Mitigating glyphosate levels in surface waters: long-term assessment in an agricultural catchment in Belgium

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Abstract

The increasing concern over pesticide pollution in water bodies underscores the need for effective mitigation strategies to support the transition towards sustainable agriculture. This study assesses the effectiveness of landscape mitigation strategies, specifically vegetative buffer strips, in reducing glyphosate loads at the catchment scale under realistic conditions. Conducted over six years (2014-2019) in a small agricultural region in Belgium, our research involved the analysis of 732 water samples from two monitoring stations, differentiated by baseflow and event-driven sampling, and before (baseline) and after the implementation of mitigation measures.

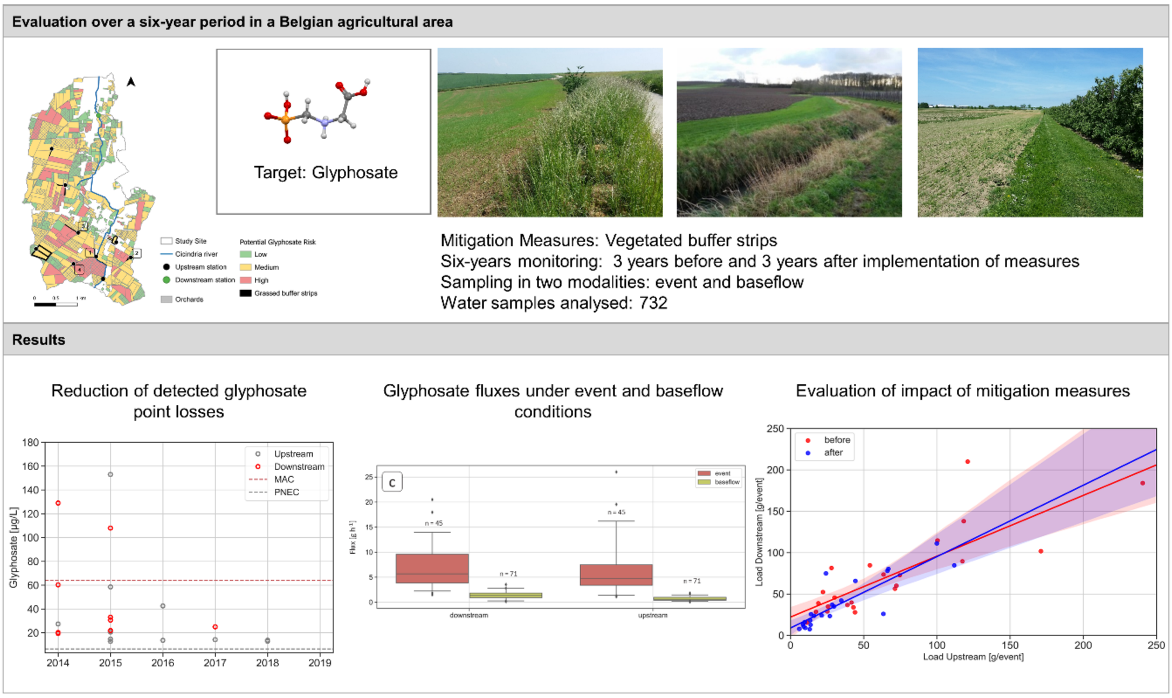
The results indicated a decline in both the number and intensity of point source losses over the years. Additionally, there was a general decrease in load intensity; however, the confluence of varying weather conditions (notably dry years during the mitigation period) and management practices (the introduction of buffer strips) posed challenges for a statistically robust evaluation of each contributing factor. A reduction of loads was measured when comparing mitigation with baseline, although this reduction is not statistically significant. Glyphosate loads during rainfall events correlated with a rainfall index and runoff ratio. Overall, focusing the mitigation strategy on runoff and erosion was a valid approach. Nevertheless, challenges remain, as evidenced by the continuous presence of glyphosate in baseflow conditions, highlighting the complex dynamics of pesticide transport.

The study concludes that while progress has been made towards reducing pesticide pollution, the complexity of interacting factors necessitates further research. Future directions should focus on enhancing farmer engagement in mitigation programs and developing experiments with more intense data collection that help to assess underlying dynamics of pesticide pollution and the impact of mitigation strategies in more detail, contributing towards the goal of reducing pesticide pollution in water bodies.

Keywords

Pesticides, mitigation, surface water; agriculture; monitoring; water quality; catchment scale.

Graphical Abstract



1 Introduction

Addressing the negative impacts of pesticide pollution on water quality is essential for moving towards sustainable agriculture. Action plans to reduce pesticide pollution contribute to the EU goal under the Water Framework Directive 2000/60/EC to improve water quality in European water bodies (European Parliament and Council, 2000). Achieving more sustainable use of pesticides while reducing risks and impacts related to pesticide use is expected under the Sustainable Use of Pesticides Directive 128/2009 (European Parliament and Council, 2009). Despite the efforts, pesticide residues frequently occur in surface waters in Europe (Navarro et al., 2024; Reemtsma et al., 2013; VMM, 2015, 2017), impacting aquatic organisms or communities.

Pesticide losses to surface water are influenced by several factors including topography, weather conditions (Daouk et al., 2013), soil characteristics (Borggaard and Gimsing, 2008), pesticide source (Wittmer et al., 2010), properties (Chaplain et al., 2011; Tang et al., 2012), and application regime (e.g., dose, timing and number of applications) (Leu et al., 2004a, 2004b), and agricultural practices (e.g., conservation tillage) (Potter et al., 2015). These factors not only determine the extent of pesticide losses but also affect the feasibility and effectiveness of mitigation strategies (Bereswill et al., 2014; Reichenberger et al., 2007). Moreover, their variable combinations and interactions make it harder to evaluate the effect of mitigation strategies (Chow et al., 2020).

There is no silver bullet to mitigate pesticides that end up in water bodies. A broadly proposed approach to reduce pollution from plant protection products is to minimise the transfer from the field where the pesticides were applied to the surface water (Carluer et al., 2017; Holvoet et al., 2007; Reichenberger et al., 2007). Vegetative buffer strips have been identified as an effective practice to mitigate the loss of nutrients, sediments and pesticides by runoff (Carvin et al., 2018; Lorenz et al., 2022; Syversen and Bechmann, 2004). Studies have shown that herbicides loads can be reduced by grassed buffer strips (Lerch et al., 2017). However, there is a large variability in effectiveness depending on buffer strip width, covering vegetation (type and coverage), location, and pesticide properties, as well as the environmental conditions, which may vary over time (e.g., over different seasons) (Prosser et al., 2020; Stehle et al., 2011; Zhang et al., 2010).

Research on the long-term effect of landscape mitigation measures, like buffer strips, at the catchment scale is limited for pesticides (Chow et al., 2020; Lorenz et al., 2022), in contrast to other substances such as nitrates, phosphorous and sediments (Bieroza et al., 2019; Boardman and Vandaele, 2020; Carvin et al., 2018; Lemke et al., 2011). Properly designed monitoring strategies at catchment scale are crucial for assessing the impact of pesticides in water bodies and the effectiveness of mitigation measures. These strategies must account for various factors affecting pesticide losses and transport, including the duration of monitoring efforts which is critical to the design. When multi-year data series are available from long term (>5 years) campaigns, it may be possible to identify trends and interpretations related to different influencing factors acting on different time scales (Chow et al., 2020).

A monitoring study was conducted on glyphosate, one of the most widely used herbicides (Benbrook, 2016), and its degradation product, aminomethylphosphonic acid (AMPA) (Borggaard and Gimsing, 2008), Glyphosate is a broad-spectrum, non-selective herbicide applied to a wide range of crops and is widely used in agriculture to control annual and perennial weeds (Duke, 2018). It is also commonly used in urban environments for weed control (Tang et al., 2015). AMPA can also be derived from the degradation of phosphonates used in household and industrial detergents, anticorrosive, and anti-scaling agents that enter surface waters via domestic and industrial wastewaters (Grandcoin et al., 2017). Glyphosate has been detected in water bodies within agricultural basins where the herbicide is commonly applied (Battaglin et al., 2014; Chang et al., 2011; Coupe et al., 2012; Navarro et al., 2024; Silva et al., 2019; VMM, 2015, 2017). Glyphosate's properties, such as high-water solubility and soil adsorption, make runoff and erosion its main transport pathways into surface waters (Coupe et al., 2012; Peruzzo et al., 2008; Rampazzo Todorovic et al., 2014; Yang et al., 2015). Understanding local use patterns, doses, and spraying schemes is vital for assessing the impact of mitigation measures (Steinmann et al., 2012; Wiese et al., 2018; Wynn et al., 2014).

To evaluate the impact of mitigation measures at catchment scale, a long-term monitoring study has been designed and carried out from 2014 to 2019 in a small agricultural catchment (~10 km^2). The 6-year study aimed to: (1) quantify the glyphosate used through a farmers survey; (2) analyse the glyphosate concentrations and loads dynamics over the different years, and (3) evaluate the effectiveness of implemented mitigation measures on glyphosate loads under realistic conditions.

2 Materials and methods

2.1 Site description

The study site is a 10.8 km^2 sub-catchment of the Cicindria river located in Sint-Truiden, Belgium (Figure 1) with altitudes of 51 to 107 m above sea level. The river flows northward with a monitored section of 6.5 km (Figure 1c). Storm and wastewater from the upstream villages (Jeuk, Borlo, Buvingen and Muizen) are discharged untreated into the river, 250 m before the upstream monitoring station. Residential wastewater from the village of Kerkom is also discharged untreated into the river in a location inside the study area.

