MEDIUM CHAIN CHLORINATED PARAFFINS IN GREAT LAKES FOOD WEBS

Derek Muir[1], Eric Braekevelt[2], Gregg Tomy[2], and Mike Whittle[3]

[1]Environment Canada, National Water Research Institute, Burlington ON
[2] Dept of Fisheries and Oceans, Winnipeg MB
[3] Dept of Fisheries and Oceans, Burlington ON

Introduction

Chlorinated Paraffins (CPs) are produced by chlorination of straight-chained paraffin fractions that are derived from distilled *n*-alkane feedstocks[1]. The products can be subdivided into three fractions depending on chain length (short-chained (C_{10-13}) chlorinated paraffins, SCCPs; medium-chained (C_{14-17}) chlorinated paraffins, MCCPs and long-chained ($C_{>17}$) chlorinated paraffins, LCCPs). MCCPs are mainly used as secondary PVC plasticisers. Further uses are as extreme pressure additives in metal working fluids, as plasticisers in paints and rubber, as additives to adhesive and sealants, in fat liquors used in leather processing, as flame retardants in other polymeric materials, and as solvents in carbonless copy paper[2]. A higher proportion of total MCCP production is used in lubricating additives and in rubber products in North America compared to the EU[3]. In 1998, production of SCCPs, MCCPs and LCCPs was 7.9, 17.8, and 12.7 kT, respectively, in North America, which highlights the importance of MCCPs compared to SCCPs and LCCPs[3].

There have been very few measurements of MCCPs in samples from the aquatic environment. Early work in the UK by Campbell and McConnell[4] reported MCCP-like compounds (C_{10}-C_{30}) using argentation –TLC (i.e. semi-quantiative). A recent study of SCCPs and MCCPs in the UK included sediments from 20 sites[5]. Both SCCPs and MCCPs were judged to be widely distributed in the UK environment[5]. Kemmlein et al.[6] determined C_{14}-C_{29} CPs in 4 coastal marine sediment samples collected near a CP manufacturer in Yarraville, Australia using carbon skeleton analysis (dechlorination of CPs to corresponding n-alkane). Their results showed about 3-fold higher concentrations of MCCPs (C_{14}-C_{17}) compared to LCCPs (C_{18}-C_{29}). In the USA, a creek near a manufacturing plant in Ohio (Sugar Creek)[7] had low ng/g (dry wt) concentrations of C_{14}-C_{17} CPs in sediment and zebra mussels. Low ng/g (dry weight) concentrations of C_{14}-C_{17} MCCPs were detected in sediment samples collected near the mouth of the Detroit River in Western Lake Erie[8]. In the same study, higher MCCP concentrations were found in catfish (904 ng/g wet wt) than in perch (82 ng/g ww).

The goal of this study was to develop a more comprehensive dataset on MCCPs in water and biota in the Great Lakes for use in exposure assessment of the compounds in Canada. A related goal was to compared results with SCCPs determined in the same samples and with other reports on MCCPs in environmental samples

Materials and Methods

Sample collection: Lake water and food web samples were collected in Lake Ontario and in northern Lake Michigan during June and August 2001, respectively (Table 1). Food web samples were collected and processed as whole individuals (lake trout) or composites of whole individuals (forage fish & invertebrates).

Table 1. Samples collected for analysis of medium chain chlorinated paraffins

Sample type	Details	N
Water	Duplicate 60L water samples;northern Lake Michigan in mid-June 2001 and from central Lake Ontario in mid-August 2001. CPs extracted using XAD-2 resin. Water prefiltered with GFF filter.	4
Zooplankton	vertical haul above thermocline with 100 um mesh net.	4
Mysis	picked from plankton net. This is a macro zooplankton with diurnal migration through water column.	4
Diporeia	Benthic invertebrate if available. Not found in northern Lake Michigan due to large number of zebra mussels.	2
Forage fish	(2 pools; smelt (omnivore), slimy sculpin (benthivore) and alewife (planktivore))	12
Lake trout	6 individuals per lake	12

