SUPPORTING INFORMATION

Nontargeted biomonitoring of halogenated organic compounds in two ecotypes of bottlenose dolphins (*Tursiops truncatus*) from the Southern California Bight

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Number of Pages (including cover page): 33

Number of Tables: 5

Number of Figures: 8

Table of Contents Page

Glossary of Acronyms

2'-MeO-BDE-68: 2'-methoxy-2,3',4,5'-tetrabrominated diphenyl ether

6-MeO-BDE-47: 6-methoxy-2,2',4,4'-tetrabrominated diphenyl ether

6'-MeO-BDE-99: 6'-methoxy-2,2',4,4',5-pentabromodiphenyl ether

B/CDE: brominated/chlorinated diphenyl ether

BDE: brominated diphenyl ether

o,p'-DDD: *o,p'*-dichlorodiphenyldichloroethane

p,p'-DDD: *p,p'*-dichlorodiphenyldichloroethane

DDE: dichlorobis(chlorophenyl)ethene

DDMU: chlorobis(chlorophenyl)ethene

DDT: dichlorodiphenyltrichloroethane

di-MeO-PBB-80: 2,2'-dimethoxy-3,3'5,5'-tetrabromobiphenyl

DMBP: 1,1'-dimethyl-2,2'-bipyrroles

EI: electron ionization

eV: electron volts

GC×GC: comprehensive two-dimensional gas chromatography

GPC: gel permeation chromatography

HOC: halogenated organic compound

MBP: 1'-methyl-1,2'-bipyrrole

MeO-B/CDE: methoxy brominated/chlorinated diphenyl ether

MeO-BDE: methoxy brominated diphenyl ether

MeO-CDE: methoxy chlorinated diphenyl ether

MS: mass spectra

NIST: National Institute of Standards and Technology

NOAA: National Oceanic and Atmospheric Administration

OH-PBDE: hydroxy polybrominated diphenyl ether

OH-PCB: hydroxy polychlorinated biphenyl

PBDE: polybrominated diphenyl ether

PBDF: polybrominated dibenzofuran

PBHD: polybrominated hexahydroxanthene derivative

PCB: polychlorinated biphenyl

PCDE: polychlorinated diphenyl ether

PCT: polychlorinated terphenyl

RT: retention time

S/N: signal-to-noise ratio

TCPM: tris(chlorophenyl)methane

TCPMOH: tris(chlorophenyl)methanol

TOF-MS: time-of-flight mass spectrometry

Materials and Methods

Materials

All of the solvents used for the extraction and cleanup procedures were residue-analysis grade.

The following reference standards were purchased from AccuStandard (New Haven, CT, USA): 3,3',4,4'-tetrabromodiphenyl ether (BDE-077S); 2,3,4,4',5,6-hexabromodiphenyl ether (BDE-166S); 6-fluoro-2,2',4,4'-tetrabromodiphenyl ether (FBDE-4003S); 4'-fluoro-2,3,3',4,5,6-hexabromodiphenyl ether (FBDE-6001S); organochlorine pesticide mixture containing α-BHC, β-BHC, heptachlor epoxide, γ-Chlordane, α-Chlordane, trans-Nonachlor, and cis-Nonachlor (M-680P); *p,p'*-DDMU (P-424S); PBDEs Standard Solution for Accuracy and Precision (BDE-AAP-A); hexabrominated biphenyl, PBB-153 (B-153S); Methylsulfonyl pentachlorinated biphenyl, 3-MeO-Sulfonyl-PCB-101 (MSCB-3101); Methoxylated bromodiphenyl ethers, 2'-MeO BDE-68 (MOBDE-4006S-0.2X), 6-MeO BDE-47 (MOBDE-4005S-0.2X), 6'-MeO BDE-99 (MOBDE-5006S-0.2X); 1,2,4-Trichlorobenzene (P-1004S); 1,2,3,4-Tetrachlorobenzene (P-999S); Pentachlorobenzene (APP-9-173); 2,2'4,5'-Tetrabromobiphenyl (B-049SS); 2,2',5,5'-Tetrabromobiphenyl; 2,2',4,5,5'-Pentabromobiphenyl (B-101S); chlordane (technical grade, APP-9-037); and DDT (technical grade, P-346N). The following reference standards were purchased from Wellington Laboratories (Guelph, Canada): 3,3',4,4',5,5'-hexachloro[$^{13}C_{12}$]biphenyl (MBP-169), 2,3,3',4,4',5,5'-heptachloro[$^{13}C_{12}$]biphenyl (MBP-189), Tris(4-chlorophenyl)methane (T4CPM); and Tris(4-chlorophenyl)methanol (T4CPME). A custom pesticide standard was purchased from Ultra Scientific (N. Kingstown, RI, USA) containing Mirex, *o,p'*-DDD, *p,p'*-DDD, and hexachlorobenzene. 5H-bromoindole; 2,4,6-tribromoanisole; tris(2-chloroethyl phosphate; and 4,4'-Dichlorobenzophenone were purchased from Sigma-Aldrich (Milwaukee, WI, USA). 4,6-Dibromoindole was purchased from SiNova

(Bethesda, MD, USA). 2,2'-Dimethoxy-3,3',5,5'-tetrabromobipehnyl, 2MeO-BB-80, was synthesized following the procedure described by Marsh et al. (2005).[S1] Polybrominated hexahydroxanthene standards were donated by Walter Vetter. All DMBP and MBP reference standards were synthesized by methods modified from Wu et al. (2002)[S2] in William Fenical's lab, except for MBP-Cl7, which was synthesized according to Wu et al. (2002).[S2]

Sample Preparation

Samples were randomly labeled 1-8 prior to extraction and analysis to eliminate analytical bias, and ecotype assignment was blinded until all halogenated organic compounds (HOCs) were identified. Approximately 2 g of blubber was homogenized, ground with kilned Na_2SO_4 and extracted by pressurized fluid extraction (Dionex ASE 300, Dionex, Sunnyvale, CA, USA) with dichloromethane (100 °C, 1500 psi). It was previously found that removal of lipids by gel permeation chromatography (GPC) only, as opposed to acidification or GPC in combination with silica-gel chromatography, resulted in the maximum number of detected compounds.[S3] Approximately 1 g of extracted blubber ("oil") was dissolved in 4.7 mL of 1:1 ethyl acetate/cyclohexane and spiked with a known amount of internal standard mixture (BDE 77, $^{13}C_{12}$-PCB 169). The solution was injected into a GPC system (J2 Scientific, Columbia, MO) to remove lipids based on a previously validated method that maximized recovery of several HOC classes.[S4] The GPC column, with a 2-cm i.d. and length of 22.5 cm, was packed with 24 g of BioBeads S-X3 in 1:1 ethyl acetate/cyclohexane. The flow rate was 5 mL/min, and the mobile phase was 1:1 ethyl acetate/cyclohexane. The eluent fraction between 8.5 and 20.5 min was collected and reduced to 1 mL under N_2 gas. The extract was brought to 4.7 mL with the mobile-phase solvent and re-injected into the GPC system to remove residual lipids. The extract was

then evaporated and solvent-exchanged to isooctane in a final volume of 50 µL. Fifty microliters of a recovery standard mixture of known concentration (6F-tetraBDE, 4F-hexaBDE, $^{13}C_{12}$-PCB 189) was then added to bring the extracts to a final volume of 100 µL prior to injection on a GC×GC/TOF-MS.

Instrumental Analysis

Sample extracts were analyzed on a Pegasus 4D GC×GC/TOF-MS (LECO, St. Joseph, MI, USA) connected to an Agilent 6890 gas chromatograph (Palo Alto, CA, USA) with a secondary oven, a split/splitless injector, and a non-moving quad-jet dual stage modulator. The first-dimension (1D) column was a Restek (Bellefonte, PA) Rtx5Sil-MS (30-m length, 0.25-mm i.d., 0.25-µm film thickness) and was integrated with 5 m of guard column. A Restek Rtx17Sil-MS (1-m length, 0.10-mm i.d., 0.10-µm film thickness) was the second-dimension (2D) column. A 2-µL splitless sample injection was conducted using an Agilent autosampler (Santa Clara, CA) at 300 °C. Research grade helium (Airgas, Radnor, PA) was used as the carrier gas at 1 mL/min. The primary oven temperature was held at 60 °C for 1 min, ramped at 10 °C/min to 300 °C and held for 3 min, and ramped at 20 °C/min to 320 °C and held for 20 min. The secondary oven temperature was programmed to be 20 °C higher than the primary oven temperature. For GC×GC, the modulation period was set to 3.5 s, with a 0.9 s hot pulse duration and a 35 °C modulator temperature offset versus the primary oven temperature. The MS transfer line and ion source temperatures were 285 °C and 250 °C, respectively. Fragmentation occurred by electron ionization (EI), with an electron energy of −70 eV and a detector voltage of 1600 V. The data acquisition rate was 150 spectra/s.

