INTERNATIONAL SYMPOSIUM

Aminophosphonates and Environments

01 and 02 October 2024
Brandenburg University of Technology
Main campus at Cottbus

Organising Committee
Ramona Riedel & Marion Martienssen
Chair of Biotechnology of Water Treatment

PREFACE

Dear Attendee,

We extend a warm welcome to all participants attending the inaugural international symposium, "Aminophosphonates and Environments," which is being held under the auspices of the Chair of Biotechnology of Water Treatment at BTU Cottbus/Senftenberg. The Chair of Biotechnology of Water Treatment at BTU Cottbus/Senftenberg has been engaged in research on aminophosphonates for the past 14 years. Nevertheless, the history of commercially available phosphonates can be traced back to the mid-twentieth century. The synthesis of glyphosate constituted a substantial advancement in the field of industrialised agriculture. The synthesis by-products, which were previously regarded as undesirable, were found to possess intriguing properties as complexing agents.

Since that time, phosphonates have become an integral part of our modern lifestyle, operating below the threshold of our conscious awareness. The absence of these valuable structures would result in considerable qualitative losses, not only in the areas of household chemicals and water treatment processes. Despite all these remarkable advantages, phosphonates have been identified on numerous occasions as a potential source of eutrophication in aquatic ecosystems. The behaviour of these compounds in aquatic environments is a topic of ongoing debate, particularly in Germany. Several research papers have been published which address a range of issues related to the analysis of phosphonates, including the challenges associated with this process, the degradation of these compounds under photochemical conditions, their behaviour during membrane filtration, the absorption phenomena that occur, the fate of these compounds in municipal wastewater treatment plants and aquatic environments, and the biodegradation of industrially relevant phosphonates.

The objective of this symposium is to facilitate a discussion between scientists, representatives from government agencies and industry on the most recent findings on the scientific state-of-art. During the oral presentation sessions, discussion of the latest research data is encouraged. During the poster session, participants will have the opportunity to exchange experiences, share successes, express opinions, and provide feedback.

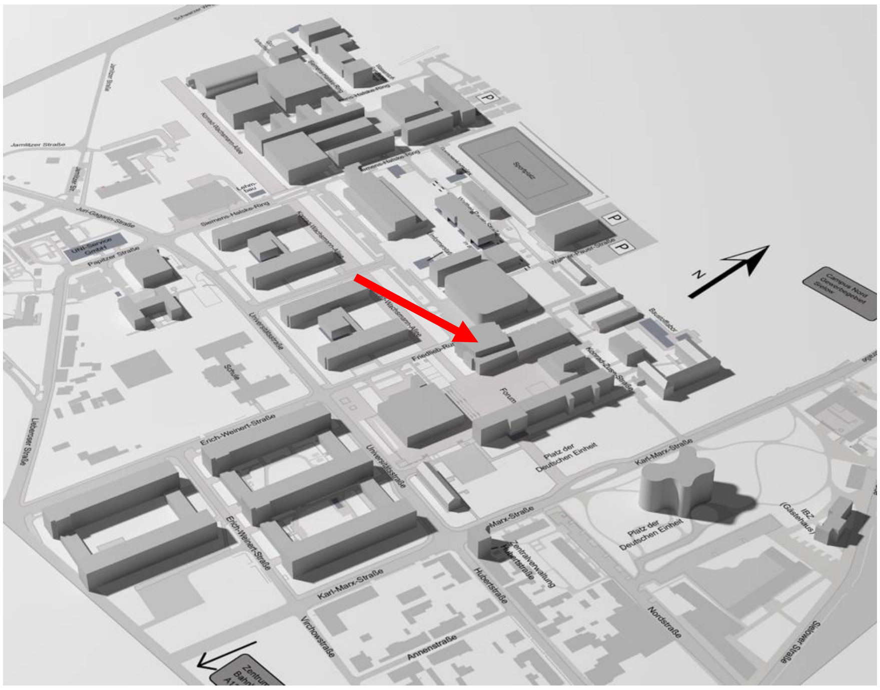
The main topics that will be presented and discussed during the symposium are the following:

- Analyses of phosphonates and application in membrane processes
- Photodegradation & Photocatalysis
- Aquatic phosphonates
- Industrial phosphonates
- Phosphonates in agriculture
- Adsorption of phosphonates
- Biodegradation of phosphonates

The Organising Committee would like to extend its gratitude to all those at BTU Cottbus/Senftenberg who were instrumental in making this event a success. We hope that you will find the event, with its diverse and engaging subject matter, both enjoyable and informative.

