Supplementary Material

# Materials and Methods

## Chemicals

Individual plastic samples were spiked with labelled internal standards (IS) of PCBs, PBDEs and organochlorine pesticides. A 13C labeled PCB mixture (MBP-MO) containing PCB #105, #114, #118, #123, #156, #157, and #167 and a 13C labeled PCB mixture (MBP-CP) containing PCB #77, #81, #126, #169 and #189, and a 13C labelled PBDE mixture (MBDE-MXC) containing PBDE #3, #15, #28, #47, #99, #153, #154 and #183 were purchased from Wellington Laboratories Inc. (Ontario, Canada). A 13C labeled persistent organic pollutant mixture (ES-5261-1.2) containing hexachlorobenzene, alpha- and gamma **hexachlorocyclohexane, lindane, aldrin, dieldrin, endrin, *trans*-chlordane, oxychlordane, *trans*-nonachlor, heptachlor, heptachlor epoxide, 4,4’-DDT, 4,4’-DDE and 4,4’-DDD was purchased from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA). Samples were spiked afterwards with labeled IS of a dioxin mixture for quantification of dioxins in the samples. The 13C labeled dioxin mixture (EN-1948ES) contained** 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, OCDF **(≥98% purity each) (Wellington Laboratories Inc.).**

**For quantification a standard containing a mixture of native and 13C labeled compounds was used. The quantification mixture contained native** 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, OCDF ( >98% purity each) (EPA-8290STN, Wellington Laboratories Inc.), PBDE #28, #47, #66, #85, #99, #100, #153, #154 and #183 (>98% purity each) (BDE-MXF, Wellington Laboratories Inc.), PCB #1, #3, #4, #8, #9, #10, #11, #12, #15, #18, #19, #28, #31, #33, #35, #37, #38, #44, #49, #52, #54, #57, #66, #70, #74, #77, #78, #79, #81, #87, #95, #99, #101, #104, #105, #110, #111, #114, #118, #123, #126, #138, #149, #153, #155, #156, #157, #162, #167, #169, #170, #174, #178, #180, #187, #188, #189, #194, #195, #199, #202, #203, #205, #206, #208 and #209 (>98-100% purity) (EC-5433, Cambridge Isotope Inc.), aldrin, cis-Chlordane, trans-Chlordane, oxy-Chlordane, **2,4′-Dichlorodiphenyldichloroethane** (2,4**′** DDD), **1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (**4,4**′** DDD), 2,4 DDE , 4,4 DDE, 2,4 DDT, 4,4 DDT, dieldrin, alpha-endosulfan, beta-endosulfan, endrin, alpha, beta, gamma, delta, and epsilon HCH, heptachlor, heptachlor exo epoxide, heptachlor endo epoxide, hexachlorobenzene, isodrin, methoxychlor, mirex, PCB #28, #52, #101, #138, #153, and #180 (94-99.9% purity) (Pesticide-Mix 13, Labor; Dr. Ehrenstorfer-Schäfers, Augsburg, Germany). 13C labeled compounds as IS in the quantification mixture contained **PBDE #28, #47, #99, #100, #153, #154, #183 (> 98% purity each) (MBDE-MXFS, Wellington Laboratories Inc.), PCB #28, #52, #70, #101, #105, #118, #138, #153, #156, #170 (97.5% purity), #180, #194, #202, #206, #209 (> 98% purity each) (Wellington Laboratories Inc.), and PCDD/Fs 13C labeled mixture EN-1948ES. As recovery standards (RS) the following 13C labeled compounds were present in the quantification standard: 1,2,3,4-TCDD, 1,2,3,7,8,9-HxCDD (> 98% purity each) (EN-1948IS, Wellington Laboratories Inc.), PCB #81, #114, #178 (> 98% purity each) (Wellington Laboratories Inc.), PBDE #77, #138 (> 98% purity each) (MBDE-MXFR, Wellington Laboratories Inc.).**

For testing of the GC-MS fractionator efficiency five different native standards of mixtures of one class of compounds were used, as well as a mixture of all the five native standards. A PAH standard mixture containing 16 PAHs (Mix 63): naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, pyrene, fluorene, fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[b]fluoranthene, chrysene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, benzo[k]fluoranthene and benzo[a]anthracene (98-99.50% purity) and a native pesticide standard mixture, Pesticide-Mix 13, of 32 compounds were purchased from Labor; Dr. Ehrenstorfer-Schärfers. A PCB native standard mixture, EC-5433, containing 66 congeners was purchased from Cambridge Isotope Laboratories, Inc. A native PBDE standard mixture, BDE-MXF, consisting of nine congeners and a native polychlorinated dibenzo-p-dioxins and dibenzofurans mixture, EPA-8290STN, containing 17 compounds were purchased from Wellington Laboratories Inc..

