

Supporting Information for:

A non-targeted GC×GC/TOF-MS method and software for inventorying persistent and bioaccumulative contaminants in marine environments

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GLOSSARY OF ACRONYMS

2MeO-BB 80: 2,2'-Dimethoxy-3,3',5,5'-tetrabromobiphenyl
BDE: brominated diphenyl ether
BFR: brominated flame retardant
DDD: dichlorodiphenyldichloroethane
DDE: 1,1-dichloro-2,2-*bis*(chlorophenyl)ethene
DDMU: 1-chloro-2,2-*bis*(chlorophenyl)ethene
DDM: 1-chloro-2,2-*bis*(chlorophenyl)ethane
DDEt: 1,1-*bis*(chlorophenyl)ethane
DDT: dichlorodiphenyltrichloroethane
DE: diphenyl ether
DMBP: 1,1'-dimethyl-2,2'-bipyrroles
DSI: direct sample introduction
GC-ECD: gas chromatography-electron capture detection
GC×GC: comprehensive two-dimensional gas chromatography
GC/MS: gas chromatography/mass spectrometry
GPC: gel permeation chromatography
HNP: halogenated natural product
MeO-PBDE: methoxy polybrominated diphenyl ether
LC-Q/TOF: liquid chromatography quadrupole time of flight mass spectrometry
MeO-PCDE: methoxy polychlorinated diphenyl ether
MBP: 1'-methyl-1,2'-bipyrroles
MRM: multiple reaction monitoring
NIST: National Institute of Standards and Technology
OCP: organochlorine pesticides
PAH: polycyclic aromatic hydrocarbon
PBB: polybrominated biphenyls
PBDE: polybrominated diphenyl ether
PBHD: polybrominated hexahydroanthene derivatives
PCB: polychlorinated biphenyl
PCDE: polychlorinated diphenyl ether
PCS: polychlorinated styrene
POP: persistent organic pollutant
SIM: selected ion monitoring
SPE: solid-phase extraction
TCPM: tris(chlorophenyl)methane
TOF-MS: time-of-flight mass spectrometry

EXPERIMENTAL SECTION

Reference Standards. The following compounds were purchased from AccuStandard (New Haven, CT, USA): standard mixtures PCB-W22 and PCB Congener Mix 6; organochlorine pesticide mixture M-680P; standard mixture BDE-CM (mixture of PBDEs) ; individual standards PCB-65, PCB-155, and PCB-204; individual standards BDE-77 and BDE-166; octachlorostyrene; 2'-MeO-BDE-68 and 6-MeO-BDE-47; hexabrominated biphenyl (BB-153); and toxaphene (technical grade). A PCB standard mixture containing $^{13}\text{C}_{12}$ -labeled PCB-77, PCB-81, PCB-126 and PCB-169; and the individual standard $^{13}\text{C}_{12}$ -PCB-189; were purchased from Wellington Laboratories (Guelph, Canada). 5H-bromoindole and 2,4,6-tribromoanisole were purchased from Sigma-Aldrich (Milwaukee, WI, USA). 4,6-Dibromoindole was purchased from SiNova (Bethesda, MD, USA). Halogenated 1'-methyl-1,2'-bipyrrole standards (MBP-HBr₅Cl, MBP-HBr₆, MBP-HBr₆Cl, and MBP-Br₇) were extracted from the blubber of a common dolphin and isolated by gel permeation chromatography (GPC) and silica column followed by preparatory capillary GC (purity >95%) (1). 2,2'-Dimethoxy-3,3',5,5'-tetrabromobiphenyl (2MeO-BB 80) was synthesized following the procedure described by Marsh et al. (2). MBP-Cl₇ and polybrominated hexahydroxanthene (PBHD) were donated by Walter Vetter. Standards of halogenated 1,1'-dimethyl-2,2'-bipyrroles (two isomers of DMBP-Br₃Cl₃, DMBP-Br₄Cl₂, DMBP-Br₅Cl, and DMBP-Br₆, purity >99%) were donated by Sheryl Tittlemier.

