


Degradation of glyphosate in water by the application of surface corona discharges

Katja Zocher ^a, Peter Gros^{b,c}, Matthias Werneburg^a, Volker Brüser^{a,*}, Juergen F. Kolb^a and Peter Leinweber^b

^a Leibniz Institute for Plasma Science and Technology (INP), Felix-Hausdorff-Strasse 2, 17489 Greifswald, Germany

^b Faculty of Agriculture and Environmental Sciences, Soil Science, University of Rostock, Justus-von-Liebig-Weg 6, 18051 Rostock, Germany

^c State Office for Agriculture and Rural Area Thuringia, Naumburger Strasse 98, 07743 Jena, Germany

*Corresponding author. E-mail: brueser@inp-greifswald.de

 KZ, 0000-0002-6353-0581

ABSTRACT

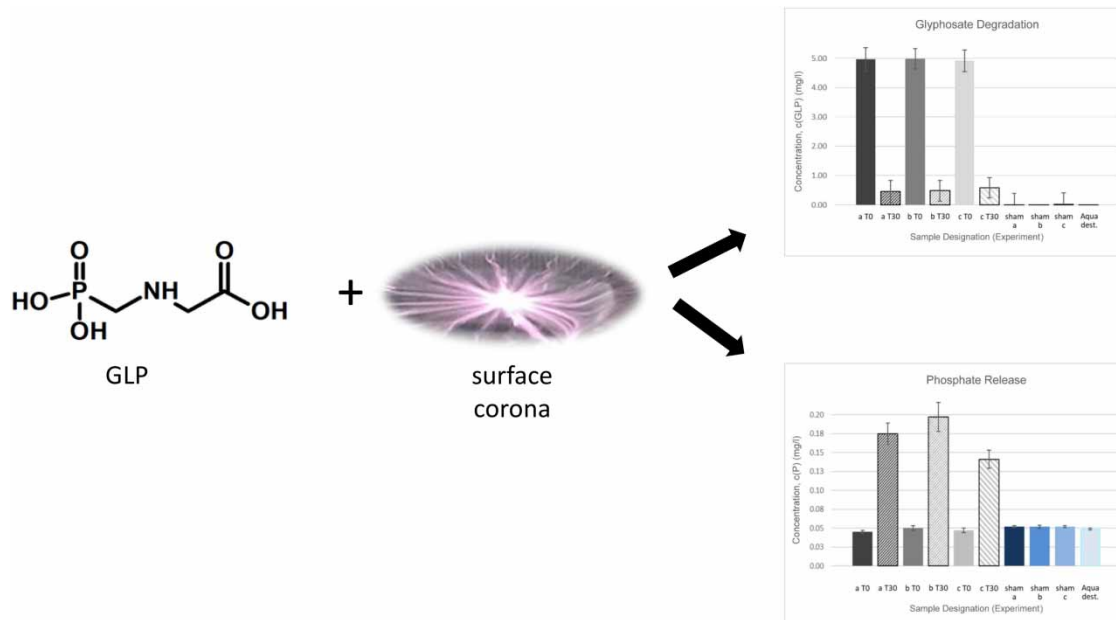
Glyphosate (GLP) is one of the most widely applied herbicides, and is found ubiquitously in the environment. The removal of glyphosate from waste water and soil is challenging and can be achieved with chemical or biological methods, which, nevertheless, suffer from different disadvantages. The application of a physical plasma for the removal of GLP in water was examined by the application of surface corona discharges in a wire-to-cylinder setup filled with argon. The plasma was ignited at the liquid surface without any additives. By applying a photometric method, GLP was detected after derivatisation with fluorenyl methoxycarbonyl chloride, whereas phosphate was determined with ammonium molybdate. A GLP degradation rate of 90.8% could be achieved within a treatment time of 30 minutes with an estimated energy efficiency of 0.32 g/kWh.

Key words: corona discharges, degradation, glyphosate, pesticide, plasma, water treatment

HIGHLIGHTS

- Corona discharges ignited at the water surface degraded glyphosate (GLP) more than 90%.
- Total carbon mineralisation was indicated by elevated free phosphate concentrations.
- Increase of liquid conductivity after plasma treatment implied the formation of ionic degradation products.

GRAPHICAL ABSTRACT



This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

1. INTRODUCTION

The herbicide glyphosate (N-(phosphonomethyl)glycine, GLP) is one of the most important agrochemicals in the world, with an annual global use of over 1 million tonnes of the active ingredient (Richmond 2018). Different environmental compartments favour its environmental distribution and environmental behaviour such as strong sorption (Glass 1987; Borggaard & Gimsing 2008), rapid microbial degradation within several days (Tang *et al.* 2019), and low toxic risk for non-target organisms. GLP detected in ground and surface waters (Struger *et al.* 2008; Battaglin *et al.* 2009; Botta *et al.* 2009; Poiger *et al.* 2017), had concentrations higher than the regulatory limit, e.g. 0.1 µg/L of EU (Van Stempvoort *et al.* 2014; Skeff *et al.* 2015) whereas in wastewaters, the concentration of GLP and its degradation product AMPA (aminomethylphosphonic acid) was reported up to 4.5 µg/L (Kolpin *et al.* 2006; Hanke *et al.* 2010; Poiger *et al.* 2020), thus demonstrating its persistence. In addition, GLP shows a slow chemical reactivity, which affects analytical detection (Gros *et al.* 2019) and chemical degradation abilities (Balci *et al.* 2009; Wang *et al.* 2019). Conversely, the interaction of GLP with organic substances (e.g. amines, carbohydrates, phenols) increases their toxicity (Tefamariam *et al.* 2009). The compound interferes in chemical reactions as matrix constituents (Ahmed *et al.* 2018) and may favour their leaching through the soil (Gros *et al.* 2017).

