Sunlight Degradation of the Aminophosphonate Diethylenetriamine Penta-(Methylenephosphonic Acid)

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Abstract: Aminophosphonate diethylenetriamine penta(methylene phosphonic acid) (DTPMP) is a scale inhibitor commonly used in several industries. DTPMP is suspected to cause anthropogenic pollution through discharge into the aquatic environment. DTPMP is assumed to be degraded by sunlight radiation. We recently predicted a preliminary degradation pathway of DTPMP applying UV treatment. Currently, we have not yet evidenced that DTPMP shows the same degradation pattern with natural sunlight. One major reason leads to the fact that the light spectrum emitted by UV lamps does not completely represent the natural sunlight spectrum, and the emitted UVB and UVA irradiation flux is much higher than for solar light. For that reason, the degradation pattern and kinetics might be different between artificial UV treatment and natural sunlight treatment. Here, we investigated whether DTPMP is degradable under natural sunlight radiation, and whether the degradation mechanisms determined through UV treatment are transferable to sunlight. We investigated five different treatment conditions, i.e., DTPMP degradation in direct or diffuse sunlight, in diffuse sunlight with addition of Ca\(^{2+}\) or Mg\(^{2+}\), and in diffuse sunlight with local TW. Our experiment was carried out from March 2021 to October 2021. We performed LC/MS analyses and measured the release of o-PO\(_4\)\(^{3-}\). DTPMP was degraded with all five treatment conditions. The fastest DTPMP degradation occurred in direct and diffuse sunlight without addition of bivalent cations. The addition of Ca\(^{2+}\) and Mg\(^{2+}\) resulted in inhibited degradation. Similar effects occurred for sunlight treatment with local TW. We evidenced different degradation mechanisms for DTPMP depending on the presence of alkaline earth metals as we previously proposed for UV-treated DTPMP. However, both degradation mechanisms of DTPMP belong to the same degradation pathway determined with UV treatment. Therefore, we conclude that DTPMP undergoes a similar degradation pathway in sunlight as compared to UV light.

Keywords: phosphonates; DTPMP; sunlight degradation; UV degradation; actinometry

1. Introduction

Synthetic phosphonate diethylenetriamine penta(methylene phosphonic acid) (DTPMP) is characterised as (poly)amino(poly)phosphonate, which interacts strongly as a complexing agent with earth alkali and transition metals [1]. Depending on varying stoichiometry, DTPMP can form multinuclear complexes increasing its efficiency extraordinarily. Because of this threshold effect, DTPMP can be dosed in very low concentrations to stabilise and delay cation metal precipitation [2,3]. Therefore, DTPMP is widely applied as commercial...
scale inhibitor in the petroleum industry [2], in cooling water systems [4], desalination processes [5], and in liquid detergents [6]. Despite its common use as scale inhibitor, DTPMP also finds application in medical approaches. Neto et al. [7] reported the development of novel DTPMP-coated nanoparticles as magnetic resonance imaging contrast agent. They also proposed other potential application such as magnetic hyperthermia, separation science, catalysis, and sensing.

During the last several years, the demand for aminophosphonates including DTPMP has continuously increased. For example, Reinhardt et al. [8] reported an increase by over 60% from 4673 tons in 2015 to 7613 tons in 2019 of phosphonates used in detergents, cleaning, and maintenance products in Germany. We recently reported an annual consumption of the DTPMP sodium salt (DTPMP-xNa) averaging 10,000 to 100,000 tons based on latest data of the European Chemical Agency [9]. Therefore, we assume that also the global consumption of DTPMP has increased within past few years.

Concern has grown that DTPMP might cause anthropogenic pollution through discharge into the aquatic environment. Rott et al. [10] emphasized the fact that the largest discharge of phosphonates to the receiving water is caused by the direct discharge of membrane concentrates and cooling water. He and his colleagues estimated discharge loads from 9000 to 18,600 tons per year to flowing rivers in Europe. Tang et al. [11] indicated that the release of untreated membrane brines could promote eutrophication of water bodies. However, membrane brines from desalination processes are not the only anthropogenic sources of DTPMP in water bodies. Municipal wastewater treatment plants (WWTP) can also be an important source of phosphonates to the aquatic environment [11,12]. Wang et al. [13] demonstrated that phosphonates are continuously released from municipal wastewater plants at trace levels. In 1998, Nowack [14] reported an influent concentration of DTPMP ranging between 74 and 109 µg L$^{-1}$ in different Swiss WWTPs. More recently, Rott et al. [15] reported an average 14 to 71 µg L$^{-1}$ DTPMP in the influent of two German municipal WWTPs. Similar to Wang et al. [13], Rott et al. [15] also showed that up to 96% of phosphonates analysed in the influents were removed during wastewater treatment. Wang et al. [13] indicated that precipitation was essential for their successful removal. Furthermore, they showed that adsorption of phosphonates on activated sludge resulted in up to 7.81 g kg$^{-1}$ in dewatered sludge, which can be of relevance during sludge disposal.

It was often reported that phosphonates can lead to eutrophication in aquatic ecosystems [4,10,16,17]. However, due to their high chemical stability, phosphonates such as DTPMP are not directly prone to immediately cause eutrophication once they are released to flowing water bodies. In addition, it was reported that most aquatic organisms show low intrinsic toxicity towards synthetic phosphonates [10,18]. Inhibition effects of DTPMP on algal growth were recently investigated by Wang et al. [18]. They found that photosynthesis was not directly inhibited by DTPMP, but by the chelator-limited free iron ions due to complexation. Free iron ions are essential for algal photosynthesis. Inhibition of algal photosynthesis resulted in serious decline in chlorophyll A, and thus a functional loss of energy generation of catabolism leading to inhibited growth. According to Wang et al. [18], impacts on the growth of autotrophic microalgae caused by phosphonates can have irreversible consequences as primary producers of aquatic ecosystems. Furthermore, Wang et al. indicated that algae growth can be recovered due to natural degradation of phosphonates releasing phosphate and trapped transition ion metals such as iron. In those cases, harmful algal blooms might easily occur because a low threshold concentration of phosphorus at only 100 µg P L$^{-1}$ was estimated [19]. Natural degradation of phosphonates in flowing water bodies is assumed to predominantly take place through photodegradation via sunlight radiation.

Several laboratory studies have been carried out that applied advanced oxidation processes (AOP) by UV irradiation, often combined with different oxidative additives to degrade phosphonates [9,17,20–23]. All authors evidenced high decomposition rates leading to release of orthophosphate (o-PO$_3^{3-}$) and other mineralisation products. Most of these authors reported AOPs as potential pretreatment of phosphate-contaminated
wastewaters prior to release into water bodies. Alternatively, photocatalysis can also be an interesting approach to degrade persistent substances such as phosphonates and/or other organic dyes [24]. However, photocatalytic degradation was predominantly reported for glyphosate degradation [25–29].

