

We thank reviewer 2 for the useful comments. We address each of these comments below:

1. There are some concerns about the consistency of parameters for flow and transport that were compiled from several studies in different environments. While this is permitted for a virtual experiment, it would be helpful to have a bit more detailed background information about the actual environments and conditions these parameters relate to.

Reply:

The study was, indeed, designed as a virtual experiment; we did not intend to simulate a specific hillslope site. However, we aimed to create a realistic hillslope by compiling a realistic parameter set for a gently sloping surface, including a declining hydraulic conductivity with increasing depth.

The hydraulic parameters for the soil were obtained from an experimental site at Canadian Forces Base Borden (north of Toronto, Ontario, Canada) because HGS has been validated against experiments at this site (Therrien et al., 2010). These simulations therefore provided verified Van Genuchten parameters for HGS simulations. We wanted to model a layered subsurface system with variable hydraulic properties, because many sites are characterized by relatively shallow soils on fractured bedrock. Previous HGS simulations of the Borden site used uniform soil parameters and only considered the upper 4 m of the profile, but we preferred to explicitly represent the bedrock. The bedrock parameters were therefore taken from simulations of the forested Coos Bay site in Oregon, USA (Mirus et al., 2011). They represent weathered bedrock and fractured sandstone. The soil parameters from this site were not used in our simulations, as this is a steep forested site, and we wanted to simulate an agricultural hillslope.

The chemical parameters governing pesticide transport, degradation and isotope fractionation were set according to values of commonly applied pesticides, which is specified in Sect. 2.4 and 2.5. Further background information about the choice of parameters will be given in the revised manuscript.

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.

Reply:

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 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 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 x 10 ⁻⁹	none	1.95	moderate
acetochlor	5	-	8.64 x 10 ⁻⁹	none	2.19	moderate
atrazine	2	-	1.20 x 10 ⁻⁷	none	2.0	moderate
bentazone	-	25 – 100	2.00 x 10 ⁻¹³	none	1.74	low
chlormequat	-	> 1000	6.50 x 10 ⁻¹³	none	2.31 ^d	moderate
chlorothalonil	12	250 – 1000	1.36 x 10 ⁻⁵	moderate	2.93	high
dichloropropene	6	-	1.50 x 10 ⁻¹	high	1.67	low
ethephon	11	100 – 250	6.11 x 10 ⁻¹³	none	0 ^e	none
glyphosate	1	> 1000	6.60 x 10 ⁻¹⁹	none	3.16	high
isoproturon	-	> 1000	3.80 x 10 ⁻⁹	none	2.68 ^f	moderate
MCPA	23	250 – 1000	1.10 x 10 ⁻⁸	none	1.0 ^e	none
metam sodium	3	-	5.27 x 10 ⁻⁹	none	1.25	low
methyl bromide	8	-	5.50 x 10 ²	high	1.59	low
s-metolachlor	4	250 – 1000	4.13 x 10 ⁻⁷	moderate	2.08	moderate
pendimethalin	10	250 – 1000	1.50 x 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.

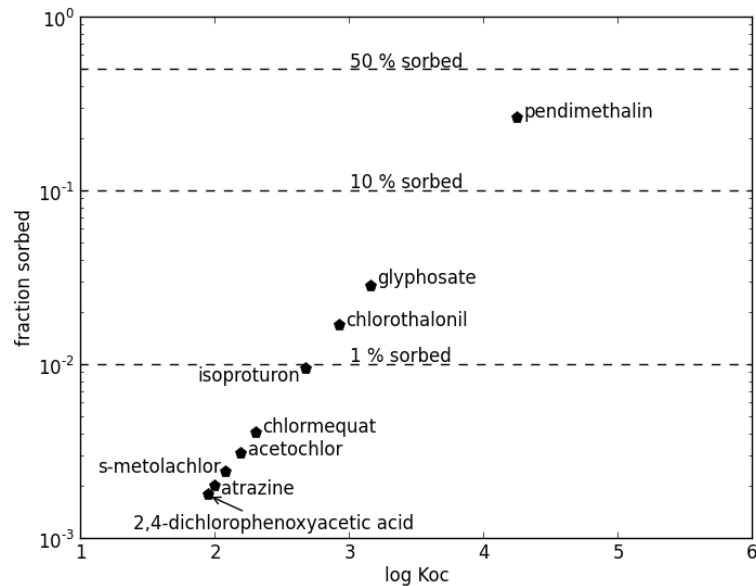


Figure 1: Comparison of concentrations in the dissolved and sorbed phase during surface runoff for pesticides with different sorption affinities.

It was briefly stated in the manuscript that we expect a minor impact of volatilization and sorption 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”).

3. This modelling study focuses on draining hillslope-river cross-sections. In real systems effluent and influent conditions alter. It is therefore recommended to also limit the conclusions drawn from this study to headwater, upstream or sections that fully correspond to model assumptions.

Reply:

This study is, indeed, mainly applicable to gaining streams and headwater catchments. We will clarify this in Section 4.3 of the revised manuscript (“Implications for the applicability of CSIA to assess pesticide transport and transformation”) and explicitly state this limitation in the conclusions as well.

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