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Organic Compounds

Chapter 2

Unreactive Phosphorus-Organophosphonates (mini review)

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Abstract

Phosphonates comprise a very large group of organophosphonates including aminophosphonates. Their main chemical feature leads to complexation of earth alkaline metals and transition metals (under stoichiometric). Therefore they are very often applied as complexing agents of detergents, as compounds of industrial cleaning products, or as antiscalants in cooling water systems and desalination processes. The high consumption of phosphonates within the past two decades leads to an increased discharge into the aquatic environment, of which the environmental risk is still uncertain. To date, there are several analytical methods published to determine phosphonates from environmental samples. However, no standard method has been defined until now. Different treatment technologies to break down phosphonates have been studied extensively such as photochemical degradation, chemical degradation and other advanced oxidation processes. The results obtained from those studies gained our chemical understanding with respect to possible implementation of such pre-treatment approaches in wastewater treatment, cooling water treatment and desalination process. The biological degradation of phosphonates has been studied for more than forty years. It was demonstrated that microorganisms are capable to breakdown the C-P bond with at least three different degradation pathways.

Keywords: Phosphonates; Photodegradation; Biodegradation; Analytical Detection

1. Introduction - Properties, Application and Production

The element phosphorus is essential for life on earth. The main chemical form available for microorganisms is orthophosphate [1]. Due to the low solubility of phosphates and their rapid conversion to insoluble forms, phosphorus is one of the major growth-limiting nutrient in ecosystems [2,3]. Commonly, the inorganic orthophosphate is categorised as soluble reactive phosphorus (SRP) while organic phosphorus is categorised as soluble unreactive phosphorus (SUP). The latter comprises a larger group of organic compounds containing phosphorus such as DNA, RNA, phospholipids in seawater and inositol hexaphosphates in lakes and sediments, phosphoamides, sugar phosphates, organic phosphorus pesticides and phosphonates [4,5]. Still, the complete identity of SUP and their bioavailability is uncertain due to a lack of analytical methods. However, it is assumed that SUP comprises up to 50-80 % of the total soluble phosphorus (TSP) in natural waters [4].

Phosphonates, one major group of SUP, have attracted a lot of attention in recent years. Their environmental relevance is currently an important issue in the scientific community because phosphonates are suspected to promote eutrophication in aquatic environments. And the most popular aminophosphonate glyphosate is currently debated to be potentially causing cancer. However, the enormous utilization of various chemically modified phosphonate structure emphasises the global role of phosphonates in modern life. With this regard, this review will focus on commercially very important organophosphonaes and aminophosphonates. Detailed reviews about glyphosate are presented elsewhere [6,7].

Organophosphonates are characterized by the presence of at least one or more phosphonic acid group. Aminophosphonates are an important subgroup of organophosphonates and contain at least one amine group, which can be primary, secondary or tertiary [8]. The direct covalent carbon-to-phosphorus bond provides high chemical stability and thereby also high resistance against chemical hydrolysis and thermal decomposition [9,10]. Commonly aminophosphonates are water-soluble, non-volatile and poorly soluble in organic solvents. The most important property leads to their complexing character of earth alkaline metals and transition metals, thus, preventing their precipitation. Aminophosphonates such as ethylenediaminetetra(methylene phosphonic acid) (EDTMP) can form multinuclear complexes that make them more efficient as compared to the better known structure-analogue ethylenediaminetetraacetic acid (EDTA). Studnik et al. [8] emphasised that in some cases only one phosphonate molecule is needed to retain 5000–10,000 calcium ions in solution. Thus, they can be utilized under substoichiometric conditions to interfere the early stages of the crystallization processes. Further useful information about the physico-chemical properties of organophosphonates are given [11 & 12].

The application range of organophosphonates and aminophosphonates is still broadening. They are often applied as complexing agents of detergents (laundry and dishwasher)

such as EDTMP and diethylenetriamine penta(methylenephosphonic acid) (DTPMP) (**Figure 1**). The aminophosphonate aminotris(methylenephosphonic acid) (ATMP) is predominantly applied as industrial detergents. The two organophosphonates hydroxyethelidene(diphosphonic acid) (HEDP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) are often applied as compounds of industrial cleaning products. Phosphonates are also often applied as dispersing agents in paper and textile industry stabilizing peroxide bleaching baths [13]. Besides, they are utilised as compound of flame redardancy [14] and in oilfield industry [15,16]. Another important application field leads to cooling water systems and desalination processes where DTPMP is often applied as scale inhibitor. Aminophosphonates such as ATMP, EDTMP, DTPMP and bis(hexamethylenetriamine) penta(methylene phosphonic acid) (BHMTPMP) were recently also reported as important base for the synthesis of environmentally friendly multifunctional mesoporous metal phosphonate materials as various absorbents in different phases such as liquid-phase and gas-phase adsorption [17]. Apart from technical applications, phosphonates such as HEDP and EDTMP are also successfully applied in medical treatments of bone diseases [9,18]. Studnik et al. [8] pointed out that at least in Europe, more than 2,700 products are registered containing phosphonates. This statement is in good agreement with the latest application data found on the database of the European Chemicals Agency (ECHA) which listed further applications as follows: “Phosphonates are also product compounds of water softeners, air care products, washing and cleaning products, fertilisers, polishes and waxes, cosmetics and personal care products, biocides (e.g. as disinfectants, pest control products), coating products and fillers, putties, plasters and modelling clay. Furthermore, they are utilized as important compounds of so-called long-life indoor materials, e.g. in flooring, furniture, toys, construction materials, curtains, foot-wear, leather products, paper and cardboard products and in electronic equipment.”

