PERSISTENT ORGANIC POLLUTANTS (POPS) IN AQUATIC ENVIRONMENTS: AN OVERVIEW

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Persistent organic pollutants (POPs) are long-lived and highly lipophilic man-made organic chemicals that have found there way into the environment. POPs possess toxic properties, resist degradation, bioaccumulate, and are transported through air, water and migratory species across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems. They have become common contaminants of fish, dairy products, and other foods around the world. Arctic ecosystems and indigenous communities are particularly at risk because of the biomagnification of these compounds and contamination of their traditional foods.

The Stockholm Convention

Because of the global risks posed by the long-range transport of POPs, the United Nations Environment Programme (UNEP) has led the development of a global legally-binding agreement to minimize releases of POPs into the environment. The first meeting on such an agreement was held in Montreal in 1998. In May 2001, after more than two years of negotiations, 120 countries concluded a new United Nations treaty, referred to as the Stockholm Convention after the final meeting in Sweden where the treaty was formally signed, to reduce or eliminate POPs (UNEP, 2001).

Twelve chemicals are internationally recognized as POPs requiring elimination and reduction. Upon ratification by 50 of the 120 participating countries, the Stockholm Convention will ban eight pesticides - aldrin, endrin, dieldrin, chlordane, heptachlor, hexachlorobenzene, mirex, and toxaphene - immediately. It will prohibit production of polychlorinated biphenyls (PCBs) immediately and phase out their use in electrical transformers and other equipment by 2025. The use of DDT will be limited to disease vector control in developing countries until effective and affordable alternatives become available in those countries. The treaty will promote actions to minimize the release of industrial chemical by-products such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs). And, using a precautionary approach, the treaty will establish a scientific POPs Review Committee to evaluate additional chemicals - based on the criteria of toxicity, persistence, bioaccumulation, and long-range transport.

Reporting on POPs at the International DIOXIN Symposium

POPs have been the subject of the annual DIOXIN international symposium series since its inception. Over the past nearly two decades, environmental monitoring programs have reported on the occurrence of PCDD/Fs, PCBs, organochlorine (OC) pesticides, and other

chemicals in aquatic biota and wildlife collected from nearly every corner of the world. Measurable concentrations of POPs reported in air, soil, and sediment samples have been linked to heavily industrialized and urban areas. Global long-range transport processes are increasingly recognized as responsible for the dispersion of these chemicals to remote environments. These subjects, together with studies of human exposure and human and animal toxicology, have been the focus of numerous studies reported annually at the annual DIOXIN symposium by members of the international scientific community.

Recognition that several environmental challenges posed by the occurrence of POPs in the aquatic environment are common to scientists worldwide was the subject of discussions among scientists at this year's DIOXIN symposium. There is growing evidence that these compounds are harmful to biota in marine and freshwater ecosystems, especially when they bioaccumulate through aquatic food webs. Impacts to one or more population of species, either through direct toxicity or more subtle disruption of endocrine hormones that may impair reproduction, is increasingly of concern to scientists, particularly because fish is an important component of the diet throughout the world.

POPs in Aquatic Environments

The purpose of this special technical session, "POPs in Aquatic Environments", was to share the experiences of scientists investigating occurrence, fate and effects of POPs in different environments worldwide. Against the backdrop of the Stockholm Convention and the shared international commitment to reduce global POP levels, presentations in this session report on POP levels in sediments and biota and ecological impacts in the North American Great Lakes, the Mediterranean Sea, the Gulf of Gdansk and in Argentina, Australia, Korea, Spain, and the United States.

Asia Pacific Region. Environmental monitoring in Australia and developing countries highlight the influence of industrial and heavily urban areas as sources of PCDD/Fs and OC pesticides in sediment and aquatic biota. According to Professor Connell, the control and phasing out of OC pesticide use in Australia beginning in the 1970s has been largely successful; the general trend has been a progressive decline in residue levels, which is strongly indicated by reductions in dietary intakes of DDT, dieldrin, and other OC pesticides. Similar trends are evident in North America and Europe.

But despite source control measures in Australia and elsewhere, impacts on aquatic and terrestrial wildlife are evident in urban estuaries and coastal waters. Professor Muller reports that high levels of OC pesticides in marine sediments continue to affect the Mai Po and Inner Deep Bay wetland ecosystems in Hong Kong, despite efforts to reduce or ban (e.g. DDT) their use. The occurrence of higher chlorinated PCDDs in sediments is similar to homologue profiles observed in sediments along the Queensland, Australia coast. In the Dagu industrial/residential area located outside the city of Tianjin, China, Professor Luksemburg traces a PCDD/F homologue pattern from a pesticide plant into Bohai Bay, located approximately 10 km from the plant. The absence of aquatic life in the area located nearest the plant's discharge canal may be attributable to the high concentrations of PCDD/Fs found in surface sediments.