Although GLP is barely found as free molecules in the environment, it binds strongly also with inorganic substances. These bindings can likewise lead to an increased toxicity for aquatic organisms. Annett *et al.* (2014) described in a review that particularly microalgae and other microorganisms are the most affected aquatic organisms. Also invertebrates, fish, or amphibians were negatively affected by GLP (Annett *et al.* 2014; and references in the review). Hence, complex interactions with a variety of possible impacts on environmental behaviour call for strategies to prevent GLP from further environmental distribution and removal from waters is thus necessary.

Different approaches have been studied to remove GLP from wastewaters, such as sorption of GLP on added Al³⁺/Mg²⁺ minerals (Li *et al.* 2005) or alum sludge (Hu *et al.* 2011). Other methods are biological degradation (Balthazor & Hallas 1986; Hallas *et al.* 1992) or chemical degradation, e.g. by photo-Fenton or electro-Fenton processes (Balci *et al.* 2009). Ozonation achieved only low degradation rates of less than 30% (Mason *et al.* 1990; Nemeth *et al.* 2019).

The previous mentioned methods are time consuming and/or need additional chemicals for water treatment. Therefore, treatment of wastewater with physical plasmas may overcome these disadvantages, since they work within minutes and require no additional chemicals. This has already been successfully demonstrated for persistent pharmaceuticals (Banaschik *et al.* 2015). In 2016, Wang *et al.* showed the successful GLP degradation in soil, using a dielectric-barrier discharge (DBD) plasma (Wang *et al.* 2016). There, GLP degradation and formation of organic intermediates, as well as inorganic end products (phosphate, ammonia), took place within an hour. However, this promising technique has so far not been applied for the treatment of GLP in wastewaters. Conversely, Fouodjouo *et al.* demonstrated that degradation of glyphosate dissolved in water was possible with a gliding arc plasma (Fouodjouo *et al.* 2015). It was found that, after 30 minutes, only traces of GLP could be detected by photospectrometry. Nevertheless, mineralisation of GLP was only obtained by adding iron salts, which is less favourable for realistic conditions.

With respect to the aforementioned disadvantages, another approach was examined in this work for the direct treatment of water containing GLP. The objective of this work was to determine whether plasma ignited in the close vicinity of the water may be able to degrade GLP and to what extent. A surface corona discharge was set up that provided a plasma along the liquid surface. The system was built in a wire-to-cylinder geometry, allowing for simple scaling. Concurrently, a method to detect degradation rates of GLP and mineralised degradation products, such as phosphate (photometric detection), was established.

2. MATERIALS AND METHODS

2.1. Sample preparation for plasma treatment

All experiments were performed with a GLP concentration of 5 mg/L. GLP (PESTANAL[®], analytical standard, Sigma Aldrich, Taufkirchen, Germany). The substance was dissolved in distilled water, stored in 1.5 L plastic bottles (1,500 mL, low density polyethylene, Laborhandel 24, Wertheim, Germany) and stored overnight between 2 and 8 °C. All controls were performed with distilled water (referred as 'sham' in the following sections). Experiments were repeated in triplicate.

2.2. Electrical setup

Corona-surface discharges were ignited in a wire-to-cylinder configuration, similar to the method described by Banaschik *et al.* (2015). In short, a tungsten wire (purity 99.95%; Good Fellow Cambridge Limited, England) with a diameter of

0.05 mm was positioned along the centre of a glass cylinder (length 70 mm; diameter 47 mm) and fixed at the top of the surrounding PMMA-housing. A stainless steel mesh (Haves & Boecker OHG, Oelde, Germany) was attached to the glass wall inside of the cylinder at a cylinder-height of approximately 35 mm. Outlets for water and gas were connected with plastic tubes at the bottom and top of the cylinder. The plasma was ignited between the tip of the wire, which touched the liquid surface, and the mesh at the cylinder wall. The wire was repositioned after every experiment. The gas space above the liquid was filled with argon at atmospheric pressure. Argon was chosen as the working gas to prevent the formation of reactive nitrogen species (RONS) that would, for example, be formed with air only instead. RONS and their rather stable products NO_3 and NO_2 are known for decreasing the pH of the liquid, which would lead to an acidification of the samples. However, acidic water would lead to acidic soils, which would be an unwanted side effect of this technique. It has to be noted that the reactor was not completely sealed and thus some gas exchange with ambient air may have been possible.

