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Glyphosate contamination in European rivers not from herbicide application?

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SUMMARY

The most widely used herbicide glyphosate contaminates surface waters around the globe. Both agriculture and urban applications are discussed as sources for glyphosate. To better delineate these sources, we investigated long-term time series of concentrations of glyphosate and its main transformation product aminomethylphosphonic acid (AMPA) in a large meta-analysis of about 100 sites in the USA and Europe. The U.S. data reveal pulses of glyphosate and AMPA when the discharge of the river is high, likely indicating mobilization by rain after herbicide application. In contrast, European concentration patterns of glyphosate and AMPA show a typical cyclic-seasonal component in their concentration patterns, correlating with patterns of wastewater markers such as pharmaceuticals, which is consistent with the frequent detection of these compounds in wastewater treatment plants. Our large meta-analysis clearly shows that for more than a decade, municipal wastewater was a very important source of glyphosate. In addition, European river water data show rather high and constant base mass fluxes of glyphosate all over the year, not expected from herbicide application. From our meta-analysis, we define criteria for a source of glyphosate, which was hidden so far. AMPA is known to be a transformation product not only of glyphosate but also of aminopolyphosphonates used as antiscalants in many applications. As they are used in laundry detergents in Europe but not in the USA, we hypothesize that glyphosate may also be a transformation product of aminopolyphosphonates.

1. Introduction

Glyphosate sales are expected to reach 900,000 t worldwide in 2025. (Maggi et al., 2020) In the USA, almost 130,000 t were used in 2012 in the agricultural sector (US EPA 2020) with 5–10 % of the annual sales applied to non-agricultural sites. (US EPA 2020; Medalie et al., 2020; US EPA 2019) Glyphosate and its main transformation product aminomethylphosphonic acid (AMPA) are frequently detected in rivers as well as in wastewater and sewage sludge (Battaglin et al., 2014; Popp et al., 2008; Wüthrich et al., 2016; Poiger et al., 2020; Ghanem et al., 2007; Desmet et al., 2016). Glyphosate is commonly perceived to enter rivers via quickflow induced by rain events with loss rates after agricultural (Hanke et al., 2010; Richards et al., 2018) or urban applications (Tang et al., 2015; Ramwell et al., 2014; Luijendijk et al., 2005) mostly reported to be below 1 %. While the importance of urban sources has been discussed, (Hanke et al., 2010; Volz, 2011; Poiger et al., 2017; Tauchnitz et al., 2020, European Commission, 2023; Kolpin et al., 2006) we do not understand the significance of the various sources nor the input pathways of glyphosate and AMPA making it impossible to judge the effectiveness of recent mitigation measures in Europe (BMEL, 2021). To delineate sources of glyphosate and AMPA in surface waters, we examined long-term time series of river water contaminations. As already the first European datasets were in stark contrast to our expectations and common hypotheses of glyphosate entering surface waters via quickflow, we extended our study to conduct a large meta-analysis of river water concentrations across Europe and the USA. We compared concentration patterns with land use and correlated glyphosate and AMPA concentration patterns to those of other agrochemicals or micropollutants derived from wastewater.

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2. Methods

Temporal patterns of glyphosate and AMPA concentrations in rivers and streams in Europe (E) and the USA (U) are compiled in Figs 1, 2 and 3 and Tables S1 and S2, which also provide information on the catchments (size, land use, impact by wastewater). The supplementary material provides additional figures and background information.

U.S. data: Sampling sites from the United States Geological Survey (https://maps.waterdata.usgs.gov/mapper/index.html) were selected based on the availability of long-term time series of glyphosate concentration data with sufficient temporal resolution (≥12 samples per year), coverage of several states and contrasting land use (urban, agricultural, mixed), see Table S1. Data for pharmaceuticals or household chemicals were not available. Glyphosate and AMPA concentration patterns in Table S1 were plotted mostly with the same scaling, often using 1.5 μg/L as the upper value. European data: Table S2 shows data plotted for 73 sites in France (38 sites), Sweden (3 sites), Germany (18 sites), the Netherlands (7 sites), the United Kingdom (1 site), Italy (2 sites) and Luxemburg (4 sites). From all available data, sites were chosen for which long time series with sufficient temporal resolution were available. We tried to cover sites all over the countries. Some sites were selected as they provide information on special aspects such as sites being impacted by wastewater treatment plants (WWTPs) receiving domestic wastewater. For European data, concentration time series were scaled according to the concentrations present at place. A comparison is made with other agricultural markers (mainly herbicides or nitrate) and wastewater markers (pharmaceuticals, especially carbamazepine, and household chemicals such as benzotriazoles or EDTA).

The choice of the micropollutants was governed by the availability of data with regard to the type of micropollutant and sufficient temporal resolution for measured concentrations above the limit of detection. For agricultural markers, a focus was set to herbicides. Data handling: When plotting data, we decided to connect the data points (except when measured concentrations in the series were < LOD) to increase clarity of the plots. Most of the data are expected to be from grab sampling; in Table S2, we indicated the rare cases, where samples mixed over several days were used. In most cases, no detailed information on the sampling was provided with the data. We use the term "sharp concentration peaks" to indicate data points with concentrations clearly exceeding both, the preceding and the subsequent data point. In contrast, the term "broad concentration maxima" is used for wastewater-derived micropollutants and more persistent transformation products of herbicides like AMPA and dechlorometolachlor, which often show elevated concentrations over several sampling dates.

We applied Spearman rank correlation to relate glyphosate concentration data to concentration patterns of AMPA, wastewater and agricultural markers for selected sites.

The logarithm of the A:G ratio, log(A:G) proved to be an elegant measure to demonstrate the differences in the AMPA vs. glyphosate concentration patterns between the USA and Europe. This ratio indicates if there is a variable or more constant concentration ratio and which compound dominates over time.

3. Results

3.1. Concentration patterns in the USA

The general assumption is that glyphosate and AMPA enter rivers after herbicide application in conjunction with rain events. (Borggaard and Gimsing, 2008) All temporal concentration patterns and mass fluxes in the USA followed this hypothesis.

