# Supplementary materials for

**Occurrence of unapproved pesticides and their ecotoxicological significance for an agriculturally influenced reservoir and its tributaries in Nepal**

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Fig. S1 Agriculture is practiced in the well-maintained terraces by the small holding farmers in Indra Sarowar catchment with (a) patchy cropping practices, (b) deposited surface sediment sampling and (c) empty pesticides containers observed in the stream of Indra Sarowar catchment.

Table S1 General characteristics of sampling sites in Indra Sarowar reservoir catchment, Nepal. For site ID location see in Fig. 1.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Name of stream/  reservoir | Site  ID | Distance from agriculture field (m)  (L = left side, R = right side) | Sample metrics | Anthropogenic impact (% agricultural land) | Flow\*  (m3 s-1) | Sediment contribution (%) from agriculture land\*\* |
| Palung | P-1 | L=10, R=15, no buffer strip in both side | Water, sediment | 10 |  |  |
| P-2 | L=20, R=22, no buffer strip in both sides | Water, sediment | 25 |  |  |
| P-3 | L=30, R=42, buffer strips present in both sides | Water, sediment | 40 |  |  |
| P-4 | L=30, R=40, buffer strip presents in left side | Water, sediment | 35 |  |  |
| Tistung | T-1 | L=10, R=10, no buffer strips in both sides | Water, sediment | 70 |  | 75 |
| T-2 | L=7, R=8, no buffer strips in both side | Water, sediment | 60 |  |  |
| T-3 | L=10, R=12, no buffer strips in both sides | Water, sediment | 65 |  |  |
| Bishenkhel | B-1 | L=10, R=11, no buffer strips in both sides | Water, sediment | 55 |  |  |
| B-2 | L= 50, R= >100, buffer strips present in both sides | Water, sediment | 65 |  |  |
| Chitlang | C-1 | L= 9, R=10, no buffer strips in both sides | Water, sediment | 21 |  | 26 |
| C-2 | L= >100, R= >100, buffer strips in both sides | Water, sediment | 30 | 0.7-4.6 | 20 |
| Indra Sarowar (Reservoir) | R-C |  | Water, cage fish | 40 |  |  |
| R-O |  | Water, open stock fish | 40 |  |  |

\*July 2003- Sep 2004 (Sangroula, 2005)

\*\* (Upadhayay et al., 2018)

Table S2 Operating conditions for LC-MS/MS and GC-ECD.

|  |  |
| --- | --- |
| LC-MS/MS | GC-ECD |
| Column Waters HSS T3 (1.8 µm)  Injection volume 10 µL  Oven temperature 40°C  Mobile phase A Water + 10 mM ammoniumacetate  Mobile phase B Acetonitrile+0.1% formic acid  Flow 0.4 mL.min-1  Gradient 0-0.25 min 2% solvent B  0-7 min linear gradient to 98% solvent B  7-8 min 98% solvent B  8-9 min linear gradient to 2% solvent B  9-10 min 2% solvent B  Detector Triple quadrupole mass spectrometer  Interface Electrospray ionization  Potential 5000 V  Temperature 500°C  Scan Type MRM (Multiple Reaction Monitoring Mode)  Collision gas Argon | Column HP-5MS (5% phenyl methyl siloxane)  30 m × 0.25 m × 0.25 µm film thickness  Mobile phase Helium  Flow 1.1 mL. min-1  Temperature gradient Initially 60 °C  20°C min-1 to 150°C  15°C min-1 to 250°C  2 min at 250 °C  30°C min-1 to 270°C  10 min at 270°C  30°C min-1 to 280°C  11 min at 280°C  Injection temperature 200°C  Injection mode Split (ratio 52.7:1)  Detector Electron Capture Detector (ECD)  Temperature detector 250°C |

