

# Interactions with freshwater biofilms cause rapid removal of common herbicides through degradation – evidence from microcosm studies

Maria Alexandra Bighiu, Willem Goedkoop

## Supplementary information

Table S1 Known metabolites of bentazone, metribuzin and metazachlor. Data from EPA and PPDB.

| Parent compound | Metabolites  | Properties                |                        |            |                       |
|-----------------|--|---------------------------|------------------------|------------|-----------------------|
|                 |  | <i>log K<sub>ow</sub></i> | <i>K<sub>foc</sub></i> | <i>BCF</i> | Vapour pressure (mPa) |
| Bentazone       | 2-amino-N-isopropylbenzamide   | 1.5                       |                        |            |                       |
|                 | N-methyl bentazone   | 1.34                      | 257.5                  |            |                       |
|                 | 8-hydroxy-bentazone  | 1.55                      |                        | 10.6       |                       |
|                 | 6-hydroxy bentazone  |                           |                        |            |                       |
|                 | 3-isopropyl-4,5-dioxo-1,3,4,5,6,7-hexahydrocyclopenta[c][1,2,6]thiadiazine-6-carboxylic acid |                           |                        |            |                       |
|                 | 2,2-dioxide  |                           |                        |            |                       |
|                 | [2-(isopropylcarbamoyl)phenyl]sulfamic acid, salts (Ref: M351H024)                           |                           |                        |            |                       |
| Metribuzin      | diketo-metribuzin (Ref: BCS-AG59919)   | 0.9                       |                        |            | 0.000081              |
|                 | desaminodiketo-metribuzin  | 1.49                      |                        |            | 0.051                 |
|                 | desamino-metribuzin (Ref: BCS-AA91084)   |                           | 43.7                   |            | 0.0065                |
|                 | 4-amino-6-(1,1-dimethylethyl)-1,2,4-triazine-5(4H)-one                                       |                           |                        |            |                       |
|                 | 6-tert-butyl-4,5-dihydro-1,2,4-triazin-5-one-3-mercaptopuric acid                            |                           |                        |            |                       |
|                 | 6-(1-hydroxy-1-methyl-ethyl)-3-methylsulfanyl-4H-[1,2,4]-triazine-5-one                      |                           |                        |            |                       |
|                 | 4-methyl-6-(1,1-dimethylethyl)-1,2,4-triazine-3,5(2H,4H)-dione                               |                           |                        |            |                       |
| Metazachlor     | metazachlor oxalic acid (Ref: BH479-4)   | 3.01                      | 24.6                   | 3.24       |                       |
|                 | metazachlor sulfonic acid (Ref: BH479-8)   |                           | 0.5                    |            |                       |
|                 | C16H19N3SO4; Metazochlor M09; 479M09   |                           |                        |            |                       |
|                 | C15H18N3SO2; Metazochlor M11; 479M011  |                           |                        |            |                       |
|                 | C14H13N3O5; Metazochlor M12; 479M012   |                           |                        |            |                       |

Table S2 Biofilm sorption of herbicides as % of initially added amount (mean  $\pm$  1 SD, n=4).

| Herbicide   | Exposure level | day 1              | day 8              | day 16             |
|-------------|----------------|--------------------|--------------------|--------------------|
| Bentazone   | high           | 0.02% $\pm$ 0.005% | 0.03% $\pm$ 0.002% | 0.01% $\pm$ 0.002% |
|             | low            | 0.02% $\pm$ 0.011% | 0.02% $\pm$ 0.004% | 0.01% $\pm$ 0.002% |
| Metazachlor | high           | 0.03% $\pm$ 0.001% | 0.09% $\pm$ 0.018% | 0.05% $\pm$ 0.005% |
|             | low            | 0.05% $\pm$ 0.007% | 0.11% $\pm$ 0.017% | 0.06% $\pm$ 0.008% |
| Metribuzin  | high           | 0.07% $\pm$ 0.009% | 0.06% $\pm$ 0.004% | 0.02% $\pm$ 0.002% |
|             | low            | 0.51% $\pm$ 0.096% | 0.23% $\pm$ 0.052% | 0.06% $\pm$ 0.022% |

