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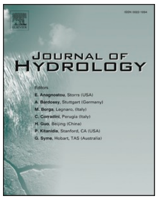

Research papers

Pesticide transport under runoff-erosion potentially dominated by small sediments: A glyphosate and AMPA experiment

Xiaomei Yang [a,b], Vera Silva [b], Darrell W.S. Tang [c,*]

[a] State Key Laboratory of Soil and Water Conservation and Desertification Control, College of Soil and Water Conservation Science and Engineering, Northwest A&F University, Yangling 712100, China
[b] Soil Physics and Land Management, Wageningen University & Research, 6700AA Wageningen, the Netherlands
[c] Water, Energy, and Environmental Engineering. University of Oulu, Finland

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ABSTRACT

Glyphosate and its degradation product AMPA, are ecotoxic, recurrent and persistent in agricultural soils, susceptible to overland transport by runoff, and sediment erosion due to their strong sorption affinities. We hypothesize that eroded sediments of different sizes have differing sorbed concentrations and relative contributions to glyphosate and AMPA transport, due to different specific surface areas and adsorption site abundances. Hence, we conducted a flume experiment of glyphosate-polluted sediment erosion in a rainfall simulator. After 1 h of rainfall (90 mm water), 10 % of applied glyphosate degraded to AMPA. The top 2 cm of soil retained 68 % of the total glyphosate-equivalent (including AMPA) mass, while runoff and eroded sediment accounted for 8 % and 10 % respectively. Amongst pesticides transported overland, runoff (61 %) and eroded sediment (39 %) were similarly important for glyphosate, but eroded sediment (95 %) transported remarkably more AMPA than runoff (5 %), although glyphosate sorption affinities are typically larger. Small sediments ($<$0.25 mm) constituted 75 % of eroded sediment counts, but carried 60 % of sediment-phase glyphosate and 85 % of sediment-phase AMPA mass. In $<$ 0.25 mm sediments, unlike glyphosate, AMPA breakthrough concentrations were substantially greater than in larger sediments. As water and pollutant mass exchanges between various environmental compartments (soil moisture, soil grains, runoff, eroded sediment, biodegradation) are highly dynamic, equilibrium sorption affinities alone may not fully characterize the predominant modes of pollutant transport, which may vary across spatio-temporal scales. Therefore, pollutants that are preferentially transported by eroded sediments, particularly small sediments, should be identified and prioritized in future research, due to potentially amplified environmental impacts.

1. Introduction

Intensive agriculture and the accompanying usage of pesticides such as glyphosate has led to widespread contamination of agricultural soils, even in fields that have no prior or recent history of pesticide application (Knuth et al., 2024). The pesticide/herbicide glyphosate, and its main degradation metabolite aminomethylphosphonic acid (AMPA), have become globally widespread in the environment. Glyphosate and AMPA are amongst the most frequently detected pesticide residues in soils, sediments, surface water, air, and indoor dust (Silva et al., 2023). Glyphosate is moderately toxic to birds, most aquatic organisms, and other diverse species of organisms including earthworms and honeybees. Glyphosate can be biodegraded by microbes and used as a phosphorus source (Panettieri et al., 2013; Sviridov et al., 2015), which perturbs the soil microbial community related to phosphorus cycling and thus the phosphorus cycle itself (Wang & Tang, 2024). The ecotoxicity of AMPA is less well-understood, but is thought to be similar or lower than the parent compound (Lewis et al., 2016). All of this has triggered significant concern regarding the environmental and ecotoxicity risks of glyphosate applications (la Cecilia et al., 2018; Zaller et al., 2014), particularly due to the wider than expected environmental spread of glyphosate and AMPA. Widespread occurrence of these pesticides, often accompanied by high levels in various environmental sinks, implies that their transport through the environment is in greater quantities than prior scientific understanding would suggest. Furthermore, the widespread detection of glyphosate and AMPA in topsoils,

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* Corresponding author.
E-mail address: darrell.tang@oulu.fi (D.W.S. Tang).

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sediments, and surface water points indicates that those compounds are prone to overland transport with surface runoff or as sorbates on eroded sediments. It has been recognized that sediment-phase overland transport of pesticides has been underappreciated in previous research, and may become increasingly more crucial in future environmental management. In recent years, strongly sorptive pesticides that are less mobile in soils have been gradually replacing non-sorptive pesticides, driven by regulatory efforts to reduce groundwater pollution (Commelin et al., 2022).

Glyphosate strongly adsorbs to aggregates of a wide variety of soils (Okada et al., 2016; van Bruggen et al., 2018), temporarily altering their environmental ecotoxicities and mobilities (Yang et al., 2015b). Glyphosate applied onto the soil surface may be infiltrated into the subsurface soil, dissolved into and washed away by surface runoff, retained as adsorbates on soil particles, or eroded along with surface soil particles (Yang et al., 2016). In the former two transport processes, the substance is transported in the aqueous phase, whereas the latter two involve sorbed phase transport. The overall transport behavior of water and aqueous phase pollutants are highly different to those of soil aggregate particles and sorbed phase pollutants. When in the sorbed phase, the biodegradation rates and ecotoxicities of glyphosate may be attenuated (Borggaard & Gimsing, 2008). Altogether, sorption affects not only the transport of glyphosate and AMPA, but also the rates at which glyphosate degrades into AMPA, and the ecotoxicities of both substances, which may have profound impacts on the overall environmental consequences of glyphosate application.

Accordingly, the capacity for soil particles to adsorb glyphosate and AMPA, as determined by the physical and chemical characteristics of soil aggregates, and the availability of adsorbent surfaces, may play important roles in the overall transport, ecotoxicity, and fate of glyphosate and AMPA in soils and the environment. For example, glyphosate and AMPA have adsorption affinities that are positively correlated to soil clay content and negatively correlated to pH and phosphorus content (Okada et al., 2016). As a result, glyphosate and AMPA may persist longer in denser soils with high clay fractions (Romano-Armada et al., 2019). Glyphosate has also been observed to persist much longer under cold and dry soil conditions than under warm and moist conditions, revealing the important role of soil microbial activity (which generally increases with increasing temperatures and humidity) in glyphosate biodegradation (Bento et al., 2016). Another crucial soil characteristic that potentially controls the fate and ecotoxicity of soil contaminants is soil aggregate sizes and the abundance of various aggregate sizes in the soil material. Currently, how the properties and sizes of soil aggregates influence glyphosate and AMPA transport and fate, as mediated by soil biogeochemical processes including adsorption, remains a major knowledge gap in pesticide research.

The various sizes of soil aggregates are associated with different physico-chemical characteristics, and may exhibit overall different reactive hydrological transport behavior of pollutants, due to changes in advection, dispersion, degradation, and adsorption processes. For example, studies have shown that the concentrations of most heavy metals such as Cd, Cu, Pb and Zn in soils increased as soil particle and aggregate size decreases (Gong et al., 2013; Fan et al., 2013; Yutong et al., 2016). Higher glyphosate and AMPA content were found in soil aggregates comprised of smaller particles (Mendez et al., 2017). Glyphosate contents in soils were observed to increase as aggregate size decreased (Haberkon et al., 2020). The distribution and degradation of glyphosate during wind erosion was studied in a wind tunnel experiment, and it was found that the adsorbed concentration of glyphosate and AMPA differed significantly across soil particle sizes, as it decreased with increasing particle size (Bento et al., 2017). Pesticide transport in the soil was found to depend substantially on the soil microstructure, which in turn depends on the soil particle size distribution (Woignier et al., 2018). An important soil biogeochemical property related to aggregate size is that smaller aggregates have larger specific surface areas and thus larger abundances of adsorption sites per unit bulk soil volume. The specific surface area may be a key mechanism that mediates the interactions between soil aggregate size and the fate and ecotoxicity of pesticides and other sorptive pollutants.