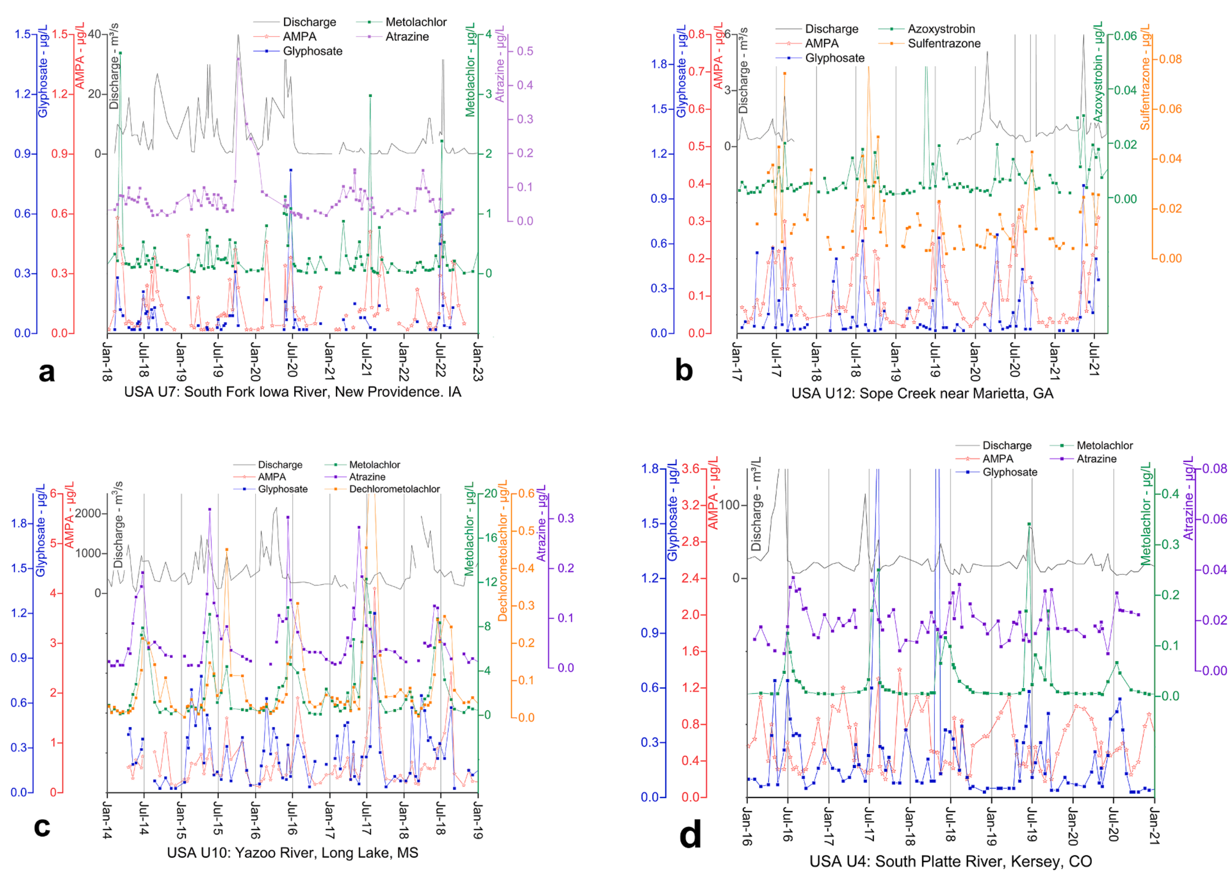

Fig. 1. Representative U.S. sites: Concentration patterns of glyphosate and AMPA and other herbicides as well as discharge in selected U.S. rivers. Details, data sources and additional data for 14 further sites are given in Table S1 (sites: U7, U12, U10, U4).

