TOXAPHENE TRANSFER IN THE MARINE FOOD WEB OF THE ST LAWRENCE ESTUARY, CANADA

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Introduction

Technical toxaphene, a pesticide made of chlorinated bornanes (CHBs), has been heavily used in North America, mainly in southern USA but also in Canada. Despite its ban in 1982, toxaphene is still one of the prominent organochlorinated contaminants in the Canadian Arctic environment[1]. Its presence in regions far away from known sources has been ascribed to long-range atmospheric transport[2]. In the St Lawrence Estuary (SLE), high concentrations of toxaphene have been reported in beluga whales[3]. However, no other studies were conducted on toxaphene in the SLE biota. There is a clear need for more information on toxaphene contamination in organisms from this specific marine system.

The aim of this study was to report concentrations of toxaphene in several organisms from the SLE and to examine the fate of this contaminant through the food web. More specifically, we have investigated if $\delta^{15}N$, an indicator of trophic level, could be used in association with contaminant levels to describe the biomagnification of toxaphene in the SLE marine food web.

Materials and Methods

Sampling: All samples were obtained from animals collected between 1997 and 2000 in the SLE. Additional information on these samples is reported in Table 1.

Table 1: Description of samples collected in the St Lawrence Estuary.

Species	Common name	Abbreviation	Tissue	Sample	Number
Nereis virens		NV	whole	pool	2
Maldane sarsi		MS	whole	pool	3
Pandalus borealis	Shrimp	SH	muscle	pool	3
	Zooplankton	ZO	whole	pool	5
Osmerus mordax	Rainbow smelt	RS	liver	pool	4
Clupea harengus harengus	Atlantic herring	AH	liver	pool	3
Anguilla rostrata	American eel	AE	muscle	individual	5
Microgadus tomcod	Atlantic tomcod	AT	liver	pool	2
Pleuronectes putnami	Smooth flounder	SF	liver	pool	3
Reinhardtius hippoglossoides	Greenland halibut	GHM	muscle	individual	3
Reinhardtius hippoglossoides	Greenland halibut	GHL	liver	individual	3
Phoca vitulina	Harbour seal	HS	blubber	individual	4
Delphinapterus leucas	Female Beluga	FB	blubber	individual	5
Delphinapterus leucas	Male Beluga	MB	blubber	individual	5

Toxaphene analysis: Seven specific toxaphene congeners (P-26, P-40, P-41, P-44, P-50, P-62 and P-69), reported as ΣCHB, were determined in biological samples according to the method described in Gouteux et al.[4]. In brief, each sample was chemically dried with anhydrous sodium sulfate and spiked with $^{13}C_{12}$ PCB (170). Contaminants and lipids were extracted with 50% dichloromethane in hexane and the extract was spiked with a labelled surrogate compound (D_8-4,4'-DDT). Lipids were then removed by gel permeation chromatography (GPC). The GPC fraction containing organochlorinated compounds was subjected to alumina/neutral silica and neutral silica column chromatographies. The final extract was concentrated and spiked with $^{13}C_{12}$ PCB (101) for instrument performance control. Analyses were performed using a gas chromatograph (GC) equipped with a programmable split/splitless injector. Chromatographic separations of 5 µL sample injections were made on a DB-5MS column. The GC was coupled with an ion trap mass detector. The ionisation was done in electronic impact mode and the ion trap was operated in MS/MS mode. The accuracy of the analytical method was evaluated using three different natural matrices spiked with a known quantity of CHBs. Recoveries of CHBs varied between 89 and 106 % (C.V.15 %).

Stable isotope analysis: Samples used for toxaphene analysis were also analysed for stable nitrogen isotopes, ^{14}N and ^{15}N, excepted that skin samples from marine mammals were used instead of blubber. Stable nitrogen isotopes were determined according to the method reported in Lesage et al.[5]. In brief, dried samples were combusted in an elemental analyser and sample gases introduced in an isochrom continuous-flow mass spectrometer. All samples were standardised against N_2 in air and ^{15}N isotope abundance expressed, by convention, in delta notation (‰). Replicates using laboratory standards indicated an analytical error of ± 0.2 ‰.