Reliable data about the individual consumption of phosphonates are very difficult to obtain because the consumption and application of phosphonates have been steadily increasing in recent decades. Studnik et al. [8] reported that more than 4000 tons of aminomethylenephosphonates were consumed in 2001. This included phosphonates such as ATMP, EDTMP and DTPMP. Gledhill and Feijtel [19] reported about an annual consumption of DTPMP with 5,270 tons in Europe. This comprised 85 % use in laundry detergents, 7 % in industrial cleaning and 2 % in industrial boiler and cooling systems, respectively. However, more detailed enquiries at the ECHA database show that the total annual production of DTPMP has increased up to an average production between 1,000 to 10,000 tons per year in 2018 [20]. Interestingly, beside the increased production of the salt free phosphonate DTPMP, the current DTPMP sodium salt (DTPMP-xNa) production averages 10,000 to 100,000 tons annually (**Table 1**). Similar production trends are found for the aminophosphonate EDTMP and the organophosphonate HEDP. The salt containing phosphonates average an annual production between 1,000 to 10,000 tons and 10,000 to 100,000 tons for EDTMP and HEDP, respectively. The production of the

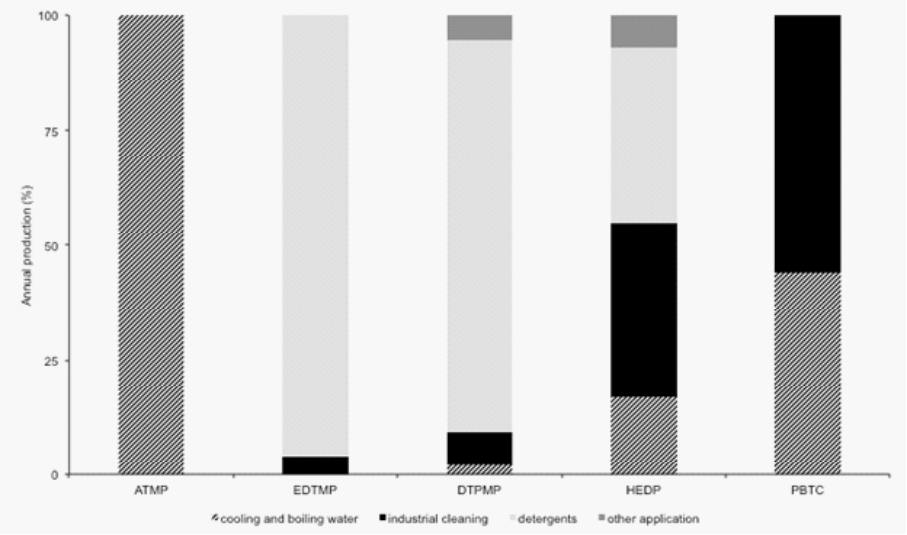
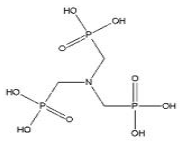
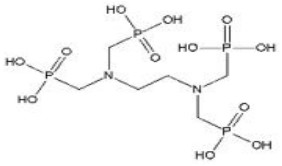
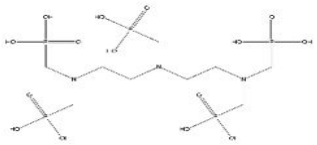
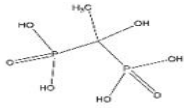
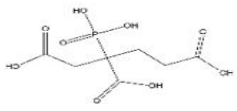


Figure 1: Annual production of selected phosphonates and their applications. Original graph is taken from [11] and slightly modified.

Table 1: Common phosphonate products and their annual production in Europe.

Phosphonate and structure	Common products*	Production (t/a)**
ATMP 	ATMP	10,000 - 100,000
	ATMP-xNa	1,000 - 10,000
	ATMP-N-Oxide, 5K	1,000 - 10,000
	ATMP-5K	1,000 - 10,000
EDTMP 	EDTMP-H	10 - 100
	Ca-Na-EDTMP	1,000 - 10,000
	Sodium EDTMP	100 - 1,000
DTPMP 	DTPMP	1,000 - 10,000
	DTPMP 5Na	100 - 1,000
	DTPMP 2-3Na	1,000 - 10,000
	DTPMP 5-7Na	10,000 - 100,000
HEDP 	HEDP	10,000 - 100,000
	HEDP 4Na	10,000 - 100,000
	HEDP (2-3Na)	100 -1,000
PBTC 	PBTC	10,000 – 100,000
	PBTC 4Na	100 – 1,000

*phosphonate products listed at the ECHA database in 2019
**manufactured and/or imported in the European economic area

salt free aminophosphonate ATMP averages an annual production between 10,000 to 100,000 tons per year and is significantly higher with respect to their salt containing products, which average 1,000 to 10,000 tons. The different production rates presented here demonstrate the high demand for different application purposes. Reliable data of the consumption of phosphonate on the American market are also difficult to obtain. Some useful data can be found [11 & 12]. Rott et al. [12] reported a worldwide consumption of phosphonates of 94,000 tons per year in 2012 with a continuous increasing trend. So far, the significance of phosphonates in modern life is currently burdened with the mainly negative publicity on the debate of glyphosate. However, all the advantages phosphonates delivered to daily life ought not be neglected.

