Addition to comment 2 from Reviewer 2 and missing reference in italics

2. Some of the assumptions for pesticide transport are quite special: non-volatility and non-sorptivity are quite unusual for pesticides. While it is a valid assumption to state that this as a hypothetical case, deviations resulting from sorption and volatility should be discussed in more detail, especially as to whether the conclusion that CSIA is working remains valid.

<u>Reply:</u>

In order to assess the relevance of sorption and volatility, we compiled literature values of commonly used organic pesticides (in the US and Germany) for the Henry's law constant and partitioning coefficient between soil organic carbon and water (K_{OC}) (Table 1). The Henry's law constant indicates the volatility of the compound. Following the classification of the PesticidePropertiesDataBase (PPDB; University of Hertfordshire, 2013) based on this constant, dichloropropene, methyl bromide, and pendimethalin are considered highly volatile, whereas volatilization is irrelevant for most of the remaining pesticides (see Table 1). The $\mathrm{K_{OC}}$-value indicates the tendency of a pesticide to be attached to the soil matrix or suspended sediment. According to the PPDB, chlorothalonil, glyphosate, and pendimethalin have $\mathrm{K_{OC}}$-values that suggest a high tendency for sorption, whereas the other compounds are moderately or non-sorptive. In summary, it seems that the assumption of negligible sorptivity and volatility is applicable for a variety of widely used pesticides.

Table 1: Physicochemical properties of commonly used pesticides. Source: PesticidePropertiesDataBase (University of Hertfordshire, 2013), unless otherwise specified

pesticide	rank (US sales in 2007)[a]	sales in Germany in 2010[b] [t]	Henry's law constant[c]	volatility according to Henry's law constant	log K_{OC} [mL g^{-1}]	sorption affinity according to log K_{OC}
2,4-dichlorophenoxyacetic acid	7	25 – 100	1.40×10^{-9}	none	1.95	moderate
acetochlor	5	-	8.64×10^{-9}	none	2.19	moderate
atrazine	2	-	1.20×10^{-7}	none	2.0	moderate
bentazone	-	25 – 100	2.00×10^{-13}	none	1.74	low
chlormequat	-	> 1000	6.50×10^{-13}	none	2.31[d]	moderate
chlorothalonil	12	250 – 1000	1.36×10^{-5}	moderate	2.93	high
dichloropropene	6	-	1.50×10^{-1}	high	1.67	low
ethephon	11	100 – 250	6.11×10^{-13}	none	0[e]	none
glyphosate	1	> 1000	6.60×10^{-19}	none	3.16	high
isoproturon	-	> 1000	3.80×10^{-9}	none	2.68[f]	moderate
MCPA	23	250 – 1000	1.10×10^{-8}	none	1.0[e]	none
metam sodium	3	-	5.27×10^{-9}	none	1.25	low
methyl bromide	8	-	5.50×10^{2}	high	1.59	low
s-metolachlor	4	250 – 1000	4.13×10^{-7}	moderate	2.08	moderate
pendimethalin	10	250 – 1000	1.50×10^{-3}	high	4.25	very high

a Grube et al. (2011)
b Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2011)
c at 20°C
d Tomlin (2003)
e U.S. Department of Agriculture-Agricultural Research Service (2006)
f Beernaerts et al. (2003)

As some pesticides in Table 1 have a moderate to high sorption tendency, we tried to assess the relevance of sorption for these compounds by calculating their concentrations in the particulate (i.e. associated to suspended matter) and aqueous phase during rainfall events. We did not include this analysis in the manuscript to reduce the length of the manuscript, but can add it if desired by the editor. Briefly, pesticide concentrations in the particulate and aqueous phase depend on the suspended matter concentration in surface runoff (C_{TSM}), the organic carbon content in the suspended matter (f_{OC}), and the partitioning coefficient between soil organic carbon and water (K_{OC}). C_{TSM} was set to 1 g L^{-1} and f_{OC} was set to 2 %, which agrees with values reported in studies of particle-bound pesticide transport during rain events (Hladik et al., 2009; Taghavi et al., 2010; Wu et al., 2004). The calculations revealed that, under the assumption of equilibrium sorption, the dissolved phase represents the main transport route for most pesticides (Fig. 1), whereas transport with suspended matter accounts for more than 10 % of the total transport only for the highly sorbing pendimethalin (log K_{OC} > 4). We therefore decided to disregard this transport route in our simulations. Besides, it was not possible to directly model pesticide sorption to suspended matter in surface runoff, as the current HGS code does not allow for the simulation of suspended matter or dissolved organic carbon in the aqueous phase.

