

POLYCHLORINATED NAFTALENES AND DLPCBs

FOOD CHAIN ACCUMULATION OF POLYCHLORINATED NAPHTHALENES IN THE RAISIN RIVER, MICHIGAN, USA

Nobuyasu Hanari¹, Kurunthachalam Kannan², Yuichi Horii¹, Sachi Taniyasu¹, Nobuyoshi Yamashita¹, David J. Jude³, John P. Giesy²

¹National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Japan

²National Food Safety and Toxicology Center, Michigan State University, East Lansing, Michigan, USA

³Center for Great Lakes and Aquatic Sciences, 501 East University, Ann Arbor, Michigan, USA

Introduction

Polychlorinated naphthalenes (PCNs) are widespread, persistent environmental pollutants. PCNs have been detected in air, water and biota samples collected from the remote oceans including the Arctic and the Antarctic oceans¹⁻³. An earlier study has reported bioaccumulation of PCNs in a marine food web of the Baltic Sea^{4,5}. Patterns of PCNs retained in biota vary widely. It has been suggested that PCNs tend to bioconcentrate and biomagnify in lower trophic level organisms including fish, while biomagnification is less (<1) in biota at the higher trophic level in the food chain such as predatory birds, marine mammals and fishes. While the earlier study has made been in the marine food web, in this study, aquatic organisms collected in the Raisin River, Michigan, were analyzed for PCN congeners to examine food chain accumulation. Food chain accumulation of PCNs was compared with those of polychlorinated biphenyls (PCBs).

Material and Methods

The food chain samples analyzed in this study include, smallmouth bass, largemouth bass, round goby, zebra mussel, amphipods, phytoplankton and benthic algae. Muscle tissues were analyzed for fishes and soft tissues were analyzed for zebra mussel. Samples were collected from the Raisin River in Michigan during Sep-Oct 1999. A few samples collected in Sep-Oct 1998 were also used. Tissues from several individuals were pooled to obtain representative samples. Chloronaphthalene (CN) and chlorobiphenyl (CB) congeners were analyzed following the method described elsewhere with some modifications⁶. PCB congeners were identified and quantified using a gas chromatograph (Perkin Elmer series 600) equipped with ⁶³Ni electron capture detector (GC-ECD). Identification and quantification of 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). The mass resolution of the spectrometer was greater than 10⁻⁴ mass units. Separation of PCN congeners was achieved by DB-17. The column oven temperature was programmed from 70 (1 min) to 180 °C at a rate of 15 °C /min, and then to 270 °C at 2 °C /min with a final hold time of 10 min. CN and CB congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster.

Results and Discussion

Concentrations of total PCNs in biota from the Raisin River were 30 to 6000 times less than those of total PCB concentrations. Total PCN concentrations were the greatest in zebra mussel and round

POLYCHLORINATED NAFTALENES AND DLPCBs

goby with concentrations as great as 24660 and 40350 pg/g, wet wt, respectively (Table 1), which can be explained by great lipid content in the tissues of these two species. Lipid-normalized concentrations of PCNs were also greater in these two species (~800 ng/g, lipid wt) than the other fishes or biota samples analyzed. Concentrations of total PCNs in zebra mussel and round goby were greater than those reported for mussels and fishes from the Baltic Sea ^{3,7}. The highest concentration of 40350 pg/g, wet wt, found in round goby muscle was greater than the highest concentration reported for fishes from the Detroit River in Michigan ⁶. These results suggest the presence of sources of PCN contamination in the Raisin River.

The wet weight based concentrations of PCNs were greater by a factor of 10 in zebra mussels and round gobies than in phytoplankton and amphipods. Lipid-normalized concentration of total PCNs in zebra mussels and round goby were 5 to 6 fold greater than those in amphipods or phytoplankton, suggesting a biomagnification factor of ~6 in zebra mussel. The diet of small round gobies (<5 cm) consists of amphipods whereas larger gobies feed on zebra mussels. Concentrations of PCNs in zebra mussels were comparable to those in round gobies suggesting their similar feeding habits. The round gobies analyzed in this study were less than 5 cm in length. A sample of benthic algae contained PCN concentration as great as 1090 ng/g on a lipid wt basis. The greatest concentration of PCNs in this primary producer may be due to its association with sediments. PCNs because of their planar structure tend to be associated with sediments. Concentrations of PCNs in smallmouth bass were less than those in round goby although it has been suggested that smallmouth bass feeds on round goby in certain locations in the Great Lakes. Both wet and lipid weight normalized concentrations of total PCBs were less in zebra mussels and round goby than in amphipods and phytoplankton. The number

Table 1. Range and mean concentrations of total PCNs (pg/g, wet wt) and total PCBs (ng/g, wet wt) in biota from the Raisin River, Michigan

Species	n	Date of collection	Lipid content (%)	Total PCNs (pg/g, wet wt)	Total PCBs (ng/g, wet wt)
Largemouth bass	1	22-Sep-99	0.98	3010	1745
Smallmouth bass	3	29-Sep-98	0.59 (0.5-0.67)	40.7 (15-78)	49.8 (44-61)
Round goby	3	15 Oct 98, 22 Sep 99	2.42 (2.18-2.61)	19670 (7740-40350)	2930 (1990-4700)
Zebra mussel	2	15 Oct 98, 20 Sep 99	2.8 (2.41-3.19)	22610 (20560-24660)	1865 (814-2900)
Phytoplankton	1	13-Oct-99	0.99	1650	10230
Amphipods	1	1-Sep-99	1.28	1842	4758
Benthic algae	1	1-Sep-99	0.25	2722	194

of samples analyzed is small and further analysis is being performed. The invasion of zebra mussels and round goby into the Great Lakes basin has resulted in alteration of food web structure, which should be examined in details to evaluate the sinks and sources of the flow of energy and toxic substances.

