

IDENTIFICATION AND DETERMINATION OF DECHLORINATION PRODUCTS OF DECHLORANE 602 IN GREAT LAKES FISH AND ARCTIC BIOTA

Shen L^{1,2*}, Jobst K^{2,3}, Helm P², Reiner E^{2,4}, McCrindle R⁵, Tomy G⁶, Letcher R⁷, Blair D⁷, Brindle I¹, Marvin C³

¹Brock University, 500 Glenridge Avenue, St. Catharines, Canada; ²Ontario Ministry of the Environment, 125 Resources Road, Toronto, Canada; ³Environment Canada, 867 Lakeshore Road, Burlington, Canada; ⁴University of Toronto, Toronto, Canada; ⁵Wellington Laboratories Inc., Guelph, Canada; ⁶Fisheries and Oceans Canada, 501 University Crescent, Winnipeg, Canada; ⁷Environment Canada, Ottawa, Canada.

Introduction

Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), Dechlorane 604 (Dec604), and Dechlorane Plus (DP) are flame retardant substitutes of mirex, which have fire retardant properties similar to mirex (<http://www.inchem.org/documents/ehc/ehc44.htm>). DP is categorized by the United States EPA as a high production chemical (<http://www.epa.gov/hpvis/index.html>). Dec 602 and 604 are on the Non-domestic Substances List published by Environment Canada (http://www.ec.gc.ca/CEPARRegistry/subs_list/NonDomestic.cfm), which means that Dec602 and 604 are likely in commercial use today. Manufacture of DP began before 1970s, and was first detected in air, sediment, and fish samples from the Laurentian Great Lakes in 2006 after being produced for four decades¹. Similar to DP, Hooker Chemicals and Plastics Corp also patented Dec602, Dec603, and Dec604 to improve the fire retardant properties of polymers in the late 1960s and 1970s (*e.g.* United States Patent 3392136, 3687983 and 3891599). These three dechloranes were recently found in sediment and fish in the Great Lakes with widespread occurrence, and Dec 602 is more bioavailable and/or bioaccumulated by fish than DP².

It is well known that Mirex undergoes successive exchanges of its chlorine atoms with hydrogen in the environment, yielding several monohydro and dihydromirex isomers. The principal photochemical product is commonly called photomirex, which has similar bioaccumulation properties to Mirex. In this study, we present new findings from our continuing efforts to identify unknown compounds present in Great Lakes fish and our preliminary analysis of remote biota samples from the Canadian Arctic. We report on the identification and concentrations of dechlorination derivatives of Dec602 in Great Lakes fish and Arctic beluga whale and polar bear observed during the analysis of Dec602, 603, 604, and DP.

Materials and methods

Dec 602 was purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). Standards of *anti*-C₁₁DP, as well as a technical mixture of Dec602 and its dechlorinated derivatives, were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada).

Fish samples in this study were collected from Lake Superior in 2002, Lake Huron in 2001, and Lake Ontario in 1998 and 1999. Beluga whale samples were collected in 2000 and 2010 from Hendrickson Island. Adult male and female polar bear samples were collected from Coral Harbour in Nunavut during subsistence harvests in 2010 and 2011.

Selected ion monitoring (SIM) experiments were performed on a Waters Autospec high resolution mass spectrometer (HRMS, Waters Milford MA USA) equipped with a Hewlett-Packard HP 6890 gas chromatograph (GC) using a 15 m DB-5HT column (0.25 mm i.d, 0.10 µm film thickness; J&W Scientific, USA). The HRMS system was operated in EI positive mode with electron energy of 40 eV and was tuned up to 10,000 resolving power (RP) according to 10% valley definition. Concentrations of target analytes in the extracts were determined by monitoring the two most abundant ions of the fragment cluster at *m/z* 271.8102/273.8072 for Dec 602 and 262.8570/264.8540 for dechlorination derivatives of Dec602. The technical mixture of Dec602 and some of the sample extracts were also analyzed using a Varian TQ-FTMS (triple quadrupole-Fourier transform mass spectrometer) (Varian Inc., Walnut Creek, CA, USA) consisting of a Varian CP-8400 autosampler, a Varian CP-3800 GC, a Varian J320-MS (triple quadrupole), a Varian 920-MS (FTIMS), and a Varian 9.4 Tesla superconducting magnet. The FTMS system was operated in the EI mode (70 eV) at a mass resolution of 30 000 – 60 000 (10 % valley definition). Mass spectra were obtained using arbitrary waveform excitation and detection from *m/z* 150 – 650.

