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New insight into pesticide partition coefficient $K_d$ for modelling pesticide fluvial transport: Application to an agricultural catchment in south-western France

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**ABSTRACT**

Pesticides applied on crops are leached with rainfall to groundwater and surface water. They threat the aquatic environment and may render water unfit for human consumption. Pesticide partitioning is one of the pesticide fate processes in the environment that should be properly formalised in pesticide fate models. Based on the analysis of 7 pesticide molecules (alachlor, atrazine, atrazine’s transformation product deethylatrazine or DEA, isoproturon, tebuconazole and trifluralin) sampled from July 2009 to October 2010 at the outlet of the river Save (south-western France), the objectives of this study were (1) to check which of the environmental factors (discharge, pH, concentrations of total suspended matter (TSM), dissolved organic carbon (DOC) and particulate organic carbon (POC) could control the pesticide sorption dynamic, and (2) to establish a relationship between environmental factors, the partition coefficient $K_d$ and the octanol/water distribution coefficient $K_{ow}$. The comparison of physico-chemical parameters values during low flow and high flow shows that discharge, TSM and POC are the factors most likely controlling the pesticide sorption processes in the Save river network, especially for lower values of TSM (below 13 mg L$^{-1}$). We therefore express $K_d$ depending on the widely literature-related variable $K_{ow}$ and on the commonly simulated variable TSM concentration. The equation can be implemented in any model describing the fluvial transport and fate of pesticides in both dissolved and sorbed phases, thus, $K_d$ becomes a variable in time and space. The $K_d$ calculation method can be applied to a wide range of catchments and organic contaminants.

**1. Introduction**

Intensive agriculture is known to have a detrimental effect on soils, surface water and groundwater quality, which leads to acute problems such as soil erosion or water contamination (Atasoy et al., 2009; Zeiger and Fohrer, 2009; Yi et al., 2012). Organic pollutants, such as excessive pesticides loading from cultivated land, are transferred to surrounding surface water either dissolved or sorbed to particles, and may be harmful to aquatic ecosystems (Polard et al., 2011; Beketov et al., 2013; Proia et al., 2013). Pesticides loads may also render stream water and groundwater unfit for drinking water provision (EC, 1998). The occurrence and the bioavailability of pesticides in water are controlled by environmental, physico-chemical, and anthropogenic factors (e.g. Imfeld et al., 2009; Lewan et al., 2009; Fenoll et al., 2011;
Rodriguez-Liébana et al., 2011). Recent studies in the south-western France area showed the role of intense rainfall events such as floods on water quality degradation regarding suspended matters and pesticides (Boithias et al., 2011; Oeurng et al., 2010, 2011; Taghavi et al., 2010, 2011). Understanding pesticide dynamics during storm events is therefore of major importance to assess surface water quality degradation risk and subsequent possible transfers to living organisms.

The relationships between pesticides and suspended sediments, dissolved or particulate organic carbon (DOC and POC), were highlighted in various studies (Gao et al., 1997; Wu et al., 2004; Thevenot et al., 2009; Taghavi et al., 2010). Adsorption of pesticides to the solid phase (organic matter and clay content) was shown to be a key process driving the mobility of pesticides in the environment, as well as pH (Hayes, 1970; Novak et al., 1997; Coquet and Barriuso, 2002; Weber et al., 2004; El Bakouri et al., 2009). Chiou et al. (1979) formalised sorption processes in terms of the organic carbon normalised partition coefficient ($K_{OC}$). The octanol/water distribution coefficient ($K_{ow}$) gives a measure of the organic molecules' hydrophobicity and partly describes the intensity of the pesticide adsorption and desorption mechanisms in water: some molecules, such as glyphosate, generally have a strong sorption although their $K_{ow}$ is low (Goss and Schwarzenbach, 2001, 2003). Relationships between $K_{OC}$ and $K_{ow}$ were found by several authors in batch conditions (Karickhoff et al., 1979; US EPA, 1996; Xu et al., 1999; Toul et al., 2003). For instance Karickhoff et al. (1979) expressed $K_{OC}$ as a function of $K_{ow}$ for non-charged organic hydrophobic compounds whose $\log(K_{ow})$ were between 2.1 and 6.3. The latter relationship is widely used to parameterise the partition coefficient $K_{d}$ in pesticide fate and transport models (e.g. SWAT – Arnold et al., 1998), by relating $K_{d}$ to $K_{OC}$ through $f_{OC-TSM}$, the fraction of POC in total suspended matter, sometimes assuming a specific value of $f_{OC-TSM}$ (Chapra, 1997). Thus, $K_{d}$ is defined for each molecule as a constant value in time and space for a whole drainage network.