The plasma was generated with rectangular high-voltage pulses from a commercial pulse generator (Eagle Harbor Technologies, Inc., Seattle, USA), i.e. with a pulse length of 260 ns, pulse amplitude of 20 kV, and a pulse repetition rate of 1 kHz. The samples were run through the system with a peristaltic pump (Meredos TL, Medorex, Germany) with a flow rate of 50 mL/min. The entire system, including tubes and expansion tank held a total volume of 200 mL. The setup is depicted in Figure 1.

Samples were treated for 30 minutes and were cooled in a water bath throughout to prevent degradation by heating. This allowed constant temperatures between 20 and 22 °C. All experiments were repeated in triplicate and results were labelled with 'T0' for initial concentrations of the samples, and 'T30' for concentrations obtained after 30 minutes treatment time. Samples without GLP, i.e. aqua dest., were treated to determine whether plasma had an effect on the sample matrix itself. These samples are labelled as 'sham' in Figures 2–4. For every set of experiments also aqua dest. itself was tested without plasma treatment, to exclude matrix effects. The samples are labelled as 'aqua dest.' in each figure, accordingly. Additionally, conductivity was determined after each plasma treatment.

2.3. Analytical methods

2.3.1. Determination of glyphosate concentration

For the photometric detection of GLP, the method was calibrated with five concentrations of the analyte in the range of 0–38.5 $\mu\text{mol GLP/L}$ (0–6.5 mg GLP/L), each in five replicates, and a blank with no GLP addition with 10 replicates. The method proposed by Waiman *et al.* (2012) was used for GLP derivatisation with slight modifications. Briefly, 0.5 mL of EDTA solution ($c = 20 \text{ mg/L}$) and borate buffer solution (pH 9) was added to 4 mL of sample solution. Next, an excess concentration of fluorenylmethoxycarbonyl chloride (FMOC-Cl; 0.5 mL, $c = 1 \text{ g/L}$; dissolved in acetonitrile) was added. After vigorous shaking, the derivatisation solution was allowed to react for 2 h while occasionally shaken again. Subsequently, by-products of FMOC-Cl (FMOC-OH) were removed by liquid–liquid extraction with 4 mL of dichloromethane. The mixture

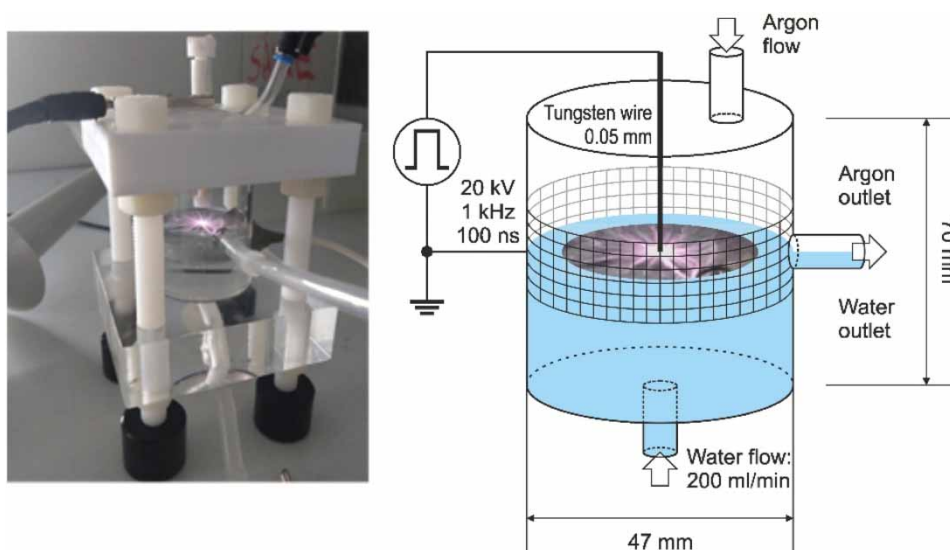


Figure 1 | Photograph and schematic (without the housing) of the electrical setup as described in section 2.2. Arrows indicate the flow direction of the liquid and of argon, respectively. High-voltage pulses were applied between the tungsten wire and the grounded metal mesh.