Insights from the existing literature thus strongly suggest that small particles may be disproportionately (relative to particle size distributions) important in the transport of sorbed phase pesticides by eroded sediments. However, existing research on sediment-phase pesticide transport has so far not addressed the effects of sorbent particle size on sediment-phase pesticide transport. Furthermore, pesticide mobility has been recognized as a key issue in the sustainability of agricultural systems, yet it remains insufficiently monitored and studied (Maggi et al., 2023). To address these knowledge gaps, we conducted a runoff-erosion experiment of pesticide transport under controlled hydrological conditions, where we apply glyphosate onto the surface of a soil within a flume under an indoor rainfall simulator. Our aims in this study are to investigate.

1) The overall glyphosate mass balance (glyphosate mass distribution across various soil layers, dissolved within runoff, adsorbed across various eroded sediment sizes, and biodegraded into AMPA), which quantifies the relative importance of the various transport and biogeochemical reaction processes in determining overall glyphosate fate.

2) The extent that the glyphosate and AMPA concentrations and fluxes in eroded sediments are sensitive to eroded sediment size.

3) Potential differences between glyphosate and AMPA transport by eroded sediments, which may arise due to differences in their biogeochemical properties such as sorption affinity and biodegradation susceptibility.

This study thus contributes towards the evaluation and risk assessment of the environmental consequences of glyphosate application and its environmental degradation into AMPA. Here, we focus on the relative importances of various aqueous phase and particulate phase hydrological transport processes, and how they potentially affect glyphosate and AMPA differently. Although we experiment on two specific compounds, glyphosate and AMPA, our research objectives also broadly pertain to the interactions between pesticide sorption, degradation, and transport by eroded sediment. Hence, the insights and conclusion derived from this study may also potentially apply to other sorptive soil pollutants that have environmental behaviors similar to glyphosate and AMPA.

2. Methods and materials

2.1. Experimental design

The experiment was conducted in the rainfall simulation hall of the Institute of Soil and Water Conservation, Northwest A&F University. The simulated rainfall is controllable by varying the water pressure and nozzle size, and the rainfall intensity was monitored with pluviographs. Soil was obtained from farmland in Yangling, Shaanxi Province, China, and is a loess loam soil, with 0.8 % organic matter, 0.65 g kg^{-1} total nitrogen, 0.72 g kg^{-1} phosphorus, and pH of 8.0. The soil was air-dried and sieved through a 10-mm mesh sieve. The wet sieving method (Sainju, 2006) with stacked sieves (2, 1, 0.5, and 0.25 mm) was used to quantify the initial fractions of soil water-stable aggregates. The initial (pre-rainfall) fractions of water-stable aggregates were: 0.65 % of $>$2 mm, 1.08 % of 1–2 mm, 8.87 % of 0.5–1 mm, 15.35 % of 0.25–0.5 mm, and 74.05 % of $<$ 0.25 mm particles. Soil was paved into hydraulic flumes (2 m length*0.5 m width*0.35 m depth) with movable platforms, adaptable slope elevators, and V-shape outlets. The soil was paved to a density of 1.25 g cm^{-3}, in six layers of 5 cm each (total thickness of 30 cm), and the soil surface was gently raked to minimise the occurrence of distinct layers and structural discontinuities. After the soil was paved, pre-wetting was conducted using 0.5 mm min^{-1} rainfall intensity, which was stopped once runoff was observed in the outlet of the flume. The flume was then covered with a plastic canvas overnight to allow for soil moisture diffusion and a spatially even distribution of soil moisture. The experimental rainfall simulations (1 h at 1.5 mm min^{-1}, corresponding to 90 L total volume) were performed the next day. Glyphosate was sprayed on the soil surface 30 min before the rain event, to represent a field scenario of a large precipitation event occurring soon after herbicide application. The experiment involved three replicates, with three flumes simultaneously under the rain simulator, each inclined to 15° from horizontal.

2.2. Pesticide application and sampling

Glyphosate was applied as Roundup® (360 g a.s. glyphosate L^{-1}; Monsanto, produced in Malaysia, Sinochem Agent), the most common formulation in the region (Yang et al., 2015b). The applied rate of glyphosate was 360 mg m^{-2}, and the surface area of the flume is 1 m^2, corresponding to 360 mg total glyphosate applied. As mentioned above, the simulated rainfall lasted one hour, and runoff samples were taken at 3-min intervals. The samples were weighed, and a sub-sample of the supernatant was collected per sample, in 10-mL plastic tubes, for further lab analyses. The sediments were sorted with the wet sieving method for 10 min at a frequency of 30 times min^{-1}. The sorted sediments (>2 mm, 2–1 mm, 1–0.5 mm, 0.5–0.25 mm, <0.25 mm) were dried in a shaded area and weighed within 48 h. After the experiment, soil samples were collected from each flume, at 0–2, 2–5, and 5–10 cm depths and at 60, 120, and 180 cm from the flume outlet. All the runoff, eroded sediments, and soil samples collected were stored at −20 °C until later retrieval for pesticide analyses.

2.3. Pesticide analyses

Glyphosate, the active substance of Roundup®, and its main metabolite aminomethylphosphonic acid (AMPA) were analysed with LC-MS/MS. The extraction procedure and the solutions used for the analysis are identical to those described in (Yang et al., 2015a; Yang et al., 2019), with the only difference being that an additional centrifuging step was done after derivatization to prevent derivatised particles from damaging the 0.45 μm PFTE filters. The quantification of glyphosate/AMPA with this method was modified (Yang et al., 2015a; Yang