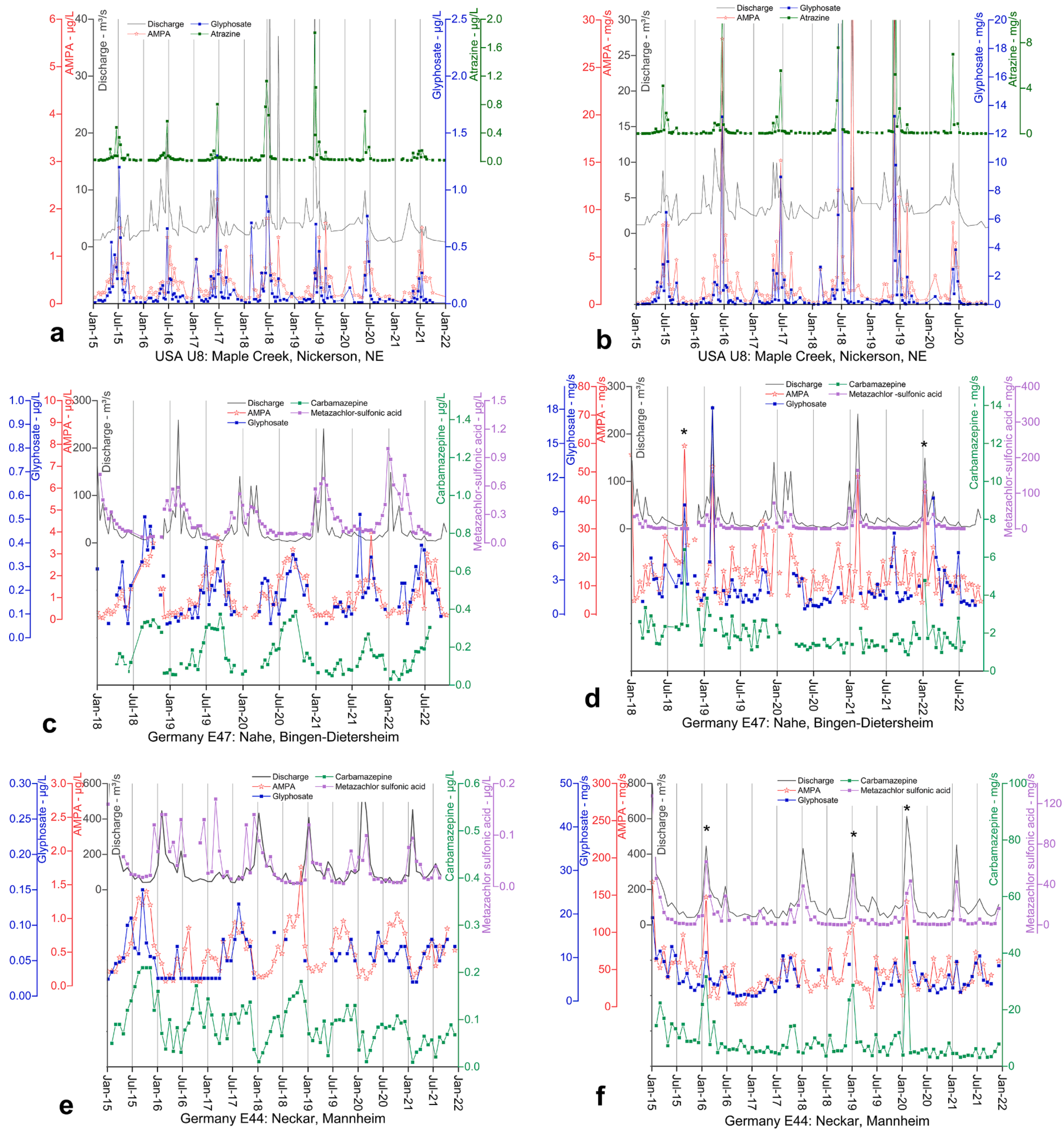

Fig. 2. Concentrations vs. mass fluxes: a, c, e: Concentration patterns and b, d, f: mass fluxes of glyphosate and AMPA in the rivers a, b Maple Creek at Nickerson, NE (Site U8); c, d Nahe at Bingen (Site E47) and e, f Neckar at Mannheim (Site E44); data sources given in Tables S1 and S2. *simultaneous increases in agricultural and urban tracers. Further examples in Fig. S3.

3.1.1. Catchments with a dominant agricultural impact

Several of the U.S. sites investigated here, have a dominantly agricultural catchment in sparsely populated areas with only small WWTPs, if any: site U7 (no WWTP), site U8 (impacted by irrigation), site U9 (small WWTP or private sewers, if any), site U13 (small WWTP <1500 inhabitants in Hookerton), site U17 (no WWTP) and site U18 (small WWTP from a village with 2300 inhabitants). Sharp concentration peaks, particularly for glyphosate are observed, exemplarily shown here for the South Fork Iowa River (Fig. 1a, site U7, other sites in Table S1). In many cases, glyphosate and AMPA peaks coincide with those of other herbicides such as metolachlor and are related with elevated discharge of the river. This clearly indicates rain-driven input as expected from agricultural runoff, likely due to first flush events after application. (Richards et al., 2018) AMPA patterns are more diverse with some sites showing predominantly sharp concentration peaks (e.g. sites U3, U5, U7, U15, U17) while others reveal broad concentration maxima over large parts of the growing season (e.g. sites U1, U4, U6, U9, U11, U16), see Table S1. Site U6, Bogue Phalia and U10, Yazoo River are described to have an intense use of glyphosate in their catchments, (Coupe et al., 2012) which may lead to the accumulation of the more persistent AMPA. (Wimmer et al., 2023) This argument is supported when looking at the broad and similar concentration maxima of dechlorometolachlor, which is also more persistent than its parent metolachlor (Table S1). (Rose et al., 2018)

At the Sope Creek (Site U12) and at the South Fork Iowa River near New Providence (U7), the logarithm of the AMPA to glyphosate concentration ratio, log(A:G), fluctuates around zero (median = 0.3) with either AMPA or glyphosate dominating at a time as can be expected for a small catchment, see Figure S1. All sites have in common that winter times show lower concentrations and lower detection frequencies, especially for glyphosate. In all cases, similar input patterns are present for glyphosate and other herbicides. In Table S3, Spearman rank correlation coefficients between glyphosate and herbicides are often > 0.6 (see also Fig. 4) (only for atrazine, lower values were often observed). Agriculture as a main source for glyphosate and AMPA can also be deduced when calculating mass fluxes, which increase during times of elevated discharge for glyphosate, AMPA and other herbicides (Fig. 2b and Fig. S3b). Agriculture as the dominant source for glyphosate input to surface waters was also discussed for Canada (Byer et al., 2008; Glozier et al., 2012) and Argentina. (Pérez et al., 2017)

Overall, we see strong differences between concentration patterns at different sites. Differences in the types of crop cultivated, management practices, catchment size and transport regimes for pesticides were discussed to be relevant for glyphosate input. As an example, we consider the work of Coupe et al. (Coupe et al., 2012), who provided application data and information on transport regimes for sites similar to some used in this meta-analysis. For the South Fork Iowa River (close to site U7) and similarly for the White River basin (with the sites U17 (Sugar Creek) and U18 (White River) located in the same catchment), Coupe et al. (Coupe et al., 2012) described a dominance of subsurface flow due to artificial drainage in 80 % of the catchment. Here, glyphosate and AMPA detections were related to their main application times and to rain events. In contrast, at the Bogue Phalia (site U9), glyphosate and AMPA were detected during the whole growing season. This can be understood from the intense use of glyphosate use in glyphosate-resistant crop grown here, which allows applications over nine months of the year. Little drainage and a surface-water-driven system is present here and thus clearly different temporal input patterns. (Coupe et al., 2012)

3.1.2. Urban catchments not impacted by wastewater

Similar concentration patterns with pronounced glyphosate peaks at elevated discharge are also present for rivers with fully urban catchments without wastewater impact (e.g., the Sope Creek in Marietta; Fig. 1b, site U12 and at Fanno Creek, site U1 (Table S1)), demonstrating intensive private and municipal use during the growing season (non-agricultural use is estimated to 5–10 % of all sales (US EPA 2020; Medalie et al., 2020; US EPA 2019)). For these sites, we also see a similar appearance of urban pesticides (e.g. Spearman rank correlation coefficients for glyphosate at the Sope Creek (U12) to azoxystrobin 0.606 and sulfentrazone 0.422, see Table S3) pointing to surface runoff as major input pathway, especially for site U12 with a significant percentage of sealed surfaces (streets, driveways) in the residential area of the catchment.

