August 2010

Marine Science Review – 388

Contaminants and pollution

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In this review:

A. Recent articles with abstracts

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Thomas, K.V. and Brooks, S. **The environmental fate and effects of antifouling paint biocides.** *Biofouling* 26(1): 73-88, 2010.

Notes: Antifouling (AF) biocides are the active ingredients in AF paints that prevent the settlement, adhesion and growth of organisms to a painted surface. A wide range of chemicals are used as AF biocides, which have very different physico-chemical properties and therefore differing environmental fates, behaviour and effects. Copper has been used as an antifoulant for centuries and extensive research has been performed to understand how copper speciation influences bioavailability and toxicity. For biocides that have been widely used over a number of decades, for example Irgarol 1051 and diuron, there are a large amount of environmental data in the public domain, including for their respective metabolites, that allows their environmental safety and potential risk to the environment to be assessed. For other biocides such as dichlofluanid, DCOIT (SeaNine 211) and zinc/copper pyrithione, there is a good understanding of their fate and effects. However, few monitoring studies have been performed and not so much is known about the fate and effects of their metabolites. There are also new or candidate biocides such as triphenylborane pyridine, Econea, capsaicin and medetomidine for which there is very little information in the public domain. This review provides an overview of the environmental fate and occurrence data that are in the public domain for AF biocides and provides some insight into the effects of these compounds on non-target organisms.

Heeb, N.V., Graf, H., Schweizer, W.B., and Lienemann, P. **Isobutoxypentabromocyclodo-decanes (IBPBCDs): A new class of polybrominated compounds.** *Chemosphere* 78(8): 950-957, 2010.

Notes: Isobutoxypentabromocyclododecanes (iBPBCDs) represent a new class of polybrominated compounds found in several flame-proofed polystyrene materials and in a technical mixture of hexabromocyclododecanes (HBCDs). Of the 64 stereoisomers possible, we now have analytical evidence for 16 different stereoisomers. By reversed- and chiral-phase liquid chromatography we distinguished 8 diastereomeric pairs of enantiomers, named α-, β-, γ-, δ-, ε-, ξ-, η-, and θ-iBPBCDs in accordance with their chromatographic retention on a C-18-RP-column. Crystal structure analysis revealed the stereochemistry of the most prominent theta-iBPBCD stereoisomers, which were determined to be (IR)-1-iso-butoxy-(2R,5R,6S,9S,10R)-2,5,6,9,10-pentabromocyclododecane and its enantiomer. The eight iBPBCD diastereomers were also found in several expanded (EPS) and extruded polystyrene materials (XPS). Stereoisomer pattern varied to a large extent with δ-, η-, and θ-iBPBCDs dominating in EPS- and α-, β-, ε-, and ξ-isomers in XPS-materials. The substitution of a bromine atom with an alkoxy group is expected to result in more lipophilic compounds than the parent HBCD compounds. The chromatographic retention on the reversed-phase column supports this assumption. Therefore, we expect that certain iBPBCD stereoisomers may also have the potential to accumulate in biota like e.g. α-HBCDs. The presented spectroscopic and chromatographic data allow the identification of 16 different iBPBCD stereoisomers in plastic materials, environmental samples, and biota. With this, the occurrence, fate, and toxicological relevance of this new class of polybrominated compounds can now be studied in more detail.

Hattenrath, T.K., Anderson, D.M., and Gobler, C.J. **The influence of anthropogenic nitrogen loading and meteorological conditions on the dynamics and toxicity of *Alexandrium fundyense* blooms in a New York (USA) estuary.** *Harmful Algae* 9(4): 402-412, 2010.

Notes: The goal of this two-year study was to explore the role of nutrients and climatic conditions in promoting reoccurring *Alexandrium fundyense* blooms in the Northport-Huntington Bay complex, NY, USA. A bloom in 2007 was short and small (3 weeks, 10^3 cells L^{-1} maximal density) compared to 2008 when the *A. fundyense* bloom, which persisted for 6 weeks, achieved cell densities $>10^6$ cells L^{-1} and water column saxitoxin concentrations $>2.4 \times 10^4$ pmol STX eq. L^{-1}. During the 2008 bloom, both deployed mussels (used as indicator species) and wild soft shell clams became highly toxic (1400 and 600 μg STX eq./100 g shellfish tissue, respectively) resulting in the closure of shellfish beds. The densities of benthic *A. fundyense* cysts at the onset of this bloom were four orders of magnitude lower than levels needed to account for observed cell densities, indicating *in situ* growth of vegetative cells was responsible for elevated bloom densities. Experimental enrichment of bloom water with nitrogenous compounds, particularly ammonium, significantly increased *A. fundyense* densities and particulate saxitoxin concentrations relative to unamended control treatments. The $\delta^{15}N$ signatures (12-23‰) of particulate organic matter (POM) during blooms were similar to those of sewage (10-30‰) and both toxin and *A. fundyense* densities were significantly correlated with POM $\delta^{15}N$ ($p<0.001$). These findings suggest *A. fundyense* growth was supported by a source of wastewater such as the sewage treatment plant which discharges into Northport Harbor. Warmer than average atmospheric temperatures in the late winter and spring of 2008 and a cooler May contributed to an extended period of water column temperatures optimal for *A. fundyense* growth (12-20 ºC), and thus may have also contributed toward the larger and longer bloom in 2008. Together this evidence suggests sewage-derived N loading and above average spring temperatures can promote intense and toxic *A. fundyense* blooms in estuaries.

Saikku, L. and Asmala, E. **Eutrophication in the Baltic Sea : the role of salmonid aquaculture, consumption, and international trade.** *Journal of Industrial Ecology* 14(3): 482-495, 2010.