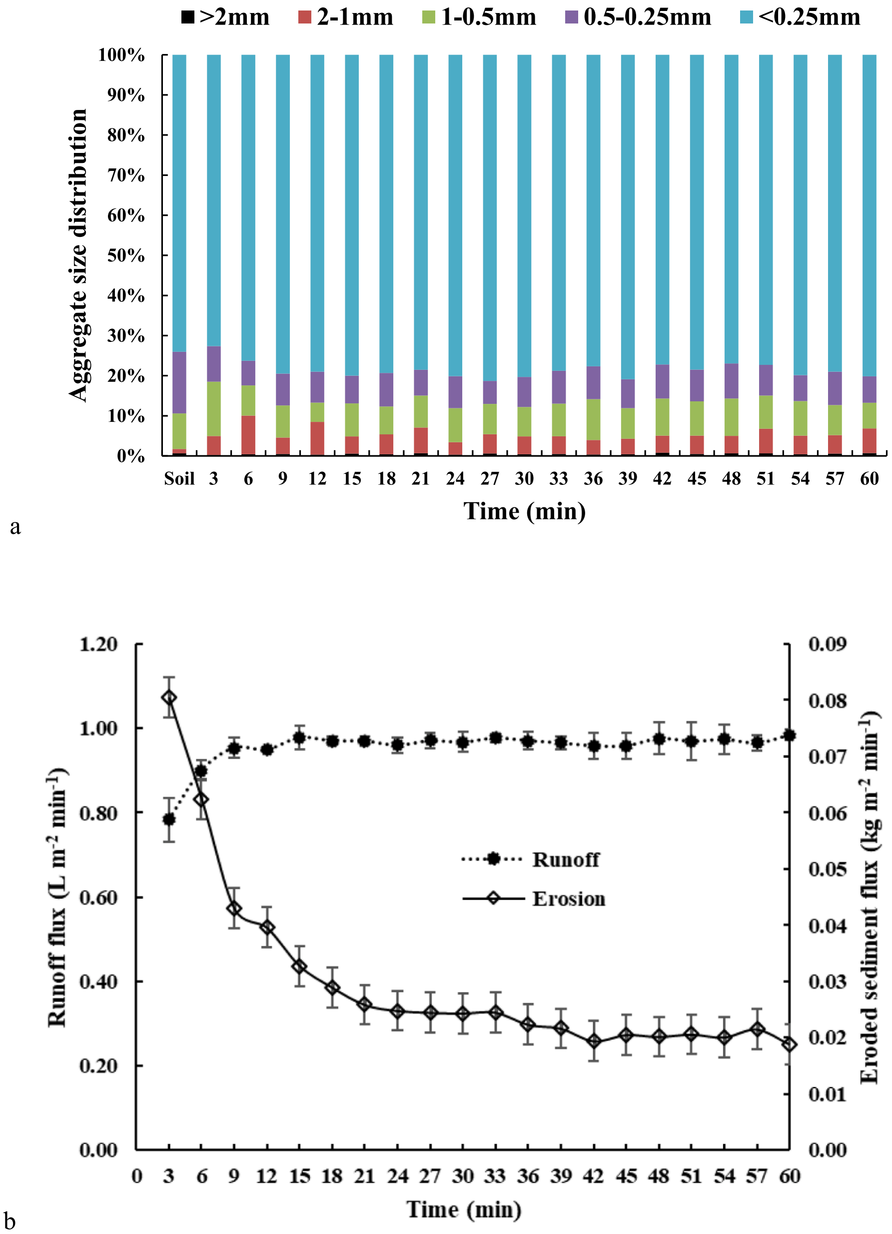

Fig. 1. (a) The aggregate size distribution of the original soil material, and that of the eroded sediment at every 3-minute interval during the rainfall event. (b) Runoff and eroded sediment fluxes at every 3-minute interval during the rainfall event.

et al., 2019), with a limit of quantification (LOQ) of 0.005 μg g^{-1} in water, and LOQ of 0.05 and 0.01 μg g^{-1} in sediment/soil for glyphosate and AMPA, respectively. Before the flume experiment, the experimental soil was tested for pre-existing glyphosate and AMPA, and found to be below the limit of quantification for both. Due to very low counts of >2 mm eroded sediments relative to all other size classes (Fig. 1a), eroded sediments with diameters >2 mm and with diameters of 1–2 mm were combined together into a new size class (>1 mm) for the purposes of the sediment-phase pesticide mass analyses.

2.4. Data analysis

The data is presented as means and standard deviations of the three replicates. Runoff rates and erosion rates were calculated from the measured runoff and sediment yield as described in (Yang et al., 2015a). The fractions of the eroded soil particles falling within the aforementioned size classes were then quantified. Power-law regression models $C = C_0 t^{-a}$ were used to characterize glyphosate and AMPA concentrations in the runoff and in the sediments of various sizes as a function of time during the rainfall event, where C is the concentration, C_0 is the initial concentration, t is time, and a is a power-law coefficient. Comparisons of the parameters of the power-law regressions for the various particle size classes were conducted using Fisher's Least Significant Difference tests (LSD; $p < 0.05$).

Total pesticide masses within the sediment/soil/runoff were calculated by multiplying the pesticide concentration by the total masses of the sediment/soil/runoff. The pesticide mass fluxes associated with the eroded sediment and runoff, and also the cumulative mass fluxes, were calculated by numerically integrating the pesticide concentrations in the sediment/runoff with the sediment/runoff discharge fluxes. In addition, in order to study the overall fate of the applied glyphosate, a glyphosate mass balance at the end of the experiment was calculated using the glyphosate masses in the soil (aqueous and sorbed), eroded sediment (sorbed), and runoff (aqueous). This mass balance calculation also takes into account the portion of glyphosate that was recovered in the chemical form of AMPA: the AMPA mass was converted to glyphosate-equivalent mass based on a parent/metabolite molecular weight coefficient of 1.52. In other words, the total glyphosate-equivalent mass is calculated as (glyphosate + 1.52*AMPA) mass. Kolmogorov–Smirnov tests were used to test data normality, followed by analysis of variance (ANOVA; $p < 0.05$) tests.

3. Results

3.1. Runoff, erosion, and eroded sediment size distribution

The smallest aggregates of <0.25 mm were relatively enriched in the eroded sediment, representing around 80 % of the eroded sediment in comparison to 74 % in the original soil material (Fig. 1a). Aggregates of 1–2 mm were also relatively enriched in the eroded material, representing around 4 %-10 % of the total count of eroded sediment in comparison to the 1 % in the original soil material. Aggregates of 1–2 mm contributed 10 times more to the eroded sediment output than > 2 mm aggregates, even though both had similar fractions in the original soil material. The fractions of 0.5–1.0 mm and 0.25–0.5 mm aggregates were similar, and both were relatively constant during the entire rainfall event, each representing around 8 % of total sediment output (Fig. 1a). The dynamics of the runoff and erosion rates during the rainfall event are presented in Fig. 1b. The results show that the runoff rate increased rapidly in the first 15 min, reaching 0.98 ± 0.03 L m^{-2} min^{-1}, whereas the erosion rate declined substantially in the first 15 min, from 0.080 ± 0.003 to 0.033 ± 0.008 kg m^{-2} min^{-1} (Fig. 1b). Both runoff and erosion rates varied substantially with time at the beginning of the rainfall, but as the rainfall event progressed the rates became nearly constant; this occurred after 15 min for runoff and after 30 min for erosion. Although the total erosion flux was dynamic and decreased during the first 30 mins of the rainfall event, the aggregate size distribution of the sediment flux became relatively constant already after 15 min of rainfall.

3.2. Glyphosate and AMPA concentrations and fluxes in runoff and eroded sediment

In runoff, the concentrations of glyphosate and AMPA changed dynamically during the rainfall event (Fig. 2 a-b). Glyphosate concentrations declined significantly within the first 30 min of rainfall, from 3.99 ± 0.64 to 0.23 ± 0.09 μg mL^{-1}, followed by a slower decrease. After 45 min of rain, glyphosate concentrations in the runoff decreased to 0.10 ± 0.02 μg mL^{-1}, and remained at similar levels until the end of the experiment. Similarly, AMPA concentrations in the runoff decreased considerably during the first 30 min and then remained around 0.005 μg mL^{-1} until the end of the experiment (Fig. 2b). The largest concentrations of glyphosate and AMPA in the runoff, and the largest concentration gradients, occurred at early experimental times, decreasing precipitously over time (Fig. 2).

The concentrations of glyphosate and AMPA in the eroded sediments were significantly different across particle sizes (Fig. 2 c-d). Glyphosate concentrations in the sediments decreased rapidly during the first 30 min of the rainfall, decreasing from 31.03 ± 4.28 to 11.87 ± 0.72 μg g^{-1} in > 1 mm sediments; from 44.86 ± 13.36 to 8.43 ± 2.51 μg g^{-1} in 1–0.5 mm sediments, and from 53.74 ± 13.29 to 10.80 ± 0.28 μg g^{-1} in 0.5–0.25 mm sediments. In the smallest sediments (<0.25 mm), glyphosate concentrations were significantly lower than in the other three sorted sediment sizes. For the < 0.25 mm sediments, glyphosate concentrations declined rapidly in the first 9 mins, from 22.95 ± 7.97 to 7.29 ± 2.64 μg g^{-1}, but later remained relatively constant with time at around 5 μg g^{-1} (Fig. 2c). No significant differences in the glyphosate concentrations across aggregate sizes were observed after 30 min of rainfall. AMPA concentrations showed a similar trend of decrease over time, but interacted differently with aggregate sizes (Fig. 2d). Specifically, AMPA concentrations in < 0.25 mm sediment were significantly higher than in the other three size classes, decreasing gradually from 14.96 ± 2.91 μg g^{-1} at the beginning of the rainfall to 3.37 ± 0.38 μg g^{-1} at the end of the rainfall event ($p < 0.05$). Although AMPA concentrations in the three larger sediment size classes also decreased with rainfall duration, most of the decrease occurred in the first 15 min, with a near-constant concentration after the first 15 min. No significant difference in AMPA concentrations was observed among these three sediment size classes (2–1 mm, 1–0.5 mm, 0.5–0.25 mm) over the entire rainfall event.