RESULTS AND DISCUSSION

De Novo Identifications. The following describes the *de novo* identification of selected uncommon compounds. The compound names correspond to those in the spectral library. The PDF report of the spectral library is a separate file in the Supporting Information. Related

compounds were assigned a number, for example chlordanes related 1 and chlordanes related 2. Chromatographic peak areas are described to indicate approximate relative concentrations. Comparisons of isomers used the same extracted ions. Comparison of non-isomeric compounds used the extracted isomers as listed.

Chlordane and heptachlor related compounds. Chlordane is a legacy insecticide. Technical chlordane contains 140 compounds (3); however, most environmental monitoring targets only a few components: α - and γ -chlordane, *cis*- and *trans*- nonachlor, and oxychlordane. In our non-targeted analysis, 15 additional chlordane related components were detected. Thirteen compounds have the formula $C_{10}H_xCl_{14-x}$, where $x = 6, 7, 8, \text{ or } 10$. Their fragmentation patterns show consecutive losses of chlorine ions. The relative intensities of the fragments in each spectrum vary, but an overall similarity to α - and γ -chlordane and *cis*- and *trans*- nonachlor suggests that they likely have the same backbone structure. The relative chromatographic peak areas of $[M-Cl]^+$ compared to γ -chlordane was significant for some compounds; chlordane related 6 (61%), chlordane related 13 (65%), and chlordane related 10 (230%). Chlordane related 14 has ions at m/z 488 (M^+) and m/z 453 ($[M-Cl]^+$) and is likely to be peak 93 found in technical chlordane (3). Chlordane related 1 contains six chlorines but two fewer hydrogens, so its suggested elemental formula is $C_{10}H_6Cl_6$. This compound may be related to chlordene according to their mass spectral similarity (γ -chlordene). The relative peak intensity of m/z 238 in Chlordane related 1 compared to γ -chlordane is 120%.

Heptachlor is also an insecticide. Most environmental monitoring targets heptachlor and heptachlor epoxide. These two compounds were detected in the blubber as expected. 1-Hydroxychlordene, a metabolite of heptachlor, was observed to co-elute with a compound identified as CAS# 69653-75-4 in the NIST library. The source of the latter compound is

unknown. The elemental formula of heptachlor is $C_{10}H_5Cl_7$. The chemical structure is similar to α - and γ -chlordane, with an additional double bond. The two main ion groups, at m/z 270 and m/z 100, correspond to $[C_5Cl_6]^+$ and $[C_5H_5Cl]^+$. Heptachlor related 1 and 2 seem to have a same elemental formula as heptachlor. The loss of chlorine is observed in both spectra, but the spectra are not exactly same as heptachlor. The two major ions in the heptachlor spectrum, at m/z 100 and m/z 270, are found in the heptachlor related 2 spectrum, but not the heptachlor related 1 spectrum. Heptachlor related 3 seems to have an additional chlorine, compared to heptachlor, and a formula of $C_{10}H_4Cl_8$. The fragment m/z 134 corresponds to $[C_5H_4Cl_2]^+$, or an additional chlorine compared to the $[C_5H_5Cl]^+$ fragment at m/z 100 observed in the heptachlor spectrum. Heptachlor related 4 contains nine chlorines. Fragments at m/z 235 and m/z 270 correspond to $[C_5Cl_5]^+$ and $[C_5Cl_6]^+$, which indicates pentachlorocyclopentadiene is a part of the chemical structure. The elemental formula of heptachlor related 4 seems to be $C_{10}H_3Cl_9$. The relative peak areas of heptachlor related 2 (m/z 337) and heptachlor related 3 (m/z 272) to heptachlor epoxide (m/z 263) were 58% and 96%, respectively.