Notes: Fish consumption is increasing globally. Overfishing puts pressure on fisheries, but aquaculture provides an alternative to satisfy the growing need for seafood. However, nutrient emissions from aquaculture contribute to eutrophication, and raising fish from the top of the food chain is inefficient. Here we use the approach of industrial ecology and report ImPACT decomposition analysis of the drivers of nutrient emissions to the Baltic Sea from rainbow trout aquaculture in Finland during 1980-2007. During this period, the nitrogen load studied increased markedly and was 522 tonnes in 2007. The phosphorus load quadrupled and then returned to its original level of about 65 tonnes. The Finnish population increased slightly, while the average affluence level increased significantly. Total salmonid consumption increased substantially during the period. The increasing percentage of imported salmonids and improvements in domestic aquaculture technology ended the period of strong growth of emissions in the 1980s. Decreasing the nutrient load through reductions in salmonid consumption in the future is unlikely, due to health benefits and consumer preferences. Replacing domestic production with import of salmonids raises questions regarding outsourcing of the environmental impact, and regarding rural development in Finland. Major improvements in production technology are not in sight. New perspectives on rainbow trout aquaculture may be needed, including using feed from the Baltic Sea, thus closing the nutrient cycle or changing consumption and production to herbivorous fish species.

Lemaire, B., Priede, I.G., Collins, M.A., Bailey, D.M., Schtickzelle, N., Thome, J.P., and Rees, J.F. **Effects of organochlorines on cytochrome P450 activity and antioxidant enzymes in liver of roundnose grenadier *Coryphaenoides rupestris*.** *Aquatic Biology* 8(2): 161-168, 2010.

Notes: Oceans function as a sink for organochlorine compounds (OCs) such as PCBs and DDTs. Deep-sea fish bioaccumulate OCs to levels 10 to 100 times higher than shallow-water species. OCs induce the cytochrome P450 (CYP) system, the activity of which may increase reactive oxygen species (ROS) production in liver cells. However, the susceptibility of fish to the oxidative stress likely caused by OCs remains unclear. We analysed whether PCB and DDT contamination of roundnose grenadier *Coryphaenoides rupestris* was associated with higher ethoxyresorufin-O-deethylase (EROD) activity (CYP1A-related), and activities of antioxidant enzymes such as catalase (CAT), superoxide dismutases (SOD) and glutathione peroxidases (GPX). Biological parameters affecting EROD patterns (e.g. gender, ontogeny) were also investigated. Citrate

synthase (CS) was used as a proxy for oxidative metabolism, responsible for basal ROS production and recruitment of antioxidant enzymes in liver cells. Hepatic OC levels were determined in individuals of different sizes (89 to 2016 g) from northern Atlantic slopes (depth range = 1000 to 1900 m). Median PCB and DDT values were 2.39 and 1.48 μg g^{-1} lipid weight, respectively, while median EROD activity was 15 pmol min^{-1} mg^{-1} protein. Gender greatly influenced OC levels (females were less contaminated), whilst weight (linked to ontogeny) positively affected DDT levels. EROD increased with PCB levels, and to some extent SOD and CAT were more influenced by EROD than CS, indicating that PCBs strongly affect the redox balance of roundnose grenadier liver cells through increased CYP1A activity. Therefore, OC-related CYP1A induction may be a major source of cellular ROS in liver of roundnose grenadier.

Tanabe, S. and Minh, T.B. **Dioxins and organohalogen contaminants in the Asia-Pacific region.** *Ecotoxicology* 19(3): 463-478, 2010.

Notes: This article reviews the outcome of comprehensive investigations conducted in our laboratory at CMES, Ehime University over the past three decades on the distribution, sources, temporal trends and toxic impacts of the persistent and bioaccumulative organohalogen contaminants in Asia-Pacific region with a particular emphasis on developing countries. Results of multi-media monitoring studies were compiled and discussed to provide in-depth understanding on various issues of dioxins and organohalogen contamination in both ambient environment and animals including humans. Prominent contaminations were found in the regions where they have been heavily used. The eastern Asian region is probably a potential source of pollution, particularly by the new contaminants such as polybrominated diphenyls ethers. These groups of contaminants, together with polychlorinated biphenyls, exhibited either decreasing or increasing trends depending on the extent of industrialization in Asian developing region, indicating the necessity for long term monitoring. The open dumping sites for municipal wastes in major cities are significant sources of many toxic chemicals, and these areas are probably one of the challenges for future research due to the long term impacts on the environmental quality and human health. The formation of dioxins and related compounds in such dumping sites and their elevated residues found in breast milk of residents living in and around warrant long term impacts of dioxins upon next generations. Comprehensive and long term monitoring programs are urgently needed with close collaboration and proper capacity building in Asian developing countries in order to mitigate dioxin and organohalogen emission and their risk on ecosystems and human health.

Chen, D. and Hale, R.C. **A global review of polybrominated diphenyl ether flame retardant contamination in birds.** *Environment International* 36(7): 800-811, 2010.