Results and Discussion

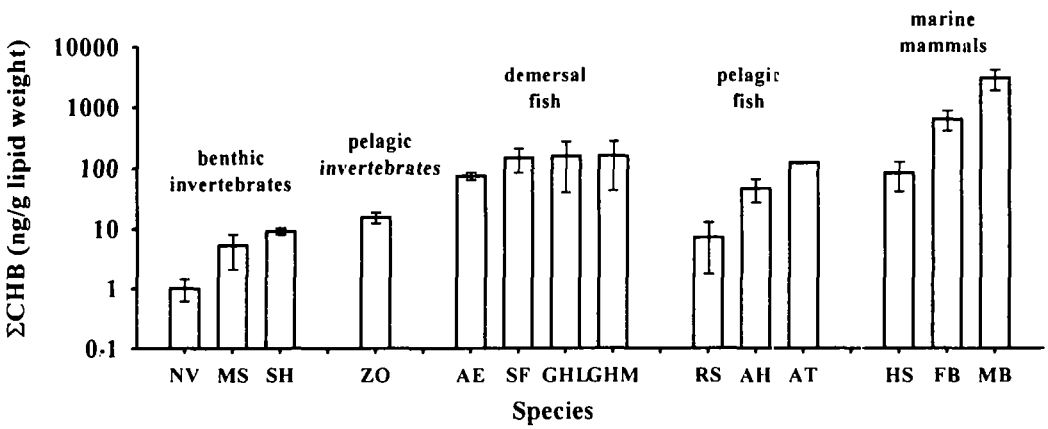

Figure 1: Mean concentrations of ΣCHB (lipid weight) in biota from the SLE. Ranges and standard deviations are indicated for species represented by two or more than three samples, respectively.

Concentrations of toxaphene in the St Lawrence Estuary food web. Toxaphene was detected in all organisms analysed. Mean concentrations of ΣCHB ranged from about 1 ng/g lipid weight in worms to 3000 ng/g lipid weight in male beluga whales, increasing from benthic invertebrates to marine mammals (Figure 1). Congeners P-50 and P-26 were predominant in all samples, representing in average 80% of ΣCHB, whereas P-69 was not detected in any samples. ΣCHB

concentrations in the same samples were about 10 to 100 times lower than those observed for ΣPCB and ΣDDT.

Relationship between toxaphene concentrations and $\delta^{15}N$. Stable nitrogen isotope ratios ($\delta^{15}N$) increase from prey to predator because of the enrichment of ^{15}N relative to ^{14}N. Then, $\delta^{15}N$, an index of trophic level, can be used in relation with contaminant levels to describe biomagnification of organochlorinated contaminants in marine food webs[6]. Linear regression relationship of the logarithm of ΣCHB (ng/g wet weight) in organisms from the SLE versus $\delta^{15}N$, is shown in Figure 2. The weak positive correlation between ΣCHB and $\delta^{15}N$ indicates that $\delta^{15}N$ is not a good predictor of toxaphene concentrations in the organisms from the SLE marine food web. Very similar results ($r^2 = 0.22$; $p = 0.09$) were obtained with ΣCHB concentrations reported on a lipid weight basis. The complexity of the SLE food web could explain the lack of relationship between ΣCHB and $\delta^{15}N$ in the examined organisms. For instance, the two top consumers in the SLE food web, beluga whales and harbour seals, are believed to have a different diet. Apparently, beluga whales depend mainly on a benthic food web whereas harbour seals feed mostly on pelagic organisms[5]. Although beluga whales and harbour seals are permanent residents of the SLE, many fish species migrate during the year (e.g. American eel, Atlantic herring). Therefore, fish species with high mobility capacities are possibly part of several food webs (*e.g.* Great Lakes, Gulf of St Lawrence). Better knowledge of the basic structure of pelagic and benthic food webs prevailing in the SLE is mandatory to properly assess the relationship between ΣCHB and $\delta^{15}N$. In addition, factors such as the age of the organisms and their lipid content are known to have an effect on the levels of ΣCHB bioaccumulated by the organisms. Variation of these factors in organisms from a given trophic level is expected to obscure the possible relationship between ΣCHB and $\delta^{15}N$.