VENUE (Audimax at BTU Cottbus-Senftenberg)

Map of BTU main campus (red arrow shows the conference building)



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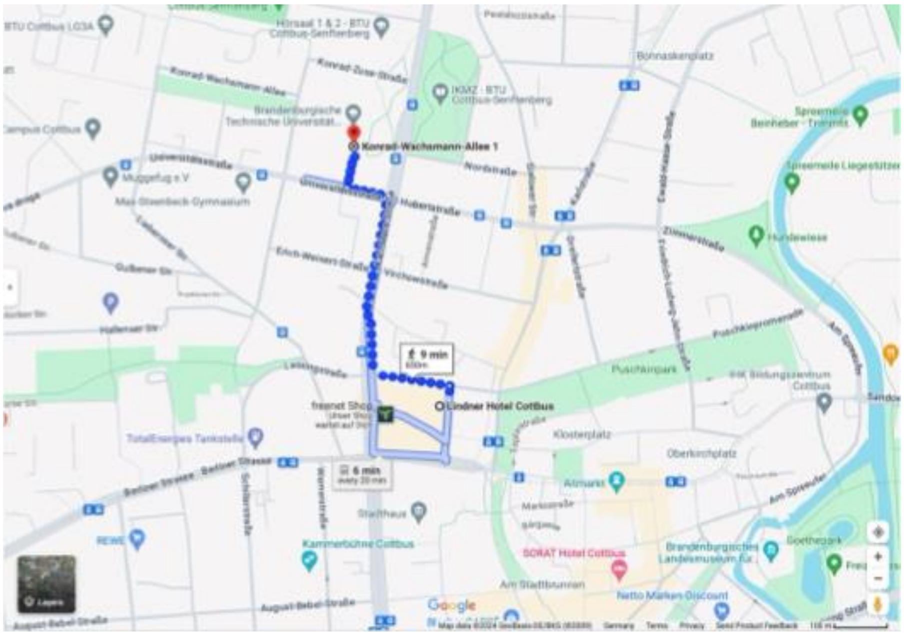

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SCIENTIFIC PROGRAM

October 01 and 02 – 2024 at BTU Cottbus/Senftenberg

Full conference days on science (including lunch and coffee breaks)

Tuesday October 01

9:30 - 9:50 Registration

9:50 - 10:00 Opening remarks

Wednesday October 02

13:10 – 13:30 Closing remarks

PROGRAM INFORMATION

Information for speakers

In order to be able to keep the symposium schedule, we would be very grateful if you could save the presentations on the computer in the lecture room during the registration and the coffee breaks. Please ensure that the presentation time does not exceed 20 minutes. For scientific discussion, please plan about 10 min.

Information for poster presenters

The poster session will be on Tuesday evening. There is no numbering for the posters, they can be attached to free poster walls. We will provide the materials for attaching the posters to the poster walls. We recommend that you create the poster in DIN A0 format (84.1 cm x 118.9 cm or 841 mm x 1189 mm).

The best poster will be awarded (250 €)!

