Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

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

Laurie Boithias [*], Sabine Sauvage, Georges Merlina, Séverine Jean, Jean-Luc Probst, José Miguel Sánchez Pérez

University of Toulouse; INPT, UPS; Laboratoire Ecologie Fonctionnelle et Environnement (EcoLab), ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan Cedex, France
CNRS, EcoLab, 31326 Castanet Tolosan Cedex, France

HIGHLIGHTS

- Water managers need to assess contaminant's bioavailability and surface water contamination risk.
- We present a novel method of pesticide partition coefficient K_d assessment.
- K_d is expressed as a function of K_{ow} and total suspended matter concentration.
- This method can be applied to a wide range of organic contaminants and catchments.
- The resultant equation is suggested to be implemented in pesticide fate models.

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;

* Corresponding author. Present address: Catalan Institute of Water Research, Emili Grahit 101, Scientific and Technological Park of the University of Girona, 17003 Girona, Spain (L. Boithias). Tel.: +34 972 18 33 80; fax: +34 972 18 32 48.
E-mail address: l.boithias@gmail.com (L. Boithias).

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 POC and to K_{oc} through $f_{OC\text{-}TSM}$, the fraction of POC in total suspended matter, sometimes assuming a specific value of $f_{OC\text{-}TSM}$ (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 $f_{OC\text{-}TSM}$. The K_{oc} metric is often related to the organic fraction to estimate the corresponding K_d. 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_{ow} 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. Calcic 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-calcic 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
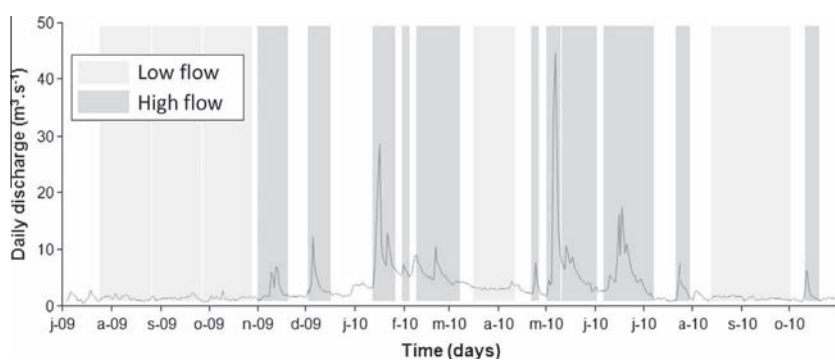
Fig. 1. Location of the river Save catchment.

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).

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.

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 ($f_{OC\text{-}TSM}$) 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:

$$K_d = \frac{C_{sorbed}}{C_{soluble}} \tag{1}$$

where C_{sorbed} ($\mu g\,mg^{-1}$ or $mg\,g^{-1}$) and $C_{soluble}$ ($\mu g\,L^{-1}$) are the observed pesticide concentrations in sorbed and dissolved phases respectively. $C_{soluble}$ was directly obtained from the analysis of the filtered samples and C_{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 $C_{soluble}$ or C_{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_{oc} and $f_{OC\text{-}TSM}$ through the following relationship:

$$K_d = f_{OC\text{-}TSM} \cdot K_{oc} \tag{2}$$

where $f_{OC\text{-}TSM}$ is in gC g^{-1} and K_{oc} is in ((mg gC^{-1}/(mg m^{-3})). The K_{oc} of the 7 molecules was calculated at each hydrological event based on the corresponding K_d and $f_{OC\text{-}TSM}$ values.

The graphical relationship between K_{oc} and K_{ow} ((mg m$_{octanol}^{-3}$)/ (mg m$_{water}^{-3}$)) 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 $f_{OC\text{-}TSM}$ and TSM is established for each sample grabbed from 2007 to 2010. Observed TSM concentration ranges from 6 to 15 743 mg L^{-1}. Observed $f_{OC\text{-}TSM}$ ranges from 0.25% to 8%. $f_{OC\text{-}TSM}$ 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:

$$f_{OC\text{-}TSM} = \frac{0.094}{TSM - 5} + 0.021 \qquad (3)$$

At high concentrations of TSM, the Eq. (3) converges on a minimal value of $f_{OC\text{-}TSM}$ 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 $f_{OC\text{-}TSMtopsoil}$. $f_{OC\text{-}TSMtopsoil}$ is a catchment-specific constant. Fig. 4 also shows about 12 samples with $f_{OC\text{-}TSM}$ below $f_{OC\text{-}TSMtopsoil}$ ($f_{OC\text{-}TSM} \approx 1.6\%$) 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 (TSM$_{min}$) of 5 mg L^{-1}. TSM$_{min}$ 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. TSM$_{min}$ 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 NUM.