The site is situated in the Belgian Loess plateau. Loess is very susceptible to soil erosion. The hilly topography and loamy soils make the area vulnerable to erosion. During heavy rainfall, low infiltration results in high runoff and 'muddy floods' (water flowing from agricultural fields carrying large quantities of soil as suspended sediment or bedload) to downhill areas (Boardman and Vandaele, 2020; Evrard et al., 2007).

The area is not artificial drain and includes a sediment retention zone and a flooding buffer area located close to the downstream monitoring station to mitigate sediment and flood impacts. The sediment zone is dredged usually once a year. The flooding area was active eight times during the project (informed by Watering van Sint-Truiden, local authorities).

Agricultural land dominates the area (72% of the total area, 766 ha), comprising mainly arable crops (cereals, beets, maize, potatoes, 55% of the agricultural surface),orchards (35%) and grassland (10%) (Land cover data 2014, Flemish department of Agriculture and Fisheries), with the remainder being urban areas and roads. Railways are not present within the sub-catchment. A headwater catchment upstream of the upstream monitoring station (Muizen), used as a control, covers 13.5 km^2 and has similar land use (77% agriculture, including 260 ha orchards) (Figure 1c).

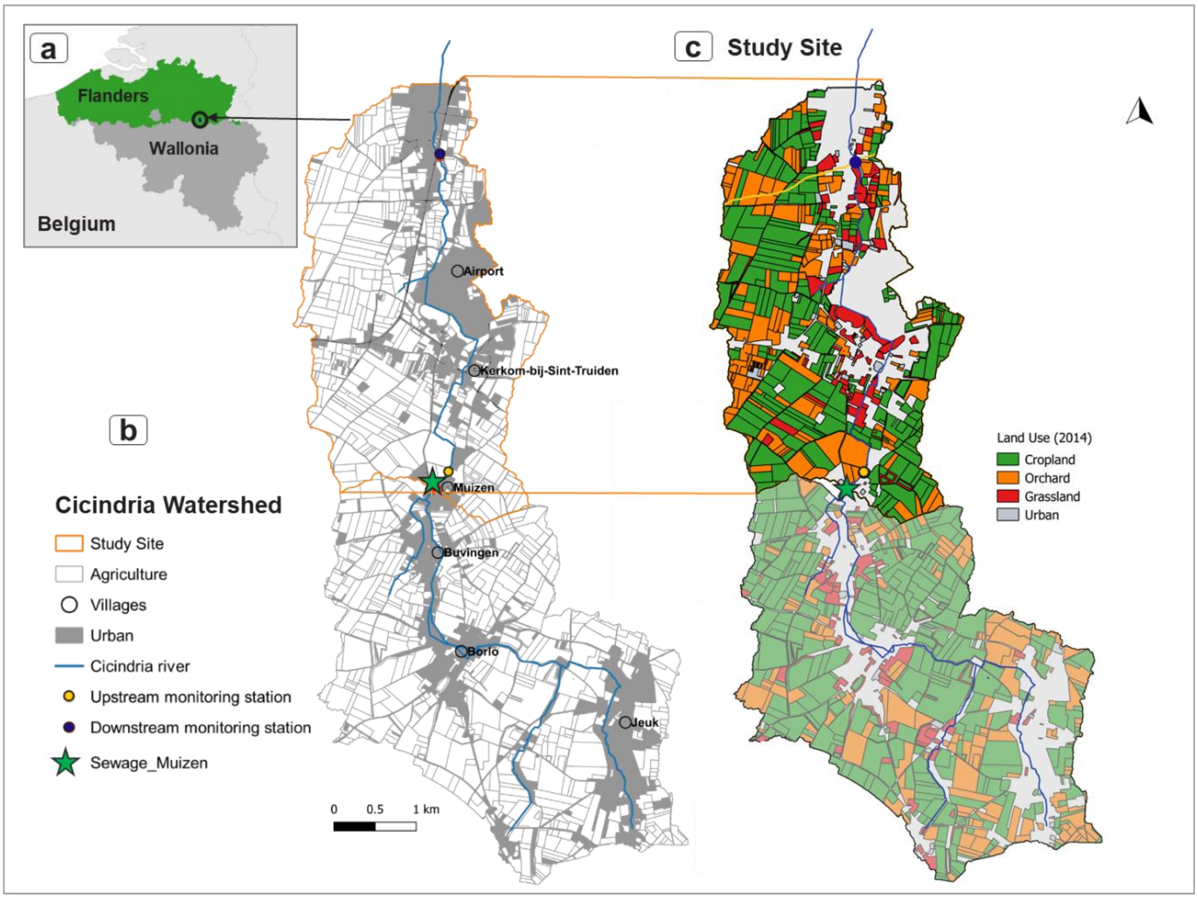


Figure 1 (a) Location of the study site, (b) Cicindria watershed (24.3 km^2). Cicindria river flows from South to North. The untreated waste and stormwater from the villages Jeuk, Borlo, Buvingen and Muizen are discharged into the river at the location identified with a star upstream of the monitoring station, (c) Study site (Cicindria river sub-catchment, 10.8 km^2) identified with stronger colours with the location of the two monitoring stations Muizen (upstream, inlet), Sint-Truiden (downstream, outlet). The land cover (2014) shows similar pattern in the whole watershed.

2.2 Sampling and analytical methods

The Cicindria river was sampled during a 6-year campaign (2014-2019). Monitoring stations were installed at the inlet/upstream of the catchment in Muizen and close to the outlet/downstream in Sint-Truiden (Figure 1c). The monitoring setup followed a Before-After-Control-Impact experimental design (Dressing and Meals, 2005), with upstream data considered as control, while downstream monitoring allows the evaluation of changes within the monitored river stretch Both the sub-catchment under study and the upstream one have similar characteristics regarding size and land use.[1] Although this was not closely monitored,

[1] Size: study area: 10.8 km^2, upstream area: 13.5 km^2. Land use: study area: 72% agriculture and 267 ha orchards, upstream area: 77% agriculture and 260 ha orchards.

it was assumed that the sub-catchment used as control (upstream/headwater area) did not show considerable changes in land use and glyphosate application during the studied period.

Discharge data was collected every 5-min using flow meters (Sontek IQ-plus) installed at both stations. An additional 15-min discharge dataset was available from a permanent monitoring station maintained by the Flemish Environment Agency (Vlaamse Milieumaatschappij, VMM) located a few meters north from the upstream station. Rainfall data was recorded at 15-min interval at a weather station located 4 km southwest of the study area.

Water samples were collected in two types: daily time-integrated (*baseflow samples*) and runoff-triggered time-integrated samples (e*vent samples)*. Baseflow samples involved collecting 20mL of water every two hours over a 24-hour period, accumulating in a glass bottle. This sampling occurred, at both locations, continuously throughout the monitoring period, regardless of water discharge, using an automated, refrigerated (< 4ºC) sampler (Isco Avalanche, Teledyne Isco) and the bottles were collected weekly.

Event samples were collected by samplers (6712 Portable samplers, Teledyne Isco) at both stations, triggered when a predefined critical discharge was exceeded. When triggered, samples were taken every 15-min and combined into a glass bottle for every 90-min. Sampling continues as long as the discharge remains above the threshold. Field technicians were alerted via automatic phone messages to collect these samples within 36 hours of the event.

For all samples, a subsample was taken from the decanted collected bottles and transferred into high-density polyethylene bottles, and frozen (-18°C) for storage until analysis for glyphosate and AMPA.

The sampling campaigns were conducted during the growing seasons, from April-May to October-November, each year from 2014 to 2019. Due to the high cost of the analysis, after sampling, only selected events and samples were analysed annually. An event qualified for analysis if (1) samples were collected at both stations during an event, and (2) complete discharge data were available for those samples. Event samples, along with daily baseflow samples related to each event, were then sent for laboratory analysis, ensuring daily samples represented baseflow conditions. Additionally, to assess sewage influence, grab samples were collected under baseflow conditions near the upstream monitoring station.

All samples were analysed at the VITO laboratory using the EMIS – VITO (2012) protocol, based on ISO 16308 standards. Glyphosate and its degradation product AMPA were determined through ultra-high-performance liquid chromatography (UHPLC) with tandem mass spectrometry (MS/MS), as detailed in the Supplementary materials. Due to the high concentrations found, samples were diluted (10x), raising the Limit of Quantification (LOQ) to 0.5 µg L^{-1}. Out of 732 samples processed, only two registered glyphosate levels below detection threshold (<0.5 µg L^{-1}).

2.3 Priority areas and mitigation strategy

To identify priority fields for the installation of buffer strips, spatial risk evaluations were conducted following methods described in Quaglia et al.,(2019), comprising both a model-based and an observation-based approach. Both methods considered the use of glyphosate for all the major crops in the area. To further prioritise and fine-tune the results, it was considered that: (1) the main target was arable land, while orchards were excluded due to the permanent grass cover between tree rows naturally reduces erosion risk; (2) fields categorised with very high or high erosion potential on the potential soil erosion map (potentiële bodemerosiekaart per perceel) were excluded. Although farmers in these areas are mandated by Flemish erosion regulations to adopt erosion mitigation measures, they have the flexibility to choose from various options, which does not guarantee the implementation of buffer strips; and (3) fields with already installed vegetated buffer strips were excluded. Four large priority areas (with several fields each) were identified through this comprehensive analysis.