## Deployment of plastics

Table S1. Coordinates of plastic pellets deployed on 14th of February 2015, date of sampling of the four sampled time points and record of samples that were taken from the two metal cages.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Coordinates** | **Date of sampling** | **Time of deployment (months)** | **Pellets sampled from cage 1** | **Pellets sampled from cage 2** |
| 23.444966 S  151.918639 E | 13.03.2015 | 1 | LDPE, HDPE, PP | LDPE, HDPE, PP |
| 08.05.2015 | 3 | LDPE, HDPE, PP | LDPE |
| 02.08.2015 | 6 | LDPE, HDPE, PP | LDPE |
| 05.10.2015 | 8 | LDPE, HDPE, PP | LDPE |

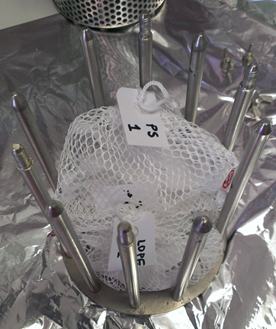
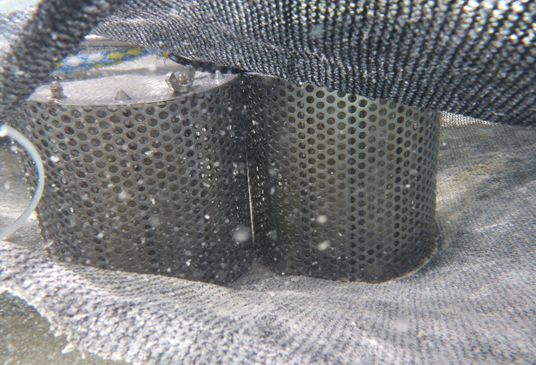
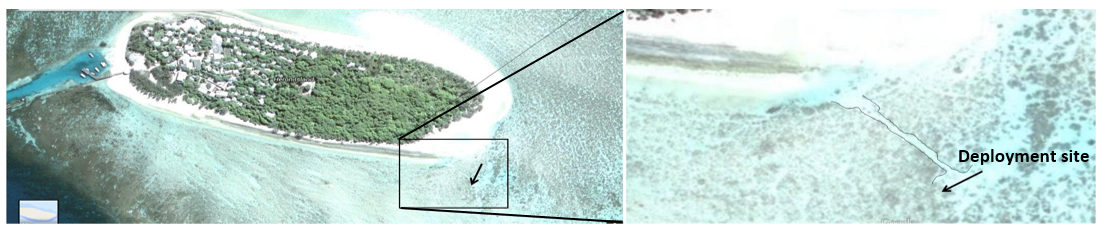


Figure S1. Pictures of the deployment site on Heron Island, AU, and metal cages with plastic pellets. The top left shows a picture of Heron Island with the deployment site indicated by an arrow on the south east part below the island. On the top right an enlarged picture of the deployment site. The bottom left shows the two metal cages deployed on the ground of the reef and covered with a black cloth for stability. The bottom right shows the opened metal cage with plastic pellets, wrapped in smaller mesh bags, in a bigger mesh bag according to the plastic type.

## Extraction of microplastics

**Table S2**. Average percentage of recoveries of 13C-labeled compounds after extraction of two replicates of each polymer type by ultrasonication and the corresponding standard deviation (SD) and relative standard deviation (RSD).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **LDPE** | | | **HDPE** | | |
|  | Recovery | SD | RSD [%] | Recovery | SD | RSD [%] |
| PCB#52 | 88 | 7.7 | 8.8 | 74 | 6.2 | 8.4 |
| PCB#70 | 46 | 11 | 25 | 84 | 4.7 | 5.6 |
| PCB#81 | 17\* |  |  | 90 | 9.3 | 10 |
| PCB#101 | 58 | 12 | 21 | 61 | 8.1 | 13 |
| PCB#105 | 35 | 8.0 | 23 | 85 | 4.7 | 5.5 |
| PCB#114 | 20 | 2.9 | 15 | 101 | 17 | 17 |
| PCB#118 | 80 | 18 | 23 | 79 | 5.5 | 7.0 |
| PCB#138 | 66 | 15 | 23 | 81 | 5.1 | 6.3 |
| PCB#153 | 42 | 8.2 | 19 | 81 | 4.8 | 5.9 |
| PCB#156 | 99 | 23 | 24 | 125 | 1.1 | 0.9 |
| PCB#170 | 79 | 18 | 22 | nd |  |  |
| PCB#178 | 18 | 2.3 | 13 | 87 | 14 | 16 |
| PCB#180 | 58 | 9.0 | 16 | 113 | 3.5 | 3.1 |
| PCB#194 | 65 | 15 | 24 | 112 | 2.4 | 2.1 |
| PCB#206 | 62 | 14 | 24 | 103 | 3.3 | 3.2 |
| PCB#209 | 62 | 16 | 25 | 96 | 3.8 | 4.0 |
| HCB | 393 | 47 | 12 | 197 | 4.1 | 2.1 |
| Cis-chlordane | 77 | 24 | 32 | 74 | 2.1 | 2.8 |
| Trans-chlordane | 105 | 27 | 26 | 74 | 0.2 | 0.3 |
| Trans-nonachlordane | 78 | 26 | 33 | 71 | 1.2 | 1.7 |
| 2,4’-DDE | 92 | 1.3 | 1.5 | 87 | 13 | 16 |
| 4,4’-DDE | 106 | 4.1 | 3.9 | 85 | 3.5 | 4.2 |
| PBDE#47 | 43 | 3.2 | 7.4 | 107 | 21 | 19 |
| OCDD | 62 | 20 | 32 | 128 | 14 | 11 |