The decrease of $f_{OC\text{-}TSM}$ together with the increase of TSM is attributed to changes in organic carbon sources (Ludwig et al., 1996; Coynel et al., 2005; Oeurng et al., 2011). A high $f_{OC\text{-}TSM}$ highlights an in-stream phytoplankton production and litter contribution during low flow periods (autochthonous sources). Low $f_{OC\text{-}TSM}$ corresponds to terrigenous POC from soil erosion during intense rainfall events, therefore from allochthonous origin. It is worth noting that the $f_{OC\text{-}TSM}$ 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 $f_{OC\text{-}TSM}$ measurements (Fig. 4) at the outlet of the Save catchment are between 1.6% and 2.4%.

Several authors have found similar relationships between $f_{OC\text{-}TSM}$ 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 $f_{OC\text{-}TSM}$ and TSM as a hyperbole, including physically understandable parameters. The term $f_{OC\text{-}TSMtopsoil}$ relates to the allochthonous carbon source, whereas the term NUM/(TSM–TSM$_{min}$) relates to the autochthonous carbon source, which is added to the base $f_{OC\text{-}TSMtopsoil}$ for total carbon content calculations.

## 3.2. Pesticide dynamics

3.2.1. Low and high flow discrepancy

The values of K_d 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_d) values plotted as boxplots for both low flow and high flow. At the river Save outlet, the range of log(K_d) is [−4.7;−0.6], which is consistent with the [−10.0;−0.1] range of log(K_d) values 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_d) values mentioned by Maillard et al. (2011) in 2009 at the outlet of a vineyard catchment in Rouffach and for pesticides within the similar log(K_{ow}) range [−1.5;4.0]. Also, the K_d values we calculated from in-stream metolachlor, trifluralin 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_d changes depending on the hydrological regime: (1) the minimal K_d value is observed during high flows and (2) the median K_d value increases during low flows, in agreement with the decrease of TSM and POC concentrations. Observed median log(K_d) 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 $f_{OC\text{-}TSM}$ (most values are between 1.6% and 2.4%), and to the regular top soil composition all over the agricultural part of the basin (Boithias et al., in
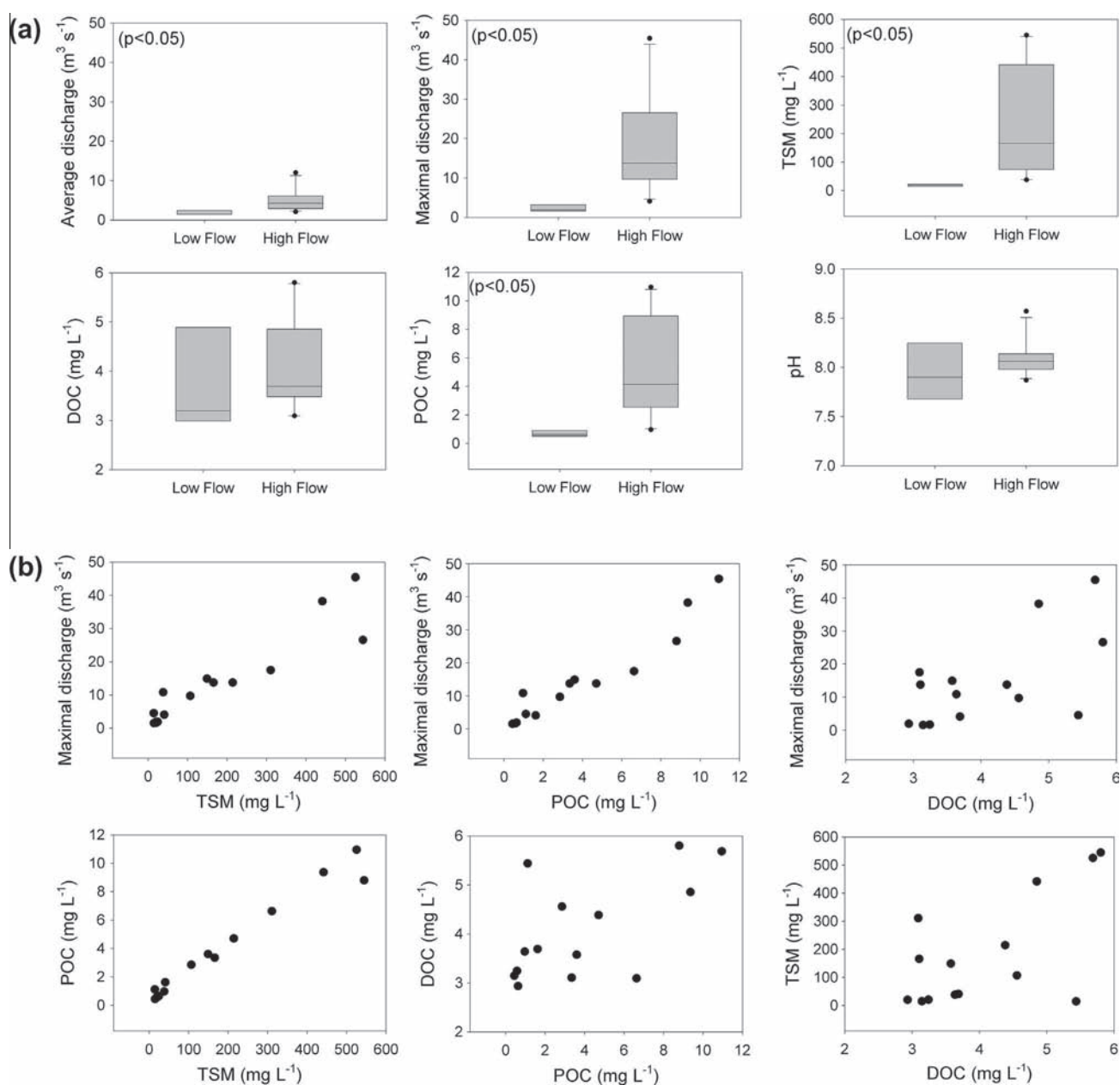
Fig. 3. (a) Boxplots of average discharge (m³ s⁻¹), maximal discharge (m³ s⁻¹), and discharge-weighted concentrations (mg L⁻¹) of Total Suspended Matter (TSM), Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC), and pH during low flow (n = 5) and high flow periods (n = 11) and (b) scatterplots of maximal discharge versus discharge-weighted TSM, POC and DOC concentrations (July 2009–October 2010).