Table S3 List of target pesticides and their recovery in various environmental compartments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Pesticides | Recovery ± SD (%) | | | Instruments |
| Sediment | Water | Fish |
| Acetamiprid | 105.5 ± 4.74 | 100.73 ± 8.65 | 126.31 ± 6.52 | LC-MS/MS |
| Alachlor | 70.87 ± 11.29 | 72.76 ± 9.57 | 145 ± 14.55 | GC-ECD |
| Aldrin | 101.44 ± 7.35 | 32.85 ± 11.06 | 82.22 ± 2.34 | GC-ECD |
| Amethryn | 81.13 ± 3.38 | 49.51 ± 11.10 | 93.45 ± 2.29 | LC-MS/MS |
| Azoxystrobine | 134.63 ± 8.49 | 117.23 ± 4.07 | 83.85 ± 9.14 | LC-MS/MS |
| Bentazon | 70.83 ± 14.06 | 85.38 ± 13.90 | 73.75 ± 7.81 | LC-MS/MS |
| Bifenthrin | 129.23 ± 4.81 | 40.65 ± 12.96 | 81.32 ± 1.41 | GC-ECD |
| Bitertanol | 39.50 ± 3.14 | 48.77 ± 4.90 | 65.00 ± 9.17 | LC-MS/MS |
| Boscalid | 111.83 ± 10.24 | 118.27 ± 10.24 | 143.43 ± 6.06 | LC-MS/MS |
| Butachlor | 92.13 ± 5.85 | 94.25 ± 14.92 | 97.95 ± 9.16 | LC-MS/MS |
| Cadusafos | 114.13 ± 2.06 | 93.70 ± 7.58 | 116.44 ± 10.21 | LC-MS/MS |
| Carbaryl | 116.44 ± 13.04 | 101.30±13.80 | 93.24±10.05 | LC-MS/MS |
| Carbendazim | 27.25 ± 1.44 | 88.75 ± 11.00 | 81.00 ± 1.22 | LC-MS/MS |
| Carbofuran | 116.75 ± 6.96 | 91.81 ± 10.07 | 120.69 ± 2.60 | LC-MS/MS |
| Chloorthalonil | 118.50 ± 1.22 | 53.65 ± 10.05 | 39.65 ± 9.26 | GC-ECD |
| Chlorpyrifos | 58.25 ± 7.12 | 52.65 ± 5.83 | 85.46 ± 27.28 | LC-MS/MS |
| Cymoxanil | 91.27 ± 11.86 | 79.78 ± 9.89 | 83.03 ± 11.60 | LC-MS/MS |
| Cypermethrin | 84.01 ± 3.29 | 38.69 ± 13.14 | 60.2 ± 3.09 | GC-ECD |
| DDD / Endosulfan-β | 109.33 ± 4.22 | 81.16 ± 6.03 | 51.77 ± 5.83 | GC-ECD |
| DDE | 133.46 ± 3.99 | 48.55 ± 8.21 | 115.45 ± 7.38 | GC-ECD |
| Deltamethrin | 86.00±4.00 | 92.00±4.00 | 76.00±4.00 | GC-ECD |
| o,p’- DDT | 117.23 ± 5.68 | 59.23 ± 9.70 | 98.05 ± 4.89 | GC-ECD |
| p,p’- DDT | 148.19 ± 3.32 | 33.76 ± 3.31 | 95.01 ± 8.46 | GC-ECD |
| Diazinon | 87.25 ± 2.75 | 81.99 ± 3.20 | 91.08 ± 4.95 | LC-MS/MS |
| Dieldrin | 110.72 ± 3.95 | 87.20 ± 8.36 | 75.37 ± 2.89 | GC-ECD |
| Difenconazole | 58.38 ± 7.60 | 41.93 ± 13.23 | 79.84 ± 9.27 | LC-MS/MS |
| Dimethoate | 87.38 ± 5.91 | 90.30 ± 4.89 | 60.72 ± 2.60 | LC-MS/MS |
| Dimethomorph | 84.44 ± 2.38 | 102.96 ± 14.01 | 92.60 ± 12.22 | LC-MS/MS |
| Diuron | 83.81 ± 4.30 | 108.53 ± 6.78 | 79.96 ± 6.08 | LC-MS/MS |
| Endosulfan-α | 138.32 ± 3.72 | 83.66 ± 6.59 | 78.55 ± 0.91 | GC-ECD |
| Endrin | 132.62 ± 5.15 | 94.83 ± 4.4 | 125.91 ± 5.91 | GC-ECD |
| Ethoprophos | 137.50 ± 8.32 | 107.20 ± 11.54 | 137.43 ± 4.77 | LC-MS/MS |
| Fenamiphos | 92.50 ± 9.40 | 99.34 ± 11.63 | 113.19 ± 10.57 | LC-MS/MS |
| Fenbuconazole | 70.75 ± 5.87 | 60.44 ± 5.68 | 82.46 ± 9.78 | LC-MS/MS |
| Fenpropimorph | 101.67 ± 10.41 | 99.43 ± 9.31 | 57.09 ± 9.78 | LC-MS/MS |
| Hexachlorobenzen | 104.23 ± 6.28 | 76.80 ±7.89 | 102.85 ± 1.87 | GC-ECD |