nd: not determined; \*: one replicate available

## Chemical analysis

For target chemical analysis of extracts of individual plastic pellets an APGC- triple quadrupole MS was used. For analysis of PCBs and pesticides initial oven temperature was set to 180 °C (2 min), then increased at 3.5 °C/min to 260 °C, and last the oven temperature was increased at 6.5 °C/min to 300 °C. The oven temperature program for the analysis of dioxins was as follows: 180 °C (1 min); 30 °C/min to 200 °C; 4 °C/min to 260 °C; 6.5 °C/min to 300 °C; 20 °C/min to 325 °C (5 min). For analysis of PBDEs the oven program was as follows: 180 °C (2 min); 8 °C/min to 250 °C; 1.5 °C/min to 260 °C (2 min); 25 °C/min to 325 °C (5 min). Helium was used as carrier gas in a constant flow of 2 mL/min. The transfer line temperature was set to 310 °C and nitrogen (N2) was used as make-up gas at 210 mL/min. The cone gas (N2) was set to 230 L/hr and the auxillary gas (N2) was set to 220 L/hr. The atmospheric pressure chemical ionization (APCI) corona needle was operated in a constant current mode at 1.6 µA.

For fractionation of pooled plastic samples a GC-MS fractionator was used. Therefore, two µL of all samples were injected at 280 °C in splitless mode. The initial oven temperature was 90 °C and was increased at 10 °C/min to 180 °C. After that the temperature was increased at 15 °C/min to 205 °C/min and held constant for 10 min, and finally an increase at 3.7 °C/min to 325 °C where is was held constant for 5 min. The MS transfer line temperature was set to 280 °C. A helium carrier gas flow was maintained constant at 3 mL/min. Heptane was used as a trap solvent with a flow of 0.2 mL/min and preheated to 300 °C before mixing with the GC eluate.

For further analysis of fractions obtained from the GC-MS fractionator a GC- Orbitrap® MS was used. One µL of the fractions were injected at a temperature of 280 °C in splitless mode. The initial oven temperature was 70 °C and increased to 205 °C at 8 °C/min where is was held for 2 min, followed by an increase of 8 °C/min to 250 °C, and then increased at 3 °C/min to 270 °C where is was held for 2 min. Next, the temperature was increased at 9 °C/min to 279 °C, followed by an increase of 1 °C/min to 280 °C where is was kept for 3 min, and then increased at 5 °C/min to 300 °C where it was held for 2 min. Finally, the temperature was increased by 25 °C/min to 325 °C and kept for 10 min. The helium carrier gas flow was kept constant at 1.5 mL/min throughout the GC run. The MS transfer line temperature was set to 280 °C.