DDT related compounds. DDT is a legacy pesticide consisting of several isomers with chlorines in the *ortho*, *meta*, and *para* positions on the phenyl rings. DDT breaks down to DDE and DDD. We identified *p,p'*-DDE; other two DDE isomers (listed as DDE isomer 1 and 2); *p,p'*-DDT; *o,p'*-DDD; and *p,p'*-DDD. We also identified the following uncommon products. 1-Chloro-2,2-bis(chlorophenyl)ethane (DDMU) and 1-chloro-2,2-bis(chlorophenyl)ethane (DDM) are products of DDD and DDE dechlorination. 1,1-Bis(chlorophenyl)-ethane (DDEt) is a degradation product of DDT and was recently identified in river and marine sediments (4). DDT related compounds 1, 2, and 3 seem to have the same chemical backbone as DDE, but contain two or three additional chlorines on the phenyl rings. These compounds were reported as

impurities of DDT present in dicofol formulations (5). We identified two isomers of tris(chlorophenyl)methane (TCPM) (6). The chromatographic peaks of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT were saturated, and had relatively high abundance compared to other DDTs, which were not saturated. The relative peak intensities of the uncommon DDT related compounds DDEt; DDT related 1, DDT related compounds 2, and 3; and the TCPM isomers were 1% to 13% of the chromatographic peak area of *o,p'*-DDD.

Toxaphene, mirex, and other legacy chlorinated pesticides. Nine toxaphene congeners were identified based on matches to a technical mixture. Three additional congeners (toxaphene 4, toxaphene 5, and toxaphene 8) were presumptively identified based on a similar fragmentation pattern (consecutive losses of carbons or chlorines). However, these three toxaphene congeners were not present in the technical mixture. Dechlorinated mirex was identified in addition to mirex. The mirex fragment at m/z 270 corresponds to $[C_5Cl_6]^+$ and the fragment at m/z 235 corresponds to $[C_5Cl_5]^+$ or a loss of chlorine. In the two dechlorinated mirex isomers (mirex-Cl isomer 1 and 2), instead of a fragment at m/z 235, m/z 236 corresponding to $[C_5HCl_5]^+$ was detected. Similarly, the mirex-2Cl spectrum contains a fragment at m/z 202 corresponding to $[C_5H_2Cl_4]^+$, which suggests two less chlorines than mirex. The relative chromatographic peak areas of the dechlorinated mirex compounds were 104% (mirex-Cl isomer 1, extracted ion m/z 238), 50% (mirex-Cl isomer 2, extracted ion m/z 238), and 32% (mirex-2Cl, extract ion m/z 204) compared to mirex (extracted ion m/z 237). Dieldrin, hexachlorobenzene, and three hexachlorocyclohexane isomers were also identified. Pentachlorobenzene was identified with a minimal chromatographic peak intensity.

PBDE and PBB. PBDEs and polybrominated biphenyls (PBBs) are flame retardants. The predominant congeners generally observed in biota, BDE-28, 47, 99, 100, 153, 154, and 183,

were identified via comparison to reference standards. Three additional tetra-BDEs, one penta-BDE, three hexa-BDEs, and two hepta-BDEs were identified based on their mass spectral similarity to isomeric reference standards. In these mass spectra, $[M]^+$ and $[M-Br_2]^+$ were commonly observed, as well as the doubly charged $[M-Br_2]^{++}$ when the chromatographic peak was intense enough to give a clean mass spectrum. This suggests that the PBDE congeners contain at least one ortho-substituted bromine on each phenyl ring (7). The relative chromatographic peak areas of the additional PBDE congeners were generally lower compared to the major PBDE congeners, except for PBDE 6Br isomer 2 which was 92% compared to BDE-153 (contains also six bromines), and PBDE 7Br isomer 1 which was 350% compared to BDE-183 (contains also seven bromines).

BB-153 is generally observed as the predominant PBB congener. We identified BB-153 and five hexa-BBs, two penta-BBs, and two tetra-BBs. Among the hexa-BBs, the BB-153 chromatographic peak was the most intense, and the relative peak areas of the other hexa-BBs were 8% to 48% compared to BB-153. Other chromatographic peak areas relative to BB-153 were PBB 4Br isomer 1 at 223% (extracted ion m/z 310), PBB 4Br isomer 2 at 167% (extracted ion m/z 310), PBB 5Br isomer 1 at 7% (extracted ion m/z 388), and PBB 5 Br isomer 2 at 80% (extracted ion m/z 388).