We recently reported UV degradation of DTPMP and ethylenediaminetetra-(methyleneephosphonic acid) (EDTMP) without additives as a potential degradation pathway that could also occur under natural condition [9,29]. However, until now there is no scientific evidence that aminophosphonates such as DTPMP show the same degradation pattern under UV irradiation as compared with natural sunlight irradiation. One major reason leads to the fact that the treatment conditions during UV experiments are very different from environmental conditions in terms of phosphonate concentration and the high-power UV source. The latter, especially, might be of crucial importance because the light spectrum emitted by UV lamps does not completely represent the natural sunlight spectrum, and the emitted UVB and UVA irradiation flux is much higher than for solar light. For this reason, the degradation pattern and kinetics might be different between artificial UV treatment and natural sunlight treatment.

Thus, the aim of our present study was to investigate if DTPMP is degradable under natural sunlight irradiation, and, if so, whether a similar degradation pathway occurs for UV degradation recently reported. The influence of direct and diffuse sunlight irradiation on degradation of DTPMP in ultrapure water was investigated together with the influence of calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)) and local tap water. The experiments were performed for 200 days from March to October 2021.

2. Material and Methods

2.1. Chemicals

DTPMP and EABMP were provided by Zschimmer and Schwarz Mohsdorf (Burgstädt, Germany). IDMP and AMPA were purchased from Sigma Aldrich (Steinheim, Germany). Calcium chloride dihydrate (CaCl\(_2\)·2H\(_2\)O) was purchased from Fluka Chemika (Neu-Ulm, Germany). Magnesium chloride hexahydrate (MgCl\(_2\)·6H\(_2\)O) was purchased from Merck (Darmstadt, Germany). Monopotassium oxalate (KHC\(_2\)O\(_4\)) was purchased from Alfa Aesar (Karlsruhe, Germany). Iron trichloride (FeCl\(_3\)·6H\(_2\)O) was purchased from Merck (Darmstadt, Germany). H\(_2\)SO\(_4\) was purchased from Roth (Karlsruhe, Germany). Ultrapure water (LC/MS grade) was generated in-house (Adrona Sia Crystal EX, Riga, Lithuania). Acetonitrile of LC/MS grade was purchased from VWR (Dresden, Germany) and ammonium acetate of analytical grade was purchased from VWR (Leuven, Belgium). All chemicals were of analytical grade or better with purity >99%.

2.2. UV Treatment of DTPMP

A reference UV treatment with 100 mg L\(^{-1}\) DTPMP was performed to determine major breakdown products. The degradation experiment was performed in an open quartz-glass vessel providing a total liquid volume of 350 mL; the UV lamp was placed in the centre of the glass (150 W middle-pressure mercury lamp; TQ 150 Heraeus Noblelight, Hanau, Germany). The maximum emission of the lamp was at 366 nm with \(3.3 \times 10^{-5} \pm 0.2 \times 10^{-5}\) E s\(^{-1}\) incident photon flux, which corresponds to a light intensity of 1.1 mW cm\(^{-2}\). The degradation experiment was performed corresponding to system configuration 1 [30]. Liquid samples were taken at the starting point; after 10, 20, and 30 min; and then in 30 min intervals until 300 min. All samples were analysed by liquid chromatography/mass spectrometry (LC/MS) for determination of major breakdown products. In addition, all samples were analysed by spectrophotometry for the release of o-PO\(_4^{3-}\).

2.3. Actinometry to Determine the Photon Flux in Sunlight with Different Flask Materials

For the choice of a suitable vessel material for our sunlight experiments, light-sensitive potassium trisoxalato-ferrate complex (K\(_3[Fe(C_2O_4)_3]·3H_2O\) was synthesised. The com-
plete synthesis was carried out in the dark. First, 60 mM KHC$_2$H$_4$ was dissolved in 50 mL of ultrapure water. Then, 20 mM FeCl$_3$·6H$_2$O was dissolved in 50 mL ultrapure water. Both solutions were mixed in the dark at room temperature under constant stirring at 500 rpm for 30 min. For crystallisation, the solution was stored at 4 °C overnight. The resulting ferrioxalate complex crystals were passed through a cellulose acetate filter with a pore size of 0.45 µm (Sartorius; VWR, Dresden, Germany) and dried overnight at 35 °C. The dried ferrioxalate complex was stored in a light-protected vial prior to use. To determine which flask material was most suitable for the sunlight experiments, 7.5 mM ferrioxalate complex solution was dissolved in acidified ultrapure water (0.05 mol L$^{-1}$ H$_2$SO$_4$).

Four different materials were investigated for their suitability for the sunlight experiments, i.e., two different poly(ethylene terephthalate) (PET) flasks (blue and transparent), one high density polyethylene (HDPE) flask from Nalgene (Sigma Aldrich, Steinheim, Germany), and one transparent silica glass flask from Schott (VWR, Dresden, Germany). All flasks were filled with 0.25 L of the ferrioxalate complex solution and placed outside in diffuse sunlight for 80 min. Samples were taken after 10, 20, 40, 60, and 80 min. The release of ferrous iron (Fe$^{2+}$) was determined.

2.4. Sunlight Degradation Experiments

All degradation experiments were carried out with 100 mg L$^{-1}$ DTPMP in 1 L HDPE bottles. Five different treatment conditions were investigated, including degradation in direct sunlight without addition of additives, in diffuse sunlight without addition of additives, in diffuse sunlight with addition of calcium (Ca$^{2+}$), in diffuse sunlight with addition of magnesium (Mg$^{2+}$), and in diffuse sunlight with local tap water (TW). For the following, these five test conditions are named: condition 1—direct sunlight; condition 2—diffuse sunlight; condition 3—diffuse sunlight and Ca$^{2+}$; condition 4—diffuse sunlight and Mg$^{2+}$; and condition 5—diffuse sunlight and TW. All test solutions were prepared with ultrapure water except treatment condition 5, which was prepared with our local TW. Ca$^{2+}$ and Mg$^{2+}$ were added corresponding to our local tap water concentration, i.e., 221.5 mg L$^{-1}$ CaCl$_2$ (corresponding to 80 mg Ca$^{2+}$ L$^{-1}$) and 83.7 mg L$^{-1}$ MgCl$_2$·6H$_2$O (corresponding to 10 mg Mg$^{2+}$ L$^{-1}$), respectively. All five test solutions were prepared fresh. The pH was adjusted to 7.0 and subsequently all solutions were filtered using sterilised cellulose nitrate filters with a pore size of 0.2 µm (Sartorius, Göttingen, Germany). All sterilised test solutions were transferred to purified HDPE bottles and placed in either direct sunlight or diffuse sunlight conditions. A chemical control, containing only 100 mg L$^{-1}$ DTPMP without additives in ultrapure water (pH 7.0), was placed in the dark.

