Estimating Catchment Vulnerability to Diffuse Herbicide Losses from Hydrograph Statistics:

Supplementary Information

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SI-1: Rational for the combined FFI-FFVs proxy: detailed derivation of Eq.[8] and [9]

This description derives the Eq.[8] and [9] of the main text in some more detail. It builds on the main text covering Eq.[1] to [7].

It has been shown (e.g., (Ahuja and Lehman, 1983; Shalit and Steenhuis, 1996)) that herbicides losses due to fast flow originate from a thin mixing layer at the soil surface of depth \( z_{\text{mix}} \). How much is actually lost by fast flow depends on how much is left due to leaching into the underlying soil matrix and due to dissipation until fast flow sets in and on the distribution between soil matrix and the soil pore water.

Assuming sorption equilibrium and a linear sorption isotherm described by the distribution coefficient \( K_d \), the concentration of the sorbed phase \( C_{\text{sorb}}(t) \) is given at any time as

\[
C_{\text{sorb}}(t) = K_d C_{\text{sol}}(t)
\]  

with \( C_{\text{sol}}(t) \) being the concentration in solution.

Accordingly, the total mass at any given time \( M_{\text{tot}}(t) \) in the mixing layer per unit area is given as:

\[
M_{\text{tot}}(t) = V_{\text{mix}} C_{\text{tot}}(t) = V_{\text{mix}} \times (\theta C_{\text{sol}}(t) + \rho K_d C_{\text{sorb}}(t)) = V_{\text{mix}} \times C_{\text{sol}}(t) \times (\theta + \rho K_d)
\]

where \( V_{\text{mix}} = z_{\text{mix}} \times A \) is the volume of the mixing layer, \( z_{\text{mix}} \) is the depth of this volume and \( A \) is an unit area; \( \theta \) and \( \rho \) are the volumetric water content and the bulk density, respectively.

The change in mass in the mixing layer results from the two independent processes dissipation and transport. If dissipation of the compound in solution is a first order process characterized by a rate constant \( k_{\text{diss}} \) and if we assume perfect mixing and instantaneous equilibrium the rate of change of the total herbicide mass \( C(t) \) in the mixing layer is given as:

\[
\frac{d(M_{\text{tot}})}{dt} = A z_{\text{mix}} \frac{dC_{\text{tot}}}{dt} = -A z_{\text{mix}} k_{\text{diss}} \frac{C_{\text{tot}}}{\theta + \rho K_d} - A N_{\text{eff}} \frac{C_{\text{tot}}}{\theta + \rho K_d} = -A \left( \frac{z_{\text{mix}} k_{\text{diss}} + N_{\text{eff}}}{\theta + \rho K_d} \right) C_{\text{tot}}
\]

Accordingly, the total concentration decreases exponentially with time:
\[ C_{\text{tot}}(t) = C_0 \exp \left( - \frac{z_{\text{mix}} k_{\text{diss}} + N_{\text{eff}}}{z_{\text{mix}} (\theta + \rho K_d)} t \right) \]  \hspace{1cm} \text{[SI-4]}

where \( C_0 \) is the initial concentration.

The initial concentration once fast flow sets in \( C_{\text{tot \_ fast \_ ini}} \) is given as \( C_{\text{tot \_ fast \_ ini}} = C_{\text{tot}}(t = \tau_{\text{sat}} \times (\text{FFI})) \).

By combining Eq.[SI-4] with Eq.[6] in the main text one obtains:

\[ C_{\text{tot \_ fast \_ ini}} = C_0 \exp \left( - \frac{z_{\text{mix}} k_{\text{diss}} + N_{\text{eff}}}{z_{\text{mix}} (\theta + \rho K_d)} \frac{z_{\text{max}}}{N_{\text{eff}} - K_{s\_deep}} (1 - \text{FFI}) \right) \]  \hspace{1cm} \text{[SI-5]}

With defining

\[ \alpha = \frac{\left( \frac{z_{\text{mix}} k_{\text{diss}} + N_{\text{eff}}}{z_{\text{mix}} (\theta + \rho K_d)} \right) z_{\text{max}}}{N_{\text{eff}} - K_{s\_deep}} \]  \hspace{1cm} \text{[SI-6]}