**Table S3.** Target chemicals for analysis of fractionated samples with GC-HRMS.

|  |  |  |
| --- | --- | --- |
|  | **Compound** | **m/z** |
| 1 | Naphthalene | 128.06260 |
| 2 | Acenaphthylene | 152.06260 |
| 3 | Acenaphthene | 154.07830 |
| 4 | Fluorene | 166.07830 |
| 5 | Phenanthrene, anthracene | 178.07830 |
| 6 | PCB 1-3 | 188.03850 |
| 7 | Pyrene, fluoranthene | 202.07830 |
| 8 | alpha-beta-gamma-delta-epsilon HCH | 216.91450 |
| 9 | PCB 4-8-9-10-11-12-15 | 222.00030 |
| 10 | Benzo[a]anthracene/chrysene | 228.09390 |
| 11 | 2,4 - 4,4 DDD | 235.00810 |
| 12 | Mirex | 236.84130 |
| 13 | 2,4 - 4,4 DDE, DDT | 246.00030 |
| 14 | Benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene | 252.09390 |
| 15 | PCB 18-19-28-31-33-35-37-38 | 255.96130 |
| 16 | Aldrin, dieldrin | 262.85690 |
| 17 | Benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene | 276.09390 |
| 18 | Dibenz[a,h]anthracene | 278.10960 |
| 19 | Hexachlorobenzene | 283.81020 |
| 20 | PCB 44-49-52-54-57-66-70-74-77-78-79-81 | 289.92240 |
| 21 | 2,3,7,8-TeCDF | 303.90160 |
| 22 | 2,3,7,8-TeCDD | 319.89650 |
| 23 | PCB 87-95-99-101-104-105-110-111-114-118-123-126 | 325.88040 |
| 24 | 1,2,3,7,8-2,3,4,7,8-PeCDF | 339.86000 |
| 25 | Methoxychlor | 344.01380 |
| 26 | 1,2,3,7,8-PeCDD | 355.85500 |
| 27 | PCB 138-149-153-155-156-157-162-167-169 | 359.84150 |
| 28 | Isodrin | 361.87570 |
| 29 | Heptachlor | 369.82110 |
| 30 | Cis-Trans-chlordane | 372.82600 |
| 31 | 1,2,3,4,7,8-1,2,3,6,7,8-1,2,3,7,8,9-2,3,4,6,7,8-HxCDF | 373.82100 |
| 32 | Endrin | 377.87060 |
| 33 | Heptachlor exo-endo epoxide | 385.81600 |
| 34 | 1,2,3,4,7,8-1,2,3,6,7,8-1,2,3,7,8,9-HxCDD | 389.81600 |
| 35 | PCB 170-174-178-180-187-189-189 | 393.80250 |
| 36 | alpha-beta-endosulfan | 403.81690 |
| 37 | BDE 28 | 405.80260 |
| 38 | 1,2,3,4,6,7,8-1,2,3,4,7,8,9-HpCDF | 407.78200 |
| 39 | oxy-chlordane | 419.77700 |
| 40 | 1,2,3,4,6,7,8-HpCDD | 423.77700 |
| 41 | PCB 194-195-199-202-203-205 | 427.76350 |
| 42 | OCDF | 441.74300 |
| 43 | OCDD | 457.73800 |
| 44 | PCB 206-208 | 461.72460 |
| 45 | BDE 47-66-77 | 485.71110 |
| 46 | PCB 209 | 497.68260 |
| 47 | BDE 85-99-100 | 563.62150 |
| 48 | BDE 153-154-138 | 643.53000 |
| 49 | BDE 183 | 721.44050 |

**Table S4.** List of analyzed suspect chemicals in fractionated samples (Carlos F. Jasso-Gastinel and Kenny 2016)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Type of additive** | **Commercial name** | **Molecular formula** | **m/z** |
| 1 | Antioxidant | ANOX 29 | C32H52O3 | 484.3911 |
| 2 | Antioxidant | Sipax DLTDP | C30H58O4S | 514.40503 |
| 3 | Antioxidant | EVERFOS 168 | C42H63O3P | 646.4515 |
| 4 | Antioxidant | ALKANOX 240 | C42H63O3P | 646.45093 |
| 5 | Antioxidant | Songnox DSTDP | C42H82O4S | 682.59283 |
| 6 | Antioxidant | IRGANOX PS 800 | C30H58O4S | 514.40503 |
| 7 | Photo-stabilizer | LOWLITE 20 | C14H12O3 | 228.0781 |
| 8 | Photo-stabilizer | TINUVIN 1130 | C13H11N3O | 225.08966 |
| 9 | Photo-stabilizer | SUNSORB 5411 | C20H25N3O | 323.19921 |
| 10 | Photo-stabilizer | |  | | --- | | KRITILEN UV 17 | |  | | C13H10O | 182.07262 |
| 11 | Flame retardants | BE-51 | C21H20Br4O2 | 619.81913 |
| 12 | Flame retardants | DECHLORAN plus 25 | C18H12Cl12 | 647.71958 |
| 13 | Flame retardants | BIOFR IPP-35 | C27H44O4P | 463.29717 |
| 14 | Plasticizer | Dioctylphthalate | C24H38O4 | 390.27646 |
| 15 | Plasticizer | Diisononylphthalate | C26H42O4 | 418.30776 |
| 16 | Plasticizer | Diisodecylphthalate | C28H46O4 | 446.33906 |
| 17 | Plasticizer | Di-n-butylphtalate | C16H22O4 | 278.15126 |
| 18 | Plasticizer | ADIMOLL BO | C21H32O4 | 348.22951 |
| 19 | Plasticizer | BENZOFLEX 2088 | C18H18O5 | 314.1154 |
| 20 | Plasticizer | BENZOFLEX 2088 | C20H22O5 | 342.1467 |
| 21 | Plasticizer | BENZOFLEX 2088 | C20H22O6 | 358.1416 |
| 22 | Plasticizer | K-FLEX 500 | C20H22O5 | 342.14618 |
| 23 | Plasticizer | K-FLEX 500 | C18H18O5 | 314.11488 |
| 24 | Plasticizer | KLJ-TCP-100 | C21H21O4P | 368.1172 |
| 25 | Bio-based additives | CAPLIG-770 | C28H52N2O4 | 480.3927 |
| 26 | Bio-based additives | Baerostab LSA | C28H52N2O4 | 480.39216 |
| 27 | Bio-based additives | CITROFOL AHII | C32H58O8 | 570.41262 |