The sunlight degradation experiment was carried out for 200 days from mid-March 2021 to the beginning of October 2021 at the campus of the Brandenburg University of Technology (BTU). Orthophosphate samples were taken frequently in intervals of 3 days within the first 30 days and subsequently at an interval of 7 days. Samples for total phosphorus (TP) analyses were taken once a month. Samples for LC/MS analyses were taken after 10 days after starting the test and then at intervals of approximately 20 to 30 days. The sunlight intensity was measured five days a week with a Lux meter LX1330B (Dr. Meter, Hong Kong, China). Daily measurements included a measurement in the morning, at noon, and in the afternoon. The sunlight intensity data were integrated over time to weekly sunlight irradiation hours. Our sunlight intensity measurements in so-called direct sunlight included direct sunlight radiation and partly reflected sunlight. Furthermore, our direct sunlight did not fulfil the requirement of a free horizon as it is common for global radiation. The latter was measured at the meteorological station of the BTU campus. The global sunlight intensity determined was measured 2 m above the ground, avoiding influences of reflected sunlight and with a free horizon. The measurements obtained from global sunlight radiation were used to verify plausibility of the light meter recordings for direct exposition of the treatment flask to sunlight (i.e., condition 1).
2.5. Analytics

DTPMP and its degradation breakdown products were analysed with liquid-chromatography electrospray-ionization mass-spectrometry (LC–ESI–MS) using a Finnigan MAT LC/MS (LC spectral system P4000, LCQ MS Detector, autosampler AS 3000, and metal PEEK-coated column (SeQuant ZIC-HILIC 150 × 2.1 mm, 3.5 µm/100 Å); Merck, Darmstadt, Germany). All liquid samples were mixed with 50% acetonitrile before injection. Gradient elution was performed with solvent A (100% ultrapure water) and solvent B (10% ultrapure water/90% acetonitrile) at 35 °C and at a flow rate of 0.2 mL min⁻¹. Solvent A contained 100 mM ammonium formate formate and solvent B contained 10 mM ammonium formate. The analysis was run for 43 min by first holding 100% of solvent B for 2 min. The gradient was then concavely increased to 10% A within 1 min and was held for 2 min. The gradient was further concavely increased to 30% A within 1 min and held again for 2 min. Subsequently, the gradient was again concavely increased to 50% A within 2 min and held for 10 min. Afterwards, the gradient was concavely increased to 60% A within 5 min and held for another 5 min, before the gradient was decreased back to 100% B within 3 min and held for 10 min before starting the next experiment. The MS detector settings were as follows: negative polarity ionization at 3.5 kV and spray capillary at 220 °C. Selected ion monitoring (SIM) was chosen for quantification. The following mass-to-charge (m/z) ratios were used for identification: DTPMP 572, EABMP 232, IDMP 204, Glyphosate 168, AMPA 110. Glyphosate was used as the internal standard. Area ratio of nonquantifiable breakdown products m/z 247, m/z 341, and m/z 478 were also determined.

TP was determined after chemical digestion. Therefore, 200 mg of Oxisolv (Merck, Darmstadt, Germany) was added into a 5 mL sample volume. The samples were treated using the microwave digestion unit MARS 5 (CEM, Kamp-Lintfort, Germany). The samples were linearly heated to 170 °C within 5 min and were held for another 3 min and subsequently cooled to room temperature. After digestion, TP was measured as orthophosphate (o-PO₄³⁻) with a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan) according to the European standard procedure EN ISO 6878:2004. The release of PO₄⁻P was also measured with the same European standard procedure. Fe²⁺ was determined with the ferrozine method [31] and measured with the spectrophotometer.

2.6. Data Evaluation

We assumed a degradation of a first-order reaction of the parent following Equation (1), where c(t) is the DTPMP concentration at time t and c₀ is the initial concentration (all in mg L⁻¹), and k is the degradation constant rate (d⁻¹).

\[ c(t) = c_0 \exp(-k \cdot t) \]  

(1)

The degradation rate constant k was assumed to follow the Arrhenius law. Therefore, k was assumed to be controlled by temperature T and by the relative effective energy density \( \frac{w_{\text{eff}}}{w_{QF}} \), with

\[ k = A \exp \left( \frac{-E_a w_{\text{eff}}}{RT w_{QF}} \right) \]  

(2)

where A is the pre-exponential frequency factor (representing the frequency of collisions between reactant molecules at a standard concentration), \( E_a \) is the activation energy (kJ mol⁻¹), \( w_{\text{eff}} \) is the effective photon energy density (kJ cm⁻²), R is the universal gas constant (0.008314 kJ K⁻¹ mol⁻¹), T is the temperature (K), and \( w_{QF} \) is the total photon energy density (kJ cm⁻²). The total photon energy density \( w_{QF} \) was estimated using a light meter, where the measured direct or diffuse sunlight radiation was used. The daily temperature and global sunlight radiation was taken from a meteorological station at the BTU campus. Global radiation (W m⁻²) was integrated over time and the term \( T \times w_{QF} \) was calculated for both light meter and meteorological station measurements (Supplementary Materials, Figure S1).
3. Results and Discussion

3.1. Degradation Pathway of DTPMP during UV Treatment

We first determined the degradation of 100 mg L\(^{-1}\) DTPMP (corresponding to 18.9 mg C L\(^{-1}\)) during UV irradiation including quantifiable and nonquantifiable breakdown products (Figure 1). The degradation of DTPMP under UV irradiation follows a first-order reaction [9]. Therefore, we determined a first-order degradation constant rate of \(2.8 \cdot 10^{-4} \text{s}^{-1} \pm 1.5 \cdot 10^{-5}\) corresponding to a half-life of 42.2 ± 2.4 min, respectively.

DTPMP degraded rapidly within 300 min UV irradiation and released IDMP, EABMP, and AMPA as major quantifiable breakdown products (Figure 1A). IDMP was released at highest concentration compared with EABMP and AMPA. However, the sum of organic carbon of the three major breakdown products was always below 6.0 mg C L\(^{-1}\) during the UV treatment. In fact, the carbon balance of the sum of IDMP, EABMP, and AMPA confirmed that only 5.8 mg C L\(^{-1}\) of DTPMP (corresponding to 31.7%) was converted to those after 150 min. At the end of the UV treatment, the sum of organic carbon of IDMP, EABMP, and AMPA averaged only 4.2 mg C L\(^{-1}\) (corresponding to 23.2%). We calculated the corresponding carbon gap and found it continuously increasing until the end of the UV experiment.

On the one hand, these results indicate that the quantifiable breakdown products comprised only 20% to 30% of converted organic carbon of DTPMP. We also assume that higher quantities of converted DTPMP were released as carbon dioxide (CO\(_2\)), which was not determinable due to the open reactor vessel. For example, we demonstrated that UV degradation of ethylenediaminetetra(methylenephosphonic acid) (EDTMP) resulted in carbon conversion of 68.0% after 300 min [29]. Thus, release of higher quantities of CO\(_2\) during DTPMP UV treatment is conceivable. On the other hand, we also assume the formation of nonquantifiable breakdown products, as recently proposed [9]. Using MS full scans, we detected high area ratios for the three \(m/z\) ratios 478, 341, and 247, which were not further quantifiable due to no synthesized phosphonate standards available.

We assume that \(m/z\) 478 corresponds to a breakdown product which is most likely cleaved through a nucleophilic attack at the central amine of DTPMP, leading to release one phosphonic acid group. Hence, the free amino group is then sensitive to another radical attack and cleaves to \(m/z\) 247 and EABMP. The \(m/z\) ratio 247 can then further attack releasing EABMP, IDMP, and /or AMPA.

