Water, Air, & Soil Pollution

The occurrence of glyphosate and its degradation products in the urban stormwater: A short review

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Abstract:	Due to urbanisation and industrialisation, water pollution is now one of the major environmental challenges of the twenty-first century. Considering the increasing of agricultural and non-agricultural settings in the last decades, the investigation of the relationship between such pesticides and urban stormwater is critical to understand how urban, residential, and industrialized areas can affect environmental safety. Recently, scientific interest has grown in stormwater chemical characterization with the aim to define its impacts in the environment and possibly to make it potable water. In this context, glyphosate, glufosinate and their degradation products have been identified as the key knowledge gap for the chemical characterization of stormwater. Research investments are needed for a better understanding of the highly polar pesticides to estimate their load, source, and dispersion of urban runoff due to residential use of herbicides. Furthermore, a more comprehensive study of wet and dry deposition and spray drift should be considered for a correct evaluation of source apportionment.
Response to Reviewers:	Reviewer #1: Thank you very much for giving me the opportunity to review your paper. In general I find your work could be a valuable contribution to Water, Air and Soil Pollution journal A: Thank to Reviewer #1 for the comment. 1. Line 86. Add a table with the physical and chemical characteristics of these herbicides (glufosinate, AMPA and glyphosate): vapor pressure, solubility, adsorption coefficient, molecular mass, etc. A: We agree with Reviewer #1, we added a table with the characteristics of each target

compound. We also better explain the degradation pathways of glyphosate (lines 83-86) as follows: “Glyphosate degradation processes in soil are mediated by microorganisms producing AMPA, sarcosine, and glycine (Figure 2). The first pathway involves C-N bond oxidation, with a consequent release of AMPA and glyoxylate. Another degradation pathway is possible through sarcosine oxidase, which leads to sarcosine and phosphate formation. Sarcosine is further processed to glycine (van Bruggen et al. 2018).”
2. Line 118. Abbreviations should be given in full name at their first appearance. EFSA? Table 1 LQO?
A: Sorry for this. All the abbreviation are now given in full name at their first appearance.
3. A variable to discuss would be the flow rate. The authors make this point (peaks line 209-211) but I think this variable needs to be addressed in their discussion of results. It is another variable to study in future research.
It must be borne in mind that before studying the behavior of these pollutants, it is necessary to know the behavior of the water flow. A first step would be to apply the concepts of urban hydrology.
A: Thank to Reviewer #1 for pointing it out. We carefully addressed the impact of flow rate and mobility of target pesticides (lines 226-236) as follows: “Overall, pesticides behaviour in urban catchments is poorly known and the often-unknown use by local residents increases the difficulty in quantifying and characterizing glyphosate. Some studies quantified the loss of glyphosate and investigated the wide range of influencing factors in urban areas (Hanke et al. 2010; Ramwell et al. 2014b; Tang et al. 2015). These studies showed how the loss rate is often very low (<17%) due to their relatively high percentage of permeable surfaces, high fraction of concrete blocks, and strong adsorption of glyphosate onto concrete and deposits. To better understand the run-off processes, a complete knowledge in the pesticide behaviour in the selected urban environments is needed, including how pesticides interact with different surface materials, their load and the characteristics of rainfall events with a consequent runoff volume and flow rate interpretation. Additionally, literature multivariate analyses suggest that rainfall and application cannot be used as a single parameter for interpreting the concentration variations (Tang et al. 2015).”

Reviewer #2: Unfortunately, this brief review adds little to our knowledge of glyphosate and related compounds in stormwater. Soil adsorption and complexation properties, and their critical impacts on fate and transport, as well as precipitation variables in relation to chemical application are inadequately addressed. Overall, the manuscript lacks detail and is plagued by broad statements and generalities, repetition, irrelevant information, contradictions, and inaccuracies. There is inappropriate, frequent use of "etc." as a catchall, when no further items or examples is apparent.
A: Thank to the Reviewers #2 for her/his point of view. As Reviewer #1 suggested, we carefully addressed the herbicide mobility, we improved the description of first flush, and we described the water pollution diagnostic as a tool for evaluating the interaction of pollutants with the ecosystem. We also face the efficiency of removal processes as suggested by Reviewer #3. We also deleted several “etc” from the entire manuscript, thanks for pointing it out. Thanks to the constructive suggestion of Reviewers #1 and #3, we improved the quality of the manuscript.
Reviewer #3: The study is about review of occurrence of glyphosate and its degradation products in the urban stormwater. The following comments can be considered:
1-I recommend author consider more quantitative approach in this review.
A: As suggested by Reviewer #3, we tried to be more quantitative through the manuscript (Table 1, lines 226-236). We think also that stressing too much the manuscript with several numbers and concentrations can make it not easy to read. We prefer to summarize this information in Table 2, to help the reader without complicating the manuscript.
2-It would be interesting if some figures and graphical images related to topic be added to this review paper.
A: We added the Figure 1 that summarizes the global glyphosate use trend. Furthermore, as suggested by Reviewer #3, we added the Figure 2 for summarizing the degradation pathways of glyphosate.
3-Can biological processes remove glyphosate efficiently? If so, please mention some of the processes.
A: As suggested by Reviewer #3 we faced the biological removal of glyphosate (lines

	274-279) as follows: “Biodegradation of organic compounds is known as an efficient method to remove organic pollutants from the aqueous environment. Glyphosate can be efficiently removed by biodegradation process with the formation of sarcosine, AMPA and acetyl-glyhposate (Feng et al. 2020). These processes require long residence time and suitable microorganisms' growth conditions to achieve high removal efficiency. Although the biodegradation of glyphosate has been extensively studied, the information on glyphosate biodegradation kinetics and by-product, is still rarely present on literature (Tazdaït et al. 2018).” 4-What is the first flush interpretations? Please elaborate about it. A: We better addressed the first flush approaches (lines 172-178) to read: “The first flush is defined as the initial volumes of runoff in urban catchments during rainfall events that contain the highest pollutant levels (Bertrand-Krajewski et al. 1998). There are two main methods for the first flush applicability: 1) the half-inch rule (which assumes that 90% of an event’s total pollutant load is transported in the first half inch of runoff) as a relevant volume for treatment, with a dimensionless cumulative pollutant load vs. cumulative runoff volume curves; 2) the Mass First Flush Ratio, which is the division of the proportion of mass by the cumulative runoff volume at a defined point. However, this still relies on the same dimensionless curves and an arbitrary definition (Bach et al. 2010).” 5-what type of filtration is appropriate for the glyphosate removal? Can ultrafiltration be used? A: As suggested by Reviewer #3, we face the filtration procedures from line 283 to line 292, to read: “Several methods for glyphosate and AMPA removal have been applied in the literature (Jönsson et al. 2013) and both compounds are readily degraded or removed by a number of common treatment steps like bank and dune filtration, aluminium and iron coagulant, sand and membrane filtration, chlorination, ozonation, UV irradiation, oxidation, activated carbon adsorption and air stripping. Biodegradation and adsorption processes can be highly effective in degrading or removing glyphosate and AMPA in bank filtration and sand filtration. Ultrafiltration can also be effective in removing glyphosate and AMPA but the cut-off needs careful consideration. In addition, large scale production of water by these methods is expensive and not commonly used (Speth 1993). No studies were conducted on the removal of other degradation products of glyphosate and glufosinate and no information were provided regarding the possible formation of such by-products during removal processes.” Additional Comments: In the Introduction include a brief note on the water pollution diagnostics - Krapivin, V. F., et al., (2021). Operational diagnosis of arctic waters with instrumental technology and information modeling. Water, Air, & Soil Pollution, 232(4), 1-7 - Krapivin, V. F., et al., (2017). A modeling system for monitoring water quality in lagoons. Water, Air, & Soil Pollution, 228(10), 1-12. A: Thanks to the Reviewers #3 for these citations. We added a brief note about water pollution diagnostics (lines 35-37), to read: “Tools for the water quality diagnostics were also developed in last years for different environments (V. F. Krapivin et al. 2017, 2021) with the aim to describe the interactions of pollutants with components of ecosystems.”
Additional Information:	
Question	**Response**
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Venice, 16/03/2022

Dear Editor,

We are pleased to send you a copy of the review paper entitled “The occurrence of glyphosate and its degradation products in the urban stormwater: A short review” by Matteo Feltracco (corresponding), Beatrice Rosso, Martina Favarin, Francesca Sambo, Elena Barbaro, Stefano Biondi, Andrea Gambaro, to be consider for publication in *Water, Air and Soil Pollution*. This article has not yet been published and it is not under consideration by any other journal. All authors are aware of the manuscript, and they accept responsibility for it.

This paper presents an overview of the determination of the urban runoff load of glyphosate, glufosinate and their metabolites, pointing out actual concerns and future challenges. We think that *Water, Air and Soil Pollution* is the appropriate journal to propose our research because it can improve knowledge of specific pesticides in stormwater.

Best regards,
Matteo Feltracco

The occurrence of glyphosate and its degradation products in the urban stormwater: A short review

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Keywords: stormwater, runoff, glyphosate, metabolites

Abstract

Due to urbanisation and industrialisation, water pollution is now one of the major environmental challenges of the twenty-first century. Considering the increasing of agricultural and non-agricultural settings in the last decades, the investigation of the relationship between such pesticides and urban stormwater is critical to understand how urban, residential, and industrialized areas can affect environmental safety. Recently, scientific interest has grown in stormwater chemical characterization with the aim to define its impacts in the environment and possibly to make it potable water. In this context, glyphosate, glufosinate and their degradation products have been identified as the key knowledge gap for the chemical characterization of stormwater. Research investments are needed for a better understanding of the highly polar pesticides to estimate their load, source, and dispersion of urban runoff due to residential use of herbicides. Furthermore, a more comprehensive study of wet and dry deposition and spray drift should be considered for a correct evaluation of source apportionment.

1. Introduction

Anthropogenic synthetic chemicals are an emerging issue, as they have been identified as contaminants of emerging concern (CECs) in different water environments, e.g. groundwater, surface water, drinking water and marine water (Menger et al. 2020). The presence of CECs such as current used pesticides (CUPs), endocrine disrupting chemicals (ECDs), benzothiazoles, per- and polyfluoroalkyl substances (PFAS) and microplastics are classified as emerging micro-pollutants as they may have significant adverse effects on environment and human health. In this review, the occurrence of highly polar anionic pesticides in urban and highway runoff and stormwater are discussed in detail. It is well documented that CUPs are scarcely removed during the conventional wastewater treatment, with the consequent their reintroduction into the environment. The need for treatment technologies that can provide safe treated effluents led to implement new competing technologies for the degradation of organic matter (Rosal et al. 2010). Tools for the water quality diagnostics were also developed in last years for different environments (V. F. Krapivin et al. 2017, 2021) with the aim to describe the interactions of pollutants with components of ecosystems. In addition to these strategies, the investigation of highly polar anionic pesticides needs to be focused on the chemical characterization of road dust, soil and aerosol and adjacent water bodies, together with water.