Analysis: XAD column extracts of lake water were eluted with methanol and DCM. The combined extract was washed with precleaned water to remove methanol. The DCM was dried over sodium sulfate, evaporated to small volume in a rotary evaporator, exchanged into hexane and then prepared for GC-ECNIMS analysis without further cleanup. Biota samples were extracted using procedures identical to other studies on PCBs and persistent organochlorines in biological samples [9]. In brief: Homogenized tissue was mixed with precleaned sodium sulfate to form a dry powder and Soxhlet extracted for 6 hrs with dichloromethane (DCM). Gel permeation chromatography was used to remove lipids using hexane: DCM (1:1) as elution solvent. Extractable lipids were determined gravimetrically on the first 150 mL of GPC eluate by evaporating off the solvent. The GPC eluate was reduced to small volume and chromatographed on activated Silica Gel (8 g in a 1.1 cm dia chromatographic column) to separate PCBs from CPs and other organochlorines. Reagent blanks were analysed for each batch of samples. An NIST 1974a mussel reference material was used although at the present time we have no certified values for SCCPs or MCCPs. All results were blank subtracted prior to reporting.

Sample were analysed by GC-high resolution electron capture negative ion MS using the procedure of Tomy and Stern[8]. Prior to instrumental analysis they were reduced to an appropriate final volume under gentle nitrogen stream and $^{13}C_8$-mirex was added as an internal standard. This method involved monitoring of $[M\text{-}Cl]^-$ ions of specific m/z values corresponding to the molecular formulas of all major C_{14}-C_{17} MCCPs i.e. Cl_5 to Cl_{10} substituted homologs. Corrections were made for the fractional abundance of specific m/z value and number of Cl atoms. Quantitation was performed by comparing the response for specific m/z values in the sample to that of an external standard. The external standard was a commercial C_{14}-C_{17} MCCP with 53% chlorine.

Results and Discussion

MCCPs were not detected in filtered samples of surface water from Lake Ontario or Lake Michigan (DL=20 pg/L for total MCCPs). However SCCPs were present at concentrations ranging from 300-1200 pg/L in Lake Ontario, similar to previous results[10]. SCCPs were undetectable in northern Lake Michigan surface waters (<100 pg/L).

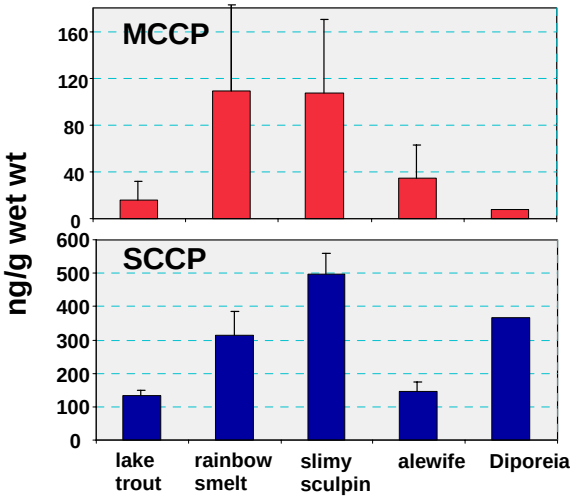

Figure 1. Mean concentrations (± SD) of MCCPs and SCCPs in Lake Ontario food web samples

MCCPs were detected in all food web samples from Lake Ontario and northern Lake Michigan at low ng/g concentrations. In Lake Ontario, highest concentrations were found in slimy sculpin and rainbow smelt and lowest concentrations in lake trout and Diporeia (Figure 1). MCCP concentrations in lake trout (whole fish) ranged widely from 1.8 to 43 ng/g ww. There was no clear relationship of MCCP concentration with age or size of lake trout. Proportions of various MCCP chain length groups also differed among species. The C_{15} MCCPs predominated in smelt, sculpin and alewife while the C_{14} group predominated in lake trout.

SCCPs were also present in the same samples from Lake Ontario at similar or higher concentrations than the MCCPs (Figure 1). C_{12} SCCPs predominated in lake trout while C_{11} was the major SCCP in sculpin and smelt. SCCP concentrations were about 2.5x lower in the samples from 2001 compared to lake trout of similar age collected in 1996 and reported on previously[10]. The lower average % lipid in the 2001 samples may account from some of the difference. MCCPs were not determined in the samples from 1996.