Table S5. Parameters defined in XCMS online website for data analysis of fractionated samples.

|  | Parameter | Description | EI ionization |
| --- | --- | --- | --- |
| General | Polarity | Mode of data acquisition | Positive |
| Retention time format | Time unit (minutes or seconds) | Minutes |
| Feature detection | Method | Feature detection method | Matched Filter |
| FWHM | full width at half maximum of matched filtration gaussian model peak | 30 |
| step | step size to use for profile generation | 10 |
| maximum peak width | maximum chromatographic peak width in seconds | 60 |
| Signal/Noise threshold | Signal to noise ratio cutoff | 2 |
| mzdiff | minimum difference in m/z for peaks with overlapping retention times, can be negative to allow overlap | 0.01 |
| max # chrom. peaks | maximum number of peaks per extracted ion chromatogram | 10 |
| Retention time correction | Method | Retention time correction method | Obiwarp |
| ProfStep | Step size (m/z) to use for profile generation from the raw data files | 0.1 |
| Alignment | Grouping method |  | Density |
| Bw | Bandwidth: Tolerated RT deviations (sec) | 5 |
| m/z width | Width of overlapping m/z slices to use for creating peak density chromatograms and grouping peaks across samples | 0.025 |
| Minfrac | Minimum fraction of samples necessary in at least one of the sample groups for it to be a valid group | 0 |
| Minsamp | minimum number of samples necessary in at least one of the sample groups for it to be a valid group | 1 |
| Max | maximum number of groups to identify in a single m/z slice | 100 |
| Statistics | Statistical test | Statistical test method. Can be paired/unpaired and parametric/non-parametric | ANOVA parametric |
| p-value threshold | Highly significant features have a p-value lower than this | 0.01 |
| Fold change threshold | Highly significant features have a fold change greater than this | 1.5 |
| Diffreport value | Into= integrated peak intensities are used for the diffreport Maxo=maximum peak intestities are used | Into |
| Normalization | Normalize the intensity values by either probabilistic quotient or cyclic loess normalization. | None |

# Results

**Table S6.** Calculated bio-TEQs based on effective concentrations for 25% (EC25) (unless otherwise noted) given as the mean of number of replicates (**n**) in pg/g of plastic extracts following a 24 h exposure and calculated potency balance (%) between bio-TEQ values and derived chem-TEQ values of analyzed PCBs and PCDD/Fs.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **n** | **bio-TEQ [pg/g]** | **Standard deviation** | **Potency balance [%]** |
| *Blank LDPE* | 4 | n.d. |  |  |
| *LDPE I 1m* | 4 | 15 | 3.1 | 7×10-6 |
| *LDPE II 1m* | 3 | 17 | 2.8 | 4.3×10-6 |
| *LDPE I 3m* | 3 | 44 | 15 | 2×10-6 |
| *LDPE II 3m* | 3 | 40 | 4.5 | 5.2×10-6 |
| *LDPE I 6m* | 3 | 60 | 1.7 | 1.3×10-6 |
| *LDPE II 6 m* | 3 | 42 | 3.4 | 1.6×10-6 |
| *LDPE I 8m* | 3 | 57 | 11 | 6×10-5 |
| *LDPE II 8m* | 3 | 41 | 25 | 1.6×10-4 |
| *Blank HDPE* | 3 | 7.6\* | 4.9 | 2.8×10-6 |
| *HDPE I 1m* | 3 | 35 | 5.3 | 7.9×10-4 |
| *HDPE II 1m* | 3 | 16 | 10 | 9.7×10-4 |
| *HDPE I 3m* | 3 | 40 | 11 | 2.6×10-6 |
| *HDPE I 6m* | 3 | 30 | 9.8 | 9.8×10-5 |
| *HDPE I 8m* | 3 | 100 | 2.3 | 3.2×10-5 |
| *Blank HIPS* | 4 | n.d. |  |  |
| *HIPS I 1m* | 3 | n.d. |  |  |
| *HIPS II 1m* | 3 | n.d. |  |  |
| *HIPS I 3m* | 2 | 51\*,a | 6.5 |  |
| *HIPS I 6m* | 2 | 50\*,b. | 26 |  |
| *HIPS I 8m* | 2 | 69\*,b | 17 |  |

n.d. = below EC20; \* = calculated at EC20; a = calculated at the second greatest concentration tested; b = calculated at the third greatest concentration tested