Infiltration excess overland flow was identified as an important transport process for glyphosate, under the climatic conditions and the characteristics of the area, based on local expertise and previous studies (Boardman et al., 2019; Evrard et al., 2008; Vandaele et al., 1996). To mitigate this, landscape mitigation measures (e.g., vegetated buffer strips, retention structures like vegetated dams) were planned to be installed in specific fields in the four priority areas (Wouters and Vandaele, 2014). Due to the thick unsaturated zone, saturation excess overland flow seems unlikely. Moreover, during heavy rainfall events, roads were observed to channel water, sediments, and consequently, pollutants, underscoring the importance of targeted landscape mitigation measures in the prioritised areas.

The study was divided into a baseline period (“before”, 2014-2016), with no interventions or farmer communication, and a mitigation period (“after”, 2017-2019), marked by the voluntary installation of vegetated buffer strips to prevent runoff and erosion following outreach by the local authority (Flemish Land Agency, VLM) starting in late 2015. Farmers were encouraged to participate in a voluntary program to install buffer strips with financial compensation under a 5-year contract. This approach aimed to significantly reduce pesticide runoff and erosion, with 2016 serving as a transitional year between the baseline and mitigation periods. Additionally, several activities (events and training) were organised to disseminate best management practices to reduce point losses and raise awareness regarding pesticides' use. Participation was not restricted to farmers from the studied area.

2.4 Data analysis

For analysis, glyphosate concentrations below the detection threshold were assigned a value of zero, affecting only 2 out of the 732 samples analysed. The relationship between variables, such as concentration and loads, was evaluated using Spearman's correlation coefficient, with a Type I error (α) set at 0.05, ensuring a 95% confidence interval.

High concentrations during dry periods could indicate point losses (e.g., resulting from accidental spills, improper disposal of pesticides, or overspray). Within the baseflow sample dataset, point losses are outliers. A sample was identified as point loss if its concentration exceeds a certain threshold defined by the interquartile range (IQR) method (Barbato et al., 2011), specifically employing the 1.5 IQR method or Tukey's fence with k=1.5. This method is a moderate approach to detect outliers. Baseflow samples with concentrations above the upper quartile value (Q75) plus 1.5 times the IQR were classified as point losses, a criterion only applied to the baseflow samples. High concentrations during rainfall events are expected as pesticides are mobilised by runoff and erosion (Leu et al., 2004a). Therefore, peak concentrations were excluded as outliers in the event sample dataset. The proposed approach identifies sporadic spills related to pesticide handling on the farm and/or the farmyard, but may not capture other types of point losses, such as continuous pesticide discharge from sewage.

Pesticide loads (eq. 1) are calculated as the product of concentration and discharge, summed over a time interval:

$$Load_{(t=i \rightarrow t=j)} = \sum_{i}^{j} C_t \times Q_t \times \Delta_t \qquad [\mathrm{g}] \qquad (1)$$

where C_t (µg L^{-1}) is the concentration of the sample at time *t*, Q_t is the discharge (L s^{-1}) at time *t*, and Δt is the sampling time step. Loads entering (inlet) and leaving (outlet) were calculated. To assess the flux of glyphosate entering the river from the surrounding land between the two monitoring stations, the load difference between the upstream (inlet) and downstream (outlet) border of the study area was calculated. Dividing the downstream-upstream load difference by the corresponding time interval provides the glyphosate influx (eq. 2)

$$Influx = \frac{Load_{Outlet} - Load_{Inlet}}{time} \qquad [\mathrm{g\,h^{-1}}] \qquad (2)$$

Events with multiple peaks were classified as separate events in the data analysis.

To evaluate and compare the intensity of the events, two ratios were analysed: the event index and the runoff index. The **event index (EVI**) (eq. 3) combines three-rainfall characteristics: maximum precipitation intensity (P_{max}; mm h^{-1}), total precipitation (P_{total}; mm), and total duration (D, hour) (Baartman et al., 2012; Lefrancq et al., 2017):

$$EVI = \frac{P_{max} \cdot P_{total}}{D} = P_{max} \cdot P_{mean} \qquad [\mathrm{mm\ h^{-1} * mm\ h^{-1}}] \ (3)$$

where P_{mean} is the average precipitation intensity of the event. A high EVI represents a short and intense rainfall event, whereas a low EVI indicates an event with long duration and with low intensity. EVI is used as an index, but it is not dimensionless.

The **runoff index (RI)** (eq. 4) was calculated for each event by dividing the cumulative event discharge Q_{event} by the drainage area $A_{drainage}$ multiplied by the total precipitation P_{total} of the event:

$$RI\ (\%) = \frac{Q\ _{event}}{A_{drainage} \cdot P_{total}} \cdot 100 \qquad (4)$$

The start and end of the event were visually determined based on the hydrograph. The runoff index helps to determine the response of the area to rainfall and compare the different events.

To assess the impact of the mitigation strategy, we followed the approach of Carvin et al. (2018), by pairing event loads (upstream/downstream) and conducting separate analyses for the periods before and after implementing mitigation measures. Linear regression was used to investigate the relationship between upstream and downstream loads for each period. A significant change in slope and/or intercept could suggest that the mitigation strategy had an impact on the downstream loads. Since each pair of loads occurred under similar weather conditions, the analysis circumvents the influence of these conditions. For example, a dry period would result in a reduced load in both stations, while the effect of mitigation efforts should only show in the outlet load assuming no significant changes occurred in the upstream sub-catchment determining the inlet load.

2.5 Glyphosate use estimation

To assess agricultural glyphosate usage in the Cicindria area, a detailed survey through in-depth interviews was conducted. In May 2019, 110 farmers were contacted via letter about the survey and subsequently phoned to schedule the interview. Of these, 42 farmers participated providing detailed information on glyphosate use from 2014-2018, including specifics on crops, product formulations, dosages, application dates, sprayer systems, application practices, soil management, and the adoption of buffer strips. The face-to-face interviews were an excellent opportunity to raise awareness about point pollution.

The annual glyphosate use in agriculture in the study site was estimated by combining the average dose per crop (g ha^{-1}) as derived from the survey with the land cover data from the Flemish Department of Agriculture and Fisheries, using maps obtained from www.geopunt.be.

To estimate the urban use of glyphosate in the study area, key potential users were contacted, including the municipality for use in public spaces and the local airport for weed control on runways. Additionally, literature review and urban land mapping helped estimate glyphosate application on hard surfaces like sidewalks and around houses. A detailed land cover map from 2015, with 1 m resolution by the Flemish Agency of Information was used to identify potential application areas of glyphosate.

3 Results and discussion

3.1 Precipitation and discharge

Figure 2 gives an overview of the precipitation measured at the Niel-bij-Sint-Truiden weather station and the discharge in the Cicindria river measured at the VMM station, from 2014 to 2019. The annual precipitation for this period was 635 mm ± 84 mm, closely aligning with a 15-year mean of 627 ± 91 mm recorded from 2005 to 2019 at the same station. The year 2019 experienced the highest annual rainfall at 725 mm, while 2018 saw the lowest at 500 mm. The initial three years of the study were characterised by normal to wet hydrological conditions, but 2017 and 2018 were notably dry. The year 2018 was extremely dry, with an extreme drought from May to November, including a record-low 8 mm of rainfall in July.

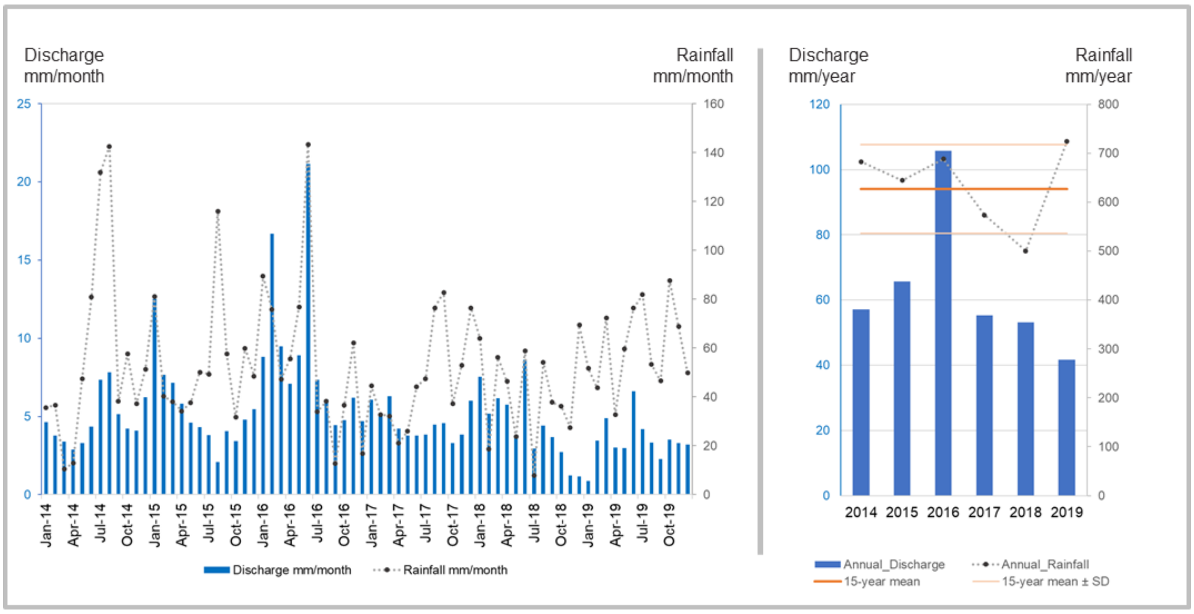


Figure 2 Left: Monthly discharge (blue bars) at the VMM station and precipitation (black dots) at the Niel-bij-Sint-Truiden station. Right. Annual discharge (blue bars), precipitation (black dots), 15-years mean precipitation (orange) ± SD (light orange line). Dashed lines between dots in precipitation were added for better readability.