To our knowledge, very few studies focused on $K_{d}$ stemming from in-stream pesticides concentration measurements (e.g. Maillard et al., 2011; Taghavi et al., 2010, 2011). In this paper we handle the hypothesis that $K_{d}$ varies over time and space following the dynamics of suspended matters and specifically the dynamics of organic fraction estimated as $f_{OC-TSM}$. The $K_{d}$ metric is often related to the organic fraction to estimate the corresponding $K_{OC}$. However, the dependency of $K_{OC}$ on the nature of the involved organic matter (Toul et al., 2003) does not authorise to keep $K_{OC}$ as a constant parameter along the river course. To take into account the possible interactions of the pesticide molecules with the organic matter, we introduced instead the widely literature-related variable $K_{ow}$. Using data sampled at the outlet of an agricultural catchment in south-western France, the river Save catchment, our study goals were (1) to check which of the environmental factors (i.e. discharge, total suspended matter, organic carbon, pH) was significantly different between high flow and low flow at the outlet of the catchment, (2) to highlight which one(s) of those factors could control the pesticide partition between dissolved and sorbed phases, and (3) to establish a relationship between $K_{d}$, $K_{OC}$ and environmental factors, suitable to the local environmental context of a wide range of catchments where the $\log(K_{ow})$ of detected molecules is below 5. Thus the pesticide-specific $K_{d}$ parameter could become a variable in time and space, implementable in pesticide fate and transport models.

2. Materials and methods

2.1. Study area

The river Save is located in south-western France and drains an area of 1110 km$^2$ (Fig. 1). The geological substratum is built from impermeable molassic deposits stemming from the erosion of the Pyrenees Mountains during the end of the Tertiary period. Calcin soils stem from molasses and represent 61% of the whole catchment area with a clay content ranging from 35% to 50%. They are located on the top of the hills and on their slopes. Non-calce silty soils represent 30% of the soil in this area (40–60% silt). They are mainly located downstream, close to the Garonne alluvial plain. Alluvial deposits are found along the streams and represent 9% of the catchment area (Boithias et al., in press). Top soil organic matter content is about 2% (Veyssy et al., 1999).

The climate is temperate oceanic. The river Save hydrological regime is mainly pluvial with a maximum discharge in May and low flows during the summer (July–September). The annual precipitation is of 600 to 900 mm with an annual evapotranspiration of 500–600 mm (1998–2010). Mean annual discharge measured by the hydrometric station at the catchment outlet is about 6.1 m$^3$ s$^{-1}$ (1998–2010) (see gauging station in Fig. 1). During low flows, the river flow is sustained upstream by the Neste canal (about 1 m$^3$ s$^{-1}$) that derives water from a Pyrenean river, namely the river Neste, for irrigation purpose (data from Compagnie d’Aménagement des Coteaux de Gascogne – CACG).

Approximately 90% of the catchment surface is devoted to agriculture. The upstream part of the catchment is a hilly agricultural area mainly covered with pasture and forest associated to cereals and corn on small plateaus (Macary et al., 2013). The downstream part is devoted to intensive agriculture with mainly both corn grown as monoculture and a 4-year crop rotation alternating winter wheat with sunflower and corn, sorghum or soybean. The 110 km$^2$ of corn are irrigated with 210 mm yr$^{-1}$ of water from July to September (Boithias et al., in press).

2.1.1. Observed discharge

The river Save discharge was monitored from 2007 to 2010. At the hydrometric station (Fig. 1), hourly discharges ($Q$) were obtained from CACG. The hourly discharge was plotted by the rating curve $Q=f(H)$ in which the water level ($H$) was measured continuously and then averaged for each day. Fig. 2 shows the daily aggregated discharge data.