TUESDAY OCTOBER 01

Session 1 – Analyses of phosphonates and application in membrane processes

Chair: Prof. Thomas Fischer (Central analytical Lab, BTU Cottbus/Senftenberg)

10:00 – 10:30	Talk 1 – Lecture by Dominc Armbruster (TZW Karlsruhe, Germany): "Overview on the status quo in the analysis of phosphonates"
10:30 – 10:50	Talk 2 – Sarah A. Bieger (Eberhard Karls University Tübingen, Germany): *"Critical transformation products of aminopolyposphonates in different processes"*
11:00 – 11:20	Talk 3 – Martin Futterlieb (University Duisburg-Essen, Germany): *"Incipient $CaCO_3$-scaling detection for antiscalant free high recovery reverse osmosis operation"*
11:30 – 12:30	Lunch break

Session 2 – Photodegradation & photocatalysis

Chair: Prof. Martienssen (BTU Cottbus/Senftenberg)

12:30 – 12:50	Talk 4 – Ramona Riedel (BTU Cottbus/Senftenberg, Germany): *"Photochemical degradation of phosphonates – what we know so far"*
13:00 – 13:20	Talk 5 – Julia Schowarte (BTU Cottbus-Senftenberg, Germany): *"Photocatalysis of the aminophosphonate EDTMP"*

Session 3 – Aquatic phosphonates

Chair: Dr.-Ing. Ramona Riedel (BTU Cottbus/Senftenberg)

13:30 – 13:50	Talk 6 – Anna M. Röhnelt (Eberhard Karls University Tübingen, Germany): *"DTPMP oxidation by MnO_2 leads to glyphosate as a minor transformation product"*

14:00 – 14:30	Tea and coffee break
14:30 – 14:50	Talk 7 – Vojtěch Kubíček (Charles University, Prague, Czech Republic): “Metal complexes of aminophosphonates in solution – stability constants and speciation

Session 4 – Industrial phosphonates

Chair: Dr. Jörg Böllmann (BTU Cottbus/Senftenberg)

15:00 – 15:20	Talk 8 – Graciela Gonzalez-Gil (King Abdullah University of Science and Technology, Saudi Arabia): *“Antiscalant Secrets: Unraveling their impact on microbial growth in seawater”*
15:30 – 15:50	Talk 9 – Gerd Braun (University of Technology Cologne, Germany): *“Considerations for the selection and dosing of inhibitors for* $CaCO_3$*-scaling in reverse osmosis and nanofiltration plants”*
16:00 -16:20	Talk 10 – Stephan Liebsch (Zschimmer & Schwarz, Germany): “The benefits of phosphonates for everyone - property profile and applications of this substance class”
16:30 – 17:00	Tea and coffee break
17:00 – 18:00	Lab visit at the Chair of Biotechnology of Water Treatment at BTU
18:00 – 19:00	Poster session
19:30	Dinner at Spree-Waldhotel Cottbus (address please see last page)

WEDNESDAY OCTOBER 02

Session 5 – Phosphonates in agricultures

Chair: Ramona Riedel (BTU Cottbus/Senftenberg)

09:00 – 09:20 Talk 11 – Werner Nader
(Eurofins Dr. Specht Express Testing & Inspection GmbH, Germany):
"Phosphonic acid in organic food and feed – residue, contaminant or natural metabolite?"

Session 6 – Adsorption

Chair: Dr. Jörg Böllmann (BTU Cottbus/Senftenberg)

09:30 – 09:50 Talk 12 – Marion Martienssen
(BTU Cottbus/Senftenberg, Germany):
"Adsorption of phosphonates on activate sludge"

Session 7 – Biodegradation of phosphonates

Chair: Prof. Martienssen (BTU Cottbus/Senftenberg)

10:00 – 10:30 Talk 13 – Lecture (by Ramona Riedel)
(BTU Cottbus/Senftenberg, Germany):
"Overview on enzymatic mechanisms to break down phosphonates"

10:40 – 11:00 Talk 14 – Karsten Meißner
(UBA, Section Water Tretament, Germany):
"Phosphonate degradation by laundry isolate *Delftia* sp. UMB14"

11:10 – 11:30 Talk 15 – Dirk Benndorf
(University of Applied Science Anhalt, Germany):
"Proteome-based elucidation of phosphonate degradation"