The impact of the dry years can be observed in the annual discharge plot (Figure 2, right). The considerably reduced rainfall in 2017 corresponds to lower discharge volumes, with 2018 showing an even further reduction in the second half of the year. Despite the total precipitation in 2019 was above the mean plus the standard deviation, marking it as a wet year, the annual discharge remained very low. This can be attributed to the fact that 2017 and 2018 were already dry years creating very dry antecedent conditions in the catchment and, hence, rainfall in 2019 mainly infiltrated and recharge groundwater. An overview of precipitation, discharge, and glyphosate concentrations is provided in supplementary materials.

3.2 Glyphosate use

The survey to estimate agricultural use of glyphosate covered 366 ha, 48% of the 766 ha of agriculture area within the study site. The 42 interviews accounted for 98 fields and informed on the glyphosate use across various crops, including orchards (apple, pears, and cherries), arable crops (cereals, maize, beets), and grasslands. Details on the survey coverage by crop type are available in the Supplementary materials, Table S1.

Glyphosate is commonly applied in the orchards of the study area for apples, pears and cherries, mainly applied under the fruit tree canopy to maintain bare soil. Application rates range from 2 L ha^{-1} to 2.5 L ha^{-1} of formulated products containing 360 g L^{-1} of glyphosate active ingredient. Also, it was found that glyphosate (28.8%) is often used in combination with another herbicide, such as Flazasulfuron. The survey revealed average doses of glyphosate calculated considering glyphosate active ingredient (a.i.) of the different formulations for orchards, detailed in Table 1. The findings indicate the highest glyphosate usage in cherries, followed by apples and pears. All doses remain below the maximum allowed rate of 3600 g ha^{-1} $year^{-1}$. However, practical experience from local advisors contradicts the high dose in cherries and recognises that less glyphosate is usually applied in cherry orchards than apple and pear, as cherry trees are more sensitive to glyphosate compared to apple and pear.

The application rates for orchards found in this study are in line with previous studies for vineyards (Daouk et al., 2013; Lefrancq et al., 2017), aiming similarly to maintain weed-free soil beneath the trees. Glyphosate is mainly applied twice a year, although the exact application dates are not always documented. Nonetheless, for most fields, the application month was reporting allowing for the delineation of an application window. There is an application window of 4-5 months with over 95% of the volume applied in the period Mar-Jun (2014, 2015, 2018), Mar-Jul (2016) or Apr-Jul (2017), with maximum volume in May. Applications made post-July contribute very little to the total application volume in the area.

Table 1 Survey results regarding glyphosate usage are presented as average doses of active ingredient (a.i.) per hectare, considering the different formulations applied in the area. The provided percentages indicate the fraction of the area treated with glyphosate relative to its overall surveyed area for each specific crop.

Crop	2014		2015		2016		2017		2018	
	a.i. g ha^{-1}	%	a.i. g ha^{-1}	%	a.i. g ha^{-1}	%	a.i. g ha^{-1}	%	a.i. g ha^{-1}	%
Apples	1074	100	1175	90	1114	98	1028	98	1008	98
Pears	806	79	912	56	951	71	1074	59	841	56
Cherries	1545	82	1545	82	1473	84	1532	84	1576	84

In the surveyed area, farmers reported limited use of glyphosate on arable land, specifically on field borders of wheat/barley fields on less than 10% of the wheat/barley surveyed area. This very low use was confirmed by technical advisors from the Provinciaal Instituut voor Biotechnisch Onderwijs, (PIBO), highlighting that glyphosate use is not always necessary, as it depends on crop rotation. Therefore, a yearly application cannot be assumed. Instead, arable farmers in the area often use selective herbicides. The technical advisors mentioned an occasional use of glyphosate to eliminate cover crops pre-sowing, depending on the type and density of the cover crop, winter frost presence, and subsequent crop rotation, in line with other studies (Wiese et al., 2018; Wynn et al., 2014).

Notably, the practice of using glyphosate for pre-harvest treatment in cereals, which is still used in other regions in Europe (Wiese et al., 2018), was discontinued in Belgium in 2017. The results of this survey were compared against data from an annual survey of approximately 700 farmers by the Flemish Department of Agriculture and Fisheries (Lenders et al., 2013; Van Esch et al., 2012), revealing glyphosate application rates in cereals (202 g ha^{-1}), potatoes (270 g ha^{-1}), maize (104 g ha^{-1}) and beets (277 g ha^{-1}) at the provincial level for the years 2014-2016 (doses between brackets are the mean values).

Table 2 shows the annual glyphosate use estimated by combining an estimated dose (Table 1) with the land use information from each year and compared with the estimation calculated with the doses informed in the Flemish survey with provincial averages, illustrating both local and regional trends.

Table 2 Annual use glyphosate (a.i. kg) for the study area estimated with the results from the local survey and the Flemish survey

Annual glyphosate use	2014	2015	2016	2017	2018
Estimation using the doses from this survey	264	285	292	301	283
Estimation using the doses from the Flemish survey	307	376	442	n.a.	n.a.

In the urban context, both the municipality and the local airport confirmed having ceased glyphosate usage for years. Flanders (Belgium) banned the non-professional use of glyphosate in 2018, though its professional application remained legal. Consequently, it was presumed that glyphosate might still be applied on hard surfaces within the study area during the monitoring period. An estimated annual use of 35 kg of glyphosate was roughly estimated for the area, assuming that 45% of the identified hard surfaces (21 ha) were treated with glyphosate with a mean dose of 3.7 kg ha^{-1}, following Tang et al. (2015) in an urban study in Belgium. This estimation can be considered a worst-case scenario, as lower use was documented in the literature, such as 14% in the US and 27% in the UK (Tang et al., 2015), suggest reduced estimates to 21 kg and 11 kg, respectively. The use of pesticides for non-professional users is also expected to decline due to the effort made by the government and the industry (Fevery et al., 2016).

3.3 Glyphosate detection and characterisation

Between 2014 and 2019, fifty events were initially selected for analysis (

Table 3). However, five events were excluded from the loads/influx analysis due to missing discharge data, resulting in 45 events being considered for further analysis (detailed in Supplementary material, Table S2). These events encompassed a broad spectrum of rainfall intensities and durations, varied catchment responses, and different glyphosate concentrations and load discharges into the Cicindria river. In total, 732 samples were analysed: 529 were collected during rainfall events, termed *event samples*, and 203 were collected under baseflow conditions, referred to as *baseflow samples.*

Table 3 Summary of the analysed events from 2014 to 2019

	2014		2015		2016		2017		2018		2019	
Sampling period	13 June	31 Oct	24 Apr	31 Oct	21 Apr	6 Nov	1 May	7 Nov	26 Apr	5 Nov	3 Apr	20 Oct
Rainfall events	8		8		9		8		6		11	
Station	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Event samples	44	49	44	46	48	49	41	44	34	34	47	49
Baseflow samples	40		34		32		41		21		35	

Glyphosate was detected in 730 of the 732 analysed samples; two (baseflow samples) were below LOQ (<0.5 µg L^{-1}). To assess the environmental risk, concentrations were compared to environmental quality standards for Flanders proposed by the Flemish Environmental Agency (VMM): Maximum Acceptable Concentration (MAC) for potential acute effects on aquatic organisms (MAC) of 64 µg L^{-1} and the Predicted Non-observed Effect Concentration (PNEC) of 6.4 µg L^{-1} for possible chronic effects from glyphosate presence (VMM, 2017). Concentrations exceeding the PNEC indicate a probable risk of chronic toxic to aquatic organisms. In our study, only three samples (0.4%) exceeded the MAC (Figure 3). These concentrations deviate much from other observations under similar weather conditions, and likely can be attributed to point losses.

Over the six years, mean glyphosate concentrations for event samples were 9.6 µg L^{-1} upstream and 7.8 µg L^{-1} downstream. Baseflow conditions showed averages of 5.5 µg L^{-1} upstream and 6.4 µg L^{-1} downstream, with a decreasing trend over the studied period (Supplementary material, table S4 and table S5). Generally, concentrations tend to be higher in small streams than measured in larger rivers, as is illustrated in Table 4. Annual mean concentrations of upstream baseflow samples and the six-year mean of 5.5 µg L^{-1} remained below the PNEC threshold of 6.4 µg L^{-1}. Downstream annual averages were below the PNEC in 2016 and 2019, with a six-year mean of 6.6 µg L^{-1}, indicating occasional exceedances of chronic toxicity thresholds.