Biomagnification of MCCPs and SCCPs in the Lake Ontario food web is examined in Table 2. MCCPs and C_{14} to C_{17} chain-length groups had very low BMFs between the three forage fish species and lake trout compared with the SCCPs. By comparison large BMFs were observed between Diporeia and sculpin especially for C_{15}-C_{17} MCCPs. The SCCPs, in contrast, had much higher BMFs especially for C_{12} and C_{13} SCCPs in the same food web. The alewife to lake trout BMF exceeded 1 as did the results for these chain length groups in Diporeia to sculpin.

The present study is the first to examine food web transfer of chlorinated paraffins. The high

Table 2. Biomagnification factors[1] for MCCPs and SCCPs in the Lake Ontario food web

Group	LT – alewife	LT - smelt	LT-sculpin	Sculpin-Diporeia
MCCPs	0.09	0.05	0.05	5.2
SCCPs	0.91	0.43	0.27	1.4
C_{10}	0.43	0.27	0.17	1.3
C_{11}	0.94	0.35	0.22	1.6
C_{12}	1.1	0.56	0.37	1.2
C_{13}	1.5	0.68	0.35	1.1
C_{14}	0.27	0.16	0.10	2.7
C_{15}	0.04	0.02	0.03	9.56
C_{16}	0.01	0.01	0.01	14.5
C_{17}	0.00	0.00	0.00	11.5

[1]Biomagnification factor = lipid wt concentration in predator/lipid wt concentration in prey

BMFs for MCCPs from Diporeia to sculpin are consistent with the BMFs found in laboratory feeding studies[11, 12], however, the transfer to lake trout from forage fish has a BMF <1 indicating that degradation is occurring both in the predator and possibly in the prey species. Biotransformation of MCCPs by major lake trout prey species, the alewife and smelt, as well as by the lake trout could explain the low BMFs.

Acknowledgments
We thank Steve Cagampan and Mike Comba for sediment extraction and Camilla Teixeira and Maxim Chigak for extraction of water samples.

References
[1]Tomy, G.T., Fisk, A.T., Westmore, J.B., and Muir, D.C.G. (1998) Rev. Environ. Contam. Toxicol. 158, 53.
[2]OSPAR (Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic) (2001). OSPAR 01/4/8-E. 65 pp.
[3]CPIA (Chlorinated Paraffin Industry Association) (2000). Unpublished data. CPIA, 1250 Connecticut Ave., NW, Suite 700,Washington, DC 20036
[4]Campbell, I. and McConnell G. (1980). Environ. Sci. Technol. 14,1209.
[5]Nicholls, C.R., Allchin, C.R., and Law, R.J. (2001). Environ. Pollut. 114, 415.
[6]Kemmlein, S., Hermeneit, A., and Rotard, W. (2002). Organohalogen Compounds 59, 279.
[7]Murray, T.M., Frankenberry, D.H., Steele, D.H., and Heath, R.G. (1988) U.S. Environmental Protection Agency, EPA/560/5 87/012. Vol.1, 150pp.
[8]Tomy, G.T. and Stern, G.A. (1999). Anal. Chem. 71, 4860.
[9]Muir, D.C.G., Jones, P.D., Karlsson, H., Koczansky, K., Stern, G.A., Kannan, K., Ludwig, J.P., Reid, H., Robertson, C. J.R. and Giesy, J.P. (2002). Environ. Toxicol. Chem. 21, 413.
[10]Muir, D., Bennie, D., Teixeira, C., Fisk, A., Tomy, G., Stern, G., and Whittle, M. (2000). In: *Persistent Bioaccumulative and Toxic Substances*, Vol 2. Lipnick, R., Jansson, B., Mackay, D., and Patreas, M. (Eds). ACS Books, Washington DC, pp. 184-202.
[11]Fisk, A.T., Cymbalisty, C.D., Tomy, G.T., and Muir, D.C.G. (1998). Aquat. Toxicol. 43, 209.
[12]Fisk, A.T., Tomy, G.T., Cymbalisty, C.D., and Muir, D.C.G. (2000). Environ. Toxicol. Chem. 19, 1506.