



selective detector (70 eV ionization energy). ECNI experiments employed methane as a reagent gas. The concentration of MBP-Br<sub>6</sub>Cl was estimated relative to a pure standard hexachloro 1,1'-dimethyl-2,2'-bipyrrole, by GC-FID, using HP 5890 Series II GC, with a CP-Sil 5CB column (60 m, 0.25 mm i.d., 0.25 µm film thickness). Comparable relative response factors by FID have been observed for compounds with a similar number of carbons and a high degree of halogenation hence the standard used should adequately represent the response of MBP-Br<sub>6</sub>Cl.<sup>7,8</sup>

## Results and Discussion

The HOC fraction isolated from *D. delphis* was analyzed by low resolution GCMS with both EI and ECNI. In addition to observing many PCBs and pesticides (and their metabolites), several halogenated compounds whose spectra did not match any reported bioaccumulated HOCs were observed (Figure 2). The most abundant of these UHCs observed by GCMS had an isotopic cluster resembling a compound containing one chlorine and six bromine atoms (Figure 3) at 647 Da. This was confirmed as the molecular ion by GCMS-ECNI, for which no ions heavier than those in this ion cluster were seen. The exact molecular formula was determined by HR-GCMS. The measured accurate mass of the molecular ion was compared to masses calculated for species with the following isotopic restrictions: H (0-20), C (7-14), N (0-3), Cl (0-5), Br (0-7), O (0-4), S (0-2). The elemental composition with the smallest difference between the measured and calculated masses, also containing an appropriate number of bromine and chlorine atoms to explain the observed isotopic pattern, was deemed the most probable molecular formula. According to these criteria the most abundant UHC was identified as C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Br<sub>6</sub>Cl. Table 1 lists the measured and calculated masses for the molecular ion and the [M-Br] ion, which are within 2 ppm.

A literature search revealed no compounds with the elemental composition C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Br<sub>6</sub>Cl. Clues about the molecular structure were revealed by low resolution MS, which shows fragmentation by loss of Br<sup>•</sup>, Cl<sup>•</sup> and CH<sub>3</sub><sup>•</sup> (Figure 1). This information, in combination with the similarity of the elemental composition to that of Q1 and the propensity of both compounds to accumulate in marine mammal blubber, lead us to suspect that C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Br<sub>6</sub>Cl also contains a 1'-methyl 1,2'-bipyrrole (MBP) skeleton. There are five possible isomers of MBP-Br<sub>6</sub>Cl, but only one of these was observed in the *D. delphis* tissue examined. We do not currently have sufficient information to identify the location of the chlorine atom. A more thorough examination by HR-GCMS, isolation of sufficient quantities for single crystal X-ray analysis and/or synthesis of authentic standards should help in identification of the specific isomer.

The concentration of MBP-Br<sub>6</sub>Cl in *D. delphis* was estimated to be 1.8 µg/ g of lipid, using GC-FID. A cursory investigation of a selection of marine mammals from the Northeastern United States indicated the concentration MBP-Br<sub>6</sub>Cl is almost an order of magnitude higher in the three species of dolphin species studied (*Lagenorhynchus actutus* and *Tursiops truncatus* in addition to *D. delphis*) than in the other five animals examined, including two species of whale (*Balaenoptera physalus* and *Delphinapterus leucas*), two species of seal (*Phoca vitulina* and *Halichoerus grypus*) and one porpoise (*Phocoena phocoena*). In most cases the concentration of PCB-153 was 4 to 15 times that of MBP-Br<sub>6</sub>Cl.

High resolution GCMS of another UHC observed in *D. delphis* is consistent with C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Br<sub>7</sub> and is likely the fully brominated analogue of Q1. These results suggest there may be a family of MBPs, with identical carbon skeletons but differing in their halogenation patterns, akin to the DMBPs reported by Tittlemier *et al.*<sup>1</sup>

Table 1. Measured and calculated masses for the molecular ion and [M-Br] ion of MBP-Br<sub>6</sub>Cl, determined by HR-GCMS.

Ion	Measured mass (Da)	Calculated mass (Da)	Error (ppm)
C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> Br <sub>6</sub> Cl	647.5093	647.5085	1.3
C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> Br <sub>5</sub> Cl	574.5747	574.5841	-1.7

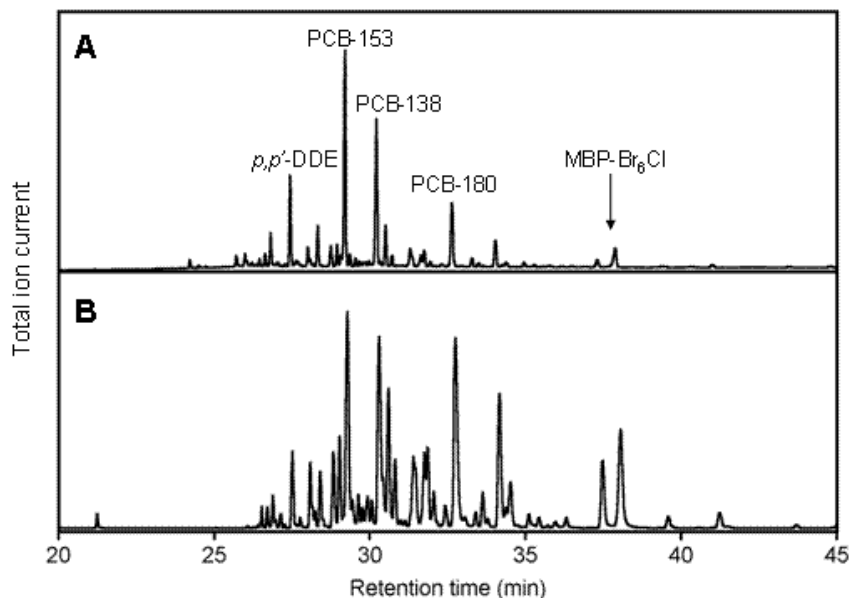


Figure 2. GCMS chromatograms of the HOCs extracted from *D. delphis*, using A) EI and B) ENCI as ionization sources.

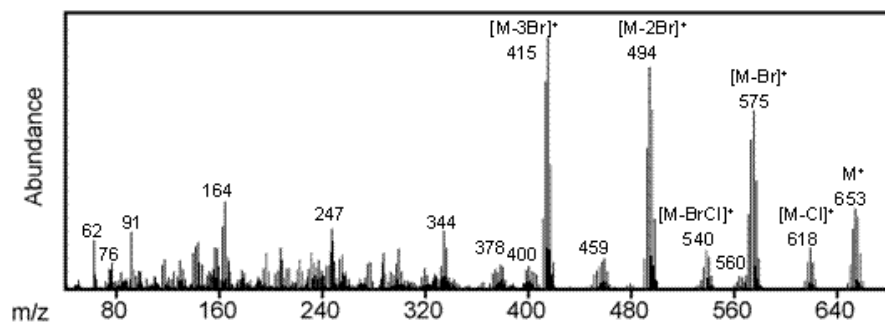


Figure 3. GCMS-EI spectrum for MBP-Br<sub>6</sub>Cl.

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