Compound Identification

Data processing for the nontargeted analysis included automatic peak finding using mass spectral deconvolution (within ChromaTOF) and spectral searching versus mass spectral libraries at a signal-to-noise threshold (S/N) of 10 or higher for the first sample analyzed (selected at random). The two mass spectral libraries used were the NIST 2011 EI mass spectral library and a previously established custom mass spectral library for HOCs identified in an Atlantic dolphin blubber sample.[S5] Identification through spectral searching was based on the common presence of characteristic identifiable fragment ions (often halogenated isotopic clusters) and the spectral similarity score. All PCB congeners and oversaturated DDT and DDE peaks were excluded from identification. Initially in this first sample, 326 peaks were identified as potential HOCs of interest at S/N 10 out of 17,038 total peaks.

These HOC peaks were then used to create a reference standard data processing method that searched the remaining seven samples for the 326 HOCs found in sample 1 (S/N 50), matching based on retention time and spectral similarity. This method also searched 'new' peaks equal or above S/N 50 and within a retention time deviation of the modulation time, ±3.5 s in 1^{st} GC and ±0.05 s in 2^{nd} GC. This resulted in a list of peaks for samples 2-8 that either matched to peaks in the reference standard (i.e., sample 1) or represented 'new' peaks that were not of similar spectra/retention time as those selected from sample 1. Reference standard matches for the compounds from sample 1 were confirmed in these remaining seven samples, and 'new' peak spectra were scrutinized for any HOCs different from those in sample 1. This resulted in a total of 395 unique HOCs from eight dolphin samples. As a final confirmation, a second reference standard data processing method containing these 395 peaks was created and used to process all

eight samples again (S/N 50). Hits to these 395 peaks were then confirmed. The final library resulted from further curation and scrutiny of these peaks (e.g., compounds identified as different isomers in different samples determined to be the same compound) and ultimately consisted of 327 unique compounds.

Compounds in the final library were ranked based on the degree of identification following previously defined categories in Hoh et al. (2012),[S5] with the category names found in the library in brackets: "(1) The experimental mass spectrum and retention times were matched to those of a reference standard analyzed under the same conditions [authentic MS RT]. (2) The experimental spectrum, but not the retention times, was matched to a reference standard, indicating the experimental spectrum is that of an isomer [authentic MS]. (3) The experimental spectrum was matched to one within the NIST Electron Ionization Mass Spectral Library [reference database MS]. (4) The experimental spectrum was matched to one found in the literature [literature MS]. (5) The experimental mass spectrum was identified as potentially belonging to a class of congeners on the basis of comparison to that of a reference standard within the same class of congeners [manual-congener group]. (6) A presumptive identification was made by manual interpretation of the experimental spectrum [manual]. (7) The experimental spectrum was identified as belonging to a halogenated compound, but the chemical structure could not be further identified [unknown]."

Ecotype Clustering

Differences in compound profiles between the coastal and offshore ecotypes were assessed using three methods: hierarchical clustering (using R function hclust) displayed as a heatmap

(Supplemental Material, Figures S2-S4), *k*-means clustering (R function kmeans) with two centers specified (Supplemental Material, Tables S2-S4), and principal components analysis (PCA, R function prcomp, Figures S5-S7). PCA plot symbols were encoded using the two clusters identified by the *k*-means clustering, and labeled by ecotype. Anthropogenic, natural, and unknown compounds were analyzed separately because we hypothesized the sources may vary spatially and impact the two ecotypes differently (with anthropogenic sources primarily along the coast). Prior to analysis, the concentration data, with non-detects set at zero, was log transformed as $\log_{10}(x+1)$, where x was the normalized abundance. We concluded there was a difference between coastal and offshore ecotype contaminant profiles only if all three methods identified two sample clusters corresponding to the two ecotypes.

References

S1. Marsh, G.; Athanasiadou, M.; Athanassiadis, I.; Bergman, A.; Endo, T.; Haraguchi, K. Identification, quantification, and synthesis of a novel dimethoxylated polybrominated biphenyl in marine mammals caught off the coast of Japan. *Environ. Sci. Technol*. **2005**, *39*, 8684-8690.

S2. Wu, J.; Vetter, W.; Gribble, G.W.; Schneekloth, J.S.; Blank, D.H.; Gorls, H. Structure and synthesis of the natural heptachloro-1'-methyl-1,2'-bipyrrole (Q1). *Angew. Chem. Int. Edit*. **2002**, *41*, 1740-1743.

S3. Hoh, E.; Lehotay, S.J.; Mastovska, K.; Ngo, H.L.; Vetter, W. Capabilities of direct sample introduction-comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry to analyze organic chemicals of interest in fish oils. *Environ. Sci. Technol*. **2009**, *57*, 2653−2660.

S4. Hoh, E.; Lehotay, S.J.; Mastovska, K.; Huwe, J.K. Evaluation of automated direct sample introduction with comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry for the screening analysis of dioxins in fish oil. *J. Chromatogr. A* **2008**, *1201*, 69−77.

S5. Hoh, E.; Dodder, N.G.; Lehotay, S.J.; Pangallo, K.C.; Reddy, C.M.; Maruya, K.A. Nontargeted Comprehensive Two-Dimensional Gas Chromatography/Time-of-Flight Mass Spectrometry Method and Software for Inventorying Persistent and Bioaccumulative Contaminants in Marine Environments. *Environ. Sci. Technol*. **2012**, *46*, 8001-8008.

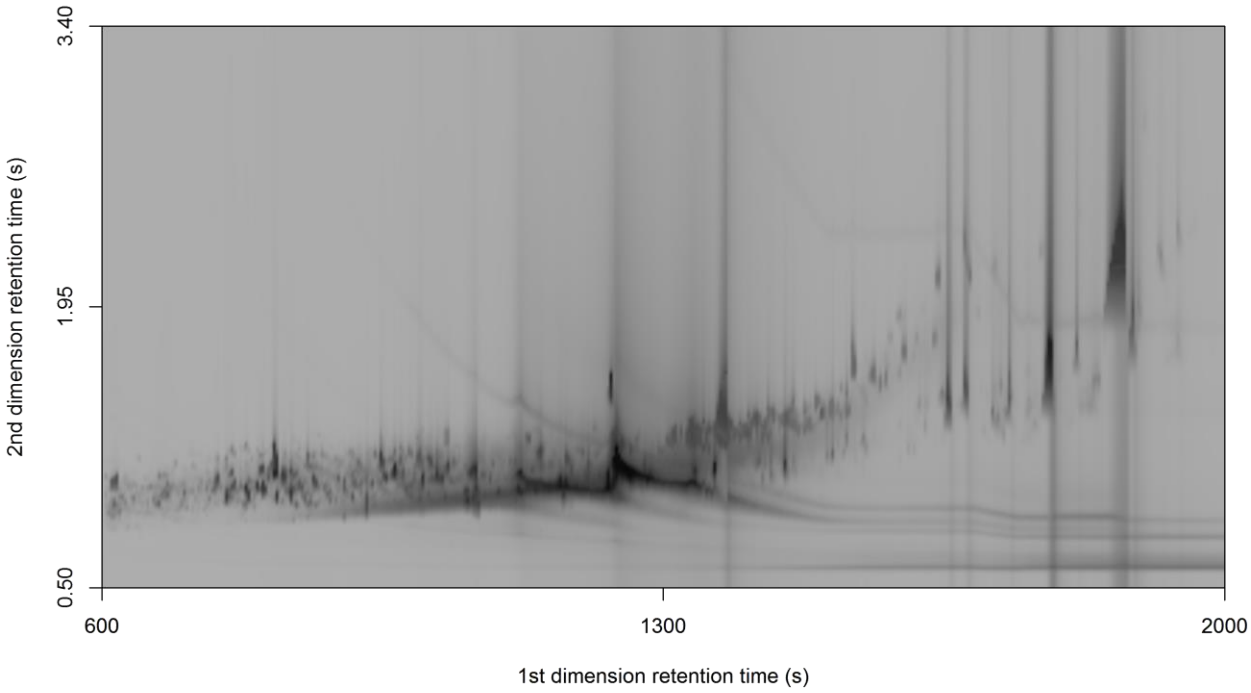

Figure S1. Representative GC×GC chromatogram of a dolphin blubber extract.