2.1.2. Water quality monitoring

At the catchment outlet gauging station, Total Suspended Matter (TSM), Dissolved Organic Carbon (DOC), Particulate Organic Carbon (POC), and pH were monitored from July 2009 to October 2010, both manually and automatically, as described in previous studies on the river Save catchment (Oeurng et al., 2011). An automatic water sampler, connected to a probe, was programmed to activate pumping water for 30 cm water level variations during high flows, for the rising and falling stages, thus providing 1–29 river 4 L water samples in 1 L glass jars per stormflow event depending on its intensity. Grab sampling was also undertaken near the probe position at weekly intervals during low flow. TSM, DOC, POC and pH laboratory analysis were performed as described in Oeurng et al. (2011) Additional POC and TSM concentrations measured from January 2007 to March 2009 (Oeurng et al., 2011) were used in this study.

In the same way, water samples for pesticides residues analyses were collected in the glass jars of the automatic water sampler. Pesticide laboratory analysis of 170 samplings was performed as described by Taghavi et al. (2010, 2011) on both filtered and unfiltered extracts of the same sample of water with a limit of detection (LOD) ranging between 0.001 and 0.003 µg L$^{-1}$ depending on the molecule. A total of 7 non-charged molecules with $\log(K_{ow})$ values ranging from 1.5 to 4.8 (mean = 3 ± 1) were considered in this study (alachlor, atrazine, deethylatrazine (DEA – metabolite of atrazine), isoproturon, metolachlor, tebuconazole and trifluralin). Pesticides concentration data are available at...
2.2. Low and high flow discrepancy

To find out if TSM, POC and DOC concentrations and log($K_d$) of the 7 molecules (see Section 2.4 for $K_d$ calculation) were significantly different between high and low flow during the 2009–2010 period, event-scale aggregation was chosen in order to avoid the bias stemming from the data sampling frequency, i.e. to make the average concentration during a high or low flow event independent from the number of sampled grabbed during that event. To separate high flow periods, discharge peak was considered as a high flow event when the discharge was back to its base level. Because of the relative small amount of samples, we considered the base level as being the smallest discharge between two peaks, provided that the number of available samples was at least 3 to calculate averages. To increase the number of samples, low flow periods were separated with an autocorrelation method. The autocorrelation was sought after shifting the discharge signal from day to day till the resulting $R^2$ was found to be below 0.2, indicating that the discharge signal could be considered as being no more correlated. For each period, the average observed DOC, POC, TSM concentrations and pH (2009–2010), were weighted by the corresponding observed discharge. The discrepancy of those values between high and low flow events was sought with Fisher’s statistical test (software: SigmaPlot 11.0). The same approach was performed for $K_d$ analysis, based on discharge-weighted pesticide concentrations.

2.3. Relationship between POC and TSM

A graphical relationship between the TSM and the fraction of POC in TSM ($f_{OC-TSM}$) was sought out of the 332 measurements of TSM and POC grabbed from 2007 to 2010 (data from this study and from Oeurng et al. (2011)).

2.4. Relationship between $K_d$, $K_{ow}$ and TSM

Event-scale calculations were also performed on pesticide concentrations at catchment outlet: average pesticide concentrations weighted by the observed discharge were calculated for each hydrological period. The partition coefficient $K_d$ (L mg$^{-1}$ or m$^3$ g$^{-1}$) of each molecule was calculated as follows:

$$K_d = \frac{C_{\text{sorbed}}}{C_{\text{soluble}}} \quad (1)$$

where $C_{\text{sorbed}}$ (µg mg$^{-1}$ or mg g$^{-1}$) and $C_{\text{soluble}}$ (µg L$^{-1}$) are the observed pesticide concentrations in sorbed and dissolved phases respectively. $C_{\text{soluble}}$ was directly obtained from the analysis of the filtered samples and $C_{\text{sorbed}}$ was calculated as the difference of concentration between the unfiltered and the filtered samples, and related to the TSM concentration. $K_d$ could be calculated when $C_{\text{soluble}}$ or $C_{\text{sorbed}}$ were both over the detection limit. Therefore, the percentage of samples grabbed from 2009 to 2010 that could be considered for $K_d$ calculations was ranging between 9% (tebuconazole) and 41% (metolachlor).

$K_d$ is assumed to be a function of $K_{ow}$ and $f_{OC-TSM}$ through the following relationship:

$$K_d = f_{OC-TSM} \cdot K_{ow} \quad (2)$$

http://www.aguaflash-sudoe.eu. Pesticide measurements all along the year allowed covering the full variability of pesticides exportations, from their application till their sinking.

Fig. 1. Location of the river Save catchment.