Table 1
Determination coefficient R^2 of compared physico-chemical parameters (discharge (m³ s⁻¹), TSM, POC and DOC concentrations in mg L⁻¹) at the outlet of the river Save catchment (July 2009–October 2010). "n" is the number of observations. Each observation is an average weighted by the discharge for each hydrological event (both high flow and low flow periods).

	TSM		POC		DOC	
	R^2	n	R^2	n	R^2	n
Average discharge	0.40 ($p < 0.05$)	15	0.48 ($p < 0.05$)	15	0.21	14
Maximal discharge	0.86 ($p < 0.05$)	15	0.92 ($p < 0.05$)	15	0.39 ($p < 0.05$)	14
pH	0.02	14	0.02	14	0.13	14
POC	0.97 ($p < 0.05$)	15	–		–	
DOC	0.39 ($p < 0.05$)	14	0.39 ($p < 0.05$)	14	–	

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
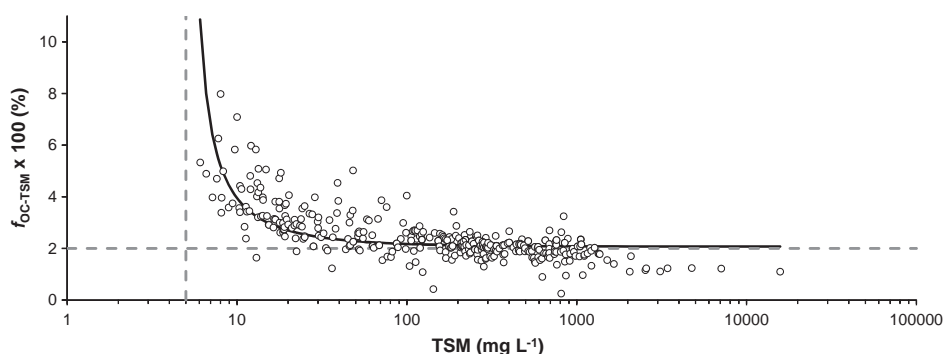
Fig. 4. Relationship between Total Suspended Matter (TSM) concentration (mg L^{-1}) and Particulate Organic Carbon (POC) content ($f_{OC\text{-}TSM}$ x 100 in % of TSM dry weight) at river Save catchment outlet (332 samples from January 2007 to October 2010). Asymptotes to the hyperbolic equation are 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).