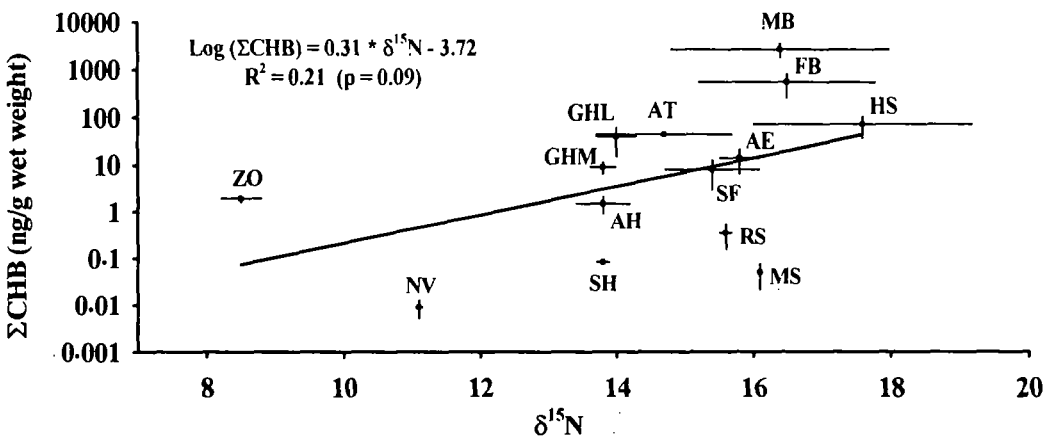

Figure 2: Mean concentrations of ΣCHB versus $\delta^{15}N$ in biota from the SLE. Ranges and standard deviations are indicated for species represented by two or more than three samples, respectively.

Relationship between toxaphene concentrations and lipids. Lipid content appears to be a key factor in explaining toxaphene concentrations in organisms, even more important in some food webs than the trophic level of the organisms[7,8]. Linear regression relationship of the logarithm of ΣCHB (ng/g wet weight) in organisms from the SLE versus logarithm of the lipid content (%), is

shown in Figure 3. Significant positive correlation between ΣCHB and lipid content indicates that lipid content does represent a very good predictor of toxaphene concentrations in the biota of the SLE marine food web.

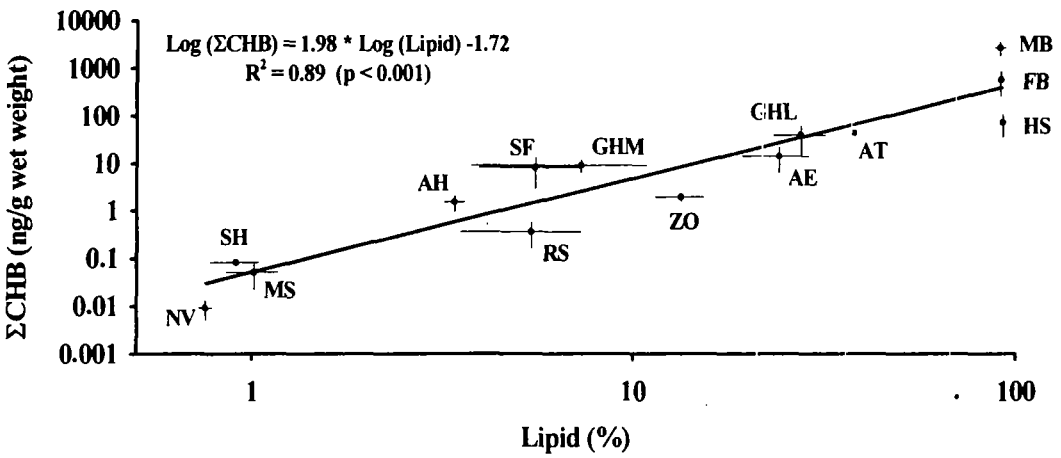

Figure 3: Mean concentrations of ΣCHB versus lipid content in biota from the SLE. Ranges and standard deviations are indicated for species represented by two or more than three samples, respectively.

In summary, toxaphene was detected in all organisms examined from the SLE. As expected, the highest concentrations were found in marine mammals. In such a complex food web, however, lipid content is better than trophic level to describe concentrations of toxaphene in the organisms.

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