11:40 – 12:30 Lunch break

12:40 – 13:00 Talk 16 – Lisa Engelbart
(Eberhard Karls University Tübingen):
„DTPMP transformation in sewage sludge yields AMPA and glyphosate"

13:10 – 13:30 Closing remarks and poster award

REGISTERED POSTERS

1. Lisa Engelbart (Eberhard Karls University Tübingen, Germany)
   "The possible role of aminopolyphosphonates for glyphosate contamination of European rivers"

2. Tomáš Bakalár (Technical University of Košice, Slovakia)
   "Phosphonates in Phosphorus Management: A Comprehensive Overview"

3. Ruoning Guo (Eberhard Karls University Tübingen, Germany)
   "Overestimation of phosphate concentration in molybdenum blue method – The interference of polyphosphonates"

4. Oliver Happel (TZW Karlsruhe, Germany)
   "Phosphonates and active carbon"

5. Matej Šuránek (Matej Bel University, Slovakia)
   "Recent advances and future perspectives on adsorbents in removal of polyphosphonates"

6. Burga Braun (TU Berlin, Germany)
   "Utilisation of industrially relevant phosphonates by laundry isolate Bosea sp."

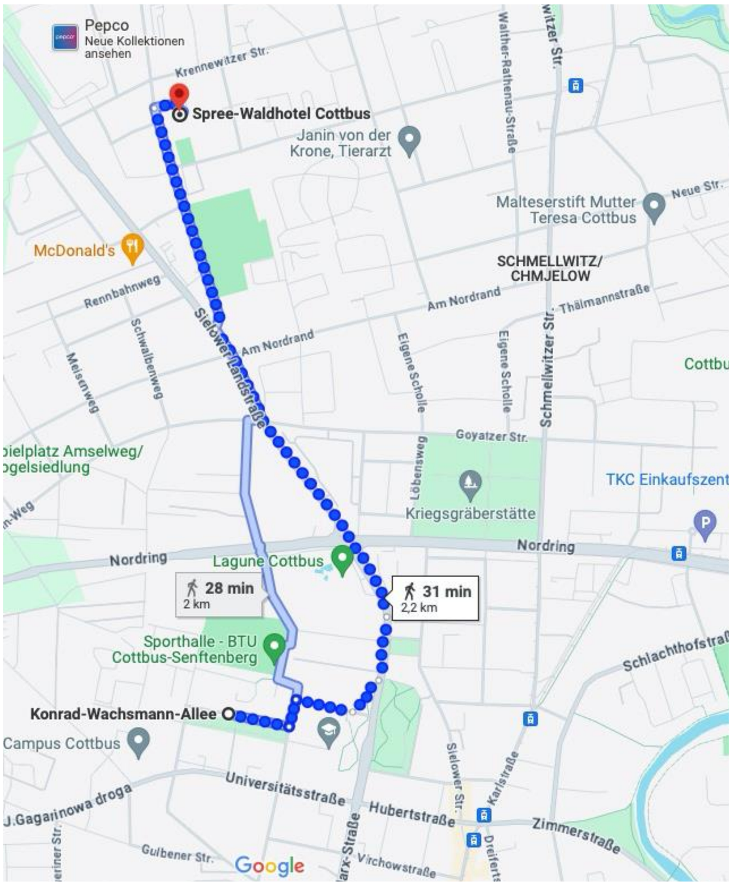
7. Kleanthi Kourtaki (Eberhard Karls University Tübingen, Germany)
   „Effect of organophosphonates as alternative P-sources on the bacterial transformation of glyphosate"

VENUE FOR THE DINNER ON OCTOBER 01

Address

Spree-Waldhotel Cottbus
Drachhausener Straße 70
03044 Cottbus

How to get there by feed?