Concern about the occurrence of pesticides in various matrices started in the 1960s with the detection of persistent and volatile substances such as DDT, dieldrin, and aldrin far from their application sites (FOCUS 2008). In this context, the invention of highly polar anionic pesticides was a big breakthrough in that era. Highly polar anionic pesticides are widely used in agricultural production with glyphosate, one of the highest used herbicides in the world. Residues of glyphosate and other anionic pesticides, such as glufosinate, fosetyl-aluminium, ethephon, chlorinated compounds, triazine and the metabolites, have been detected in vegetables, cereals, and processed foods (Ehling and Reddy 2015; Tseng et al. 2004). Perchlorate is another contaminant in some fertilizers, while chlorate is commonly used as biocides in food preparation facilities. Glyphosate is widely used throughout the growing season in intensive and perennial cultures, such as that of vine, and significant runoff loss of glyphosate and aminomethylphosphonic acid (AMPA) from vineyard catchments was observed previously (Maillard et al. 2011). During rainfall events, wetland systems can intercept and retain the related pesticides (Imfeld et al. 2013).

Over the last few decades, the occurrence of highly polar anionic pesticides in stormwater has become an emerging issue of protecting the environment. Much of the pollution in stormwater can be due to pesticide use in crop and soil management practices in the agriculture sector. During rainfall events, contaminants are washed into the stormwater system and then discharged into urban rivers or rural environments. In an urban environment, the pollutant loads introduced during rainfall into the aquatic ecosystem can induce mechanical, trophic and microbial degradation of this environment (Lamprea and Ruban 2011). Furthermore, in recent studies (Ravier et al. 2019; de F. Sousa et al. 2019, Feltracco et al. 2022 submitted) glyphosate was detected in the atmospheric aerosol, pointing out the need to implement an extensive air monitoring network for glyphosate control. Particularly, this situation is an emerging concern due to the worldwide intensive urbanization that has been altering the hydrological cycle and subsequently, led to increasing stormwater runoff with deteriorated water quality. Though their major sources are agricultural use, glyphosate and glufosinate are also the most widely used herbicides for urban and residential weed control in many European countries (Tang et al. 2015). The extensive urban use of glyphosate in may result in concentration anomalies in the stormwater, particularly when the herbicides are directly applied on hard surfaces. Since pavements are semi- or totally impermeable, the runoff phenomena is enhanced than agricultural areas.

The presence of trace metals, hydrocarbons and other major ions in water have been widely described and their impact on human health and the environment are known (Deblonde et al. 2011). Despite growing recognition of highly polar anionic pesticides impacts (and glyphosate) from stormwater, a review of recent advances that directly evaluates the sources, occurrence, and removal processes remains rare.

2. The herbicides glyphosate and glufosinate

Glyphosate [N-(phosphonomethyl)glycine] has been one of the world's most widely applied herbicides since its commercial introduction in 1974. It is a non-selective herbicide, usually formulated as a salt. Glyphosate is currently the most widely used herbicide in the United States and throughout the world (Benbrook 2016). Worldwide glyphosate use was modest in the 1970s compared to the applied herbicides then on the market (e.g., metolachlor). Total worldwide use (agricultural plus non-agricultural) of glyphosate increased from about 67 million kg in 1995 to 826 million kg in 2014. Over the last decade, 6.1 billion kg of glyphosate have been applied, 71.6 % of total use worldwide from 1974–2014 (Figure 1).

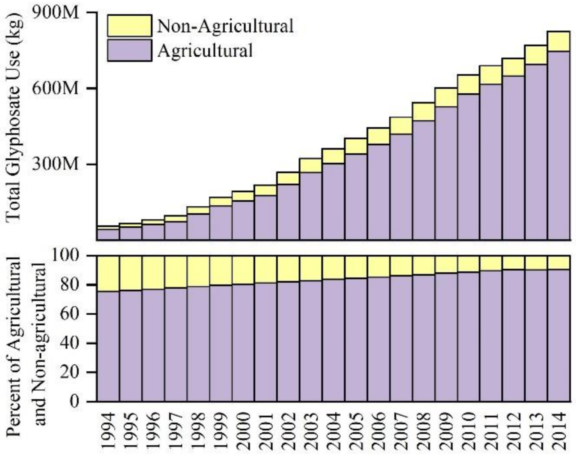

Figure 1. Global glyphosate usage. Adapted from Benbrook et al. (2016).

Given that glyphosate is moderately persistent and mobile, levels in surface and groundwater will likely rise in step with use, and this will increase the diversity of potential routes of animal and human exposure. Glyphosate degradation processes in soil are mediated by microorganisms producing AMPA, sarcosine, and glycine (Figure 2). The first pathway involves C-N bond oxidation, with a consequent release of AMPA and glyoxylate. Another degradation pathway is possible through sarcosine oxidase, which leads to sarcosine and phosphate formation. Sarcosine is further processed to glycine (van Bruggen et al. 2018).

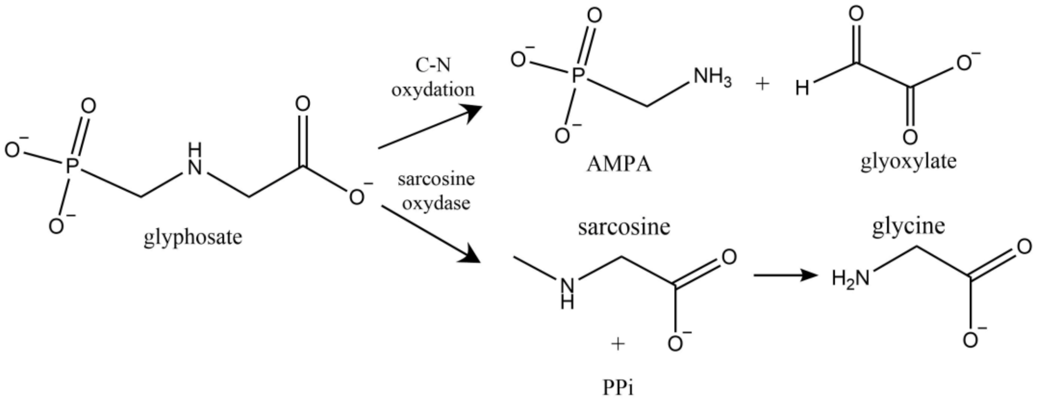

Figure 2. Pathways of glyphosate degradation by C-N oxidation and sarcosine oxidase.

Glufosinate [2-amino-4-(hydroxymethylphosphinyl)butanoic acid] is an herbicide used as an alternative pesticide in glyphosate-resistant crops. It was introduced in 1993 and it is formulated as ammonium-salt. The estimated treated area with glufosinate in the world was approximately 12 million hectares per year in 2014 in the USA (Zhou et al. 2020). Thus, glufosinate is widely used in the United States where the majority of glufosinate-resistant soybean and in South America, especially due to the large adoption of no-till cropping systems (Takano and Dayan 2020). Few information are reported regarding the degradation products and metabolites of glyphosate and glufosinate, especially related to runoff transport and wet and dry atmospheric deposition. Table 1 shows the physical and chemical characteristics of glyphosate, AMPA and glufosinate.

Table 1. Properties of glyphosate, AMPA and glufosinate (Borggaard and Gimsing 2008; Rodriguez et al. 2020; Singh and Singh 2016; van Bruggen et al. 2018).

Common name	**Glyphosate**	**AMPA**	**Glufosinate**
Chemical name	N-(phosphonomethyl) glycine	aminomethyl phosphonic acid	2-amino-4-(hydroxymethylphosphinyl) butanoic acid
CAS number	1071-83-6	1066-51-9	51276-47-2
Molecular formula	$C_3H_8NO_5P$	CH_6NO_3P	$C_5H_{12}NO_4P$
Exact mass	169.01 g mol^{-1}	111.01 g mol^{-1}	181.13 g mol^{-1}
Vapour pressure (25 °C)	1.31×10^{-5} Pa	8.44×10^{-4} Pa	3.10×10^{-5} Pa
Henry’s law volatility constant (25 °C)	2.1×10^{-7} Pa m^3 mol^{-1}	2.6×10^{-3} Pa m^3 mol^{-1}	4.48×10^{-9} Pa m^3 mol^{-1}
Solubility in water (20 °C)	10.5 g L^{-1}	1467 g L^{-1}	500 g L^{-1}
Solid/water distribution coefficient (K_d)	5.3–900 L kg^{-1}	15–1554 L kg^{-1}	/ (slightly mobile)
Soil organic carbon normalized adsorption coefficient (Koc)	884–60 000 L kg^{-1}	1160–24 800 L kg^{-1}	~600 L kg^{-1}
Half-life (DT_{50}) in soil	1–197 days	23–958 days	6-11 days

3. Sources

Studies in the literature reported that pesticides applied to the soil surface may be transported rapidly to the groundwater, thereby bypassing soils (Vereecken 2005). Due to their bioaccumulation ability, they have been detected in surface and ground water (Battaglin et al. 2014; Lapworth et al. 2006; van Stempvoort et al. 2014), sediment (Pandey et al. 2019; Skeff et al. 2018), aquatic organisms (Feltracco et al. 2021; Mercurio et al. 2014) and aerosols (Ravier et al. 2019).

Glyphosate and similar product (like glufosinate, bialaphos and etephon) are atomized with sprayers directly to target weeds (Stephenson et al. 2006). The most common routes of pesticide entry into the atmosphere could be the drift during their application and volatilization during spraying or from plants (Tzanetou and Karasali 2020), depending on the physicochemical properties of the pesticide (vapor pressure, solubility, adsorption coefficient and molecular mass). On the other hand, although herbicides containing glyphosate are not intentionally applied directly to the soil, they may contaminate soils in and around the treated areas, via spray drift during their application and after being washed off from leaf surfaces with rainfall.