	K_{ow} ((mg m$^{-3}_{octanol}$)/(mg m$^{-3}_{water}$))	Log (K_{ow})[a]	K_d (m^3 g^{-1})	K_{oc} ((mg gC^{-1})/(mg m^{-3}))
Alachlor	1259	3.1	0.004 ± 0.006	0.147 ± 0.198
Atrazine	501	2.7	0.013 ± 0.018	0.481 ± 0.668
DEA	32	1.5	0.006 ± 0.012	0.268 ± 0.636
Isoproturon	316	2.5	0.020 ± 0.032	0.579 ± 0.999
Metolachlor	794	2.9	0.010 ± 0.021	0.310 ± 0.669
Tebuconazole	5012	3.7	0.016 ± 0.019	0.633 ± 0.720
Trifluralin	63 096	4.8	0.044 ± 0.082	1.265 ± 2.061

[a] Tomlin (2009).
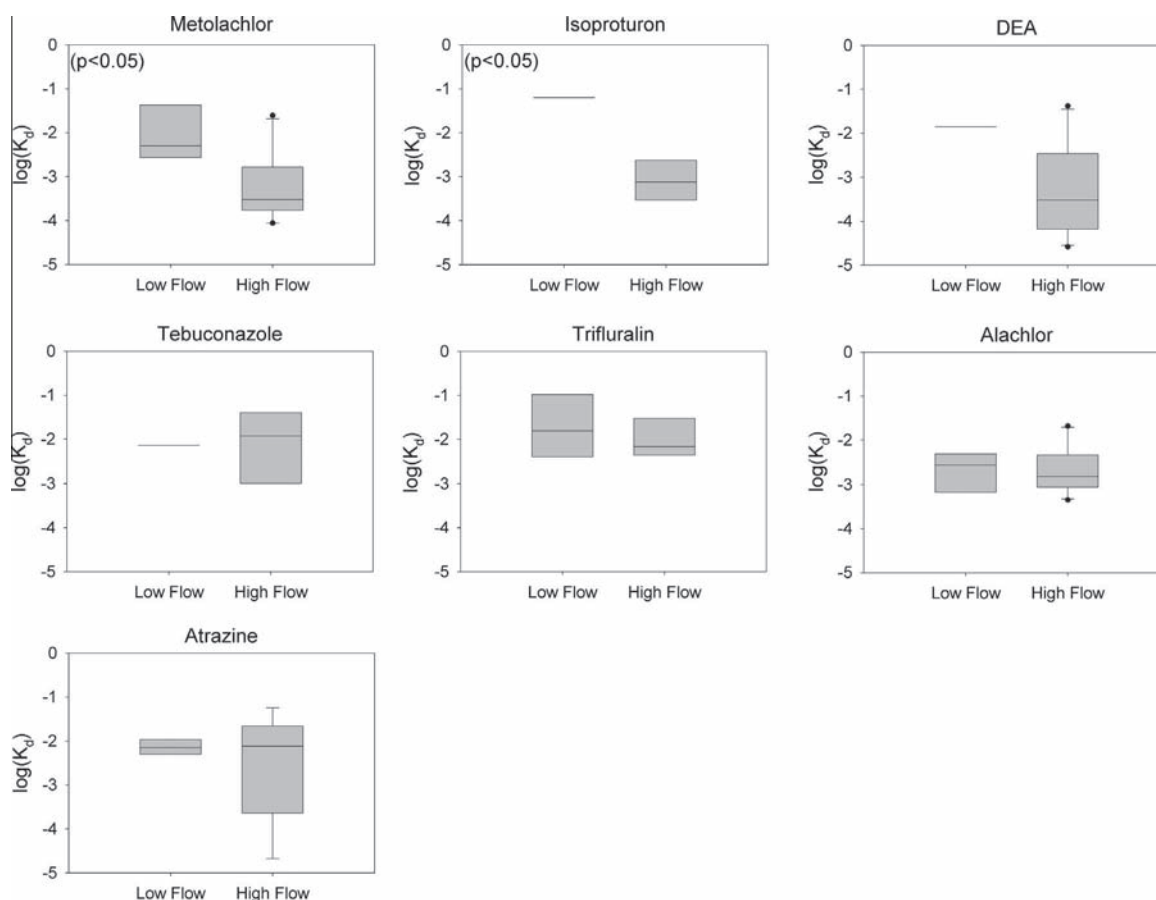
Fig. 5. Boxplots of average K_d (m^3 g^{-1}) weighted by the discharge for 7 pesticides during low flow (2 < n < 5) and high flow periods (5 < n < 11) (July 2009–October 2010).