2. Environmental Impact of Phosphonates

The worldwide increasing demand of phosphonates and broad application range underline the importance of this specific subgroup of the unreactive phosphorus fraction. However, parallel to the high demand also the increased environmental impact is currently under discussion [12,21]. Phosphonates are chelating agents with the potential to remobilise heavy metals from sediments. At the early beginning of the 21 century, Jaworska et al. [22] described the first environmental risk assessment of phosphonates in the Netherlands. She pointed out that the use pattern of phosphonates in the US and Europe was different. In the US phosphonates are many used in industrial cooling and boiling processes and therefore their release to the environment is more limited. The situation in Europe is very different because phosphonates are commonly used in detergents and thereby continuously introduced to the wastewater or surface water. Jaworka et al. [22] calculated the total phosphonate exposure concentration for surface water for HEDP, ATMP, EDTMP and DTPMP and concluded that the low concentration of about 0.03 mg L^{-1} are not high enough for expected metal remobilisation. This assumption was recently again confirmed by other scientists [12].

Nevertheless, these calculations are almost 20 years old and might be revised since the phosphonate release to the environment has certainly increased as well as their demand. Rott et al. [12] stated that in Europe 20,900 tons per year of phosphonate from detergents of laundry and dishwasher are introduced to municipal wastewater treatment. Industrial detergents are indirectly discharged to the municipal wastewater and comprise up to 3,700 tons per year. Overall 1.2 to 1.5 $g_{phosphonate}$ $kg^{-1}{}_{dry\ substance}$ (80 % to 95 %) is removed by adsorption onto the sludge in the sewage plant. The main fraction of the sludge (50 % - 60 %) is recycled and incinerated. Another fraction of 30 % to 35 % is used for agriculture as fertilizer and soil improvement. Approximately 5 % up to 20 % is discharged into the receiving water resulting in concentrations between 0.5 to 5 µg L^{-1}. Consequently these concentrations are higher as modelled by Jaworska et al. [22], therefore, the impact and the fate in the environment ought not to be underscored. Even though, Rott et al. emphasized the fact that the largest discharge of phosphonates to the receiving water is not caused by municipal wastewater plants but by

the direct discharge of membrane concentrates and cooling water. He averaged discharge loads from 9,000 to 18,600 tons per year to the streaming rivers in Europe. For that reason, the impact to the environment is even more an important issue and requires more intensive investigations.

3. Analytical Challenges

In the past three decades, several analytical methods have been reported and highlighted being applicable to analyse for organophosphonates and aminophosphonates. Nevertheless, reliable and reproducible analyses of phosphonates and their possible degradation products are generally difficult to realise due to very low concentrations in the environment. At the moment, there is no standard method defined as a routine for detecting and quantifying phosphonates at trace levels [10]. Thus, different phosphonate detection approaches with different detection limits have been reported (**Table 2**). For example, first methods for ion chromatography (IC) followed by post-column derivatisation of the column effluent forming detectable Fe-complexes [22,23] or followed by indirect photometric detection [25,26] were described. These methods were mainly restricted to the analyses of standard solutions or samples with minimal concentration of disturbing background matrix. Another limit led to the concentration of natural water samples, which are expected at trace level concentrations as above-mentioned. Frigge and Jackwerth [27] were the first authors who officially dedicated their attention to this problem and published a method to pre-concentrate different organophosphonates from natural waters by absorption or precipitation. They reported successful enrichment factors from 10 to 25 in solution with low chloride contents by absorbing the phosphonates HEDP, ATMP and EDTMP on bismuth hydroxide. Higher enrichment factors of 50 to 400 were achieved for the same phosphonates using exchange cellulose or exchange resins. The sample was also analysed by IC. Another method also based on indirect photometric detection was reported for capillary electrophoresis [28]. The method was applied to soaps and toothpaste and showed excellent results. The authors highlighted the possibility to apply the developed CE method to routine analysis of samples having phosphorus-containing polyvalent anions. However, the use of this method to environmental samples as screening methods was not reported until nowadays.

In 1995, Tewari et al. [29] pointed out that detection methods based on Fe(III) complexation suffered much from the large background noise and that the expected limits of detection were too high for analysing environmental samples. In addition, the sample preparation was too laborious. Therefore, they introduced a new method again based on IC but with an amperometric detector. They highlighted in their publication that this detector should provide higher selectivity and should be less influenced by disturbing anions in the background sample matrix. The authors pointed out that their method showed excellent selectivity and sensitivity but the robustness still required further optimisation. Nevertheless, the IC and CE methods mentioned here were mainly limited due to interferences by major cations and anions

in the water [13].

For that reason, Nowack [30] developed another method for the determination of phosphonates in natural waters based on high performance liquid chromatography (HPLC) with limits of detection (LOD) between 15 to 100 μg L^{-1} for different phosphonates. The identification was based on the individual retention times of the eluting compounds. This obstacle was overcome by first methods reported applying liquid chromatography (LC) coupled with mass spectrometry (MS). Klinger et al. [31] introduced a very promising analytical method for determining phosphonates in natural and surface water samples by coupling LC/MS by particle-beam interface (PB) (LC/PB-MS). This method described the first time successful derivatisation of phosphophonates such as PBTC, HEDP, ATMP, EDTMP and DTPMP with diazomethane. This method showed also very low LOD and appeared very promising for the analyses of natural water samples. However, the authors indicated that higher amounts of inorganic salts decreased the sensitivity of the method which was also a great problem to the former method [30]. Another attempt to further enhance the sample purity was reported by Vreeken et al. [32] who included derivatisation followed by solid phase extraction prior to LC/MS-MS analysis. In the past 18 years, only three other methods were published focusing the analysis of phosphonates apart from glyphosate [33, 34, 35]. The authors of the last two publications highlighted the analysis of aminophosphonates without derivations. The method published by Schmidt et al. [34] included a pre-concentration step applying SPE followed by sample separation with IC and inductively coupled plasma mass spectrometry (ICP-MS). The authors demonstrated successfully the applicability of their developed method for trace-level analysis of phosphonates without derivatisation in natural water samples. The advantage of this method was that there is no negative effect by interferences caused by the sample nature. Unfortunately, identification of unknown structures was not possible applying ICP-MS as it is a common feature of MS approaches. Instead, the identification via ICP-MS is based on the retention time of a standard sample as reference and therefore unknown structure and/or important metabolites from natural samples cannot be identified.

