Validating analytical protocols to determine selected pesticides and PCBs using routine samples.

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This Electronic Supplementary Material enhances the understanding of the scientific article. This document summarise all the comments that could not be included into the text. This document is divided in 3 sections, including 4 figures and 11 tables.

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Fig. S1: Flow diagram of the trials for the calculation of proportional bias.



Fig. S2: Flow diagram of the trials for the calculation of constant bias.

Table S1: Results from analyses of two masses of sub-sample (A=0.587 g, B=1.573 g) and calculations to estimate constant bias.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Mass average (ng) | | Standard deviation (ng) | | Constant bias | U(x)/X | | Uncert. rel constant bias | Relative constant bias | | Statistic “t” | |
|  | **A** | **B** | **A** | **B** | **A-B** | **A** | **B** | **A-B** | **A** | **B** | **A** | **B** |
| **α-HCH** | 2.9 | 15 | 0.1  ..14.6 | 2.6 | -4.1 | 0.013 | 0.10 | 0.066 | -1.41 | -0.28 | -22 | -4.26 |
| **β-HCH** | 6 | 145 | 4.6 | 28.9 | 11 | 0.044 | 0.11 | 0.1 | 0.18 | 0.07 | 1.82 | 0.76 |
| **γ-HCH** | 8.2 | 18 | 1.7 | 1.9 | 2.5 | 0.12 | 0.063 | 0.19 | 0.30 | 0.14 | 1.59 | 0.73 |
| **HCB** | 3524 | 8451 | 209 | 198 | 594 | 0.034 | 0.014 | 0.055 | 0.17 | 0.07 | 3.06 | 1.28 |
| **o-p’-DDE** | 4.3 | 11 | 0.3 | 0.4 | 0.5 | 0.036 | 0.022 | 0.059 | 0.11 | 0.04 | 1.86 | 0.75 |
| **p-p’-DDE** | 23. | 52 | 2.1 | 1.6 | 6.5 | 0.053 | 0.018 | 0.085 | 0.28 | 0.13 | 3.30 | 1.49 |
| **o-p’-DDD** | 44 | 102 | 5.2 | 5.2 | 10 | 0.068 | 0.029 | 0.11 | 0.24 | 0.1 | 2.16 | 0.94 |
| **p-p’-DDD** | 45 | 99 | 3.4 | 12.1 | 14 | 0.043 | 0.07 | 0.08 | 0.30 | 0.14 | 3.75 | 1.72 |
| **PCB-28** | 442 | 997 | 49 | 77 | 112 | 0.064 | 0.045 | 0.11 | 0.25 | 0.11 | 2.41 | 1.07 |
| **PCB-52** | 143 | 352 | 18 | 25 | 19 | 0.073 | 0.042 | 0.12 | 0.13 | 0.05 | 1.13 | 0.46 |
| **PCB-101** | 68 | 178 | 5.8 | 16 | 2.8 | 0.049 | 0.052 | 0.085 | 0.04 | 0.02 | 0.48 | 0.18 |
| **PCB-118** | 30 | 63 | 5.0 | 4.4 | 11 | 0.095 | 0.04 | 0.15 | 0.036 | 0.17 | 2.33 | 1.12 |
| **PCB-138** | 3.3 | 8 | 0.2 | 0.6 | 0.6 | 0.027 | 0.044 | 0.05 | 0.20 | 0.08 | 3.93 | 1.67 |
| **PCB-153** | 10 | 22 | 0.6 | 2.1 | 3.0 | 0.036 | 0.053 | 0.065 | 0.29 | 0.13 | 4.49 | 2.05 |
| **PCB-180** | 14 | 25 | 2.1 | 2.6 | 7.2 | 0.088 | 0.06 | 0.14 | 0.52 | 0.29 | 3.61 | 2.00 |

Table S2: Results from analyses of two masses of sub-sample (B=1.573 g, C=2.558 g) and calculations to estimate constant bias.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Mass average (ng) | | Standard deviation (ng) | | Constant bias | U(x)/X | | Uncert. rel constant bias | Relative constant bias | | Statistic “t” | |
|  | **B** | **C** | **B** | **C** | **B-C** | **B** | **C** | **B-C** | **B** | **C** | **B** | **C** |
| **α-HCH** | 15 | 41 | 2.6 | 6.0 | 27 | 0.10 | 0.10 | 0.32 | 1.88 | 0.67 | 5.88 | 2.10 |
| **β-HCH** | 145 | 261 | 28.9 | 15.6 | 40 | 0.11 | 0.042 | 0.31 | 0.28 | 0.15 | 0.90 | 0.50 |
| **γ-HCH** | 18 | 40 | 1.9 | 11.8 | 18 | 0.063 | 0.21 | 0.37 | 0.99 | 0.44 | 2.66 | 1.19 |
| **HCB** | 8451 | 13832 | 198 | 421 | 154 | 0.014 | 0.022 | 0.05 | 0.02 | 0.01 | 0.37 | 0.23 |
| **o-p’-DDE** | 11 | 17 | 0.4 | 3.4 | -0.6 | 0.022 | 0.14 | 0.23 | -0.05 | -0.03 | -0.23 | -0.15 |
| **p-p’-DDE** | 52 | 78 | 1.6 | 10.9 | -8.9 | 0.018 | 0.10 | 0.16 | -0.17 | -0.11 | -1.05 | -0.69 |
| **o-p’-DDD** | 102 | 160 | 5.2 | 27.6 | -7.5 | 0.029 | 0.12 | 0.21 | -0.07 | -0.05 | -0.35 | -0.22 |
| **p-p’-DDD** | 99 | 143 | 12.1 | 8.3 | -29 | 0.07 | 0.041 | 0.19 | -0.29 | -0.20 | -1.50 | -1.04 |
| **PCB-28** | 997 | 1607 | 77 | 138 | -23 | 0.045 | 0.061 | 0.15 | -0.02 | -0.01 | -0.15 | -0.09 |
| **PCB-52** | 352 | 576 | 25 | 59 | 7.1 | 0.042 | 0.072 | 0.16 | 0.02 | 0.01 | 0.13 | 0.08 |
| **PCB-101** | 178 | 252 | 16 | 2.8 | -60 | 0.052 | 0.008 | 0.14 | -0.34 | -0.24 | -2.50 | -1.77 |
| **PCB-118** | 63 | 104 | 4.4 | 5.5 | 1.5 | 0.04 | 0.038 | 0.12 | 0.02 | 0.01 | 0.20 | 0.12 |
| **PCB-138** | 8 | 13 | 0.6 | 1.1 | 1.4 | 0.044 | 0.060 | 0.15 | 0.18 | 0.1 | 1.19 | 0.69 |
| **PCB-153** | 22 | 40 | 2.1 | 3.0 | 5.2 | 0.053 | 0.053 | 0.16 | 0.23 | 0.13 | 1.43 | 0.81 |
| **PCB-180** | 25 | 38 | 2.6 | 3.4 | -3.8 | 0.06 | 0  .063 | 0.19 | -0.15 | -0.1 | -0.82 | -0.54 |