Eq.[SI-5] simplifies to:

\[ C_{\text{tot \_ fast \_ ini}} = C_0 \exp(- \alpha (1 - \text{FFI})) \]  \hspace{1cm} \text{[SI-7]}

Once fast flow has set in, its generation occurs at the same rate irrespective of the FFI (Eq.[SI-7]). Accordingly, it takes a constant period of time \( \Delta t = t - \tau_{\text{sat}} \) to generate a given volume of FFVs once fast flow has set in and the cumulative mass of herbicide that is lost with fast flow is given as:

\[ M_{\text{loss}} = \left( N_{\text{eff}} - K_{s\_deep} \right) \frac{C_{\text{tot \_ fast \_ ini}}}{\theta + K_d} \rho \times \int_{\tau_{\text{sat}}}^{t-\tau_{\text{sat}}} \exp \left( - \frac{z_{\text{mix}} k_{\text{diss}} + N_{\text{eff}}}{z_{\text{mix}} (\theta + K_d \rho)} t \right) dt \]  \hspace{1cm} \text{[SI-8]}

The only term in Eq.[SI-8] - corresponding to Eq.[8] in the main text - that depends on the FFI is the initial concentration \( C_{\text{tot \_ fast \_ ini}} \). Hence, the herbicide losses for a given FFVs depend exponentially on the FFI according:

\[ M_{\text{loss}} = \exp(- \alpha (1 - \text{FFI})) \times FFV = \varphi \times FFVs \]  \hspace{1cm} \text{[SI-9]}

This equation corresponds to Eq.[9] in the main text. A range for parameter \( \alpha \) can be obtained by inserting empirical values for the parameters in Eq.[SI-9] (see below).
Figure SI-1: Map with the location of the two Swiss study catchments of lakes Murten and Greifen.
Figure SI-2: Map of the four North American catchments.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Lake Greifen(^\dagger)</th>
<th>Lake Murten (years)</th>
<th>Maumee(^\dagger) (years)</th>
<th>Sandusky(^\dagger) (years)</th>
<th>Honey(^\dagger) (years)</th>
<th>Rock(^\dagger) (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetochlor</td>
<td>9</td>
<td>8</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Alachlor</td>
<td>21</td>
<td>20</td>
<td>21</td>
<td>21</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Atrazine</td>
<td>11</td>
<td>6</td>
<td>21</td>
<td>20</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>6</td>
<td>6</td>
<td>21</td>
<td>20</td>
<td>21</td>
<td>20</td>
</tr>
</tbody>
</table>

\(^\dagger\) no atrazine data for 1992, 1995, 1996

\(\dagger\) no data for 1999 and 2001

\(\dagger\) no data for 1999
Table SI-2: Characterization of study catchments by area, land use and precipitation

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Area [km²]</th>
<th>Land use † [%]</th>
<th>Precipitation‡ (1960-1990) [mm/y]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cropland</td>
<td>Pasture</td>
</tr>
<tr>
<td>Lake Greifen</td>
<td>167</td>
<td>19</td>
<td>35</td>
</tr>
<tr>
<td>Lake Murten</td>
<td>392</td>
<td>31</td>
<td>34</td>
</tr>
<tr>
<td>Rock Creek</td>
<td>88</td>
<td>81</td>
<td>2</td>
</tr>
<tr>
<td>Honey Creek</td>
<td>386</td>
<td>83</td>
<td>1</td>
</tr>
<tr>
<td>Sandusky</td>
<td>3240</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>Maumee</td>
<td>16395</td>
<td>76</td>
<td>3</td>
</tr>
</tbody>
</table>

† from Richards and Baker (1993) and Singer et al. (2005)

‡ Swiss meteo (http://www.meteoschweiz.admin.ch) for Swiss catchments and Casey et al. (1997) for Lake Erie catchments
SI-2: Statistical analysis of regressions between FFVs and loss rates $M_{\text{rel}}$

The relationships between $FFV$ and loss rates $M_{\text{rel}}$ were analyzed according to Eq. [4] by linear regressions for all catchments and all herbicides for which loss data were available. Regressions were calculated for the unweighted and weighted (by the inverse of the $FFV$) $M_{\text{rel}}$. Furthermore, we tested for the influence of outliers by removing the $M_{\text{rel}}$ from the data sets of each compound and catchment. Figure SI-3a to Figure SI-3f and Table SI-3a to Table SI-3f on the following pages show the results of this statistical analysis.
**Figure SI-3a:** Linear regressions between herbicide losses and the FFVs for the Lake Murten catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

**Table S3-a:** Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the catchment of lake Murten: u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset.