We further analysed the trends of \(m/z\) 478, 341, and 247 during the UV degradation of DTPMP to specify their participation in the degradation pathway of DTPMP (Figure 1B). The development of the area ratio \(m/z\) 478 and 247 during 300 min UV irradiation confirmed that first \(m/z\) 478 is released from degraded DTPMP and reaches its maximum after 15 min.
UV irradiation. In comparison, the release of \( m/z \) 247 initializes when \( m/z \) 478 starts to be further broken down. Thus, the area ratio of \( m/z \) 247 increased rapidly within 60 min, reached its maximum at 120 min, and subsequently degraded only slowly. This may also explain the constant intermediate concentrations of IDMP, EABMP, and AMPA during the UV degradation experiment. We assume that the constant degradation of breakdown products with higher molecular weight (independent if quantifiable or not) resulted in constant conversion rates of EABMP, IDMP, and/or AMPA.

Apart from the formation of \( m/z \) 478 as initial breakdown product of DTPMP, we also detected \( m/z \) ratio 341. The chemical structure of \( m/z \) 341 is similar to that recently identified as a major breakdown product of EDTMP [29]. Therefore, we assume that \( m/z \) ratio 341 corresponds to ethylenediaminetri(methylene phosphonic acid). Similar to \( m/z \) 478, \( m/z \) 341 also seems to occur only within the initial 60 min of the UV treatment, showing its maximum area ratio at 15 min. The formation of \( m/z \) 341 can be attributed to further decomposition of \( m/z \) 478 or by direct decomposition of the parent compound. Both degradation pathways are possible to release \( m/z \) 341.

Obviously, \( m/z \) 341 is further converted to smaller breakdown products such as EABMP, IDMP, and/or AMPA, but also to \( m/z \) 247. Thus, both \( m/z \) 478 and \( m/z \) 341 can contribute to the release of these breakdown products, especially in the initial phase of the UV treatment of DTPMP. Therefore, we propose that the major degradation pathway of DTPMP during our UV treatment is initialized by cleaving the C-N bond of the central amine of DTPMP, leading to either \( m/z \) 478 or \( m/z \) 341 (Figure 2). According to our determined area ratios, cleavage through nucleophilic attack to release the phosphonic acid group of the central amine leading to \( m/z \) 478 seems to be the dominant pathway during our UV treatment. Independent of the dominant pathway, both \( m/z \) 478 and \( m/z \) 341 can further be broken down either to \( m/z \) 247, EABMP, IDMP, and/or AMPA, which finally is converted to the mineralization products \( \text{H}_2\text{PO}_4^- \), \( \text{NH}_4^+ \), and \( \text{CO}_2 \), as recently demonstrated.

![Figure 2. Proposed degradation pathway of UV-treated DTPMP. Red arrows highlight the proposed dominant pathway. Grey arrows indicate the underrepresented pathway. The breakdown production \( m/z \) 341 can be released either by breaking down the parent compound or as a transformation byproduct of degradation (\( m/z \) 478). Orange, yellow, and green arrows indicate the degradation to smaller breakdown products up to complete mineralisation.](image-url)

### 3.2. Actinometry for the Determination of Suitable Material for the Sunlight Degradation Test

Prior to our sunlight degradation experiments with DTPMP, we investigated the influence of the flask materials during sunlight degradation with the light-sensitive potassium trisoxalato-ferrate complex (Figure 3A). The ferioxalate complex is a common actimeter to
determine the photon flux of light sources from photochemical reactors. This complex is sensitive to light absorbed in a wavelength range from 250 to 500 nm [32]. We chose this actimeter because we previously used the ferrioxalate complex to determine the photon flux and corresponding light intensity of our UV lamp (maximum emission 366 nm).

Figure 3. Choice of test flasks for sunlight degradation experiments. (A) Test bottles used for actinometry starting from the left glass bottle, HDPE bottle, blue PET bottle and transparent bottle. (B) Release of ferrous iron from the ferrioxalate complex through sunlight irradiation in different bottles tested.

Therefore, it was reasonable to also use this actimeter to compare the light penetration in our different flask materials, i.e., three based on common PE polymers and one on silica glass. We expected that the latter does not allow UV light to penetrate the reaction flask. In consequence, we assumed that photochemical degradation of the light-sensitive complex in the glass bottle is a result of adsorbed light with an active range from 360 to 500 nm. For the polymeric flasks, we assumed that both UV light and visible light (VIS) can penetrate them. However, the UV light content in terrestrial sunlight averages only 8% and consists mainly of UVA [33]. In addition, the spectral distribution and irradiation of the sunlight can change through adsorption, reflection processes, and scattering at the Earth’s surface [33]. For our investigation on the choice of a suitable flask material, we did not consider those effects.

Therefore, we expected that the influence of UV light to generate ferrous iron of the ferrioxalate complex in our polymeric flasks would be very low. In fact, our results indicate that in all four flasks ferrous iron was continuously released within 80 min and the difference between them was very low (Figure 1B). However, the highest release of ferrous iron in the HDPE flask occurred from 40 to 80 min. The reaction rates determined also confirmed our finding (Table 1). We compared the reactions rates of our four flasks with the reaction rate of our UV lamp, which was almost two orders of magnitude larger. In other words, the ferrioxalate complex was degraded 36.7 times faster and 45.2 times faster under UV irradiation than with sunlight irradiation in the HDPE flask and with the transparent PET flask, respectively. Finally, we decided to use HDPE flasks of our sunlight degradation experiment with DTPMP.

Table 1. Reaction rates of different vials during sunlight degradation of ferrioxalate complex.

| Reaction rate (mol s⁻¹) | Glass  | HDPE  | PETblue | PETtransparent | UV Lamp |
|------------------------|-------|-------|---------|----------------|---------|
| 3.6 × 10⁻⁷             | 4.2 × 10⁻⁷ | 3.9 × 10⁻⁷ | 3.4 × 10⁻⁷ | 1.5 × 10⁻⁷ |
| Ratio UV vs. Sun (-)   | 42.5  | 36.7  | 39.3    | 45.3           | -       |
3.3. Influence of Sunlight on the Degradation of DTPMP

The aim of our sunlight experiment was twofold. The first aim was to verify if our determined degradation pathway of DTPMP during UV irradiation is transferable to conditions with sunlight radiation. Should the degradation pathway be transferable, we also wanted to investigate the influence of Ca\(^{2+}\) and Mg\(^{2+}\) on the degradation mechanisms and reaction rate as previously demonstrated [9]. Therefore, we investigated five different treatment conditions, i.e., DTPMP degradation in direct or diffuse sunlight, in diffuse sunlight with addition of Ca\(^{2+}\) or Mg\(^{2+}\), and in diffuse sunlight with local TW.