Table S3: Calibration parameters and limits for selected compounds

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Compound | Number calibrations | Range of r2 | Linear range  (ng L-1) | LOD  (ng L-1) | LOQ  (ng L-1) |
| **Aldrin** | 7 | 0.997 - 0.99997 | 50 – 1000 | 2 | 5 |
| **Atrazine** | 9 | 0.994 - 0.9997 | 50 – 2000 | 4 | 7 |
| **o-p’-DDD** | 9 | 0.991 - 0.9997 | 50 – 1000 | 3 | 21 |
| **p-p’-DDD** | 13 | 0.997 - 0.99995 | 50 – 1000 | 3 | 8 |
| **o-p’-DDE** | 9 | 0.990 - 0.9991 | 50 – 1000 | 4 | 18 |
| **p-p’-DDE** | 13 | 0.990 - 0.99993 | 50 – 1000 | 1 | 3 |
| **o-p’-DDT** | 9 | 0.990 - 0.9998 | 50 – 1000 | 2 | 4 |
| **p-p’-DDT** | 13 | 0.991 - 0.9992 | 50 – 1000 | 2 | 5 |
| **Dieldrin** | 15 | 0.991 - 0.99998 | 50 – 1000 | 3 | 5 |
| **Endrin** | 15 | 0.992 - 0.99993 | 50 – 1000 | 2 | 4 |
| **Hexachlorobencene** | 7 | 0.995 - 0.997 | 50 – 1000 | 1 | 2 |
| **α-HCH** | 16 | 0.994 - 0.99996 | 50 – 1000 | 3 | 5 |
| **β-HCH** | 16 | 0.991 - 0.99997 | 50 – 1000 | 3 | 5 |
| **γ-HCH** | 16 | 0.993 - 0.999999 | 50 – 1000 | 2 | 5 |
| **Isodrin** | 7 | 0.997 - 0.99996 | 50 – 1000 | 2 | 3 |
| **Metolachlor** | 9 | 0.995 - 0.99997 | 50 – 2000 | 4 | 7 |
| **Pentachlorobencenee** | 8 | 0.990 - 0.9997 | 50 – 1000 | 4 | 13 |
| **PCB-28** | 8 | 0.994 - 0.9998 | 50 – 1000 | 2 | 15 |
| **PCB-52** | 8 | 0.994 - 0.99991 | 50 – 1000 | 2 | 9 |
| **PCB-101** | 8 | 0.997 - 0.99993 | 50 – 1000 | 2 | 12 |
| **PCB-118** | 8 | 0.993 - 0.99995 | 50 – 1000 | 3 | 22 |
| **PCB-138** | 8 | 0.992 - 0.99991 | 50 – 1000 | 3 | 19 |
| **PCB-153** | 8 | 0.991 - 0.99998 | 50 – 1000 | 3 | 19 |
| **PCB-180** | 8 | 0.993 - 0.99998 | 50 – 1000 | 4 | 21 |
| **Simazine** | 9 | 0.992 - 0.9997 | 50 – 2000 | 6 | 13 |
| **Terbutylazine** | 9 | 0.997 - 0.9997 | 50 – 2000 | 4 | 7 |

Table S4: Accuracy evaluated by the analysis of two certified reference materials

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Water (WatRTM 713) | | Sediment (CNS391) | |
| Compound | **Acceptance limits**  **(µg/L)** | **Value measured**  **(µg/L) n=2** | **Certified value**  **(ng/g)** | **Value measured**  **(ng/g) n=4** |
| **Aldrin** | 0.82 – 2.32 | 1.17 ± 0.04 | - | - |
| **Atrazine** | 1.92 – 5.08 | 2.86 ± 0.14 | - | - |
| **Dieldrin** | 0.86 – 2.28 | 1.34 ± 0.04 | - | - |
| **o-p’-DDD** | - | - | 15.5 | 14±2.3 |
| **p-p’-DDD** | - | - | 13.9 | 12±2.0 |
| **o-p’-DDE** | - | - | 39.5 | 31±5.8 |
| **p-p’-DDE** | - | - | 18.8 | 17 ±2.5 |
| **o-p’-DDT** | - | - | 43 | 24 ± 5.25 |
| **p-p’-DDT** | - | - | 10.2 | 11 ± 0.80 |
| **Endrin** | 2.27 – 2.95 | 2.87 ± 0.11 | - | - |
| **Hexachlorobencene** | 1.41 – 3.50 | 1.72 ± 0.11 | 34.5 | 35 ± 3.3 |
| **α-HCH** | - | - | 37.1 | 26 ± 2.6 |
| **β-HCH** | - | - | 21.1 | 25 ± 1.0 |
| **γ-HCH** | 1.18 – 3.10 | 2.07 ± 0.02 | 9.5 | 12 ± 1.0 |
| **Metolachlor** | 5.61 – 14.8 | 7.41 ± 0.22 | - | - |
| **PCB-28** | - | - | 44.9 | 41 ± 3.1 |
| **PCB-52** | - | - | 64.6 | 67 ± 11 |
| **PCB-101** | - | - | 45.7 | 44 ± 9.3 |
| **PCB-118** | - | - | 24 | 28 ± 5.1 |
| **PCB-138** | - | - | 34.6 | 34 ±7.8 |
| **PCB-153** | - | - | 50.1 | 34±5.2 |
| **PCB-180** | - | - | 54.7 | 41±5.2 |
| **PCB-28** | - | - | 44.9 | 41 ± 3.1 |
| **Simazine** | 1.99 – 5.23 | 2.31 ± 0.07 | - | - |