PCDE and PCS. Polychlorinated diphenyl ethers (PCDEs) are byproduct of industrial combustion and chlorophenol production (8). Fifteen penta- through octa-PCDE congeners were manually identified based on similar fragmentation to PBDEs, but with chlorine loss instead of bromine loss. Both $[M]^+$ and $[M-Cl_2]^+$ were abundant ions in most spectra, except only $[M]^+$ was detected in hepta-CDE isomer 1 and hepta-CDE isomer 2. The presence of $[M-Cl_2]^+$ ions indicates formation of dibenzofuran via loss of two chlorines at the *ortho*-position of each phenyl

ring (7). Therefore, it is likely that the two PCDE congeners missing $[M-Cl_2]^+$ do not contain two *ortho*-substituted chlorines.

The source of polychlorinated styrenes (PCS) is uncertain and there are multiple possibilities (9, 10). The identity of octachlorostyrene was confirmed via a reference standard, with abundant $[M]^+$, $[M-Cl]^+$, $[M-Cl_2]^+$, and $[M-Cl_2]^{++}$ ions. Ten penta- through hepta substituted PCS were identified through literature mass spectra (11), and four additional tri- and tetra substituted PCS were identified based on similar fragmentation patterns. The most abundant ion in the $[M]^+$ cluster was used to compare the peak areas of the 14 PCS compounds to octachlorostyrene. The relative peak areas varied from 3% to 246%, with heptachlorostyrene isomer 1, 2, and 3 at 246%, 62%, and 107%, respectively.

Methoxy polybrominated/chlorinated diphenyl ether (MeO-B/CDE). Some methoxy polybrominated diphenyl ethers (MeO-PBDEs) are known to be natural products produced by marine algae/sponges (12). Seven MeO-PBDEs were identified. 2'-MeO-BDE68 and 6'-MeO-BDE47 were confirmed via reference standards and ions $[M]^+$, $[M-CH_3Br]^+$, and $[M-Br_2]^+$ were prominent in both mass spectra. Loss of CH_3Br produces a stable brominated dibenzo-*p*-dioxin ion, and the presence of $[M-CH_3Br]^+$ indicates both the methoxy group and a bromine atom are *ortho* to the aromatic ether linkage (7). A similar fragmentation pattern was observed in the other five tri- through penta- brominated MeO-PBDEs, suggesting they also have the methoxy group and a bromine atom at the *ortho* positions. Three congeners of methoxy polychlorinated diphenyl ethers (MeO-PCDEs) were identified (MeO-CDE 7Cl, MeO-CDE 8Cl isomer 1 and 2) via loss of CH_3Cl and Cl_2 , similar to that observed for the MeO-PBDEs. In literature, MeO-PCDEs were identified as impurities in technical pentachlorophenol (13). Two mixed halogenated MeO-B/CDEs were also identified (MeO-B/CDE Br3Cl and MeO-B/CDE Br4Cl) via loss of CH_3Br

and BrCl and are likely natural products (14). Fragmentation of MeO-B/CDE Br4Cl matched that of isomers of MeO-DE with four bromines and one chlorine (15). The most abundant ion in the $[M-CH_3Br]^+$ or $[M-CH_3Cl]^+$ clusters was used to compare the relative peak areas, with 2'-MeO-BDE68 at 89% of the 6'-MeO-BDE47 peak area. The relative peak areas of the other MeO-B/CDE congeners were low, at 1% to 9%.