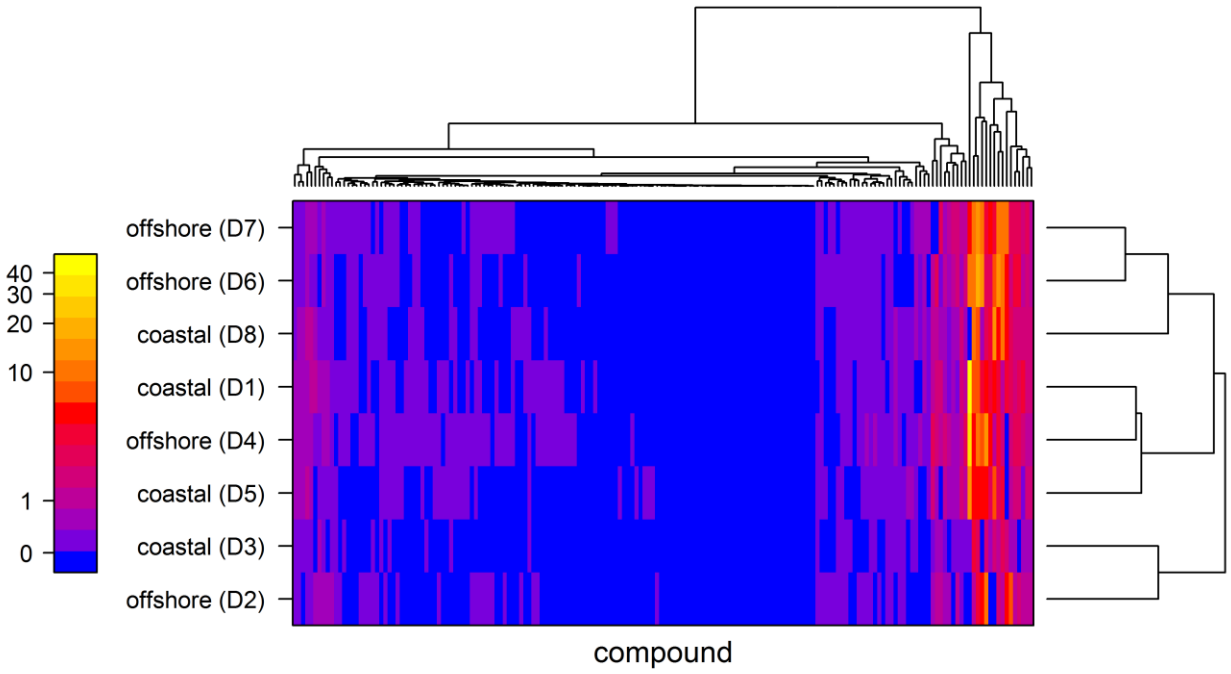

Figure S2. Hierarchical clustering results for the anthropogenic compounds. The color key indicates the normalized compound abundance and the dendrograms indicate the clustering results. Each compound has at least one detect among the eight samples, although some compounds with low abundance were binned as having apparent values of zero.

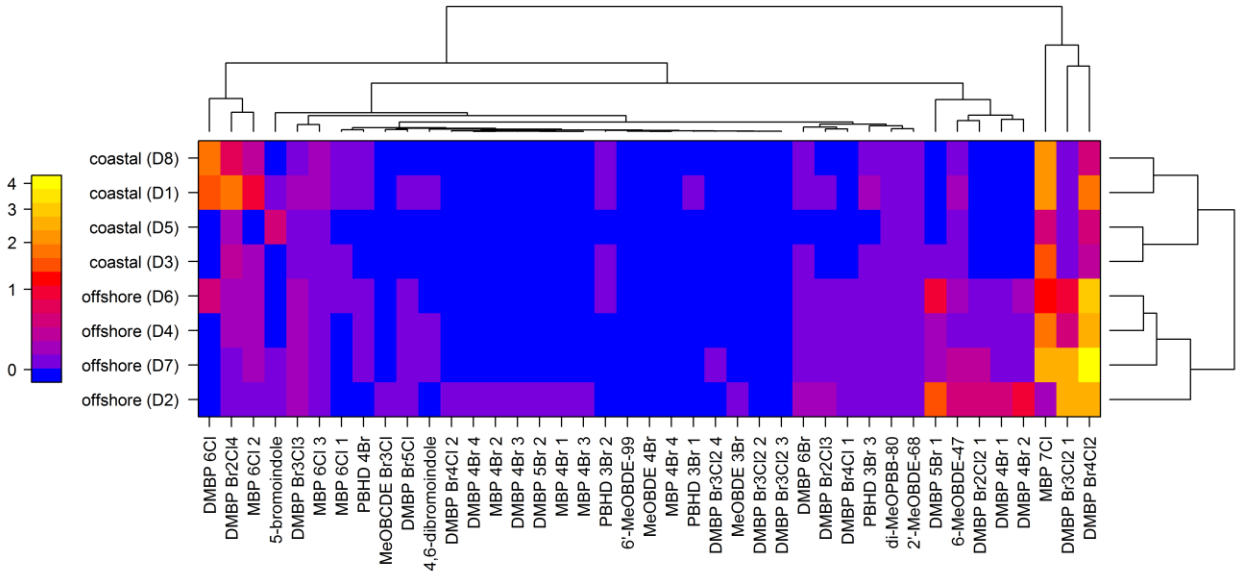

Figure S3. Hierarchical clustering results for the natural compounds. The color key indicates the normalized compound abundance and the dendrograms indicate the clustering results. Each compound has at least one detect among the eight samples, although some compounds with low abundance were binned as having apparent values of zero.

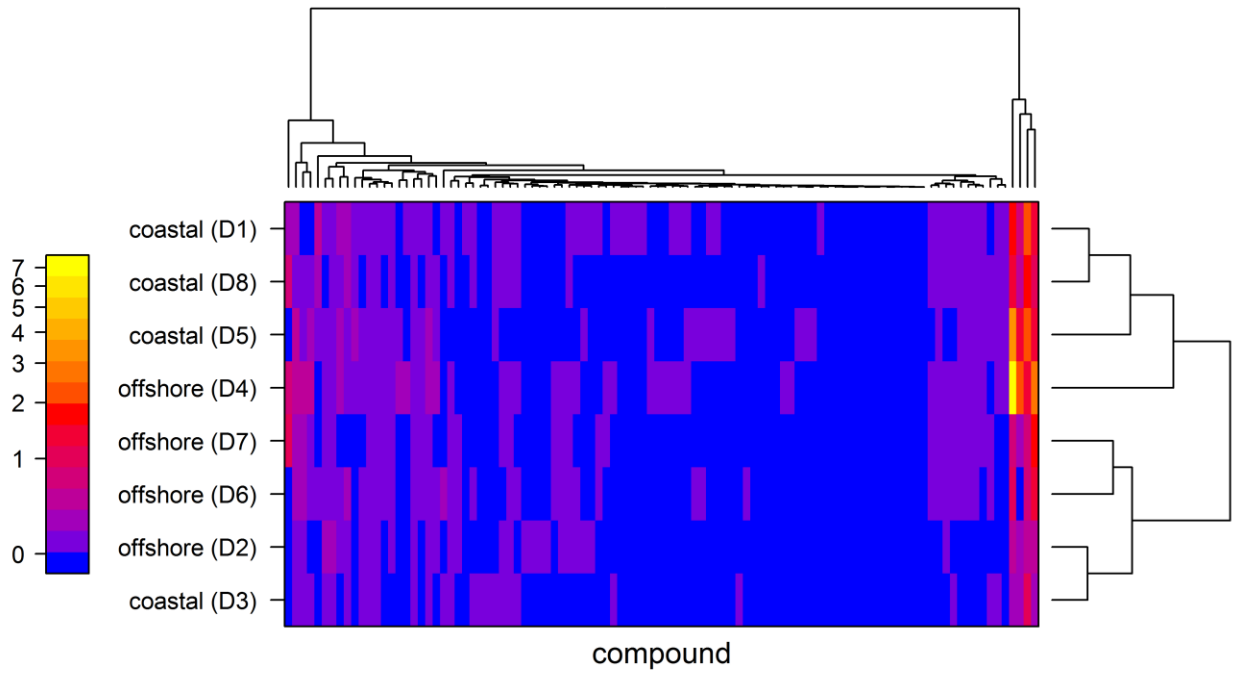

Figure S4. Hierarchical clustering results for the unknown compounds. The color key indicates the normalized compound abundance and the dendrograms indicate the clustering results. Each compound has at least one detect among the eight samples, although some compounds with low abundance were binned as having apparent values of zero.