Notes: As a consequence of substantial, long-term usage, polybrominated diphenyl ethers (PBDEs) have contaminated humans, wildlife, and abiotic matrices around the world. Although several reports have reviewed PBDE contamination in general, none have focused specifically on birds. Birds have long been recognized as invaluable monitoring species for organohalogen contamination. This review summarizes most available PBDE data in birds and emphasizes several specific aspects, i.e., inter-regional differences in PBDE contamination, the extent of BDE-209 contamination, differences in congener composition patterns between piscivorous and terrestrial-feeding birds, trophic biomagnification and temporal changes in PBDE contamination. A meta-analysis of PBDE congener profiles reveals distinctly different patterns between birds utilizing terrestrial and aquatic food webs. Terrestrial-feeding birds appear to exhibit heightened Deca-BDE contamination. Inter-regional comparisons reveal elevated PBDE burdens in North American aquatic birds compared to those from the rest of the world, likely related to greater Penta-BDE demand there. Examination of North American and Chinese terrestrial birds also exhibited some of the highest BDE-209 concentrations ever reported in wildlife, and suggested that urban environments in general and some commercial activities (e.g., electronic recycling) may increase exposure of wildlife and humans to Deca-BDE. Summaries of temporal trend studies suggest that varying usage histories and regulations have influenced PBDE contamination patterns at different regions. As a consequence of continued usage of Deca-BDE around the world, significant increases in BDE-209 burdens have been observed in both North American and European birds. Examination of both wild and laboratory-exposed birds also indicated potential degradation of BDE-209 to less brominated, but more bioavailable/toxic congeners. Therefore, it would be wise to reduce releases of Deca-BDE, the only PBDE formulation remaining in production, to the environment.

Mehinto, A.C., Hill, E.M., and Tyler, C.R. **Uptake and biological effects of environmentally relevant concentrations of the nonsteroidal anti-inflammatory pharmaceutical diclofenac in rainbow trout (*Oncorhynchus mykiss*).** *Environmental Science and Technology* 44(6): 2176-2182, 2010.

Notes: Diclofenac, a nonsteroidal anti-inflammatory drug, is widely detected in surface waters and can potentially cause deleterious effects in fish. Here, we investigated the biological effects of 21-day exposure to waterborne diclofenac at environmentally relevant concentrations (0, 0.5, 1, 5, and 25 μg/L) in rainbow trout. Accumulation of diclofenac in the bile was measured and responses in selected tissues were assessed via changes in the expression of selected genes (cytochrome P450 (cyp) 1a1, cyclooxygenase (cox) 1 and 2, and p53) involved in metabolism of xenobiotics, prostaglandin synthesis, and cell cycle control, respectively, together with histopathological alterations in these tissues. Diclofenac accumulated in the bile by a factor of between 509 ± 27 and 657 ± 25 and various metabolites were putatively identified as hydroxydiclofenac, diclofenac methyl ester, and the potentially reactive metabolite hydroxydiclofenac glucuronide. Expression levels of both cox1 and cox2 in liver, gills, and kidney were significantly reduced by diclofenac exposure from only 1 μg/L. Expression of cyp1a1 was induced in the liver and the gills but inhibited in the kidney of exposed fish. Diclofenac exposure induced tubular necrosis in the kidney and hyperplasia and fusion of the villi in the intestine from 1 μg/L. This study demonstrates that subchronic exposure to environmental concentrations of diclofenac can interfere with the biochemical functions of fish and lead to tissue damage, highlighting further the concern about this pharmaceutical in the aquatic environment.

Hagg, H.E., Humborg, C., Morth, C.M., Medina, M.R., and Wulff, F. **Scenario analysis on protein consumption and climate change effects on riverine N export to the Baltic Sea.** *Environmental Science and Technology* 44(7): 2379-2385, 2010.

Notes: This paper evaluates possible future nitrogen loadings from 105 catchments surrounding the Baltic Sea. Multiple regressions are used to model total nitrogen (TN) flux as a function of specific runoff (*Q*), atmospheric nitrogen deposition, and primary emissions (PE) from humans and livestock. On average cattle contributed with 63%, humans with 20%, and pigs with 17% of the total nitrogen PE to land. Compared to the reference period (1992-1996) we then evaluated two types of scenarios for year 2070. i) An increased protein consumption scenario that led to 16% to 39% increased mean TN flux (kg per km^{-2}). ii) Four climate scenarios addressing effects of changes in river discharge. These scenarios showed increased mean TN flux from the northern catchments draining into the Gulf of Bothnia (34%) and the Gulfs of Finland and Riga (14%), while the mean TN flux decreased (-27%) for catchments draining to the Baltic Proper. However, the net effect of the scenarios showed a possible increase in TN flux ranging from 3-72%. Overall an increased demand for animal protein will be instrumental for the Baltic Sea ecosystem and may be a major holdback to fulfill the environmental goals of the Baltic Sea Action Plan.

O'Hara, P.D. and Morandin, L.A. **Effects of sheens associated with offshore oil and gas development on the feather microstructure of pelagic seabirds.** *Marine Pollution Bulletin* 60(5): 672-678, 2010.

Notes: Operational discharges of hydrocarbons from maritime activities can have major cumulative impacts on marine ecosystems. Small quantities of oil (i.e., 10 ml) results in often lethally reduced thermoregulation in seabirds. Thin sheens of oil and drilling fluids form around offshore petroleum production structures from currently permissible operational discharges of hydrocarbons. Methodology was developed to measure feather microstructure impacts (amalgamation index or AI) associated with sheen exposure. We collected feather samples from two common North Atlantic species of seabirds; Common Murres (*Uria aalge*) and Dovekies (*Alle alle*). Impacts were compared after feather exposure to crude oil and synthetic lubricant sheens of varying thicknesses. Feather weight and microstructure changed significantly for both species after exposure to thin sheens of crude oil and synthetic drilling fluids. Thus, seabirds may be impacted by thin sheens forming around offshore petroleum production facilities from discharged produced water containing currently admissible concentrations of hydrocarbons.

Saito, L., Rosen, M.R., Roesner, L., and Howard, N. **Improving estimates of oil pollution to the sea from land-based sources.** *Marine Pollution Bulletin* 60(7): 990-997, 2010.