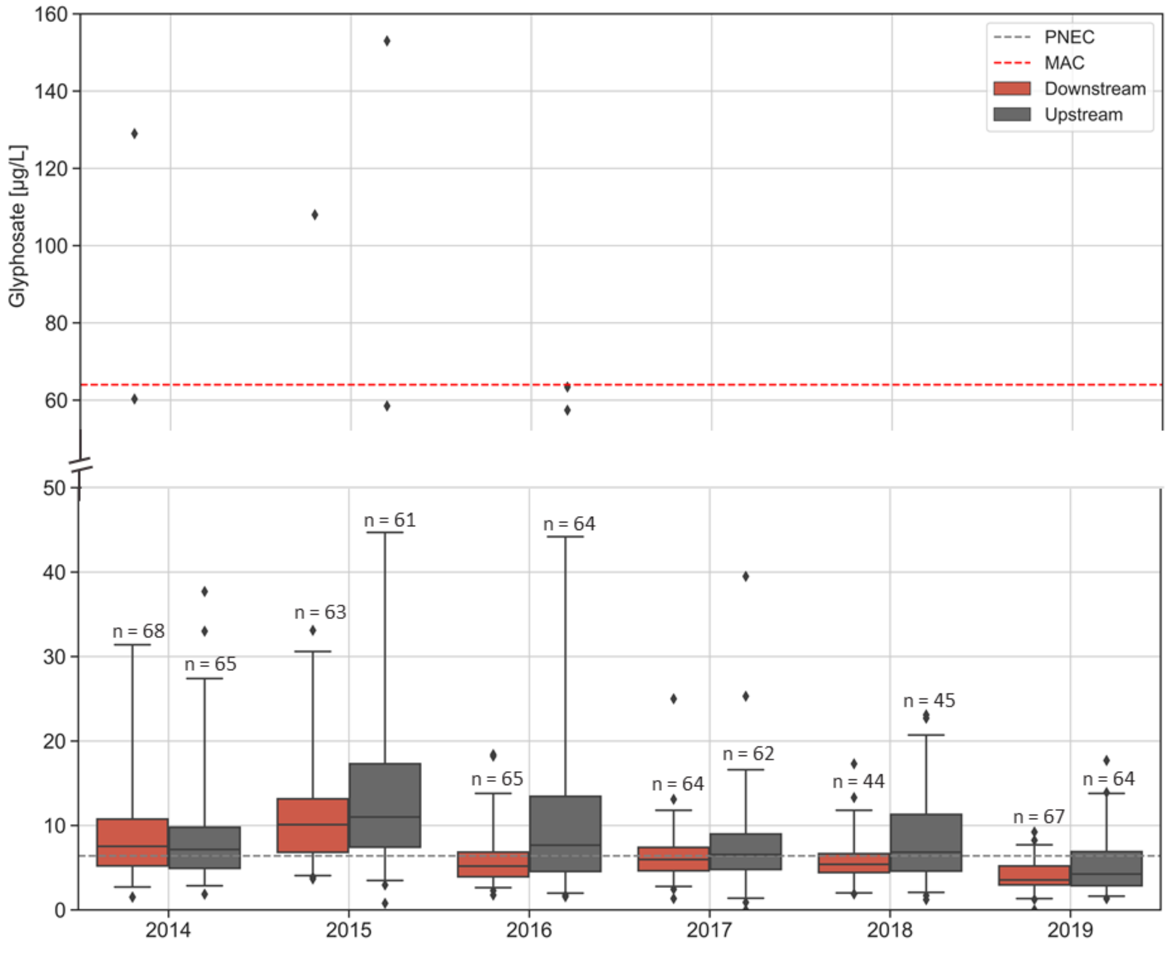


Figure 3 Boxplot for glyphosate concentrations (baseflow and event) sampled at both stations (downstream in red and upstream in grey) against MAC and PNEC (before removing point losses) grouped by year. The boxes indicate the first and third quartiles (25%, 75%) and the median is shown as a solid black line. The whiskers indicate 1.5IQR, and the dots are the outliers. Only three samples exceed 64 µg L^{-1} (MAC) over the 6-years (top). The larger top box halves and whiskers indicate right-skewed distributions, the most commonly occurring shape for water quality data (Helsel and Hirsch, 2002).

Despite glyphosate use being limited to fruit growers in the area, glyphosate was detected in >99% of the samples. Ervard et al. (2008) found that grassed buffer strips between trees in orchards exhibit higher runoff than most cultivated soils, possibly due to soil compaction from agricultural machinery. This may facilitate the movement of glyphosate dissolved in water from the orchards. Additionally, several orchard fields were located very close to the river and in areas with a steep slope. Daouk et al. (2013) observed that vineyards on steep slopes contribute to higher loads of glyphosate in runoff.

The Cicindria river receives untreated waste and stormwater from the upstream catchment, only 250 m before the upstream monitoring station. Additionally, the village of Kerkom-bij-Sint-Truiden, located between the two monitoring stations, also discharges untreated water. Consequently, the herbicide applied on hard surfaces, farmyards, and other urban use could contribute to measured concentrations of glyphosate as shown in previous studies (Hanke et al., 2010; Tang et al., 2015).

Table 4 Glyphosate concentrations in other rivers and streams

Location	**Concentration (Min-Max; Mean μg L^{-1})**	**Area (km^2)**	**Time of collection**	**Land Use**	**Reference**
Cicindria river, Belgium	0.78-153; 8.7	10.7	Apr/May – early Nov 2014-2019	72% agriculture (33% orchards).	Present study
Lutrieve river, Switzerland	0.015-4.97	6.4	Apr-Sep 2011	45% agriculture, 31% impervious surfaces, 24% forests.	(Daouk et al., 2013)
Lake Greifen Catchment, Switzerland	Max: 4.2 Baseflow: 0.0024-0.13	25	Mar-Nov 2007	75% agriculture	(Hanke et al., 2010)
Mess river, Luxembourg	Max: 6.22; 1.65	32.5	Oct 2006-Jan 2010	58% grassland, 22.7% arable land, 9.7% forest, 8.7% urban, 2.3% roads and rail network.	(Meyer et al., 2011)

Meuse River, Belgium	Max: 0.7 upstream Max: 0.3 downstream	Large basin. 250 km river stretch under study	monthly or biweekly 1995-2011	54-60% agriculture, 11-34% urban,12-28% nature/forest/water	(Desmet et al., 2016)

3.3.1 Point losses

Baseflow samples exceeding 14.6 µg L^{-1} downstream and 12.5 µg L^{-1} upstream were classified as point losses, identified using the interquartile range (IQR) method from six years of data. The frequency and intensity of point losses have decreased over time, with none detected in 2019 (Figure 4), likely due to increased awareness of the issue and the implementation of improved filling/spraying practices among farmers. The reduction was slightly greater downstream. Nevertheless, actions taken could influence both the control and monitored area. The yearly count of point losses versus baseflow samples analysed shows a notable increase in point losses percentage in 2018 due to fewer samples being analysed during a dry period (Supplementary materials, Table S12).

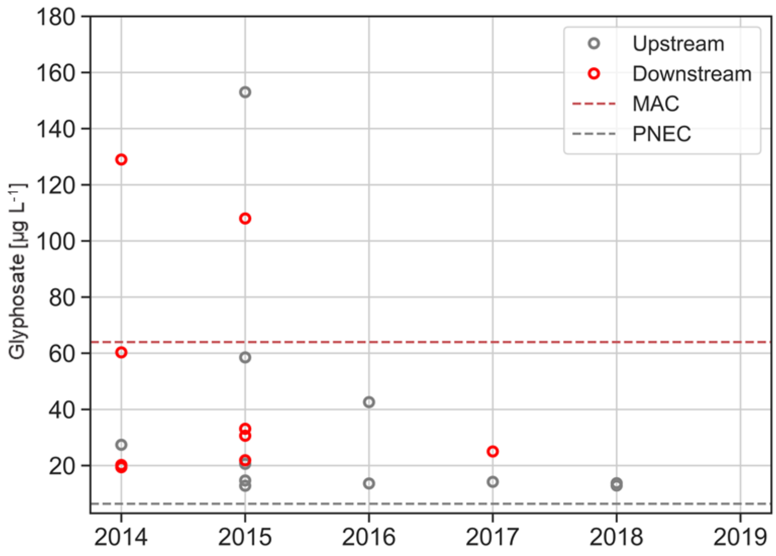


Figure 4 Measured concentrations related to point losses for 2014-2019 .

The analysis of selected baseflow samples does not provide a complete assessment of point losses but, due to consistent sampling and the sample selection over the 6-year study period, it supports a reliable trend analysis.

3.3.2 Concentration dynamics

Two ratios, event index (EVI) and runoff index, were used to analyse glyphosate dynamics in the study area. The maximum concentration per event positively correlates with the EVI ($p<0.01$) (Figure 5). Events with high EVI, meaning intense and short rainfall, mobilised and transported larger amounts of glyphosate into the river. This relationship corresponds well to the findings of Lefrancq et al. (2017), who found a positive correlation of glyphosate with EVI in a monitoring study in France. However, the results from our study are scattered. High concentrations with low EVI may originate from hard surfaces losses (Tang et al., 2015). No significant correlation was found between the runoff index and maximum glyphosate concentration per event.

Rainfall events near application dates might enhance pesticide runoff from fields (Daouk et al., 2013). This study assessed whether the proximity of rainfall to application dates influences glyphosate levels in the river by comparing event concentrations at both stations during and outside the application period, as identified by the farmers' survey. The analysis revealed no significant difference (Kruskal-Wallis non-parametric test), indicating no attenuation in the events outside of the spring or early summer usage period when agricultural applications occur. This could be due to the broad application window and the possible contribution of urban sources of glyphosate. The latter more concretely relates to the wash off after application on hard surfaces and direct stormwater discharge into the river.