**Table S7.** Concentrations in pg/g of detectable HOCs in plastic pellets. Numbers in red indicate values above LOD but below LOQ. The sum of concentration of PCBs, the sum of concentrations of pesticides, and the sum of concentrations of PBDEs include only values above LOQ.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | **Blank LDPE** | | **Blank HDPE** | | **Blank HIPS** | | **LDPE I 1 m** | | **LDPE II 1 m** | | **LDPE I 3 m** | | **LDPE II 3 m** | | **LDPE I 6 m** | | **LDPE II 6 m** | | **LDPE I 8 m** | | **LDPE II 8 m** | | **HDPE I 1 m** | | **HDPE II 1 m** | | **HDPE I 3 m** | | **HDPE I 6 m** | | **HDPE I 8 m** | |
| **PCB 52** | | 81 | | <0.6 | | 32 | | <0.9 | | <0.5 | | <0.6 | | <0.6 | | <0.6 | | <0.6 | | 46 | | <0.8 | | <0.7 | | <0.7 | | <0.6 | | <0.6 | | <0.6 | |
| **PCB 49** | | 24 | | 46 | | 14 | | 48 | | 101 | | 38 | | 48 | | 37 | | 20 | | 13 | | 52 | | 102 | | 37 | | 20 | | 15 | | 16 | |
| **PCB 44** | | 42 | | <2.5 | | 19 | | <3.5 | | <2.2 | | <2.4 | | <2.6 | | <2.4 | | <2.5 | | 17 | | <3.3 | | <2.8 | | <2.7 | | <2.4 | | <2.4 | | <2.4 | |
| **PCB 74** | | 18 | | <1.3 | | <1.2 | | <1.8 | | <1.2 | | <1.2 | | <1.4 | | <1.2 | | <1.3 | | 7.7 | | <1.8 | | <1.5 | | <1.4 | | <1.3 | | <1.3 | | <1.3 | |
| **PCB 70** | | 31 | | <1.2 | | <1.1 | | <1.7 | | <1.1 | | <1.1 | | 11 | | 10 | | <1.2 | | 15 | | <1.6 | | 16 | | 11 | | 5.7 | | 4.5 | | <1.1 | |
| **PCB 66** | | 24 | | <1.1 | | <1.0 | | 13 | | <1.0 | | 2.9 | | <1.2 | | 10 | | <1.1 | | 14 | | <1.5 | | <1.3 | | 1.6 | | <1.1 | | <1.1 | | <1.1 | |
| **PCB 79** | | <1.4 | | <1.6 | | <1.4 | | <2.2 | | <1.4 | | <1.5 | | <1.6 | | <1.5 | | <1.6 | | <1.6 | | <2.1 | | <1.8 | | <1.7 | | <1.5 | | <1.5 | | <1.5 | |
| **PCB 95** | | 6.1 | | 6.1 | | 4.9 | | 7.1 | | 11 | | 5.2 | | 7.7 | | 5.3 | | 2.7 | | 7.6 | | 9.2 | | 20 | | 7.1 | | 2.9 | | 3.2 | | 2.9 | |
| **PCB 101** | | < 21 | | < 23 | | < 21 | | < 32 | | < 21 | | < 22 | | < 24 | | < 22 | | < 23 | | < 23 | | < 30 | | 38 | | < 25 | | < 22 | | < 22 | | < 22 | |
| **PCB 99** | | < 12 | | 18 | | <12 | | < 18 | | < 12 | | < 12 | | 20 | | < 12 | | < 13 | | 16 | | 25 | | 73 | | 28 | | < 13 | | < 13 | | < 13 | |
| **PCB 87** | | 1.6 | | < 1.2 | | <1.0 | | <1.6 | | 1.3 | | 2.1 | | 2.3 | | <1.1 | | <1.2 | | 2.6 | | <1.5 | | 4.9 | | 2.1 | | 1.1 | | 1.1 | | 1.1 | |
| **PCB 110** | | 3.6 | | <2.5 | | <2.3 | | <3.5 | | 5.4 | | < 2.4 | | 3.0 | | < 2.4 | | < 2.5 | | 2.9 | | < 3.3 | | <2.9 | | < 2.8 | | <2.5 | | <2.4 | | <2.4 | |
| **PCB 118** | | 4.9 | | <1.2 | | <1.0 | | 11 | | 7.3 | | 9.1 | | 18 | | 8.0 | | 6.6 | | 19 | | 26 | | 62 | | 24 | | 11 | | 9.8 | | 9.4 | |
| **PCB 105** | | <1.7 | | 2.2 | | <1.7 | | <2.6 | | < 1.7 | | <1.8 | | 2.5 | | < 1.8 | | <1.9 | | 2.9 | | 2.9 | | 8.5 | | 3.6 | | < 1.8 | | < 1.9 | | < 1.1 | |
| **PCB 155** | | <0.6 | | < 0.7 | | <0.6 | | <1.0 | | <0.6 | | <0.6 | | <0.7 | | <0.6 | | <0.7 | | <0.7 | | <0.9 | | <0.8 | | < 0.7 | | <0.7 | | <0.6 | | <0.6 | |
| **PCB 149** | | 15 | | 18 | | 19 | | <3.3 | | 8.7 | | <2.2 | | 19 | | 11 | | 7.3 | | 19 | | 25 | | 53 | | 24 | | 8.9 | | 10 | | 11 | |
| **PCB 153** | | <26 | | 155 | | <26 | | 115 | | 22 | | 83 | | 202 | | 114 | | 85 | | 220 | | 304 | | 673 | | 332 | | 102 | | 128 | | 104 | |