The fate of these compounds in the soil is complex and attributed to degradation, immobilization, mineralization and leaching (Mesnage et al. 2019). Glyphosate and similar products can plausibly contaminate surface waters through erosion, and when rainfall occurs, ionic pesticides are easily dissolved by rain, or rain washes granules containing adsorbed pesticides (Richards et al. 2018). Even when adsorbed to soil particles, it may dissolve back into the water in the presence of phosphates (Tzanetou and Karasali 2020). The wet and dry depositions on surfaces are also collected by stormwater flows during rainfall events (Popp et al. 2008).

4. Glyphosate, glufosinate and their metabolites in urban stormwater

Urban runoff consists of a collection from various input sources, including rain, road and highways runoff, domestic garden runoff, etc. Urbanization has led to an increase in urban runoff, accompanied by a decline in water quality during rainfall. Urban runoff occurs from the road surface, the application zone, and the adjacent vegetated environment (Chen et al. 2019). Sources of glyphosate and its metabolites from stormwater runoff are various and many of these originate from site applications for pesticides control purposes in both urban and agricultural areas. The degradation pathway of glyphosate into AMPA through laboratory experiments is well studied and is mainly determined by microbial processes in soil and water (Mercurio et al. 2014). Another metabolite of glyphosate is N-acetyl AMPA through the action of N-phenylacetyltransferase. Glyphosate is inactivated by converting it to N-acetyl glyphosate and further N-acetyl AMPA and AMPA (Nørskov et al. 2019). Low acute toxicity was observed by European Food Safety Authority (EFSA) when glyphosate was administered to mammals and no skin irritation or potential for skin sensitisation were attributed to the active substance (EFSA 2015). On the other hand, the International Agency for Research on Cancer (IARC) classified glyphosate as ‘probably carcinogenic to humans’ (IARC 2015). Furthermore, it has been established by researchers that glyphosate can persist in the environment (Ighalo et al. 2021). Despite a wide range of organophosphates derivates are applied and found in agriculture environments, most of the studies in stormwaters focused on glyphosate occurrence and toxicology and its main metabolite AMPA. Table 2 reports all studies considered in the present review.

Huang et al. (2004) determined the concentrations of glyphosate and AMPA in stormwater from USA for up to 11 storms following herbicide application. Both glyphosate and AMPA were detected, but the latter was detected at higher concentrations, in more storm events, and at greater depth in the soil profile, due to its high mobility. The authors suggested that glyphosate tends to readily transform to AMPA because only AMPA was detected in the last storm events. Zgheib et al. (2011) described the occurrence of glyphosate and AMPA on both dissolved and particulate phases in stormwater of France suburbs. Again, only AMPA was measured in all samples in both phases. After entering in the stormwater, organophosphate with a strong adsorption propensity can easily adsorb to the suspended particulate matter (Doong et al. 2002), explaining the non-negligible presence of AMPA in particulate matter. The undetected pesticides in this study are the same as those reported previously for wastewater in Paris and Nantes (J. Gasperi et al. 2014; Johnny Gasperi et al. 2009). Lamprea et al. (2011) conducted a two-year study of glyphosate and AMPA in both the stormwater and wastewater of urban watersheds of France. In this case, glyphosate reached a maximum value of 71 µg L^{-1}, this was due to the wide use of glyphosate as an herbicide in the sampled area, which underscores this difference. Those results agree with a previous study conducted similarly in the suburban catchment basin of Saint Joseph de Porterie, North of Nantes (Ruban et al. 2005) where only glyphosate was studied. Both studies conducted in Nantes showed high concentrations especially in spring and autumn when glyphosate use is maximum. Martin et al. (2012) quantified glyphosate, AMPA and glufosinate at the inlet of the stormwater wetland from April to September in Rouffach (Alsace, France). Values of these three organophosphates were very variable and the study did not explain such variability, even though the trend seems to follow the pesticides application route. Imfeld et al. (2013) pointed out that transport of stormwater-associated glyphosate and AMPA largely vary over time. A wetland attenuation efficiency of glyphosate and AMPA loadings was also tested for the first time. Reduction of glyphosate and AMPA concentrations was 80% and correlated with larger vegetation cover, and likely with gradual adaptation of glyphosate-degrading microorganisms. Richards et al. (2018) performed four high-frequency sampling campaigns (from 2015 to 2017) following controlled spray applications in the state of New York. The campaigns were also grouped according to dry and wet initial conditions at the time of spraying. The aim of such study was mainly to understand how runoff events were linked with pesticides spraying, considering the role of soil moisture conditions. Any adsorbed glyphosate in the stormwater would potentially increase the total efflux, as pointed out by the author. Two investigations were conducted by Okada et al. (2019, 2020) in Melbourne where the levels of glyphosate and AMPA were quantified in environmental samples from diverse surface stormwater sources. Surprisingly, no glyphosate or AMPA was present in water samples taken from rural streams. However, glyphosate and AMPA were detected urban wetland samples, suggesting that household use might be an important source of glyphosate contamination in urban stormwaters. Hanke et al. (2010) monitored the glyphosate and AMPA contamination of stormwaters after moderate and strong rainfall in Switzerland. Here, the concentration of glyphosate was dominated by first flush peak from sealed, while AMPA may result of the degradation of phosphonates used as detergents (Botta et al. 2009). The first flush is defined as the initial volumes of runoff in urban catchments during rainfall events that contain the highest pollutant levels (Bertrand-Krajewski et al. 1998). There are two main methods for the first flush applicability: 1) the half-inch rule (which assumes that 90% of an event's total pollutant load is transported in the first half inch of runoff) as a relevant volume for treatment, with a dimensionless cumulative pollutant load vs. cumulative runoff volume curves; 2) the Mass First Flush Ratio, which is the division of the proportion of mass by the cumulative runoff volume at a defined point. However, this still relies on the same dimensionless curves and an arbitrary definition (Bach et al. 2010). Tang et al. (2015) investigates the use and loss of glyphosate from a typical Belgian residential area, aiming to quantify glyphosate loss via stormwater runoff. The overall loss rate of glyphosate was <0.5% and varied considerably among rainfall events. Further statistical analyses suggested that rainfall land application did not explain the concentration variations, and surface material and connectivity to the drain inlets of the application sites must be considered. Ramwell et al. (2014) quantify glyphosate and AMPA concentrations in surface stormwater drain that could be attributed to amateur, non-professional usage alone. The study found out that glyphosate concentrations in drain flow were lower than concentrations reported elsewhere from professional use in urban areas.

As reported in Table 2, glyphosate and AMPA are very often detected in urban stormwater, and glufosinate, when studied, is also often present. This suggests that highly polar pesticides are widely used both in urban and residential areas, with direct implication of stormwater pollutants. Many studies are focusing on removal processes of glyphosate (Hossaini et al. 2014; Hu et al. 2013; Jönsson et al. 2013; Pereira et al. 2021), but a more responsible use of urban herbicides is mandatory to contain their load in the environment. Such removal processes performances varied significantly depending on pH, glyphosate or AMPA concentrations, temperature, etc. Thus, many variables should be considered, and many treatment plants are not designed to deal with this approach. If other variables are considered, such as metabolites, degradation products of glyphosate and glufosinate, or new pesticides, removal processes should be further updated.

Only one study was found for the quantification of glyphosate and AMPA in the suspended particulate matter of stormwater (Zgheib et al. 2011). As described in other studies (mac Loughlin et al. 2020; Ronco et al. 2016), the presence of glyphosate is very often associated with the suspended particulate matter and its trend can be associated to water-to-colloid transfer during transport. This is might due to the glyphosate adsorbing properties to soil particles (Feltracco et al. 2021). These transfer phenomena should be also considered in future studies in order to better understand the behaviour of highly polar pesticides during runoff.

5. The unexplored degradation products

Detailed studies about the presence of other highly polar pesticides in stormwater runoff originated from various sources are now missing. Amongst the hundreds and thousands of pesticides sought in the environment, the so-called highly anionic polar pesticides are particularly difficult to analyse due to ultratrace concentrations (Melton et al. 2019). Apart from AMPA, a metabolite of glyphosate is also N-acetyl AMPA through the action of N-phenylacetyltransferase. Furthermore, one of the degradation products of glufosinate is N-acetyl glufosinate, found as the main metabolite in transgenic sugar beet cells. Another metabolite of glufosinate is 3-methylphosphinicopropionic acid (MPPA), which it has similar biological and toxicological effects to the parent compound (Aris and Leblanc 2011). Few studies are present regarding the quantification of organophosphorus pesticides (Pedersen et al. 2006; Shimabuku et al. 2022; Sumon et al. 2018), but not directly related to glyphosate and its degradation products. Furthermore, it is known how AMPA can also derive from the degradation of other molecules than glyphosate. Detergents as ethylene diamine tetramethylene phosphonate can be degraded in AMPA and found in the environment (Botta et al. 2009). The detergent by-product should be deeply investigated, considering their massive use in urban and residential environments. Their investigation can serve as proxy to understand how glyphosate, glufosinate and detergents are degraded through runoff.

6. Variables affecting highly polar pesticides in stormwater and mitigation strategies

The concentration and distribution of highly polar pesticides can be affected by many factors, including precipitation, use pattern, and properties of the application surface. The presence of pesticides in stormwater is directly dependent on rainfall patterns. Moderate but frequent rain may contribute to delivering many pollutants from highway pavements (Hwang and Weng 2015).

Table 2. A summary of glyphosate and related pesticides in stormwater (SW= stormwater, SPM = suspended particulate matter, LOQ = limit of quantification).