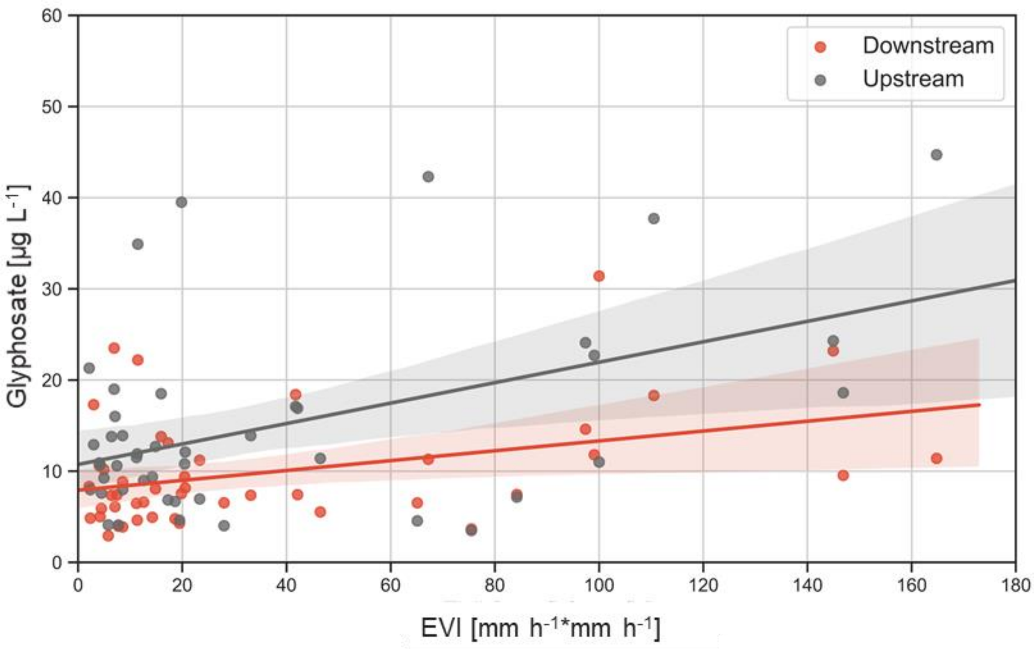


Figure 5 Maximum glyphosate concentration measured per event versus EVI index (maximum precipitation intensity, total precipitation, and duration). Significant Pearson correlation ($p<0.01$, Upstream $r=0.5$, Downstream $r=0.4$). Regression line: R^2 Upstream= 0.22, Downstream= 0.14, confidence interval bands 95%.

3.4 Glyphosate and AMPA

AMPA was detected in all the samples with increasing concentrations over the years, from 14.3 ± 5.8 µg L^{-1} in 2014 to 59.9 ± 37.0 µg L^{-1} in 2019 at the downstream station. Notably, during dry conditions in 2019, AMPA concentrations reached peak levels of 210 µg L^{-1} downstream and 303 µg L^{-1} upstream (Supplementary material, table S8 and table S9). Contrastingly, glyphosate concentrations showed the opposite trend (Figure 3). AMPA exceed glyphosate concentrations in 95% of the samples during dry conditions and in 85% during rainfall events. Similar results were found by Struger et al. (2015).

A weak correlation between AMPA and glyphosate concentrations ($r=0.3$, $p<0.005$) was observed upstream over the six years, with no significant correlation downstream. However, the correlations calculated for each year showed different results (Table 5). A strong correlation was found during the dry period for both stations, while no correlation or lower values were found during events downstream. These patterns suggest AMPA might also originate from other phosphonate compounds in sewage (Grandcoin et al., 2017), not just glyphosate degradation, indicating diverse transport processes for both substances during rainfall events.

Table 5 Correlation between glyphosate and AMPA. A strong significant correlation ($R>0.7$) were identified in grey.

	DOWNSTREAM	**UPSTREAM**

Year	R Baseflow	P	R Event	P	R Baseflow	P	R Event	P
2014	0.02	N.S.	0.35	<0.05	0.28	N.S.	0.19	N.S.
2015	0.31	N.S.	-0.08	N.S.	0.72	<0.05	0.65	<0.05
2016	0.73	<0.05	0.35	<0.05	0.75	<0.05	0.58	<0.05
2017	0.56	<0.05	0.00	N.S.	0.52	<0.05	0.55	<0.05
2018	0.77	<0.05	0.64	<0.05	0.90	<0.05	0.81	<0.05
2019	0.68	<0.05	0.67	<0.05	0.71	<0.05	0.46	<0.05

The AMPA to glyphosate ratios offer insight into the sources, fate, and transport processes of glyphosate and its metabolite. Battaglin et al. (2003) show that lower concentration ratios in runoff samples, observed shortly after application or near the application area, might indicate the proximity of the pesticide source in terms of space or time. In this study, increasing ratios were found, ranging from 3 ± 2 in 2014 to 23 ± 11 in 2019 at the downstream station. A temporal variation over the months was observed for downstream samples with lower ratios during the application window of glyphosate in May, June and July (Figure 6).

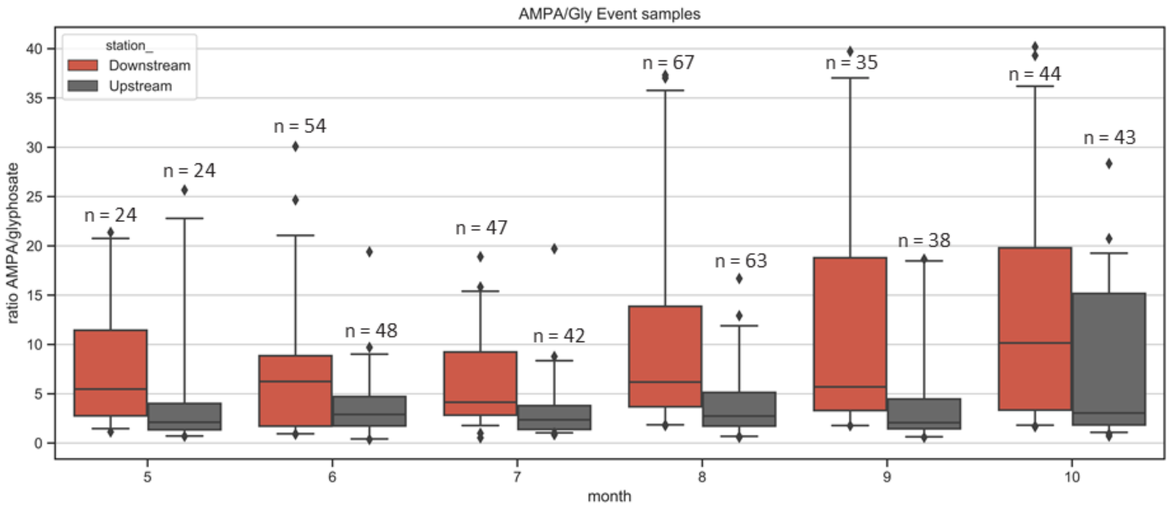


Figure 6 Ratio AMPA/glyphosate for samples taken during rainfall events (2014-2019). Lower ratios at the downstream station can be observed in May, June and July during the window of application of glyphosate.

3.5 Glyphosate loads and flux dynamics

Loads were calculated for 45 events at both stations, as detailed in the Supplementary material, Table S2. The relation between the calculated event loads and both indexes, runoff index and EVI, was evaluated (Figure 7). Event loads for both stations are positively weakly correlated with both EVI ($r=0.4$, $p<0.05$) and the runoff index ($r_{downstream}=0.3$, $r_{upstream}=0.5$, $p<0.05$). This proves the importance of the runoff processes in generating the observed loads. These results also corroborate the strategy followed in the choice for mitigation measures focused on runoff. Previous studies in the region (Evrard et al., 2008; Vandaele et al., 1996) have identified runoff, driven by infiltration excess, as a key factor in water and sediment transport. Our study adds that runoff also mobilizes glyphosate from the field and transports it into the stream. Furthermore, it was observed that some roads could transport water and sediments during heavy rainfall events, additionally contributing to glyphosate loads. The range of loads and the range of runoff index and EVI are much smaller in the period after implementation of the mitigation measures than in the period before, where the most extreme events corresponded with loads larger than 150 g/event.