| Hexaconazole | 46.63 ± 2.56 | 64.60 ±10.09 | 86.58 ±10.56 | LC-MS/MS |
| Imazalil | 84.83 ± 8.56 | 76.17± 8.80 | 75.96 ±12.21 | LC-MS/MS |
| Imidacloprid | 103.25 ± 5.32 | 56.69 ± 8.77 | 120.69 ± 5.12 | LC-MS/MS |
| Iprodione | 44.75 ±14.50 | 76.83 ± 4.64 | 84.98 ± 9.62 | LC-MS/MS |
| Kresoxim-methyl | 72.66 ± 4.59 | 81.53 ± 10.34 | 78.78 ± 8.02 | LC-MS/MS |
| β-HCH | 47.19 ± 6.31 | 96.26 ± 11.85 | 98.53 ± 3.28 | GC-ECD |
| Linuron | 89.50 ± 5.15 | 109.65 ± 4.26 | 104.45 ± 12.21 | LC-MS/MS |
| Malathion | 92.17 ± 9.52 | 106.70 ± 12.71 | 90.37 ± 9.33 | LC-MS/MS |
| Metalaxyl | 131.13 ± 9.45 | 136.49 ± 9.80 | 139.81 ± 5.66 | LC-MS/MS |
| Methiocarb | 100.00 ± 11.30 | 69.15 ± 9.61 | 100.07 ± 4.31 | LC-MS/MS |
| Methoxychlor | 49.56 ± 9.91 | 84.21 ± 7.59 | 62.86 ± 5.98 | LC-MS/MS |
| Methsulfuron methyl | 96.25 ± 9.46 | 71.91 ± 5.43 | 88.53 ± 9.04 | LC-MS/MS |
| Metribuzin | 93.75 ± 7.23 | 61.11 ± 7.27 | 100.07 ± 2.56 | LC-MS/MS |
| Monocrotophos | 76.00 ± 4.81 | 38.45 ± 9.02 | 108.70 ± 4.66 | LC-MS/MS |
| Nicosulfuron | 79.50 ± 8.60 | 70.50 ± 8.61 | 90.11 ± 5.22 | LC-MS/MS |
| Oxamyl | 75.13 ± 6.16 | 87.93 ± 11.29 | 62.97 ± 25.44 | LC-MS/MS |
| Pendimethanil | 67.70± 9.77 | 80.27 ± 12.47 | 68.41 ± 12.97 | LC-MS/MS |
| Pirimicarb | 41.50 ± 5.57 | 79.24 ± 5.64 | 95.95 ± 3.24 | LC-MS/MS |
| Prochloraz | 31.50 ± 4.77 | 36.30 ± 7.63 | 86.96 ± 7.14 | LC-MS/MS |
| Profenofos | 70.25 ± 1.85 | 83.80 ± 8.43 | 81.96 ± 6.92 | LC-MS/MS |
| Propanil | 80.88 ± 5.74 | 104.38 ± 5.00 | 91.45 ± 10.49 | LC-MS/MS |
| Propiconazole | 74.38±6.34 | 73.28±8.28 | 76.38 ± 12.26 | LC-MS/MS |
| Propoxur | 115.75 ± 4.77 | 89.07 ± 8.13 | 126.44 ± 2.29 | LC-MS/MS |
| Pyraclostrobine | 92.25 ± 5.01 | 109.20 ± 12.30 | 121.44 ± 14.30 | LC-MS/MS |
| Pyrazosulfuron ethyl | 57.13 ± 9.20 | 79.11 ± 8.20 | 89.13 ± 5.58 | LC-MS/MS |
| Pyrimethanil | 134.17 ± 9.24 | 80.28 ± 5.78 | 86.12 ± 9.79 | LC-MS/MS |
| Spinosad A | 81.10 ± 2.97 | 37.23 ± 0.48 | 58.21 ± 1.21 | LC-MS/MS |
| Spinosad D | 73.10 ± 6.11 | 39.55 ± 0.29 | 70.50 ± 7.01 | LC-MS/MS |
| Spiroxamine | 78.17 ± 10.52 | 57.67 ± 10.78 | 33.98 ± 2.29 | LC-MS/MS |
| Tebuconazole | 55.63 ± 3.28 | 71.36 ± 6.00 | 78.96 ± 16.85 | LC-MS/MS |
| Tebuthiuron | 92.38 ± 5.14 | 95.05 ± 6.98 | 100.82 ± 4.64 | LC-MS/MS |
| Terbuthryn | 73.00 ± 6.07 | 41.43 ± 6.33 | 101.95 ± 8.48 | LC-MS/MS |
| Thiabendazole | 85.59 ± 6.62 | 98.42 ± 8.01 | 75.12 ± 3.76 | LC-MS/MS |
| Thiametoxam | 87.00 ± 4.30 | 74.26 ± 6.78 | 117.44 ± 4.82 | LC-MS/MS |
| Thifensulfuron | 40.65 ± 5.78 | 122.72 ± 12.80 | 25.99 ± 0.87 | LC-MS/MS |
| Thiodicarb | 77.25 ± 5.95 | 77.91 ± 8.40 | 51.47 ± 7.55 | LC-MS/MS |
| Triademinol | 50.50 ± 4.38 | 69.76 ± 7.38 | 67.09 ± 6.97 | LC-MS/MS |
| Triazophos | 118.83 ± 9.83 | 107.90 ± 9.69 | 124.44 ± 9.00 | LC-MS/MS |
| Trifloxystrobine | 87.13 ± 9.20 | 64.45 ± 8.96 | 122.44 ± 13.44 | LC-MS/MS |