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_{oc} 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:

$$K_{oc} = 7.55 \times 10^{-3} \cdot K_{ow}^{0.36} \tag{4}$$

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_{ow} and K_{oc} 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 parameterise 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,
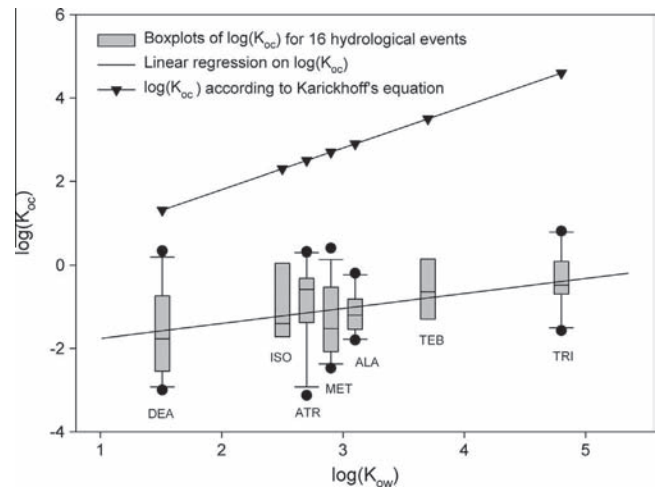
Table 3
Determination coefficient R^2 between observed $\log(K_d)$ (K_d in m^3 g^{-1}) and observed physico-chemical parameters (TSM, POC and DOC concentrations in mg L^{-1}) for 7 pesticides detected at the outlet of the river Save catchment (July 2009–October 2010). "n" is the number of observations. Each observation is an average weighted by the discharge for each hydrological event (both high flow and low flow periods).

	TSM		POC		DOC	
	R^2	n	R^2	n	R^2	n
K_d alachlor	0.06	14	0.05	14	0.09	13
K_d atrazine	0.04	13	0.05	13	0.04	12
K_d DEA	0.00	12	0.00	12	0.01	12
K_d isoproturon	0.53	7	0.52	7	0.01	7
K_d metolachlor	0.47 ($p < 0.05$)	15	0.47 ($p < 0.05$)	15	0.16	14
K_d tebuconazole	0.17	7	0.08	7	0.51	6
K_d trifluralin	0.30	10	0.29	10	0.09	9

Fig. 6. Relationship between K_{oc} ((mg gC^{-1})/(mg m^{-3})) and K_{ow} ((mg m$_{octanol}^{-3}$)/(mg m$_{water}^{-3}$)) at river Save catchment outlet for the 16 hydrological periods, and for 7 pesticide molecules (alachlor, atrazine, deethylatrazine, isoproturon, metolachlor, tebuconazole and trifluralin) (July 2009–October 2010).

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 $f_{OC\text{-}TSM}$ and K_{oc} with their respective equations Eqs. (3) and (4):

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

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 $\log(K_d)$ is correlated to $\log(K_{ow})$ of respective molecules ($R^2 = 0.74$, $p < 0.05$, $n = 7$) but the correlation between average observed $\log(K_d)$ 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.
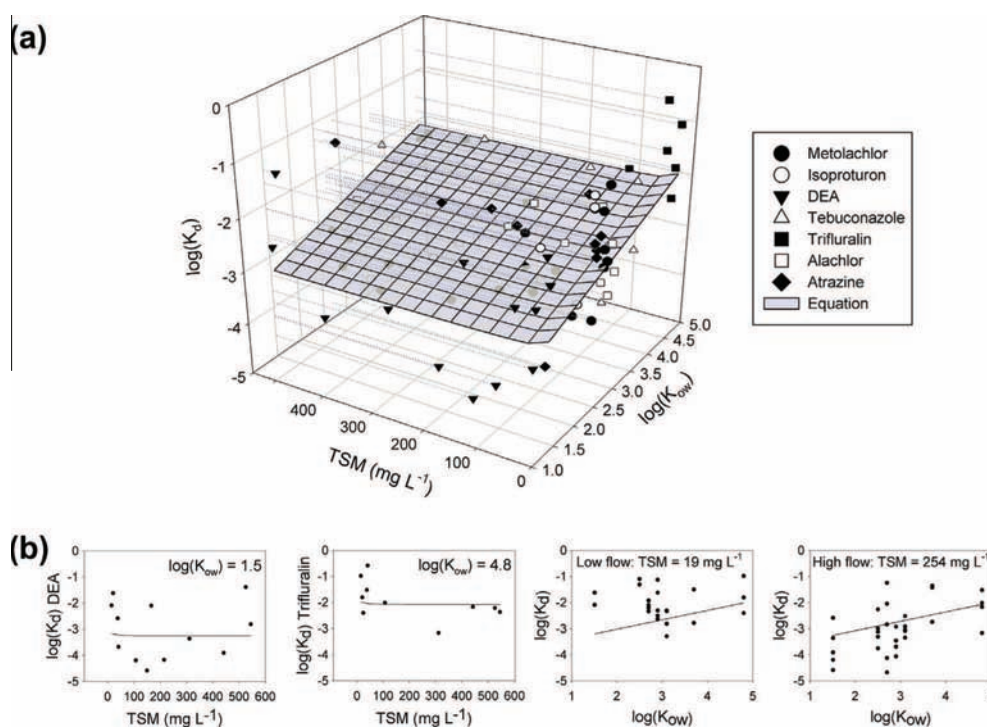
The values of K_d (Figs. 5 and 7) together with the results in Section 3.1.2 suggest that pesticides are mostly sorbed to allochthonous matter during stormflow events whereas they are mostly sorbed to autochthonous matter during low flow. K_d value decreases when concentration in allochthonous material 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; Lefrancq 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 $f_{OC\text{-}TSM}$ (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 $\log(K_d)$ become less than 1% for a TSM concentration