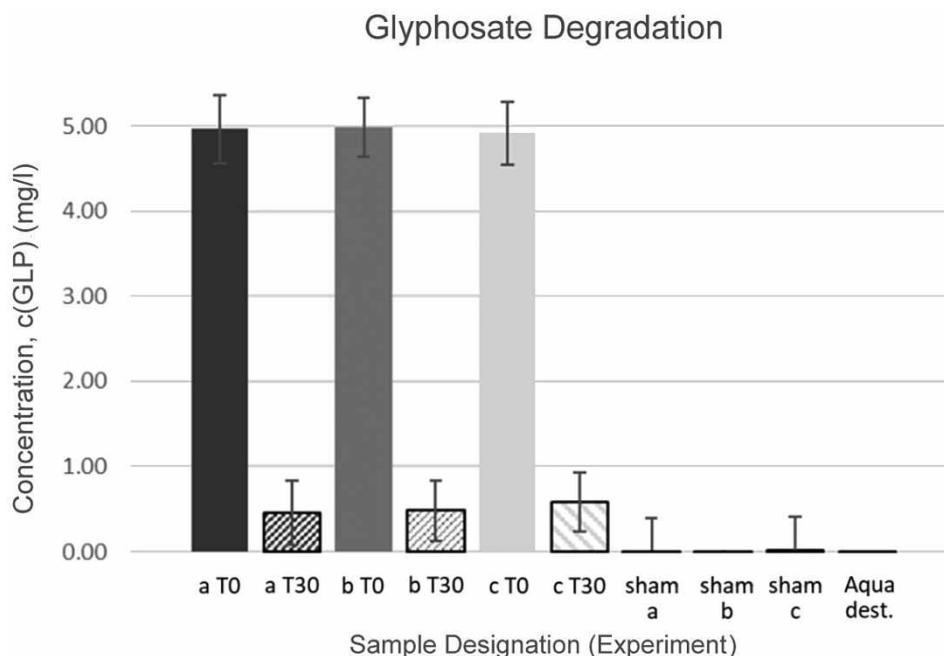


Figure 2 | Glyphosate concentrations, $c(\text{GLP})$, before (a T0, b T0, c T0, solid fill) and after plasma treatment (a T30, b T30, c T30, hatched fill), respectively, as well as the corresponding sham samples, and aqua dest.

was centrifuged (10 min, $1,558 \times g$) to separate the two phases. The supernatant aqueous phases of each derivatisation solution were used for photospectroscopy at $\lambda = 264 \text{ nm}$ (Specord200, Analytik Jena AG, 07745 Jena, Germany). The averaged signals of the calibration series of the respective analyte were corrected by subtracting the signal intensity of the blank level, which contained no analyte. In this way, effects on signal intensity resulting from matrix constituents were eliminated.

2.3.2. Determination of phosphate concentration

Soluble reactive phosphorus was determined via the ammonium molybdate spectrometric method (DIN EN 1189 D11) using a Cary 1E Spectrophotometer (Varian Medical Systems, Inc.).

2.3.3. Determination of conductivity

The conductivity of the samples ($20 \text{ }^\circ\text{C}$) was measured in 50 mL centrifuge tubes, used for sample storage, by a WTW LF3000 conductivity meter (Xylem Analytics Germany Sales GmbH & Co. KG).

3. RESULTS AND DISCUSSION

3.1. Glyphosate

The evaluation of the calibration series showed a level of detection (LOD) of $0.95 \mu\text{mol GLP/L}$ (0.16 mg GLP/L) and a level of quantitation (LOQ) of $1.83 \mu\text{mol GLP/L}$ (0.31 mg/L). The results for the tested samples are presented in Figure 2. No impurities were detected, which could otherwise contribute to false-positive or background signals, including for the treatment of pH-adjusted water samples without GLP addition (sham a–c). Therefore, plasma treatment did not create any artefacts in the experiments. Full recovery was achieved for the untreated GLP samples (a T0; b T0; c T0, $4.92\text{--}4.98 \text{ mg/L}$), indicating the suitability for evaluating the degradation. After plasma treatment (a T30; b T30; c T30, see Figure 2), GLP concentration decreased to $0.46\text{--}0.48 \text{ mg/L}$, which corresponded to a degradation rate of $88.3\text{--}90.8\%$ within 30 min.

3.2. Phosphate

The evaluation of the calibration series showed LOD for phosphate of $0.13 \mu\text{mol P}_i/\text{L}$ (0.16 mg/L) and LOQ of $0.20 \mu\text{mol P}_i/\text{L}$ (0.31 mg/L). The results are presented in Figure 3. The aqua dest. sample showed only small impurities of $0.5 \mu\text{mol P}_i/\text{L}$ (0.049 mg/L P_i). In addition, the pH-adjusted samples investigated after plasma treatment (sham a–c) and those with GLP