Along the Korean coast, Professor Koh reports the spatial distributions and relative abundance of POPs in sediment trends from nonylphenol> polycyclic aromatic hydrocarbons (PAHs) > PCBs ≈ octylphenol > bisphenol A > OC pesticides; the highest concentrations occurring in developed estuaries and harbors. Organic extracts from several sediment samples were capable of eliciting significant *in vitro* bioactivity in both dioxin-like and estrogenic responses that could not be explained entirely by chemical concentrations. With regard to the occurrence of PCDD/Fs, Professor Moon suggests that the dominance of octachlorinated dioxins in the homologue profile encountered in marine sediments from the East Sea and South Sea is consistent atmospheric deposition of particulate matter generated from various combustion processes.

North America. The Great Lakes region is the focus of the largest research efforts currently underway in North America on the significance of anthropogenic discharges of POPs on populations of aquatic wildlife and strategies to mitigate ecological impacts. Professor Marvin summarizes Environment Canada's current monitoring program to assess the occurrence and spatial distribution of PCDD/Fs, non-ortho substituted and co-planar PCBs, and polychlorinated naphthalenes (PCNs) in suspended sediments in the Detroit River corridor located between Lake Erie and Lake St. Clair.

Professor Iannuzzi reports on similar efforts to evaluate PCDD/F, PCBs, and OC pesticides in intertidal reaches of the Passaic River and Newark Bay located in northeastern New Jersey. Tissue concentrations of POPs in sedentary, less migratory organisms representing lower trophic levels in the food web in affected aquatic environments tend to reflective of levels occurring in surface sediments. Correlating sediment concentrations and tissue levels in biota representing higher trophic levels or more migratory species is more difficult and contributes a significant amount of the uncertainty in ecological assessments of POPs and other environmental contaminants.

Northern Europe and the Mediterranean Sea. Environmental monitoring of POPs in fish and marine mammals along the European continent over the past several decades has provided important clues on global trends and the success of regional and international source control efforts. According to Professor Jimenez, the widespread occurrence of octachlorinated CDD/Fs and 2,3,4,7,8-PnCDF in cetacean populations living in the Mediterranean Sea are indicative of combustion sources and discharges from large continental watersheds (e.g., the Rhone River). The presence of 1,2,3,7,8-PnCDD, 2,3,4,7,8-PnCDF and 1,2,3,7,8-PnCDF found in all liver samples is consistent with the general findings in European samples. In most cases the largest percentage contribution to total dioxin toxic equivalents (TEQ) is from mono-ortho PCBs; in Pilot whales, practically all of the total TEQ is from mono-ortho PCBs, the contribution of PCDD/Fs and non-ortho PCBs being almost negligible.

The contribution from non-point sources of POPs to the aquatic environment is widely recognized by scientists as a significant environmental challenge. Reporting on monitoring programs in Spain, Professor Rivera establishes the presence of PCDD/Fs, PCBs, PAHs, polyethoxylated nonylphenols, and OC pesticides in nearly all samples of surface and ground waters, sewage sludge, biota tissues, and marine and river sediments. Much further north in the Gulf of Gdansk region of the Baltic Sea, Professor Falandysz reports widespread PCB and OC pesticide

contamination in sediments and sewage sludge, which are believed to have been discharged directly to the Gulf prior to the early 1990's.

South America. According to Professor Carvalhaes, the occurrence of PAHs, OC pesticides, and PCDD/Fs in surface water and sediment samples collected from the Cunha Channel, which discharges into Guanabara Bay, Rio de Janeiro, follows a similar trend to that observed in Northern Europe and in the Asia Pacific region. The presence of carboxylic acids and several sterol compounds strongly suggests sewage waste inputs. Similar studies in this region and in developed coastal areas located elsewhere in South America are needed to evaluate the introduction of industrial and/or domestic wastes containing these and other chemical contaminants.

From Occurrence to Ecological Impacts: Future Research Efforts

There is general agreement among scientists that future environmental monitoring efforts need to include the collection of data representing measurable impacts of adverse affects to one or more aquatic species. These data should be correlated with data describing the concentrations of POPs – as well as other chemical and geochemical parameters (e.g., organic carbon, grain size, ammonia) - in surface waters and surface sediments. Other potential stressors also should be included in assessments of aquatic environments to gain a full appreciation of exposures and risks to aquatic wildlife posed by the occurrence of POPs in the environment.

To further appreciate the impact of the occurrence of POPs in bottom sediment and resuspended material on aquatic organisms, scientists also must understand how chemicals can elicit various overt and subtle adverse effects on aquatic organisms. As Professor Koh observes, ecological risk assessment based solely on the results of chemical measurements may underestimate the potential hazard associated with sediment contamination. It is anticipated that scientists at future international DIOXIN symposiums will continue to bridge the current gaps in our knowledge between environmental occurrence and adverse impacts on aquatic wildlife.

Literature Cited

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