3.1.3. Catchments with mixed land used and impact by wastewater

Also for U.S. sampling sites with larger catchments and a mixed urban and agricultural input, most of them impacted by wastewater (U3-6, U10, U11, U14–16, details on WWTPs and disinfection protocols are provided in Table S1), similar concentration patterns are present. We included disinfection processes commonly implemented in U.S. WWTPs because chlorination was shown to efficiently eliminate glyphosate (and partially AMPA). (Brosillon et al., 2006; Mehrsheikh et al., 2006; Navee and Kim, 2009) Many WWTPs were equipped with this technique in the USA, but its use declined from 95 % in 1997 to 75 % of U.S. WWTPs in 2003. (Bischoff, 2013) The alternative UV disinfection (21 % of U.S. plants in 2003 (Bischoff, 2013)) can be expected to be less efficient in glyphosate removal. (Assalin et al., 2010; Espinoza-Montero et al., 2020) Comparing data from different sites, we neither observe relevant differences in concentration patterns due to the type of disinfection nor differences in time upon changes in disinfection protocols, e.g. from chlorination to reaction with peracetic acid in Denver (Newhart et al., 2020) (site U4, see Table S1). The sharp concentration peaks visible for sites U3, U5, U10, U14, U15 and the (continued) frequent switching of the log(A:G) from positive to negative values at many sites, see Fig. S1, demonstrate that the input of WWTPs does not principally change the concentration patterns in receiving waters. As glyphosate is only rarely detected and if, only at low concentrations in WWTP effluents in the USA, (Kolpin et al., 2006; Battaglin et al., 2005) either efficient elimination may be present or input via the sewer system is of minor importance. In contrast, AMPA is more frequently detected in WWTP effluents. AMPA was consistently discussed to be a transformation product of aminopolyphosphonates, (Struger et al., 2015; Fürhacker et al., 2005) used e.g. in cooling circles and laundry products (see discussion in Section 4.3). But this source would be expected to lead to rather constant base mass fluxes and an inverse relationship to discharge due to dilution, but the opposite is observed along with patterns consistent to other herbicides. Impressive examples can be found at Site U4 at Kersey (catchment 28,800 km^2, WWTP 2.2 Mio IE) with up to 85 % treated municipal wastewater in the South Platte River (Spearman rank correlation of glyphosate and metolachlor of 0.632, see Table S3) or at Site U6 at Hastings on the Mississippi (catchment 95,083 km^2, 1.8 Mio IE). At U6, concentrations patterns of glyphosate and metolachlor are similar with a Spearman rank correlation coefficient of 0.607 ($n = 125$). This also holds true for the patterns of AMPA and dechlorometolachor (0.648, $n = 125$).

3.2. Concentration patterns in Europe

By contrast, the features described for the USA are not at all representative of the European data (Fig. 3 and Table S2). The typical agricultural input patterns visible in the USA are rarely observed among the more than 70 sites investigated in Europe (e.g., at sites E2, E5, E24 (France), sites E39 (Fig. 3a) and E40 (Sweden), sites E61 and E65 (the Netherlands), see Table S2). For these sites, input patterns for glyphosate (reaching concentrations of up to 57 μg/L (Site E40 with a very small purely agricultural catchment)) and other agricultural markers (diflufenican (sites E2 and 5) or MCPA (E61)) resemble the hydrograph. In the large dataset available from France, we would expect agricultural concentration patterns especially in the sparsely populated headwater regions of river catchments, but detection frequencies and/or temporal resolution are too low.

In contrast, most of the sites investigated, especially those with average concentrations >> LOD, show distinctly different patterns with a strong seasonality. Representative examples are shown in Fig. 3b-d (all other sites in Table S2). During winter months (November-March) with expected low use of glyphosate (see U.S. data), concentrations are lowest but often still well above LOD and with high detection frequencies. Concentrations regularly increase in April or May, reach a maximum mostly during July-October, when the discharge is lowest and then decline again (see Fig. 3 and Table S2). The anticyclical patterns of discharge on the one hand and glyphosate and AMPA concentrations on the other hand is particularly well visible in Fig. 3b (Site E47, Nahe at Bingen-Dietersheim). Similar temporal concentration patterns were shown for sites in France, (Carles et al., 2019; Piel et al., 2021) the Netherlands, (Desmet et al., 2016; Volz, 2011) and Switzerland. (Poiger et al., 2017; Sinniger and Niederhauser, 2013) Seemingly, this similar contamination pattern all over (Western) Europe is independent from differences in land use (urban or agricultural), crop type, management practices or climate conditions, which surely prevail at the different sites (for catchment information, see Table S2). For example, site E29 (Aude a la Redorte, FR) has a catchment dominated by vineyards whereas the catchment for site E46 (Emscher, DE) is dominantly urban. Sometimes, sharp glyphosate peaks superimpose the seasonal pattern, but are limited to single events (sites E3, E10, E17, E18, E43 and E59). Glyphosate peaks are observed at sampling sites along the Helme (E53 a-d) at the same days, but in contrast to other points in time, AMPA concentrations did not increase in parallel, making rain-driven glyphosate input from the large neighboring fields likely.