Notes: This paper presents improvements to calculation methods used in the National Research Council's (NRC) Oil in the Sea reports from 2003 and 1985 to estimate land-based contributions of petroleum hydrocarbons to the sea from North America. Using procedures similar to the 2003 report, but with more robust methods for handling non-detections, estimated land-based contributions for 1977 and 2000 were over 50% lower than the best 1996 estimate in the NRC report. The largest loads were from the northeastern United States and the Gulf of Mexico region for both the 2003 report and updated calculations. Calculations involved many sources of uncertainty, including lack of available data, variable methods of measuring and reporting data, and variable methods of reporting values below detection limits. This updated analysis of land-based loads of petroleum hydrocarbons to the sea highlights the continued need for more monitoring and research on inputs, fates and effects of these sources.

Bernabeu, A.M., Rey, D., Lago, A., and Vilas, F. **Simulating the influence of physicochemical parameters on subsurface oil on beaches: Preliminary results.** *Marine Pollution Bulletin* 60(8): 1170-1174, 2010.

Notes: Monitoring of sandy beaches after the Prestige oil spill revealed thick subsurface layers (up to 1 m thick) of grey-coloured sand. These horizons were sometimes found under more than 3 m of clean sand. Examination of the sand by electron microscopy confirmed that the colouring was due to oil-coated sand grains, and revealed a sequence of degradation of buried oil. Further analysis of the sand revealed high concentrations of hydrocarbon in the oil-coated sand and that the main biomarkers were indicative of biodegradation, even though the oil was buried. A set of experiments was designed to analyze the evolution of oil from tar balls to coatings. The results revealed that biodegradation is a secondary process in the changes that take place in the buried oil, and that water flow slows down the appearance of grey sand and that low salinity may hinder the oil degradation process.

Camphuysen, K.C.J. **Declines in oil-rates of stranded birds in the North Sea highlight spatial patterns in reductions of chronic oil pollution.** *Marine Pollution Bulletin* 60(8): 1299-1306, 2010.

Notes: Strandings of oiled seabirds are used to signal the problem of chronic oil pollution. Species-specific oil rates reflect the risk for marine birds to become oiled at sea. High oil rates were characteristic for seabirds common in areas with frequent oil spills; low oil rates for birds wintering away from the busiest shipping lanes. Declining trends in oil-rates were found, reflecting a reduction in the amount of oil intentionally discharged over the past 50 years. Spatial patterns in the risk to become oiled could be identified, when the winter distribution patterns of the affected birds were incorporated in the analysis. Declines in oil rates were most pronounced in coastal birds. These trends were consistent with tendencies to police nearshore waters more effectively than offshore waters. While levels of chronic oil pollution are much reduced, future emphasis should be to reduce chronic oiling more effectively in offshore waters.

Baker, A.R., Lesworth, T., Adams, C., Jickells, T.D., and Ganzeveld, L. **Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field sampling: Fixed nitrogen and dry deposition of phosphorus.** *Global Biogeochemical Cycles* 24: art. GB3006, 2010.

Notes: Atmospheric nitrogen inputs to the ocean are estimated to have increased by up to a factor of three as a result of increased anthropogenic emissions over the last 150 years, with further increases expected in the short- to mid-term at least. Such estimates are largely based on emissions and atmospheric transport modeling, because, apart from a few island sites, there is very little observational data available for atmospheric nitrogen concentrations over the remote ocean. Here we use samples of rainwater and aerosol we obtained during 12 long-transect cruises across the Atlantic Ocean between 50°N and 50°S as the basis for a climatological estimate of nitrogen inputs to the basin. The climatology is for the 5 years 2001-2005, during which almost all of the cruises took place, and includes dry and wet deposition of nitrate and ammonium explicitly, together with a more uncertain estimate of soluble organic nitrogen deposition. Our results indicate that nitrogen inputs into the region were ~850-1420 Gmol (12-20 Tg) N yr^{-1}, with ~78-85% of this in the form of wet deposition. Inputs were greater

in the Northern Hemisphere and in wet regions, and wet regions had a greater proportion of input via wet deposition. The largest uncertainty in our estimate of dry inputs is associated with variability in deposition velocities, while the largest uncertainty in our wet nitrogen input estimate is due to the limited amount and uneven geographic distribution of observational data. We also estimate a lower limit of dry deposition of phosphate to be ~0.19 Gmol P yr^{-1}, using data from the same cruises. We compare our results to several recent estimates of N and P deposition to the Atlantic and discuss the likely sources of uncertainty, such as the potential seasonal bias introduced by our sampling, on our climatology.

Yan, W., Mayorga, E., Li, X., Seitzinger, S.P., and Bouwman, A.F. **Increasing anthropogenic nitrogen inputs and riverine DIN exports from the Changjiang River basin under changing human pressures.** *Global Biogeochemical Cycles* 24: art. GB0A06, 2010.

Notes: In this paper, we estimate the inputs of nitrogen (N) and exports of dissolved inorganic nitrogen (DIN) from the Changjiang River to the estuary for the period 1970–2003, by using the global NEWS-DIN model. Modeled DIN yields range from 260 kg N km^{-2} yr^{-1} in 1970 to 895 kg N km^{-2} yr^{-1} in 2003, with an increasing trend. The study demonstrated a varied contribution of different N inputs to river DIN yields during the period 1970–2003. Chemical fertilizer and manure together contributed about half of the river DIN yields, while atmospheric N deposition contributed an average of 21% of DIN yields in the period 1970–2003. Biological N fixation contributed 40% of DIN yields in 1970, but substantially decreased to 13% in 2003. Point sewage N input also showed a decreasing trend in contribution to DIN yields, with an average of 8% over the whole period. We also discuss possible future trajectories of DIN export based on the Global NEWS implementation of the Millennium Ecosystem Assessment scenarios. Our result indicates that anthropogenically enhanced N inputs dominate and will continue to dominate river DIN yields under changing human pressures in the basin. Therefore, nitrogen pollution is and will continue to be a great challenge to China.