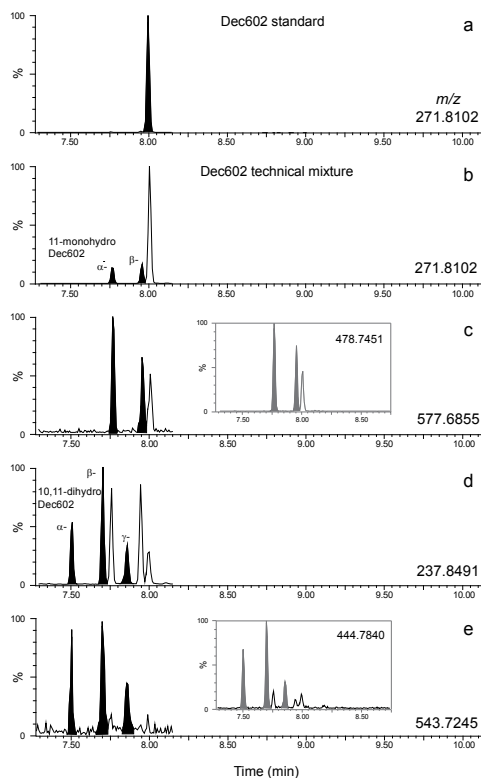


Figure 1. GC-HRMS selected ion chromatograms of (a) Dec 602 and (b – e) the monohydro- and dihydro-analogues of Dec 602 in the prepared technical mixture.

Results and discussion

Identification of the dechlorination products of Dec602. In the course of our previous studies of Dec602 in Great Lakes fish, we observed several unknown chromatographic peaks by monitoring $C_5Cl_6^{++}$ (m/z 271.8102 / 273.8072) and $C_5Cl_5H^{++}$ (237.8491 / 239.8462) with GC/HRMS. These unknowns eluted between Mirex and Dec602, and each had isotope distributions consistent with the theoretical values of $C_5Cl_6^{++}$ and $C_5Cl_5H^{++}$. This indicated that Dec602 may also undergo dechlorination in the environment, akin to the behaviour of Mirex. To investigate this further, a genuine standard of Dec602 and a technical mixture of its mono- and dihydroDec602 analogues were examined using GC-HRMS and GC-FTMS.

The GC-HRMS selected ion chromatograms of Dec602 and the technical mixture are shown in Figure 1. Three peaks are observed in the m/z 271.8102 selected ion chromatogram of the technical mixture (Figure 1b), which correspond to Dec602 and two diastereomers of 11-monohydroDec602 that are referred to α - and β -11-monohydroDec602 in this study for the first- and second-eluting isomers, respectively. The mass spectrum of Dec602 generated using FTMS is dominated by a peak at m/z 271.8093. The mass spectrum of the α -isomer is identical to that of the β -isomer, and shows that the isomers of monohydroDec602 generally produce $C_5Cl_6^{++}$ and $C_5Cl_5H^{++}$ in equal abundance. In addition to the chlorinated cyclopentadiene fragments, a significant peak at m/z 479 is also observed, which corresponds to the generation of ions M-Cl-HCl-CO. The selected ion chromatogram of Figure 1c shows that the molecular ion (M, m/z 577.6855) of monohydroDec602 can also be detected by GC-HRMS, but these ions are far less abundant than the cyclopentadiene fragments. The technical mixture also contains three more peaks in the m/z 237.8491 selected ion chromatogram labelled as α -, β -, and γ -10,11-dihydroDec602 (Figure 1d). These isomers each have identical mass spectra, which display m/z 238 ($C_5Cl_5H^{++}$) as the base peak. Similar to monohydroDec602, the molecular ion for dihydroDec602 (M, m/z 543.7245) and the M-Cl-HCl-CO (m/z 444.7840) ions are also observed (Figure 1e).

The selected ion chromatogram for m/z 237.8491 obtained from a tissue extract of Lake Ontario lake trout clearly indicates the presence of isomers of monohydro-Dec602 (α - and β -Cl₁₁Dec602) based on the following

criteria: a) the isotope distributions consistent with the theoretical values of $C_5Cl_5H^+$, b) the closely matched retention times, and c) mass spectra to those of the α - and β - isomers detected in the technical mixture. DihydroDec602 isomers were not identified in the lake trout extract according to the above criteria.