For more than a decade (longest data sets reach back to 1997, Site

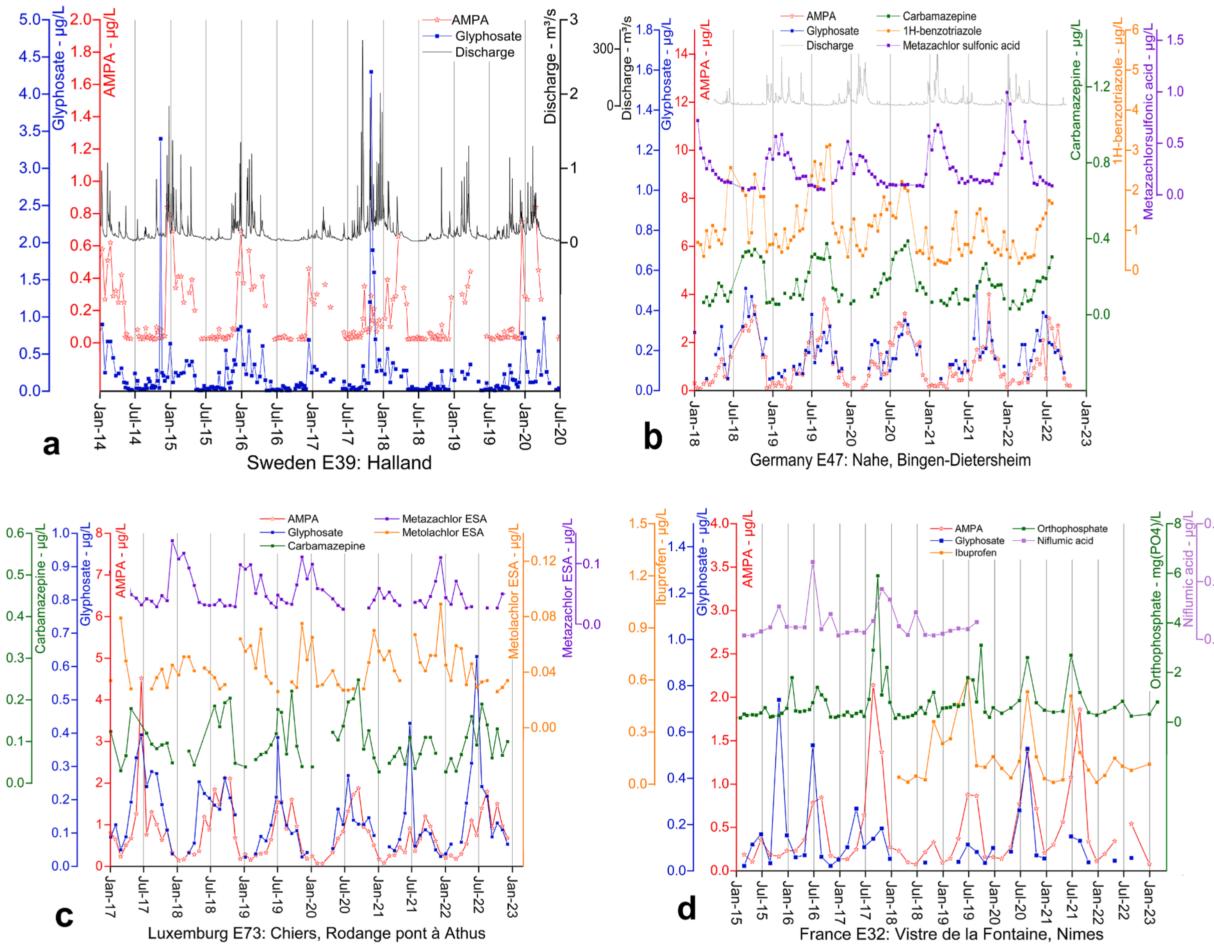

Fig. 3. Representative European sites: a-d: Concentration patterns of glyphosate and AMPA compared to concentrations of agrochemicals (herbicides, nitrate) or wastewater-derived substances (triazoles, pharmaceuticals, phosphate) and discharge where available in Swedish, French, Luxembourgish and German rivers. Details, data sources and additional data for almost 70 further sites are given in Table S2. Sites: a: E39 (SE), b: E47 (DE), c: E73 (LU), d: E32 (FR).

E49), at most European sites, concentration patterns are not consistent with the main glyphosate application times for stubble and pre-sowing treatments in spring and late summer/autumn (for details, see Section S2). Genetically modified glyphosate-resistant crops are not approved in the EU. This limits summer applications of glyphosate to special crops (e.g. wine, legumes) or to pre-harvest (siccation) applications in crops such as oilseed rape, maize or cereals. Siccation applications, however, were strongly restricted since 2016 in Germany, fully banned there in 2021 and are now banned in the whole EU, see Section S4. (Dickeduisberg et al., 2012) For Germany, it was stated that glyphosate was used on about 37 % of agricultural land, but only on 2 % for siccation (6 % of all sales) in 2017. (Deutscher Bundestag, 2017) Restrictions were implemented for municipal and private use (starting in 2017 in the EU) up to the full ban of glyphosate in Luxembourg from January 2021 until the ban was stopped again by a court decision end of March 2023. However, no reduction of glyphosate and AMPA contaminations in rivers can be seen (see Fig. 3c and Table S2 (sites E70–73)).

4. Discussion

4.1. Comparison of U.S. and European concentration patterns in rivers

We here summarize surface water data ranging from 1997 to 2023, mostly with 10 and more samplings per year for about 100 sampling sites in total. Samples at monthly intervals cannot clearly be attributed to distinct phases of processes such as the beginning, the peak, or the recession of a runoff event. However, we are confident that the high number of data points support more general conclusions despite the haphazard nature of grab sampling. This is supported by the strong differences seen in European and U.S. data. In addition, some time series reveal strong jumps in the concentrations of micropollutants at times of strongly elevated river discharge. This shows that in the large data set, both, base mass fluxes and increased mass fluxes during heavy rain events were sampled.

European data reveal an approximately inverse relationship of glyphosate and AMPA patterns to discharge or nitrate as a marker for diffuse input from agriculture (e.g. sites E16, E17, E44, E47). The concentration patterns of other herbicides such as metolachlor and metazachlor and their transformation products clearly differ (sites E7, E15, E17, E22, E23, E25, E44, E47, E62, E70–73), indicated also by low to negative Spearman rank correlation coefficients, see Fig. 4 and Table S4. This is in stark contrast to the USA (see Fig. 2a and b, Fig. S3a and b) and the agricultural catchment in Sweden (Fig. 3a, Fig. S3 c-d), where glyphosate and AMPA concentrations and mass fluxes increased upon elevated discharge just like other herbicides, and are corroborated by high Spearman rank coefficients (Fig. 4 and Table S3).

Glyphosate use is higher in the USA than in European countries with application rates in terms of total agricultural area of 138 kg/km^2 in the USA (statista 2023) and of 26 kg/km^2 on average for European countries (ranging from 17 kg/km^2 for Luxemburg/UK to 32 kg/km^2 for France) (eurostat 2023) (details in Section S1). However, the concentration ranges of glyphosate in rivers are similar among USA, France and Germany (Fig. S2). European sites with a pure agricultural catchment have log(A:G) values fluctuating around a median of −0.1 to 0.1 over time

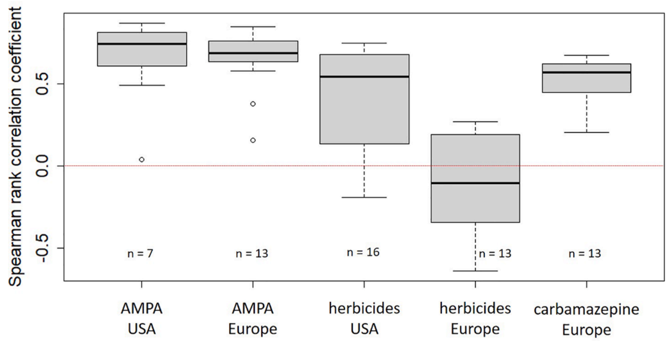

Fig. 4. Box-whisker-plots of Spearman rank correlation coefficients for rank correlation analysis of glyphosate with AMPA, with available data on herbicides and carbamazepine from selected sites in the USA and Europe. A correlation coefficient of 1 indicates a perfect positive, a coefficient of −1 a perfect negative relationship of the variables' ranks. The number of analyzed time series is indicated by n. Data in Tables S3 and S4.

similar to U.S. sites with small catchments (sites E39, U3 and U12, Fig. S1). By contrast, the log(A:G) ratios of most European sites are dominated by AMPA with values >1 (sites E3, E6, E8, E15, E16) and even >1.5 (AMPA concentrations >30 times glyphosate) for sites with larger catchments such as E33, E56, E62 (Fig. S1). Among the U.S. sites chosen here, median values up to 0.5 were only reached for the Red River (site U5, 70,000 km^2) and the Yazoo River (U10, 34,227 km^2). Here the fluctuations in log(A:G) were not as pronounced as in rivers with smaller catchments (see Figure S1), likely due to the more frequent application of glyphosate in the catchment compared to small catchments. This finding is a first hint to a more constant source also for glyphosate present in Europe. Indeed, when calculating long-term glyphosate mass fluxes (Fig. 2c-f and Fig. S3e-f), we observe rather constant base mass fluxes for glyphosate and AMPA in Europe but not in the USA. This includes periods outside the growing season and even periods of extended droughts (e.g., summers of 2013 and 2018) when mobilization by rain is unlikely.