Seitzinger, S.P., Mayorga, E., Bouwman, A.F., Kroeze, C., Beusen, A.H.W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B.M., Garnier, J., and Harrison, J.A. **Global river nutrient export: A scenario analysis of past and future trends.** *Global Biogeochemical Cycles* 24: art. GB0A08, 2010.

Notes: An integrated modeling approach was used to connect socioeconomic factors and nutrient management to river export of nitrogen, phosphorus, silica and carbon based on an updated Global NEWS model. Past trends (1970-2000) and four future scenarios were analyzed. Differences among the scenarios for nutrient management in agriculture were a key factor affecting the magnitude and direction of change of future DIN river export. In contrast, connectivity and level of sewage treatment and P detergent use were more important for differences in DIP river export. Global particulate nutrient export was calculated to decrease for all scenarios, in part due to increases in dams for hydropower. Small changes in dissolved silica and dissolved organics were calculated for all scenarios at the global scale. Population changes were an important underlying factor for river export of all nutrients in all scenarios. Substantial regional differences were calculated for all nutrient elements and forms. South Asia alone accounted for over half of the global increase in DIN and DIP river export between 1970 and 2000 and in the subsequent 30 years under the Global Orchestration scenario (globally connected with reactive approach to environmental problems); DIN river export decreased in the Adapting Mosaic (globally connected with proactive approach) scenario by 2030, although DIP continued to increase. Risks for coastal eutrophication will likely continue to increase in many world regions for the foreseeable future due to both increases in magnitude and changes in nutrient ratios in river export.

Yasin, J.A., Kroeze, C., and Mayorga, E. **Nutrients export by rivers to the coastal waters of Africa: Past and future trends.** *Global Biogeochemical Cycles* 24: art. GB0A07, 2010.

Notes: We analyze past and future trends in nitrogen (N), phosphorus (P), and carbon (C) export by rivers to the coastal waters of Africa as calculated by the Global Nutrient Export to WaterShed (NEWS) models for the period 1970-2050. Between 1970 and 2000 the total nutrient export by African rivers increased by 10-80%. For future years (2000-2050) we calculate an increase in the total loads of dissolved forms of N and P, but decreasing trends for dissolved organic C and particulate forms of N and P. There are large regions that deviate from these pan-African trends. We explore the regional

patterns and the underlying processes, in particular for the Nile, Zaire, Niger, and Zambezi. In the future, anthropogenic sources may, in large parts of Africa, become larger contributors to riverine nutrient loads than natural sources.

Harrison, J.A., Bouwman, A.F., Mayorga, E., and Seitzinger, S. **Magnitudes and sources of dissolved inorganic phosphorus inputs to surface fresh waters and the coastal zone: A new global model.** *Global Biogeochemical Cycles* 24: art. GB1003, 2010.

Notes: As a limiting nutrient in aquatic systems, phosphorus (P) plays an important role in controlling freshwater and coastal primary productivity and ecosystem dynamics, increasing frequency and severity of harmful and nuisance algae blooms and hypoxia, as well as contributing to loss of biodiversity. Although dissolved inorganic P (DIP) often constitutes a relatively small fraction of the total P pool in aquatic systems, its bioavailability makes it an important determinant of ecosystem function. Here we describe, apply, evaluate, and interpret an enhanced version of the Global Nutrient Export from Watersheds (NEWS)-DIP model: NEWS-DIP-Half Degree (NEWS-DIP-HD). Improvements to NEWS-DIP-HD over the original NEWS DIP model include (1) the preservation of spatial resolution of input data sets at the 0.5 degree level and (2) explicit downstream routing of water and DIP from half-degree cell to half-degree cell using a global flow-direction representation. NEWS-DIP explains 78% and 62% of the variability in per-basin DIP export (DIP load) for U.S. Geological Survey (USGS) and global stations, respectively, similar to the original NEWS-DIP model and somewhat more than other global models of DIP loading and export. NEWS-DIP-HD output suggests that hot spots for DIP loading tend to occur in urban centers, with the highest per-area rate of DIP loading predicted for the half-degree grid cell containing Tokyo (6366 kg P km^{-2} yr^{-1}). Furthermore, cities with populations >100,000 accounted for 35% of global surface water DIP loading while covering less than 2% of global land surface area. NEWS-DIP-HD also indicates that humans supply more DIP to surface waters than natural weathering over the majority (53%) of the Earth's land surface, with a much larger area dominated by DIP point sources than nonpoint sources (52% versus 1% of the global land surface, respectively). NEWS-DIP-HD also suggests that while humans had increased DIP input to surface waters more than fourfold globally by the year 2000, human activities such as dam construction and consumptive water use have somewhat moderated the effect of humans on P transport by preventing (conservatively) 0.35 Tg P yr^{-1} (~20% of P inputs to surface waters) from reaching coastal zones globally.

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van der Struijk, L.F. and Kroeze, C. **Future trends in nutrient export to the coastal waters of South America: Implications for occurrence of eutrophication.** *Global Biogeochemical Cycles* 24: art. GB0A09, 2010.

Notes: We analyze future trends in nutrient export to the coastal waters of South America, with a special focus on the causes of nutrient export and their potential effects. Nutrient Export from Watersheds (NEWS) model results for South America are presented, including trends in human activities and the associated river export of nutrients for the period 1970-2050. For 25 areas in coastal waters of South America where eutrophication or hypoxia has been observed, we investigate how these relate to NEWS model output. For selected watersheds we discuss the causes of increased nutrient loadings of rivers and future trends as projected by the NEWS models.

Billen, G., Beusen, A., and Bouwman, L. **Anthropogenic nitrogen autotrophy and heterotrophy of the world's watersheds: Past, present, and future trends.** *Global Biogeochemical Cycles* 24: art. GB0A11, 2010.