As stated in the introduction, the phosphonate glyphosate is not the major focus of this review. However, it should be noticed that there is a tremendous number of published analytical methods available in the current scientific literature. More in detail, in 2001 Stalikas et al. [36] published a very comprehensive review focusing only on the analysis of glyphosate and AMPA. They summarised more than 16 different methods for detecting both aminophosphonates via gas chromatography (GC) and 18 methods via HPLC. All methods are based on derivatisation. It is expected that the number of applicable methods for the analysis of glyphosate from environmental samples has still increased within the past years.

Table 2: Overview of different analytical methods for the detection of diverse phosphonates.

Phosphonates	Pretreatment	Acquisition	Target	LOD (µg L^{-1})	Ref.
Diverse organophosphonates	Fe(III)-complexation	IC	Complex mixtures	Not reported	23
HEDP, ATMP, EDTMP and others	Fe(III)-complexation	IC	Standard solution	Not reported	24
HEDP, ATMP, EDTMP, DTPMP	Fe(III)-complexation	IC	Standard solution	Not reported	25
Diverse organophosphonates	none	HPLC	Standard solution	Not reported	26
HEDP, ATMP, EDTMP	Ion exchange resin	IC	Natural waters	0.5	27
HEDP, ATMP, EDTMP, HDTMP*, DTPMP	Organic/inorganic modifier	CE	Natural waters	100 - 200	28
EDTMP, DTPMP	Sulphite	HPLC-PAD	Detergents	250	29
HEDP, ATMP, EDTMP, DTPMP	Fe(III) complexation	HPLC	Wastewater, drinking water	15 - 100	30
PBTC, HEDP, ATMP, EDTMP, DTPMP	Derivatisation	LC/PB-MS	Surface water	2 - 13	31
Glyphosate, glyfosinate, AMPA	Derivatisation & SPE	LC/MS-MS	Various types of water	0.05 - 3.0	32
FIDMP, IDMP	Derivatisation	HPLC	Wastewater	2 - 4	33
HEDP, ATMP, EDTMP, HDTMP, DTPMP	Ion exchange resin	IC-ICP-MS	Natural waters	0.006 – 0.025	34
Glyphosate, AMPA	Ion exchange resin	LC-MS/MS	Saline natural waters	0.8 – 4.0	35

* Hexamethylenediamine tetra (methylenephosphonic acid) (HDTMP)

Overall, the analysis of aminophosphonates has caught a lot of attention and scientists have continuously developed and optimised new methods to detect these very challenging compounds from natural water samples. It is, therefore, reasonable to expect that the development of even more selective and sensitive analytical methods will progress within the following years.

4. Photochemical Degradation

Due to the slow biodegradability, phosphonates are categorised as being rather persistent [21, 37]. Similar to other chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), it is expected that phosphonates also enrich over long periods in anthropogenically influenced streams and most rivers in industrial countries [11]. One major degradation pathway of phosphonates leads to photolysis as earlier described also for ferric complexes of EDTA and NTA [38,39]. The first study on the photolysis with monochromatic light (i.e. at 254 nm and 365 nm) of an aminophosphonate was reported in 1989 [40]. The authors evidenced the rapid degradation of ferric EDTMP of which 75 % of orthophosphate (o-PO_4) was released. The formation of a photostable transformation product was confirmed

and identified as N-methyl-aminomethylenephosphonic acid. The authors emphasized that photodegradation of ferric phosphonates ought to be the major degradation pathway in aquatic environment since these complexes absorb light. In view of this, the authors expected no conversion of uncomplexed EDTMP through photolysis because the uncomplexed phosphonate does not absorb visible or ultra-violet (UV) light. This consideration is still in agreement with other scientists [13,41,42].

However, even if the photodegradation of phosphonates appears as the major degradation pathways in the aquatic environment, almost 20 years were required until another study about the photodegradation of phosphonates such as ATMP, EDTMP and DTPMP was published. An explanation might be to the fact that the direct measurement of the parent compounds and identification of released intermediate by-products was impeded through limited analytical methods available. Perhaps that was why the main scientific focus rather turned on the development of new analytical methods than on deciphering the photochemical reaction mechanisms of phosphonate taking place in aquatic environments. In 2005, Lesueur et al. [41] published a fundamental study about the influence of ferric iron (Fe^{3+}) at different pH during UV treatment of common organophosphonates. Different to the study of Matthijs et al. [40], the authors applied polychromatic light having a wavelength range from 190 nm to 650 nm to treat the phosphonates. They clearly identified AMPA as the intermediate by-product and thereby underlined that the release of AMPA in aquatic environments is not only due to the degradation of glyphosate. Others scientists confirmed this important finding later [42,43]. Thus, the presence of AMPA does not automatically lead to conclude that this intermediate by-product is the tracer for glyphosate. Scientists justified their conclusion by the fact that the popular intermediate by-product is also a common by-product of other phosphonates such as detergents and antiscalants. The latter are often directly discharged without pre-treatment from cooling water or membrane concentrates [44], therefore, AMPA formation from other phosphonates is feasible.