| **PCB 138** | | <7.1 | | 111 | | <7.0 | | 71 | | 22 | | 48 | | 120 | | 77 | | 54 | | 146 | | 170 | | 408 | | 223 | | 63 | | 79 | | 72 | |
| **PCB 162** | | <1.0 | | 6.1 | | <0.9 | | <1.5 | | <0.9 | | <1.0 | | <1.1 | | <1.0 | | <1.1 | | <1.1 | | <1.4 | | <1.2 | | <1.1 | | <1.0 | | <1.0 | | <1.0 | |
| **PCB 156** | | <1.3 | | <1.4 | | <1.3 | | <2.0 | | <1.3 | | < 1.3 | | <1.5 | | < 1.3 | | <1.4 | | 1.6 | | 3.2 | | 7.9 | | 4.2 | | < 1.4 | | 1.4 | | 1.6 | |
| **PCB 157** | | <1.3 | | <1.5 | | <1.3 | | <2.0 | | <1.3 | | <1.4 | | <1.5 | | <1.4 | | <1.4 | | <1.5 | | <1.9 | | 2.8 | | 1.7 | | <1.4 | | <1.4 | | <1.4 | |
| **∑ PCBs** | | 239 | | 355 | | 84 | | 142 | | 133 | | 97 | | 419 | | 267 | | 81 | | 519 | | 577 | | 1427 | | 652 | | 210 | | 248 | | 214 | |
|  | | | | | | | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |
| Continuation of Table S7. | | | | | | | | | | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |  | |
|  | **Blank LDPE** | | **Blank HDPE** | | **Blank HIPS** | | **LDPE I 1 m** | | **LDPE II 1 m** | | **LDPE I 3 m** | | **LDPE II 3 m** | | **LDPE I 6 m** | | **LDPE II 6 m** | | **LDPE I 8 m** | | **LDPE II 8 m** | | **HDPE I 1 m** | | **HDPE II 1 m** | | **HDPE I 3 m** | | **HDPE I 6 m** | | **HDPE I 8 m** | |
| **Heptachlor** | 3.6 | | <3.7 | | <3.3 | | <5.1 | | <3.3 | | <3.4 | | <3.8 | | <3.4 | | <3.7 | | 60 | | <4.9 | | <4.2 | | <4.0 | | <3.6 | | <3.5 | | <3.5 | |
| **t-chlordane** | <1.9 | | <2.1 | | <1.9 | | <2.9 | | <1.9 | | <2.0 | | <2.2 | | <2.0 | | <2.1 | | 2.8 | | <2.8 | | <2.4 | | <2.3 | | <2.0 | | <2.0 | | <2.0 | |
| **p,p'-DDD** | 8.8 | | <2.3 | | <2.1 | | <3.2 | | <2.1 | | 6.3 | | 4.2 | | 4.3 | | 2.3 | | 5.7 | | 9.1 | | 7.3 | | 7.3 | | 3.4 | | 2.2 | | 3.3 | |
| **∑ Pesticides** | 8.8 | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | | 60 | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | | <LOD | |
| **OCDD** | <0.1 | | <0.1 | | <0.1 | | <0.2 | | 0.4 | | <0.1 | | <0.2 | | <0.1 | | <0.1 | | <0.1 | | <0.2 | | <0.2 | | <0.2 | | <0.1 | | <0.1 | | <0.1 | |
| **BDE#28** | <0.1 | | 0.4 | | <0.1 | | 1.1 | | 9.8 | | 1.0 | | 2.3 | | 1.1 | | 0.9 | | 2.1 | | 2.0 | | 0.2 | | 0.3 | | 0.6 | | 0.4 | | 0.5 | |
| **BDE#47** | 2.6 | | 9.8 | | <0.1 | | 7.8 | | 43 | | <0.1 | | 20 | | 6.1 | | 13 | | 31 | | 26 | | 1.7 | | 1.5 | | 3.1 | | 1.5 | | 3.6 | |
| **BDE#100** | <0.1 | | 1.4 | | <0.1 | | <0.1 | | 5.6 | | <0.1 | | 1.8 | | <0.1 | | <0.1 | | 5.1 | | 2.7 | | 0.2 | | <0.1 | | 0.1 | | 0.1 | | <0.1 | |
| **BDE#99** | <0.5 | | 2.5 | | < 0.5 | | 1.5 | | 23 | | <0.5 | | 5.6 | | 1.2 | | <0.6 | | 12 | | 5.1 | | <0.1 | | 0.8 | | < 0.5 | | < 0.5 | | < 0.5 | |
| **BDE#85** | <0.5 | | <0.6 | | <0.5 | | <0.8 | | < 0.5 | | <0.5 | | <0.6 | | <0.5 | | <0.6 | | 1.0 | | <0.7 | | <0.6 | | <0.6 | | < 0.5 | | < 0.5 | | < 0.5 | |
| **BDE#154** | 0.1 | | 1.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | 2.9 | | 0.9 | | <0.0 | | 0.1 | | <0.1 | | 0.1 | | 0.2 | |
| **BDE#183** | <0.1 | | <0.1 | | <0.1 | | 1.9 | | 1.6 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.1 | | <0.0 | | 1.1 | | <0.1 | | 0.1 | | 0.1 | |
| **∑ PBDEs** | 2.6 | | 15 | | <LOD | | 11 | | 83 | | 1.0 | | 30 | | 7.2 | | 14 | | 53 | | 36 | | 1.7 | | 2.9 | | 3.7 | | 1.9 | | 4.1 | |