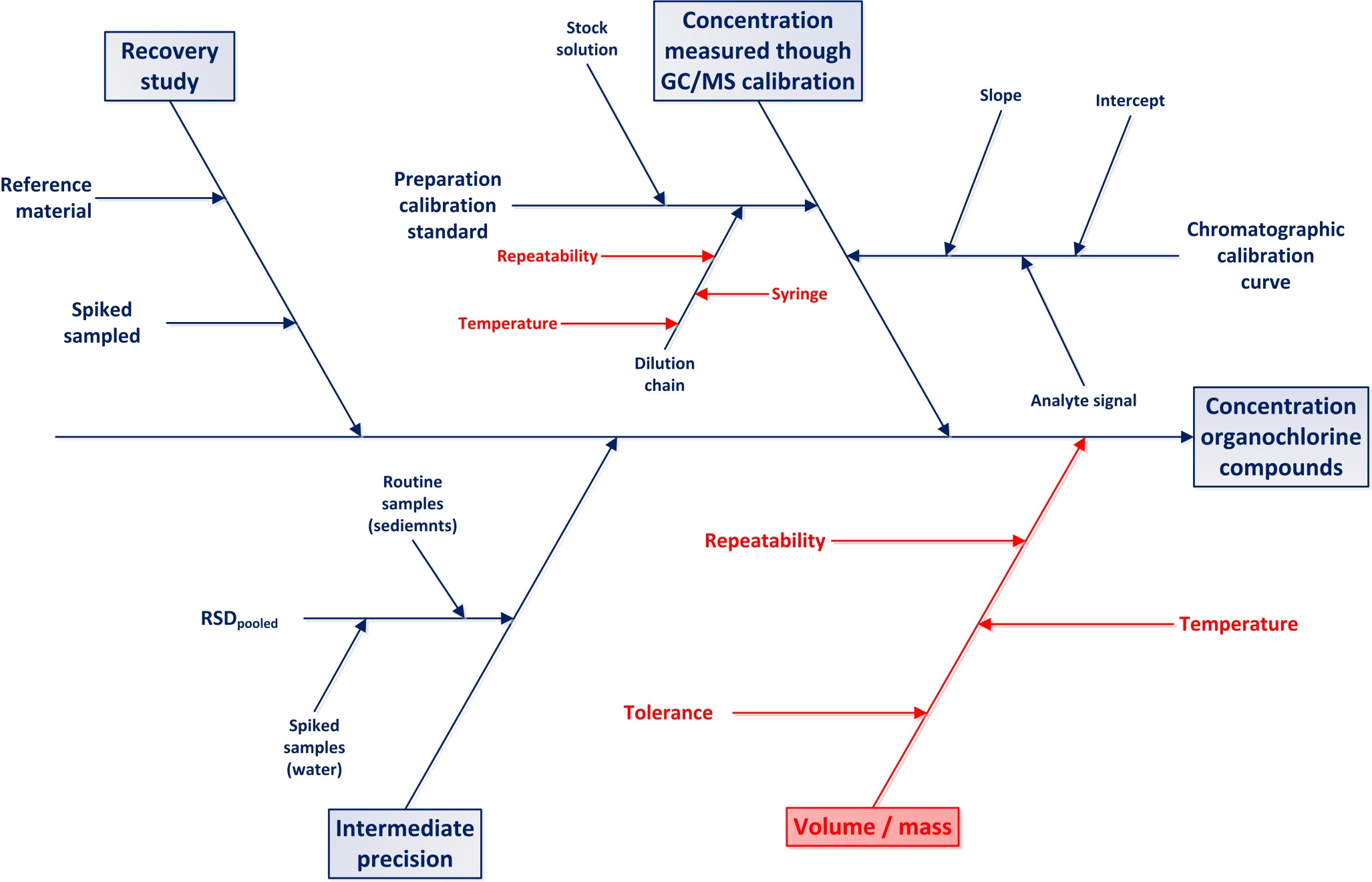


Fig. S3: Cause and effect diagram

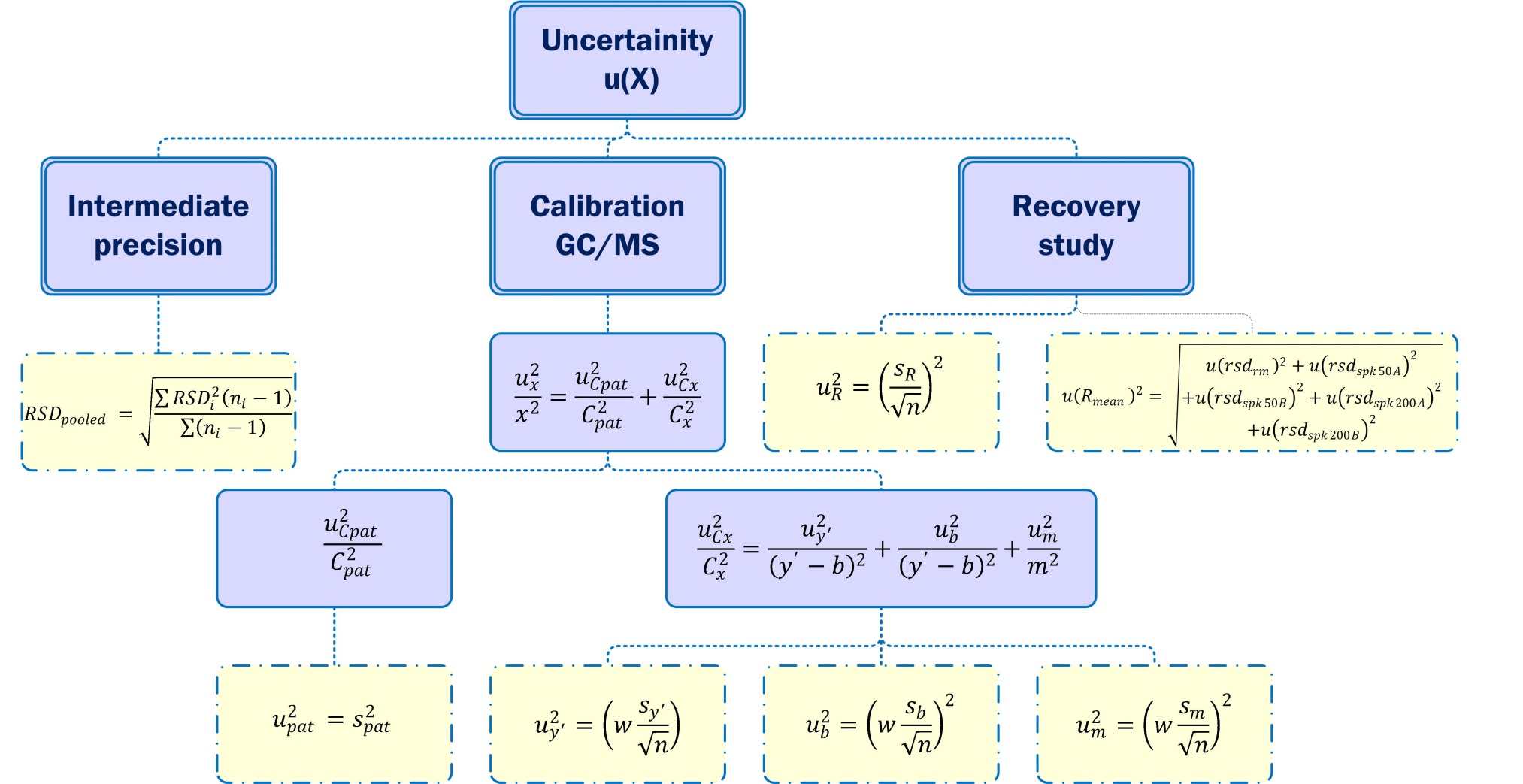


Fig. S4: Equations to calculate uncertainty

Table S5: Uncertainty from analytical signal (uy2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | y’ | sy | n | uy2 |
| **Aldrin** | 0.006 | 0.001 | 11 | 8.9 10-7 |
| **Atrazine** | 0.011 | 0.0012 | 18 | 1.0 10-6 |
| **Dieldrin** | 0.012 | 0.0046 | 17 | 2.0 10-5 |
| **o-p’-DDD** | 0.027 | 0.0035 | 13 | 1.2 10-5 |
| **p-p’-DDD** | 0.027 | 0.0068 | 14 | 3.4 10-5 |
| **o-p’-DDE** | 0.03 | 0.0029 | 21 | 4.8 10-6 |
| **p-p’-DDE** | 0.022 | 0.0027 | 20 | 5.1 10-5 |
| **o-p’-DDT** | 0.023 | 0.0032 | 11 | 9.9 10-6 |
| **p-p’-DDT** | 0.024 | 0.0029 | 11 | 1.2 10-5 |
| **Endrin** | 0.053 | 0.0253 | 12 | 6.20 10-4 |