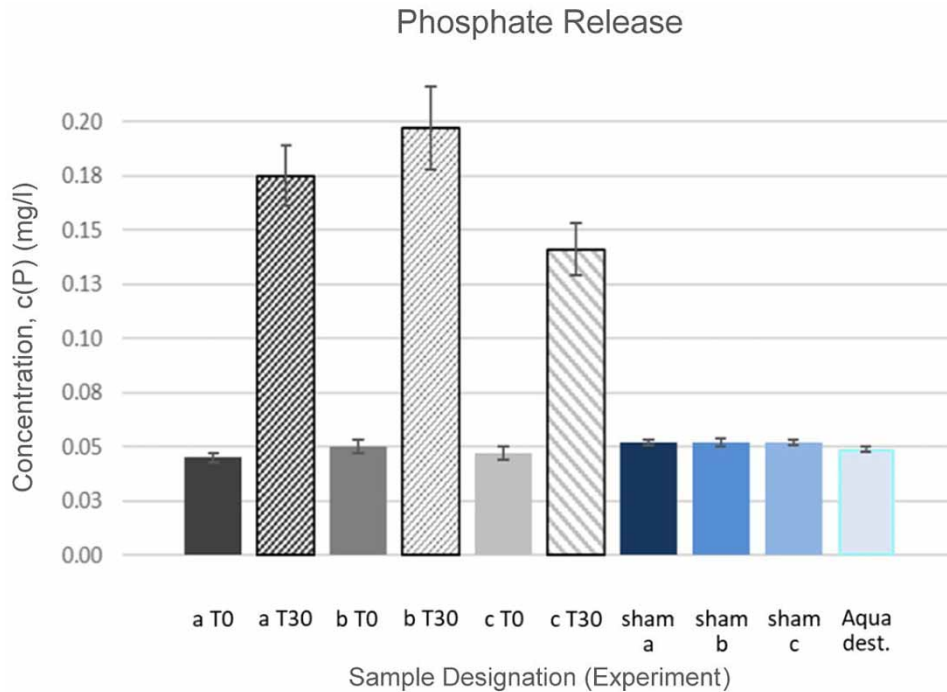


Figure 3 | Phosphate concentration, $c(P_i)$, before (a T0, b T0, c T0, solid fill) and after plasma treatment (a T30, b T30, c T30, hatched fill), as well as the corresponding sham samples, and aqua dest.

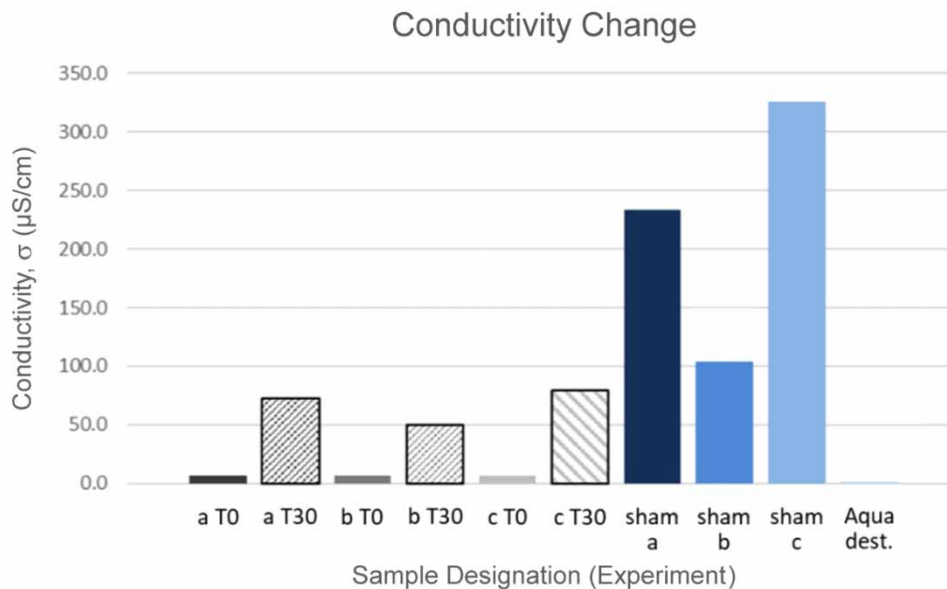


Figure 4 | Conductivity, σ , before (a T0, b T0, c T0, solid fill) and after plasma treatment (a T30, b T30, c T30, hatched fill), as well as the corresponding sham samples, and aqua dest.

addition studied before plasma treatment (a T0; b T0; c T0) had P_i impurities at levels of the treated aqua dest. ($0.47\text{--}0.55 \mu\text{mol } P_i/\text{L}$, or $0.045\text{--}0.052 \text{ mg/L}$). For the plasma-treated samples (a T30; b T 30; c T30), the concentration of P_i rose strongly to $1.48\text{--}2.07 \mu\text{mol } P_i/\text{L}$ ($0.14\text{--}0.175 \text{ mg/L}$). This clearly indicated a degradation of GLP into mineralised end products.

3.3. Electrical conductivity

Aqua dest., as a reference sample, showed no relevant conductivity ($1.77 \mu\text{S}/\text{cm}$; see Figure 4), whereas after addition of sulphuric acid (sham a–c) for pH-adjustment conductivity rose to $104\text{--}324 \mu\text{S}/\text{cm}$, since the number of free charged atoms or molecules (sulphate ions and protons) increased. The addition of GLP led to decreased conductivities between 6.41 and $7.18 \mu\text{S}/\text{cm}$ (samples a T0; b T0; c T0), indicating that the number of free charged ions decreased due to compensation of positive and negative ions and/or clusters of ions that were formed, which were less mobile due to their size. Formation of GLP clusters previously reported by Daniele *et al.* may explain this observation (Daniele *et al.* 1997). The conductivity increased from 50.2 to $79.1 \mu\text{S}/\text{cm}$ after plasma treatment (samples a T30; b T30; c T30), which could be an indicator for the formation of additional charged degradation products.