Halogenated methyl bipyrrroles (MBP) and halogenated dimethyl bipyrrroles (DMBP). MBPs and DMBPs are considered natural products (16, 17). MBPs in the blubber of this sample were reported previously (18). We identified 28 MBPs with various degrees of halogenation. Fully chlorinated MBP-Cl7, also referred to as Q1 (19), MBP-Br6, MBP-Br7, two isomers of MBP-Br5Cl, and MBP-Br6Cl, were confirmed via reference standards. Two MBP-6Cl were identified based on their similarity to literature mass spectra (19). The other MBPs were identified based on spectral similarity to the reference standards and comparison to theoretical isotopic ratios. The halogenation varied among 6-7 chlorines, 4-7 bromines, and mixtures of bromines and chlorines. Among the 28 halogenated MBPs, MBP-6Br isomer 2, MBP-Br5Cl isomer 2, and MBP-Br6Cl were most abundant based on a relative peak area comparison using the most intense ion $> m/z$ 300.

Ten halogenated DMBPs were identified. The halogenations varied among 4-6 bromines and mixtures of bromines and chlorines. Similar to other halogenated compounds, fragments generated by a loss of halogens, such as one or two bromine or chlorine ions, were commonly observed in the mass spectra. Ion $[M-120]^+$, which may correspond to $[M-BrCNCH_3]^+$, was found at a high intensity in all the mass spectra. This fragment distinguishes DMBPs from MBPs. DMBP-Br4Cl2 was the most abundant congener in this class based on a relative peak area comparison using the most intense ion $> m/z$ 300.

Miscellaneous compounds. A tribromophenol; 2,4,6-tribromoanisole; a monobromoindole and two dibromoboindoles; dimethoxy brominated biphenyl (2MeO-BB-80); and tri/tetrabrominated hexahydroxanthenes (PBHDs) were identified. These compounds are likely to be natural halogenated products, except for tribromophenol which has both natural and anthropogenic sources (20). Pentachloro-ethylbenzene's source is uncertain. Tetraphenyltin, a non-halogenated compound, was identified and is used in agrochemical mixtures, antifouling paints, and as stabilizers (21). Its accumulation in marine mammals has not been reported.

Mixed halogenated diphenyl ether (B/CDE). Seven diphenyl ether congeners containing mixtures of 3 to 5 bromines and one chlorine were presumptively identified based on fragment masses and isotopic ratios, and the consistent presence of $[M]^+$ and $[M-Br_2]^+$ ions. The presence of $[M-Br_2]^+$ suggests that the bromines are positioned *ortho* to the ether linkage between the phenyl rings. These mixed B/CDEs have not been reported in the literature, although B/CDEs containing nine bromines and one chlorine only have been reported (22, 23). The relative peak areas of these compounds, using $[M-Br_2]^+$ as the extracted ion, was $\leq 10\%$ of BDE-99. The two isomers of B/CDE Br₃Cl were 6% and 10% of BDE-99.

Unidentified compounds. We cataloged 27 relatively clean mass spectra that were not identifiable through spectral database or literature searches, or through *de novo* interpretation. The number of halogens was estimated by comparing the observed isotopic ratios to theoretical isotopic ratios. Based on their spectral similarity, unknowns 1-(1-4) may belong to the same chemical class. Three of the spectra were reported in dietary cod liver oil (24) and two of the spectra in Mediterranean sponges (25), but were not identified. Unknowns 2-(1-3) show similarity to Unknown group 1, but the major fragments are 2 *m/z* units higher. This suggests unknown group 2 contains two more hydrogens due to the presence of a single rather than double

bond. The GC×GC retention times of the unknown groups 1 and 2 support this hypothesis. As shown in Figure 2-B, compounds in the same class are typically clustered. In Figure 2-C, unknown groups 1 and 2 are each clustered, indicating similar structures with each group. Unknown groups 3 and 4 may each contain similar structures based on common fragment ions and retention time clustering (Figure 2-C). Unknown 5 was previously reported in dietary cod liver oil and presumed to be 2,2',3,3'-tetra-bromo-4,4',5,5'-tetrahydroxy diphenyl methane (24). Unknowns 6 to 14 contain chlorine only, and Unknowns 15 to 17 contain either bromine only, or bromine and chlorine.

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