Monohydro-Dec602 in Great Lakes fish and Arctic beluga whale and polar bear. Quantification of $Cl_{11}Dec602$ were conducted via SIM mode by monitoring m/z 237.8491/239.8462 as they were the most abundant isotope ions at the EI energy of 38 eV. Dec602 were also quantified using m/z 271.8102/273.8072. Reported concentrations of the α - and β - $Cl_{11}Dec602$ isomers detected in the sample extracts should be considered semi-quantitative as there are currently no quantitative analytical standards available. The average of response factors of photomirex and $\alpha Cl_{11}DP$ generated using m/z 237.8491/239.8462 was used to quantify concentrations of α - and β - $Cl_{11}Dec602$ isomers in the samples.

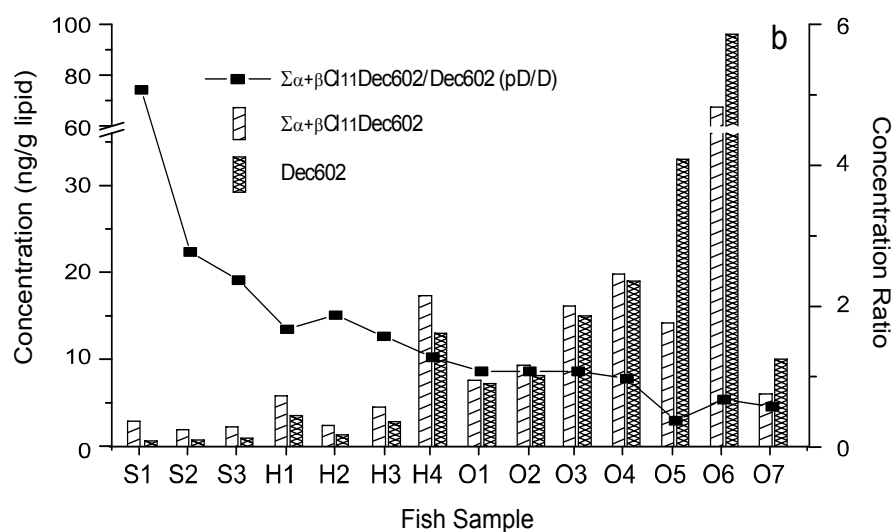


Figure 2. Concentrations and ratios of Dec602 and its monohydro-analogues in fish from Lakes Superior (S), Huron (H), and Ontario (O).

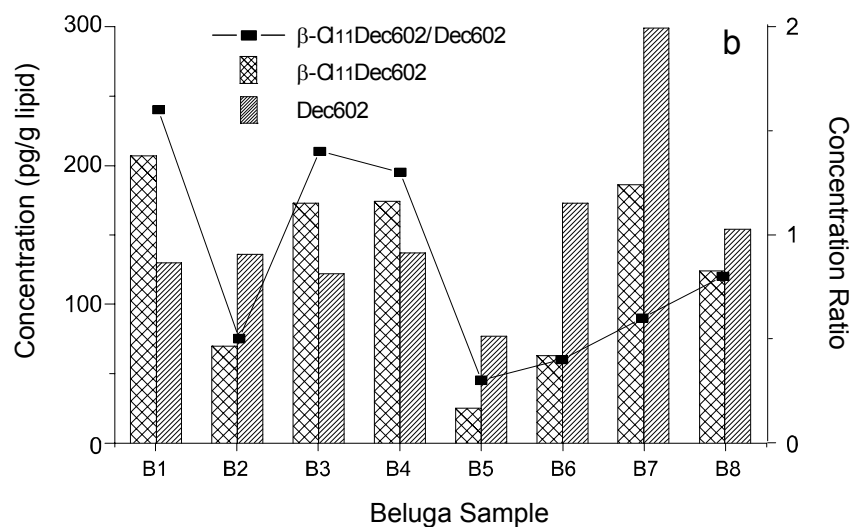


Figure 3. Concentrations and ratios of Dec602 and its monohydro analogues in Arctic Beluga.

