Polychlorinated Naphthalenes and Polychlorinated Biphenyls in Benthic Organisms of a Great Lakes Food Chain

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Received: 6 June 2003 / Accepted: 5 August 2003

Abstract. Invasion of zebra mussels, Dreissena polymorpha, and round gobies, Neogobius melanostomus, into the Great Lakes has altered the food web structure and thereby the pathways of toxic contaminants such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). In this study, concentrations of PCNs and PCBs were measured in organisms of a Great Lakes benthic food chain encompassing zebra mussels. PCNs were found in all of the benthic organisms, including phytoplankton, algae, amphipods, zebra mussels, round gobies, and smallmouth bass, Micropterus dolomieui. Concentrations of PCNs were greater in samples collected from the Raisin River than in samples from the St. Clair River. Biomagnification factors (BMF) for tetra- through octa-CN congeners in going from algae to zebra mussels from the St. Clair River ranged from 3 to 10. No major biomagnification of PCNs was found in round gobies, when concentrations were related to those in their prey species, zebra mussels. The biomagnification potential of PCNs appears to be similar to that of PCBs in the benthic food chain investigated in this study, despite the fact that PCNs may be metabolized by organisms higher in the food chain. Among several congeners, the BMFs of PCN congeners 35, 42, 43/44, 52/60, 58, and 66/67 were highest in round gobies. PCNs accounted for 1–22% of the total TEQs (toxic equivalents) of PCBs and PCNs in benthic organisms analyzed in this study. PCB congener 126 was the major contributor to TEQs, accounting for 72–99% of the PCB-TEQs in the food chain organisms analyzed.

Polychlorinated naphthalenes (PCNs), like polychlorinated biphenyls (PCBs), are widespread, persistent environmental pollutants. PCNs have been detected in samples of air, water, and biota collected from the remote oceans, including the Arctic Ocean (Harner et al. 1998; Helm et al. 2002; Corsolini et al. 2002). Although PCNs are ubiquitous pollutants, reports of their accumulation in the food chain are scarce, compared with PCBs. Biomagnification of PCNs in pelagic and benthic food chains of the Baltic Sea has been documented (Falandysz et al. 1996; Falandysz 1998; Lundgren et al. 2002). These studies have shown that, among 75 PCN congeners, only a few biomagnify in the food chain (Falandysz et al. 1997; Lundgren et al. 2002). Hexachloronaphthalene congeners 66/67, 69, and 71/72 were the most bioaccumulative in four-horned sculpins, Myoxocephalus quadricornis, when concentrations were compared with those in their prey species, amphipods (Lundgren et al. 2002). In sea eagles and cormorants, chloronaphthalene (CN) congeners 42, 52/60, 54, 58, 61, 64/68, 66/67, 69, and 71/72 were the most bioaccumulative ones (Falandysz et al. 1997). Moreover, patterns of PCN congeners retained in biota, particularly those at the lower trophic levels in the food chain, vary considerably, depending on the source of exposure (Falandysz et al. 1996; Järnberg et al. 1997; Kannan et al. 1998, 2000). Therefore, biomagnification of PCN congeners is expected to vary depending on location and species. Differences in CN congener composition in benthic organisms, coupled with congener-specific biomagnification, necessitate a site-specific approach to the evaluation of food chain transfer of PCNs. While earlier studies have examined trophic transfer of PCNs in the Baltic Sea (Falandysz et al. 1997; Lundgren et al. 2002), no information on the accumulation of PCNs in organisms in a Great Lakes food chain has been reported prior to this study. In this study, freshwater aquatic organisms were collected from the International Joint Commission (IJC) designated Areas of Concern (AOC) including the Raisin River (a tributary of Lake Erie), the Saginaw River (a tributary to Lake Huron), and the St. Clair River, Michigan, USA. The major objective of this study was to examine the concentrations and transfer of PCNs and PCBs in the zebra mussels, Dreissena polymorpha–round gobies, Neogobius melanostomus–smallmouth bass, Micropterus dolomieui, food chain.

This study is of particular significance because the invasion
of the Great Lakes by zebra mussels in the late 1980s and round gobies in the early 1990s (Jude et al. 1992) represents a new mechanism for the mobilization of toxic organic contaminants, such as PCNs and PCBs, from benthic organisms to higher trophic levels. Zebra mussels are filter feeders and feed primarily on algae, plankton, and other suspended materials in the water column (Bruner et al. 1994). Large round gobies (> 50-mm length) feed primarily on zebra mussels less than 20 mm in length (Jude et al. 1995; French and Jude 2001). Prior to the invasion of round gobies into the Great Lakes, relatively few species there consumed zebra mussels (French 1993). Therefore, toxic substances accumulated in zebra mussels were released to decomposers only after the mussels died. Because zebra mussels are an important component of the round goby diet, the invasion and spread of round gobies created a mechanism for the transfer of toxic substances in zebra mussels to higher trophic levels. This is because round gobies are reported in the diets of game fishes such as walleye, smallmouth bass, and rock bass (Jude et al. 1995). The effects of the invasion of zebra mussels and of round gobies on the movement of toxic substances from benthic organisms to higher trophic levels are a subject of potential public and environmental health concern (Morrison et al. 1998).

