



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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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.

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ABSTRACT

Pesticides applied on crops are leached with rainfall to groundwater and surface water. They threaten 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.

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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

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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-Liévana 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-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. Mailard 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_{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 km² (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 m³ 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 m³ 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 km² 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 $\mu\text{g L}^{-1}$ 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

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