| **Hexachlorobencene** | 0.02 | 0.0032 | 13 | 9.60 10-6 |
| **Isodrin** | 0.012 | 0.0028 | 11 | 1.20 10-5 |
| **α-HCH** | 0.006 | 0.0009 | 15 | 8.10 10-7 |
| **β-HCH** | 0.005 | 0.0005 | 15 | 2.20 10-7 |
| **γ-HCH** | 0.005 | 0.0007 | 15 | 4.10 10-7 |
| **Metolachlor** | 0.024 | 0.004 | 14 | 1.60 10-5 |
| **PCB-28** | 0.02 | 0.0035 | 13 | 1.20 10-5 |
| **PCB-52** | 0.018 | 0.0037 | 13 | 1.30 10-5 |
| **PCB-101** | 0.04 | 0.0114 | 13 | 1.20 10-4 |
| **PCB-118** | 0.053 | 0.0154 | 13 | 2.30 10-4 |
| **PCB-138** | 0.044 | 0.0172 | 15 | 2.80 10-4 |
| **PCB-153** | 0.045 | 0.0107 | 15 | 1.10 10-4 |
| **PCB-180** | 0.032 | 0.0042 | 16 | 1.70 10-5 |
| **Pentachlorobencene** | 0.017 | 0.004 | 13 | 2.80 10-5 |
| **Simazine** | 0.008 | 0.0023 | 17 | 4.90 10-6 |
| **Terbuthylazine** | 0.018 | 0.0022 | 18 | 3.60 10-6 |