4.2. Glyphosate and AMPA entering surface waters via wastewater

A strong seasonality in concentration data and rather constant base mass fluxes are well known for micropollutants derived from wastewater such as phosphate, pharmaceuticals such as the antiepileptic carbamazepine or pain killers (niflumic acid or ibuprofen), and household chemicals (such as (benzo)triazoles used e.g. in dishwashing agents). (Comber et al., 2020) An impressive example is that of glyphosate and benzotriazole at the Teltowkanal (site E58, Table S2). Their seasonal concentration pattern can easily be explained by constant mass fluxes from a point source diluted during winter by river discharges elevated due to low evapotranspiration (Yua et al., 2009). Unfortunately, suitable data for wastewater markers are lacking in the U.S. data.

Comparative Spearman rank correlation analysis was performed for selected sites in the USA (7 sites, Table S3) and Europe (13 sites, Table S4). The distribution of the Spearman rank correlation coefficients is depicted as box-whisker-plots in Fig. 4. They demonstrate equally high correlations between glyphosate and AMPA concentrations for both continents, while herbicides were highly correlated with glyphosate only in the USA. In constrast, glyphosate concentrations at the European sites show a correlation with the wastewater-derived carbamazepine in a similar range as with AMPA but mostly low to negative coefficients for other pesticides, here mainly herbicides.

The relevance of wastewater for European river contamination by glyphosate and AMPA is further stressed by the fact that all European sites showing the seasonal concentration patterns are impacted by wastewater (see catchment information in Table S2). In addition, glyphosate concentrations increase upon passing a WWTP discharge point and decrease with distance to the next WWTP upstream (e.g. along the Seine (FR) (sampling sites Charrey sur Seine to Saint-Lye and Mery-sur-Seine and further downstream for Saint Fargeau-Ponthierry to Conflans-Sainte Honorine (site E18)) and at the Aude (sampling sites Trebes to La Redorte) (data not shown)). In Berlin, glyphosate and AMPA were hardly detected in the Dahme (site E57) but detection frequencies and concentrations strongly increased (to 0.05–0.5 μg/L glyphosate and 1–7 μg/L AMPA) in its branch Teltowkanal (site E59) after the discharge points of Berlin's largest WWTP Waßmannsdorf (1.3 Mio IE), WWTP Stahnsdorf (320 000 IE) and Ruhleben during summer months (1.6 Mio IE), see Table S2. The relevance of wastewater as a source is also visible by the number of positive detects in surface waters in Berlin (8 % / 35 % / 56 % for glyphosate and 22 % / 55 % / 95 % for AMPA) with no / seasonal / permanent wastewater inputs, respectively (Fig. 5) (wastewater discharge alternates into different rivers during the year).

For the USA, only very few data on glyphosate and AMPA concentrations in WWTP effluents were published: 1 of 11 (9 of 11) (Battaglin et al., 2014) and 3 of 11 (9 of 11) (Kolpin et al., 2006) effluent samples were tested positive for glyphosate (AMPA). The median glyphosate concentration was <LOD (LOD = 0.02 (Battaglin et al., 2014) and 0.1 μg/L (Kolpin et al., 2006)) and for AMPA, 0.45 μg/L (Battaglin et al., 2014) or < LOD (Kolpin et al., 2006) (LOD = 0.1 μg/L (Kolpin et al., 2006)) in the two studies. This is in strong contrast to Europe, where almost all WWTP effluents were tested positive for glyphosate and AMPA: In Switzerland, the median glyphosate concentration in 42 of 45 WWTPs was 0.34 μg/L with a range of 0.06–3.8 μg/L in 2016 (AMPA, 45 of 45 WWTPs, median 0.78 μg/L, range 0.054–8.40 μg/L). (Wüthrich et al., 2016) Similarly, a German WWTP revealed a median glyphosate concentration of 0.55 μg/L (range <LOD to 5.4 μg/L) from monthly sampling (AMPA: median 1.35 μg/L, range 0.05–5.0 μg/L), data kindly provided by the Bayerisches Landesamt für Umwelt, Germany. WWTP effluents along the Meuse and its tributaries in the Netherlands had average concentrations of 1.6 μg/L glyphosate (up to 29.2 μg/L) (AMPA 3.5 μg/L, up to 50 μg/L) in 2010. (Volz, 2011) Poiger et al. (Poiger et al., 2020) detected glyphosate (and AMPA) from April to November in a Swiss WWTP with average effluent concentrations of 0.16 μg/L (range 0.047–0.58 μg/L). The most intriguing observations were made by Ghanem et al., (Ghanem et al., 2007) who determined glyphosate and AMPA over one year in dried sewage sludge in a French WWTP with moderate industrial activity and fed by *separate* sewer systems: Concentrations reached up to 3 mg/kg glyphosate and 20 mg/kg AMPA, see Fig. S4. Glyphosate and AMPA patterns were very similar to each other. (Poiger et al., 2020; Ghanem et al., 2007) A certain seasonality of concentrations in WWTP effluents, visible in the data of these two studies, may arise from sewer infiltration or storm water inputs during wet seasons or periods (Comber et al., 2020). Hence, dilution effects may also occur in the sewer system but this does not contradict the assumption of rather constant mass fluxes. Finally, Märki et al. (Märki, 2015) detected glyphosate in WWTP samples also during dry weather periods. These findings question glyphosate contamination in streams to be derived only from rain-driven mobilization after herbicide applications. The rather constant log(A:G) ratios in receiving rivers, sometimes over decades, seem to reflect rather constant ratios in WWTP effluents. (Poiger et al., 2020; Ghanem et al., 2007; Märki, 2015) Changes may be related to changes in the performance of WWTPs (e.g. at the Neckar in Mannheim (E44) and at the Main in Bischofsheim (E55).