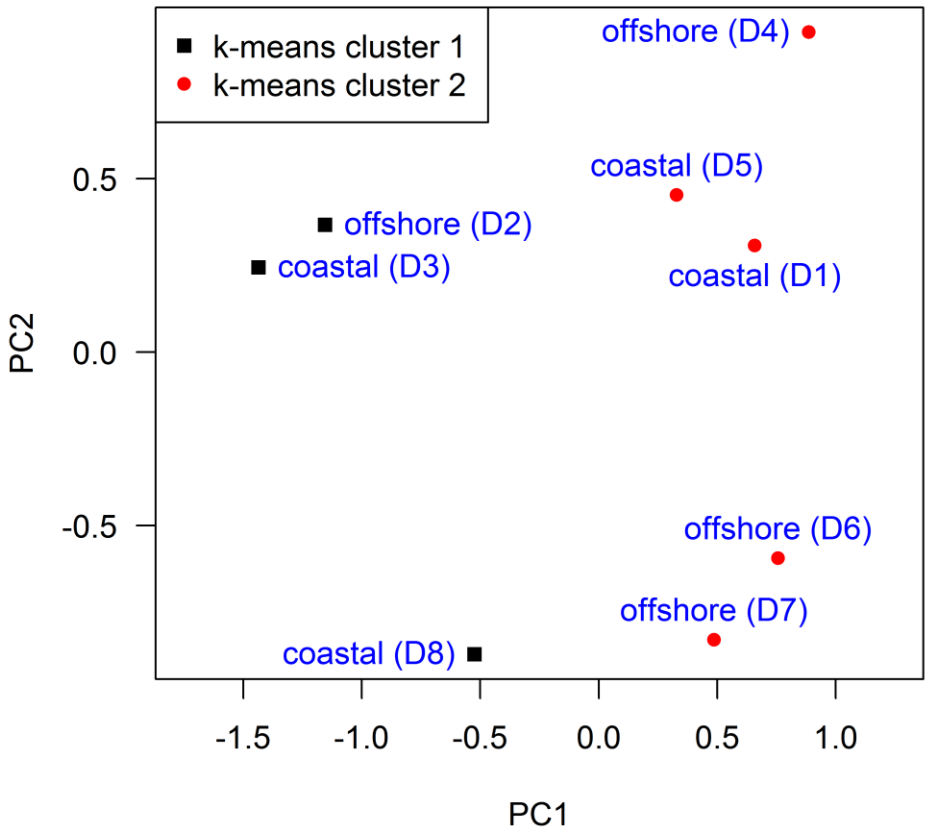

Figure S5. Principal components analysis results for the anthropogenic compounds. Together, the first two principal components (PC1 and PC2) represented 68% of the variance.

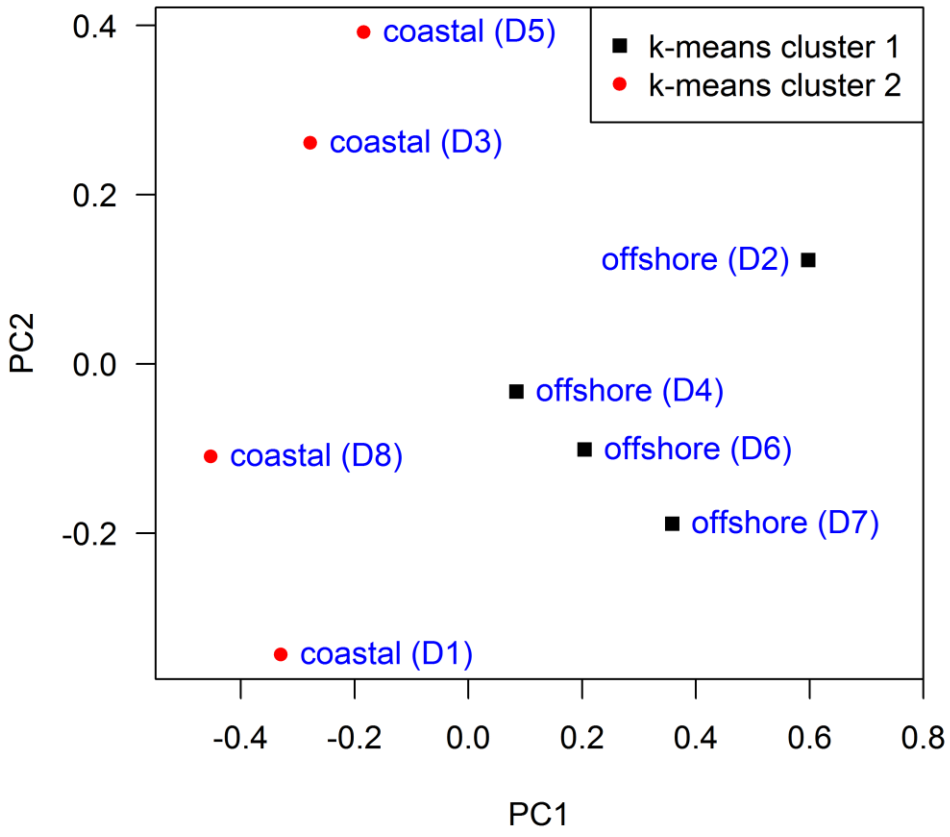

Figure S6. Principal components analysis results for the natural compounds. Together, PC1 and PC2 represented 81% of the variance.

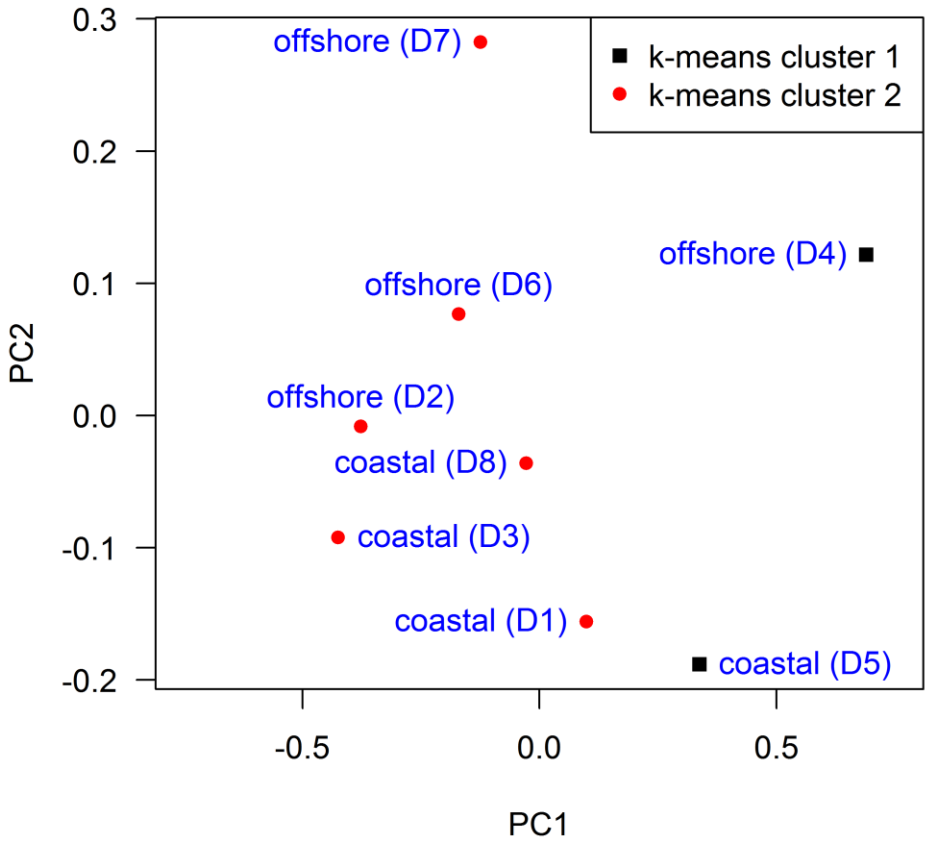

Figure S7. Principal components analysis results for the unknown compounds. Together, PC1 and PC2 represented 84% of the variance.