Table S6: Uncertainty from slope (um2) and y-intercept (ub2)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | b | m | sb | sm | ub2 | um2 |
| **Aldrin** | -0.003 | 1.20 10-4 | 0.0038 | 8.30 10-6 | 1.60 10-6 | 7.70 10-12 |
| **Atrazine** | -0.0051 | 2.70 10-4 | 0.0057 | 1.10 10-5 | 2.60 10-6 | 9.30 10-12 |
| **Dieldrin** | -0.0008 | 2.40 10-4 | 0.012 | 2.30 10-5 | 1.50 10-5 | 5.50 10-11 |
| **o-p’-DDD** | -0.0229 | 8.00 10-4 | 0.0188 | 3.60 10-5 | 3.40 10-5 | 1.30 10-10 |
| **p-p’-DDD** | -0.0248 | 8.40 10-4 | 0.0193 | 3.80 10-5 | 3.60 10-5 | 1.40 10-10 |
| **o-p’-DDE** | -0.0024 | 6.40 10-4 | 0.0056 | 1.10 10-5 | 2.20 10-6 | 8.60 10-12 |
| **p-p’-DDE** | -0.0028 | 5.20 10-4 | 0.0051 | 1.00 10-5 | 1.80 10-6 | 6.90 10-12 |
| **o-p’-DDT** | -0.0256 | 7.10 10-4 | 0.0193 | 3.80 10-5 | 4.90 10-5 | 1.90 10-10 |
| **p-p’-DDT** | -0.025 | 7.20 10-4 | 0.0167 | 3.30 10-5 | 3.70 10-5 | 1.50 10-10 |
| **Endrin** | 0.0032 | 8.50 10-5 | 0.0049 | 1.00 10-5 | 2.90 10-6 | 1.20 10-11 |
| **Hexachlorobencene** | -0.0007 | 3.40 10-4 | 0.0038 | 8.20 10-6 | 1.60 10-6 | 7.50 10-12 |
| **Isodrin** | -0.0067 | 1.80 10-4 | 0.0103 | 2.00 10-5 | 9.50 10-6 | 3.50 10-11 |
| **α-HCH** | -0.0041 | 1.40 10-4 | 0.0033 | 5.90 10-6 | 9.80 10-7 | 3.10 10-12 |
| **β-HCH** | -0.0049 | 1.30 10-4 | 0.0037 | 6.50 10-6 | 1.20 10-6 | 3.90 10-12 |
| **γ-HCH** | -0.0046 | 1.30 10-4 | 0.0045 | 7.90 10-6 | 1.80 10-6 | 5.70 10-12 |
| **Metolachlor** | -0.0207 | 6.60 10-4 | 0.0121 | 2.10 10-5 | 1.50 10-5 | 4.40 10-11 |
| **PCB-28** | -0.003 | 4.00 10-4 | 0.0047 | 1.00 10-5 | 2.40 10-6 | 1.10 10-11 |
| **PCB-52** | 0.0004 | 3.20 10-4 | 0.0044 | 9.60 10-6 | 2.20 10-6 | 1.00 10-11 |
| **PCB-101** | 0.0026 | 4.10 10-4 | 0.0067 | 1.40 10-5 | 5.00 10-6 | 2.30 10-11 |
| **PCB-118** | 0.0018 | 5.70 10-4 | 0.0097 | 2.10 10-5 | 1.00 10-5 | 4.80 10-11 |
| **PCB-138** | 0.001 | 4.80 10-4 | 0.0111 | 2.10 10-5 | 1.20 10-5 | 4.40 10-11 |
| **PCB-153** | -0.0021 | 5.30 10-4 | 0.0108 | 2.10 10-5 | 8.90 10-6 | 3.30 10-11 |
| **PCB-180** | 0.0007 | 4.90 10-4 | 0.0117 | 2.50 10-5 | 1.50 10-5 | 7.10 10-11 |
| **Pentachlorobencene** | 0.002 | 2.80 10-4 | 0.0012 | 2.50 10-6 | 1.50 10-7 | 6.90 10-13 |
| **Simazine** | -0.0048 | 1.90 10-4 | 0.0039 | 7.20 10-6 | 1.30 10-6 | 4.40 10-12 |
| **Terbuthylazine** | -0.0073 | 4.20 10-4 | 0.0094 | 1.80 10-5 | 7.10 10-6 | 2.50 10-11 |

Table S7: Uncertainty associated to concentration measured through calibration

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | uy2/(y-b)2 | ub2/(y-b)2 | um2/m2 | uCx2/Cx2 |
| **Aldrin** | 0.011 | 0.0202 | 1.90 10-4 | 0.032 |
| **Atrazine** | 0.004 | 0.0099 | 1.20 10-4 | 0.014 |
| **Dieldrin** | 0.121 | 0.0894 | 9.40 10-4 | 0.212 |
| **o-p’-DDD** | 0.005 | 0.0137 | 2.00 10-4 | 0.019 |
| **p-p’-DDD** | 0.013 | 0.0133 | 2.00 10-4 | 0.026 |
| **o-p’-DDE** | 0.005 | 0.0021 | 2.10 10-5 | 0.007 |
| **p-p’-DDE** | 0.008 | 0.0029 | 2.60 10-5 | 0.011 |
| **o-p’-DDT** | 0.004 | 0.0206 | 3.80 10-4 | 0.025 |
| **p-p’-DDT** | 0.005 | 0.0153 | 2.80 10-4 | 0.021 |
| **Endrin** | 0.248 | 0.0012 | 1.70 10-3 | 0.251 |
| **Hexachlorobencene** | 0.023 | 0.0039 | 6.50 10-5 | 0.027 |
| **Isodrin** | 0.033 | 0.0269 | 1.10 10-3 | 0.061 |
| **α-HCH** | 0.008 | 0.0098 | 1.60 10-4 | 0.018 |
| **β-HCH** | 0.002 | 0.0129 | 2.50 10-4 | 0.015 |
| **γ-HCH** | 0.004 | 0.018 | 3.20 10-4 | 0.022 |
| **Metolachlor** | 0.008 | 0.0076 | 1.00 10-4 | 0.016 |
| **PCB-28** | 0.022 | 0.0045 | 7.10 10-5 | 0.027 |
| **PCB-52** | 0.43 | 0.0071 | 9.70 10-5 | 0.05 |
| **PCB-101** | 0.089 | 0.0036 | 1.40 10-4 | 0.093 |
| **PCB-118** | 0.086 | 0.0039 | 1.50 10-4 | 0.09 |
| **PCB-138** | 0.152 | 0.0063 | 1.90 10-4 | 0.158 |
| **PCB-153** | 0.049 | 0.004 | 1.20 10-4 | 0.053 |
| **PCB-180** | 0.017 | 0.0156 | 2.90 10-4 | 0.033 |
| **Pentachlorobencene** | 0.119 | 0.0006 | 8.70 10-6 | 0.12 |
| **Simazine** | 0.032 | 0.0085 | 1.20 10-4 | 0.04 |
| **Terbuthylazine** | 0.006 | 0.0115 | 1.40 10-4 | 0.017 |