Since the applied method cannot distinguish between GLP itself, or its derivatisable degradation product AMPA, it is not clear, which species contributed to the remaining signals. The comparison of amounts of degraded GLP ($26.0\text{--}26.8 \mu\text{mol GLP}/\text{L}$ or $4.43\text{--}4.50 \text{ mg}/\text{L}$) with the amounts of created phosphate ($1.48\text{--}2.07 \mu\text{mol P}_i/\text{L}$, or $0.094\text{--}0.147 \text{ mg}/\text{L}$) show that, although GLP was almost completely degraded, only a small portion was mineralised. Hence, the formation of smaller organic intermediates, according to the microbial degradation pathway described by Giesy *et al.* (see Figure 5), can be assumed (Giesy *et al.* 2000). The formed intermediates after plasma treatment can be considered ionic, contributing to the increased conductivity of the solution, and contained no secondary amine group (e.g. sarcosine) and/or phosphorous fragments (e.g. N-methylphosphonate). Fouodjouo *et al.* postulated that hydroxyl radicals, generated during plasma treatment might be the main reactive agents which degrade GLP. They further stated that hydroxyl radicals and the recombined hydrogen peroxide (H_2O_2) are most likely responsible for plasma-degraded GLP and observed by-products (Fouodjouo *et al.* 2015). Wang *et al.* also described that hydroxyl radicals might be the main reason for GLP degradation during DBD plasma treatment (Wang *et al.* 2016). Hydroxyl-mediated removal of organic compounds was recently also demonstrated for pharmaceuticals in water that were treated by corona discharges similar to the presented experiments (Banaschik *et al.* 2018). Comparable findings were also reported for the degradation of dyes or phenol (Hoeben *et al.* 2000; Sugiarto *et al.* 2003). It is likely that analogous pathways can be postulated for GLP reduction by surface corona discharges. In addition, a contribution by a certain amount of ozone that might be generated at the plasma-liquid surface was possible, which was enhanced by the formation from oxygen either dissolved in water or provided from the dissociation of water molecules. Lukes *et al.* have found that in a corona discharge over a water surface, with an Ar/ O_2 atmosphere above the liquid, the ozone production is increased in the presence of argon. Argon is a monoatomic and chemical inert gas, which hinders quenching of oxygen. The participation as a third collision partner might explain an increased ozone production under argon atmosphere (Lukes *et al.* 2005). It is thus likely that a mixture of hydroxyl radicals and ozone are responsible for

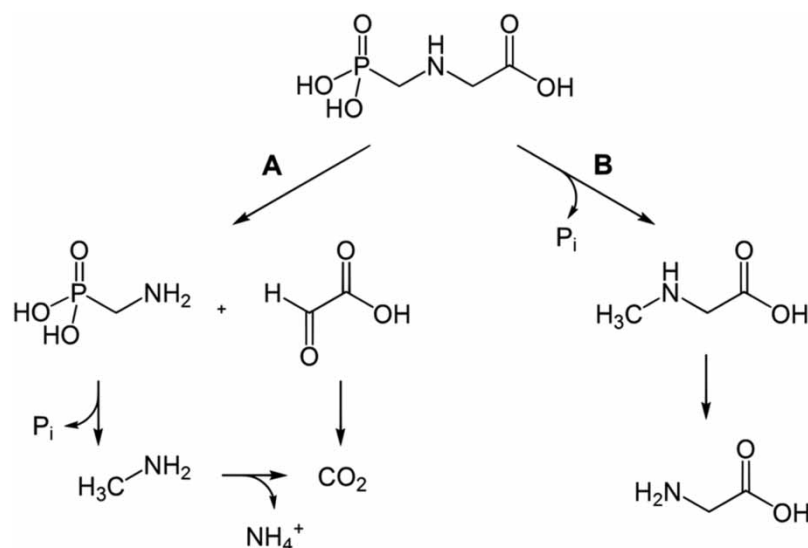


Figure 5 | Microbial degradation pathways of glyphosate according to Giesy *et al.* (2000). A similar degradation pathway can be assumed for plasma treatment.

the observed degradation. However, the degradation by hydroxyl radicals can be assumed to be more efficient and prominent, considering that degradation by ozonation achieved only low degradation rates (Mason *et al.* 1990; Nemeth *et al.* 2019). An in-depth analysis of generated radicals and possible toxic degradation by-products is therefore necessary for further research.

There are different treatment options to degrade GLP in water (Jönsson *et al.* 2013). In comparison with these options, the present plasma-based degradation method achieved similar rates in a shorter time, but without additives. For instance, chemical-based methods for GLP removal, such as electro-Fenton-like processes or H₂O₂/UV treatment, reached degradation rates of 40–90% in 40–300 min for highly contaminated (0.3–1 mmol GLP/L) media (Balci *et al.* 2009; Manassero *et al.* 2010). Sorption-based methods also require the addition of chemical substrates to the media, e.g. Al³⁺/Mg²⁺ minerals or alum sludge. They achieved an equilibrium for the degradation of an initial load of 0.2–0.6 mmol GLP/L after 24–52 hours. With Al³⁺/Mg²⁺-minerals, a GLP degradation by 95% was achieved (Li *et al.* 2005), and more than 91% for alum sludge (Hu *et al.* 2011). Biological methods for contaminated wastewaters (0.03–1.2 mmol GLP/L) reached degradation rates higher than 95% within several days (Hallas *et al.* 1992). In comparison, a study of GLP removal from contaminated soil (initial concentration of 1.2 mmol GLP/kg soil) by plasma treatment yielded a degradation rate of more than 95% within 45 min after the application of a DBD plasma (Wang *et al.* 2016). Also Fouodjouo *et al.* stated a high degradation rate after the application of a gliding arc after 30 minutes of treatment time (Fouodjouo *et al.* 2015). In the study presented here, a GLP degradation of more than 90% was achieved for an initial concentration of 5 mg GLP/L within 30 minutes. The energy consumption was calculated with 25–30 mJ/pulse, resulting in total energy of about 50 kJ for the treatment. Thus, an energy efficiency of 0.32 g/kWh could be obtained, which is similar to observations for the degradation of dyes, and other organic compounds by corona discharges (Locke & Shih 2011). The findings and the results presented here indicate that plasma treatment is a fast and efficient method for the degradation of glyphosate, which is suitable for different environmental compartments.