Results show that indeed the pesticide breakthrough curves in the runoff and in the sediments, both in terms of concentrations (Fig. 3a) and mass fluxes (Fig. 3b), conform to power-law functions, yielding linear relationships in log–log space. Parameters of the power-law function fitted to the concentrations of glyphosate and AMPA in the runoff and the various sediment size classes are given in Table 1. The results show significant differences in the glyphosate and AMPA residuals between the runoff and the different sizes of sorted sediment ($p < 0.01$). The glyphosate and AMPA regression curves in the runoff differed significantly in their initial concentrations and power coefficients compared to those in the sorted sediments. For both glyphosate and AMPA, the power coefficients for < 0.25 mm sediments were the smallest (0.48 to 0.5), those for the other sediment size were at intermediate values, and those for runoff were the largest (0.94 to 1.26). This implies that in relative terms, glyphosate and AMPA concentrations decreased with time most rapidly in the runoff, and most slowly in the smallest sediments. Accordingly, the ratio of concentrations in sediment/runoff increased substantially over the course of the rainfall event, for both glyphosate and AMPA (Fig. 3c). Although pesticide concentrations in the runoff decreased with time faster than concentrations in the sediment (Fig. 3a), the pesticide fluxes in the runoff decreased at similar rates as fluxes in the sediment (Fig. 3b), because the sediment mass flux decreased over time whereas the runoff remained nearly

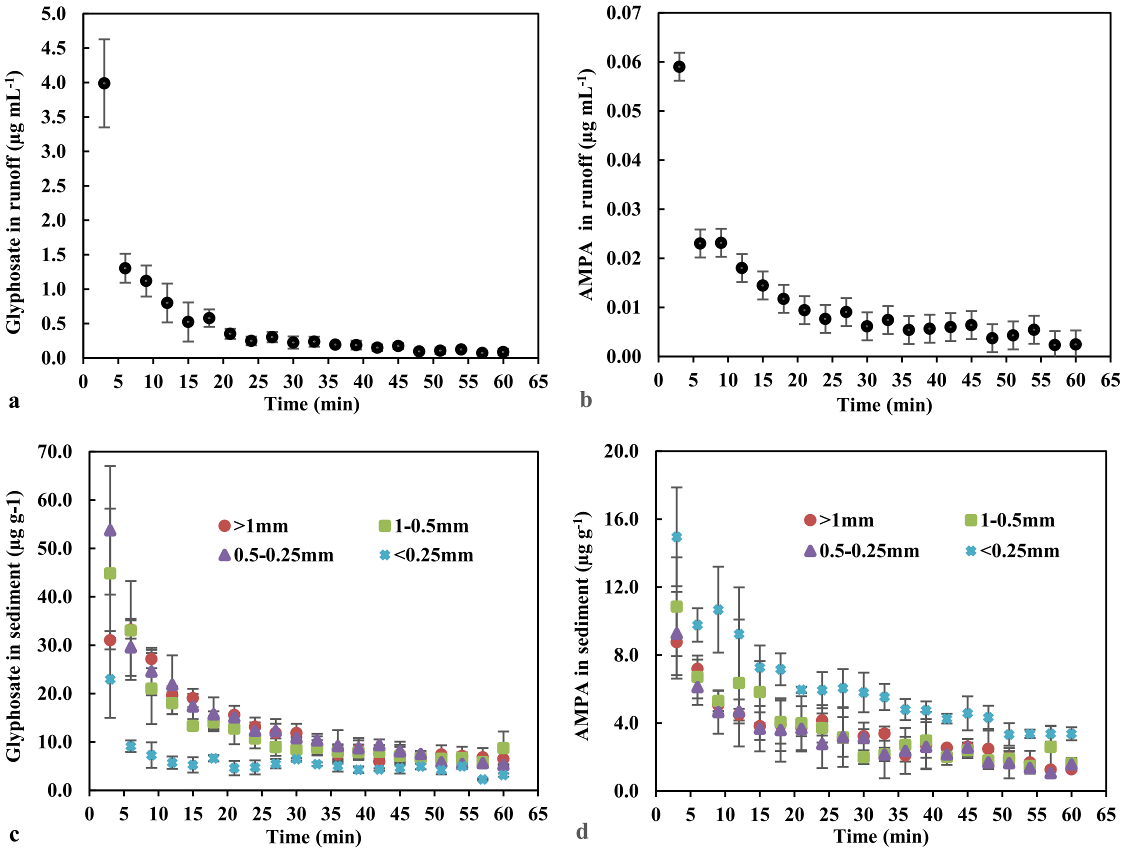

Fig. 2. Glyphosate (a) and AMPA (b) concentrations in the runoff. Glyphosate (c) and AMPA (d) concentrations in the eroded sediments of different sizes.

constant (Fig. 1). Glyphosate fluxes in the runoff and sediment were similar, whereas AMPA fluxes in sediment were an order of magnitude larger than that in the runoff (Fig. 3b). Altogether, 50 % more glyphosate was cumulatively transported in the runoff than in the sediment, whereas 20 times as much AMPA was transported in the sediment than in the runoff (Fig. 3d).

When the pesticide fluxes of the various sediment size classes are individually considered (Fig. 4a), it becomes evident that glyphosate fluxes are around half an order of magnitude greater than AMPA fluxes for all sediment sizes, except for < 0.25 mm sediments, for which glyphosate and AMPA fluxes are similar throughout the experiment (Fig. 4c). The same is observed for the cumulative fluxes (Fig. 4b), where < 0.25 mm sediments transported almost as much AMPA as did glyphosate, whereas other sediment sizes were associated with much larger glyphosate than AMPA fluxes (Fig. 4d). Glyphosate fluxes in the runoff were around 70 times AMPA concentrations at $t = 3$, but this ratio decreased to around 30 times by $t = 60$, suggesting that AMPA becomes relatively enriched in the runoff over time (Fig. 4c). Similarly, glyphosate fluxes through sediment flow were around 2 times AMPA concentrations at $t = 3$, but this ratio decreased to around 1 by $t = 60$, suggesting that AMPA becomes relatively enriched in the sediment flow over time (Fig. 4c). Similar ratios are observed in the cumulative fluxes (Fig. 4d). For both the fluxes (Fig. 4c) and cumulative fluxes (Fig. 4d), the ratio of glyphosate to AMPA was much larger in the runoff than in the intermediate-sized sediments, which were in turn much larger than in the smallest sediments of < 0.25 mm size.

3.3. Water and solute mass balances

Numerically integrating the runoff fluxes (Fig. 1b) over time yields a total runoff volume of 57.3 L, which is 63.7 % of the total rainfall volume of 90 L. Thus, assuming that all non-runoff water infiltrated the soil, then 32.7 mm of water infiltrated into the soil. Given a soil porosity between 0.3 and 0.4, the mean wetting front would be expected to reach a depth of 8 cm to 10 cm. This is in agreement with the experimentally observed wetting front depths, which ranged from 7 cm to 10 cm depth, which implies that other possible aspects of the water balance (e.g., evaporation) were negligible. However, glyphosate and AMPA concentrations in the flume soil were exponentially higher in the top 2 cm than in deeper layers, and decreased significantly with depth ($p < 0.05$), indicating substantial retardation of the infiltration of glyphosate and AMPA. Pesticide concentrations in the soil in the 0–2 cm, 2–5 cm and 5–10 cm deep layers were 8.50 ± 0.17, 0.10±<0.01, 0.06 ± 0.01 µg g^{-1} for glyphosate, and 0.71 ± 0.05, 0.04 ± 0.01, and 0.01 ± 0.002 µg g^{-1} for AMPA, respectively.