Another important outcome of the study of Lesueur et al. [41] was that the concentration of ferric iron was enough to promote phosphonate conversion induced by sunlight in natural waters. Chen et al. [45] investigated also the influence of ferric iron during photolysis but they used glyphosate for the treatment. Interestingly, they postulated a reaction mechanism which was similar to the chemical degradation based on oxidation by manganese oxide [46]. Finally, photochemical and metal-catalysed degradation can both lead to similar reaction pathways.

More recently, the complete degradation pathway of EDTMP during photolysis was identified by applying LC/MS analysis [47]. For the first time, the direct degradation of the parent compound and the formation of the major intermediate by-products was reported. The authors demonstrated that beside AMPA iminodi(methylenephosphonic acid) (IDMP) and e thylaminobis(methylenephosphonic acid) (EABMP) also were important intermediate by-

products. The formation of IDMP as major breakdown product was also reported earlier for the conversion of other aminophosphonates [48,49]. In spite of this, the authors emphasised that they were capable to convert uncomplexed EDTMP. They showed that a nucleophilic attack by hydroxyl radicals as previously reported for the photolysis of glyphosate was responsible for the degradation [37]. In another photochemical study, the same authors investigated the influence of the ferrous iron (Fe^{2+}), magnesium (Mg^{2+}) and calcium (Ca^{2+}) during the photolysis of DTPMP [20]. They demonstrated that ferrous DTPMP was converted four times faster as compared to uncomplexed DTPMP. Interestingly, the presence of ferrous iron accelerated predominantly the degradation of the parent compound but did not further promote the rapid degradation of the intermediate by-products. It was speculated that the by-products might not efficiently coordinate the metal ion, therefore, no further metal-catalysed degradation takes place as recently described for the treatment of NTA [50].

Obviously, photochemical degradation attempts for better understanding possible reaction mechanisms of phosphonates in the aquatic environment have also attacked other scientist in the past five years. These studies, however, were more focussed on combining different approaches including UV treatment to remove phosphonates from process waters such as industrial wastewater [44], domestic wastewater [51] or membrane concentrates [52]. Rott et al. [44] investigated intensively the effect of UV/Fe^{2+}, Fenton and UV/Fenton treatment for the implementation of a specific phosphonate treatment in a continuously operated wastewater treatment plant. They stated that the Fenton reagent resulted in only 20 % phosphonate conversion. In order to enhance the degradation to a higher extent UV irradiation was proposed to support. Furthermore, they recommended UV/Fe^{2+} process only if the unreactive phosphorus was present as nitrogen-free phosphonate due to the high selectivity of this process. Alternatively, they proposed to apply the Fenton principle to degrade and absorb the phosphonates (vie sludge sedimentation and filtration) from industrial wastewaters. Sun et al. [51] followed a similar strategy but they paid more attention of replace Ca^{2+} from the phosphonate complex by Fe^{3+}, which is the higher photo-active complex. UV treated ferric phosphonates were then simply removed from the wastewater by co-precipitation. Applying this treatment strategy, more than 60 % of ATMP was converted to o-PO_4 and overall more than 90 % of the total phosphorus was removable from the wastewater effluent.

Huang et al. [52] treated a synthetic membrane concentrate containing HEDP with UV/chlorine and found highest conversion at low chlorine doses. They proposed the implementation of this treatment strategy as possible pre-treatment of membrane concentrates controlling the environmental risk by antiscalants. Wang et al. [53] introduced another combined advanced oxidation process (AOP) for the treatment of ATMP from desalination concentrates. They showed that UV treatment with monochromatic light (254 nm) was insufficient to breakdown ATMP. The addition of persulfate resulted in efficient ATMP removal under standardised condition, i.e. batch experiments. When they applied their set-up to real reverse osmosis (RO)

concentrate, the degradation efficiency decreased due to matrix effects. They identified Cl^- and HCO_3^- playing a major role in reducing the removal of ATMP during the AOP treatment. Therefore, they proposed to remove those anions prior to the UV/persulfate treatment.

Summarizing, the presented studies evidenced that aminophosphonate undergo photochemical conversion with or without complexation of metal ions. The formation of different intermediate by-products was proven. Still, little is known about their effects in the aquatic environment. Apart from the consensus that AMPA is not only delivered from glyphosate, the environmental relevance of the other major intermediate by-products such as IDMP, FIDMP and EABMP is still underestimated. Further, it was clearly demonstrated that results obtained from UV irradiation experiments are, to a certain extent, transferable to reaction mechanisms taking place in natural waters. Bearing in mind that phosphonates replaced initially polyphosphates in detergents due to their high efficiency to soften the water hardness during laundry process by reducing tremendously the input amounts. However, their high stability and various applications make them serve as a continuous long-term contamination in the environment where they could potentially release higher quantities of o-PO_4 as SRP. For that reason, phosphonates are still suspected to promote eutrophication of natural water and surface waters. Certainly, more basic research has to be carried out to better understand the reaction mechanisms of the parent compound but also of the intermediate by-products.

5. Chemical Degradation and Ozonation

There are some interesting studies focussing exclusively on the degradation of phosphonates in presence of catalytic transition metals and/or by adsorption onto mineral surfaces. Doubtlessly, Nowack and Stone have contributed most in describing the reaction mechanism that occurs during chemical degradation [10,49,53]. They focussed mainly on the degradation mediated by manganese (Mn) and showed that only Mn^{2+} catalysed the autooxidation of ATMP [53]. They concluded that Mn^{2+} is also responsible for the degradation of ATMP in natural water. However, they underlined that the degradation rate is dependent on the presence of Mn^{2+} concentration. In cases where phosphonates form complexes with other metal ions the degradation rate might be significantly reduced. Interestingly, the intermediate by-products IDMP and FIDMP and also the organophosphonate HEDP were not subjected to autooxidation. This observation is in agreement with those of Kuhn et al. [20]. As stated before, the latter performed UV degradation and found this effect mainly for the treatment with ferrous iron. Nowack and Stone also pointed out that Klinger et al. [31] have made similar observation when they treated HEDP with ozone.