Notes: Anthropogenic nitrogen autotrophy of a territory is defined as the nitrogen flux associated with local production of harvested crops and grass consumed by livestock grazing (in kg N/km^2/yr). Nitrogen heterotrophy is the nitrogen flux associated with local food and feed consumption by humans and domestic animals. These two summarizing characteristics (anthropogenic nitrogen autotrophy and heterotrophy (ANAH)) indicate the degree of anthropogenic perturbation of the nitrogen cycle by agriculture and human consumption: their balance value provides information on either the potential for commercial export or the need to import agricultural goods; in a watershed, their vector sum is related to the nitrogen flux delivered to the sea. These indicators were calculated for all the watersheds in the Global Nutrient Export from Watersheds (NEWS) database for 1970 and 2000, as well as for 2030 and 2050, according to Millennium Ecosystem Assessment scenarios. During this 30 year period, many watersheds shifted from relatively balanced situations toward either more autotrophic or more heterotrophic conditions. This trend is predicted to become more pronounced over the next 50 years.

Bianchi, T.S., DiMarco, S.F., Cowan, J.H., Hetland, R.D., Chapman, P., Day, J.W., and Allison, M.A. **The science of hypoxia in the Northern Gulf of Mexico: A review.** *The Science of the Total Environment* 408(7): 1471-1484, 2010.

Notes: The Mississippi River is one of the world's 10 largest rivers, with average freshwater discharge into the northern Gulf of Mexico (GOM) of 380 km^3 $year^{-1}$. In the northern GOM, anthropogenic nitrogen is primarily derived from agricultural fertilizer and delivered via the Mississippi River. The general consensus is that hypoxia in the northern Gulf of Mexico is caused primarily by algal production stimulated by excess nitrogen delivered from the Mississippi-Atchafalaya River Basin and seasonal vertical stratification of incoming stream flow and Gulf waters, which restricts replenishment of oxygen from the atmosphere. In this paper, we review the controversial aspects of the largely nutrient-centric view of the hypoxic region, and introduce the role of non-riverine organic matter inputs as other oxygen-consuming mechanisms. Similarly, we discuss non-nutrient physically-controlled impacts of freshwater stratification as an alternative mechanism for controlling in part, the seasonality of hypoxia. We then explore why hypoxia in this dynamic river-dominated margin (RiOMar) is not comparable to many of the other traditional estuarine systems (e.g., Chesapeake Bay, Baltic Sea, and Long Island Sound). The presence of mobile muds and the proximity of the Mississippi Canyon are discussed as possible reasons for the amelioration of hypoxia (e.g., healthy fisheries) in this region. The most recent prediction of hypoxia area for 2009, using the current nutrient-centric models, failed due to the limited scope of these simple models and the complexity of this system. Predictive models should not be the main driver for management decisions. We postulate that a better management plan for this region can only be reached through a more comprehensive understanding of this RiOMar system — not just more information on river fluxes (e.g., nutrients) and coastal hypoxia monitoring programs.

Rigét, F., Bignert, A., Braune, B., Stow, J., and Wilson, S. **Temporal trends of legacy POPs in Arctic biota, an update.** *The Science of the Total Environment* 408(15): 2874-2884, 2010.

Notes: A statistically robust method was applied to 316 time-series of 'legacy' persistent organic pollutants (POPs) in Arctic biota from marine, freshwater and terrestrial ecosystems with the purpose of generating a 'meta-analysis' of temporal trend data collected over the past two to three decades for locations from Alaska in the west to northern Scandinavian in the east. Information from recently published temporal trend studies was tabulated and comparisons were also drawn with trends in arctic air. Most of the analysed time-series of legacy POP compounds showed decreasing trends, with only a few time-series showing significantly increasing trends. Compounds such as α-HCH, γ-HCH and ΣDDT had a relatively high proportion of time-series showing significantly decreasing trends; ΣCHL had the lowest proportion. β-HCH was an exception, where long-range transport through the ocean, and not the atmosphere, may explain several increasing trends that were detected in the Canadian Arctic. Moving east from the Canadian Arctic there was a trend towards a greater proportion of significantly decreasing trends. Several time-series for DDE and ΣDDT showed significantly non-exponential trends, most often with a period of relative stability followed by a decrease. The median 'minimum detectable annual change within a 10-year period' for all of the time-series considered was 12% which did not meet the desirable level of statistical power capable of detecting a 5% annual change with a significance level of 5% within a 10-year period. The trends observed in the biota were consistent with decreasing trends of legacy POPs reported for Arctic air which appear to follow historic decreases in emissions. However, recent decreases in air are also starting to show signs of levelling off which may be an indication that atmospheric concentrations and, consequently those in the biota, are being less driven by primary sources and more by environmental processes and degradation.

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de Wit, C.A., Herzke, D., and Vorkamp, K. **Brominated flame retardants in the Arctic environment — trends and new candidates.** *The Science of the Total Environment* 408(15): 2885-2918, 2010.