Fig. 2. Daily observed discharge (m$^3$ s$^{-1}$) at river Save catchment outlet, with 11 high flow periods and 5 low flow periods (July 2009–October 2010).
where \( f_{OC-TSM} \) is in gC g\(^{-1}\) and \( K_{oc} \) is in \( (\text{mg g}^{-1})(\text{mg m}^{-3}) \). The \( K_{oc} \) of the 7 molecules was calculated at each hydrological event based on the corresponding \( K_{av} \) and \( f_{OC-TSM} \) values.

The graphical relationship between \( K_{oc} \) and \( K_{ow} \) \( (\text{mg g}^{-1})(\text{mg m}^{-3}) \) was then sought for the river Save catchment based on 2009–2010 data for the 7 molecules.

### 3. Results and discussion

#### 3.1. Physico-chemical parameters dynamics

##### 3.1.1. Low and high flow discrepancy

Eleven high flow periods, i.e. 11 flood events, and 5 low flow periods, are identified from July 2009 to October 2010 (Fig. 2). Fig. 3(a) shows event-scale aggregations of average and maximal discharge, TSM, DOC, and POC concentrations, and pH. They are plotted as boxplots for both low flow and high flow. Average and maximal discharge, TSM and POC concentrations are significantly different between low flow and high flow periods \((p<0.05)\) (Fig. 3(a)). The concentrations of DOC are very similar in both flow conditions. This physico-chemical parameter is not linearly related to flow (Wagner et al., 2008; Oeurng et al., 2011). Strong correlations are found between POC and TSM \((R^2=0.97, p<0.05, n=15)\) and between POC and maximal discharge \((R^2=0.92, p<0.05, n=15)\) (Table 1, Fig. 3(b)). High correlation between POC and TSM has been already shown at global scale by Ludwig et al. (1996). High discrepancies for TSM and POC between low and high flows are related to the control of runoff on the erosion of the upper soil layers, as shown by Oeurng et al. (2010, 2011) in a previous study at the river Save outlet. Changes of pH are insignificant between low flow and high flow, eliminating its possible effect on the ionisation of the pesticide molecule. So the environmental factors liable to drive pesticide partition between dissolved and sorbed phases in the river Save are POC and TSM concentrations, observed under a wide range of discharge values.

##### 3.1.2. Relationship between POC and TSM

A relationship between \( f_{OC-TSM} \) and TSM is established for each sample grabbed from 2007 to 2010. Observed TSM concentration ranges from 6 to 15743 mg L\(^{-1}\). Observed \( f_{OC-TSM} \) ranges from 0.25% to 8%. \( f_{OC-TSM} \) and TSM are correlated through a hyperbolic regression \((R^2=0.5, p<0.05, n=332)\), the Eq. (3), which is illustrated in Fig. 4:

\[
 f_{OC-TSM} = \frac{0.094}{\text{TSM} – 0.021} 
\]

At high concentrations of TSM, the Eq. (3) converges on a minimal value of \( f_{OC-TSM} \) to be related to the gradual increase of mineral constituents in fluvial TSM during erosive rainy events. The value of 2.1% is in agreement with the top soil POC rates observed in south-western France catchments (2% – Probst, 1992; Veyssy et al., 1999). This value will be later mentioned as \( f_{OC-TSMtopsoil}. \) \( f_{OC-TSMtopsoil} \) is a catchment-specific constant. Fig. 4 also shows about 12 samples with \( f_{OC-TSM} \) below \( f_{OC-TSMtopsoil} \) \( \left( f_{OC-TSM} \approx 1.6\% \right) \) for TSM concentrations beyond 1000 mg L\(^{-1}\), for discharges higher than 40 m\(^3\) s\(^{-1}\). This may be related to the desorption of DOC from POC during high flow (Bass et al., 2011). Conversely, lowest TSM concentrations measured at the outlet of the river Save tends to a minimum value \( (\text{TSM}_{\text{min}}) \) of 5 mg L\(^{-1}\). \( \text{TSM}_{\text{min}} \) depends on the supply of TSM together with the water flow of the Neste canal, regulated by the upstream Neste reservoir that consequently regulates the sediments flux. \( \text{TSM}_{\text{min}} \) is a catchment-specific constant, including an anthropogenic impact in the Save case. At last, the numerator, which value is 9.4%, is a catchment-specific constant related to the primary production of the river and to the land cover of the basin (Martins and Probst, 1991). This constant will be later called \( K_{av} \).