Finally, Nowack and Stone concluded that the presence of the amine group plays a major role in the initial cleavage of the parent compound. It is assumed that the bivalent transition metal ion transfers an electron to the nitrogen of the amine, which results in changing the electron density distribution around the nitrogen centre. This affects the C-N bond and

makes it more vulnerable to the nucleophilic attack as above-mentioned for the UV treatment with ferrous iron and also for the manganese-catalysed autooxidation. Furthermore, Nowack and Stone also expect autooxidation of other commercially relevant aminophosphonates such as EDTMP, HDTMP and DTPMP in natural waters. Obviously, aminophosphonate are more predestined to rapid cleavage, thereby, release metabolites with increased resistant to chemical degradation. For that reason, their potential accumulation in natural water bodies is conceivable.

Despite chemical degradation, AOP such as ozonation was also investigated. Ozonation, however, was predominantely studied as promising treatment for rapidly breaking down phosphonates. Klinger et al. showed the rapid degradation of EDTMP (less than 1 min) in ultra-pure water and tap water through ozonation [55]. They showed further that ozonation of EDTMP can lead to formation of glyphosate and AMPA. The degradation of AMPA was more difficult as compared to glyphosate which was mainly determined at the beginning of the oxidation process. They suggested a reaction pathway for the oxidation of EDTMP which included at least another eleven metabolites which were still not determinable due to the lack of analytical methods. More recently, ozonation applied to phosphonates was commonly used as antiscalants for RO [56,57]. Greenlee et al. [56] showed that the presence of multivalent cations affected the antiscalant oxidation, i.e. complexation with Ca^{2+} seemed to enhance the degradation in presence of ozone. They concluded that only low ozone doses between 1-10 mg L^{-1} O_3^{-1} are necessary to oxidise the phosphonates ATMP, HDTMP and DTPMP. Xu et al. [57] applied different AOPs to breakdown 2-Phosphonobutane-1,2,4-tricarboxylic (PBTCA) and found only significant degradation by applying ozone (40 mg L^{-1} O_3^{-1}) and UV/H_2O_2. They described every detailed the reaction kinetics and showed that the oxidation of PBTCA by ozone was dominated through hydroxyl radical, especially, at higher pH. The released o-PO_4 was removed at a coagulant dose of 40 mg L^{-1} of ferric chloride and achieved up to 95 %. The authors concluded that combining ozonation followed by coagulation is a suitable pre-treatment dealing with the phosphorus in PBTCA.

Chemical degradation and ozonation can be both applied to pre-treat waters containing phosphonates. Most reaction mechanisms are meanwhile well understood and therefore the degradation pathway and kinetics can be simulated and predicted. For future application, several promising approaches are now available. Nevertheless, they will always require specific optimisation regarding their specific target treatment aim, i.e. phosphonate degradation and/or simultaneous SRP removal.

6. Adsorption of Phosphonate

Apart from AOP to remove phosphonates from process waters, only a few studies focussed on adsorption process which is also practically applicable. First studies investigating basic adsorption of phosphonates were reported in 1984 and 1986. Müller et al. [58] investigated the

potential of HEDP of both remobilisation of selected metals and adsorption of the phosphonate from activated sludge. It was found that only iron was remobilised in the primary clarifier and mainly adsorbed in conventional activated sludge (CAS) process of the treatment plant. Rott et al. [12] concluded from these findings that metal remobilisation from activated sludge (AS) might be insignificant. Nowack pointed out that phosphonates show strong adsorption onto almost all mineral surfaces and also sludge [13]. Steber et al. [48,59] investigated the adsorption potential for both HEDP and ATMP on AS. For the adsorption experiments three different sludges were tested and all delivered similar results by means of a maximum elimination of > 90 % HEDP adsorption. From the experimental dataset, 25 % - 60 % adsorptive HEDP removal was calculated for CAS. Steber pointed out that for the calculation not only the adsorption coefficient of the AS is required but also the surplus sludge wastage has to be included. The elimination of ATMP by adsorption on AS was lower compared with HEDP. Unfortunately, Steber did not show more detailed results. He based this conclusion mainly on the model calculation of [60]. Steber calculated also the mobility of HEDP and ATMP in sediments and concluded that different to aminocarboxylates, the two investigated phosphonates showed moderated or rather low mobility in soil and sediments.

Adsorption on selected mineral surfaces seems to be more intensive investigated. Nowack summarised overall eleven studies focussing on adsorption on calcite, clay, aluminium oxides, iron oxides, zinc oxide, hydroxyapatite and barite [13]. According to Nowack all these mineral surfaces showed very high potential adsorbing phosphonates if the pH was in a range similar to natural waters.