Notes: Polybrominated diphenyl ethers (PBDEs) containing two to 10 bromines are ubiquitous in the Arctic, in both abiotic and biotic samples. Hexabromocyclododecane (HBCD) is also ubiquitous in the Arctic, with the γ-HBCD isomer predominating in air, the α-HBCD isomer predominating in biota and similar concentrations of α-, β- and γ-HBCD found in marine sediments. Other brominated flame retardants (BFRs) found in some Arctic samples are polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HxBBz), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH). Temporal trends of tetra- to heptaBDEs and HBCD show increasing concentrations or a tendency to levelling off depending

on the matrix (air, sediment, biota) and location, but no uniform picture for the Arctic emerges. BDE-209 concentrations are increasing in air. PBDEs and HBCD spatial trends in seabirds and marine mammals are similar to those seen previously for polychlorinated biphenyls (PCBs), with highest concentrations found in organisms from East Greenland and Svalbard. These trends indicate western Europe and eastern North America as important source regions of these compounds via long range atmospheric transport and ocean currents. Latitudinal trends showed lower concentrations and fluxes of PBDEs at higher latitudes. The tetra-hexaBDEs and α-HBCD biomagnify in Arctic food webs. Results for BDE-209 are more conflicting, showing either only low or no biomagnification potential. PBDE and HBCD concentrations are lower in terrestrial organisms and higher in marine top predators such as some killer whale populations in Alaska and glaucous gulls from the Barents Sea area. Higher concentrations are seen near populated areas indicating local sources. Findings of BTBPE, HxBBz, PBEB, PBT and TBECH in seabirds and/or marine mammals indicate that these compounds reach the Arctic, most probably by long range atmospheric transport and accumulate in higher trophic level organisms and that increasing use as PBDE replacements will lead to increasing concentrations.

Bidleman, T.F., Helm, P.A., Braune, B.M., and Gabrielsen, G.W. **Polychlorinated naphthalenes in polar environments − A review.** *The Science of the Total Environment* 408(15): 2919-2935, 2010.

Notes: Polychlorinated naphthalenes (PCNs) consist of naphthalene substituted with 1-8 chlorines, yielding 75 possible congeners. They were formerly used in industry, occur at trace levels in commercial PCB mixtures, and have current sources in combustion processes. PCNs are widespread in arctic air with higher levels in the European Arctic. Concentrations were higher during the cold months in arctic Canada and Russia, but no seasonality was noted in subarctic Canada and Greenland. "Marker" congeners indicative of combustion were evident at some sites. Total toxic equivalents (TEQ) in air due to PCNs + dioxin-like PCBs were dominated by PCNs in arctic Canada and Russia, but not in subarctic Canada. Deposition of PCNs in snow was measured in northern Norway and Svalbard. Surveys of PCNs in the lower food web are limited to the northern Baltic Sea and lakes/rivers of northern Scandinavia. PCNs showed little or no biomagnification in lower food webs of the northern Baltic and discrimination among congeners suggested preferential metabolism. There are no reports of PCNs in fish and invertebrates from the Arctic Ocean, and only one from Antarctica. Total PCNs in marine mammals followed the order: harbour seal ~ pilot whale ≥ polar bear > beluga > ringed seal ~ Weddell seal. Total PCNs in seabirds varied over 100-fold, with higher concentrations in glaucous gull eggs and plasma from Bear Island, and livers of northern fulmar from the eastern Canadian Arctic. Lower concentrations occurred in eggs of glaucous gull from Svalbard and black-backed gull from the Faroe Islands. PCNs accounted for <1% of total TEQ in ringed seal, Weddell seal, seabirds and polar bear, but up to 6-15% in beluga and pilot whale. TEQ due to PCNs were generally low in harbour seal, but up to 9% of total TEQ in some animals.

Butt, C.M., Berger, U., Bossi, R., and Tomy, G.T. **Levels and trends of poly- and perfluorinated compounds in the arctic environment.** *The Science of the Total Environment* 408(15): 2936-2965, 2010.

Notes: Poly- and perfluorinated organic compounds (PFCs) are ubiquitous in the Arctic environment. Several modeling studies have been conducted in attempt to resolve the dominant transport pathway of PFCs to the arctic − atmospheric transport of precursors versus direct transport via ocean currents. These studies are generally limited by their focus on perfluorooctanoate (PFOA) fluxes to arctic seawater and thus far have only used fluorotelomer alcohols (FTOHs) and sulfonamide alcohols as inputs for volatile precursors. There have been many monitoring studies from the North American and European Arctic, however, almost nothing is known about PFC levels from the Russian Arctic. In general, there are very few measurements of PFCs from the abiotic environment. Atmospheric measurements show the widespread occurrence of PFC precursors, FTOHs and perfluorinated sulfonamide alcohols. Further, PFCAs and PFSAs have been detected on atmospheric particles. The detection of PFCAs and PFSAs in snow deposition is consistent with the volatile precursor transport hypothesis. There are very limited measurements of PFCs in seawater. PFOA is generally detected in the greatest concentrations. Additional seawater measurements are needed to validate existing model predications. The bulk of the monitoring efforts in biological samples have focused on the perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs), although there are very few measurements of PFC precursors. The marine food web has been well studied, particularly the top predators. In contrast, freshwater and terrestrial ecosystems have been poorly studied. Studies show that in wildlife perfluorooctane sulfonate (PFOS) is generally measured in the highest concentration, followed by either perfluorononanoate (PFNA) or perfluoroundecanoate (PFUnA). However, some whale species show relatively high levels of perfluorooctane sulfonamide (PFOSA) and seabirds are typically characterized by high proportions of the C11-C15 PFCAs. PFOA is generally

infrequently detected and is present in low concentrations in arctic biota. Food web studies show high bioaccumulation in the upper trophic-level animals, although the mechanism of PFC biomagnification is not understood. Spatial trend studies show some differences between populations, although there are inconsistencies between PFC trends. The majority of temporal trend studies are from the Northern American Arctic and Greenland. Studies show generally increasing levels of PFCs from the 1970s, although some studies from the Canadian Arctic show recent declines in PFOS levels. In contrast, ringed seals and polar bears from Greenland continue to show increasing PFOS concentrations. The inconsistent temporal trends between regions may be representative of differences in emissions from source regions.

Hoferkamp, L., Hermanson, M.H., and Muir, D.C.G. **Current use pesticides in Arctic media; 2000-2007.** *The Science of the Total Environment* 408(15): 2985-2994, 2010.