<table>
<thead>
<tr>
<th>Regression</th>
<th>Slope (u)</th>
<th>Slope (w)</th>
<th>Slope (w,m)</th>
<th>R² (u)</th>
<th>R² (w)</th>
<th>R² (w,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.71</td>
<td>0.70</td>
<td>0.57</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.014</td>
<td>0.014</td>
<td>0.009</td>
<td>0.55</td>
<td>0.52</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Figure SI-3b: Linear regressions between herbicide losses and the FFVs for the Lake Murten catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

Table S1-3b: Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the Greifensee catchment: u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(u)</td>
<td>(w)</td>
<td>(w,m)</td>
<td>(u)</td>
<td>(w)</td>
<td>(w,m)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>0.010</td>
<td>0.010</td>
<td>0.008</td>
<td></td>
<td>0.67</td>
<td>0.72</td>
<td>0.60</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.017</td>
<td>0.009</td>
<td>-0.005</td>
<td></td>
<td>0.69</td>
<td>0.30</td>
<td>0.29</td>
</tr>
</tbody>
</table>
Figure SI-3c: Linear regressions between herbicide losses and the FFVs for the Maumee catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

Table SI-3c: Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the Maumee catchment. u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Slope</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>(u) 0.021</td>
<td>(w) 0.028</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.020</td>
<td>0.023</td>
</tr>
<tr>
<td>Alachlor</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>0.002</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Figure SI-3d: Linear regressions between herbicide losses and the FFVs for the Sandusky catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

Table S1-3d: Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the Sandusky catchment:. u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset

<table>
<thead>
<tr>
<th>Regression</th>
<th>Slope (u)</th>
<th>Slope (w)</th>
<th>Slope (w,m)</th>
<th>R² (u)</th>
<th>R² (w)</th>
<th>R² (w,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.038</td>
<td>0.034</td>
<td>0.029</td>
<td>0.56</td>
<td>0.70</td>
<td>0.69</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.040</td>
<td>0.031</td>
<td>0.027</td>
<td>0.65</td>
<td>0.70</td>
<td>0.68</td>
</tr>
<tr>
<td>Alachlor</td>
<td>0.005</td>
<td>0.007</td>
<td>0.006</td>
<td>0.21</td>
<td>0.47</td>
<td>0.55</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>0.010</td>
<td>0.005</td>
<td>-0.013</td>
<td>0.08</td>
<td>0.03</td>
<td>0.57</td>
</tr>
</tbody>
</table>
**Figure S1-3e:** Linear regressions between herbicide losses and the FFVs for the Honey Creek catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

**Table S1-3e:** Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the Honey creek catchment. u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset.

<table>
<thead>
<tr>
<th></th>
<th>sacrifice</th>
<th>(u)</th>
<th>(w)</th>
<th>(w,m)</th>
<th>(u)</th>
<th>(w)</th>
<th>(w,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.036</td>
<td>0.034</td>
<td>0.030</td>
<td></td>
<td>0.54</td>
<td>0.71</td>
<td>0.67</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.028</td>
<td>0.026</td>
<td>0.024</td>
<td></td>
<td>0.58</td>
<td>0.72</td>
<td>0.67</td>
</tr>
<tr>
<td>Alachlor</td>
<td>0.010</td>
<td>0.010</td>
<td>0.009</td>
<td></td>
<td>0.44</td>
<td>0.60</td>
<td>0.56</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>0.042</td>
<td>0.031</td>
<td>0.012</td>
<td></td>
<td>0.39</td>
<td>0.43</td>
<td>0.24</td>
</tr>
</tbody>
</table>
**Figure SI-3f:** Linear regressions between herbicide losses and the FFVs for the Rock Creek catchment. The different regression lines correspond to a) different weighting of the data and b) the exclusion data with the highest loss rate. black: unweighted regression, all data; red: data weighted by fast flow volume (FFVs), all data; light red: data weighted by FFVs, maximum loss rate excluded.