Pesticide	Country	Site	Season	Mean	Range	Citation
Glyphosate	California (USA)	Highway	Winter	2.69 µg L^{-1}	1.36 – 9.44 µg L^{-1}	Huang et al. 2004
	Paris (FRA)	Suburb	Winter	0.98 µg L^{-1} SW	ND – 1.9 µg L^{-1} SW	Zgheib et al. 2011
	Paris (FRA)	Suburb	Winter	<LOQ SPM	<LOQ SPM	Zgheib et al. 2011
	Pin Sec, Nantes (FRA)	Residential	Autumn	3.27 µg L^{-1}	1.1 – 71 µg L^{-1}	Lamprea and Ruban 2011
	Gohards, Nantes (FRA)	Residential/Commercial	Autumn	2.15 µg L^{-1}	<0.10 – 3.8 µg L^{-1}	Lamprea and Ruban 2011
	Nantes (FRA)	Urban	Autumn/Winter	2.71 µg L^{-1}	–	Ruban et al. 2005
	Rouffac (FRA)	Urban/wetland	Spring	4.13 µg L^{-1}	0.3 – 11.0 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Summer	5.95 µg L^{-1}	0.2 – 15.0 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Spring	19.9 µg L^{-1}	0.1 – 150 µg L^{-1}	Imfeld et al. 2013
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.34 µg L^{-1}	–	Gasperi et al. 2014
	State of New York (USA)	Urban/Rural	Spring/Autumn	–	ND – 90 µg L^{-1}	Richards et al. 2018
	Melbourne (AUS)	Urban	Autumn	–	1.95 – 2.96 µg L^{-1}	Okada et al. 2019
	Melbourne (AUS)	Urban	Autumn/Winter	1.1 µg L^{-1}	0.25 – 14.2 µg L^{-1}	Okada et al. 2020
	North-East of Switzerland (SWI)	Urban	Spring/Summer/Autumn	–	ND – 4.2 µg L^{-1}	Hanke et al. 2010
	Flanders, Belgium (BEL)	Residential	Spring/Summer	2.3 µg L^{-1}	0.6 – 6.1 µg L^{-1}	Tang et al. 2015
	York (UK)	Residential	Summer	–	ND – 8.99 µg L^{-1}	Ramwell et al. 2014
AMPA	California (USA)	Highway	Winter	2.75 µg L^{-1}	–	Huang et al. 2004
	Paris (FRA)	Suburb	Winter	0.45 µg L^{-1} SW	0.32 – 0.66 µg L^{-1} SW	Zgheib et al. 2011
	Paris (FRA)	Suburb	Winter	0.78 µg L^{-1} SPM	0.23 – 1.60 µg L^{-1} SPM	Zgheib et al. 2011
	Pin Sec, Nantes (FRA)	Residential	Autumn	0.35 µg L^{-1}	0.2 – 1.5 µg L^{-1}	Lamprea and Ruban 2011
	Gohards, Nantes (FRA)	Residential/Commercial	Autumn	0.23 µg L^{-1}	<0.1 – 0.4 µg L^{-1}	Lamprea and Ruban 2011
	Rouffac (FRA)	Urban/wetland	Spring	1.37 µg L^{-1}	0.2 – 2.3 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Summer	2.53 µg L^{-1}	ND – 21 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Spring	3.3 µg L^{-1}	–	Imfeld et al. 2013
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.82 µg L^{-1}	–	Gasperi et al. 2014
	Melbourne (AUS)	Urban	Autumn	–	0.55 – 2.42 µg L^{-1}	Okada et al. 2019
	Melbourne (AUS)	Urban	Autumn	1.3 µg L^{-1}	0.25 – 10 µg L^{-1}	Okada et al. 2020
	North-East of Switzerland	Urban	Spring/Summer/Autumn	–	0.04 – 1.11 µg L^{-1}	Hanke et al. 2010
	Flanders, Belgium (BEL)	Residential	Spring/Summer	2.5 µg L^{-1}	0.2 – 16 µg L^{-1}	Tang et al. 2015
	York (UK)	Residential	Summer	–	ND – 1.15 µg L^{-1}	Ramwell et al. 2014
Glufosinate	Rouffac (FRA)	Urban/wetland	Spring	0.85 µg L^{-1}	ND – 6.3 µg L^{-1}	Martin et al. 2012
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.76 µg L^{-1}	–	Gasperi et al. 2014

On the other hand, less frequent but intense rainfalls produce lower pollutant loads (Pereira et al. 2021). For example, a long dry period allows some pesticides to be degraded (Chinen et al. 2016). Therefore, an evaluation of the typical half-life of the various degradation products of glyphosate and glufosinate can provide information about their formation during dry periods. Overall, pesticides behaviour in urban catchments is poorly known and the often-unknown use by local residents increases the difficulty in quantifying and characterizing glyphosate. Some studies quantified the loss of glyphosate and investigated the wide range of influencing factors in urban areas (Hanke et al. 2010; Ramwell et al. 2014b; Tang et al. 2015). These studies showed how the loss rate is often very low (<17%) due to their relatively high percentage of permeable surfaces, high fraction of concrete blocks, and strong adsorption of glyphosate onto concrete and deposits. To better understand the run-off processes, a complete knowledge in the pesticide behaviour in the selected urban environments is needed, including how pesticides interact with different surface materials, their load and the characteristics of rainfall events with a consequent runoff volume and flow rate interpretation. Additionally, literature multivariate analyses suggest that rainfall and application cannot be used as a single parameter for interpreting the concentration variations (Tang et al. 2015).

Although the capture of stormwater from the first flush is considered as a useful measure in controlling pollutions, inefficiency of the treatment system still prevails when a large volume of storm runoff is captured from large catchments (>10 ha) (Mamun et al. 2020). Despite this, concentration dynamics of glyphosate at sub-catchments <10 ha was dominated by first flush peaks followed by lower concentration peaks from diffuse sources (Hanke et al. 2010). These discrepancies are due to the approach to first flush interpretations (McCarthy 2009). As a result, various strategies have been formed to help manage urban stormwater pollution by maximising treatment for the initial part of storm events. For robust analyses of different factors or for obtain management insights, a spatially distributed hydrological model is beneficial to account for the spatial properties and urban hydrology.

The pesticides use pattern can be proportioned among the following routes: the proportion of the pesticide deposited onto the target area; the proportion deposited onto the adjacent non-target area; and the proportion lost to the atmosphere during application (FOCUS 2008). Apart from runoff removal, dry and wet deposition should be also considered. Wet deposition is determined by the precipitation rate, the air/water partition coefficient, and the washout ratio for particles, while dry deposition is due to the deposition of dry aerosols, which contain adsorbed substances (Asman et al. 2005). Although herbicides containing glyphosate are not intentionally applied directly to the soil, they may contaminate surfaces around the treated areas, via the so-called spray drift during their application. In addition, it was estimated that 97% of glyphosate existing in the atmosphere could be removed by weekly rainfall greater than 30 mm (Tzanetou and Karasali 2020). Generally, few monitoring studies have been conducted for the determination of glyphosate and glufosinate residues in atmospheric samples, and strong variation in collection time and duration, the analytes selected, the analytical methods used were found (van Dijk and Guicherit 1999).

Solid adsorption is the most cost-effective techniques for removing glyphosate in an aqueous solution. Despite this, the methodology is followed by time consuming modelling processes (Pereira et al. 2021). The performance of coagulation for incorporation of particulates from the stormwater is strongly dependent on pH and coagulant concentration. Some studies report that filtration is more efficient rather than flotation for the removal of adsorbed particles (Jönsson et al. 2013). Other results indicate that the foulants can be effectively removed by nanofiltration from water. Addition of intermediate concentrations of NaCl results in better foulant separation (Yuan et al. 2018). This method was applied on drinking water and is likely difficult to use with a complex matrix like stormwaters. Mayakaduwa et al. (2016) studied the use of woody biochar obtained as waste from a bioenergy industry plant. The kinetic curves showed that the adsorption equilibrium time is relatively short, less than 1 h. Various laboratory tests have shown that glyphosate and AMPA are both degraded or removed by a number of common treatment (chlorination, ozonation, UV irradiation and air stripping) steps at drinking water treatment plants, but few studies investigated the stormwater in order to understand if an efficient removal of glyphosate, glufosinate and degradation products is possible (Feng et al. 2020).

Biodegradation of organic compounds is known as an efficient method to remove organic pollutants from the aqueous environment. Glyphosate can be efficiently removed by biodegradation process with the formation of sarcosine, AMPA and acetyl-glyhposate (Feng et al. 2020). These processes require long residence time and suitable microorganisms' growth conditions to achieve high removal efficiency. Although the biodegradation of glyphosate has been extensively studied, the information on glyphosate biodegradation kinetics and by-product, is still rarely present on literature (Tazdaït et al. 2018).

The efficient evaluation of removal plants is not the main aim of this review, but as most of the studies were conducted at the lab scale, further research is still needed to study the practical application of these technologies. The energy consumption and cost of these technologies also need to be systematically analysed. Several methods for glyphosate and AMPA removal have been applied in the literature (Jönsson et al. 2013) and both compounds are readily degraded or removed by a number of common treatment steps like bank and dune filtration, aluminium and iron coagulant, sand and membrane filtration, chlorination, ozonation, UV irradiation, oxidation, activated carbon adsorption and air stripping. Biodegradation and adsorption processes can be highly effective in degrading or removing glyphosate and AMPA in bank filtration and sand filtration. Ultrafiltration can also be effective in removing glyphosate and AMPA, but the cut-off needs careful consideration. In addition, large scale production of water by these methods is expensive and not commonly used (Speth 1993). No studies were conducted on the removal of other degradation products of glyphosate and glufosinate and no information were provided regarding the possible formation of such by-products during removal processes.

7. Conclusions

This review wants to highlight future research directions in this field: additional studies involving impact of stormwater runoff of urban areas, with a deeper apportioning of sources, also considering the spray drift phenomenon and wet and dry deposition. In most cases, the occurrences, and concentrations of pesticides varied considerably, and these were related to the load precipitation, pesticides use and national legislation. Moreover, future studies on highly polar pesticides occurrence in stormwater should be focused on the degradation products that can be formed during transport. This could be a key knowledge gap hindering the development of control measures for pesticides in stormwater runoff, which is vital both for the protection of ecosystems and the future use of stormwater as a potable water resource.

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The occurrence of glyphosate and its degradation products in the urban stormwater: A short review

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Abstract

Due to urbanisation and industrialisation, water pollution is now one of the major environmental challenges of the twenty-first century. Considering the increasing of agricultural and non-agricultural settings in the last decades, the investigation of the relationship between such pesticides and urban stormwater is critical to understand how urban, residential, and industrialized areas can affect environmental safety. Recently, scientific interest has grown in stormwater chemical characterization with the aim to define its impacts in the environment and possibly to make it potable water. In this context, glyphosate, glufosinate and their degradation products have been identified as the key knowledge gap for the chemical characterization of stormwater. Research investments are needed for a better understanding of the highly polar pesticides to estimate their load, source, and dispersion of urban runoff due to residential use of herbicides. Furthermore, a more comprehensive study of wet and dry deposition and spray drift should be considered for a correct evaluation of source apportionment.