4. CONCLUSIONS

The aim of this study was to evaluate whether surface corona discharges are able to degrade GLP dissolved in water. A removal rate of over 90% could be achieved within a short time, which makes this method interesting for application in wastewater treatment plants. However, for further research, it is necessary to study whether less expensive gases instead of argon can achieve similar degradation rates. A more in-depth analysis of intermediates and end products after GLP degradation is recommended, which will also help to improve the system and tailor the plasma source for scaling.

ACKNOWLEDGEMENT

This research was conducted within the scope of the Leibniz Science Campus Phosphorus Research Rostock.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Ahmed, A. A., Gros, P., Kühn, O. & Leinweber, P. 2018 Molecular level investigation of the role of peptide interactions in the glyphosate analytics. *Chemosphere* **196**, 129–134.
- Annett, R., Habibi, H. R. & Hontela, A. 2014 Impact of glyphosate and glyphosate-based herbicides on the freshwater environment. *Journal of Applied Toxicology* **34** (5), 458–479.
- Balci, B., Oturan, M. A., Oturan, N. & Sires, I. 2009 Decontamination of aqueous glyphosate, (aminomethyl) phosphonic acid, and glufosinate solutions by electro-Fenton-like process with Mn²⁺ as the catalyst. *Journal of Agricultural and Food Chemistry* **57** (11), 4888–4894.
- Balthazor, T. M. & Hallas, L. E. 1986 Glyphosate-degrading microorganisms from industrial activated sludge. *Applied and Environmental Microbiology* **51** (2), 432–434.
- Banaschik, R., Lukes, P., Jablonowski, H., Hammer, M. U., Weltmann, K.-D. & Kolb, J. F. 2015 Potential of pulsed corona discharges generated in water for the degradation of persistent pharmaceutical residues. *Water Research* **84**, 127–135.
- Banaschik, R., Jablonowski, H., Bednarski, P. J. & Kolb, J. F. 2018 Degradation and intermediates of diclofenac as instructive example for decomposition of recalcitrant pharmaceuticals by hydroxyl radicals generated with pulsed corona plasma in water. *Journal of Hazardous Materials* **342**, 651–660.