Overall, we determined DTPMP degradation for all five treatment conditions including the release of EABMP and IDMP as major quantifiable breakdown products within 200 days (Figure 4A–E and Figure 5A). Further, we found for the direct and diffuse sunlight treatment almost similar degradation of DTPMP. In direct sunlight more than 14.0 mg C L\(^{-1}\) DTPMP was degraded within 200 days, corresponding to 74.5% of total organic carbon concentration (Figure 4A). In diffuse sunlight we determined more than 14.5 mg C L\(^{-1}\), corresponding to 77.0% (Figure 4B). For the other three treatment conditions, the DTPMP degradation was significantly reduced. Thus, for diffuse sunlight with Ca\(^{2+}\) addition and diffuse sunlight Mg\(^{2+}\) addition, we determined 10.3 mg C L\(^{-1}\) and 5.8 mg C L\(^{-1}\) DTPMP degradation, corresponding to 54.7% and 30.7%, respectively (Figure 4C,D). For DTPMP degradation in diffuse sunlight with our local TW, we determined 7.8 mg C L\(^{-1}\) DTPMP degradation, corresponding to 41.6% (Figure 4E).

Figure 4. Cont.
Figure 4. Total quantities of 100 mg L\(^{-1}\) DTPMP, its major breakdown products, and nonquantifiable breakdown products during sunlight photolysis. (A1, A2) Sunlight photolysis in direct sunlight. (B1, B2) Sunlight photolysis in diffuse sunlight without addition of bivalent cations. (C1, C2) Sunlight photolysis in diffuse sunlight with addition of 80 mg Ca\(^{2+}\) L\(^{-1}\). (D1, D2) Sunlight photolysis in diffuse sunlight with addition of 10 mg Mg\(^{2+}\) L\(^{-1}\). (E1, E2) Sunlight photolysis in diffuse sunlight with local TW of Cottbus.
We also determined the release of $\text{O-PO}_4^{3-}$ and found in the direct sunlight treatment the highest release of 4.4 mg P L$^{-1}$, corresponding to 16.2% P release of DTPMP (Table 2). Interestingly, the release of $\text{O-PO}_4^{3-}$ in diffuse sunlight without addition of bivalent ions was lower as compared to the treatment condition with Ca$^{2+}$. Overall, we found that only small amounts of $\text{O-PO}_4^{3-}$ were released within 200 days of sunlight treatment (Figure 5B). Nevertheless, as abovementioned algae blooms can occur easily if the threshold concentration of phosphorus is above 0.1 mg P L$^{-1}$ [19], the small concentration released can affect negatively fragile ecosystems. However, from our results we cannot conclude that sunlight photolysis of DTPMP automatically leads to harmful algae blooms. We used a high concentration of DTPMP that is not a common concentration for application. We chose the high concentration to achieve treatment conditions comparable to our UV treatment. Common concentrations for application range from 2.5 to 5.0 mg L$^{-1}$ DTPMP, which would also result in significant lower release of free phosphorus. Therefore, we cannot state that DTPMP resulting from sunlight photolysis leads to higher loads of $\text{O-PO}_4^{3-}$ in aquatic environments.

Table 2. DTPMP degradation and P release after 200 days of sunlight treatment.

| Test Condition               | DTPMP (%) | $\text{O-PO}_4^{3-}$ (%) | $\text{O-PO}_4^{3-}$ (mg P L$^{-1}$) |
|------------------------------|-----------|--------------------------|-------------------------------------|
| Direct sunlight              | 74.6      | 16.2                     | 4.4                                 |
| Diffuse sunlight             | 77.1      | 8.9                      | 2.4                                 |
| Diffuse sunlight and Ca$^{2+}$| 54.7      | 10.3                     | 2.8                                 |
| Diffuse sunlight and Mg$^{2+}$| 30.7      | 6.4                      | 1.7                                 |
| Diffuse sunlight and tap water| 48.5      | 6.9                      | 1.9                                 |

As mentioned above, we found similar degradation rates of DTPMP for both treatments in direct and diffuse sunlight. However, our results from LC/MS measurements indicate that the degradation of DTPMP exposed to direct sunlight occurred rapidly within the first two to four weeks while DTPMP exposed to diffuse sunlight occurred stably and degraded only slowly. Afterwards, DTPMP exposed to diffuse sunlight also degraded rapidly and reached similar degradation rates as compared with direct sunlight. Both treatment conditions resulted in almost similar releases of IDMP and EABMP but in small amounts (Figure 4A1,B1). The calculated carbon gap was very high compared to the other three sunlight treatments, i.e., diffuse sunlight with Ca$^{2+}$ addition, Mg$^{2+}$ addition, and use of our local TW. We assume that the higher carbon gap for direct and diffuse sunlight photolysis of DTPMP is a result of higher conversion of the parent compound (which also might result in further release of nonquantifiable and detectable breakdown products). We also detected $m/z$ 478 as the dominant nonquantifiable breakdown product for these two sunlight treatment conditions (Figure 4A2,B2). This result indicates that sunlight
photolysis of DTPMP also leads to initial cleavage of the C-N bond of the central amine as demonstrated by our UV treatment (Figure 2). As the degradation rates of DTPMP and the release of IDMP, EABMP, and m/z 478 are very similar for both treatment conditions, we conclude that DTPMP indeed undergoes the same degradation mechanism in direct and diffuse sunlight as shown for UV treatment.

The second aim of our study was to investigate the individual influence of Ca\(^{2+}\) and/or Mg\(^{2+}\) during sunlight photolysis of DTPMP compared with sunlight treatment containing our local TW. We recently reported that the degradation mechanism of DTPMP during UV photolysis can be affected through the complexing properties and molecular stability caused by these alkaline earth metals [9]. Both have high complex formation constants for DTPMP, i.e., 10.7 and 10.8 for Ca\(^{2+}\) and Mg\(^{2+}\), respectively [6,9]. We assume that the formation of stable phosphonate–metal complexes was the major reason for inhibited sunlight degradation of DTPMP in the initial 60 days of the experiment for the treatment of diffuse sunlight with Ca\(^{2+}\), Mg\(^{2+}\), and local TW (Figure 5A). The high concentration of both alkaline earth metals in our treatment conditions (i.e., 80 mg Ca\(^{2+}\) L\(^{-1}\) and 10 mg Mg\(^{2+}\) L\(^{-1}\)) certainly increased the resistance of DTPMP to sunlight photolysis as we also recently proposed for UV-treated DTPMP [9]. This correlates well with our finding that the degradation rates of DTPMP were significantly slower compared with direct and diffuse sunlight treatment (Figure 4C–E). Thus, Ca\(^{2+}\) and Mg\(^{2+}\) affect the degradation kinetics of DTPMP due to complexation.