The decrease of \( f_{OC-TSM} \) together with the increase of TSM is attributed to changes in organic carbon sources (Ludwig et al., 1996; Coux et al., 2005; Oeurng et al., 2011). A high \( f_{OC-TSM} \) highlights an in-stream phytoplankton production and litter contribution during low flow periods (autochthonous sources). Low \( f_{OC-TSM} \) corresponds to terrigenous POC from soil erosion during intense rainfall events, therefore from allochthonous origin. It is worth noting that the \( f_{OC-TSM} \) of 40% (Chapra, 1997), characteristic of the phytoplankton organic carbon content, is never reached at river Save outlet (maximum is about 8%), thus highlighting the dilution of POC by mineral suspended sediments during low flow (when water is mainly supplied by the Neste canal) that is also the irrigation period. The latter also explains why 49% of the \( f_{OC-TSM} \) measurements (Fig. 4) at the outlet of the Save catchment are between 1.6% and 2.4%.

Several authors have found similar relationships between \( f_{OC-TSM} \) and TSM (Ittekkot, 1988; Martins and Probst, 1991; Ludwig et al., 1996; Veyssy et al., 1999; Oeurng et al., 2011; Cerro et al., in press). Cerro et al. (in press) and Ludwig et al. (1996) have published the related equation but none of them have expressed the relationship between \( f_{OC-TSM} \) and TSM as a hyperbole, including physically understandable parameters. The term \( f_{OC-TSMtopsoil} \) relates to the autochthonous carbon source, whereas the term \( \text{NUM}/(\text{TSM} – \text{TSM}_{\text{min}}) \) relates to the allochthonous carbon source, which is added to the base \( f_{OC-TSMtopsoil} \) for total carbon content calculations.

#### 3.2. Pesticide dynamics

##### 3.2.1. Low and high flow discrepancy

The values of \( K_{av} \) for the 7 molecules are calculated with Eq. (1) using the samples grabbed from July 2009 to October 2010 during the 11 high flow periods and 5 low flow periods (Table 2). Fig. 5 shows event-scale aggregations of log(\( K_{av} \)) values plotted as boxplots for both low flow and high flow. At the river Save outlet, the range of log(\( K_{av} \)) is \([-4.7; -0.6]\), which is consistent with the \([-10.0; -0.1]\) range of log(\( K_{av} \)) previously mentioned by Taghavi (2010) and Taghavi et al. (2010) from 2008 to 2009 in the river Save catchment and for pesticides having a similar range of \( \log(K_{ow}) \), i.e. \([2.5; 5.2]\). Our calculated values are also consistent with the \([-3.3; 1.1]\) range of log(\( K_{av} \)) values mentioned by Maillard et al. (2011) in 2009 at the outlet of a vineyard catchment in Rouffiac and for pesticides within the similar \( \log(K_{ow}) \) range \([-1.5; 4.0]\). Also, the \( K_{av} \) values we calculated from in-stream metolachlor, triflurilin and atrazine measurements are in the range of the one reported by Tomlin (2009) in the environment \([-6.7; -3.2]\).

Because of the small number of available sample measurements during low flow periods, some molecules (DEA, isoproturon and tebuconazole) are less detected and their results are therefore less significant. A dominant trend for all molecules (Fig. 5) is however that \( K_{av} \) changes depending on the hydrological regime: (1) the minimal \( K_{av} \) value is observed during high flows and (2) the median \( K_{av} \) value increases during low flows, in agreement with the decrease of TSM and POC concentrations. Observed median \( \log(K_{av}) \) values of atrazine, alachlor and trifluralin are similar during both low and high flows. The latter has to be related to the homogeneity of the river Save catchment highlighted by the stable pH (Fig. 3(a)), to a constant dissolved organic matter contain (DOC between 3 and 6 mg L\(^{-1}\) – Fig. 3(a)), to the small range of variation of \( f_{OC-TSM} \) (most values are between 1.6% and 2.4%), and to the regular top soil composition all over the agricultural part of the basin (Bothias et al., in
press). Significant changes in metolachlor log(K_d) could be attributed to its high solubility (470 mg L^{-1}).