Fig. 7. Relationship between K_d (m³ g⁻¹), K_{ow} ((mg m$_{octanol}^{-3}$)/(mg m$_{water}^{-3}$)) and Total Suspended Matter (TSM in mg L⁻¹) concentration: (a) equation and scatterplot of the K_d calculated from the concentration measurements of 7 pesticide molecules at the outlet of the river Save catchment (July 2009–October 2010) and (b) 2-dimension projections of extreme values for fixed K_{ow} and TSM concentrations.

over 13 mg L⁻¹ in the river Save, considering the 7 molecules' K_{ow} range. The K_d 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_{OC-TSM} and TSM appears suitable for future implementation in computer models: both the TSM$_{min}$ and the $f_{OC-TSMtopsoil}$ 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_{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_{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_{oc} by the use of K_{ow} since K_{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_{oc} and K_d may broadly differ depending on the sorbed substance and on the sorbent. Using K_{ow} frees us from the uncertainty of the sorbent. For a modelling purpose, the parameters of the equation linking K_{oc} to K_{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_{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_{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.

References

Arnold, J.G., Srinivasan, R., Muttiah, R.S., Williams, J.R., 1998. Large area hydrologic modeling and assessment. I. Model development. J. Am. Water Resour. Assoc. 34 (1), 73–89.

Atasoy, A.D., Mermut, A.R., Kumbur, H., İnce, F., Arslan, H., Avcı, E.D., 2009. Sorption of alpha and beta hydrophobic endosulfan in a Vertisol from southeast region of Turkey. Chemosphere 74, 1450–1456.

Bass, A.M., Bird, M.I., Liddell, M.J., Nelson, P.N., 2011. Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment. Limnol. Oceanogr. 56, 2282–2292.

Beketov, M.A., Kefford, B.J., Schafer, R.B., Liess, M., 2013. Pesticides reduce regional biodiversity of stream invertebrates. PNAS 110, 11039–11043.

Boithias, L., Sauvage, S., Taghavi, L., Merlina, G., Probst, J.L., Sánchez Pérez, J.M., 2011. Occurrence of metolachlor and trifluralin losses in the Save river agricultural catchment during floods. J. Hazard. Mater. 196, 210–219.

Boithias, L., Srinivasan, R., Sauvage, S., Macary, F., Sánchez Pérez, J.M., 2013. Daily nitrate losses: implication on long term river quality in an intensive agricultural catchment (south-western France). J. Environ. Qual. http://dx.doi.org/10.2134/jeq2011.0367 (in press).

Cerro, I., Sánchez Pérez, J.M., Ruiz-Romera, E., Antigüedad, I., 2013. Variability of particulate (SS, POC) and dissolved (DOC, NO3) matter during storm events in the Alegria agricultural watershed. Hydrol. Process. http://dx.doi.org/10.1002/hyp.9850 (in press).

Chapra, S.C., 1997. Surface Water-Quality Modeling. McGrawHill, Boston, USA.

Chiou, C.T., Peters, L.J., Freed, V.H., 1979. A physical concept of soil–water equilibria for nonionic organic compounds. Science 206 (4420), 831–832.

Coquet, Y., Barriuso, E., 2002. Spatial variability of pesticide adsorption within the topsoil of a small agricultural catchment. Agronomie 22, 389–398.

Coynel, A., Etcheber, H., Abril, G., Maneux, E., Dumas, J., Hurtrez, J.E., 2005. Contribution of small mountainous rivers to particulate organic carbon input in the Bay of Biscay. Biogeochemistry 74 (2), 151–171.