**Table S1-3f:** Regression slopes between the volume of fast flow (FFVs) and the herbicide losses relative to the applied amounts for the Rock creek catchment. u: unweighted regression, w: data weighted by inverse FFVs, m: largest loss rate excluded from the dataset

<table>
<thead>
<tr>
<th>Regression</th>
<th>Slope</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(u)</td>
<td>(w)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>0.043</td>
<td>0.038</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>0.060</td>
<td>0.059</td>
</tr>
<tr>
<td>Alachlor</td>
<td>0.004</td>
<td>0.006</td>
</tr>
<tr>
<td>Acetochlor</td>
<td>0.031</td>
<td>0.022</td>
</tr>
</tbody>
</table>
SI-3: Prediction of a plausible range for the dependence of the loss rate on the FFI

Based on Eq.[SI-9] derived in the previous section it is possible to estimate a plausible range for the values of the parameter $\alpha$. For that purpose, minimum and maximum values for the parameters of Eq.[SI-9] are defined based on literature data and our own experience (Table SI-4). We obtained the plausible range upon randomly selecting parameter values from uniform distributions of all single parameters within the bounds defined by the extreme values in Table SI-2 and inserting these values into Eq.[SI-9]. Finally, we defined the 5% and 95% percentile of the resulting distribution of the alpha values as the plausible range (see Figure 4 in the main text).

Table SI-4: Range of parameter values used to calculate the range of plausible values of $\alpha$ (Eq.[SI-9]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Unit</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>zmix</td>
<td>Thickness Mixing Layer</td>
<td>[m]</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>thalf</td>
<td>Herbicide$^\dagger$ half-life in the mixing layer</td>
<td>[d]</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Neff</td>
<td>Rate of effective rainfall</td>
<td>[m d$^{-1}$]</td>
<td>0.002</td>
<td>0.005</td>
</tr>
<tr>
<td>theta</td>
<td>Volumetric water content</td>
<td>[m$^3$ m$^{-3}$]</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>$K_d$</td>
<td>Herbicide$^\ddagger$ distribution coefficient</td>
<td>[m$^3$ kg$^{-1}$]</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Bulk density</td>
<td>[kg m$^{-3}$]</td>
<td>1100</td>
<td>1400</td>
</tr>
<tr>
<td>$K_s$</td>
<td>Saturated hydraulic conductivity of the geologic underground below the soil profile</td>
<td>[m d$^{-1}$]</td>
<td>0</td>
<td>0.002</td>
</tr>
<tr>
<td>zmax</td>
<td>Maximum drainable porosity</td>
<td>[m]</td>
<td>0.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^\dagger$ generic moderately persistent herbicide
$^\ddagger$ generic moderately sorbing herbicide
Figure SI-4: Spatial distribution of the estimated FFI across Europe based on the European soil map (see Schneider et al. (2007) for more details). Areas under Mediterranean, Boreal and Alpine climates (according to Biogeographical regions of Europe 2005, European Environment Agency, http://www.eea.europa.eu/data-and-maps/data/biogeographical-regions-europe-2005) and areas without relevant corn production (basically < 0.5% of agricultural land under corn, based on Eurostat cropping statistics) were excluded.
Table SI-5: Organic carbon normalized soil/water sorption coefficient and field dissipation half-life values in soil for acetochlor, alachlor, atrazine, metolachlor, and s-metolachlor. Mean values from the footprint pesticide properties database (FOOTPRINT, 2006)

<table>
<thead>
<tr>
<th></th>
<th>$\text{DT}_{50\text{Field}} (\text{d})$</th>
<th>$\text{K}_{\text{OC}} \text{ (ml g}^{-1}\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetochlor</td>
<td>12.1</td>
<td>156</td>
</tr>
<tr>
<td>Alachlor</td>
<td>14</td>
<td>124</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>21</td>
<td>200</td>
</tr>
<tr>
<td>S-Metolachlor</td>
<td>22</td>
<td>226</td>
</tr>
<tr>
<td>Atrazine</td>
<td>29</td>
<td>100</td>
</tr>
</tbody>
</table>

References


FOOTPRINT. 2006. The FOOTPRINT Pesticide Properties Data Base. Database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704).