To investigate the role of both the sorbed and the dissolved phases in the pesticide dynamics, the average value of log(K_d) is compared to the physico-chemical parameters of the river Save catchment (Table 3). Isoproturon and metolachlor have an affinity with the particulate carbon fraction (POC). Trifluralin shows an intermediate affinity with the POC. Conversely, tebuconazole is

Table 1

<table>
<thead>
<tr>
<th></th>
<th>TSM R^2</th>
<th>POC R^2</th>
<th>DOC R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average discharge</td>
<td>0.40 (p &lt; 0.05)</td>
<td>0.48 (p &lt; 0.05)</td>
<td>0.21</td>
</tr>
<tr>
<td>Maximal discharge</td>
<td>0.86 (p &lt; 0.05)</td>
<td>0.92 (p &lt; 0.05)</td>
<td>0.39 (p &lt; 0.05)</td>
</tr>
<tr>
<td>pH</td>
<td>0.02</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>POC</td>
<td>0.97 (p &lt; 0.05)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DOC</td>
<td>0.39 (p &lt; 0.05)</td>
<td>0.39 (p &lt; 0.05)</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Boxplots of average discharge (m^3 s^{-1}), maximal discharge (m^3 s^{-1}), and discharge-weighted concentrations (mg L^{-1}) of Total Suspended Matter (TSM), Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC), and pH during low flow (n = 5) and high flow periods (n = 11) and (b) scatterplots of maximal discharge versus discharge-weighted TSM, POC and DOC concentrations (July 2009–October 2010).
Fig. 4. Relationship between Total Suspended Matter (TSM) concentration (mg L$^{-1}$) and Particulate Organic Carbon (POC) content ($f_{OC-TSM} \times 100$ in % of TSM dry weight) at river Save catchment outlet (332 samples from January 2007 to October 2010). Asymptotes to the hyperbolic equation are presented as dashed lines.

Table 2
Average and standard deviation of $K_d$ (m$^3$ g$^{-1}$) and $K_{oc}$ ((mg gC$^{-1}$)/(mg m$^3$)) for 7 pesticides detected at the outlet of the river Save catchment (July 2009–October 2010), and their respective $K_{ow}$ ((mg m$^3$ octanol)/(mg m$^3$ water)) values (Tomlin, 2009).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>$K_{ow}$ $(\text{mg m}^3 \text{ octanol}/\text{mg m}^3 \text{ water})$</th>
<th>$\log (K_{ow})^*$</th>
<th>$K_d$ (m$^3$ g$^{-1}$)</th>
<th>$K_{oc}$ ((mg gC$^{-1}$)/(mg m$^3$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>1259</td>
<td>3.1</td>
<td>0.004 ± 0.006</td>
<td>0.147 ± 0.198</td>
</tr>
<tr>
<td>Atrazine</td>
<td>501</td>
<td>2.7</td>
<td>0.013 ± 0.018</td>
<td>0.481 ± 0.668</td>
</tr>
<tr>
<td>DEA</td>
<td>32</td>
<td>1.5</td>
<td>0.006 ± 0.012</td>
<td>0.268 ± 0.636</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>316</td>
<td>2.5</td>
<td>0.020 ± 0.032</td>
<td>0.579 ± 0.999</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>794</td>
<td>2.9</td>
<td>0.010 ± 0.021</td>
<td>0.310 ± 0.669</td>
</tr>
<tr>
<td>Tebuconazole</td>
<td>5012</td>
<td>3.7</td>
<td>0.016 ± 0.019</td>
<td>0.633 ± 0.720</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>63096</td>
<td>4.8</td>
<td>0.044 ± 0.082</td>
<td>1.265 ± 2.061</td>
</tr>
</tbody>
</table>

$^*$ Tomlin (2009).

Fig. 5. Boxplots of average $K_d$ (m$^3$ g$^{-1}$) weighted by the discharge for 7 pesticides during low flow (2 < n < 5) and high flow periods (5 < n < 11) (July 2009–October 2010).
correlated with the dissolved carbon fraction (DOC). Except for tebuconazole, and although the $R^2$ are poorly significant, as the correlation of the pesticide molecules with POC is very similar to the correlation with TSM, all molecules sorbed to TSM are actually sorbed to the POC included in TSM. As the TSM parameter is easily measurable and predictable, and strongly correlated to POC (Table 1), it appears relevant expressing $K_d$ depending on TSM instead of POC.