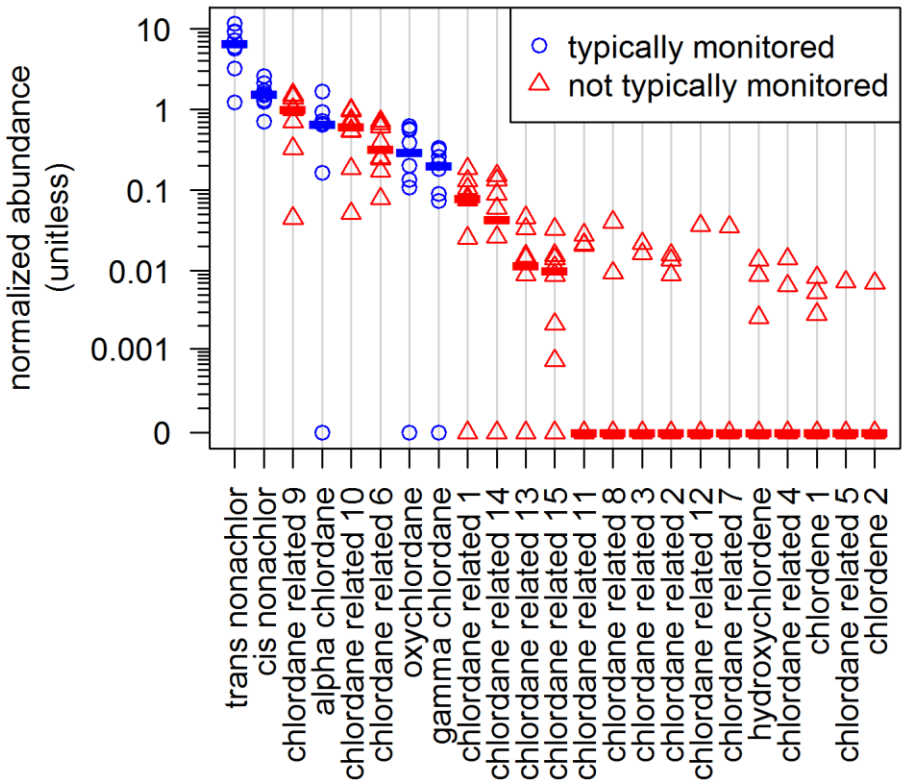

Figure S8. Abundance (normalized peak area) of the chlordane compounds. Each point represents a single dolphin blubber sample (n = 8). The line is the median abundance. Compounds along the x-axis are sorted by median abundance. The monitoring status of each chlordane is shown in the legend. Non-detects are shown with a value of zero (multiple non-detects overlap). Note the three unmonitored chlordanes with similar abundance to the typically monitored chlordanes: chlordane related 9 (page 13 in the mass spectral library), chlordane related 10 (page 15), and chlordane related 6 (page 10).

Table S1. Mean and median normalized abundances and frequency of detection for all individual compounds (alphabetical order by class, then compound).

Compound	Compound Class	Mean Area	Median Area	Frequency	Identification
PBCDE Br3Cl 1	B/CDE	0.0095	0.0078	5	Manual-Congener Group
PBCDE Br3Cl 2	B/CDE	0.015	0.017	5	Manual-Congener Group
PBCDE Br3Cl 3	B/CDE	0.015	0.015	6	Manual-Congener Group
2,4,6-tribromo anisole	Brominated anisole	0.038	0.042	8	Authentic MS RT
4,6-dibromoindole	Brominated indole	0.023	0.02	4	Authentic MS RT
5-bromoindole	Brominated indole	0.093	0.015	7	Authentic MS RT
bromomethyl biphenyl	Bromomethylbiphenyl	0.022	0.015	4	Reference Database MS
alpha chlordane	Chlordane-related	0.78	0.67	7	Authentic MS RT
chlordane related 1	Chlordane-related	0.098	0.082	7	Manual
chlordane related 10	Chlordane-related	0.59	0.62	8	Manual-Congener Group
chlordane related 11	Chlordane-related	0.024	0.022	3	Manual-Congener Group
chlordane related 12	Chlordane-related	0.037	0.037	1	Manual-Congener Group
chlordane related 13	Chlordane-related	0.024	0.015	5	Manual-Congener Group
chlordane related 14	Chlordane-related	0.093	0.09	5	Manual-Congener Group
chlordane related 15	Chlordane-related	0.012	0.011	7	Literature MS
chlordane related 2	Chlordane-related	0.013	0.014	3	Reference Database MS
chlordane related 3	Chlordane-related	0.019	0.019	2	Manual-Congener Group
chlordane related 4	Chlordane-related	0.01	0.01	2	Manual-Congener Group
chlordane related 5	Chlordane-related	0.0072	0.0072	1	Manual-Congener Group
chlordane related 6	Chlordane-related	0.39	0.32	8	Manual-Congener Group
chlordane related 7	Chlordane-related	0.035	0.035	1	Manual-Congener Group
chlordane related 8	Chlordane-related	0.025	0.025	2	Manual-Congener Group
chlordane related 9	Chlordane-related	0.94	1	8	Manual-Congener Group
chlordene 1	Chlordane-related	0.0055	0.0053	3	Reference Database MS
chlordene 2	Chlordane-related	0.007	0.007	1	Reference Database MS
cis nonachlor	Chlordane-related	1.6	1.6	8	Authentic MS RT
gamma chlordane	Chlordane-related	0.21	0.22	7	Authentic MS RT
hydroxychlordene	Chlordane-related	0.0083	0.0088	3	Reference Database MS
oxychlordane	Chlordane-related	0.37	0.39	7	Reference Database MS

trans nonachlor	Chlordane-related	6.7	6.6	8	Authentic MS RT
1,2,3,4-tetrachlorobenzene	Chlorinated benzene	0.041	0.025	5	Authentic MS RT
1,2,4-trichlorobenzene	Chlorinated benzene	0.12	0.079	3	Authentic MS RT
hexachlorobenzene	Chlorinated benzene	2.3	2	8	Authentic MS RT
pentachlorobenzene	Chlorinated benzene	0.081	0.049	4	Authentic MS RT
chlorinated PAH	Chlorinated PAH	0.0017	0.0017	2	Authentic MS
ethenyl benzene 3Cl	Chlorinated styrene	0.052	0.048	5	Reference Database MS
polychlorinated styrene 7Cl	Chlorinated styrene	0.019	0.02	8	Authentic MS
chlorobenzaldehyde	Chlorobenzaldehyde	0.046	0.044	7	Reference Database MS
tris(2-chloroethyl)phosphate	Chlorophosphate	0.013	0.0095	4	Authentic MS RT
DDMU 1	DDT-related	0.19	0.21	6	Authentic MS
DDMU 2	DDT-related	0.73	0.53	8	Authentic MS
DDMU 3	DDT-related	7	5.8	7	Authentic MS RT
DDMU 4	DDT-related	0.15	0.16	6	Authentic MS
DDT related 1	DDT-related	0.016	0.016	7	Reference Database MS
DDT related 10	DDT-related	0.051	0.054	6	Reference Database MS
DDT related 11	DDT-related	0.29	0.18	5	Manual
DDT related 12	DDT-related	0.43	0.42	7	Reference Database MS
DDT related 13	DDT-related	6.1	5.7	7	Reference Database MS
DDT related 14	DDT-related	0.085	0.045	3	Manual-Congener Group
DDT related 15	DDT-related	0.055	0.055	2	Manual-Congener Group
DDT related 16	DDT-related	0.023	0.023	1	Manual-Congener Group
DDT related 17	DDT-related	0.044	0.04	4	Manual-Congener Group
DDT related 18	DDT-related	0.045	0.039	8	Manual-Congener Group
DDT related 19	DDT-related	0.033	0.031	5	Manual-Congener Group
DDT related 2	DDT-related	0.077	0.072	6	Reference Database MS
DDT related 20	DDT-related	0.12	0.094	8	Manual-Congener Group
DDT related 21	DDT-related	0.1	0.098	4	Manual
DDT related 22	DDT-related	0.15	0.1	7	Manual
DDT related 23	DDT-related	0.023	0.016	8	Manual-Congener Group
DDT related 3	DDT-related	1.3	1.2	8	Reference Database MS
DDT related 4	DDT-related	0.094	0.12	5	Reference Database MS

