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

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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
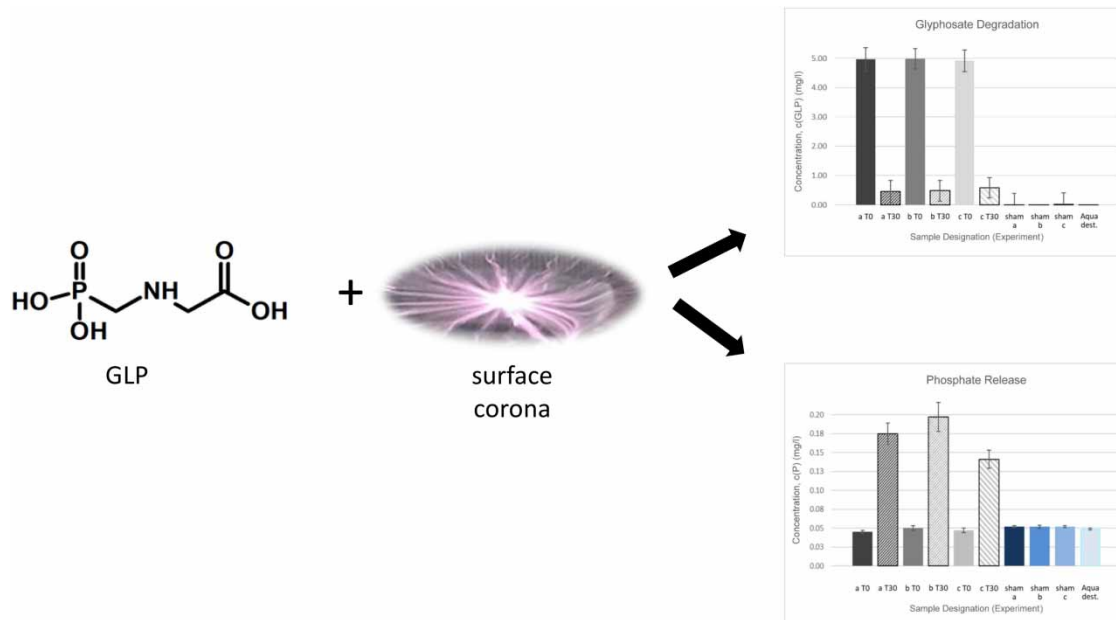
1. INTRODUCTION

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 (Tesfamariam 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 Al^{3+}/Mg^{2+} 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 μmol 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 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 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
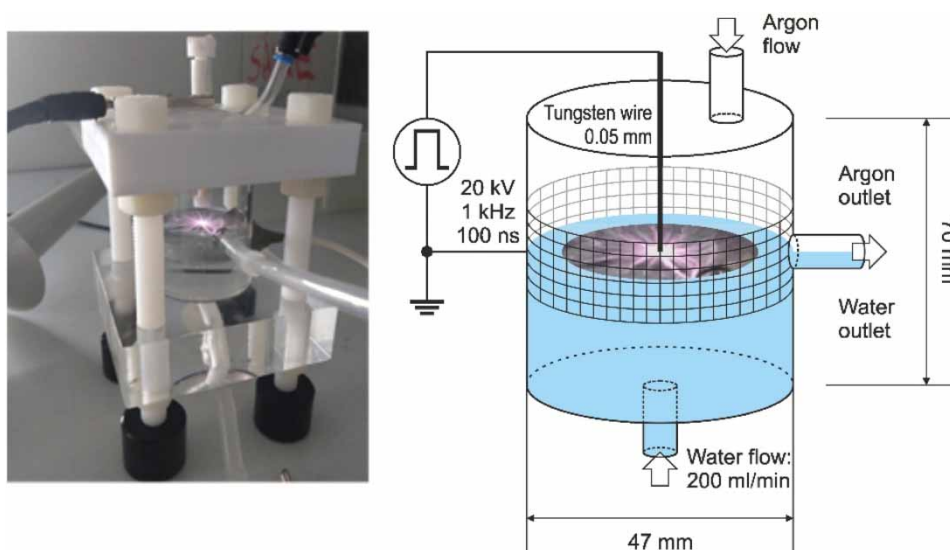