1. Introduction

Anthropogenic synthetic chemicals are an emerging issue, as they have been identified as contaminants of emerging concern (CECs) in different water environments, e.g. groundwater, surface water, drinking water and marine water (Menger et al. 2020). The presence of CECs such as current used pesticides (CUPs), endocrine disrupting chemicals (ECDs), benzothiazoles, per- and polyfluoroalkyl substances (PFAS) and microplastics are classified as emerging micro-pollutants as they may have significant adverse effects on environment and human health. In this review, the occurrence of highly polar anionic pesticides in urban and highway runoff and stormwater are discussed in detail. It is well documented that CUPs are scarcely removed during the conventional wastewater treatment, with the consequent their reintroduction into the environment. The need for treatment technologies that can provide safe treated effluents led to implement new competing technologies for the degradation of organic matter (Rosal et al. 2010). Tools for the water quality diagnostics were also developed in last years for different environments (V. F. Krapivin et al. 2017, 2021) with the aim to describe the interactions of pollutants with components of ecosystems. In addition to these strategies, the investigation of highly polar anionic pesticides needs to be focused on the chemical characterization of road dust, soil and aerosol and adjacent water bodies, together with water.

Concern about the occurrence of pesticides in various matrices started in the 1960s with the detection of persistent and volatile substances such as DDT, dieldrin, and aldrin far from their application sites (FOCUS 2008). In this context, the invention of highly polar anionic pesticides was a big breakthrough in that era. Highly polar anionic pesticides are widely used in agricultural production with glyphosate, one of the highest used herbicides in the world. Residues of glyphosate and other anionic pesticides, such as glufosinate, fosetyl-aluminium, ethephon, chlorinated compounds, triazine and the metabolites, have been detected in vegetables, cereals, and processed foods (Ehling and Reddy 2015; Tseng et al. 2004). Perchlorate is another contaminant in some fertilizers, while chlorate is commonly used as biocides in food preparation facilities. Glyphosate is widely used throughout the growing season in intensive and perennial cultures, such as that of vine, and significant runoff loss of glyphosate and aminomethylphosphonic acid (AMPA) from vineyard catchments was observed previously (Maillard et al. 2011). During rainfall events, wetland systems can intercept and retain the related pesticides (Imfeld et al. 2013).

Over the last few decades, the occurrence of highly polar anionic pesticides in stormwater has become an emerging issue of protecting the environment. Much of the pollution in stormwater can be due to pesticide use in crop and soil management practices in the agriculture sector. During rainfall events, contaminants are washed into the stormwater system and then discharged into urban rivers or rural environments. In an urban environment, the pollutant loads introduced during rainfall into the aquatic ecosystem can induce mechanical, trophic and microbial degradation of this environment (Lamprea and Ruban 2011). Furthermore, in recent studies (Ravier et al. 2019; de F. Sousa et al. 2019, Feltracco et al. 2022 submitted) glyphosate was detected in the atmospheric aerosol, pointing out the need to implement an extensive air monitoring network for glyphosate control. Particularly, this situation is an emerging concern due to the worldwide intensive urbanization that has been altering the hydrological cycle and subsequently, led to increasing stormwater runoff with deteriorated water quality. Though their major sources are agricultural use, glyphosate and glufosinate are also the most widely used herbicides for urban and residential weed control in many European countries (Tang et al. 2015). The extensive urban use of glyphosate in may result in concentration anomalies in the stormwater, particularly when the herbicides are directly applied on hard surfaces. Since pavements are semi- or totally impermeable, the runoff phenomena is enhanced than agricultural areas.

The presence of trace metals, hydrocarbons and other major ions in water have been widely described and their impact on human health and the environment are known (Deblonde et al. 2011). Despite growing recognition of highly polar anionic pesticides impacts (and glyphosate) from stormwater, a review of recent advances that directly evaluates the sources, occurrence, and removal processes remains rare.

2. The herbicides glyphosate and glufosinate

Glyphosate [N-(phosphonomethyl)glycine] has been one of the world's most widely applied herbicides since its commercial introduction in 1974. It is a non-selective herbicide, usually formulated as a salt. Glyphosate is currently the most widely used herbicide in the United States and throughout the world (Benbrook 2016). Worldwide glyphosate use was modest in the 1970s compared to the applied herbicides then on the market (e.g., metolachlor). Total worldwide use (agricultural plus non-agricultural) of glyphosate increased from about 67 million kg in 1995 to 826 million kg in 2014. Over the last decade, 6.1 billion kg of glyphosate have been applied, 71.6 % of total use worldwide from 1974–2014 (Figure 1).

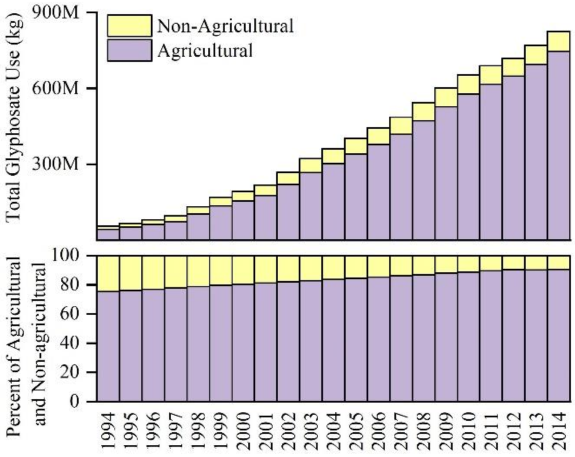

Figure 1. Global glyphosate usage. Adapted from Benbrook et al. (2016).

Given that glyphosate is moderately persistent and mobile, levels in surface and groundwater will likely rise in step with use, and this will increase the diversity of potential routes of animal and human exposure. Glyphosate degradation processes in soil are mediated by microorganisms producing AMPA, sarcosine, and glycine (Figure 2). The first pathway involves C-N bond oxidation, with a consequent release of AMPA and glyoxylate. Another degradation pathway is possible through sarcosine oxidase, which leads to sarcosine and phosphate formation. Sarcosine is further processed to glycine (van Bruggen et al. 2018).

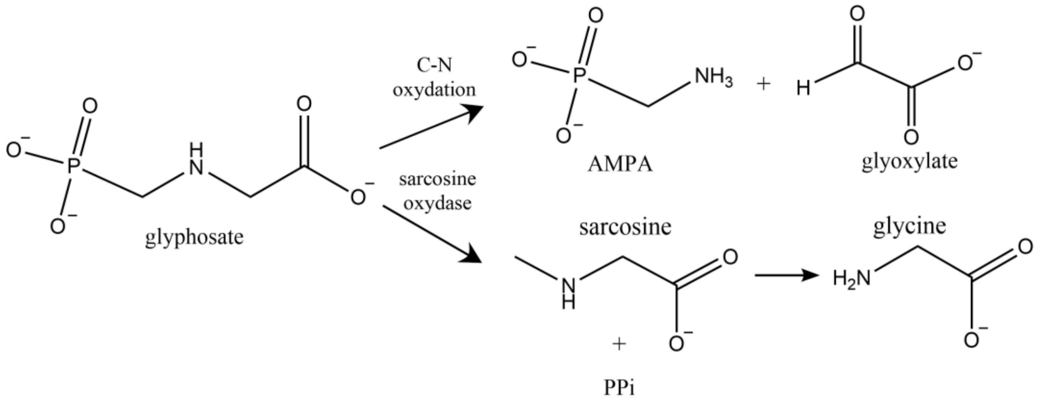

Figure 2. Pathways of glyphosate degradation by C-N oxidation and sarcosine oxidase.

Glufosinate [2-amino-4-(hydroxymethylphosphinyl)butanoic acid] is an herbicide used as an alternative pesticide in glyphosate-resistant crops. It was introduced in 1993 and it is formulated as ammonium-salt. The estimated treated area with glufosinate in the world was approximately 12 million hectares per year in 2014 in the USA (Zhou et al. 2020). Thus, glufosinate is widely used in the United States where the majority of glufosinate-resistant soybean and in South America, especially due to the large adoption of no-till cropping systems (Takano and Dayan 2020). Few information are reported regarding the degradation products and metabolites of glyphosate and glufosinate, especially related to runoff transport and wet and dry atmospheric deposition. Table 1 shows the physical and chemical characteristics of glyphosate, AMPA and glufosinate.

Table 1. Properties of glyphosate, AMPA and glufosinate (Borggaard and Gimsing 2008; Rodriguez et al. 2020; Singh and Singh 2016; van Bruggen et al. 2018).

Common name	**Glyphosate**	**AMPA**	**Glufosinate**
Chemical name	N-(phosphonomethyl) glycine	aminomethyl phosphonic acid	2-amino-4-(hydroxy-methylphosphinyl) butanoic acid
CAS number	1071-83-6	1066-51-9	51276-47-2
Molecular formula	$C_3H_8NO_5P$	CH_6NO_3P	$C_5H_{12}NO_4P$
Exact mass	169.01 g mol^{-1}	111.01 g mol^{-1}	181.13 g mol^{-1}
Vapour pressure (25 °C)	1.31×10^{-5} Pa	8.44×10^{-4} Pa	3.10×10^{-5} Pa
Henry's law volatility constant (25 °C)	2.1×10^{-7} Pa m^3 mol^{-1}	2.6×10^{-3} Pa m^3 mol^{-1}	4.48×10^{-9} Pa m^3 mol^{-1}
Solubility in water (20 °C)	10.5 g L^{-1}	1467 g L^{-1}	500 g L^{-1}
Solid/water distribution coefficient (K_d)	5.3–900 L kg^{-1}	15–1554 L kg^{-1}	/ (slightly mobile)
Soil organic carbon normalized adsorption coefficient (Koc)	884–60 000 L kg^{-1}	1160–24 800 L kg^{-1}	~600 L kg^{-1}
Half-life (DT_{50}) in soil	1–197 days	23–958 days	6-11 days

3. Sources

Studies in the literature reported that pesticides applied to the soil surface may be transported rapidly to the groundwater, thereby bypassing soils (Vereecken 2005). Due to their bioaccumulation ability, they have been detected in surface and ground water (Battaglin et al. 2014; Lapworth et al. 2006; van Stempvoort et al. 2014), sediment (Pandey et al. 2019; Skeff et al. 2018), aquatic organisms (Feltracco et al. 2021; Mercurio et al. 2014) and aerosols (Ravier et al. 2019).

Glyphosate and similar product (like glufosinate, bialaphos and etephon) are atomized with sprayers directly to target weeds (Stephenson et al. 2006). The most common routes of pesticide entry into the atmosphere could be the drift during their application and volatilization during spraying or from plants (Tzanetou and Karasali 2020), depending on the physicochemical properties of the pesticide (vapor pressure, solubility, adsorption coefficient and molecular mass). On the other hand, although herbicides containing glyphosate are not intentionally applied directly to the soil, they may contaminate soils in and around the treated areas, via spray drift during their application and after being washed off from leaf surfaces with rainfall.