A study at the Meuse in 2010 (Volz, 2011) suggested that wastewater is a dominant source of glyphosate contamination: loads in the Meuse at a sampling point close to the French border in Tailfer (650,000 inhabitants in the catchment) were 0.28 kg/day glyphosate and 1.28 kg/day AMPA. Close to the estuary at Keizersveer (7.7. Mio inhabitants in the catchment), loads increased to 0.9 kg/day glyphosate and 19 kg/day AMPA. Thus, for glyphosate, the loads increased by 0.62 kg/day. A significant fraction of this increase in glyphosate mass flux can be explained by input via WWTPs: an additional load of 0.7 kg/day

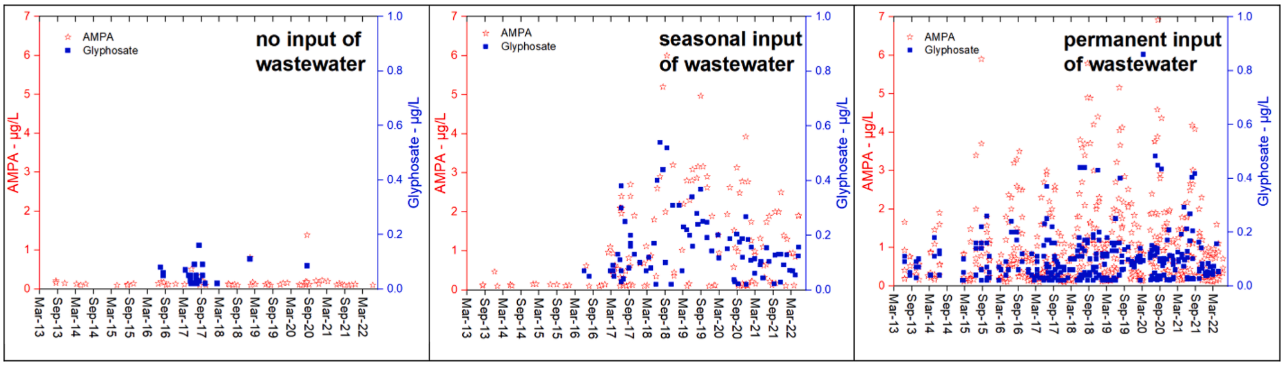

Fig. 5. Glyphosate and AMPA contamination in Berlin surface waters, plotting data for several rivers as point clouds classified regarding the temporal patterns of wastewater input. Data and information kindly provided by the Berliner Wasserbetriebe.

glyphosate was determined for several (25) but not all WWTPs discharging into the Meuse and its tributaries. (Volz, 2011) For AMPA, this load from the WWTPs was 1.36 kg/day. Aminopolyphosphonates were discussed to be an additional source, especially with regard to one tributary with very high AMPA loads (3.7 kg/day) presumed to stem from the use of phosphonates as antiscalants in cooling waters of chemical industries.

Our meta-analysis provides indications, that combined sewer overflow may be a relevant source for peak concentrations of glyphosate and AMPA in rivers. We see events of elevated discharge, where glyphosate and AMPA concentrations increase together with both wastewater and agricultural markers (see asterisks in Fig. 2d and f). A sampling with a very high temporal resolution during heavy rainfall in France showed glyphosate and AMPA concentrations to increase simultaneously with those of fecal indicators due to sewer overflow but hardly with the subsequent concentration peak of agrochemicals. (Reoyo-Prats et al., 2017)

4.3. An unknown source for glyphosate?

The importance of urban sources for glyphosate and AMPA has been discussed before, (Volz, 2011; Botta et al., 2009) especially in the Netherlands. (Desmet et al., 2016; Volz, 2011) As mentioned, AMPA is a known transformation product also of aminopolyphosphonates, which are intensely used in Europe as antiscalants, bleach stabilizers, and corrosion inhibitors mainly in laundry products, in the textile and paper industries, and in cooling circles. (Struger et al., 2015; Fürhacker et al., 2005; Studnik et al., 2015; Martin et al., 2020; Röhnelt et al., 2023) AMPA formation from aminopolyphosphonates in WWTPs was discussed by Wang et al. (Wang et al., 2019) We may thus assume that aminopolyphosphonates are the dominant source for AMPA. Then, the impressive differences between U.S. and European river contamination patterns and residues in WWTPs can easily be explained for AMPA: Opposite to Europe, the most popular U.S. laundry detergent brands do not contain aminopolyphosphonates (web search 6/2023). Sales numbers for aminopolyphosphonates were reported to be significantly lower in the USA compared to Europe. (Gledhill and Feijtel, 1992; Rott et al., 2018)

But how to explain the findings for glyphosate? The common perception is that glyphosate enters WWTPs after private or municipal urban herbicide applications, or from applications along railway tracks. However, looking into more detail (see detailed discussion in Section S3), none of these applications would explain rather constant base mass fluxes all over the year, especially not during long dry periods. E.g. in Germany, the number of permits for municipal and industrial glyphosate applications are very low and comprise maximal two applications during the growing season (Section S3.1). Similarly, railway tracks were reported to be treated only once per year (Deutscher Bundestag 2021) with low findings of glyphosate at larger distance to the tracks. (Cederlund, 2022) Sorption to soil particles and thus lowered bioavailability for transformation as well as possible long sludge retention times in WWTPs could be expected to broaden peak input after applications and rain events, but this is clearly not observed in the USA despite intense urban and agricultural use. Urban use in the EU became more and more restricted in recent years but mitigation strategies did not change surface water concentrations (see Section S4). Input via diet and urine would be a possible constant source for glyphosate in WWTPs, however, modeled loads for this source are too low to explain field data (see Section S3.3).

Some rough model calculations may aid to judge the loads that can be expected from urban herbicide applications. We can assume 80–90 % elimination rates in WWTPs (Poiger et al., 2020) and low loss rates of 1–2 % reported for glyphosate from residential areas (Tang et al., 2015; Ramwell et al., 2014) (see also Section S3.1). At the Teltowkanal in Berlin (site E59), the average yearly load of glyphosate in the canal is 28 kg/year (2015–2021). Considering elimination and loss rates, we can estimate an amount of the herbicide theoretically applied in the range of 2.8–28 tons of glyphosate per year in the catchment. This is high with regard to sales numbers for non-occupational use in Germany having declined from 95 tons per year in 2014 to 17 tons in 2021 (statistics from the German Bundesamt für Verbraucherschutz und Lebensmittelsicherheit 2022). With the estimate, a theoretical area of 41–390 km^2 could have been treated in the catchment of the WWTPs Waßmannsdorf and Stahnsdorf (and seasonaly Ruhleben, see Section 4.2) (calculated using: recommended doses of 0.17 g/m^2 (garden applications) or 0.072 g/m^2 for agricultural use (application in volunteer grain)). For comparison, the total area of Berlin is about 1000 km^2. Similarly, we estimate a load of 8 kg/year glyphosate at Site E54 with an old WWTP near a small village (500 inhabitants). Calculating with only 50 % elimination for the two sewage ponds, 0.8–1.6 tons of glyphosate and a theoretical application area of 4.7–9.4 km^2 are estimated. The area covered by the village is only 0.7 km^2 (simply using a rectangle in the map). We want to stress that to explain surface water concentrations, the application of glyphosate must evoke a rather constant input throughout the year.