## Performance of the GC-MS fractionation platform

The suitability of the GC-column and the set GC parameters for separation and retention of different classes of organic compounds were evaluated (see above). The column and the GC settings were found to provide a sufficient separation of a wide range of compounds. All compounds were eluted from the column between 5.14 min (naphthalene) and 50.74 min (indeno[1,2,3,- c,d]pyrene).

**Table S8.** Detected compounds (118 out of 134) in 17 collected fractions of a defined mixture.

|  |  |  |
| --- | --- | --- |
| **Fraction** | **Retention time [min]** | **Detected compounds by GC-HRMS** |
| 1 | 4.12 – 7.12 | Naphthalene |
| 2 | 7.12 – 10.12 | Acenaphthylene, acenaphthene, PCB #1 |
| 3 | 10.12 – 13.12 | Fluorene, PCB #3, #4, #8, #9, #10, #11, #12, #15, #18, #19, hexachlorobenzene, alpha and gamma hexachlorocyclohexane |
| 4 | 13.12 – 16.12 | Phenanthrene, anthracene, PCB #12, #15, #28, #31, #33, #35, #37, #38, #44, #49, #52, #54, #104, beta, delta and epsilon hexachlorocyclohexane |
| 5 | 16.12 – 19.12 | PCB #37, #57, #70, #74, #95, #101, #155, trans-chlordane, cis-chlordane |
| 6 | 19.12 – 22.12 | Fluoranthene, PCB #66, #78, #79, #87, #99, #101, 2,4-DDE, 4,4-DDE, cis-chlordane |
| 7 | 22.12 – 25.12 | Pyrene, PCB #77, #81, #110, , #118, #123, #149, #153, #188, 2,4-DDD, 4,4-DDD |
| 8 | 25.12 – 28.12 | PCB #105, #114, #138 #153, #178, #187, 4,4-DDD, 2,4-DDT, 4,4-DDT, PBDE #28 |
| 9 | 28.12 – 31.12 | 2,3,7,8-TeCDF, 2,3,7,8-TeCDD, PCB #126, #156, #162, #167, #174, #202 |
| 10 | 31.12 – 34.12 | Benzo[a]anthracene, chrysene, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, PCB #157, #169, #170, #180, #199, #203, PBDE #47, Mirex |
| 11 | 34.12 – 37.12 | 1,2,3,4,7,8-HxCDF, PCB #189, #194, #195, #205, #208, PBDE #66 |
| 12 | 37.12 – 40.12 | 1,2,3,6,7,8- HxCDF, 1,2,3,7,8,9- HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8- HxCDD, 1,2,3,6,7,8- HxCDD, 1,2,3,7,8,9-HxCDD, PCB #206, #209, PBDE #100 |
| 13 | 40.12 – 43.12 | Benzo[b]fluoranthene, benzo[k]fluoranthene, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD |
| 14 | 43.12 – 46.12 | Benzo[a]pyrene, 1,2,3,4,7,8,9-HpCDF, OCDD, PBDE #154 |
| 15 | 46.12 – 49.12 | OCDF |
| 16 | 49.12 – 52.12 | Benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene |
| 17 | 52.12 – 54.12 | None |



**Figure S2**. Principal component analysis of GC-HRMS data of 17 fractions of pooled HIPS and 17 fractions of HIPS blank illustrating score plot and loading plot results.

# References

Carlos F. Jasso-Gastinel, Kenny JM. 2016. Chapter: 4 additives in polymers. In: Modification of polymer properties:Elsevier, p 87-108.

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