3.2.2. Contribution of the $K_d$ approach

The values of $K_{oc}$ calculated with Eq. (2) are given for the 7 molecules in Table 2. The boxplots of log($K_{oc}$) depending on log($K_{ow}$) are shown in Fig. 6: boxplots integrate measurements of all hydrological periods from July 2009 to October 2010. A linear regression is drawn based on log($K_{oc}$) and log($K_{ow}$) values, leading to the following equation:

$$K_{oc} = 7.55 \times 10^{-3} \cdot K_{ow}^{0.36}$$

(4)

$R^2$ of the relationship between averages of $K_{oc}$ and averages of $K_{ow}$ is 0.8 ($n = 7$, $p < 0.05$). The standard deviations of the average $K_{oc}$ for the 7 molecules are higher than the average $K_{oc}$ of all 7 molecules (Table 2) because the high variability of the POC concentration of the river Save (Fig. 3).

The log($K_{oc}$) values we calculated from in-stream metolachlor, trifluralin and atrazine measurements are in the range of the one reported by Tomlin et al. (2009) in the environment [–4.4;–1.4]. Fig. 6 also shows that the relationship found between $K_{oc}$ and $K_{ow}$ in the river Save is strongly different from the one drawn with the equation published by Karickhoff et al. (1979), i.e. log($K_{oc}$) = log($K_{ow}$) - 0.21 ($K_{oc} = 0.63 \cdot K_{ow}$), and suggested to parameterize the SWAT model (Neitsch et al., 2009). The log($K_{oc}$) values predicted by their equation applied to the river Save outlet do not fit with the calculated log($K_{oc}$) from observed data considering the differences in intercept and slope. They are more than two logarithmic units higher than the calculated average log($K_{oc}$) values with Eq. (4), and they are in any case out of the range of the calculated log($K_{oc}$) values from river sampling. The conditions of experiments described in Karickhoff et al. (1979) were different to ours in the river Save catchment. Karickhoff et al. (1979) worked in batch laboratory conditions and reported $K_{oc}$ depending on $K_{ow}$ for coarse silt fractions (20–50 μm) at a concentration of 20000 mg L$^{-1}$. In the river Save, 23.9% of the measured suspended sediment particles (Merlina et al., personal communication) are from the fine fraction (i.e. below 63 μm according to the OSPAR commission criterion). Since the average TSM concentration is 20 mg L$^{-1}$, the interaction factor is 4000 times lower. Therefore, the shift in the TSM concentration can impact the required level of the involved Gibbs free energy of partition, considering the same concentration of organic contaminant (Goss and Schwarzenbach, 2003). Our system is not energetically favourable for a strong interaction of the neutral pesticides molecules with the particulate organic matter. At last, the effectiveness of the hydrophobic binding of the 7 molecules in our study (log($K_{ow}$) of 3 ± 1) is decreased since they are less lipophilic than the aromatic hydrocarbons and chlorinated hydrocarbons used elsewhere (log($K_{ow}$) of 5 ± 1 in (Karickhoff et al. 1979)).

3.2.3. Relationship between $K_d$, $K_{ow}$ and TSM

$K_d$ is expressed as a function (Eq. (5), from Eq. (2)) of TSM and $K_{ow}$, by replacing $f_{oc-TSM}$ and $K_{oc}$ with their respective equations Eqs. (3) and (4):

$$K_d = \left( \frac{0.094 \cdot (TSM - 5)}{TSM + 0.021} \right) \cdot \left( 7.55 \times 10^{-3} \cdot K_{ow}^{0.36} \right)$$

(5)

Fig. 7(a) shows a representation of Eq. (5) in a 3D plot and shows the scatterplot for the 7 molecules depending on $K_d$, $K_{ow}$ and TSM. Fig. 7(b) shows 2-dimension projections of extreme values for fixed $K_{ow}$ and TSM concentrations, for an easier visualisation. The uncertainty of the resulting equation mostly relies on the uncertainty on the relationship between $K_d$ and TSM: average observed log($K_{oc}$) is correlated to log($K_{ow}$) of respective molecules ($R^2 = 0.74$, $p < 0.05$, $n = 7$) but the correlation between average observed log($K_{oc}$) and observed TSM concentration is weaker ($0.00 < R^2 < 0.53$ depending on the molecule ($7 < n < 15$), Table 3). As such, Eq. (5) refines the linear relationship between $K_d$ and $K_{ow}$ previously established by Taghavi et al. (2010), as they considered an average TSM concentration per event.