For comparison, the model calculation can be reversed: If we estimate urban glyphosate use from sales numbers for non-occupational use to 10–100 tons of glyphosate (a broad range to account for the high uncertainty) (Section S3.1), a loss rate of 1 %, 80 % elimination rate and 10 billion m^3 wastewater in Germany, we could expect average WWTP effluent concentrations of glyphosate of 0.002–0.02 µg/L. This is clearly lower than the concentrations observed in European WWTPs (Section 4.2) and often even lower than river water concentrations (Table S2 and Fig. S2), for which further dilution by mixing of the WWTP effluent with river water would have to be considered.

Our meta-analysis clearly shows that municipal wastewater is important (see discussion for the Teltowkanal, Site E58), but provides further hints that domestic wastewater must be relevant: At site E53a (catchment only ca. 25 km^2), the seasonal pattern of AMPA is clearly visible and slightly indicated also for glyphosate. The site is about 8 km downstream of the Helme spring and downstream of the small WWTP of Stöckey (400 inhabitants). There is no industrial input. Similarly, only wastewater from households is relevant for sites E16, E41 and site E19 (600 m downstream of the Aubance spring in the village of Louerre (500 inhabitants). Finally, clear seasonal patterns of glyphosate and AMPA (concentrations up to 0.8 and 2 μg/L, respectively), flanked by the patterns of painkillers and phosphate are visible at the Vistre de la Fontaine in Nîmes (site E32, catchment of 41 km^2) with its spring in the city center. The river is mainly diverted through still existing Roman sewers used as the modern city's sewer system for a long time. It is known that some houses are still connected to this old sewer system, (Collet, 2014) making domestic wastewater a likely constant source for glyphosate.

5. Conclusion

Our meta-analysis on U.S. and European river water concentrations and additional information presented show that the dominant source for glyphosate in Europe cannot be herbicide application but is wastewater - the major indications being that, **1)** in contrast to the USA, seasonal patterns in Europe are not consistent with a dominant input from agricultural or urban herbicide applications. **2)** Only in Europe, rather constant base mass fluxes of glyphosate are present even during long dry summer periods and outside the application period of herbicides. **3)** Glyphosate and AMPA are detected in WWTPs connected to separate sewer systems receiving mainly domestic wastewater (Ghanem et al., 2007) and during dry weather periods. (Märki, 2015) **4)** High and constant loads shown to stem from WWTPs are difficult to relate to urban herbicide use. **5)** Model calculations for WWTP effluent concentrations of glyphosate from sales for non-occupational use are much lower than actual field data. **6)** Mitigation strategies did not change surface water concentrations or patterns. **7)** Concentration patterns of AMPA and glyphosate are very similar, which is unexpected given the different input pathways for AMPA, which are related to surface runoff (formation from glyphosate) and municipal wastewater (formation from aminopolyphosphonates).

What might this as yet unknown source for glyphosate be? Our results give rise to the following criteria:

1) A discharge into watercourses via WWTPs;
2) An origin in municipal and domestic wastewater;
3) An application/usage over the entire year;
4) An application/usage in most (Western) European countries but not in the USA;
5) A source for both glyphosate and AMPA; and
6) Relevant since at least 1999 (see site E49, Selz at Ingelheim).

We are not aware of any technical or domestic glyphosate applications evoking a constant input into wastewater and rivers leading to a rather constant log(A:G). As discussed, all aspects of this meta-analysis regarding AMPA concentration patterns can well be explained by its formation from aminopolyphosphonates. However, accepting aminopolyphosphonates as the dominant source for AMPA in Europe, raises the hypothesis that also glyphosate originates from these chemicals, making aminopolyphosphonates used e.g. in laundry detergents a common precursor for both AMPA and glyphosate. This hypothesis is further substantiated by the lack of aminopolyphosphonates in U.S. detergents and by the work of Klinger et al., (Klinger et al., 1998) demonstrating the formation of glyphosate during ozonation of the aminopolyphosphonate EDTMP already in 1998. Our ongoing experimental work addresses the formation of glyphosate under environmentally relevant conditions.

Author contributions

Carolin Huhn developed the hypothesis of wastewater input of glyphosate inspired by our sediment core data analyzed by Benedikt Wimmer. Together with Wolfgang Schulz, she organized the data collection for the meta-analysis. Carolin Huhn conducted most of the investigations on agricultural land use, informational aspects of selected sites, and management practices. She screened all data and made the selections included in this manuscript, which she prepared. Lisa Engelbart and Sarah Bieger aided in preparing the figures and took part in literature search. Marc Schwientek contributed to the catchment-specific interpretation of concentration time series, rank correlation and, aided by Hermann Rügner, supported the data interpretation, e.g., by calculating cumulative mass fluxes and by identifying discharge-related seasonal patterns. They both contributed to intense discussions throughout the study. Wolfgang Schulz supported the work with his expertise in markers for wastewater and agriculture. Stefan Haderlein critically considered all findings of the study and intensely edited the manuscript. All authors were active in improving the manuscript with discussions, further information, and editing.

CRediT authorship contribution statement

M. Schwientek: Writing – review & editing, Visualization, Validation, Resources, Investigation, Formal analysis. **H. Rügner:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis. **S.B. Haderlein:** Writing – review & editing, Visualization, Investigation. **W. Schulz:** Writing – review & editing, Validation, Resources. **B. Wimmer:** Writing – review & editing, Validation, Investigation. **L. Engelbart:** Writing – review & editing, Visualization, Validation, Investigation. **S. Bieger:** Writing – review & editing, Validation, Investigation. **C. Huhn:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

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

Data availability

The headers for Tables S1 and S2 provide information on all data sources used. A large share of the data is available online, some data sets can be provided upon request by the different institutions.

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Supplementary materials

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