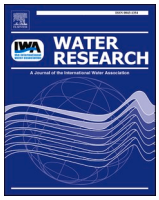
Water Research 272 (2025) 122965

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres



Comment on "Glyphosate contamination in European rivers not from herbicide application?" By M. Schwientek, H. Rügner, S.B. Haderlein, W. Schulz, B. Wimmer, L. Engelbart, S. Bieger, C. Huhn; Water Research Volume 263, 1 October 2024, 122140, page 1–10☆

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ARTICLE INFO

Keywords
Wastewater treatment
Glyphosate
Polyphosphonates
AMPA
Herbicide

1. Use of glyphosate

Schwientek et al. carried out a large meta-analysis of sites in Europe and the USA, and noticed differences in glyphosate and AMPA concentration patterns. They hypothesized that the presence of measured concentrations glyphosate and its transformation product AMPA in WWTP effluent cannot be attributed to the use of glyphosate as a herbicide. For this study they used data over the years 2014 until January 2023. The use of glyphosate as a herbicide in urban settings has been banned in some member states of the EU now, but this ban on use by private individuals is a recent development (Belgium 2018, Germany 2021, the Netherlands 2023), so at least would not be visible in large part of their data. Schwientek et al. restrict their analysis of the glyphosate use in Europe to the comparison of glyphosate sales for non-occupational use between 2014 and 2020/2021 in Berlin. However, in Germany the total sales of glyphosate were 4315 tonnes in 2015, 4700 in 2017, 3058 in 2019 and 4097 in 2021 (Wehde, 2023), which does not indicate a large decrease. Citizens and/or municipalities will have continued to use glyphosate as long as it could be legally bought, and probably will have kept some supplies for later use. Therefore, it is to be expected that glyphosate will have been used on roads and railways during most of the period studied. Grandcoin et al. (2017) and Botta et al. (2009) have shown that this application results in high glyphosate concentrations in WWTP effluent through storm sewers, contrarily to the assumption made by Schwientek et al.. This, however, is in accordance with the conclusion drawn by Schwientek et al., that municipal wastewater treatment plants significantly contribute to the release of AMPA and glyphosate.

Polyphosphonates are used in several industrial and household applications, and in water treatment processes (Studnik et al., 2015; Grandcoin et al., 2017), but only 15 % of the polyphosphonates originates from detergents. Even if these compounds would be converted into glyphosate on a significant scale, this could still not account for the concentration differences observed by Schwientek et al.

☆ The paper of Schwientek et al. suggests that there may be other sources of glyphosate contamination in rivers than its use as a herbicide. The authors hypothesize that glyphosate may be formed during treatment of polyphosphonate containing wastewater. We disagree with this hypothesis, as we will explain below. Furthermore, throughout the article the terms 'AMPA' and 'glyphosate' are constantly being mixed up, which contributes to a wrong interpretation of the results presented.

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https://doi.org/10.1016/j.watres.2024.122965
Received 30 August 2024; Received in revised form 7 December 2024; Accepted 10 December 2024
Available online 11 December 2024

2. Formation of AMPA

AMPA can be formed by microbial degradation of glyphosate in soils and from photo-degradation of amino polyphosphonates in water (Grandcoin et al., 2017; Wang et al., 2020). These authors did not indicate the formation of glyphosate from amino phosphonates. Biodegradation of phosphonates is not or only slightly possible (Horstmann and Grohmann, 1988; Nowack and Baumann, 1998; Drzyzga et al., 2017). In a recent paper Riedel et al. (2024) managed to identify a bacterial strain that can use phosphonates like AMPA as sole phosphorus source, but this work did not show the formation of glyphosate during this process. Chen et al. (2022) have shown the biodegradation of glyphosate via the AMPA pathway but they did not find any evidence of the (microbially mediated) formation of glyphosate from AMPA or other phosphonates. It has been shown, though, that glyphosate can be formed through ozonation of phosphonates (Klinger et al., 1998). However, as the large majority of European wastewater treatment plants only apply biological degradation processes and no ozonation, conversion of polyphosphonates from detergents into significant concentrations of glyphosate in WWTP effluent is very unlikely, although some conversion into AMPA, by photo-degradation, cannot be excluded. Volz (2011) showed that the degradation of glyphosate into AMPA depends on local conditions like time and temperature. Thus, concentrations of glyphosate in wastewater and surface water should always be expressed in relation to the total concentrations of glyphosate and AMPA, as AMPA is a known transformation product of glyphosate. Schwientek et al., however, mix up glyphosate and AMPA throughout the paper. In this way they misinterpret the AMPA and glyphosate concentrations, and confuse the discussion. They do not present any data on the reliability/reproducibility of sampling, sample preparation and analytical methods. It certainly will not be easy to do this for a large set of data, but on the other hand in this way it cannot be judged to what extend these data can be compared*, especially as in the paper AMPA and glyphosate often are being confused*. Besides, the ratio of AMPA to glyphosate is calculated on a logarithmic scale. All this may result in large inaccuracies in their comparisons. Furthermore, they have shown no physical proof beyond their meta-analysis, to support their conclusion. Therefore, what they present as a conclusion in fact is a hypothesis, that is hardly supported by data on glyphosate and other polyphosphonates use in the EU, and totally not supported by any (bio) chemical proof.