The values of $K_d$ (Figs. 5 and 7) together with the results in Section 3.1.2 suggest that pesticides are mostly sorbed to autochthonous matter during stormflow events whereas they are mostly sorbed to autochthonous matter during low flow. $K_d$ value decreases when concentration in autochthonous material increases. This is consistent with the fact that pesticides are transferred from land to river network mostly with surface runoff (Dur et al., 1998; Boithias et al., 2011; Lefrançais et al., 2013; Ulrich et al., 2013) and that the transfer depends on the nature of the sorbent (Niederer et al., 2007). For that purpose, the hyperbolic proxy for f_{oc-TSM} (i.e. TSM) integrates all the components involved in the sorption processes: mineral fraction and organic matter of either terrestrial or aquatic origin. According to $K_d$ values modelled through Eq. (5), variations in log($K_{oc}$) become less than 1% for a TSM concentration
over 13 mg L\(^{-1}\) in the river Save, considering the 7 molecules’ \(K\) range. The \(K\) is conversely sensitive to TSM changes for small values of TSM concentrations, as it happens at the beginning and at the fall of the storm event.

3.3. Modelling pesticide fate at basin scale

The study shows that the partition coefficient \(K_d\) varies depending on the river’s physico-chemical parameter POC, included in TSM. Pesticide transport and fate computer models as SWAT focus on TSM and do not simulate the fate of organic carbon in river networks. Since the controlling factors discharge, POC and TSM concentrations are correlated among each other, it is relevant to seek a simplified equation of \(K_d\) expressed in terms of TSM and not POC. A hyperbolic relationship between \(f_{\text{OC-TSM}}\) and TSM appears suitable for future implementation in computer models: both the TSM\(_{\text{min}}\) and the \(f_{\text{OC-TSM(topsoil)}}\) parameters are physically comprehensible and easy to parameterise if previously measured. Only the NUM parameter is kept as a calibration parameter, based on the catchment properties understanding. The equation appears suitable to other rivers where \(f_{\text{OC-TSM}}\) and TSM are known to be the main controlling factors of pesticide partition. As such, the pesticide dynamics control of in-stream particulate organic matter can be introduced into the model (e.g. SWAT).

The study also shows that introducing \(K_{\text{oc}}\) values stemming from the equation of Karickhoff et al. (1979) into the pesticide fate model (e.g. SWAT) may not be adapted for pesticides fate modelling in every catchment. We replace the use of \(K_{\text{oc}}\) by the use of \(K_{\text{ow}}\) since \(K_{\text{ow}}\) is a standard pesticide-specific value easily found in the literature (e.g. Tomlin, 2009). As reported by Toul et al. (2003), the observed values of \(K_{\text{oc}}\) and \(K_d\) may broadly differ depending on the sorbed substance and on the sorbent. Using \(K_{\text{ow}}\) frees us from the uncertainty of the sorbent. For a modelling purpose, the parameters of the equation linking \(K_{\text{oc}}\) to \(K_{\text{ow}}\) (Eq. (4)) may be recalculated depending on the available data set for all modelled molecules.

4. Conclusions

This pesticide environmental fate study is a promising first attempt to characterise the dynamic of organic contaminant sorption processes depending on river hydrological regime, provided the sorption processes are mostly driven by hydrophobic interactions. We expressed the partition coefficient \(K_d\) as a function of the widely literature-related variable \(K_{\text{ow}}\) and the total suspended matter (TSM) concentration, that is easily measurable and commonly simulated in pesticide fate models. The equation therefore provides both catchment-specific and molecule-specific values of \(K_d\). The equation can be implemented in any model describing the fluvial transport and fate of pesticides in both dissolved and sorbed phases, where \(K_d\) becomes a variable in time and space. In case of catchment scale models, the \(K_d\) parameter becomes a channel spatialised variable based on local TSM variations and appropriate \(K_{\text{ow}}\) value of the modelled molecule. In addition to bring an insight to pesticide fate modelling, we propose a method for \(K_d\) assessment based on measurements carried out directly in the river course. The \(K_d\) calculation method described here can be applied to any catchments, when (1) a sufficient water quality data set is available, and (2) the catchments are not influenced by reservoirs, lakes or wetlands, that might imply different pesticides behaviours by trapping the suspended matters (e.g. Locke et al., 2011). The \(K_d\) calculation method can be extended to other families of non-charged organic contaminants such as some pharmaceuticals, and can be further adapted to inorganic contaminants, such as complexed metals. For a risk assessment purpose, the \(K_d\) calculations can also be used to quantify the bioavailable dissolved concentration of contaminants in a river channel based on contaminant inputs into the hydrological system.
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