PHOSPHONATES EUROPE

INFORMATION PAPER

November 2024

A Tübingen University study[1] suggests that aminophosphonates contribute to glyphosate in surface waters, but leaves key questions unanswered. Phosphonates Europe supports further research to identify all potential sources.

A recent publication[1] of the University of Tübingen concludes that industrial aminophosphonates, especially DTPMP used in detergents, contribute to the occurrence of glyphosate in the environment. This study consists of a statistical analysis of the concentration levels of glyphosate and aminomethylphosphonic acid (AMPA) found in surface waters at about 70 locations in Central and Western Europe. AMPA is a degradation product of both glyphosate and DTPMP. Unlike in the USA, where DTPMP is not used, no seasonal fluctuations in the occurrence of both substances (glyphosate and AMPA) are observed in the EU. In the USA, these fluctuations correlate well with agricultural glyphosate use. Based on these observations, the University of Tübingen concludes that the glyphosate found in surface waters in the EU originates from the degradation of DTPMP used in detergents.

To substantiate their findings, the University of Tübingen released an additional study[2] describing a known process by which DTPMP is completely degraded into AMPA.

Phosphonates Europe, representing the European manufacturers of phosphonates, supports any efforts to identify the origins of glyphosate in the environment and intends to play an active role in this process. As such, there are some concerns we would like to address in relation to these two studies:

- In wastewater treatment plants, glyphosate and AMPA strongly attach to the sludge, rather than degrade into discharge waters.
- The Tübingen University study 'Glyphosate contamination in European rivers not from herbicide application?'
    - does not consider the impact of the hardness of the water

[1] C. Huhn et al, 2024, Glyphosate contamination in European rivers not from herbicide application? https://www.sciencedirect.com/science/article/pii/S004313542401039X?via%3Dihub

[2] C. Huhn, 2024, Glyphosate is a transformation product of a widely used aminopolyphosphonate complexing agent, https://www.researchgate.net/publication/383176943_Glyphosate_is_a_transformation_product_of_a_widely_used_aminopolyphosphonate_complexing_agent

Phosphonates Europe
Rue Belliard 40, b15, B-1040 Brussels, Belgium
Tel. +32.2.436.93.00 - phosphonates@cefic.be - www.phosphonates.org
A sector group of Cefic
European Chemical Industry Council - Cefic aisbl
EU Transparency Register: 64879142323-90

    - does not seek to validate the mass balance between the levels of DTPMP used in EU detergents and the glyphosate and AMPA levels in surface waters.

- The Tübingen University study 'Glyphosate is a transformation product of a widely used aminopolyphosphonate complexing agent' is conducted under largely artificial experimental conditions, significantly deviating from natural conditions.
- In addition to industrial agriculture, other sources of glyphosate, such as urban applications, are well documented.
- The levels addressed are below the recommended limits, and are considered safe for human health and the environment.

In wastewater treatment plants, glyphosate and AMPA strongly attach to the sludge, rather than degrade into discharge waters.

Scientific studies[3,4] have established that glyphosate is frequently detected in municipal wastewater, indicating significant urban use, but is not significantly degraded during the wastewater treatment. Instead, glyphosate attaches strongly to the sludge thanks to its property to bind to metal ions like iron, aluminium or calcium and to the organic matter that are present in the sludge. This adsorption mechanism allows for a removal efficiency ranging from 71-96%. Some recycling processes can be applied to the sludge afterwards to recover phosphorus[5] or other nutrients. Alternatively, under certain conditions it can be used in agriculture, otherwise be incinerated. The consistent detection of glyphosate and AMPA in municipal wastewater and their strong adsorption to sludge suggest that their presence in surface waters is largely attributable to glyphosate use rather than DTPMP.

The Tübingen University study 'Glyphosate contamination in European rivers not from herbicide application?' does not consider the impact of the hardness of the water

The persistence of glyphosate and its metabolite AMPA in water is influenced by the hardness of the water. In hard water, which contains high levels of minerals like calcium and magnesium, glyphosate forms stable complexes with these metals. These complexes are difficult to break down, meaning that glyphosate and AMPA remain in the water for a long time.

The Tübingen University study 'Glyphosate is a transformation product of a widely used aminopolyphosphonate complexing agent' is conducted under largely artificial experimental conditions, significantly deviating from natural conditions.