DDT related 5	DDT-related	0.031	0.016	3	Reference Database MS
DDT related 6	DDT-related	0.036	0.024	5	Reference Database MS
DDT related 7	DDT-related	0.061	0.026	6	Reference Database MS
DDT related 8	DDT-related	0.048	0.044	6	Reference Database MS
DDT related 9	DDT-related	0.022	0.023	6	Reference Database MS
o,p'-DDD	DDT-related	5.1	4.9	6	Authentic MS RT
p,p'-DDD	DDT-related	5.9	4.6	8	Authentic MS RT
4,4'-dichlorobenzophenone	Dichlorobenzophenone	3.4	3.8	7	Authentic MS RT
DMBP 4Br 1	DMBP	0.17	0.073	4	Authentic MS
DMBP 4Br 2	DMBP	0.23	0.087	6	Authentic MS
DMBP 4Br 3	DMBP	0.011	0.0032	3	Authentic MS RT
DMBP 4Br 4	DMBP	0.019	0.019	1	Authentic MS RT
DMBP 5Br 1	DMBP	0.36	0.11	8	Authentic MS RT
DMBP 5Br 2	DMBP	0.009	0.0033	3	Authentic MS RT
DMBP 6Br	DMBP	0.047	0.021	8	Authentic MS RT
DMBP 6Cl	DMBP	1.2	1.5	3	Authentic MS RT
DMBP Br2Cl2 1	DMBP	0.15	0.06	7	Manual-Congener Group
DMBP Br2Cl3	DMBP	0.048	0.036	7	Manual-Congener Group
DMBP Br2Cl4	DMBP	0.44	0.18	8	Authentic MS RT
DMBP Br3Cl2 1	DMBP	0.82	0.36	8	Authentic MS RT
DMBP Br3Cl2 2	DMBP	0.0032	0.0044	6	Authentic MS
DMBP Br3Cl2 3	DMBP	0.0034	0.0032	6	Authentic MS
DMBP Br3Cl2 4	DMBP	0.0064	0.0068	4	Authentic MS
DMBP Br3Cl3	DMBP	0.13	0.15	8	Authentic MS RT
DMBP Br4Cl 1	DMBP	0.05	0.033	4	Authentic MS RT
DMBP Br4Cl 2	DMBP	0.012	0.0048	4	Authentic MS RT
DMBP Br4Cl2	DMBP	1.9	2.2	8	Authentic MS RT
DMBP Br5Cl	DMBP	0.021	0.016	8	Authentic MS RT
alpha BHC	HCH-related	0.13	0.13	8	Authentic MS RT
beta BHC	HCH-related	1.6	1.6	8	Authentic MS RT
cyclohexene 4Cl 1	HCH-related	0.057	0.043	5	Reference Database MS
cyclohexene 4Cl 2	HCH-related	0.015	0.02	5	Reference Database MS

heptachlor epoxide	Heptachlor-related	0.52	0.42	8	Authentic MS RT
heptachlor related 1	Heptachlor-related	0.026	0.028	3	Manual
heptachlor related 2	Heptachlor-related	0.043	0.048	8	Manual-Congener Group
heptachlor related 3	Heptachlor-related	0.17	0.18	3	Manual-Congener Group
MBP 4Br 1	MBP	0.012	0.012	2	Manual-Congener Group
MBP 4Br 2	MBP	0.011	0.011	2	Manual-Congener Group
MBP 4Br 3	MBP	0.023	0.023	1	Manual-Congener Group
MBP 4Br 4	MBP	0.0043	0.0043	1	Manual-Congener Group
MBP 6Cl 1	MBP	0.027	0.027	6	Authentic MS
MBP 6Cl 2	MBP	0.31	0.22	7	Authentic MS
MBP 6Cl 3	MBP	0.11	0.12	8	Authentic MS
MBP 7Cl	MBP	1.4	1.5	8	Authentic MS RT
MeOBCDE Br3Cl	MeO-B/CDE	0.059	0.059	1	Manual-Congener Group
2'-MeOBDE-68	MeO-BDE	0.037	0.037	8	Authentic MS RT
6-MeOBDE-47	MeO-BDE	0.21	0.16	8	Authentic MS RT
6'-MeOBDE-99	MeO-BDE	0.0022	0.0022	2	Authentic MS RT
MeOBDE 3Br	MeO-BDE	0.0043	0.0037	7	Authentic MS
MeOBDE 4Br	MeO-BDE	0.0026	0.0016	4	Authentic MS
MeOCDE 8Cl 1	MeO-CDE	0.016	0.0073	3	Manual-Congener Group
MeOCDE 8Cl 2	MeO-CDE	0.012	0.0092	7	Manual-Congener Group
di-MeOPBB-80	MeO-PBB	0.055	0.052	8	Authentic MS RT
methylenebistrichloroanisole	Methylenebistrichloroanisole	0.63	0.59	7	Reference Database MS
methylsulfonylPCB 5Cl 1	Methylsulfonyl-PCB	0.027	0.028	4	Authentic MS
methylsulfonylPCB 5Cl 2	Methylsulfonyl-PCB	0.049	0.037	5	Authentic MS
methylsulfonylPCB 5Cl 3	Methylsulfonyl-PCB	0.013	0.0084	4	Authentic MS
methylsulfonylPCB 6Cl 1	Methylsulfonyl-PCB	0.0062	0.0068	3	Authentic MS
methylsulfonylPCB 6Cl 2	Methylsulfonyl-PCB	0.0048	0.0049	3	Authentic MS
methylsulfonylPCB-101	Methylsulfonyl-PCB	0.16	0.094	7	Authentic MS RT
mirex	Mirex-related	1.3	1.3	7	Authentic MS RT
mirex 1Cl	Mirex-related	0.061	0.045	7	Manual-Congener Group
mirex 2Cl 1	Mirex-related	0.093	0.063	4	Manual-Congener Group
mirex 2Cl 2	Mirex-related	0.038	0.035	7	Manual-Congener Group