The total mass balance of the applied glyphosate was calculated for the runoff, sorted sediment and soil flume (Fig. 5a). AMPA was considered in the glyphosate mass balance by using the parent-metabolite molecular weight ratio, such that every 1 g AMPA is equivalent to 1.52 g glyphosate. In terms of total glyphosate-equivalent mass (glyphosate + 1.52*AMPA), 8.3 % and 10.4 % was exported in the runoff and sediment, respectively. Around 7 % of the mass balance was associated with transport in the sorbed phase of the smallest sediments of < 0.25 mm size, whereas the other sediment size classes contributed around 1 % each. Meanwhile, the soil compartment of the mass balance was dominated by shallow layers, with contribution rates of 68.1 %, 1.9 % and 1.5 % in top 2 cm, 2–5 cm and 5–10 cm depths of the soil, respectively. In total, 90 % of the applied glyphosate was found in the runoff, eroded sediment or in the flume soil after the short-term rainfall event. Approximately 10 % of the total applied glyphosate mass existed in AMPA form by the end of the experiment. Of the total AMPA mass, around 60 % was in the soil, 40 % was in the eroded sediment, and 2 % was in the runoff. Considering that the AMPA concentration in the eroded sediment was much higher than in the runoff, and that AMPA

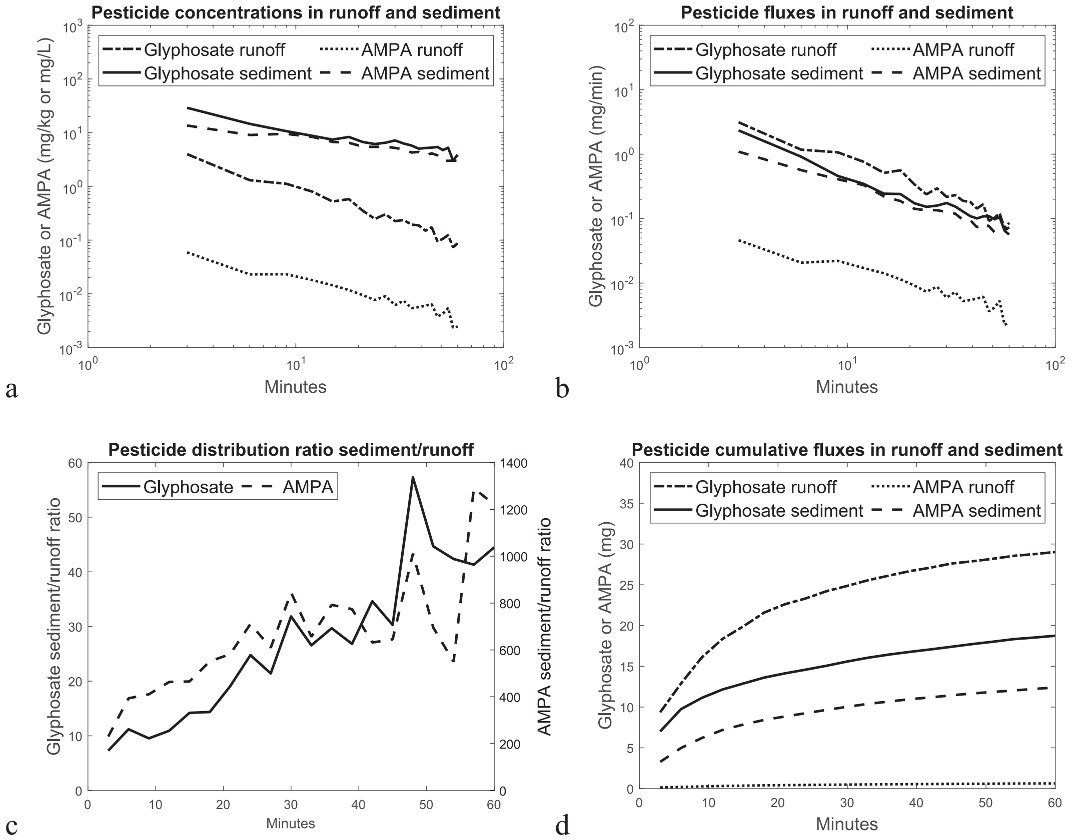

Fig. 3. Pesticide (a) concentration and (b) flux breakthrough curves in the runoff and in the eroded sediment in log–log space. Linear breakthrough curves in log–log space imply power-law breakthrough curves in linear space, and the parameters of these curves are given in Table 1. (c) Sediment/runoff ratio of pesticide concentrations. (d) Cumulative fluxes of pesticides in the runoff and sediment.

Table 1
Fitted curves of glyphosate and AMPA concentrations in the runoff and eroded sediments of various sizes.

		Glyphosate		AMPA	
Runoff	–	$C_{gly} = 16.27\ t^{-1.26}$ ($R^2 = 0.97$)	a	$C_{ampa} = 0.17\ t^{-0.94}$ ($R^2 = 0.93$)	a –
Sediment	>1 mm	$C_{gly} = 94.82\ t^{-0.66}$ ($R^2 = 0.92$)	b	$C_{ampa} = 19.62\ t^{-0.58}$ ($R^2 = 0.86$)	b
	1–0.5 mm	$C_{gly} = 93.00\ t^{-0.67}$ ($R^2 = 0.96$)	b	$C_{ampa} = 23.92\ t^{-0.63}$ ($R^2 = 0.88$)	b
	0.5–0.25 mm	$C_{gly} = 130.40\ t^{-0.75}$ ($R^2 = 0.97$)	b	$C_{ampa} = 20.09\ t^{-0.62}$ ($R^2 = 0.89$)	b
	<0.25 mm	$C_{gly} = 24.87\ t^{-0.48}$ ($R^2 = 0.74$)	c	$C_{ampa} = 28.61\ t^{-0.50}$ ($R^2 = 0.94$)	c

Letters represent significant differences in the time exponent across the sediment size classes, or between the eroded sediment and runoff.

exhibited strongly retarded infiltration in the soil, this implies that we can estimate that most AMPA mass (between 40 % to 95 %) was partitioned in the adsorbed phase upon sampling. Around 10 % of the applied glyphosate was lost to outcomes that were not accounted for, such as leaching to deeper soil layers, vaporization, measurement error, biodegradation of AMPA, or biodegradation of glyphosate to other product substances (Bergström et al., 2011).

For transported glyphosate (excluding AMPA), 60.8 % of the total was due to runoff and 22.8 % was due to < 0.25 mm eroded sediments (Fig. 5b). For transported AMPA, 4.85 % of the total was due to runoff and 80.9 % was due to < 0.25 mm eroded sediments (Fig. 5b). For transported glyphosate equivalents (glyphosate + 1.52*AMPA), 44.4 % was due to runoff and 39.8 % was due to < 0.25 mm eroded sediments (Fig. 5b). Hence, most transported glyphosate was transported by runoff, whereas most transported AMPA was transported by < 0.25 mm eroded sediments. The three larger sediment size classes (>1 mm, 1–0.5 mm, 0.5–0.25 mm) combined accounted for 16.4 %, 14.2 %, and 15.8 % of the total transport of glyphosate, AMPA, and glyphosate equivalents (glyphosate + 1.52*AMPA) respectively (Fig. 5b).

4. Discussion

4.1. Sorption facilitates the retention and dispersal of pesticides across the surface and near-surface environment

In this study, we observed strong retardation of glyphosate and AMPA infiltration into the soil, and the occurrence of substantial quantities of glyphosate and AMPA as sorbates on eroded sediment. This is consistent with glyphosate and AMPA being strongly sorptive solutes (Skeff et al., 2018; Zhang et al., 2024). As this study confirms, transport by eroded sediments is an important component of glyphosate and AMPA overland transport and spreading throughout the environment, through several key mechanisms: 1) these pesticides infiltrate soils very slowly due to sorption-induced retardation, and thus remain in the topsoil susceptible to erosion as sorbates on surface soil particles; 2) these pollutants occur substantially in the sorbed phase, where they may be physically occluded or chemically protected from degradation processes that would otherwise be more rapid in the highly oxygen-rich and microbe-rich conditions of topsoils (Borggaard & Gimsing, 2008; Tang et al., 2024); and 3) these pollutants desorb slowly even if the surrounding runoff or soil moisture has low pollutant concentrations.