More recently, the removal potential of phosphonates by adsorption on coated mineral surfaces, ion exchangers and natural absorbents has been investigated [61,62,63]. It was found that iron-coated waste filtration sand outcompeted anion exchange resin and activated carbon [61]. The metal-coated surface did not show the adsorption suppression at increasing ionic strength as the ion exchanger. The authors emphasized the application of iron-coated surfaces for membrane concentrates as a low-cost absorbent. For ATMP removal from industrial waters, Kołodyńska et al. [62] recommended chelating ion exchangers and strongly basic anion exchangers. She pointed out that commonly ATMP has to be removed as metal complexes (i.e. often preferred with cadmium, lead, copper or zinc) from industrial waters. Their adsorptive removal is strongly dependent on the contact time, pH and temperature. The maximum removal of complexed ATMP with interfering salts achieved about 85 %. In contrast, Kumar et al. [63] recommended the removal of phosphonates by powdered laterite stone as a low-cost and easy available natural absorbance source. They achieved 40 % removal within 15 min residence time. Extending the residence time improved the removal efficiency significantly.

Overall, the available database concerning adsorption of phosphonates, especially, under environmental conditions, is still very rare and insufficient. For better understanding the

adsorption potential, more research is required to also estimate the environmental behaviour.

7. Biodegradation of Phosphonates By Different Microorganisms

Possible biodegradation by microorganisms is a pertinent aspect of breaking down phosphonates in aquatic habitats. There are many studies dedicated to biodegradation of phosphonates and especially to specific enzyme regulation. However, in current literature it appears that most scientists focus on deciphering the enzyme regulation of successfully isolated and cultured bacteria. In this presented section the focus will be on the determination of biodegradation. The enzymatic repertoire of bacteria is discussed more detailed in the section below.

Commonly, chemical substances are tested for their biodegradation applying OECD degradation tests. Rott et al. [12] summarised the possible biodegradation of some common phosphonates based on recent literature. Most results were obtained in the 80's and 90's of the past century. Overall, it was found that neither the tested organophosphonates PBTC and HEDP nor the tested aminophosphonates ATMP, EDTMP and DTPMP were inherently biodegradable. Those results are not very surprising since phosphonates provide very high phosphorus content with respect to their carbon content. The OECD biodegradation tests are considered for easy biodegradation, i.e. chemical substances are degraded at least to 75% within 28 days. The biodegradation covers only the conversion of organic carbon and considers not the removal of nitrogen or phosphorus. For that reason, the experimental set-up investigating the biodegradation of phosphonates with the OECD test strategies might be adapted favouring biological phosphorus removal rather than the removal of organic carbon. In view of this, Schowanek and Verstraete [64] applied test condition with phosphorus limitation forcing bacteria to utilise phosphonates as sole P source. They found only one of thirteen tested pure cultures (strain *Arthrobacter* sp.) was capable to degrade almost all tested synthetic aminophosphonates. The authors emphasized that the biodegradation of the natural synthesised phosphonate 2-aminoethylphosphonate (2-AEP) was the most accessible phosphonates, i.e. most bacterial strains showed the highest degradation activity on this P substrate.

There are some earlier studies reporting the biodegradation of glyphosate and other phosphonates with different bacterial strain such as *Pseudomonas* sp., *Bacillus cereus* or *Escherichia coli* [65-69]. The tested phosphonates served mainly as phosphorus source. Successful biodegradation was reported in terms o-PO_4 release and methane production as simple indicator for the enzymatic cleavage of the C-P bond. Moore et al. noticed that the biodegradation of glyphosate required a longer lag phase and greater generation time for the bacteria as compared with other phosphorus sources [65]. In 1992, McMullan et al. [70] isolated a gram-negative bacterium from activated sludge capable to utilise phosphonates not only as phosphorus source but also as carbon source. However, the strain did not grow on synthetic aminophosphonates such as glyphosate. McGrath et al. [71] showed that *Rhizobium huakuii*

utilises phosphonates such as phosphonomycin as carbon source and Obojska et al. isolated the wild-type *Streptomyces* sp., which grew on phosphonates as carbon and nitrogen source [72]. Ternan et al. [73,74] demonstrated that *Burkholdria cepacia* cleaved phosphonopyruvate and *Pseudomonas putida* NG2 cleaved 2-AEP independent of the supplement of phosphate or phosphorus starvation in the media. More recently, Fox et al. [75] investigated biodegradation of phosphonate through Gram-positive bacteria, Gram-negative bacteria and fungi. Gram-negative bacteria represented the largest group capable to degrade almost all three served phosphonates. Gram-positive bacteria and fungi degraded phosphonates only partly. Biodegradation of phosphonates through yeast was also reported [76]. More detailed information about general biodegradation of aminophosphonates are summarised in [77].

Finally, all these different studies have evidenced that biodegradation of phosphonates is not restricted to some few bacterial strains and therefore seems to be more ubiquitous as previously expected. More comprehensive studies on the impact of biodegradation in aquatic environments are urgently required on estimating or rather predicting the environmental risk of phosphonates more precisely.

8. Enzymes to Breakdown Phosphonates

Overall, there are three different cleavage mechanisms very detailed reported in recent literature concerning the degradation of phosphonates: 1. Hydrolytic cleavage (phosphonoacetate hydrolase; phosphonopyruvate hydrolase, phosphonoacetaldehyde hydrolase), 2. oxidative cleavage (phosphonates) and 3. radical mediated cleavage (C-P-lyase) (**Table 3**; **Figure 2**).

In many cases, it was reported that the cleavage of phosphonates depend on the available P uptake and P starvation. Hsieh and Wanner showed very detailed the biochemical mechanism of the phosphate regulon (Pho; phosphate starvation regulon) signal transduction under conditions of surplus phosphate and phosphate limitation [78]. As Villarreal-Chiu et al. [79] pointed out, the enzymatic regulation of the C-P cleavage during available P uptake and/or P starvation are both under direct control of the Pho regulon.