---

[3] E. Rott, 2020, Influence of Wastewater Discharge on the Occurrence of PBTC, HEDP, and Aminophosphonates in Sediment, Suspended Matter, and the Aqueous Phase of Rivers, https://www.mdpi.com/2073-4441/12/3/803

[4] Poiger et al, Chimia, 2020, 74, No. 3, 156160, Behaviour of Glyphosate in Wastewater Treatment Plants, https://www.chimia.ch/chimia/article/view/2020_156

[5] More about the phosphorus recovery technologies under development at ESPP: https://www.phosphorusplatform.eu/activities/p-recovery-technology-inventory

While the first study suggests that the occurrence of glyphosate in the environment is also due to DTPMP used in detergents, due to the absence of seasonality, the second study, currently only available as a non-reviewed pre-publication, describes an already known process where DTPMP is completely degraded on manganese oxide surfaces, into AMPA, and glyphosate to a lesser extent. The experiments of this study were conducted under very controlled and artificial conditions to ensure the complete degradation of DTPMP:

- using ten times more manganese oxide than DTPMP - unlikely in natural conditions
- using pure water - absence of hardness or other transition metal ions that would already neutralise a part of the glyphosate
- using a buffer (morpholine ethane sulfonic acid) to maintain a stable pH during the experiments - to ensure optimal chemical reaction
- over a maximum period of four days - which is too short to determine the environmental persistence of glyphosate and AMPA, knowing that the average half-life of glyphosate under normal conditions is approx. 30 days.

The study did not include any experiments that would approach natural conditions, and the maximum amount of glyphosate produced in these very specific conditions is about 0,16% of the original DTPMP - a very low ratio.

The Tübingen University study 'Glyphosate contamination in European rivers not from herbicide application?' does not seek to validate the mass balance between the levels of DTPMP used in EU detergents and the glyphosate and AMPA levels in surface waters.

The study is lacking a comparison of the concentration levels of glyphosate and AMPA observed in the surface waters analysed, with a calculation of the DTPMP used in detergents within the EU, multiplied by the proposed degradation factor (max 0,16% in laboratory conditions). This would have given a first impression on the plausibility of this hypothesis.

According to Eurostat, total sales of pesticides in the EU amounted around 322.000 mt in 2022. Glyphosate represents about a third of the total volume of herbicides sold in the EU, slightly above 100.000 mt. In comparison, we can only provide an approximation of the maximum volume of DTPMP used in EU detergents, that would amount about 10.000 mt.

In addition to industrial agriculture, other sources of glyphosate, such as urban applications, are well documented.

The scientific paper[6] by Hanke et al. makes reference to the presence of glyphosate in waters that are not connected to waste water treatment plants. This attests of alternative sources of glyphosate, not linked to aminophosphonates in detergents. These alternative sources could come from:

[6] Hanke et al, Chemosphere 81 (2010) 422-429, Relevance of urban glyphosate use for surface water quality, https://www.sciencedirect.com/science/article/abs/pii/S0045653510007411

- urban applications like treatment of railway embankments, roadsides, professional & domestic gardeners.
- improper cleaning of glyphosate-containing work equipment
- groundwater containing glyphosate, reaching surface waters
- shaft drainage in fields, that help to remove the excess water from the soil
- heavy rainfalls or irrigation

The levels addressed are below the recommended limits, and are considered safe for human health and the environment.

The concentrations of glyphosate in surface waters determined over the past few years in Central and Western Europe average 0.1-0.5 µg/l, and are far below the limit value of 86.7 µg/l specified in the European Commission's proposal[7] amending the Environmental Quality Standards Directive. This value is assumed to be the value below which no harmful effects on aquatic organisms are to be expected. In the reporting and discussions about the conversion of DTPMP, the small amounts of glyphosate that are (supposedly) produced as an intermediate product from DTPMP, should only be a tiny portion of it, if any, which has not been calculated by the Tübingen University researchers. These concentrations are not critical for either human health or the environment.

In conclusion, Tübingen University's study proposes a new perspective, but leaves too many uncertainties at this stage. We recommend further research on the diverse sources of glyphosate mentioned above, to clarify the origins and quantities of glyphosate encountered in surface waters. The members of Phosphonates Europe, in association with other stakeholders, are keen to see the work of the Tübingen University continued, and fully support initiatives to the scope out the environmental fate of their products.

For more information please contact:
Peng Paternostre
Phosphonates Europe Sector Group Manager, ppa@cefic.be

About Cefic
Cefic, the European Chemical Industry Council, is the forum of large, medium and small chemical companies across Europe, accounting for 1.2 million jobs and 14% of world chemicals production.
On behalf of its members, Cefic's experts share industry insights and trends, and offer views and input to the EU agenda. Cefic also provides members with services, like guidance and trainings on regulatory and technical matters, while also contributing to the advancement of scientific knowledge.

[7] COM(2022) 540 final, Annex V, https://environment.ec.europa.eu/publications/proposal-amending-water-directives_en