Table S8: Uncertainty associated to recovery of selected pesticides in water samples

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | Recovery | s | n | urec | urec/R | urec/R (%) |
| **Aldrin** | 0.85 | 0.040 | 6 | 0.016 | 0.019 | 2 |
| **Atrazine** | 1.11 | 0.141 | 12 | 0.041 | 0.037 | 4 |
| **o-p’-DDD** | 0.55 | 0.134 | 12 | 0.039 | 0.070 | 7 |
| **p-p’-DDD** | 0.72 | 0.220 | 18 | 0.052 | 0.072 | 7 |
| **o-p’-DDE** | 0.37 | 0.079 | 12 | 0.023 | 0.062 | 6 |
| **p-p’-DDE** | 0.44 | 0.151 | 16 | 0.038 | 0.086 | 9 |
| **o-p’-DDT** | 0.40 | 0.082 | 8 | 0.029 | 0.073 | 7 |
| **p-p’-DDT** | 0.65 | 0.256 | 12 | 0.074 | 0.114 | 11 |
| **Dieldrin** | 0.82 | 0.202 | 18 | 0.048 | 0.058 | 6 |
| **Endrin** | 0.81 | 0.443 | 18 | 0.104 | 0.130 | 13 |
| **Hexachlorobencene** | 0.93 | 0.149 | 6 | 0.061 | 0.066 | 7 |
| **α-HCH** | 1.28 | 0.338 | 18 | 0.080 | 0.062 | 6 |
| **β-HCH** | 1.17 | 0.254 | 18 | 0.060 | 0.051 | 5 |
| **γ-HCH** | 1.20 | 0.273 | 18 | 0.064 | 0.054 | 5 |
| **Isodrin** | 0.88 | 0.071 | 6 | 0.029 | 0.033 | 3 |
| **Metolachlor** | 0.98 | 0.120 | 12 | 0.035 | 0.035 | 4 |
| **Simazine** | 1.17 | 0.181 | 12 | 0.052 | 0.044 | 4 |
| **Terbutylazine** | 0.91 | 0.188 | 12 | 0.054 | 0.060 | 6 |

Table S9: Uncertainty associated to recovery of selected pesticides in sediment samples

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | u(rsd)rm | u(rsd)spk50A | u(rsd)spk50B | u(rsd)spk200A | u(rsd)spk200B | u(Rmean) |
| **p-p’-DDD** | 0.083 |  | 0.021 |  | 0.099 | 0.097 |
| **p-p’-DDE** | 0.073 | 0.003 | 0.001 | 0.001 | 0.005 | 0.073 |
| **p-p’-DDT** | 0.036 | 0.001 | 0.001 |  |  | 0.036 |
| **Hexachlorobencene** | 0.047 | 0.124 | 0.143 | 0.050 | 0.043 | 0.205 |
| **α-HCH** | 0.049 | 0.062 | 0.012 | 0.037 | 0.017 | 0.090 |
| **β-HCH** | 0.019 | 0.044 | 0.037 | 0.043 | 0.033 | 0.081 |
| **γ-HCH** | 0.042 | 0.007 | 0.038 | 0.030 | 0.006 | 0.065 |
| **PCB-28** | 0.038 | 0.009 | 0.024 | 0.011 | 0.011 | 0.049 |
| **PCB-52** | 0.080 | 0.018 | 0.042 | 0.041 | 0.116 | 0.154 |
| **PCB-101** | 0.106 | 0.008 | 0.020 | 0.019 | 0.053 | 0.122 |
| **PCB-118** | 0.092 | 0.008 | 0.023 | 0.025 | 0.031 | 0.103 |
| **PCB-138** | 0.113 | 0.028 | 0.026 | 0.017 | 0.012 | 0.121 |
| **PCB-153** | 0.076 | 0.010 | 0.033 | 0.008 | 0.008 | 0.084 |
| **PCB-180** | 0.063 | 0.005 | 0.026 | 0.013 | 0.011 | 0.071 |

Table S10: Uncertainty associated to intermediate precision for the analysis of selected compounds in water samples