Despite kinetic effects, we also studied in detail the potential influence on the degradation mechanism of DTPMP. The gap of total organic carbon and release of major breakdown products were good indicators for the degradation mechanism of DTPMP. In particular, we found the highest carbon gap for sunlight treatment with Ca\(^{2+}\) and the lowest for Mg\(^{2+}\) (Figure 4C1,D1). Obviously, the low carbon gap for the latter was caused by the slow degradation of DTPMP. All three carbon gaps for the three treatment conditions were below the carbon gaps of direct and diffuse sunlight treatment without bivalent cation addition. This result indicates that both alkaline earth metals are relevant for degradation rates of DTPMP during sunlight photolysis, as recently proposed [9]. Interestingly, we also determined significantly higher releases of EABMP for these sunlight treatments as compared to direct and diffuse sunlight photolysis. Only the release of IDMP was significantly different for the sunlight treatment with our local TW (Figure 4E1). Furthermore, the trend of the release of nonquantifiable breakdown products was significantly different. We detected \(m/z\) 478 and \(m/z\) 341 for all three treatment conditions (Figure 4C2,D2,E2). The area ratio of \(m/z\) 478 increased only slowly within the initial 60 days of sunlight photolysis of DTPMP. In comparison, \(m/z\) 478 was immediately released during the direct and diffuse treatment without bivalent cation addition. We assume that the inhibited release of \(m/z\) 478 during the treatment in diffuse sunlight with Ca\(^{2+}\), Mg\(^{2+}\), and in local TW was a result of the slow degradation of the parent compound. Further, we assume that the detection of \(m/z\) 341 was not the result caused through reduced degradation rates of DTPMP. The detection of \(m/z\) 341 indicates to us that the second proposed degradation pathway occurring during UV treatment of DTPMP also occurred in these three sunlight photolysis treatments. In our opinion, the higher releases of EABMP and the detection of \(m/z\) 341 are indicators for a different degradation mechanism of DTPMP. Therefore, we conclude that both alkaline earth metals significantly influence the degradation mechanism and the kinetic of DTPMP during sunlight photolysis.

Further investigations are urgently required to better understand the influence of the different degradation mechanism caused by Ca\(^{2+}\) and Mg\(^{2+}\). Both the C-N bond of DTPMP and presence of alkaline earth metals seem to play an important role in the degradation mechanism. Recently, Jaisi et al. [34] also investigated the mechanistic details of the C-N cleavage of aminophosphonates but during UV irradiation. They stated that the mechanism is still poorly understood, and they proposed a hydroxyl-radical-mediated attack for glyphosate, as proposed by Sandy et al. [35]. Recently, we demonstrated that the degradation mechanism of aminophosphonates such as EDTMP and DTPMP during
UV treatment is underlying a radical attack of both hydroxyl radicals and superoxide radicals [29].

The mechanistic role of alkaline earth metals and a potentially radical driven degradation mechanism must be addressed in future work. For example, scavenger experiments could help to evidence the presence of different radical species and their potential influence on the degradation in combination with alkaline earth metals.

In our previous studies using UV treatment for different aminophosphonates, we demonstrated that the breakdown product IDMP occurred commonly as the major breakdown product [9,29,36]. Additionally, Nowack and Stone reported on the formation of IDMP as one of the major breakdown products of aminotris (methylenephosphonic acid) (ATMP) [37]. They further concluded that the degradation of IDMP might be limited due to lower log K values, resulting in slower metal-catalysed degradation. We previously proposed that IDMP could be a relevant breakdown product also occurring during sunlight photolysis of aminophosphonates. Our current investigation further confirms our assumption that this breakdown product may play an important role during sunlight photolysis of commercial aminophosphonates if released to aquatic environment without reliable pretreatment. In consequence, continuous enrichment of IDMP in stream sediments may occur.

3.4. Influence of Sunlight Intensity on DTPMP Degradation Kinetics

Apart from the degradation mechanism of DTPMP, we also investigated the influence of different sunlight intensities on the degradation kinetics of DTPMP. The global sunlight radiation was measured from the meteorological station at our BTU campus. For the first four weeks of our sunlight experiments, data from this station were not available due to technical problems. However, our measurements of the global sunlight radiation were always higher than our measurements for direct and diffuse sunlight (Figure 6A). Our results of the sunlight intensity measurements show that both global and direct sunlight intensities seemed to be more influenced by fluctuations than diffuse sunlight. The latter showed more clearly the influence of seasons and the angle of light incidence, i.e., the highest light intensity was achieved after 15 to 20 weeks (100 to 130 days). The calculated sum of daily light intensities evidenced that our chosen position for the direct sunlight photolysis indeed provided significantly higher light intensities, allowing penetration of the treatment flask (Figure 6B). After 200 days of sunlight photolysis, the sum of daily sunlight intensity in diffuse sunlight averaged almost half that of direct sunlight. The differences in the sunlight intensities have direct influence on the degradation kinetics of DTPMP. Less penetrating sunlight corresponds to lower photon flux in the treatment flasks, and therefore decreased degradation kinetics. Based on our meteorological and analytical measurements (LC/MS), we calculated the degradation constant rate $k$ for the five sunlight treatment conditions during 200 days (Figure 7). We assumed a reaction according to first order because the main degradation pathway of DTPMP in sunlight was similar to that found with UV treatment. Based on this postulation, we found good correlation between $k$ and the decrease in DTPMP. The degradation kinetic of DTPMP in diffuse sunlight without addition of bivalent cations was highest from day 60 to 160, which correlates well with the temporary increase in diffuse sunlight intensity (Figure 6A). Obviously, the degradation kinetics of sunlight-treated DTPMP are not directly dependent on very high sunlight intensities, but possibly on a specific threshold intensity and/or temperature. For the latter, we did not find direct proof for the dependence of DTPMP degradation on temperature.
Figure 6. Global sunlight intensity measurement at the BTU meteorological station and direct sunlight measurement with a lux meter in direct and diffuse sunlight at test flasks. (A) Sum of weekly sunlight intensity and (B) sum of daily sunlight intensity. The sum of the daily sunlight intensity of global sunlight is below direct and diffuse sunlight in the first 12 weeks because of missing initial data within the first four weeks of the sunlight experiments. These data are not available due to technical problems during this period.

Figure 7. Degradation rate constant over time for different sunlight treatment conditions of 100 mg L\(^{-1}\) DTPMP.

We further evaluated the different determined pre-exponential frequency factor \(A\), the products of activation energy \(E_a\), and effective photon energy density \(w_{eff}\) (Table 3). Our calculated results confirm that the degradation of DTPMP in diffuse sunlight had the highest frequency of collisions with the parent compound, leading to rapid degradation. In contrast, we determined the lowest collision frequency for the sunlight treatment condition with diffuse sunlight and addition of Mg\(^{2+}\). For the results of the product of \(E_a \cdot w_{eff}\), we first assumed that the activation energy for the degradation of DTPMP is the same in direct and diffuse sunlight. Therefore, we can conclude that differences in the calculated product \(E_a \cdot w_{eff}\) are only the result of differences in the effective photon energy density responsible for the degradation of DTPMP. For the sunlight treatment of DTPMP in direct and diffuse sunlight without additions the higher calculated \(E_a \cdot w_{eff}\) correlates well with our expectation since the sum of direct sunlight intensity was significantly higher over the complete treatment time. Thus, a higher sum of daily sunlight intensity corresponds with a higher photon energy density penetrating the treatment flask.
Table 3. Parameters determined from the sunlight degradation experiment of DTPMP.

| Treatment Condition | A         | \(E_a \cdot w_{eff}\) (kJ mol\(^{-1}\) cm\(^{-2}\)) | \(R^2\) | RSS * |
|---------------------|-----------|-----------------------------------------------|--------|-------|
| Direct sunlight     | \(2.1 \times 10^{-4}\) | 2.8 \(\times 10^4\) | 0.97   | 313.9 |
| Diffuse sunlight    | \(2.7 \times 10^{-4}\) | 2.0 \(\times 10^4\) | 0.99   | 163.4 |
| Diffuse sunlight and Ca\(^{2+}\) | \(1.8 \times 10^{-4}\) | 2.3 \(\times 10^4\) | 0.99   | 98.9  |
| Diffuse sunlight and Mg\(^{2+}\) | \(0.4 \times 10^{-4}\) | 1.4 \(\times 10^4\) | 0.96   | 57.1  |
| Diffuse sunlight and tap water | \(1.4 \times 10^{-4}\) | 2.4 \(\times 10^4\) | 0.99   | 45.0  |

* Residual sum of squares of the fitting curves for data evaluation (see more in the Supplementary Materials, Figures S2–S6).