- Battaglin, W. A., Rice, K. C., Focazio, M. J., Salmons, S. & Barry, R. X. 2009 The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005–2006. *Environmental Monitoring and Assessment* **155** (1–4), 281–307.
- Borggaard, O. K. & Gimsing, A. L. 2008 Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. *Pest Management Science: Formerly Pesticide Science* **64** (4), 441–456.
- 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.
- Daniele, P. G., De Stefano, C., Prenesti, E. & Sammartano, S. 1997 Copper (II) complexes of N-(phosphonomethyl) glycine in aqueous solution: a thermodynamic and spectrophotometric study. *Talanta* **45** (2), 425–431.
- Fouodjouo, M., Laminsi, S., Kamgang, G. Y., Mengue, M. T. & Debacher, N. A. 2015 Non-thermal plasma induced total mineralization of glyphosate in water in the presence of iron II ions. *Journal of the Brazilian Chemical Society* **26** (3), 411–419.
- Giesy, J. P., Dobson, S. & Solomon, K. R. 2000 Ecotoxicological risk assessment for Roundup® herbicide. In: George W. Ware (eds) *Reviews of Environmental Contamination and Toxicology*. Springer, Tucson USA, pp. 35–120.
- Glass, R. L. 1987 Adsorption of glyphosate by soils and clay minerals. *Journal of Agricultural and Food Chemistry* **35** (4), 497–500.
- Gros, P., Ahmed, A., Kühn, O. & Leinweber, P. 2017 Glyphosate binding in soil as revealed by sorption experiments and quantum-chemical modeling. *Science of the Total Environment* **586**, 527–535.
- Gros, P., Ahmed, A. A., Kühn, O. & Leinweber, P. 2019 Influence of metal ions on glyphosate detection by FMOC-Cl. *Environmental Monitoring and Assessment* **191** (4), 244.
- Hallas, L., Adams, W. & Heitkamp, M. 1992 Glyphosate degradation by immobilized bacteria: field studies with industrial wastewater effluent. *Applied and Environmental Microbiology* **58** (4), 1215–1219.
- Hanke, I., Wittmer, I., Bischofberger, S., Stamm, C. & Singer, H. 2010 Relevance of urban glyphosate use for surface water quality. *Chemosphere* **81** (3), 422–429.
- Hoeben, W., Van Veldhuizen, E., Rutgers, W., Cramers, C. & Kroesen, G. 2000 The degradation of aqueous phenol solutions by pulsed positive corona discharges. *Plasma Sources Science and Technology* **9** (3), 361.
- Hu, Y., Zhao, Y. & Sorohan, B. 2011 Removal of glyphosate from aqueous environment by adsorption using water industrial residual. *Desalination* **271** (1–3), 150–156.
- Jönsson, J., Camm, R. & Hall, T. 2013 Removal and degradation of glyphosate in water treatment: a review. *Journal of Water Supply: Research and Technology - AQUA* **62** (7), 395–408.
- Kolpin, D. W., Thurman, E. M., Lee, E. A., Meyer, M. T., Furlong, E. T. & Glassmeyer, S. T. 2006 Urban contributions of glyphosate and its degradate AMPA to streams in the United States. *Science of the Total Environment* **354** (2–3), 191–197.
- Li, F., Wang, Y., Yang, Q., Evans, D. G., Forano, C. & Duan, X. 2005 Study on adsorption of glyphosate (N-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution. *Journal of Hazardous Materials* **125** (1–3), 89–95.
- Locke, B. R. & Shih, K.-Y. 2011 Review of the methods to form hydrogen peroxide in electrical discharge plasma with liquid water. *Plasma Sources Science and Technology* **20** (3), 034006.
- Lukes, P., Clupek, M., Babicky, V., Janda, V. & Sunka, P. 2005 Generation of ozone by pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor. *Journal of Physics D: Applied Physics* **38**, 409–416.
- Manassero, A., Passalia, C., Negro, A. C., Cassano, A. E. & Zalazar, C. S. 2010 Glyphosate degradation in water employing the H₂O₂/UVC process. *Water Research* **44** (13), 3875–3882.
- Mason, Y. Z., Choshen, E. & Rav-Acha, C. 1990 Carbamate insecticides: removal from water by chlorination and ozonation. *Water Research* **24** (1), 11–21.
- Nemeth, J., Sebestyen, V., Juzsakova, T., Cretescu, I., Domokos, E. & Redey, A. 2019 Study of the glyphosate-amine pesticide mineralization in wastewater by ozonation treatment. *Environmental Engineering & Management Journal (EEMJ)* **18** (9), 1867–1873.
- Poiger, T., Buerge, I. J., Bächli, A., Müller, M. D. & Balmer, M. E. 2017 Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS. *Environmental Science and Pollution Research* **24** (2), 1588–1596.
- Poiger, T., Keller, M., Buerge, I. J. & Balmer, M. E. 2020 Behavior of glyphosate in wastewater treatment plants. *CHIMIA International Journal for Chemistry* **74** (3), 156–160.
- Richmond, M. E. 2018 Glyphosate: a review of its global use, environmental impact, and potential health effects on humans and other species. *Journal of Environmental Studies and Sciences* **8** (4), 416–434.
- Skeff, W., Neumann, C. & Schulz-Bull, D. E. 2015 Glyphosate and AMPA in the estuaries of the Baltic Sea method optimization and field study. *Marine Pollution Bulletin* **100** (1), 577–585.
- Struger, J., Thompson, D., Staznik, B., Martin, P., McDaniel, T. & Marvin, C. 2008 Occurrence of glyphosate in surface waters of southern Ontario. *Bulletin of Environmental Contamination and Toxicology* **80** (4), 378–384.
- Sugiarto, A. T., Ito, S., Ohshima, T., Sato, M. & Skalny, J. D. 2003 Oxidative decoloration of dyes by pulsed discharge plasma in water. *Journal of Electrostatics* **58** (1), 135–145.
- Tang, F. H., Jeffries, T. C., Vervoort, R. W., Conoley, C., Coleman, N. V. & Maggi, F. 2019 Microcosm experiments and kinetic modeling of glyphosate biodegradation in soils and sediments. *Science of the Total Environment* **658**, 105–115.

- Tesfamariam, T., Bott, S., Cakmak, I., Römheld, V. & Neumann, G. 2009 Glyphosate in the rhizosphere—role of waiting times and different glyphosate binding forms in soils for phytotoxicity to non-target plants. *European Journal of Agronomy* **31** (3), 126–132.
- Van Stempvoort, D., Roy, J., Brown, S. & Bickerton, G. 2014 Residues of the herbicide glyphosate in riparian groundwater in urban catchments. *Chemosphere* **95**, 455–463.
- Waiman, C. V., Avena, M. J., Garrido, M., Band, B. F. & Zanini, G. P. 2012 A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to adsorption isotherms on soils and goethite. *Geoderma* **170**, 154–158.
- Wang, T., Ren, J., Qu, G., Liang, D. & Hu, S. 2016 Glyphosate contaminated soil remediation by atmospheric pressure dielectric barrier discharge plasma and its residual toxicity evaluation. *Journal of Hazardous Materials* **320**, 539–546.
- Wang, G., Huang, R., Zhou, A. & Xu, Q. 2019 Degradation of methyl orange by a new catalyst glyphosate ferrous. *Solid State Sciences* **95**, 105933.

First received 29 April 2021; accepted in revised form 30 July 2021. Available online 11 August 2021