Figure 1 | Photograph and schematic (without the housing) of the electrical setup as described in section 2.2. Arrows indicate the flow direction of the liquid and of argon, respectively. High-voltage pulses were applied between the tungsten wire and the grounded metal mesh.
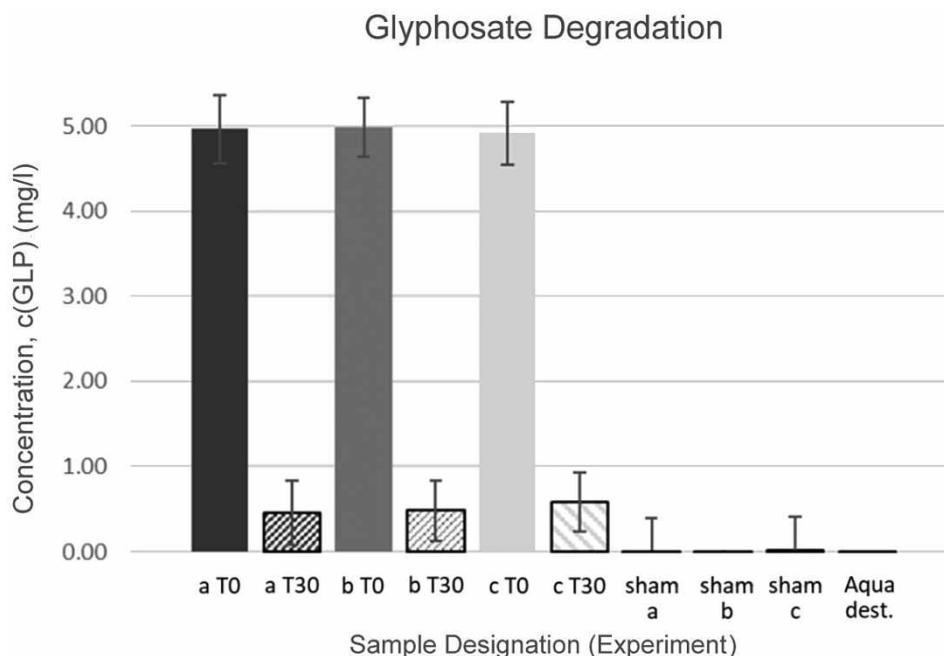
Figure 2 | Glyphosate concentrations, c(GLP), before (a T0, b T0, c T0, solid fill) and after plasma treatment (a T30, b T30, c T30, hatched fill), respectively, as well as the corresponding sham samples, and aqua dest.

was centrifuged (10 min, 1,558 × g) to separate the two phases. The supernatant aqueous phases of each derivatisation solution were used for photospectroscopy at $\lambda = 264$ 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 °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 μmol GLP/L (0.16 mg GLP/L) and a level of quantitation (LOQ) of 1.83 μmol 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, 4.92–4.98 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 0.46–0.48 mg/L, which corresponded to a degradation rate of 88.3–90.8% within 30 min.

3.2. Phosphate

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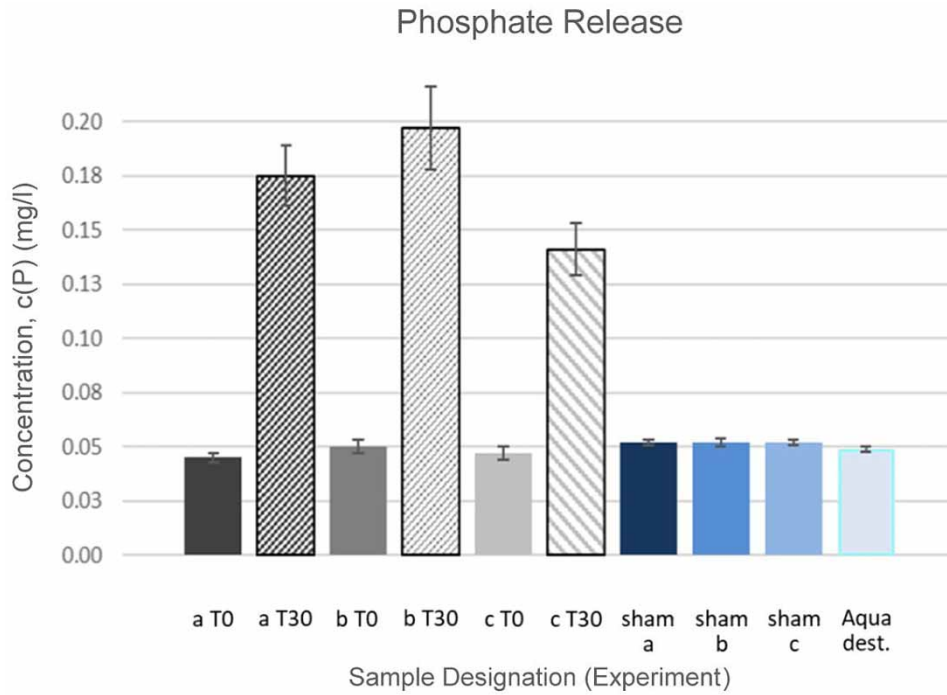
Phosphate Release

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.