The fate of these compounds in the soil is complex and attributed to degradation, immobilization, mineralization and leaching (Mesnage et al. 2019). Glyphosate and similar products can plausibly contaminate surface waters through erosion, and when rainfall occurs, ionic pesticides are easily dissolved by rain, or rain washes granules containing adsorbed pesticides (Richards et al. 2018). Even when adsorbed to soil particles, it may dissolve back into the water in the presence of phosphates (Tzanetou and Karasali 2020). The wet and dry depositions on surfaces are also collected by stormwater flows during rainfall events (Popp et al. 2008).

4. Glyphosate, glufosinate and their metabolites in urban stormwater

Urban runoff consists of a collection from various input sources, including rain, road and highways runoff, domestic garden runoff, etc. Urbanization has led to an increase in urban runoff, accompanied by a decline in water quality during rainfall. Urban runoff occurs from the road surface, the application zone, and the adjacent vegetated environment (Chen et al. 2019). Sources of glyphosate and its metabolites from stormwater runoff are various and many of these originate from site applications for pesticides control purposes in both urban and agricultural areas. The degradation pathway of glyphosate into AMPA through laboratory experiments is well studied and is mainly determined by microbial processes in soil and water (Mercurio et al. 2014). Another metabolite of glyphosate is N-acetyl AMPA through the action of N-phenylacetyltransferase. Glyphosate is inactivated by converting it to N-acetyl glyphosate and further N-acetyl AMPA and AMPA (Nørskov et al. 2019). Low acute toxicity was observed by European Food Safety Authority (EFSA) when glyphosate was administered to mammals and no skin irritation or potential for skin sensitisation were attributed to the active substance (EFSA 2015). On the other hand, the International Agency for Research on Cancer (IARC) classified glyphosate as ‘probably carcinogenic to humans’ (IARC 2015). Furthermore, it has been established by researchers that glyphosate can persist in the environment (Ighalo et al. 2021). Despite a wide range of organophosphates derivates are applied and found in agriculture environments, most of the studies in stormwaters focused on glyphosate occurrence and toxicology and its main metabolite AMPA. Table 2 reports all studies considered in the present review.

Huang et al. (2004) determined the concentrations of glyphosate and AMPA in stormwater from USA for up to 11 storms following herbicide application. Both glyphosate and AMPA were detected, but the latter was detected at higher concentrations, in more storm events, and at greater depth in the soil profile, due to its high mobility. The authors suggested that glyphosate tends to readily transform to AMPA because only AMPA was detected in the last storm events. Zgheib et al. (2011) described the occurrence of glyphosate and AMPA on both dissolved and particulate phases in stormwater of France suburbs. Again, only AMPA was measured in all samples in both phases. After entering in the stormwater, organophosphate with a strong adsorption propensity can easily adsorb to the suspended particulate matter (Doong et al. 2002), explaining the non-negligible presence of AMPA in particulate matter. The undetected pesticides in this study are the same as those reported previously for wastewater in Paris and Nantes (J. Gasperi et al. 2014; Johnny Gasperi et al. 2009). Lamprea et al. (2011) conducted a two-year study of glyphosate and AMPA in both the stormwater and wastewater of urban watersheds of France. In this case, glyphosate reached a maximum value of 71 µg L^{-1}, this was due to the wide use of glyphosate as an herbicide in the sampled area, which underscores this difference. Those results agree with a previous study conducted similarly in the suburban catchment basin of Saint Joseph de Porterie, North of Nantes (Ruban et al. 2005) where only glyphosate was studied. Both studies conducted in Nantes showed high concentrations especially in spring and autumn when glyphosate use is maximum. Martin et al. (2012) quantified glyphosate, AMPA and glufosinate at the inlet of the stormwater wetland from April to September in Rouffach (Alsace, France). Values of these three organophosphates were very variable and the study did not explain such variability, even though the trend seems to follow the pesticides application route. Imfeld et al. (2013) pointed out that transport of stormwater-associated glyphosate and AMPA largely vary over time. A wetland attenuation efficiency of glyphosate and AMPA loadings was also tested for the first time. Reduction of glyphosate and AMPA concentrations was 80% and correlated with larger vegetation cover, and likely with gradual adaptation of glyphosate-degrading microorganisms. Richards et al. (2018) performed four high-frequency sampling campaigns (from 2015 to 2017) following controlled spray applications in the state of New York. The campaigns were also grouped according to dry and wet initial conditions at the time of spraying. The aim of such study was mainly to understand how runoff events were linked with pesticides spraying, considering the role of soil moisture conditions. Any adsorbed glyphosate in the stormwater would potentially increase the total efflux, as pointed out by the author. Two investigations were conducted by Okada et al. (2019, 2020) in Melbourne where the levels of glyphosate and AMPA were quantified in environmental samples from diverse surface stormwater sources. Surprisingly, no glyphosate or AMPA was present in water samples taken from rural streams. However, glyphosate and AMPA were detected urban wetland samples, suggesting that household use might be an important source of glyphosate contamination in urban stormwaters. Hanke et al. (2010) monitored the glyphosate and AMPA contamination of stormwaters after moderate and strong rainfall in Switzerland. Here, the concentration of glyphosate was dominated by first flush peak from sealed, while AMPA may result of the degradation of phosphonates used as detergents (Botta et al. 2009). The first flush is defined as the initial volumes of runoff in urban catchments during rainfall events that contain the highest pollutant levels (Bertrand-Krajewski et al. 1998). There are two main methods for the first flush applicability: 1) the half-inch rule (which assumes that 90% of an event's total pollutant load is transported in the first half inch of runoff) as a relevant volume for treatment, with a dimensionless cumulative pollutant load vs. cumulative runoff volume curves; 2) the Mass First Flush Ratio, which is the division of the proportion of mass by the cumulative runoff volume at a defined point. However, this still relies on the same dimensionless curves and an arbitrary definition (Bach et al. 2010). Tang et al. (2015) investigates the use and loss of glyphosate from a typical Belgian residential area, aiming to quantify glyphosate loss via stormwater runoff. The overall loss rate of glyphosate was <0.5% and varied considerably among rainfall events. Further statistical analyses suggested that rainfall land application did not explain the concentration variations, and surface material and connectivity to the drain inlets of the application sites must be considered. Ramwell et al. (2014) quantify glyphosate and AMPA concentrations in surface stormwater drain that could be attributed to amateur, non-professional usage alone. The study found out that glyphosate concentrations in drain flow were lower than concentrations reported elsewhere from professional use in urban areas.

As reported in Table 2, glyphosate and AMPA are very often detected in urban stormwater, and glufosinate, when studied, is also often present. This suggests that highly polar pesticides are widely used both in urban and residential areas, with direct implication of stormwater pollutants. Many studies are focusing on removal processes of glyphosate (Hossaini et al. 2014; Hu et al. 2013; Jönsson et al. 2013; Pereira et al. 2021), but a more responsible use of urban herbicides is mandatory to contain their load in the environment. Such removal processes performances varied significantly depending on pH, glyphosate or AMPA concentrations, temperature, etc. Thus, many variables should be considered, and many treatment plants are not designed to deal with this approach. If other variables are considered, such as metabolites, degradation products of glyphosate and glufosinate, or new pesticides, removal processes should be further updated.

Only one study was found for the quantification of glyphosate and AMPA in the suspended particulate matter of stormwater (Zgheib et al. 2011). As described in other studies (mac Loughlin et al. 2020; Ronco et al. 2016), the presence of glyphosate is very often associated with the suspended particulate matter and its trend can be associated to water-to-colloid transfer during transport. This is might due to the glyphosate adsorbing properties to soil particles (Feltracco et al. 2021). These transfer phenomena should be also considered in future studies in order to better understand the behaviour of highly polar pesticides during runoff.

5. The unexplored degradation products

Detailed studies about the presence of other highly polar pesticides in stormwater runoff originated from various sources are now missing. Amongst the hundreds and thousands of pesticides sought in the environment, the so-called highly anionic polar pesticides are particularly difficult to analyse due to ultratrace concentrations (Melton et al. 2019). Apart from AMPA, a metabolite of glyphosate is also N-acetyl AMPA through the action of N-phenylacetyltransferase. Furthermore, one of the degradation products of glufosinate is N-acetyl glufosinate, found as the main metabolite in transgenic sugar beet cells. Another metabolite of glufosinate is 3-methylphosphinicopropionic acid (MPPA), which it has similar biological and toxicological effects to the parent compound (Aris and Leblanc 2011). Few studies are present regarding the quantification of organophosphorus pesticides (Pedersen et al. 2006; Shimabuku et al. 2022; Sumon et al. 2018), but not directly related to glyphosate and its degradation products. Furthermore, it is known how AMPA can also derive from the degradation of other molecules than glyphosate. Detergents as ethylene diamine tetramethylene phosphonate can be degraded in AMPA and found in the environment (Botta et al. 2009). The detergent by-product should be deeply investigated, considering their massive use in urban and residential environments. Their investigation can serve as proxy to understand how glyphosate, glufosinate and detergents are degraded through runoff.

6. Variables affecting highly polar pesticides in stormwater and mitigation strategies

The concentration and distribution of highly polar pesticides can be affected by many factors, including precipitation, use pattern, and properties of the application surface. The presence of pesticides in stormwater is directly dependent on rainfall patterns. Moderate but frequent rain may contribute to delivering many pollutants from highway pavements (Hwang and Weng 2015).

Table 2. A summary of glyphosate and related pesticides in stormwater (SW= stormwater, SPM = suspended particulate matter, LOQ = limit of quantification).