mirex related 1	Mirex-related	0.21	0.18	4	Manual
BB 4Br 1	PBB	0.13	0.094	8	Manual-Congener Group
BB 4Br 2	PBB	0.0041	0.004	7	Manual-Congener Group
BB 4Br 3	PBB	0.0018	0.0018	2	Manual-Congener Group
BB 5Br 1	PBB	0.00016	0.00016	1	Manual-Congener Group
BB 5Br 2	PBB	0.036	0.022	8	Manual-Congener Group
BB 5Br 3	PBB	0.0058	0.0058	1	Manual-Congener Group
BB 5Br 4	PBB	0.0024	0.0019	3	Manual-Congener Group
BB 6Br 1	PBB	0.0033	0.0022	3	Authentic MS
BB 6Br 2	PBB	0.0013	0.0013	1	Authentic MS
BB-101	PBB	0.03	0.026	8	Authentic MS RT
BB-153	PBB	0.1	0.077	6	Authentic MS RT
BB-49	PBB	0.028	0.029	4	Authentic MS RT
BB-52	PBB	0.059	0.057	7	Authentic MS RT
BDE 2Br 1	PBDE	0.01	0.0088	6	Authentic MS
BDE 3Br 1	PBDE	0.01	0.01	6	Authentic MS
BDE 3Br 2	PBDE	0.081	0.07	8	Authentic MS
BDE 4Br 1	PBDE	0.018	0.0032	7	Authentic MS
BDE 5Br 1	PBDE	0.041	0.043	8	Authentic MS
BDE-100	PBDE	2.1	2.1	8	Authentic MS RT
BDE-116	PBDE	0.0056	0.0047	7	Authentic MS RT
BDE-153	PBDE	0.069	0.069	8	Authentic MS RT
BDE-154	PBDE	0.29	0.26	8	Authentic MS RT
BDE-155	PBDE	0.049	0.053	8	Authentic MS RT
BDE-17/25	PBDE	0.0057	0.0044	6	Authentic MS RT
BDE-28/33	PBDE	0.31	0.25	7	Authentic MS RT
BDE-47	PBDE	5	3.5	8	Authentic MS RT
BDE-49	PBDE	0.15	0.12	8	Authentic MS RT
BDE-66	PBDE	0.061	0.051	8	Authentic MS RT
BDE-75	PBDE	0.038	0.037	5	Authentic MS RT
BDE-99	PBDE	1.2	0.99	8	Authentic MS RT
dibromobenzofuran 1	PBDF	0.014	0.013	8	Authentic MS

dibromobenzofuran 2	PBDF	0.0066	0.0062	4	Authentic MS
PBHD 3Br 1	PBHD	0.0062	0.0066	5	Authentic MS
PBHD 3Br 2	PBHD	0.01	0.01	7	Authentic MS
PBHD 3Br 3	PBHD	0.078	0.067	7	Authentic MS RT
PBHD 4Br	PBHD	0.024	0.02	8	Authentic MS RT
terphenyl 4Cl 1	PCT	0.017	0.017	2	Literature MS
terphenyl 4Cl 2	PCT	0.027	0.027	2	Literature MS
terphenyl 4Cl 3	PCT	0.01	0.0055	3	Literature MS
terphenyl 4Cl 4	PCT	0.022	0.013	4	Literature MS
terphenyl 4Cl 5	PCT	0.12	0.095	6	Literature MS
terphenyl 4Cl 6	PCT	0.13	0.093	8	Literature MS
terphenyl 4Cl 7	PCT	0.025	0.025	4	Literature MS
terphenyl 4Cl 8	PCT	0.025	0.016	5	Literature MS
terphenyl 4Cl 9	PCT	0.069	0.068	8	Literature MS
terphenyl 5Cl 1	PCT	0.05	0.015	5	Manual-Congener Group
terphenyl 5Cl 2	PCT	0.037	0.037	1	Manual-Congener Group
terphenyl 5Cl 3	PCT	0.018	0.018	1	Manual-Congener Group
terphenyl 5Cl 4	PCT	0.025	0.023	6	Manual-Congener Group
terphenyl 5Cl 5	PCT	0.049	0.023	8	Manual-Congener Group
terphenyl 5Cl 6	PCT	0.063	0.042	3	Manual-Congener Group
terphenyl 6Cl 1	PCT	0.0017	0.0017	2	Manual-Congener Group
terphenyl 6Cl 2	PCT	0.0063	0.0063	2	Manual-Congener Group
terphenyl 6Cl 3	PCT	0.0058	0.0054	4	Manual-Congener Group
terphenyl 6Cl 4	PCT	0.003	0.003	2	Manual-Congener Group
terphenyl 6Cl 5	PCT	0.0085	0.0085	2	Manual-Congener Group
terphenyl 6Cl 6	PCT	0.0077	0.0097	3	Manual-Congener Group
terphenyl 6Cl 7	PCT	0.012	0.012	2	Manual-Congener Group
terphenyl 6Cl 8	PCT	0.0041	0.0041	1	Manual-Congener Group
terphenyl 7Cl 1	PCT	0.0034	0.0035	4	Manual-Congener Group
terphenyl 7Cl 2	PCT	0.018	0.016	5	Manual-Congener Group
terphenyl 7Cl 3	PCT	0.011	0.0083	3	Manual-Congener Group
terphenyl 7Cl 4	PCT	0.0058	0.0058	2	Manual-Congener Group

terphenyl 7Cl 5	PCT	0.011	0.011	2	Manual-Congener Group
terphenyl 7Cl 6	PCT	0.014	0.013	4	Manual-Congener Group
terphenyl 7Cl 7	PCT	0.012	0.011	4	Manual-Congener Group
terphenyl 7Cl 8	PCT	0.0067	0.0067	2	Manual-Congener Group
terphenyl 7Cl 9	PCT	0.0059	0.0052	4	Manual-Congener Group
terphenyl 8Cl 1	PCT	0.0017	0.002	5	Manual-Congener Group
terphenyl 8Cl 2	PCT	0.0034	0.0034	2	Manual-Congener Group
terphenyl 8Cl 3	PCT	0.015	0.018	3	Manual-Congener Group
terphenyl 8Cl 4	PCT	0.011	0.011	3	Manual-Congener Group
terphenyl 8Cl 5	PCT	0.0029	0.0025	3	Manual-Congener Group
pyrrolidinecarbonyl chloride	Pyrrolidinecarbonyl chloride	0.047	0.034	3	Reference Database MS
TCPM 1	TCPM	0.12	0.095	8	Authentic MS
TCPM 2	TCPM	0.12	0.12	1	Authentic MS
TCPM 2Cl	TCPM	0.022	0.014	7	Manual-Congener Group
TCPM 3	TCPM	2.1	1.8	8	Authentic MS
TCPM 4	TCPM	0.7	0.66	8	Authentic MS
TCPM 4Cl 1	TCPM	0.1	0.055	7	Manual-Congener Group
TCPM 4Cl 2	TCPM	0.063	0.032	6	Manual-Congener Group
TCPM 4Cl 3	TCPM	0.046	0.054	6	Manual-Congener Group
TCPM 5	TCPM	5.3	3.6	8	Authentic MS
TCPM 6	TCPM	1.1	1.2	7	Authentic MS
TCPM 7	TCPM	0.33	0.38	5	Authentic MS
Tris(4-chlorophenyl)methane (TCPM)	TCPM	8.1	7.7	8	Authentic MS RT
Tris(4-chlorophenyl)methanol (TCPME)	TCPMOH	18	13	6	Authentic MS RT
toxaphene 1	Toxaphene	0.41	0.36	5	Manual
toxaphene 10	Toxaphene	1.1	0.86	7	Authentic MS RT
toxaphene 11	Toxaphene	0.13	0.13	6	Authentic MS RT
toxaphene 12	Toxaphene	0.4	0.4	6	Manual
toxaphene 13	Toxaphene	0.25	0.18	5	Manual
toxaphene 14	Toxaphene	0.12	0.081	4	Manual
toxaphene 15	Toxaphene	0.28	0.24	7	Manual
toxaphene 16	Toxaphene	0.27	0.27	8	Authentic MS RT

toxaphene 17	Toxaphene	0.44	0.49	8	Authentic MS RT
toxaphene 18	Toxaphene	0.0077	0.0092	3	Authentic MS
toxaphene 19	Toxaphene	0.026	0.026	5	Authentic MS
toxaphene 2	Toxaphene	0.06	0.065	3	Authentic MS RT
toxaphene 3	Toxaphene	0.017	0.016	5	Authentic MS RT
toxaphene 4	Toxaphene	0.013	0.013	2	Authentic MS RT
toxaphene 5	Toxaphene	0.027	0.024	5	Manual
toxaphene 6	Toxaphene	0.08	0.065	3	Manual
toxaphene 7	Toxaphene	0.009	0.0076	4	Manual
toxaphene 8	Toxaphene	0.072	0.071	4	Manual
toxaphene 9	Toxaphene	0.054	0.054	2	Reference Database MS
benzonitrile 3Cl	Trichloro benzonitrile	0.73	0.75	4	N/A
unknown-10	Unknown	0.025	0.025	1	N/A
unknown-11	Unknown	0.05	0.052	6	N/A
unknown-12	Unknown	0.02	0.02	1	N/A
unknown-13	Unknown	0.036	0.038	6	N/A
unknown-14	Unknown	0.14	0.14	1	N/A
unknown-15	Unknown	0.018	0.017	8	N/A
unknown-16	Unknown	0.023	0.023	3	N/A
unknown-17	Unknown	0.026	0.024	5	N/A
unknown-18	Unknown	0.061	0.049	4	N/A
unknown-19	Unknown	0.071	0.061	3	N/A
unknown-20	Unknown	0.01	0.0053	4	N/A
unknown-21	Unknown	0.11	0.035	3	N/A
unknown-22	Unknown	0.098	0.064	8	N/A
unknown-23	Unknown	0.017	0.017	1	N/A
unknown-24	Unknown	0.0025	0.0025	1	N/A
unknown-25	Unknown	0.013	0.013	2	N/A
unknown-26	Unknown	0.17	0.17	2	N/A
unknown-27	Unknown	0.004	0.004	1	N/A
unknown-28	Unknown	0.011	0.011	2	N/A
unknown-29	Unknown	0.0083	0.0083	2	N/A