The α - and β -Cl₁₁Dec602 isomers were found in all fish samples as shown in Figure 2. Concentrations were in the range (all ng/g lipid) of 1.6 - 50 for α -Cl₁₁Dec602, 0.65 - 20 for β -Cl₁₁Dec602, and 0.60 - 96 for Dec602. Manufacturing plants in Niagara Falls, NY, are important sources of Mirex and Dec602 to the Great Lakes, especially to Lake Ontario³. Similar to Mirex and Dec602, α - and β -Cl₁₁Dec602 were significantly greater in fish from Lake Ontario than the mean concentrations in fish from the upper Great Lakes (Lakes Superior and Huron) ($p < 0.05$; Student's t-test). The ratios of the sum of α - and β -Cl₁₁Dec602 to Dec602 (pD/D) in fish also showed differences between the upper Great Lakes and Lake Ontario. The total Cl₁₁Dec602 concentrations were greater than Dec602 concentrations in fish from the upper lakes, resulting in pD/D ratios ranging 1.3 - 5.1 compared to 0.43 - 1.1 in the Lake Ontario fish.

Dec602 was detected in all ten beluga whale and twenty three polar bear samples. Unlike the Great Lakes fish samples, only β -Cl₁₁Dec602 was found in Arctic biota. Lower concentrations were found for the Dec602-related compounds in beluga with β -Cl₁₁Dec602 ranging from 25 - 210 pg/g lipid and Dec602 ranging from 80 to 300 pg/g lipid. The ratio of β -Cl₁₁Dec602 to Dec602 ranged from 0.33 to 1.60 with an average of 0.9 (Figure 3). For the polar bear samples, the average ratio of β -Cl₁₁Dec602 to Dec602 is similar to that of beluga whale, but the concentrations of β -Cl₁₁Dec602 and Dec602 are much higher ranging from 0.2 - 15 ng/g lipid and 0.1 to 14 ng/g lipid, respectively.

Fate and dechlorination pathway. Mirex has been reported to be very resistant to biodegradation and metabolism in most terrestrial and aquatic organisms and environments, but it can slowly loses chlorine in the environment via indirect phototransformation in the presence of dissolved organic matter (DOM) in water⁴, yielding photomirex that has similar bioaccumulation properties and resistance to metabolism as Mirex. This study is the first to report the identification of hydroDec602 derivatives in biota, while there are no reports on the photochemical fate or transport of Dec602. As a poorly soluble compound in water, Dec602 may sorb to DOM and undergo phototransformation within the hydrophobic zones of DOM in a similar way to Mirex. Long range atmospheric transport of persistent organic pollutants such as organochlorine pesticides and polychlorinated biphenyls to the Great Lakes basin and to the Canadian arctic is well established. However, there are few reports detailing the direct measurement of Mirex and photomirex in the atmosphere of these areas. This limits confirmation of photochemical mechanisms acting upon Mirex, and compounds such as Dec602 and DP with similar chemistry during transport. The occurrence of Dec602 and β -Cl₁₁Dec602 in arctic beluga and polar bear in this study provides evidence of long range transport of Dec602 and its bioavailability to biota in remote environments. Further, only β -Cl₁₁Dec602 was detected in the arctic biota samples and was found in higher proportions in Lake Superior compared to Lake Ontario fish. These results indicate that the photochemical dechlorination mechanism of Dec602 might differ from Mirex, or may occur at a higher rate. The β -Cl₁₁Dec602 may also be the more persistent isomer, or may be more bioaccumulative than other Cl₁₁Dec602 isomers.

Acknowledgements

We thank Liad Haimovici (Ministry of Environment), Kerri Pleskach and Bruno Rosenberg (Fisheries & Oceans) for preparing the beluga samples for analysis. L. Shen and K. Jobst gratefully acknowledge financial support provided in part through the Canada-Ontario Agreement respecting the Great Lakes program. KJJ thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Visiting Fellowship.

References:

1. Hoh E, Zhu L, Hites RA. (2006) *Environ Sci Technol* 40:1184–1189
2. Shen L, Reiner EJ, Helm PA, Marvin CH, Hill B, Zhang X, MacPherson KA, Kolic TM, Tomy GT, Brindle ID (2011) *Environ Sci Technol* 45:3333–3340
3. Shen L, Reiner EJ, MacPherson KA, Kolic TM, Helm PA, Richman LA, Marvin CH, Burniston DA, Hill B, Brindle ID, McCrindle R, Chittim BG (2011) *Environ Sci Technol* 45:693–699
4. Burns SE, Hassett JP, Rossi MV (1996) *Environ Sci Technol* 30:2934–2941