Interestingly, diffuse sunlight treatment with addition of Ca\(^{2+}\) and with our local TW resulted in higher calculated products of \(E_a \cdot w_{eff}\) than the sunlight treatment in diffuse sunlight without addition. All treatment flasks exposed to diffuse sunlight treatment were placed in the same sunlight condition. Therefore, we conclude that all treatment flasks in diffuse sunlight must have the same penetrating photon energy density. If \(w_{eff}\) is constant for all treatment flasks in diffuse sunlight, the activation energy must be different. This finding correlates well with our abovementioned postulation of a different degradation mechanism for DTPMP with addition of Ca\(^{2+}\), Mg\(^{2+}\), and in local TW. This also explains well that we determined highest \(E_a \cdot w_{eff}\) for diffuse sunlight with local TW compared with diffuse sunlight treatment with addition of Ca\(^{2+}\) and Mg\(^{2+}\). The high values of \(E_a \cdot w_{eff}\) with local TW indicates it is close to that of diffuse sunlight with Ca\(^{2+}\). This might indicate that Ca\(^{2+}\) in our local TW played an important role in influencing both the degradation kinetics and mechanism, but perhaps not exclusively. Other unknown influences may further impact the activation energy of sunlight-treated DTPMP.

4. Conclusions

We investigated the sunlight photolysis of DTPMP under five different treatment conditions. We determined DTPMP degradation for all treatment conditions within 200 days. We determined the highest DTPMP degradation in direct sunlight and diffuse sunlight without addition of alkaline earth metals. The addition of both Ca\(^{2+}\) and Mg\(^{2+}\) resulted in inhibited degradation within the initial 60 days of the sunlight treatment. Similar effects occurred for sunlight treatment with local TW. This finding can be explained by the high complex formation constants for DTPMP with Ca\(^{2+}\) and Mg\(^{2+}\), which have direct influence on the activation energy of the reaction to breakdown the parent compound. Therefore, different degradation kinetics and degradation rate constants \(k\) dominate the different treatment conditions. Furthermore, we evidenced different degradation mechanisms for DTPMP depending on the presence of alkaline earth metals as we previously proposed for UV-treated DTPMP. We further conclude that DTPMP undergoes a similar degradation pathway in sunlight as compared to UV light. Therefore, our previous results obtained from UV treatment are transferable to those for sunlight. For this reason, we can conclude that our setup for UV treatment of the aminophosphonates is reliable and can be used to predict the degradation pathway through sunlight radiation in natural aquatic conditions.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/solar2020009/s1, Figure S1: Correlation between measured sunlight intensity at the meteorological station at BTU campus and the luxmeter, Figure S2: Data fitting for condition 1 (direct sunlight radiation), Figure S3: Data fitting for condition 2 (diffuse sunlight radiation without bivalent cation addition), Figure S4: Data fitting for condition 3 (diffuse sunlight radiation with addition of 80 mg Ca\(^{2+}\) L\(^{-1}\)), Figure S5: Data fitting for condition 3 (diffuse sunlight radiation with addition of 10 mg Mg\(^{2+}\) L\(^{-1}\)), Figure S6: Data fitting for condition 3 (diffuse sunlight radiation with local tap water providing 80 mg Ca\(^{2+}\) L\(^{-1}\) and 10 mg Mg\(^{2+}\) L\(^{-1}\)).
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References

1. Studnik, H.; Liebsch, S.; Forlani, G.;Wieczorek, D.; Kafarski, P.; Lipok, J. Amino polyphosphonates—Chemical features and practical uses, environmental durability and biodegradation. *New Biotechnol.* 2015, 32, 1–6. [CrossRef]

2. Liu, Y.; Dai, Z.; Kan, A.T.; Tomson, M.B.; Zhang, P. Investigation of sorptive interaction between phosphonate inhibitor and barium sulfate for oilfield scale control. *J. Petrol. Sci. Eng.* 2022, 208, 109425. [CrossRef]

3. Mpelwa, M.; Tang, S.F. State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: A review. *Petrol. Sci.* 2019, 16, 830–849. [CrossRef]

4. Nowack, B. Environmental chemistry of phosphonates. *Water Res.* 2003, 37, 2533–2546. [CrossRef]

5. Greenlee, L.F.; Testa, F.; Lawler, D.F.; Freeman, B.D.; Moulin, P. Effect of antiscalant degradation on salt precipitation and solid/liquid separation of RO concentrate. *J. Membr. Sci.* 2011, 366, 48–61. [CrossRef]

6. Knepper, T.P. Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment. *Trends Anal. Chem.* 2003, 22, 707–724. [CrossRef]

7. Neto, D.M.; da Costa, L.S.; de Menezes, F.L.; Fechine, L.M.; Freire, R.M.; Denardin, J.C.; Banobre-López, M.; Vasconcelos, I.F.; Ribeiro, T.S.; Leal, L.K.A.; et al. A novel amino phosphonate-phosphate-coated magnetic nanoparticle as MRI contrast agent. *Appl. Surf. Sci.* 2021, 543, 148824. [CrossRef]

8. Reinhardt, T.; Rott, E.; Schneider, P.A.; Minke, R.; Schönberger, H. Fixed-bed column studies of phosphonate and phosphate adsorption on granular ferric hydroxide (GFH). *Process Saf. Environ. Conserv.* 2021, 135, 301–310. [CrossRef]

9. Kuhn, R.; Jensch, R.; Bryant, I.M.; Fischer, T.; Liebsch, S.; Martiennsen, M. The influence of selected bivalent metal ions on the photolysis of diethylenetriamine penta(methylenephosphonic acid). *Chemosphere* 2018, 210, 726–733. [CrossRef] [PubMed]

10. Rott, E.; Steinmetz, H.; Metzer, J.W. Organophosphonates: A review on environmental relevance, biodegradability and removal in wastewater treatment plants. *Sci. Total Environ.* 2018, 615, 1176–1191. [CrossRef] [PubMed]

11. Tang, X.; Kum, S.; Liu, H. Inland desalination brine disposal: A baseline study from southern California on brine transport infrastructure and treatment potential. *ACS EST Engg.* 2021, 2, 456–464. [CrossRef]

12. Armbruster, D.; Rott, E.; Minke, R.; Happel, O. Trace-level determination of phosphonates in liquid and solid phase of wastewater and environmental samples by IC-ESI-MS/MS. *Anal. Bioanal. Chem.* 2019, 412, 4807–4825. [CrossRef] [PubMed]