Pesticide	Country	Site	Season	Mean	Range	Citation
Glyphosate	California (USA)	Highway	Winter	2.69 µg L^{-1}	1.36 – 9.44 µg L^{-1}	Huang et al. 2004
	Paris (FRA)	Suburb	Winter	0.98 µg L^{-1} SW	ND – 1.9 µg L^{-1} SW	Zgheib et al. 2011
	Paris (FRA)	Suburb	Winter	<LOQ SPM	<LOQ SPM	Zgheib et al. 2011
	Pin Sec, Nantes (FRA)	Residential	Autumn	3.27 µg L^{-1}	1.1 – 71 µg L^{-1}	Lamprea and Ruban 2011
	Gohards, Nantes (FRA)	Residential/Commercial	Autumn	2.15 µg L^{-1}	<0.10 – 3.8 µg L^{-1}	Lamprea and Ruban 2011
	Nantes (FRA)	Urban	Autumn/Winter	2.71 µg L^{-1}	–	Ruban et al. 2005
	Rouffac (FRA)	Urban/wetland	Spring	4.13 µg L^{-1}	0.3 – 11.0 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Summer	5.95 µg L^{-1}	0.2 – 15.0 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Spring	19.9 µg L^{-1}	0.1 – 150 µg L^{-1}	Imfeld et al. 2013
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.34 µg L^{-1}	–	Gasperi et al. 2014
	State of New York (USA)	Urban/Rural	Spring/Autumn	–	ND – 90 µg L^{-1}	Richards et al. 2018
	Melbourne (AUS)	Urban	Autumn	–	1.95 – 2.96 µg L^{-1}	Okada et al. 2019
	Melbourne (AUS)	Urban	Autumn/Winter	1.1 µg L^{-1}	0.25 – 14.2 µg L^{-1}	Okada et al. 2020
	North-East of Switzerland (SWI)	Urban	Spring/Summer/Autumn	–	ND – 4.2 µg L^{-1}	Hanke et al. 2010
	Flanders, Belgium (BEL)	Residential	Spring/Summer	2.3 µg L^{-1}	0.6 – 6.1 µg L^{-1}	Tang et al. 2015
	York (UK)	Residential	Summer	–	ND – 8.99 µg L^{-1}	Ramwell et al. 2014
AMPA	California (USA)	Highway	Winter	2.75 µg L^{-1}	–	Huang et al. 2004
	Paris (FRA)	Suburb	Winter	0.45 µg L^{-1} SW	0.32 – 0.66 µg L^{-1} SW	Zgheib et al. 2011
	Paris (FRA)	Suburb	Winter	0.78 µg L^{-1} SPM	0.23 – 1.60 µg L^{-1} SPM	Zgheib et al. 2011
	Pin Sec, Nantes (FRA)	Residential	Autumn	0.35 µg L^{-1}	0.2 – 1.5 µg L^{-1}	Lamprea and Ruban 2011
	Gohards, Nantes (FRA)	Residential/Commercial	Autumn	0.23 µg L^{-1}	<0.1 – 0.4 µg L^{-1}	Lamprea and Ruban 2011
	Rouffac (FRA)	Urban/wetland	Spring	1.37 µg L^{-1}	0.2 – 2.3 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Summer	2.53 µg L^{-1}	ND – 21 µg L^{-1}	Martin et al. 2012
	Rouffac (FRA)	Urban/wetland	Spring	3.3 µg L^{-1}	–	Imfeld et al. 2013
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.82 µg L^{-1}	–	Gasperi et al. 2014
	Melbourne (AUS)	Urban	Autumn	–	0.55 – 2.42 µg L^{-1}	Okada et al. 2019
	Melbourne (AUS)	Urban	Autumn	1.3 µg L^{-1}	0.25 – 10 µg L^{-1}	Okada et al. 2020
	North-East of Switzerland	Urban	Spring/Summer/Autumn	–	0.04 – 1.11 µg L^{-1}	Hanke et al. 2010
	Flanders, Belgium (BEL)	Residential	Spring/Summer	2.5 µg L^{-1}	0.2 – 16 µg L^{-1}	Tang et al. 2015
	York (UK)	Residential	Summer	–	ND – 1.15 µg L^{-1}	Ramwell et al. 2014
Glufosinate	Rouffac (FRA)	Urban/wetland	Spring	0.85 µg L^{-1}	ND – 6.3 µg L^{-1}	Martin et al. 2012
	Paris, Nantes and Lyon (FRA)	Urban/Idustrial	Year-round	0.76 µg L^{-1}	–	Gasperi et al. 2014

On the other hand, less frequent but intense rainfalls produce lower pollutant loads (Pereira et al. 2021). For example, a long dry period allows some pesticides to be degraded (Chinen et al. 2016). Therefore, an evaluation of the typical half-life of the various degradation products of glyphosate and glufosinate can provide information about their formation during dry periods. Overall, pesticides behaviour in urban catchments is poorly known and the often-unknown use by local residents increases the difficulty in quantifying and characterizing glyphosate. Some studies quantified the loss of glyphosate and investigated the wide range of influencing factors in urban areas (Hanke et al. 2010; Ramwell et al. 2014b; Tang et al. 2015). These studies showed how the loss rate is often very low (<17%) due to their relatively high percentage of permeable surfaces, high fraction of concrete blocks, and strong adsorption of glyphosate onto concrete and deposits. To better understand the run-off processes, a complete knowledge in the pesticide behaviour in the selected urban environments is needed, including how pesticides interact with different surface materials, their load and the characteristics of rainfall events with a consequent runoff volume and flow rate interpretation. Additionally, literature multivariate analyses suggest that rainfall and application cannot be used as a single parameter for interpreting the concentration variations (Tang et al. 2015).

Although the capture of stormwater from the first flush is considered as a useful measure in controlling pollutions, inefficiency of the treatment system still prevails when a large volume of storm runoff is captured from large catchments (>10 ha) (Mamun et al. 2020). Despite this, concentration dynamics of glyphosate at sub-catchments <10 ha was dominated by first flush peaks followed by lower concentration peaks from diffuse sources (Hanke et al. 2010). These discrepancies are due to the approach to first flush interpretations (McCarthy 2009). As a result, various strategies have been formed to help manage urban stormwater pollution by maximising treatment for the initial part of storm events. For robust analyses of different factors or for obtain management insights, a spatially distributed hydrological model is beneficial to account for the spatial properties and urban hydrology.

The pesticides use pattern can be proportioned among the following routes: the proportion of the pesticide deposited onto the target area; the proportion deposited onto the adjacent non-target area; and the proportion lost to the atmosphere during application (FOCUS 2008). Apart from runoff removal, dry and wet deposition should be also considered. Wet deposition is determined by the precipitation rate, the air/water partition coefficient, and the washout ratio for particles, while dry deposition is due to the deposition of dry aerosols, which contain adsorbed substances (Asman et al. 2005). Although herbicides containing glyphosate are not intentionally applied directly to the soil, they may contaminate surfaces around the treated areas, via the so-called spray drift during their application. In addition, it was estimated that 97% of glyphosate existing in the atmosphere could be removed by weekly rainfall greater than 30 mm (Tzanetou and Karasali 2020). Generally, few monitoring studies have been conducted for the determination of glyphosate and glufosinate residues in atmospheric samples, and strong variation in collection time and duration, the analytes selected, the analytical methods used were found (van Dijk and Guicherit 1999).

Solid adsorption is the most cost-effective techniques for removing glyphosate in an aqueous solution. Despite this, the methodology is followed by time consuming modelling processes (Pereira et al. 2021). The performance of coagulation for incorporation of particulates from the stormwater is strongly dependent on pH and coagulant concentration. Some studies report that filtration is more efficient rather than flotation for the removal of adsorbed particles (Jönsson et al. 2013). Other results indicate that the foulants can be effectively removed by nanofiltration from water. Addition of intermediate concentrations of NaCl results in better foulant separation (Yuan et al. 2018). This method was applied on drinking water and is likely difficult to use with a complex matrix like stormwaters. Mayakaduwa et al. (2016) studied the use of woody biochar obtained as waste from a bioenergy industry plant. The kinetic curves showed that the adsorption equilibrium time is relatively short, less than 1 h. Various laboratory tests have shown that glyphosate and AMPA are both degraded or removed by a number of common treatment (chlorination, ozonation, UV irradiation and air stripping) steps at drinking water treatment plants, but few studies investigated the stormwater in order to understand if an efficient removal of glyphosate, glufosinate and degradation products is possible (Feng et al. 2020).

Biodegradation of organic compounds is known as an efficient method to remove organic pollutants from the aqueous environment. Glyphosate can be efficiently removed by biodegradation process with the formation of sarcosine, AMPA and acetyl-glyhposate (Feng et al. 2020). These processes require long residence time and suitable microorganisms' growth conditions to achieve high removal efficiency. Although the biodegradation of glyphosate has been extensively studied, the information on glyphosate biodegradation kinetics and by-product, is still rarely present on literature (Tazdaït et al. 2018).

The efficient evaluation of removal plants is not the main aim of this review, but as most of the studies were conducted at the lab scale, further research is still needed to study the practical application of these technologies. The energy consumption and cost of these technologies also need to be systematically analysed. Several methods for glyphosate and AMPA removal have been applied in the literature (Jönsson et al. 2013) and both compounds are readily degraded or removed by a number of common treatment steps like bank and dune filtration, aluminium and iron coagulant, sand and membrane filtration, chlorination, ozonation, UV irradiation, oxidation, activated carbon adsorption and air stripping. Biodegradation and adsorption processes can be highly effective in degrading or removing glyphosate and AMPA in bank filtration and sand filtration. Ultrafiltration can also be effective in removing glyphosate and AMPA, but the cut-off needs careful consideration. In addition, large scale production of water by these methods is expensive and not commonly used (Speth 1993). No studies were conducted on the removal of other degradation products of glyphosate and glufosinate and no information were provided regarding the possible formation of such by-products during removal processes.

7. Conclusions

This review wants to highlight future research directions in this field: additional studies involving impact of stormwater runoff of urban areas, with a deeper apportioning of sources, also considering the spray drift phenomenon and wet and dry deposition. In most cases, the occurrences, and concentrations of pesticides varied considerably, and these were related to the load precipitation, pesticides use and national legislation. Moreover, future studies on highly polar pesticides occurrence in stormwater should be focused on the degradation products that can be formed during transport. This could be a key knowledge gap hindering the development of control measures for pesticides in stormwater runoff, which is vital both for the protection of ecosystems and the future use of stormwater as a potable water resource.

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Reviewer #1: Thank you very much for giving me the opportunity to review your paper. In general I find your work could be a valuable contribution to Water, Air and Soil Pollution journal

A: Thank to Reviewer #1 for the comment.

1. Line 86. Add a table with the physical and chemical characteristics of these herbicides (glufosinate, AMPA and glyphosate): vapor pressure, solubility, adsorption coefficient, molecular mass, etc.

A: We agree with Reviewer #1, we added a table with the characteristics of each target compound. We also better explain the degradation pathways of glyphosate (lines 83-86) as follows: "Glyphosate degradation processes in soil are mediated by microorganisms producing AMPA, sarcosine, and glycine (Figure 2). The first pathway involves C-N bond oxidation, with a consequent release of AMPA and glyoxylate. Another degradation pathway is possible through sarcosine oxidase, which leads to sarcosine and phosphate formation. Sarcosine is further processed to glycine (van Bruggen et al. 2018)."

