Supplementary material

# Organochlorine pesticides and polychlorinated biphenyls along an east-to-west gradient in subtropical North Atlantic surface waters

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## S1 Methodology

### S1.1 Sampling

Table S1. Sampling parameters during cruise M113, sections I-II, of RV Meteor

| Cruise # Sea region | M113-I Azores region | | M113-II East-west (40-67°W) transect | | | |
|---|---|---|---|---|---|---|
| Sample # | I4 + I5 pooled | I6 + I7 pooled | II1 | II2 | II3 | II4 |
| Latitude / longitude | 37.9°N/ 28.1°W | 38.1°N/ 29.7°W | 33.0°N/ 40.0°W | 30.0°N/ 50.0°W | 27.0°N/ 60.0°W | 24.0°N/ 66.6°W |
| Date<br>Time (UTC) | 7 Jan 15<br>19:00-23:00 h | 16 Jan 15<br>16:00-18:30 h | 28 Jan 15<br>07:41 h | 31 Jan 15<br>19:48 h | 3 Feb 15<br>22:30 h | 6 Feb 15<br>08:19 h |
| Volume (L) | 32.0 | 32.4 | 17.3 | 17.2 | 17.5 | 17.2 |
| Salinity (PSU) | 36.18 | 36.15 | 36.69 | 37.00 | 36.63 | 36.54 |
| Wind (Bf) | 4 | 5 | 5 | 5 | 3 | 4 |
| $T_{air}$ (°C) | 16.5-16.6 | 15.8-16.3 | 19.9 | 20.1 | 23.9 | 24.2 |
| $T_{water}$ (°C) | 16.7-17.1 | 16.8-17.7 | 20.7 | 22.8 | 24.8 | 25.5 |

**S1.2 Organic trace analytical quality assurance parameters**

The instrument limit of quantification (ILOQ; Table S2) was based on 3 times the instrument limit of detection, which in turn is based on 3 times the chromatogramme baseline noise level.

Table S2: Instrument limits of quantification (LOQ) and blank values, given as masses and concentrations, the latter for the biggest (32 L) sample

| Analyte | iLOQ mass (ng) | iLOQ concentration (pg $L^{-1}$) | Mean blank (ng) |
|---|---|---|---|
| PCB 28 | 0.00507 | 0.275 | 0.019 |
| PCB 52 | 0.01047 | 0.908 | 0.024 |
| PCB 101 | 0.01949 | 0.158 | 0.056 |
| PCB 118 | 0.01243 | 0.327 | 0.037 |
| PCB 153 | 0.0137 | 0.609 | 0.122 |
| PCB 138 | 0.02092 | 0.388 | 0.094 |
| PCB 180 | 0.01144 | 0.428 | 0.071 |
| Pentachlorobenzene | 0.00847 | 0.654 | 0.000 |
| Hexachlorobenzene | 0.01216 | 0.358 | 0.019 |
| $\alpha$-HCH | 0.01404 | 0.265 | 0.035 |
| $\beta$-HCH | 0.01669 | 0.380 | 0.000 |
| $\gamma$-HCH | 0.01485 | 0.439 | 0.540 |
| $\delta$-HCH | 0.02229 | 0.522 | 0.000 |
| *o,p'*-DDE | 0.01559 | 0.464 | 0.000 |
| *p,p'*-DDE | 0.00805 | 0.697 | 0.038 |
| *o,p'*-DDD | 0.01099 | 0.487 | 0.000 |
| *p,p'*-DDD | 0.00872 | 0.252 | 0.000 |