In this study, samples were collected from the Raisin, Saginaw, and St. Clair Rivers, where both zebra mussels and round gobies have invaded. Phytoplankton, amphipods, and benthic algae were also collected from the Raisin and St. Clair Rivers for determination of the extent and profile of PCN accumulation in these lower trophic level organisms. PCBs, including coplanar congeners, were also analyzed in the samples for comparison of their trophic transfer with those of PCNs in zebra mussels and round gobies. 2,3,7,8-Tetrachloro-dibenzo-p-dioxin equivalents (TEQs) of PCNs (PCN-TEQs) and PCBs (PCB-TEQs) were calculated for evaluation of the relative importance of these two class of organochlorine pollutants in the benthic chain of the Great Lakes.

Materials and Methods

Sampling

Smallmouth bass, largemouth bass, round gobies, and zebra mussels were collected from various locations within 1 km of the Raisin River mouth to Lake Erie (Figure 1). Smallmouth bass were collected near the mouth of the Raisin River and below the highway 24 bridge dam. Amphipods, phytoplankton, and benthic algae were collected at one site within 1 km of the river mouth. Smallmouth bass, round gobies, zebra mussels, phytoplankton, and benthic algae were collected from the St. Clair River at its confluence with the Belle River, at Marine City, and at Algonac (Figure 1). Round gobies and zebra mussels were collected from the Saginaw River. All of the samples were collected during July–November 1998 and 1999 (Table 1). Several hundreds of zebra mussels were collected from their rocky substrates at each location by snorkeling or SCUBA diving. Zebra mussels ranged in size from 3 to 24 mm. Round gobies generally eat zebra mussels ranging in size from 3 to 12 mm (Jude et al. 1995). Fish were collected by seineing or by electroshocking. Amphipods were collected by turning over rocks and using forceps to collect individual organisms. Phytoplankton was collected using a 10-μm plankton net. The phytoplankton samples collected using the 10-μm net may contain zooplankton and suspended particles. Nevertheless, zooplankton levels are generally low in these rivers. Benthic algae were collected by scraping hard surfaces with a toothbrush (for nonfilamentous forms), or by hand-picking tufts of filamentous algae. Skinless fillets were analyzed for fish except round gobies, for which the whole body was analyzed. Soft tissues were analyzed for zebra mussels. Tissues from several individuals per species were pooled to obtain adequate mass for extraction.

Chemical Analysis

Chloronaphthalene (CN) and chlorobiphenyl (CB) congeners were analyzed following the method described elsewhere, with some modifications (Kannan et al. 2000). Samples (approximately 20 g for fish and zebra mussels, 1–4 g for phytoplankton, algae, and amphipods) were homogenized with anhydrous sodium sulfate and extracted in a Soxhlet apparatus for 16 h using dichloromethane and hexane (400 mL, 3:1). An aliquot of the concentrated extract was used for the determination of fat content by gravimetry. Extracts were then treated with sulfuric acid in a separatory funnel. The solution was concentrated to 2 ml and passed through silica gel packed glass columns. Aliquots of extracts were injected into a gas chromatograph (Perkin Elmer series 600) equipped with a 63Ni electron capture detector (GC-ECD) for the determination of total PCB concentrations.

Identification and quantification of di-, mono-, and non-ortho PCBs and individual PCN congeners were accomplished with a Hewlett Packard 6890 series high-resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700D high-resolution mass spectrometer (HRMS). Di-, mono-, and non-ortho coplanar PCBs and PCN congeners were separated from other ortho-substituted PCBs and pesticides by passing the extracts through a porous Hypercarb graphite carbon column (100 × 4.6 mm, 7-μm particle size; Thermo Hypersil-Keystone, Bellefonte, PA). Details of the fractionation procedure have been described elsewhere (Horii et al. 2001). A Shimadzu liquid chromatograph pump (LC-10AD) was employed to deliver solvents. The first fraction, eluted with 50% dichloromethane in hexane at a rate of 2.5 ml/min (20 ml), contained di- and mono-ortho substituted PCBs. The graphite column was then reversed and eluted with toluene (50 ml) to collect non-ortho coplanar PCBs and PCNs. The toluene fraction was further fractionated by passing the extracts through a Cosmosil 5-PYE column (pyrenyl ethyl group; 250 × 4.6 mm, 5-μm particle size; Nacalai Co., Osaka, Japan). The first fraction, eluted with 10 ml 10% dichloromethane in hexane, contained non-ortho coplanar congeners 77, 81, 126, and 169, and lower CNs. The second and third fractions, eluted with the same solvent mixture, contained more highly chlorinated naphthalenes. The fourth fraction contained the remaining...