Dur, J.C., Gouy, V., Calvet, R., Belamie, R., Chaplain, V., 1998. Influence of adsorption–desorption phenomena on pesticide runoff measured under controlled conditions. Comptes Rendus de l'Académie des Sciences: Earth Planet Sci. 327, 405–411.

EC, 1998. Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Off. J. Eur. Communities L330, Off. J. Eur. Communities L330.

El Bakouri, H., Morillo, J., Usero, J., Ouassini, A., 2009. Natural attenuation of pesticide water contamination by using ecological adsorbents: application for chlorinated pesticides included in European Water Framework Directive. J. Hydrol. 364 (1–2), 175–181.

Fenoll, J., Ruiz, E., Flores, P., Hellín, P., Navarro, S., 2011. Reduction of the movement and persistence of pesticides in soil through common agronomic practices. Chemosphere 85, 1375–1382.

Gao, J.P., Maguhn, J., Spitzauer, P., Kettrup, A., 1997. Distribution of pesticides in the sediment of the small Teufelsweiher pond (Southern Germany). Water Res. 31 (11), 2811–2819.

Goss, K.-U., Schwarzenbach, R.P., 2001. Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. Environ. Sci. Technol. 35, 1–9.

Goss, K.-U., Schwarzenbach, R.P., 2003. Rules of thumb for assessing equilibrium partitioning of organic compounds: successes and pitfalls. J. Chem. Educ. 80, 450–455.

Hayes, M.H., 1970. Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic matter chemistry. Residue Rev. 32, 131–174.

Imfeld, G., Braeckevelt, M., Kuschk, P., Richnow, H.H., 2009. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere 74, 349–362.

Ittekkot, V., 1988. Global trends in the nature of organic matter in river suspension. Nature 332, 436–438.

Karickhoff, S.W., Brown, D.S., Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13 (3), 241–248.

Lefrancq, M., Imfeld, G., Payraudeau, S., Millet, M., 2013. Kresoxim methyl deposition, drift and runoff in a vineyard catchment. Sci. Total Environ. 442, 503–508.

Lewan, E., Kreuger, J., Jarvis, N., 2009. Implications of precipitation patterns and antecedent soil water content for leaching of pesticides from arable land. Agric. Water Manage. 96, 1633–1640.

Locke, M.A., Weaver, M.A., Zablotowicz, R.M., Steinriede, R.W., Bryson, C.T., Cullum, R.F., 2011. Constructed wetlands as a component of the agricultural landscape: mitigation of herbicides in simulated runoff from upland drainage areas. Chemosphere 83 (11), 1532–1538.

Ludwig, W., Probst, J.L., Kempe, S., 1996. Predicting the oceanic input of organic carbon by continental erosion. Global Biogeochem. Cycles 10 (1), 23–41.

Macary, F., Leccia, O., Almeida Dias, J., Morin, S., Sánchez Pérez, J.M., 2013. Agro-environmental risk evaluation by a spatialised multi-criteria modelling combined with the PIXAL method. Int. J. Geomatics Spatial Anal. 23, 39–70.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S., Imfeld, G., 2011. Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment. Sci. Total Environ. 409, 2317–2324.

Martins, O., Probst, J.L., 1991. Biogeochemistry of major African rivers: carbon and mineral transport. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), SCOPE 42 – Biogeochemistry of Major World Rivers. John Wiley, Chichester, pp. 127–155.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Williams, J.R., 2009. Soil and Water Assessment Tool theoretical documentation – version 2009 (TR406).

Niederer, C., Schwarzenbach, R.P., Goss, K.U., 2007. Elucidating differences in the sorption properties of 10 humic and fulvic acids for polar and nonpolar organic chemicals. Environ. Sci. Technol. 41 (19), 6711–6717.

Novak, J.M., Moorman, T.B., Cambardella, C.A., 1997. Atrazine sorption at the field scale in relation to soils and landscape position. J. Environ. Qual. 26 (5), 1271–1277.

Oeurng, C., Sauvage, S., Sánchez Pérez, J.M., 2010. Dynamics of suspended sediment transport and yield in a large agricultural catchment, southwest France. Earth Surf. Process. Landforms 35 (11), 1289–1301.

Oeurng, C., Sauvage, S., Coynel, A., Maneux, E., Etcheber, H., Sánchez Pérez, J.M., 2011. Fluvial transport of suspended sediment and organic carbon during flood events in a large agricultural catchment in southwest France. Hydrol. Process. 25 (15), 2365–2378.