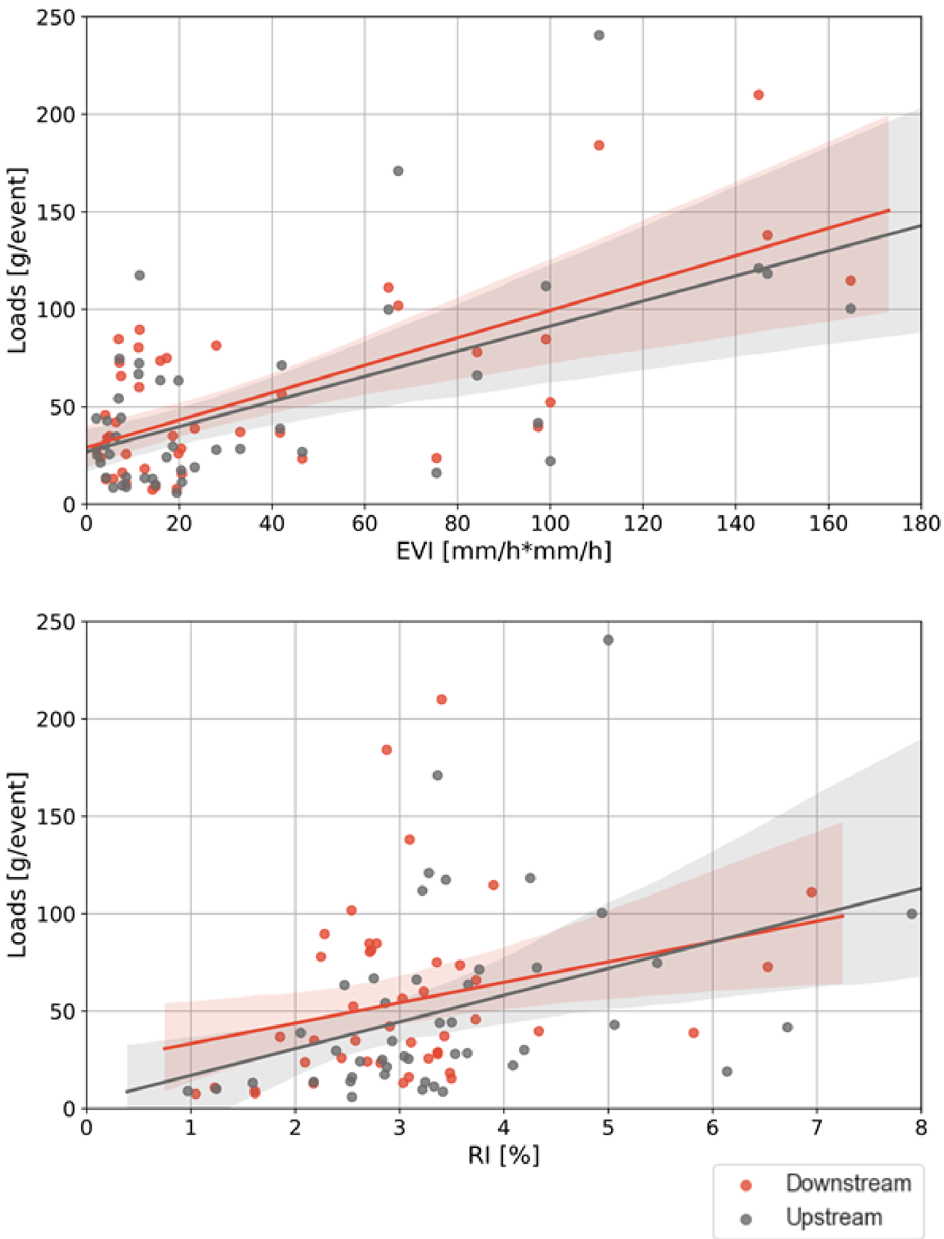


Figure 7 EVI (above) and RI (below) versus upstream (grey) and downstream (red) event loads of glyphosate (g/event). Each point corresponds to an event (45 events, table S1). Linear regression and 95% confidence interval bands are shown.

Over the 6-year study, the glyphosate load intensity during events decreased over the years (Figure 8 a). Fluxes reduced from 3.4 g h^{-1} (average 2014-2016) to 1.4 g h-1 (average 2017-2019) after implementing measures. The hydrological conditions were normal to wet in the baseline period, while after implementation, three consecutive dry years occurred. Since the change in management (mitigation measures) coincided with a change in the average hydrological (weather) conditions, a (statistically) sound evaluation of the individual contribution of each of these influencing factors based on observed fluxes could not be established.

More than 60% of the events showed a positive difference between downstream and upstream loads, meaning that the monitored sub-catchment area contributes glyphosate input between the two sampling points. The difference between the loads downstream and upstream (load intensity or flux, g h^{-1}) during events can be attributed to several processes. A positive difference can be explained by glyphosate being transported via runoff and erosion (Yang et al., 2015), the resuspension/remobilisation from river sediments, desorption from soil particles and point losses. However, the desorption of glyphosate from soil particles in sediment has been shown to be very low (Maqueda et al., 2017). A negative difference could be due to degradation or immobilisation in river sediments. Glyphosate degradation in water takes a few days (half-life: 1-35 days, (Lewis et al., 2016). Given the short travel time of the water between the upstream and downstream locations (a few hours under low flow conditions), degradation can be considered negligible (Battaglin et al., 2014). A more like explanation relates to the sediment trap located south (upstream) of the downstream monitoring location, which may retain sediment and glyphosate adsorbed to it.

Baseflow loads are observed to be relatively high, which is connected to the presence of the sewage outlet (located before the upstream station, outside of the monitoring area) considered as a principal source (Supplementary material, table S3). Over 85% of the baseflow paired samples showed a positive flux (difference downstream upstream loads) (Figure 8 b). Some possible reasons could explain the positive glyphosate baseflow fluxes. First, there is a sewage outlet of the small urban area (Kerkom-bij-Sint-Truiden) between the two monitoring stations. Second, there is a possible release of glyphosate from the sediments (riverbed and sediment trap) due to a legacy effect resulting from slower desorption dynamics. Due to the dry conditions during the last three years of monitoring, it was observed that the event fluxes tend to approach the baseflow fluxes values. To compare event and baseflow fluxes, the loads were divided by the sampling time to obtain a flux in mass per unit of time. Figure 8 c shows the different magnitudes between fluxes in baseflow and event conditions for each monitoring station.

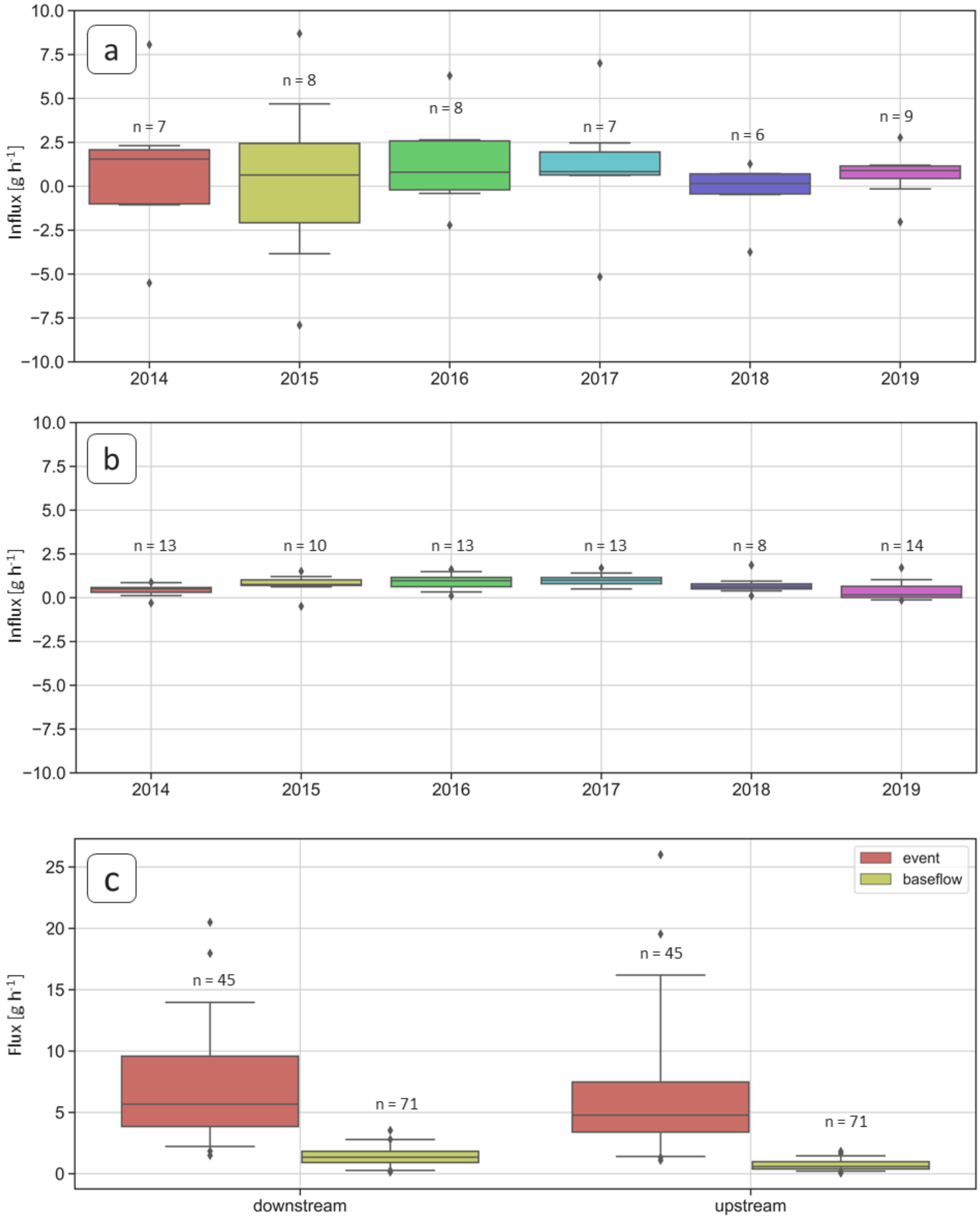


Figure 8 (a) Glyphosate influx (g h^{-1}) (loads downstream - loads upstream) in the investigated stretch over the years under event conditions. In total, 45 events were analysed, 29 events showed a positive difference. Each box, median, upper 75%, lower 25%. Whiskers 1.5*IQR. Dots: outliers, (b) Glyphosate influx (g h^{-1}) in the investigated stretch over the years under baseflow conditions. Each box, median, upper 75%, lower 25%. Whiskers 1.5*IQR. Dots: outliers, (c) Glyphosate flux (g h^{-1}) upstream and downstream under event and baseflow conditions. Each box, median, upper 75%, lower 25%. Whiskers 1.5*IQR. Dots: outliers.