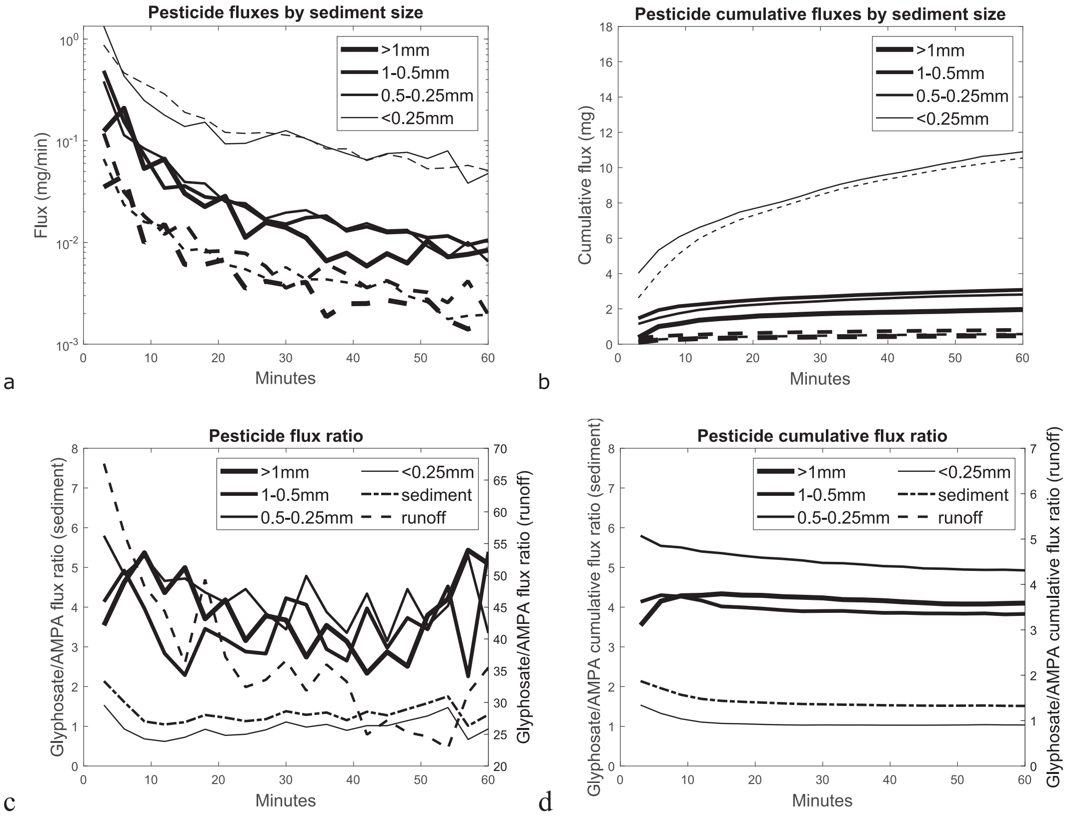

Fig. 4. (a) Pesticide flux breakthrough curves in the various sediment size classes, for glyphosate (solid lines) and AMPA (dashed lines), in semi-log space. The use of semi-log space here illustrates that glyphosate concentrations in the eroded sediment is half an order of magnitude greater than AMPA concentrations, except for the smallest size class of <0.25 mm. (b) Pesticide cumulative fluxes in the various sediment size classes, for glyphosate (solid lines) and AMPA (dashed lines). Glyphosate/AMPA (c) flux and (d) cumulative flux ratios in the sediment and runoff. For the curves related to the eroded sediment, thicker lines refer to aggregates of larger sizes.

As a result of their highly inhibited subsurface advection rates, and their high susceptibility to overland transport by runoff and erosion, risks of glyphosate and AMPA leaching to groundwater are generally low (Geng et al., 2021). Under field conditions, glyphosate and AMPA are strongly retained in the top layer of the soil (Lupi et al., 2019; Okada et al., 2016), in agreement with our experiment. The widespread high frequencies and concentrations of glyphosate and AMPA observed in surface soils and water bodies (Knuth et al., 2024; Navarro et al. 2024; Khurshid et al., 2024), may potentially be explained by the large propensity for glyphosate and AMPA to be hydrologically transported and dispersed overland rather than into the subsurface (Schwientek et al., 2024). Nevertheless, we note that the AMPA concentrations in the runoff and eroded sediment generally decreased monotonically with time (Fig. 1), instead of increasing with time or peaking at some intermediate time as would be expected if the glyphosate and AMPA were completely immobilized in the topsoil, given that glyphosate degrades faster than AMPA. This suggests that despite the strong retardation effect, the decrease over time in AMPA concentrations in the runoff and eroded sediment is primarily caused by the gradual infiltration of glyphosate and AMPA downwards into the soil, implying that infiltration remains an important determinant of the partitioning of glyphosate and AMPA between the subsurface and overland transport pathways.

The overland transport behavior of glyphosate and AMPA by runoff and eroded sediment that we have observed in this study is qualitatively consistent with preceding studies on the topic. Bento et al. (2018) observed in a flume experiment that the cumulative breakthrough flux of glyphosate was larger in the runoff than in eroded sediment at a flume outlet, and that AMPA breakthrough was primarily in the eroded sediment, in agreement with our findings. In a flume experiment with different flume orientations (slope relative to gravity), applied glyphosate concentrations, and rainfall intensities, Yang et al (2015a) found rates of glyphosate-equivalent transport by runoff and eroded sediment (14 %) that were similar to that of this study (18 %). The transport of glyphosate and AMPA by eroded sediment has also been observed to be substantial under field conditions, sometimes at rates larger than aqueous phase transport by runoff (Bento et al., 2019; Commelin et al., 2022; Commelin et al., 2024).

Our results show that the concentration and flux breakthrough curves in both the runoff and eroded sediment are well described by power-law functions. In contrast to exponential functions, which are typical for breakthrough curves in the advective–dispersive transport of solutes by large and deep surface water bodies such as rivers (Hunt, 2006), power-law concentration–time functions are more physically accurate for solute transport phenomena that involve dynamic mass exchanges of substances between multiple relatively mobile (runoff, sediment) and immobile (soil) phases (Aquino et al., 2015; Schumer et al., 2003). Such power-law breakthrough curves have also been observed for the transport of small particulate tracers and bacterial colloids in small streams under field conditions with complex mass exchange processes such as hyporheic exchange and attachment-detachment onto vegetation (Drummond et al., 2014). Therefore, the good fits of the power-law distributions in this study imply that the various water, solute, and sorption mass fluxes were dynamic and did not yet achieve steady state within the spatial and temporal scales of our experiment. This further implies that the relative importance of the various processes in glyphosate and AMPA transport may be different in scenarios with smaller or larger spatial or temporal scales, and should be addressed in future research.