Table S4 PNEC values of pesticides quantified in the water and sediment from Indra Sarowar reservoir and its tributaries.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Pesticides | Acute toxicity data (µg L-1) | | | PNEC  (µg L-1) |
| Algae | Invertebrate | Fish |
| Alachlor | 966 | 10000 | 1800 | 9.66 |
| Boscalid | 3750 | 5330 | 2700 | 27 |
| Cypermethrin | 66.7 | 0.21 | 1.51 | 0.0021 |
| DDT | - | 5 | 2500 | 0.05 |
| Deltamethrin | 0.47 | 0.56 | 0.15 | 0.0015 |
| Diuron | 2.7 | 5700 | 6700 | 0.027 |
| Endosulfan - α | 2150 | 440 | 2 | 0.02 |
| β - HCH | 2500 | 1600 | 2.9 | 0.029 |
| Iprodione | 1800 | 660 | 3700 | 6.6 |
| Metalaxyl | 420 | 3470 | 960 | 4.2 |
| Pyrimethanil | 1200 | 2900 | 10560 | 12 |

Table S5Physico-chemical properties of pesticides: solubility (S) at 20˚C, octanol-water partition coefficient (log Kow), bioconcentration factor (BCF) and aqueous hydrolysis (DT50 at 20˚C and pH 7) (Source: (Lewis et al., 2016)).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Pesticides | Class | S (mg L-1) | Log Kow | BCF (L kg-1) | DT50 (days) |
| Alachlor | Herbicide | 240 | 3.09 | 39 | 1 – 2 |
| Boscalid | Fungicide | 4.6 | 2.96 | 107 | stable |
| Cypermethrin | Insecticide | 0.009 | 5.55 | 331 | stable |
| DDT | Insecticide | 0.006 | 6.91 | 3173 | - |
| Deltamethrin | Insecticide | 0.0002 | 4.6 | 1400 | stable |
| Diuron | Herbicide | 35.6 | 2.87 | 9.45 | stable (~50) |
| Endosulfan-α | Insecticide | 0.32 | 4.75 | 2755 | non-persistent (20) |
| β-HCH | Fungicide | – | – | – | – |
| Iprodione | Fungicide | 6.8 | 3.0 | 70 | 4.5 |
| Metalaxyl | Fungicide | 8400 | 1.75 | 7 | persistent (106) |
| Pyrimethanil | Fungicide | 110 | 2.84 | Low risk | stable |

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