3. Conclusions

Schwientek et al. argue that there should be another source of glyphosate, and that AMPA or other phosphonates may well be converted into glyphosate. However, they do not take into account physical/chemical proof on glyphosate and polyphosphonate degradation and the use of glyphosate as a herbicide in the urban environment during the period they investigated. No analytical or mechanistic data are presented, and their claims contradict scientific findings. They focused more on the number of permits than on degradation data and data about the use of glyphosate as a herbicide in the urban environment. The data presented do not in any way indicate the formation of glyphosate from polyphosphonates during WWTP processes, nor that there might be another source than herbicides explaining the presence of glyphosate and AMPA in European rivers. Their data rather indicate that the use of glyphosate had not diminished yet as a result of changing legislation, and that the (illegal) use in urban areas may still be a problem to be tackled.

The hypothesis that “glyphosate may also be a transformation product of aminopolyphosphonates ” should be rejected, as it cannot be based on the data presented.

CRediT authorship contribution statement

Harry H. Tolkamp: Writing – original draft, Investigation. **Roberta (C.H.M.). Hofman-Caris:** Writing – original draft, Investigation.

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

No data was used for the research described in the article.

References

Botta, F., Lavison, G., Couturier, G., Alliot, F., Moreau-Guigon, E., Fauchon, N., Guery, B., Chevreuil, M., Blanchoud, H., 2009. Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems. Chemosphere 77 (1), 133–139.

Chen, Y., Chen, W.J., Huang, Y., Li, J., Zhong, J., Zhang, W., Zou, Y., Mishra, S., Bhatt, P., Chen, S., 2022. Insights into the microbial degradation and resistance mechanisms of glyphosate. Environ. Res. 215.

Drzyzga, D., Forlani, G., Vermander, J., Kafarski, P., Lipok, J., 2017. Biodegradation of the aminopolyphosphonate DTPMP by the cyanobacterium Anabaena variabilis proceeds via a C–P lyase-independent pathway. Environ. Microbiol. 19 (3), 1065–1076.

Grandcoin, A., Piel, S., Baurès, E., 2017. AminoMethylPhosphonic acid (AMPA) in natural waters: its sources, behavior and environmental fate. Water Res. 117, 187–197.

Horstmann, B., Grohmann, A., 1988. Investigations into the biodegradability of phosphonates. Vom Wasser 70, 163–178.

Klinger, J., Lang, M., Sacher, F., Brauch, H.J., Maier, D., Worch, E., 1998. Formation of glyphosate and AMPA during ozonation of waters containing ethylenediaminetetra (methylenephosphonic acid). Ozone Sci. Eng. 20 (2), 99–110.

Nowack, B., Baumann, U., 1998. Biodegradation of the photolysis products of FeIIIEDTA. Acta Hydrochim. Hydrobiol. 26 (2), 104–108.

Riedel, R., Commichau, F.M., Benndorf, D., Hertel, R., Holzer, K., Hoelzle, L.E., Mardoukhi, M.S.Y., Noack, L.E., Martienssen, M., 2024. Biodegradation of selected aminophosphonates by the bacterial isolate Ochrobactrum sp. BTU1. Microbiol. Res. 280.

Studnik, H., Liebsch, S., Forlani, G., Wieczorek, D., Kafarski, P., Lipok, J., 2015. Amino polyphosphonates–chemical features and practical uses, environmental durability and biodegradation. New Biotechnol. 32 (1), 1–6.

Volz, J. (2011). Glyfosaat En AMPA in Het Stroomgebied van De Maas; Resultaten van Een Internationale Meetcampagne in 2010, RIWA-Maas, Werkendam, The Netherlands.

Wang, S., Zhang, B., Shan, C., Yan, X., Chen, H., Pan, B., 2020. Occurrence and transformation of phosphonates in textile dyeing wastewater along full-scale combined treatment processes. Water Res. 184.

Wehde, G. (2023, 14-09-2023). "Bioland warnt vor weiteren fünf Jahren Glyphosat " Retrieved 28-08-2024, 2024, from https://www.bioland.de/presse/pressemitteilungen-detail/bioland-warnt-vor-weiteren-fuenf-jahren-glyphosat.