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Recovery study (1000 ng/L) | | | | | | Recovery study (500 ng/L) | | | | | | Recovery study (250 ng/L) | | | | | |  |  |
|  | **Recovery A** | | **Recovery B** | | **Recovery C** | | **Recovery A** | | **Recovery B** | | **Recovery C** | | **Recovery A** | | **Recovery B** | | **Recovery C** | |  |  |
|  | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **Avge** | **s** | **n** | **rsd pooled** |
| **Aldrin** |  |  |  |  |  |  | 0.85 | 0.04 | 0.36 | 0.10 | 0.27 | 0.04 |  |  |  |  |  |  | 3 | 0.082 |
| **Atrazine** | 1.09 | 0.06 | 1.17 | 0.07 | 0.89 | 0.14 |  |  |  |  |  |  | 1.07 | 0.04 | 1.25 | 0.15 | 1.20 | 0.03 | 6 | 0.104 |
| **op’-DDD** | 0.30 | 0.01 | 0.33 | 0.03 | 0.34 | 0.06 |  |  |  |  |  |  | 0.46 | 0.13 | 0.39 | 0.04 | 0.39 | 0.12 | 6 | 0.085 |
| **pp’-DDD** | 0.31 | 0.01 | 0.34 | 0.02 | 0.35 | 0.08 | 0.73 | 0.17 | 0.44 | 0.10 | 1.02 | 0.02 | 0.52 | 0.11 | 0.37 | 0.07 | 0.47 | 0.10 | 9 | 0.096 |
| **op’-DDE** | 0.34 | 0.01 | 0.61 | 0.05 | 0.54 | 0.14 | 1.06 | 0.27 | 0.95 | 0.27 | 0.65 | 0.15 | 0.63 | 0.13 | 0.54 | 0.09 | 0.64 | 0.15 | 9 | 0.172 |
| **pp’-DDE** | 0.57 | 0.02 | 0.63 | 0.06 | 0.52 | 0.19 |  |  |  |  |  |  | 0.77 | 0.22 | 0.57 | 0.12 | 0.74 | 0.10 | 6 | 0.150 |
| **op’-DDT** | 0.30 | 0.02 | 0.43 | 0.04 | 1.00 | 0.00 |  |  |  |  |  |  | 0.43 | 0.10 | 0.44 | 0.09 | 1.00 | 0.00 | 6 | 0.063 |
| **pp’-DDT** | 0.37 | 0.04 | 0.64 | 0.12 | 1.00 | 0.00 | 1.03 | 0.34 | 0.47 | 0.21 | 1.00 | 0.00 | 0.66 | 0.09 | 0.71 | 0.14 | 1.00 | 0.00 | 9 | 0.160 |
| **Dieldrin** | 0.73 | 0.02 | 0.91 | 0.07 | 0.83 | 0.49 | 1.46 | 0.19 | 1.20 | 0.24 | 0.31 | 0.06 | 0.70 | 0.11 | 0.06 | 0.01 | 1.06 | 0.16 | 9 | 0.217 |
| **Endrin** | 0.68 | 0.01 | 0.82 | 0.02 | 0.70 | 0.08 | 1.18 | 0.17 | 1.10 | 0.18 | 0.74 | 0.08 | 0.69 | 0.11 | 0.67 | 0.07 | 0.83 | 0.15 | 9 | 0.120 |
| **HCB** |  |  |  |  |  |  | 1.04 | 0.11 | 0.81 | 0.03 | 0.48 | 0.05 |  |  |  |  |  |  | 3 | 0.090 |
| **α-HCH** | 1.26 | 0.11 | 1.33 | 0.25 | 0.98 | 0.01 | 1.92 | 0.24 | 1.61 | 0.11 | 1.00 | 0.08 | 1.24 | 0.39 | 1.24 | 0.10 | 0.93 | 0.04 | 9 | 0.199 |
| **β-HCH** | 1.25 | 0.07 | 1.13 | 0.09 | 0.83 | 0.31 | 1.51 | 0.11 | 1.53 | 0.28 | 1.07 | 0.02 | 1.06 | 0.18 | 1.08 | 0.18 | 1.05 | 0.01 | 9 | 0.182 |
| **γ-HCH** | 1.25 | 0.07 | 1.23 | 0.18 | 0.87 | 0.21 | 1.68 | 0.02 | 1.39 | 0.19 | 0.98 | 0.06 | 1.00 | 0.35 | 1.34 | 0.03 | 1.03 | 0.01 | 9 | 0.176 |
| **Isodrin** |  |  |  |  |  |  | 0.88 | 0.07 | 0.43 | 0.16 | 0.31 | 0.01 |  |  |  |  |  |  | 3 | 0.121 |
| **Methlor** | 1.12 | 0.01 | 1.11 | 0.01 | 0.94 | 0.09 |  |  |  |  |  |  | 0.90 | 0.12 | 1.01 | 0.08 | 0.84 | 0.03 | 6 | 0.076 |
| **Simazine** | 1.43 | 0.09 | 1.27 | 0.08 | 0.97 | 0.19 |  |  |  |  |  |  | 1.05 | 0.00 | 1.24 | 0.15 | 1.09 | 0.01 | 6 | 0.121 |
| **Terbuty** | 1.12 | 0.02 | 1.13 | 0.04 | 0.90 | 0.09 |  |  |  |  |  |  | 0.73 | 0.14 | 0.84 | 0.12 | 0.71 | 0.03 | 6 | 0.095 |