2. Line 118. Abbreviations should be given in full name at their first appearance. EFSA? Table 1 LQO?

A: Sorry for this. All the abbreviation are now given in full name at their first appearance.

3. A variable to discuss would be the flow rate. The authors make this point (peaks line 209-211) but I think this variable needs to be addressed in their discussion of results. It is another variable to study in future research.

It must be borne in mind that before studying the behavior of these pollutants, it is necessary to know the behavior of the water flow. A first step would be to apply the concepts of urban hydrology.

A: Thank to Reviewer #1 for pointing it out. We carefully addressed the impact of flow rate and mobility of target pesticides (lines 226-236) as follows: "Overall, pesticides behaviour in urban catchments is poorly known and the often-unknown use by local residents increases the difficulty in quantifying and characterizing glyphosate. Some studies quantified the loss of glyphosate and investigated the wide range of influencing factors in urban areas (Hanke et al. 2010; Ramwell et al. 2014b; Tang et al. 2015). These studies showed how the loss rate is often very low (<17%) due to their relatively high percentage of permeable surfaces, high fraction of concrete blocks, and strong adsorption of glyphosate onto concrete and deposits. To better understand the run-off processes, a complete knowledge in the pesticide behaviour in the selected urban environments is needed, including how pesticides interact with different surface materials, their load and the characteristics of rainfall events with a consequent runoff volume and flow rate interpretation. Additionally, literature multivariate analyses suggest that rainfall and application cannot be used as a single parameter for interpreting the concentration variations (Tang et al. 2015)."

Reviewer #2: Unfortunately, this brief review adds little to our knowledge of glyphosate and related compounds in stormwater. Soil adsorption and complexation properties, and their critical impacts on fate and transport, as well as precipitation variables in relation to chemical application are inadequately addressed. Overall, the manuscript lacks detail and is plagued by broad statements and generalities, repetition, irrelevant information, contradictions, and inaccuracies. There is inappropriate, frequent use of "etc." as a catchall, when no further items or examples is apparent.

A: Thank to the Reviewers #2 for her/his point of view. As Reviewer #1 suggested, we carefully addressed the herbicide mobility, we improved the description of first flush, and we described the water pollution diagnostic as a tool for evaluating the interaction of pollutants with the ecosystem. We also face the efficiency of removal processes as suggested by Reviewer #3. We also deleted several "etc" from the entire manuscript, thanks for pointing it out. Thanks to the constructive suggestion of Reviewers #1 and #3, we improved the quality of the manuscript.

Reviewer #3: The study is about review of occurrence of glyphosate and its degradation products in the urban stormwater. The following comments can be considered:

1-I recommend author consider more quantitative approach in this review.

A: As suggested by Reviewer #3, we tried to be more quantitative through the manuscript (Table 1, lines 226-236). We think also that stressing too much the manuscript with several numbers and concentrations can make it not easy to read. We prefer to summarize this information in Table 2, to help the reader without complicating the manuscript.

2-It would be interesting if some figures and graphical images related to topic be added to this review paper.

A: We added the Figure 1 that summarizes the global glyphosate use trend. Furthermore, as suggested by Reviewer #3, we added the Figure 2 for summarizing the degradation pathways of glyphosate.

3-Can biological processes remove glyphosate efficiently? If so, please mention some of the processes.

A: As suggested by Reviewer #3 we faced the biological removal of glyphosate (lines 274-279) as follows: "Biodegradation of organic compounds is known as an efficient method to remove organic pollutants from the aqueous environment. Glyphosate can be efficiently removed by biodegradation process with the formation of sarcosine, AMPA and acetyl-glyhposate (Feng et al. 2020). These processes require long residence time and suitable microorganisms' growth conditions to achieve high removal efficiency. Although the biodegradation of glyphosate has been extensively studied, the information on glyphosate biodegradation kinetics and by-product, is still rarely present on literature (Tazdaït et al. 2018)."

4-What is the first flush interpretations? Please elaborate about it.

A: We better addressed the first flush approaches (lines 172-178) to read: "The first flush is defined as the initial volumes of runoff in urban catchments during rainfall events that contain the highest pollutant levels (Bertrand-Krajewski et al. 1998). There are two main methods for the first flush applicability: 1) the half-inch rule (which assumes that 90% of an event's total pollutant load is transported in the first half inch of runoff) as a relevant volume for treatment, with a dimensionless cumulative pollutant load vs. cumulative runoff volume curves; 2) the Mass First Flush Ratio, which is the division of the proportion of mass by the cumulative runoff volume at a defined point. However, this still relies on the same dimensionless curves and an arbitrary definition (Bach et al. 2010)."

5-what type of filtration is appropriate for the glyphosate removal? Can ultrafiltration be used?

A: As suggested by Reviewer #3, we face the filtration procedures from line 283 to line 292, to read: "Several methods for glyphosate and AMPA removal have been applied in the literature (Jönsson et al. 2013) and both compounds are readily degraded or removed by a number of common treatment steps like bank and dune filtration, aluminium and iron coagulant, sand and membrane filtration, chlorination, ozonation, UV irradiation, oxidation, activated carbon adsorption and air stripping. Biodegradation and adsorption processes can be highly effective in degrading or removing glyphosate and AMPA in bank filtration and sand filtration. Ultrafiltration can also be effective in removing glyphosate and AMPA but the cut-off needs careful consideration. In addition, large scale production of water by these methods is expensive and not commonly used (Speth 1993). No studies were conducted on the removal of other degradation products of glyphosate and glufosinate and no information were provided regarding the possible formation of such by-products during removal processes."

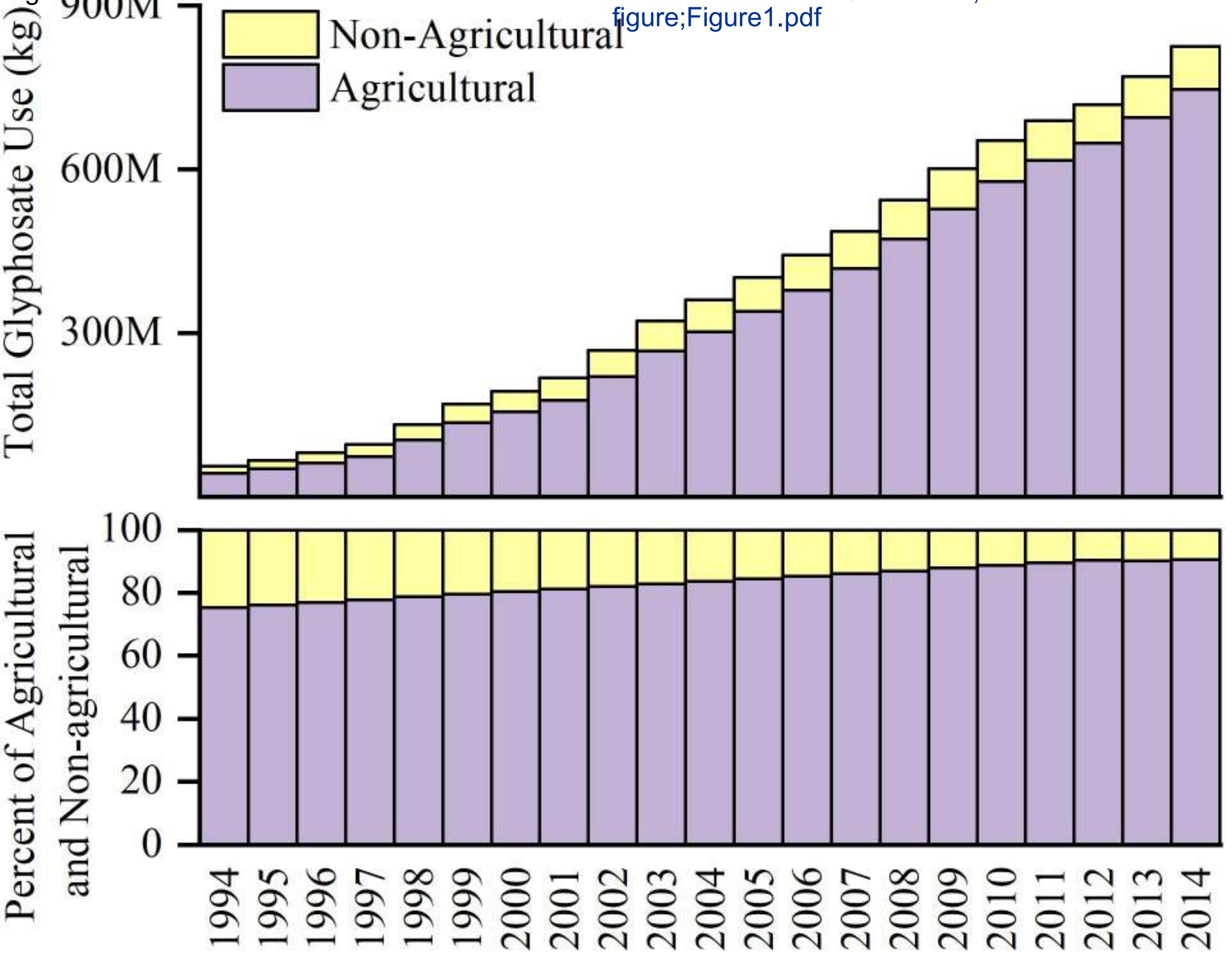
Additional Comments: In the Introduction include a brief note on the water pollution diagnostics

- Krapivin, V. F., et al., (2021). Operational diagnosis of arctic waters with instrumental technology and information modeling. Water, Air, & Soil Pollution, 232(4), 1-7

- Krapivin, V. F., et al., (2017). A modeling system for monitoring water quality in lagoons. Water, Air, & Soil Pollution, 228(10), 1-12.

A: Thanks to the Reviewers #3 for these citations. We added a brief note about water pollution diagnostics (lines 35-37), to read: "Tools for the water quality diagnostics were also developed in last years for different environments (V. F. Krapivin et al. 2017, 2021) with the aim to describe the interactions of pollutants with components of ecosystems."

Figure 1


Total Glyphosate Use (kg)
900M
600M
300M
Non-Agricultural
Agricultural
Percent of Agricultural and Non-agricultural
100
80
60
40
20
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014


glyphosate
C-N
oxydation
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oxydase
AMPA
+
glyoxylate
sarcosine
glycine
+
PPi

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The two authors listed below were added due to their expertise in pollutin determination in varoius environment matrices. Dr. Toscano and Prof. Barbante collaborated actively in the manuscript review process. Their contribution has been fundamental. The two new authors read and approved the final revised manuscript.

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