(continued)

| Analyte | iLOQ mass (ng) | iLOQ concentration (pg $L^{-1}$) | Mean blank (ng) |
|---|---|---|---|
| *o,p'*-DDT | 0.01363 | .343 | 0.000 |
| *p,p'*-DDT | 0.01203 | .272 | 0.000 |
| Heptachlor | 0.195 | 6.11 | 0.000 |
| *trans*-Heptachlorepoxide | 3.194 | 99.8 | 0.000 |
| *cis*-Heptachlorepoxide | 0.630 | 19.7 | 0.000 |
| Aldrin | 0.389 | 12.2 | 0.000 |
| Dieldrin | 0.912 | 28.5 | 0.000 |
| Endrin | 1.00 | 30.9 | 0.000 |
| Endrin aldehyde | 1.984 | 62.0 | 0.000 |
| Endrin ketone | 1.026 | 32.1 | 0.000 |
| Isodrin | 0.467 | 14.6 | 0.000 |
| Oxychlordane | 1.615 | 50.5 | 0.000 |
| $\gamma$-Chlordane | 0.10 | 3.10 | 0.000 |
| $\alpha$-Chlordane | 0.10 | 3.10 | 0.000 |
| $\alpha$-Endosulfan | 0.10 | 3.1 | 0.000 |
| $\beta$-Endosulfan | 1.00 | 30.9 | 0.000 |
| Endosulfan sulfate | 1.00 | 30.9 | 0.000 |
| Chlordecone | 20.79 | 650 | 0.000 |
| Methoxychlor | 1.290 | 40.3 | 0.000 |
| Mirex | 0.088 | 2.74 | 0.000 |

Table S3: Ions monitored for the MS analysis of target substances on (a) GC-MS/MS Agilent 7890 coupled to Agilent 7000B, (b) Agilent 6890N GC coupled to Waters Micromass Quattro Micro GC (EI+ mode) and (c) GC-QExactive-Orbitrap-MS (CI- mode)

a.

| Analyte | Quantification transition | Collision energy (eV) | Verification transition | Collision energy (eV) | $t_R$ (min) |
|---|---|---|---|---|---|
| PeCB | 252>215 | 22 | 250>215 | 22 | 11.10 |
| *α*-HCH | 219>183 | 6 | 181>145 | 13 | 15.73 |
| HCB | 285.8>213.8 | 39 | 283.8>248.9 | 18 | 16.28 |
| *γ*-HCH | 219>183 | 6 | 181>145 | 13 | 18.58 |
| *β*-HCH | 219>183 | 6 | 181>145 | 13 | 18.87 |
| *δ*-HCH | 219>183 | 6 | 181>145 | 13 | 21.95 |
| *ε*-HCH | 219>183 | 6 | 181>145 | 13 | 22.79 |
| PCB28 | 258>186 | 30 | 256>186 | 30 | 23.02 |
| PCB52 | 291.9>219.9 | 33 | 289.9>219.9 | 33 | 25.78 |
| *o,p'*-DDE | 318>248 | 24 | 246>176 | 33 | 32.09 |
| PCB101 | 327.9>255.9 | 33 | 325.9>255.9 | 33 | 32.71 |
| *p,p'*-DDE | 318>248 | 24 | 246>176 | 33 | 34.27 |
| *o,p'*-DDD | 237>165 | 22 | 235>165 | 22 | 35.10 |
| *o,p'*-DDT | 237>165 | 22 | 235>165 | 22 | 36.70 |
| PCB118 | 327.9>255.9 | 33 | 325.9>255.9 | 33 | 36.98 |
| *p,p'*-DDD | 237>165 | 22 | 235>165 | 22 | 37.49 |
| PCB153 | 361.8>289.9 | 33 | 359.8>289.9 | 33 | 37.78 |
| *p,p'*-DDT | 237>165 | 22 | 235>165 | 22 | 39.01 |
| PCB138 | 361.8>289.9 | 33 | 359.8>289.9 | 33 | 39.22 |
| PCB180 | 395.8>325.9 | 33 | 393.8>323.9 | 33 | 42.37 |

b.