Tetra and penta-CN's were the predominant congeners collectively accounting for 62 to 86% of the total PCNs in biota collected from the Raisin River (Fig. 1). Proportion of di- and tri-CN's to total PCN concentrations in phytoplankton were greater than those in fishes. Octa-CN was found in smallmouth

POLYCHLORINATED NAFTALENES AND DLPCBs

bass. Although a slight shift in congener ratios with an increase in trophic level in the food chain could be discerned, the profile of greater tetra- and penta-CN in biota appears to be a characteristic of this location. Fishes from the Detroit River contained greater proportions of penta- and hexa-CN⁶.

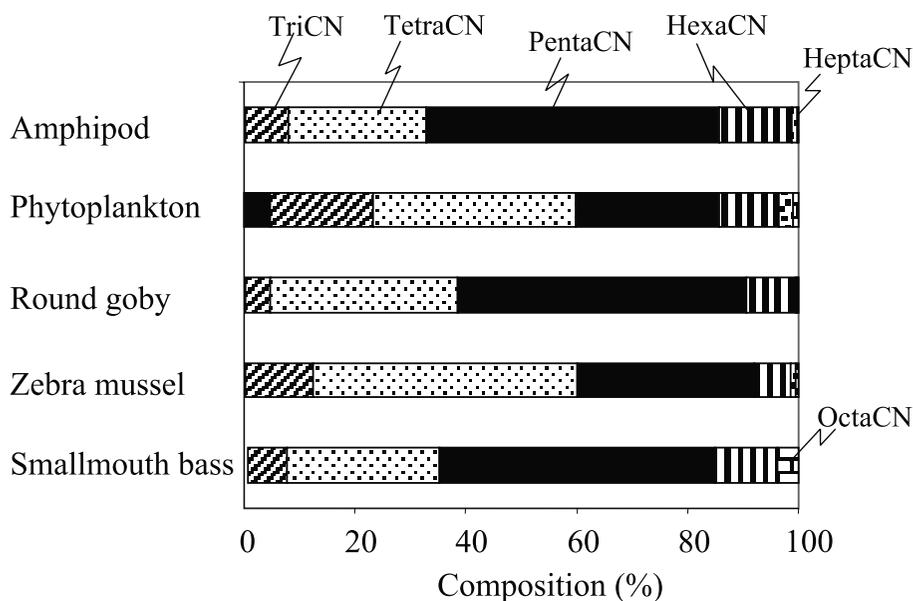


Figure 1. Homologue profile of PCNs in biota collected from the Raisin River, Michigan

PCN congeners that elicit dioxin-like activity were found in most of the biota analyzed. These include congeners 12357+12467, 12367, 12456, 12378, 123467+123567, 123568, 123578, 123456, 123678 and 1234567. The 2,3,7,8-tetrachloro-dibenzo-p-dioxin equivalents were calculated based on the relative potencies derived from H4IIE-bioassays^{8,9}. Similar to that observed for total PCN concentrations, TEQs contributed by PCNs increased with the trophic level. The greatest PCN-TEQ of 5.7 pg/g, wet wt, was found in the muscle tissue of round goby. The measured TEQs are similar to those reported in fishes from the Detroit River, where TEQs contributed by PCNs were comparable to those of the TEQs contributed by PCBs.

Table 2. Mean dioxin-like toxic equivalents (TEQs; pg/g, wet wt) contributed by PCNs in biota from the Raisin River, Michigan

Species	n	PCN-TEQs
Largemouth bass	1	0.3821
Smallmouth bass	3	0.0048
Round goby	3	3.0255
Zebra mussel	2	1.6344
Phytoplankton	1	0.23

POLYCHLORINATED NAFTALENES AND DLPCBs

Amphipods	1	0.35
Benthic algae	1	0.35

References

1. Helm, P.A., Bidleman, T.F., Stern, G.A. and Koczanski, K. (2002). *Environ. Pollut.*, 119, 69-78.
2. Harner, T., Kylin, H., Bidleman, T.F., Halsall, C., Strachan, W.M.J., Barrie, L.A. and Fellin, P. (1998). *Environ. Sci. Technol.*, 32, 3257-3265.
3. Corsolini, S., Kannan, K., Imagawa, T., Focardi, S. and Giesy, J.P. (2002). *Environ. Sci. Technol.* (in press).
4. Falandysz, J. and Rappe, C. (1997). *Environ. Sci. Technol.*, 30, 3362-3370.
5. Falandysz, J. (1998). *Environ. Pollut.*, 101, 77-90.
6. Kannan, K., Yamashita, N., Imagawa, T., Decoen, W., Khim, J.S., Day, R.M., Summer, C.L. and Giesy, J.P. (2000). *Environ. Sci. Technol.*, 34, 566-572.
7. J@rnberg, U., Asplund, L., de Wit, C., Egebäck, A-L., Wideqvist, U. and Jakobsson, E. (1997). *Arch. Environ. Contam. Toxicol.*, 32, 232-245.
8. Blankenship, A.L., Kannan, K., Villalobos, S.A., Villeneuve, D.L., Falandysz, J., Imagawa, T., Jakobsson, E., and Giesy, J.P. (2000). *Environ. Sci. Technol.*, 34, 3153-3158.
9. Villeneuve, D.L., Kannan, K., Khim, J.S., Falandysz, J., Nikiforov, V.A., Blankenship, A.L., and Giesy, J.P. (2000). *Arch. Environ. Contam. Toxicol.*, 39, 273-281.