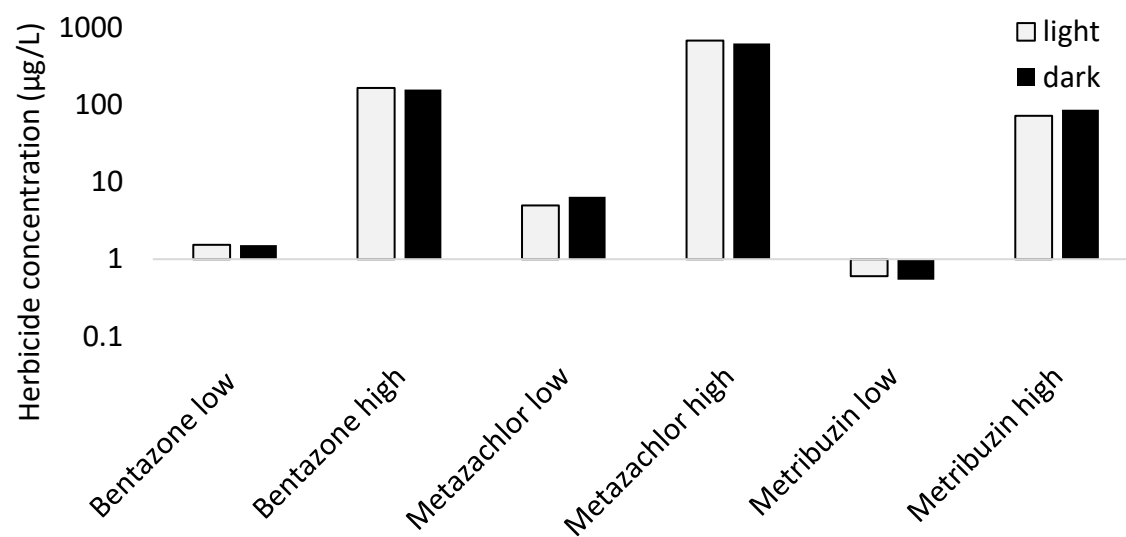


Figure S1 Herbicide water concentrations (log scale) after 16 days in light and dark treatments without biofilms.

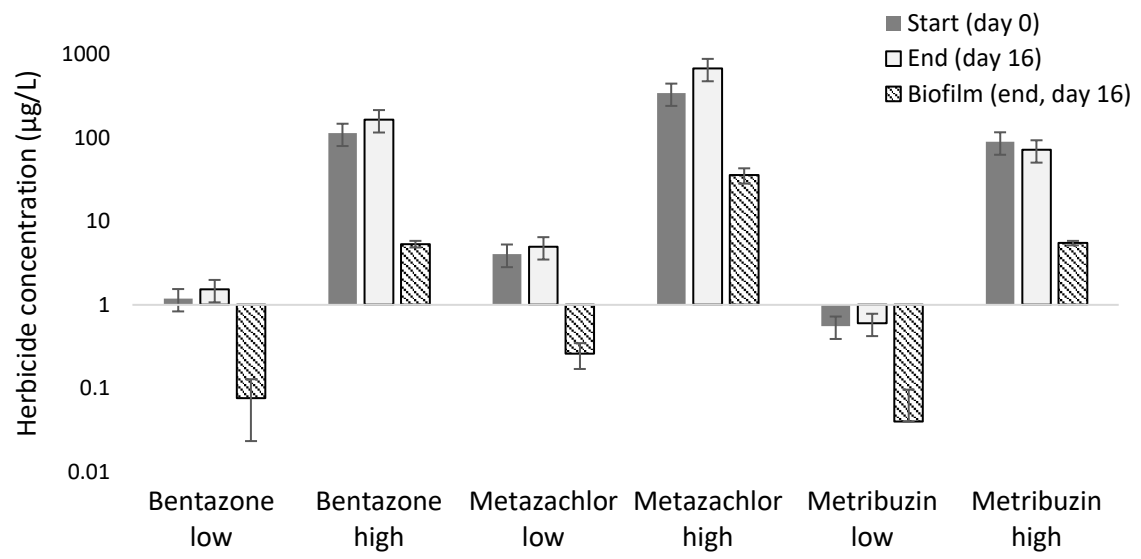


Figure S2 Herbicide water concentrations in treatments with and without biofilms (patterned and plain bars, respectively). Error bars represent measurement uncertainty for replicates without biofilm and standard deviation among replicates with biofilm. The concentrations in treatments with biofilm are calculated from DPM, disintegrations per minute (see text for details).