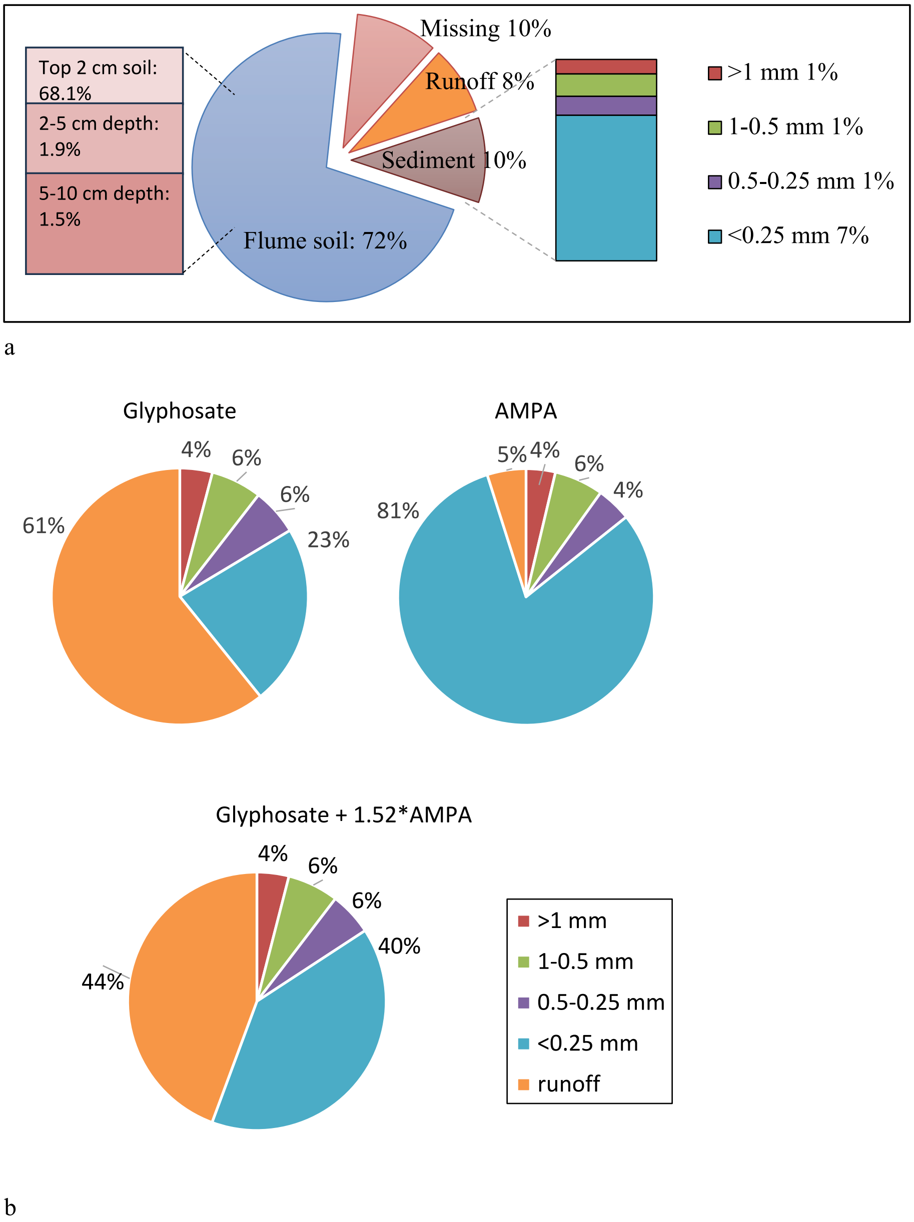

Fig. 5. (a) Mass balance of glyphosate-equivalents at the end of the experiment. (b) Proportions of total glyphosate and AMPA transported within the runoff and the eroded sediments of various sizes.

4.2. Sorption affinity may not fully characterize partitioning of solute mass between soil, runoff, and sediment

The sorption affinity (e.g., soil–water distribution coefficient) of a solute is a key controlling parameter of solute transport under runoff-erosion, and the partitioning of solute mass across the soil, runoff, and eroded sediment (Commelin et al., 2024). Both glyphosate and AMPA are strongly sorbing solutes, considered to be slightly mobile with coefficients of distribution Kd estimated to be around 209.4 mL g^{-1} (Lewis et al., 2016) for glyphosate and 88 mL g^{-1} (Yang et al., 2015b) for AMPA. Thus, a substantial portion of the overall glyphosate and AMPA in soils will become sorbed onto soil and sediment particles. Glyphosate is more sorptive than AMPA (Skeff et al., 2018; Zhang et al., 2024), though the extent of the difference depends on factors such as various soil properties and the concentrations of glyphosate and AMPA (Todorovic et al., 2010; Todorovic et al., 2014; Lupi et al., 2015; Sasal et al., 2015; Okada et al., 2016). Differences in the sorption affinity of glyphosate and AMPA may lead to different transport behavior of glyphosate and AMPA under runoff-erosion, in particular their mass partitioning across runoff and eroded sediment, as was observed in this study.

Despite the larger sorption affinity of glyphosate, we counterintuitively found that AMPA transport is dominated by the eroded sediment, whereas glyphosate transport was more evenly split across the runoff and sediment. A potential explanation for this counterintuitive finding is that soil phosphates, which may be abundant in the soil due to a relatively high phosphorus content (0.72 g kg^{-1}), compete with less abundant glyphosate (0.0001 – 0.004 g kg^{-1}) for adsorption sites, thereby reducing the sorption of glyphosate but not AMPA (Munira et al., 2018). Another possible explanation for why glyphosate is relatively depleted in sediments compared to AMPA, is that glyphosate may more favorably degrade into AMPA in the sorbed phase than in the aqueous phase, but this is inconsistent with past research that suggests that biodegradation is more favorable in the aqueous phase than sorbed phase (Wimmer et al., 2023; Borggaard & Gimsing, 2008). Several complicating factors make it challenging to isolate a direct mechanistic cause of this counterintuitive observation: 1) This experiment was conducted over 1 h, whereas the sorption equilibration time for glyphosate and AMPA can be as high as several hours to multiple days (Padilla & Selim, 2019; Gjettermann et al., 2011). This implies that the observed extents of glyphosate and AMPA sorption may not reflect their typical sorption affinities. 2) Glyphosate is constantly being removed due to degradation into AMPA, whereas both formation and removal processes apply to AMPA. Hence, glyphosate and AMPA concentrations in the soil, runoff, and eroded sediment are controlled by complex interactions between sorption kinetics, mixing between soil and runoff water, and biodegradation kinetics which differ in the aqueous and sorbed phase. 3) AMPA concentrations in the soil and runoff are much lower than glyphosate concentrations, which means that AMPA-specific sorption sites may be less saturated than glyphosate-specific sorption sites, possibly enabling AMPA to sorb more readily despite potentially lower sorption affinities.

Furthermore, in addition to the non-equilibrium nature of the sorption processes as described above, we emphasize that the hydrological processes and contaminant transport processes in our study were also highly dynamic, as evident in the successful fitting of power-law breakthrough curves. Not all processes may have reached a steady state within the spatial or temporal scale of the experiment. At the beginning of the rainfall, the soil is dry and therefore the infiltration capacity is larger. As the soil becomes increasingly saturated over time, the infiltration rate decreases as the soil's capacity to hold additional water decreases, therefore causing the runoff rate to increase over time. In the case of the erosion rate, as time progresses, the eroded sediment flux decreases because of various possible reasons. For example, by later times during the rainfall event, the easier-to-erode surface soil particles may have already been eroded away at prior times leaving a surface layer of harder-to-erode particles at the soil surface (e.g. very dense/heavy particles, particles with sizes/shapes that cause them to be physically 'hooked' onto the soil matrix, particles that are strongly chemically bonded to the rest of the soil matrix by organic matter, etc). Such processes are implied by our results, which showed that aggregates of 1–2 mm contributed 10 times more to the eroded sediment output than > 2 mm aggregates, even though both had similar fractions in the original soil material (Section 3.1). This in turn implies that 1–2 mm aggregates may be easier to erode than > 2 mm aggregates. Therefore, at later times of the rainfall event, the eroded sediment flux may decrease partially because there are fewer 1–2 mm aggregates and other easier-to-erode particles remaining at the soil surface. Although the sediment flux dynamics observed in our study are typical of loess soils, note that the sediment flux dynamics may be different for other slope angles (Yang et al., 2015a) or soil types. For example, in soils where deeper layers also contain sufficient easily erodible particles, the sediment flux may increase over time (Pan & Shangguan, 2006), instead of decrease as observed in this study.