unknown-30	Unknown	0.0068	0.0068	4	N/A
unknown-31	Unknown	0.0039	0.0039	2	N/A
unknown-32	Unknown	0.014	0.0071	3	N/A
unknown-33	Unknown	0.015	0.015	4	N/A
unknown-34	Unknown	0.014	0.0062	4	N/A
unknown-35	Unknown	0.069	0.069	1	N/A
unknown-36	Unknown	0.012	0.008	6	N/A
unknown-37	Unknown	0.0087	0.0064	4	N/A
unknown-38	Unknown	0.0058	0.0064	4	N/A
unknown-39	Unknown	0.0057	0.0023	3	N/A
unknown-40	Unknown	0.0042	0.0037	3	N/A
unknown-41	Unknown	0.0026	0.002	4	N/A
unknown-42	Unknown	0.016	0.012	7	N/A
unknown-43	Unknown	0.14	0.11	5	N/A
unknown-44	Unknown	0.007	0.0044	4	N/A
unknown-45	Unknown	0.011	0.011	3	N/A
unknown-46	Unknown	0.0054	0.0056	4	N/A
unknown-47	Unknown	0.035	0.029	8	N/A
unknown-48	Unknown	0.00022	0.00022	1	N/A
unknown-49	Unknown	0.052	0.029	5	N/A
unknown-50	Unknown	0.0089	0.0063	7	N/A
unknown-51	Unknown	0.025	0.025	1	N/A
unknown-52	Unknown	0.046	0.037	8	N/A
unknown-53	Unknown	0.0035	0.0029	4	N/A
unknown-54	Unknown	0.0048	0.0046	3	N/A
unknown-55	Unknown	0.0094	0.0079	3	N/A
unknown-56	Unknown	0.0087	0.01	3	N/A
unknown-9	Unknown	0.0025	0.0025	1	N/A
unknown-1-1	Unknown-1	0.11	0.11	1	N/A
unknown-1-2	Unknown-1	0.076	0.076	1	N/A
unknown-1-3	Unknown-1	0.0022	0.0013	3	N/A
unknown-1-4	Unknown-1	0.016	0.012	6	N/A
unknown-1-5	Unknown-1	0.054	0.045	7	N/A

unknown-1-6	Unknown-1	0.0043	0.0043	2	N/A
unknown-2-1	Unknown-2	1.3	1.3	8	N/A
unknown-2-10	Unknown-2	0.084	0.081	8	N/A
unknown-2-11	Unknown-2	0.015	0.01	4	N/A
unknown-2-2	Unknown-2	0.14	0.14	6	Authentic MS
unknown-2-3	Unknown-2	2	1.2	8	Authentic MS
unknown-2-4	Unknown-2	0.81	0.53	7	Authentic MS
unknown-2-5	Unknown-2	0.05	0.029	6	N/A
unknown-2-6	Unknown-2	0.031	0.027	3	N/A
unknown-2-7	Unknown-2	0.18	0.18	2	Authentic MS
unknown-2-8	Unknown-2	0.2	0.17	7	N/A
unknown-2-9	Unknown-2	0.23	0.15	6	N/A
unknown-3-1	Unknown-3	0.029	0.025	8	N/A
unknown-3-2	Unknown-3	0.0047	0.0042	4	N/A
unknown-3-3	Unknown-3	0.0087	0.0076	7	N/A
unknown-4-1	Unknown-4	0.032	0.031	5	N/A
unknown-4-10	Unknown-4	0.11	0.095	8	N/A
unknown-4-11	Unknown-4	0.078	0.052	7	N/A
unknown-4-12	Unknown-4	0.013	0.0097	5	N/A
unknown-4-13	Unknown-4	0.054	0.034	8	N/A
unknown-4-14	Unknown-4	0.061	0.047	8	N/A
unknown-4-15	Unknown-4	0.013	0.013	4	N/A
unknown-4-16	Unknown-4	0.035	0.02	8	N/A
unknown-4-17	Unknown-4	0.016	0.011	6	N/A
unknown-4-2	Unknown-4	0.079	0.067	8	N/A
unknown-4-3	Unknown-4	0.28	0.27	8	N/A
unknown-4-4	Unknown-4	0.16	0.17	7	N/A
unknown-4-5	Unknown-4	0.091	0.087	6	N/A
unknown-4-6	Unknown-4	0.091	0.073	5	N/A
unknown-4-7	Unknown-4	0.065	0.077	5	N/A
unknown-4-8	Unknown-4	0.19	0.15	4	N/A
unknown-4-9	Unknown-4	0.038	0.037	5	N/A

unknown-5-1	Unknown-5	0.012	0.012	2	N/A
unknown-5-2	Unknown-5	0.093	0.09	7	N/A
unknown-6-1	Unknown-6	0.056	0.028	5	N/A
unknown-6-2	Unknown-6	0.0096	0.0039	6	N/A
unknown-6-3	Unknown-6	0.012	0.0073	5	N/A
unknown-7-1	Unknown-7	0.031	0.018	7	N/A
unknown-7-2	Unknown-7	0.07	0.027	8	N/A
unknown-8-1	Unknown-8	0.04	0.029	5	N/A
unknown-8-2	Unknown-8	1.3	1.3	8	N/A

Table S2. K-means clustering results for the anthropogenic compounds.

Blubber Sample	Cluster
offshore (D2)	1
coastal (D3)	1
coastal (D8)	1
offshore (D4)	2
coastal (D5)	2
offshore (D6)	2
offshore (D7)	2
coastal (D1)	2

Table S3. K-means clustering results for the natural compounds.

Blubber Sample	Cluster
offshore (D2)	1
offshore (D4)	1
offshore (D6)	1
offshore (D7)	1
coastal (D1)	2
coastal (D3)	2
coastal (D5)	2
coastal (D8)	2

Table S4. K-means clustering results for the unknown compounds.

Blubber Sample	Cluster
offshore (D4)	1
coastal (D5)	1
coastal (D3)	2
coastal (D8)	2
offshore (D6)	2
offshore (D7)	2
coastal (D1)	2
offshore (D2)	2

Table S5. Stranding and morphometric information for the Southern California *Tursiops truncatus* blubber samples (n=8).

Blind ID	NOAA Code	Stranding Date	CA Stranding Location	Length (cm)	Weight (kg)	Age	Ecotype
D1	KZP0086	7/25/01	Imperial Beach, San Diego	310	n/a	n/a	Coastal
D2	DSJ2195	2/11/06	Dockweiler State Beach, Los Angeles	263	165	7	Offshore
D3	NEB0016	8/9/10	Imperial Beach, San Diego	319	n/a	13	Coastal
D4	JEH0504	7/21/00	Big Sycamore Canyon State Beach, Ventura	293	331	15	Offshore
D5	JEH0472	9/5/95	Solana Beach, San Diego	313	295	17	Coastal
D6	DSJ2155	5/25/04	Newport Beach	265	299	13	Offshore
D7	DSJ1765	5/1/97	Point Dume, Los Angeles	289	298	11	Offshore
D8	KXD0003	3/24/00	Coronado, San Diego	305	n/a	n/a	Coastal