| Analyte | Quantification transition | Collision energy (eV) | Verification transition | Collision energy (eV) | $t_R$ (min) |
|---|---|---|---|---|---|
| Heptachlor | 272 > 237 | 32 | 272 > 141 | 12 | 16.81 |
| *trans*-Heptachlorepoxide | 353 > 282 | 12 | 353 > 253 | 16 | 20.82 |
| *cis*-Heptachlorepoxide | 353 > 253 | 16 | 353 > 282 | 12 | 21.06 |
| Aldrin | 263 > 193 | 24 | 263 > 228 | 18 | 18.66 |
| Dieldrin | 263 > 193 | 22 | 277 > 207 | 20 | 25.15 |
| Isodrin | 193 > 157 | 18 | 263 > 193 | 24 | 20.32 |
| Oxychlordane | 387 > 263 | 14 | 387 > 287 | 16 | 20.81 |
| Methoxychlor | 227 > 141 | 30 | 227 > 169 | 24 | 36.28 |
| Mirex | 272 > 237 | 12 | 274 > 239 | 12 | 40.76 |

c.

| Analyte | Quantification Ion | Verification Ions | $t_R$ (min) |
|---|---|---|---|
| Endrin | 269.9414 | 271.9384, 273.9356 | 23.48 |
| $\gamma$-Chlordane | 299.8656 | 301.8627, 297.8685 | 21.83 |
| $\alpha$-Chlordane | 265.9045 | 241.9043, 267.9019 | 22.13 |
| $\alpha$-Endosulfan | 265.9045 | 263.9075, 267.9018 | 22.20 |
| $\beta$-Endosulfan | 241.9042 | 403.8169, 239.9067 | 23.68 |
| Endosulfan sulfate | 383.8360 | 96.9592, 385.8331 | 24.78 |

### S1.3 Dissolved organic carbon (DOC) analysis

DOC concentrations of all water samples were measured using a high temperature catalytic oxidation analyser (Shimadzu TOC-V) with a Pt catalyst at 680°C. All generated aqueous samples for DOC analysis were acidified to pH ≈ 2 with 85% $H_3PO_4$ and purged for 5 min to remove inorganic carbon prior to analysis. Synthetic air was used as a carrier gas in the TOC analyser. Standards (potassium biphthalate) were analysed immediately prior to and after analysis of 10 samples and were prepared with ultrapure water from a Microlab-Genpure system (TKA, Germany). The detection limit was found at 0.02 mg $L^{-1}$. All samples were analysed in triplicate. Precision, in terms of the relative standard deviation, was better than 2%.

**S2 Discussion - Comparison with model predictions of surface seawater concentrations**

Table S4: Dissolved phase concentrations in surface seawater of (a.) endosulfan and (b.) PCBs (pg $L^{-1}$) for January-February 2015, predicted by multicompartment chemistry-transport modelling, global multidecadal simulations starting 1950, ≈3° horizontal resolution (Lammel and Stemmler 2012; Octaviani et al. 2015, and unpublished model data).

a.

| | Azores region | East-west (40-67°W) transect |
|---|---|---|
| | 38°N/28-30°W | 24-33°N/ 40-67°W |
| $\alpha$-endosulfan low emissions [(1)] | 25-28 | 16-43 |
| $\alpha$-endosulfan high emissions [(2)] | 75-85 | 55-150 |
| $\alpha$-endosulfan high em. [(2)] conversion [(3)] | 105-119 | 126-740 |

b.

| | Azores region | East-west (40-67°W) transect |
|---|---|---|
| | 38°N/28-30°W | 24-33°N/ 40-67°W |
| PCB28 [(4)] | 5.8-12.5 | 0.55-4.7 |
| PCB101 [(4)] | 19-35 | 1.4-13.8 |
| PCB153 [(5)] | 50-145 | 4-30 |
| PCB180 [(4)] | 21-24 | 1.5-10.6 |

[(1)] based on top 8 usage countries only and reported application rates (application to crops; FAO 2009)

[(2)] based on application to crops worldwide (FAO 2009) using application rates reported from USA (USDA 2012) for most countries

[(3)] assumes conversion of $\beta$- into $\alpha$-endosulfan in seawater (Weber et al. 2010; Walse et al. 2003)

[(4)] PCB153 emissions input; model output scaled for historical emissions of this congener (Breivik et al. 2007)

[(5)] Maximum emission estimate of Breivik et al., 2007.

## References


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