The group of the phosphonate hydrolases is generally termed as phosphonates. Kamat and Raushel stated that the characteristic feature of phosphonatases is the presence of an electron withdrawing β-carbonyl group of the substrate facilitating bond delocalization and thereby initiating the heterolytic C-P cleavage [80]. The first detailed description of a phosphonatase cleaving the C-P bond of the naturally synthesized 2-AEP was reported in 1970 [81]. This degradation pathway is twofold. In the first stage 2-AEP is degraded via the enzyme 2AEP-pyruate aminotransferase to the intermediate 2-phosphonoacetaldehyde [82]. In the second stage the enzyme phosphonoacetaldehyde hydrolase (PalH) catalyses the conversion to the two final products acetaldehyde and o-PO_4 [70,82,83]. Another hydrolytic cleavage pathway was reported by Ternan and Quinn [84]. They were first who identified and

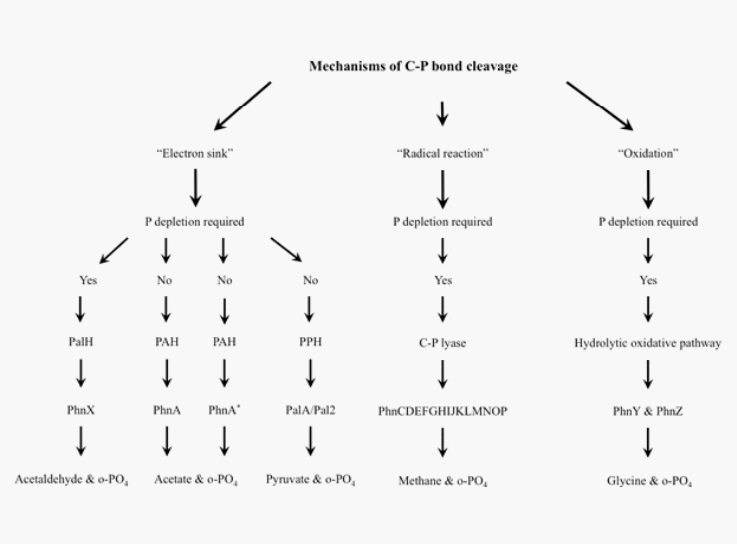
extracted phosphonopyruvate hydrolase (PPH) from *Burkholdria cepacia*, which catalyses the conversion of phosphonopyruvate to pyruvate and o-PO_4. Phosphonoacetate hydrolase (PAH), also belonging to the group of the phosphonatases, was first detected in *Pseudomonas fluorescens* 23F isolated from sludge of a laundry waste treatment plant by [70]. A similar degradation mechanism was identified for the species *Sinorhizobium meliloti* [85]. In both cases, the enzyme catalyses the conversion of phosphonoacetate to yield acetate and o-PO_4.

An alternative pathway to breakdown 2-AEP was recently discovered and described as oxidative pathway. McSorley et al. [87] demonstrated that this unusual pathway is also twofold. In the first stage, 2AEP is converted through hydroxylation to 2-amino-1-hydroxyl-ethylphosphonic acid (2A1HEP). In the second stage, 2A1HEP is further catalysed to yield glycine and o-PO_4. The oxidative cleavage of the C-P bond seems to be an important reaction mechanism typical for phosphorus-poor environments.

The radical-based homolytic cleavage of the C-P bond is catalysed through a multienzyme complex better known as C-P lyase. This enzyme complex has been studied deeply for more than four decades [88]. First evidence of the C-P lyase activity in strain *E. coli* was shown by [89]. The C-P activity was only detected during phosphorus starvation. The gene product form the enzyme complex which is localised in the cell membrane and periplasm. The enzyme complex is composed of five different functionalized groups [77]. In particular, the gene products PhnC, PhnD, PhnE and PhnK are related to transport [80]. The gene products PhnC, PhnD and PhnE are transporter proteins. The function of PhnK is still uncertain.

Table 3: Overview of C-P bond cleaving enzymes recently identified.

Enzyme	First isolated species	Superfamily	Substrate range	Metal dependency*	Ref.
Phosphonoacetaldehyde hydrolase	*Bacillus cereus*	Haloalkanoic acid dehygrogenase	2-AEP	Mg^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}	80, 86
Phosphonoacetate hydrolase	*Pseudomonas fluorescens* 23F	Alkaline phosphatase	Broad sprectrum	Zn^{2+}	70, 80
Phosphonoacetate hydrolase	*Sinorhizobium meliloti*	Alkaline phosphatase	2-AEP	Zn^{2+}, Mn^{2+}, Fe^{2+}	80, 85
Phosphonopyruvate hydrolase	*Burkholdria cepacia*	Phospho(enol)pyruvate mutase/isocitrate lyase	Phosphonopyruvate	Mg^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}	80, 84
Phosphohydolase	*Escherichia coli* (mutant)	Non-heme Fe(II)/α-ketoglutarate-dependent dioxygenase	2-AEP	Fe^{2+}	80, 87
C-P lyase	*Escherichia coli*	None (multienzyme complex)	Broad spectrum	Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}	80, 88



* gene on a megaplasmid (*Sinorhizobium meliloti*)

Figure 2: Overview of inducible enzymes for C-P cleavage with and without phosphorus limitation as prerequisite.

The two gene products PhnF and PhnO are related to the metabolism of the intermediates and products [81, 89, 90]. The five catalytic gene products PhnG, PhnH, PhnI, PhnL and PhnM are involved in preparing the final cleavage. The gene product PhnJ is finally cleaving the C-P bond through a radical reaction. The two gene products PhnN and PhnP are involved in the post-catalytic metabolisms. A very detailed description of the entire pathway with every single reaction stages is delivered by [77,80].

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