Table S11: Variance from the analysis of each sediment by duplicate.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | PClB | α-HCH | β-HCH | γ-HCH | HCB | op’-DDE | pp’-DDE | op’-DDD | pp’-DDD | op’-DDT | pp’-DDT | PCB 28 | PCB 52 | PCB 101 | PCB 118 | PCB 153 | PCB 138 | PCB 180 |
| **1** | 0.366 | 0.019 | 0.222 | 0.003 | 0.006 | 0.012 | 0.037 | 0.009 | 0.076 |  |  | 0.003 | 0.01 | 0.125 | 0.015 | 0.002 |  |  |
| **2** | 0.698 | 0.025 | 0.002 | 0.009 | 0.061 | 0.099 | 0.005 | 0.007 |  |  |  |  | 0.002 | 0.003 |  | 0.017 |  |  |
| **3** | 0.055 | 0.035 |  | 0.022 | 0.02 | 0.031 | 0.021 | 0.016 | 0.027 |  |  | 0.019 | 0.028 | 0.029 |  | 0.025 |  |  |
| **4** |  | 1.037 | 0.155 |  | 0.955 | 0.08 | 0.002 | 0.038 | 0.039 |  |  | 0.242 | 0.16 | 0.13 | 0.13 | 0.278 |  |  |
| **5** | 0.015 | 0.004 |  | 0.008 | 0.25 | 0.002 |  | 0.003 | 0.014 |  |  |  | 0.002 | 0.031 | 0.068 | 0.01 |  |  |
| **6** | 0.007 | 0.005 |  | 0.001 |  | 0.008 |  | 0.002 | 0.073 |  |  |  | 0.001 | 0.001 | 0.016 | 0.004 |  |  |
| **7** | 0.014 | 0.03 | 0.003 | 0.004 |  | 0.003 | 0.004 | 0.038 | 0.01 |  |  | 0.001 | 0.001 | 0.003 | 0.002 | 0.004 |  |  |
| **8** | 0.255 | 0.048 | 0.015 | 0.022 | 0.082 | 0.099 | 0.031 | 0.028 | 0.278 |  |  | 0.129 | 0.056 | 0.06 |  | 0.037 |  |  |
| **9** | 0.039 | 0.005 | 0.324 | 0.023 | 0.005 | 0.012 | 0.028 | 0.162 | 0.718 |  |  | 0.008 | 0.054 | 0.12 | 0.281 | 0.116 |  |  |
| **10** | 1.115 | 0.173 | 0.017 | 0.007 | 0.102 | 0.004 |  | 0.045 | 0.332 |  |  | 0.001 | 0.001 | 0.001 |  | 0.001 |  |  |
| **11** | 0.044 | 0.005 | 0.016 | 0.002 | 0.024 | 0.022 | 0.062 | 0.198 | 1.414 |  |  | 0.241 | 0.371 | 0.494 |  |  |  |  |
| **12** |  | 0.056 | 0.019 | 0.044 | 0.209 | 0.02 | 0.002 | 0.08 | 0.047 |  |  | 0.056 | 0.132 | 0.112 | 0.051 | 0.082 | 0.146 | 0.048 |
| **13** |  | 0.009 | 0.074 | 0.004 | 0.001 | 0.115 | 0.112 | 0.082 | 0.052 | 0.082 | 0.002 | 0.019 | 0.06 | 0.086 | 0.08 | 0.128 | 0.092 | 0.12 |
| **14** | 0.038 |  | 0.039 |  | 0.055 | 0.137 | 0.181 | 0.001 |  | 0.5 |  | 0.097 | 0.001 | 0.052 | 0.199 | 0.308 | 0.175 | 0.728 |
| **15** | 0.316 | 0.004 | 0.002 | 0.012 |  | 0.139 | 0.074 | 0.047 | 0.119 |  |  | 0.01 | 0.007 | 0.011 |  | 0.01 |  |  |
| **16** |  | 0.009 | 0.199 |  | 0.062 | 0.25 | 0.874 | 0.135 | 0.058 |  |  |  | 0.036 |  |  |  |  |  |
| **17** | 0.182 | 0.165 | 0.915 |  | 0.107 |  | 0.006 | 0.018 | 0.023 |  | 0.033 | 0.005 |  | 0.002 | 0.017 | 0.422 | 0.513 | 0.012 |
| **18** | 0.029 | 0.008 | 0.024 | 0.036 | 0.087 | 0.032 | 0.02 | 0.214 | 0.129 | 0.017 | 0.355 | 0.076 | 0.095 | 0.064 | 0.011 | 0.024 | 0.022 | 0.031 |
| **19** | 0.008 | 0.013 | 0.087 | 0.018 | 0.002 | 0.001 | 0.002 | 0.004 | 0.03 | 0.167 | 0.488 | 0.002 | 0.001 | 0.112 | 0.001 | 0.005 |  |  |
| **20** | 0.005 | 0.009 | 0.006 | 0.031 | 0.018 | 0.007 | 0.002 |  | 0.045 | 0.641 | 1.143 | 0.005 | 0.003 | 0.001 | 0.019 | 0.32 | 0.49 |  |
| **21** | 1.01 | 0.014 | 0.015 |  | 0.476 | 0.08 | 0.017 | 0.036 | 0.008 | 0.041 |  | 0.407 | 0.287 |  |  |  |  |  |
| **22** | 0.387 | 0.022 | 0.01 | 0.028 |  | 0.017 | 0.001 | 0.031 | 0.039 | 0.056 |  | 0.004 | 0.006 | 0.008 | 0.003 | 0.002 | 0.003 |  |
| **23** | 0.043 | 0.032 | 0.005 | 0.037 |  | 0.065 | 0.016 | 0.045 | 0.133 | 0.188 |  | 0.056 | 0.013 | 0.019 |  | 0.031 |  |  |
| **24** | 0.009 | 0.038 |  | 0.017 | 0.144 | 0.183 | 0.08 | 0.062 | 0.018 |  |  | 0.14 | 0.171 | 0.325 |  | 0.81 |  |  |
| **25** | 0.004 | 0.028 | 1.284 | 0.01 | 0.066 | 0.004 | 0.005 |  | 0.018 | 0.005 | 0.628 | 0.028 | 0.018 | 0.01 | 0.012 | 0.002 |  |  |
| **26** | 0.017 | 0.005 | 0.001 | 0.006 | 0.014 | 0.015 | 0.023 | 0.01 | 0.011 |  |  | 0.183 | 0.09 | 0.133 |  | 0.133 |  |  |
| **27** |  | 0.663 | 0.122 | 0.763 |  | 0.031 | 0.015 | 0.009 | 0.003 |  |  | 0.191 | 0.025 | 0.006 |  | 0.004 |  |  |
| **28** | 0.012 | 0.001 |  | 0.374 | 0.593 | 0.034 | 0.06 | 0.138 | 0.185 |  |  | 0.04 | 0.02 | 0.098 |  | 0.101 |  |  |
| **29** | 0.016 | 0.015 | 0.02 |  | 0.195 |  |  |  | 0.088 | 0.012 |  | 0.056 | 0.004 |  |  | 0.015 | 0.001 | 0.001 |
| **30** | 0.118 | 0.036 | 0.056 | 0.001 | 0.02 | 0.001 | 0.003 | 0.006 | 0.007 | 0.009 | 0.335 | 0.04 | 0.023 |  | 0.006 | 0.034 | 0.015 | 0.018 |
| **31** |  | 0.118 |  | 0.047 | 0.022 | 0.013 | 0.01 | 0.012 | 0.025 | 0.212 |  | 0.019 | 0.023 | 0.025 | 0.046 | 0.019 | 0.032 | 0.019 |
| **32** | 0.26 | 0.101 | 0.038 | 0.187 | 0.52 | 0.036 | 0.046 | 0.139 | 0.08 | 0.18 |  | 0.159 | 0.111 | 0.07 |  | 0.044 |  |  |
| **33** | 0.026 | 0.336 | 0.065 | 0.019 | 0.524 | 0.114 | 0.021 | 0.052 | 0.103 | 1.997 | 0.966 | 0.004 | 0.001 | 0.634 | 0.062 | 0.031 | 0.025 |  |