13. Wang, S.; Zhang, B.; Shan, C.; Yan, X.; Chen, H.; Fan, B. Occurrence and transformation of phosphonates in textile dyeing wastewater along full-scale combined treatment processes. *Water Res.* 2020, 184, 116173. [CrossRef] [PubMed]

14. Nowack, B. The behavior of phosphonates in wastewater treatment plants of Switzerland. *Water Res.* 1998, 32, 1271–1279. [CrossRef]

15. Rott, E.; Happel, O.; Armbruster, D.; Minke, R. Behavior of PBTC, HEDP, and aminophosphonates in the process of wastewater treatment. *Water 2020*, 12, 53. [CrossRef]

16. Boels, L.; Tervahauta, T.; Witkamp, G.J. Adsorptive removal of nitritolitr(is)methyleneephosphonic acid) antiscalant from membrane concentrates by iron-coated waste filtration sand. *J. Hazard. Mater.* 2010, 182, 855–862. [CrossRef] [PubMed]

17. Lesueur, C.; Pfeffer, M.; Fuerhacker, M. Photodegradation of phosphonates in water. *Chemosphere* 2005, 59, 685–691. [CrossRef] [PubMed]

18. Wang, X.X.; Zhang, T.Y.; Diao, G.H.; Xu, Z.B.; Wu, Y.H.; Hu, H.Y. Assessment and mechanisms of microalgae growth inhibition by phosphonates: Effects of intrinsic toxicity and complexation. *Water Res.* 2020, 186, 116333. [CrossRef] [PubMed]

19. Schindler, D.W.; Carpenter, S.R.; Chapra, S.C.; Hecky, R.E.; Orihel, D.M. Reducing phosphorus to curb lake eutrophication is a success. *Environ. Sci. Technol.* 2016, 50, 8923–8929. [CrossRef] [PubMed]

20. Rott, E.; Minke, R.; Ball, U.; Steinmetz, H. Removal of phosphonates from industrial wastewater with UV/Fe(II), Fenton and UV/Fenton treatment. *Water Res.* 2017, 122, 345–354. [CrossRef] [PubMed]
21. Sun, S.; Wang, S.; Ye, Y.; Pan, B. Highly efficient removal of phosphonates from water by a combine Fe(II)/UV/co-precipitation process. *Water Res.* 2019, 153, 21–28. [CrossRef] [PubMed]
22. Huang, N.; Wang, W.-L.; Xu, Z.-B.; Wu, Q.-Y.; Hu, H.-Y. UV/chlorine oxidation of the phosphonate antiscalant 1-Hydroxyethane-1,1-diphosphonic acid (HEDP) used for reverse osmosis processes: Organic phosphorus removal and scale inhibition properties changes. *J. Environ. Manage.* 2019, 237, 180–186. [CrossRef]
23. Zhu, J.; Wang, S.; Li, H.; Qian, J.; Lv, L.; Pan, B. Degradation of phosphonates in Co(II)/peroxymonosulfate process: Performance and mechanism. *Water Res.* 2021, 202, 117997. [CrossRef] [PubMed]
24. Chiu, Y.H.; Chang, T.F.M.; Chen, C.Y.; Sone, M.; Hsu, Y.J. Mechanistic insight into photodegradation of organic dyes using heterostructure photocatalysts. *Catalysts* 2019, 9, 430. [CrossRef]
25. Alulema-Pullupaxi, P.; Fernández, L.; Debut, A.; Santacruz, C.P.; Villacis, W.; Fierro, C.; Espinoza-Montero, P.J. Photoelectrochemical degradation of glyphosate on titanium dioxide synthesized by sol-gel/spin-coating on boron doped diamond (TiO$_2$/BDD) as a photoanode. *Chemosphere* 2021, 278, 130488. [CrossRef]
26. Huang, Y.; Li, Z.; Yao, K.; Chen, C.; Fang, Y.; Li, R.; Tian, H. Suppressing toxic intermediates during photocatalytic degradation glyphosate by controlling adsorption modes. *Appl. Catal. B-Environ.* 2021, 299, 120671. [CrossRef]
27. Tang, Q.Y.; Yang, M.J.; Yang, S.Y.; Yu, X.H. Enhanced photocatalytic degradation of glyphosate over 2D CoS/BiOBr heterojunctions under visible light irradiation. *J. Hazard. Mater.* 2021, 407, 124798. [CrossRef]
28. Lv, Y.R.; He, R.K.; Chen, Z.Y.; Li, X.; Xu, Y.H. Fabrication of hierarchical copper sulfide/bismuth tungstate p-n heterojunction with two-dimensional (2D) interfacial coupling for enhanced visible-light photocatalytic degradation of glyphosate. *J. Colloid Interface Sci.* 2020, 560, 293–302. [CrossRef] [PubMed]
29. Kuhn, R.; Tóth, E.; Geppert, H.; Fischer, T.; Martienssen, M. Identification of the complete degradation pathway of ethylenediaminetetra(methylenephosphonic acid) in aquatic solution. *CLEAN Air Soil Water* 2017, 45, 1500774. [CrossRef]
30. Kuhn, R.; Jensch, R.; Bryant, I.M.; Fischer, T.; Liebsch, S.; Martienssen, M. Photodegradation of ethylenediaminetetra(methylenephosphonic acid)—Effect of the system configuration. *J. Photochem. Photobiol. A Chem.* 2020, 388, 112192. [CrossRef]
31. Stookey, L.L. Ferrozine: A new spectrophotometer reagent for iron. *Anal. Chem.* 1970, 42, 779–781. [CrossRef]
32. Kuhn, H.J.; Braslavsky, S.E.; Schmidt, R. Chemical actinometry (IUPAC technical report). *Pure Appl. Chem.* 2004, 76, 2105–2146. [CrossRef]
33. Dudok de Wit, T.; Watermann, J. Solar forcing of the terrestrial atmosphere, C.R. *Geoscience* 2010, 342, 259–272. [CrossRef]
34. Jaisi, D.P.; Li, H.; Wallace, A.F.; Paudel, P.; Sun, M.; Balakrishna, A.; Lerch, R.N. Mechanisms of bond cleavage during manganese oxide and UV degradation of glyphosate: Results from phosphate oxygen isotopes and molecular simulations. *J. Agric. Food Chem.* 2016, 64, 8474–8482. [CrossRef] [PubMed]
35. Sandy, E.H.; Blake, R.E.; Chang, S.J.; Jun, Y.; Yu, C. Oxygen isotope signature of glyphosate and phosphonoacetate: Tracing source and cycling of phosphonates. *J. Hazard. Mater.* 2013, 260, 947–954. [CrossRef]
36. Kuhn, R.; Bryant, I.M.; Jensch, R.; Liebsch, S.; Martienssen, M. Photolysis of hexamethylenediaminetetra(methyleneephosphonic acid) (HDTMP) using manganese and hydrogen peroxide. *Emerg. Contam.* 2020, 6, 10–19. [CrossRef]
37. Nowack, B.; Stone, A.T. Homogeneous and heterogeneous oxidation of nitrolotrimethyleneephosphonic acid (NTMP) in the presence of manganese (II, III) and molecular oxygen. *J. Phys. Chem. B* 2002, 106, 6227–6233. [CrossRef]