Notes: This review will summarize the levels of selected current use pesticides (CUPs) that have been identified and reported in Arctic media (i.e. air, water, sediment, and biota) since the year 2000. Almost all of the 10 CUPs (chlorothalonil, chlorpyrifos, dacthal, diazinon, dicofol, lindane, methoxychlor, pentachloronitrobenzene (PCNB), pentachlorophenol, and trifluralin) examined in the review currently are, or have been, high production volume chemicals i.e. >1 M lbs/y in USA or >1000 t/y globally. Characteristic travel distances for the 10 chemicals range from 55 km (methoxychlor) to 12,100 km (PCNB). Surveys and long-term monitoring studies have demonstrated the presence of 9 of the 10 CUPs included in this review in the Arctic environment. Only dicofol has not been reported. The presence of these chemicals has mainly been reported in high volume air samples and in snow from Arctic ice caps and lake catchments. There are many other CUPs registered for use which have not been determined in Arctic environments. The discovery of the CUPs currently measured in the Arctic has been mainly serendipitous, a result of analyzing some samples using the same suite of analytes as used for studies in mid-latitude locations. A more systematic approach is needed to assess whether other CUPs might be accumulating in the arctic and ultimately to assess whether their presence has any significance biologically or results in risks for human consumers.

Letcher, R.J., Bustnes, J.O., Dietz, R., Jenssen, B.M., Jørgensen, E.H., Sonne, C., Verreault, J., Vijayan, M.M., and Gabrielsen, G.W. **Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish.** *The Science of the Total Environment* 408(15): 2995-3043, 2010.

Notes: Persistent organic pollutants (POPs) encompass an array of anthropogenic organic and elemental substances and their degradation and metabolic byproducts that have been found in the tissues of exposed animals, especially POPs categorized as organohalogen contaminants (OHCs). OHCs have been of concern in the circumpolar arctic for decades. For example, as a consequence of bioaccumulation and in some cases biomagnification of legacy (e.g., chlorinated PCBs, DDTs and CHLs) and emerging (e.g., brominated flame retardants (BFRs) and in particular polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs) including perfluorooctane sulfonate (PFOS) and perfluorooctanic acid (PFOA) found in Arctic biota and humans. Of high concern are the potential biological effects of these contaminants in exposed Arctic wildlife and fish. As concluded in the last review in 2004 for the Arctic Monitoring and Assessment Program (AMAP) on the effects of POPs in Arctic wildlife, prior to 1997, biological effects data were minimal and insufficient at any level of biological organization. The present review summarizes recent studies on biological effects in relation to OHC exposure, and attempts to assess known tissue/body compartment concentration data in the context of possible threshold levels of effects to evaluate the risks. This review concentrates mainly on post-2002, new OHC effects data in Arctic wildlife and fish, and is largely based on recently available effects data for populations of several top trophic level species, including seabirds (e.g., glaucous gull (*Larus hyperboreus*)), polar bears (*Ursus maritimus*), polar (Arctic) fox (*Vulpes lagopus*), and Arctic charr (*Salvelinus alpinus*), as well as semi-captive studies on sled dogs (*Canis familiaris*). Regardless, there remains a dearth of data on true contaminant exposure, cause-effect relationships with respect to these contaminant exposures in Arctic wildlife and fish. Indications of exposure effects are largely based on correlations between biomarker endpoints (e.g., biochemical processes related to the immune and endocrine system, pathological changes in tissues and reproduction and development) and tissue residue levels of OHCs (e.g., PCBs, DDTs, CHLs, PBDEs and in a few cases perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs)). Some exceptions include semi-field studies on comparative contaminant effects of control and exposed cohorts of captive Greenland sled dogs, and performance studies mimicking environmentally relevant PCB concentrations in Arctic charr. Recent tissue concentrations in several arctic marine mammal species and populations exceed a general threshold level of concern of 1 part-per-million (ppm), but a clear evidence of a POP/OHC-related stress in these populations remains to be

confirmed. There remains minimal evidence that OHCs are having widespread effects on the health of Arctic organisms, with the possible exception of East Greenland and Svalbard polar bears and Svalbard glaucous gulls. However, the true (if any real) effects of POPs in Arctic wildlife have to be put into the context of other environmental, ecological and physiological stressors (both anthropogenic and natural) that render an overall complex picture. For instance, seasonal changes in food intake and corresponding cycles of fattening and emaciation seen in Arctic animals can modify contaminant tissue distribution and toxicokinetics (contaminant deposition, metabolism and depuration). Also, other factors, including impact of climate change (seasonal ice and temperature changes, and connection to food web changes, nutrition, etc. in exposed biota), disease, species invasion and the connection to disease resistance will impact toxicant exposure. Overall, further research and better understanding of POP/OHC impact on animal performance in Arctic biota are recommended. Regardless, it could be argued that Arctic wildlife and fish at the highest potential risk of POP/OHC exposure and mediated effects are East Greenland, Svalbard and (West and South) Hudson Bay polar bears, Alaskan and Northern Norway killer whales, several species of gulls and other seabirds from the Svalbard area, Northern Norway, East Greenland, the Kara Sea and/or the Canadian central high Arctic, East Greenland ringed seal and a few populations of Arctic charr and Greenland shark.

Muir, D.C.G. and de Wit, C.A. **Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations.** *The Science of the Total Environment* 408(15): 3044-3051, 2010.

Notes: This article provides an overview of key findings in the reviews in this special issue on the assessment of persistent organic pollutants (POPs) under the Arctic Monitoring and Assessment Program (AMAP), identifies knowledge gaps, and presents conclusions and recommendations for future work. The articles in this special issue summarize the peer reviewed literature and selected technical reports on trends of concentrations and possible biological effects of POPs in the Arctic published up to early 2009.