Polard, T., Jean, S., Gauthier, L., Laplanche, C., Merlina, G., Sánchez Pérez, J.M., Pinelli, E., 2011. Mutagenic impact on fish of runoff events in agricultural areas in south-west France. Aquat. Toxicol. 101 (1), 126–134.

Probst, J.L., 1992. Geochemistry and hydrology of continental erosion mechanisms present-day global budget and fluctuations during the last 500 million years. Sci. Geol. Mem. Strasbourg 94. 161p..

Proia, L., Osorio, V., Soley, S., Köck-Schulmeyer, M., Pérez, S., Barceló, D., Romaní, A.M., Sabater, S., 2013. Effects of pesticides and pharmaceuticals on biofilms in a highly impacted river. Environ. Pollut. 178, 220–228.

Rodriguez-Liébana, J.A., Mingorance, M.D., Peña, A., 2011. Sorption of hydrophobic pesticides on a Mediterranean soil affected by wastewater, dissolved organic matter and salts. J. Environ. Manage. 92, 650–654.

Taghavi, L., 2010. Dynamique de transfert des pesticides en périodes de crue sur les bassins versants agricoles gascons. PhD diss. Institut National Polytechnique de Toulouse. 302p (PhD thesis).

Taghavi, L., Probst, J.L., Merlina, G., Marchand, A.L., Durbe, G., Probst, A., 2010. Flood event impact on pesticide transfer in a small agricultural catchment (Montousse at Aurade, south west France). Int. J. Environ. Anal. Chem. 90 (3), 390–405.

Taghavi, L., Merlina, G., Probst, J.-L., 2011. The role of storm flows in concentration of pesticides associated with particulate and dissolved fractions as a threat to aquatic ecosystems. Case study: the agricultural watershed of Save river (Southwest of France). Knowl. Manage. Aquat. Ecosyst. 400 (06), 11.

Thevenot, M., Dousset, S., Hertkorn, N., Schmitt-Kopplin, P., Andreux, F., 2009. Interactions of diuron with dissolved organic matter from organic amendments. Sci. Total Environ. 407 (14), 4297–4302.

Tomlin, C.D.S., 2009. The Pesticide Manual. fifteenth ed. A World Compendium. C.D.S. Tomlin Ed. BCPC Publications Alton, Hampshire, UK, 1457 p.

Toul, J., Bezdek, J., Kovarova, M., Bohacek, Z., Hanák, J., Milicka, J., Müller, P., 2003. Sorption of hydrophobic organic pollutants on soils and sediments. Bull. Geosci. 78 (3), 205–223.

Ulrich, U., Dietrich, A., Fohrer, N., 2013. Herbicide transport via surface runoff during intermittent artificial rainfall: a laboratory plot scale study. Catena 101, 38–49.

US EPA, 1996. Soil organic carbon (K_{oc})/octanol–water (K_{ow}) partition coefficients. In: Soil screening guidance: technical background document. EPA/540/R 95/128 Appendix K.

Veyssy, E., Etcheber, H., Lin, R.G., Buat-Menard, P., Maneux, E., 1999. Seasonal variation and origin of particulate organic carbon in the lower Garonne River at La Reole (southwestern France). Hydrobiologia 391, 113–126.

Wagner, L., Vidon, P., Tedesco, L.P., Gray, M., 2008. Stream nitrate and DOC dynamics during three spring storms across land uses in glaciated landscapes of the Midwest. J. Hydrol. 362 (3–4), 177–190.

Weber, J.B., Wilkerson, G.G., Reinhardt, C.F., 2004. Calculating pesticide sorption coefficients (K_d) using selected soil properties. Chemosphere 55, 157–166.

Wu, Q., Riise, G., Lundekvam, H., Mulder, J., Haugen, L., 2004. Influences of suspended particles on the runoff of pesticides from an agricultural field at Askim, SE-Norway. Environ. Geochem. Health 26 (2), 295–302.

Xu, F., Liang, X.M., Su, F., Zhang, Q., Lin, B.C., Wu, W.Z., Yediler, A., Kettrup, A., 1999. A column method for determination of soil organic partition coefficients of eight pesticides. Chemosphere 39 (5), 787–794.

Yi, A.X., Leung, K.M.Y., Lam, M.H.W., Lee, J.S., Giesy, J.P., 2012. Review of measured concentrations of triphenyltin compounds in marine ecosystems and meta-analysis of their risks to humans and the environment. Chemosphere 89, 1015–1025.

Zeiger, M., Fohrer, N., 2009. Impact of organic farming systems on runoff formation processes – a long-term sequential rainfall experiment. Soil Tillage Res. 102 (1), 45–54.