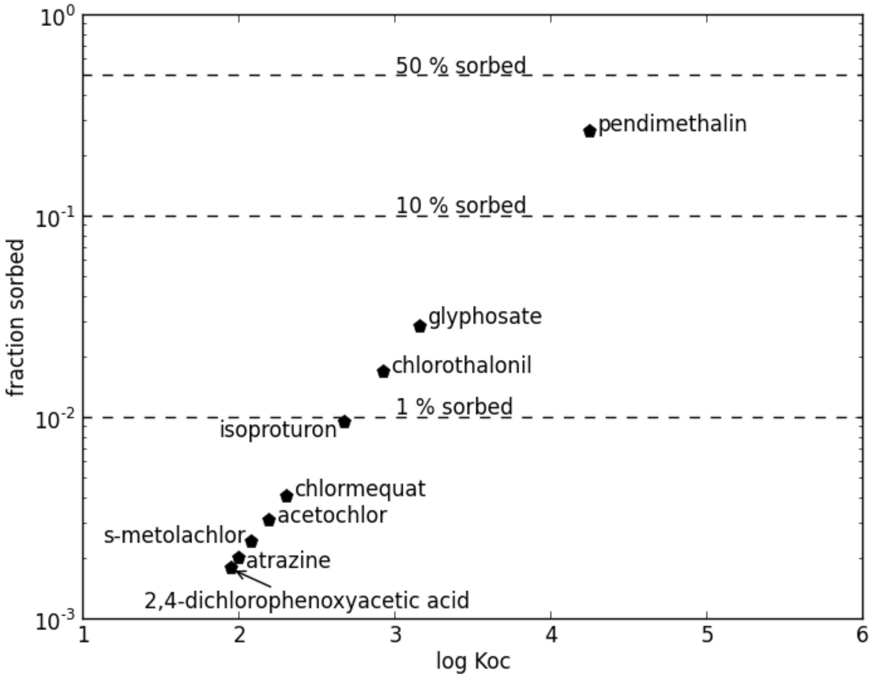

Figure 1: Comparison of concentrations in the dissolved and sorbed phase during surface runoff for pesticides with different sorption affinities.

In contrast to the simulation of sorption to solid matter in the aqueous phase, the HGS code allows for the simulation of equilibrium sorption of solutes to the soil matrix. Simulation of sorption to the soil matrix would have had a retardation effect on pesticide transport to the hillslope outlet. If sorption had been included, it would have been possible to also simulate sorption-induced isotope fractionation in the soil matrix. This can result in an enrichment in heavy isotopes at the front and a depletion at the tail of a migrating groundwater plume (Kopinke et al. 2005). If isotopic enrichment is only attributed to degradation, CSIA can thus yield an overestimation of degradation for the plume front. However, we did not explicitly simulate sorption-related isotope fractionation, as this is only relevant in non-stationary plumes when degradation is slow (van Breukelen and Prommer 2008) (see P8801-L10), and would thus be insignificant in the modelled hillslope system.

It was briefly stated in the manuscript that we expect a minor impact of volatilization on the isotope ratios of the modelled pesticide (P8801-L6 to L13). Volatilization was not considered, as it would mainly lead to a decrease in the pesticide mass load at the pollution source. Moreover, rainfall occurred soon after pesticide application in the simulations, so we assumed a rapid mobilization of the recently applied compound and thus minor losses due to volatilization for the modelled system. This implies negligible isotope fractionation effects due to volatilization under comparable hydrological conditions.

Wang and Huang (2003) examined volatilization-induced isotope fractionation during vaporization of petroleum hydrocarbons; they measured no detectable carbon isotope fractionation, and considerable hydrogen isotope fractionation only for a large extent of volatilization (between 8 and 45 ‰ for vaporization of more than 90 % of the initial amount, depending on the compound). Considering the low volatility of the majority of the compounds in Table 1, we do not expect such a large extent of vaporization after application. However, depending on the properties of the pesticide, soil parameters, and meteorological conditions, volatilization losses of up to 50 % of the applied amount have been reported (van den Berg et al., 1999). If isotope fractionation at the pollution source due to volatilization is not considered in this case, CSIA might yield an inaccurate assessment of the extent of degradation.

In summary, we assumed that sorption and volatilization are only relevant for particular compounds with a high tendency for sorption or volatilization. Moreover, if sorption-induced isotope fractionation had been included, it would have overlapped with degradation-induced isotope fractionation and thus complicated the interpretation of the simulation results. Consequently, we believed that the incorporation of sorption and volatilization would add unneeded complexity and uncertainty to the modelling and the interpretation of the simulation results. We will more explicitly state in the revised manuscript that we did not include sorption and volatilization, and that our results are thus applicable only for situations where sorption and volatilization are small. The expected effects of volatilization and sorption, and the role of preferential flow (comment 8 from reviewer 1) will be added to a new discussion section in the revised manuscript ("4.2 Validity of model assumptions").

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