Although Fig. 1a shows that the runoff flux and eroded sediment flux had achieved a steady state within 15 min, other mass transfer phenomena such as soil moisture diffusion, infiltration, and dispersive solute exchange between soil moisture and runoff water may not have achieved steady state. Therefore, the sorption affinity of a substance, which provides information on its sorbed-aqueous phase partitioning under steady-state or equilibrium situations, may not be a dominant controlling factor of the sorbed-aqueous phase partitioning under our dynamic experimental conditions. Under similarly complex and dynamic experimental conditions, Yang et al (2015b) also found that a larger proportion of AMPA than glyphosate was sorbed onto sediment (as opposed to dissolved in runoff), in agreement with this study. Overall, this discussion suggests that glyphosate typically having a larger sorption affinity than AMPA does not necessarily imply that transport by eroded sediment would be more important for glyphosate than for AMPA, at least within spatio-temporal scales similar to those of our experiment.

4.3. Overland transport of some sorptive solutes may be dominated by small sediments

As revealed in this study, most of the substantial sediment-phase transport of glyphosate and AMPA occurs through the smallest sediment size class (<0.25 mm). The larger sediments with sizes greater than 0.25 mm accounted for a minority of both glyphosate and AMPA fluxes. Part of the explanation for the pesticides being strongly associated with small sediments is that small sediments comprised a majority of the eroded sediments (Fig. 1b). However, the relative importance of the small sediments in transport differs by pesticide species. Considering that the particle count of < 0.25 mm sediments was around 75 % of all eroded sediments (Fig. 1b), this means that relative to particle count, <0.25 mm sediments are disproportionately underrepresented for sediment-phase glyphosate transport, as they carried around 60 % of the sediment-phase glyphosate (Fig. 5b). However, <0.25 mm sediments are disproportionately overrepresented for sediment-phase AMPA transport, as they carried around 85 % of the sediment-phase AMPA (Fig. 5b).

The overrepresentation of small sediments in AMPA transport may be related to several factors: 1) smaller soil and sediment particles have greater specific surface areas (surface area per unit volume), which implies a greater relative abundance of adsorption sites and a larger adsorption capacity; 2) smaller soil particles may be surrounded by smaller pore spaces, which implies that substances in soil water can more rapidly diffuse from the bulk pore water to the grain surfaces of small soil particles (crucial in non-equilibrium sorption), where the substances are then readily captured by sorption-related forces (Tang & Raoof, 2024); and 3) potentially larger organic matter fractions in small sediments (Virto et al., 2008; Badin et al., 2008; Christiansen et al., 1997), which potentially contribute to increasing the sorption capacity of the soil as they are effective sorbents of organic contaminants (Kozak, 1996; Delle Site, 2001). However, we note that whether organic matter in soils and sediments increase glyphosate and AMPA sorption remains unclear, as the existing literature is divided (Sidoli et al., 2016; Garba et al., 2018; Pereira et al., 2021; Wang et al., 2023). The current sparsity of detailed mechanistic understanding of these observed outcomes highlights the uniqueness and novelty of our study, which takes a first step towards understanding the relative importances of the various processes that control the sorbed-phase overland transport of soil pollutants. A direct experimental investigation into the underlying mechanisms of these observations is beyond the scope of this study, and is a potential topic for future follow-up research.

Given the highly dynamic non-equilibrium nature of the hydrological and sorption processes within the spatio-temporal scale of this experiment, and the complexity in glyphosate and AMPA adsorption processes, it is not mechanistically clear why < 0.25 mm sediments are disproportionately overrepresented for sediment-phase AMPA transport, but underrepresented for glyphosate transport. In the above discussion, we have highlighted several possible mechanisms that could be pursued further in future studies. In any case, our study shows that small sediments may be disproportionately overrepresented in the overland transport of some contaminant species, such as AMPA. Such small sediments may settle relatively slowly in surface water, and are more readily kept in suspension for long distances and periods of time (Pähtz et al., 2020). Hence, contaminants that tend to occur as sorbates on small sediments are likely to be more effectively transported overland by various sediment flux processes associated with runoff, lakes, gullies, and rivers. Furthermore, such small sediments may also be more likely to be suspended in the air as airborne dust, and transported large distances by wind (Gillette et al., 1974). This means that the environmental reach and mass fluxes of such contaminants may be underestimated if the extent of sediment-phase transport is measured from the bulk soil, as is typical in existing literature. Small sediments are also associated with greater health risks; as they are more likely to be ingested by wildlife, and more likely to make it into human food supplies (Cao et al., 2012). This implies that potential ecotoxicity levels and public health risks posed by such contaminants may also be underestimated by studies that do not specifically account for the potentially elevated risks posed by small sediments.

This study shows that in future research, and in order to better support decision makers regarding the protection of habitats and pesticide use restrictions, it is crucial to identify contaminant species that are preferentially sorbed onto, and predominantly occurring on small sediments, especially persistent contaminant species. Furthermore, our findings also imply that it is crucial to study how other agricultural and land-management practices interact with the issue of pesticide transport by eroded sediments. For example, conventional tillage increases the proportion of smaller soil particles (Leij et al., 2002), and increases the rate of soil loss to water erosion (Mhazo et al., 2016), which may doubly exacerbate the transport of sorptive pesticides that are preferentially transported by (small) eroded sediments. Mitigating the transport of small sediments and the contaminants sorbed onto them is another key issue for environmental sustainability and public health protection, but may be especially challenging, due to their small size, large quantities, and far reach.

5. Conclusion

Glyphosate and its biodegradation metabolite AMPA are ecotoxic substances that may be retained for long periods of time in the surface or near-surface soil environment. The strong sorption affinities of glyphosate and AMPA onto soil and sediment particles impede their infiltration into deeper soil and groundwater. In this study, we show that diffuse sources of glyphosate and AMPA representing typical agricultural application scenarios are susceptible to substantial overland hydrological transport through runoff and sediment erosion. Amongst the pesticides transported overland, transport by runoff and eroded sediment were similarly important for glyphosate, but the eroded sediment was much more important than runoff for AMPA. Furthermore, the transport of contaminants sorbed onto eroded sediments may be disproportionately dominated by the smallest sediments for some contaminant species, such as AMPA, but not for others such as glyphosate.

The importance of sorption on glyphosate and AMPA transport suggests that their transport behavior may be controlled by their sorption affinities, specifically the soil–water partitioning ratio at chemical equilibrium. Although the sorption affinity of glyphosate is larger than that of AMPA, we instead found sediment-phase transport to be much more important for AMPA than glyphosate. Therefore, the sorption affinity in isolation may not be sufficient to reveal which substances are preferentially transported by eroded sediments compared to runoff, and the relative importance of small sediments in the transport process. This is because the various water, sediment, and solute flux and mass exchange processes may not have achieved steady-state or chemical equilibrium within the limited temporal and spatial scale of this study. In conclusion, it is important for future research to directly identify which hazardous substances are preferentially transported by eroded sediment, to better assess the environmental spread of the contaminants. This will aid in defining pesticide restrictions and land measures to reduce pesticide risks, which is a target of various international commitments such as the European Green Deal, Farm to Fork Strategy, and Zero Pollution Action Plan. Special attention should be paid to smaller sediments, which may become especially widely dispersed and ecotoxic in the environment, and may act as carrier particles of disproportionately large quantities of some contaminants.

CRediT authorship contribution statement

Xiaomei Yang: Writing – original draft, Investigation, Funding acquisition, Conceptualization. **Vera Silva:** Writing – review & editing. **Darrell W.S. Tang:** Conceptualization, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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