Further work is needed to properly disentangle the relative contributions of the baseflow, the in-stream processes, and the influence of the sewage discharge (inside, Kerkom-bij-Sint-Truiden, and outside upstream Muizen). The mitigation of baseflow loads and the overall water quality improvement was not the focus of this study and hence was not incorporated in the experimental design. A wastewater treatment plant is planned for this area, which may help reduce the magnitude of the overall water pollution problem in the Cicindria river. Additional measures could be proposed once the plant is operational, such as converting the flooding area into a constructed wetland.

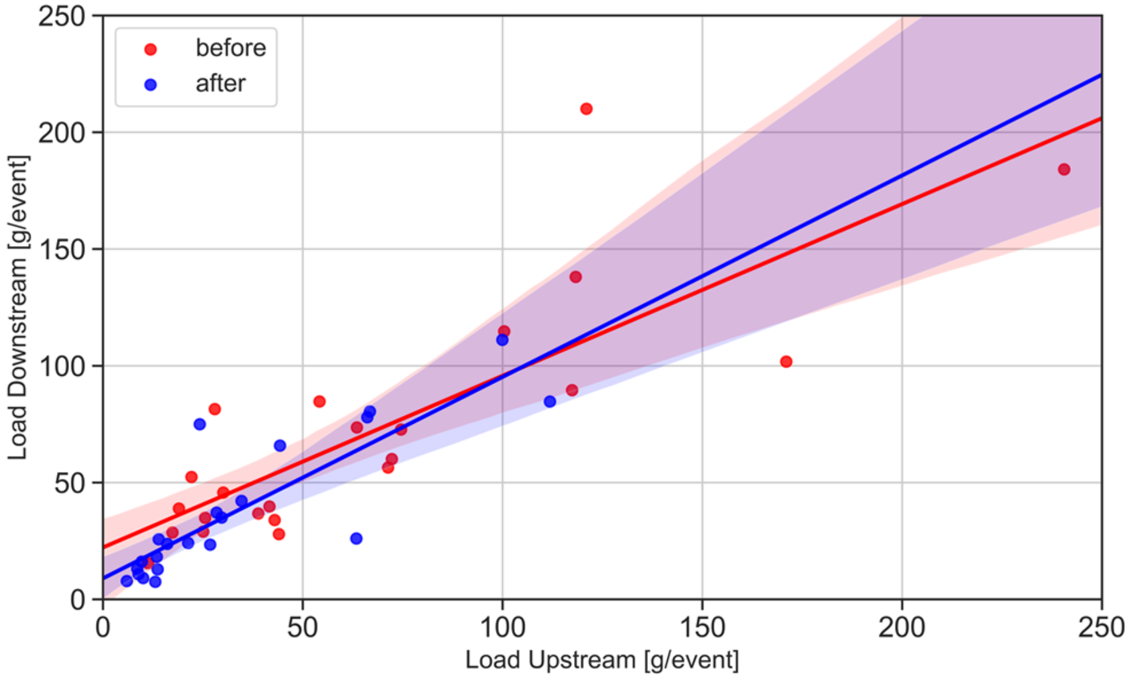
3.6 Implementation and impact evaluation

In addition to vegetated buffer strips (VBS), retention structures such as vegetated dams were considered as mitigation measures, but funding constraints led to the exclusive installation of VBS. The design of VBS, including their location within the field, cover type, and width, were tailored case by case through cooperation between local authorities and farmers. Starting in 2016, VBS covered an initial area of 57661 m^2, expanding by 12062 m^2 in 2017, totalling 69723 m^2 with well-established grass cover by May 2017. Buffer width varies from 6 to 24 m. Half of the buffers were in high erosion risk areas yet accounted for 30% of the total buffer area.

The initial assumptions of the project, particularly the widespread use of glyphosate in arable fields, were re-evaluated based on farm survey results, highlighting local practices related to the use of glyphosate differ preliminary expectations considering provincial survey. This led to recognising orchards as potential glyphosate runoff contributors, despite being initially excluded due to their low erosion potential. However, these areas could contribute and should not be neglected.

A 5% glyphosate load reduction was estimated with the updated assumptions using a project-specific decision support framework (Quaglia, 2022). Considering the natural variability of the processes contributing to generation of glyphosate loads into surface water and the uncertainties associated with their quantification (McMillan et al., 2012), the 5% potential estimated load reduction would be difficult to measure with certainty.

The loads for downstream and upstream were compared to determine if there was a change between the two periods: the calculated event loads were split into two groups, according to their observation date being before (2014-2016) or after the implementation of measures (2017-2019). For each group, the relation between the upstream and downstream loads was investigated and a linear regression was performed (Figure 9). It should be noted that there is a large overlap between the 95% confidence intervals of the regression lines before and after the implementation of the mitigation measures; the confidence interval of the former is almost entirely included in that of the latter. Consequently, the results have to be interpreted with caution. The intercept after implementation of measures is lower indicating lower glyphosate input from the monitored area, whereas the slope increased and, hence, suggests a relatively stronger load response in function of the event size. It is possible that the buffers work better for the mitigation of “small” events (<100g event^{-1}), while there is no measurable effect for “larger” events.



Before Implementation: $Load_{Down} = 0.74\ Load_{up} + 22.2$ $R^2 = 0.67$

After Implementation: $Load_{Down} = 0.86\ Load_{up} + 8.9$ $R^2 = 0.73$

Figure 9 Loads upstream and downstream before (red) and after (blue) the implementation of mitigation measures. The evaluation of the linear regression showed that the intercept after implementation is lower indicating lower losses; however, the slope has increased suggesting a stronger load response in larger event sizes. Linear regression and 95% confidence interval bands are shown.

Visual assessment of the buffer strips after storms confirmed the positive impact on soil retention, contrasting with fields lacking such measures (Supplementary material, figure S5). However, buffer strip condition and effectiveness could fluctuate seasonally and annually, as evidenced in 2018 when extreme dry conditions led to some buffers having sparse vegetation (Supplementary material, figure S6), underscoring the variability in efficiency reported in literature (Klein et al., 2023; Lerch et al., 2017; Otto et al., 2012).

4 Conclusions

The evaluation of mitigation measures for pesticide pollution was accomplished by monitoring the catchment three years before (baseline monitoring) and three years after implementing the measures.

The use of glyphosate was limited to orchards (apple, pears and cherries) to control weeds below the canopy. The window of application is wide (4-5 months). There is a need for a more nuanced understanding of pesticide application patterns and suggest that future research could focus on developing tailored strategies to collect pesticide use data that consider crop type and local practices.

The number and intensity of point losses detected per year decreased over the 6-years monitoring period. Moreover, the maximum concentration observed in point losses decreased over the years from over 100 μg L^{-1} to less than 15 μg L^{-1}. No point losses were detected in 2019. The decreasing trend could be explained due to the sensitisation of farmers to issues around point losses and possible mitigation practices. This trend is encouraging and suggests that increased farmer awareness and adoption of better management practices can significantly mitigate point source pollution.

A statistically significant correlation between the event loads, the event index (EVI) and the runoff index (RI) suggested that runoff is a relevant process explaining event loads. However, the correlation was weak in both indexes ($r<0.5$). This indicates that while runoff is a significant factor in explaining event loads, other processes such as mobilisation from river sediment and sewage discharge also play a role. Further investigation into these additional contributing factors is needed to develop a more comprehensive understanding of pesticide flux dynamics.

There was an almost constant positive flux of glyphosate in baseflow conditions. Yet, event fluxes were observed to be considerably higher with a decreasing trend over the 6 years of monitoring. Further investigation is needed on the impact of sewage discharge and interactions with the river sediment to fully explain glyphosate loads during dry conditions and propose alternative mitigation measures to reduce them. This finding points to the complexity of glyphosate transport mechanisms in river systems and underscores the importance of considering both baseflow and event conditions in water quality monitoring and management strategies.

Despite the efforts made to involve the local farmers, some critical areas were left without measures in our study, as the adoption of mitigation measures was part of a voluntary program. Future work should aim to increase participation in mitigation programs and explore additional strategies to enhance their effectiveness.

A combined effect of variable weather conditions and management changes (implementation mitigation measures) could be observed in the 6-year trend of event load intensity. The weather conditions were normal to wet in the baseline period (2014-2016), while two consecutive dry years (2017-2018) followed in the implementation period (2017-2019). Despite the high level of precipitation in 2019, it can also be considered “dry” as regards to the discharge. Since both the management and the hydrological conditions trends coincided, we were unable to make a (statistically) sound evaluation of the separate contribution of each of the influencing factors based on the event load intensity (fluxes). From the evaluation before-after the implementation, a mitigating effect was found for loads of “small” events (<100g/event), while there was no considerable effect for “larger” events (>100g/event).

The results emphasise the difficulty in evaluating the impact of mitigation measures at the catchment scale. This suggests that future research should develop more robust methodologies and tools for assessing the effectiveness of mitigation strategies in complex environmental systems.

5 Acknowledgements

This work was supported by the Glyphosate Environmental Stewardship Steering Group (GESSG); and it has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675120.

The authors would like to thank Nathalie Broers, Kris Dhaese and Raf Spiritus (pcfruit), Karel Vandaele (Watering van Sint-Truiden), Martijn Erkens (VLM, Flemish Land Agency), Guido Vanermen and Griet Jacobs (VITO). The authors thank Dr. Jan Bronders (VITO) for the constructive comments that improved our manuscript markedly.

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