Conductivity Change

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.
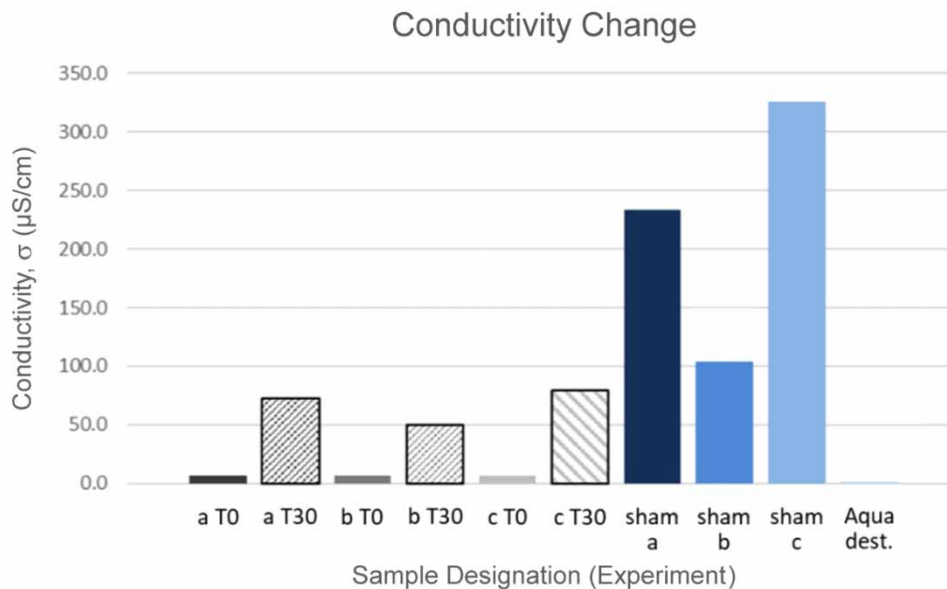
addition studied before plasma treatment (a T0; b T0; c T0) had P$_i$ impurities at levels of the treated aqua dest. (0.47–0.55 μmol P$_i$/L, or 0.045–0.052 mg/L). For the plasma-treated samples (a T30; b T 30; c T30), the concentration of P$_i$ rose strongly to 1.48–2.07 μmol P$_i$/L (0.14.–0.175 mg/L). 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 μS/cm; see Figure 4), whereas after addition of sulphuric acid (sham a–c) for pH-adjustment conductivity rose to 104–324 μS/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 μS/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 μS/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 (26.0–26.8 μmol GLP/L or 4.43–4.50 mg/L) with the amounts of created phosphate (1.48–2.07 μmol P_i/L, or 0.094–0.147 mg/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
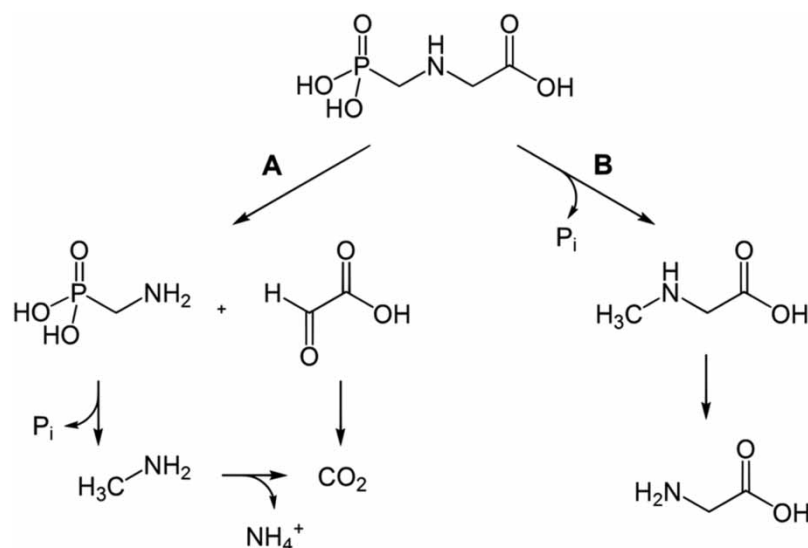

Figure 5 | Microbial degradation pathways of glyphosate according to Giesy et al. (2000). A similar degradation pathway can be assumed for plasma treatment.

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 option, 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 H_2O_2/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. Al^{3+}/Mg^{2+} 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 Al^{3+}/Mg^{2+}-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.

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DATA AVAILABILITY STATEMENT

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

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