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ABSTRACT COLLECTION OF ORAL PRESENTATION

Dominic Armbruster (Talk 1 – Lecture)

Overview on the status quo in the analysis of phosphonates

Dominic Armbruster[1,*], Beat Schmutz[1], Oliver Happel[1]

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Phosphonates are frequently applied as softeners in detergents, surface cleaners, care products and industrial processes as well as drinking water production by reverse osmosis (RO). Due to high affinity to mineral surfaces and plurivalent metal cations, phosphonates are effective water-softening agents. They are demanding analytes, possessing no chromophoric groups and low chemical reactivity. Due to their polar functional groups, phosphonates are not volatile, poorly soluble in most organic solvents but well soluble in water. In environmental samples, they are present as nonuniform complexes with plurivalent metal cations. Before quantification takes place, these complexes must be converted to a uniform state, typically the free acids by means of a cation exchange. Earlier analytical methods proved insufficiently sensitive to cover the concentration range of phosphonates in surface waters or were affected by the wastewater matrix [1].

Established separation techniques involve ion pair chromatography (IPC) on reversed phase columns with ion pair reagents [1], capillary zone electrophoresis [2] and anion exchange chromatography [3]. Based on the latter, an analytical toolset involving three IC-MS coupling techniques was developed. Detection by ICP-MS, ESI-Q-TOF and ESI-MS/MS allows the identification, characterization, and quantification of phosphonates.

Phosphorus can be detected by ICP-MS, allowing the indirect quantification of unknown phosphorus species due to the intensity being proportional to the phosphorus content and independent of the chemical phosphorus-bonding.

The coupling to ESI-Q-TOF allows the determination of exact masses and the recording fragment spectra and, thus, the characterization and identification of known as well as unknown substances, such as synthesis-derived contaminants. The combination of ICP-MS- and ESI-TOF-detection has been applied for the characterisation of technical antiscalants [4].

Sensitive and specific quantification of target analytes is achieved by ESI-MS/MS-coupling through the monitoring of substance-specific fragment ions. The implementation of isotope-labelled internal standards allows for the compensation of matrix influences and recovery during extraction and enrichment procedures.

For the trace-quantification of phosphonates from environmental samples (river sediment and suspended matter, activated sludge, wastewater (WW), and surface water) via IC-ESI-MS/MS, specific sample preparation techniques were developed. Solid samples were extracted by alkaline nitrilotriacetic acid solution, liberating over 95 % of the extractable phosphonate. An automated enrichment procedure on the analytical separation column facilitated limits of quantification (LOQs) in the range of 0,1 µg L^{-1} from surface water and RO-permeates. WW samples (LOQ: 1 µg L^{-1}) and extracts from river sediment (LOQ: 0.1 mg kg^{-1}) or activated sludge (LOQ: 1 mg kg^{-1}) were directly analysed. These methods were successfully applied for the determination of phosphonates during a research project on the environmental fate of phosphonates in municipal wastewater and allowed for the balancing of phosphonates in the process of WW treatment and liquid as well as solid matrices of the receiving rivers. Elimination rates of 80 % to 90 % during WW treatment were determined. In treated WW, phosphonates significantly contribute to the residual fraction of dissolved unreactive phosphorus and accumulate in the river sediment [5-7]. A subsequent study involving the screening of river sediments from Lower Saxony confirmed the correlation between the phosphonate content of sediments and the wastewater burden of the corresponding rivers [8].

References

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Sarah A. Bieger (Talk 2)

Critical transformation products of aminopolyphosphonates in different processes

Sarah Bieger[1,*], Lisa Engelbart[1], Markus Kramer[1], Tobias Bader[2], Markus Flörs[2], Anna Röhnelt[3], Katharine Tomsich[3], Erik Niehaves[4], Stefan Haderlein[3] Uwe Karst[4], Carolin Huhn[1]

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[2] Zweckverband Landeswasserversorgung, Laboratory for Operation Control and Research, Germany
[3] Geo- and Environmental Research Center, Department of Geosciences, University of Tübingen, Tübingen, Germany
[4] Institute of Inorganic and Analytical Chemistry, University of Münster, Münster, Germany

Aminopolyphosphonates (APPs), of which diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) is the most sold, are versatile complexing agents widely used in domestic and industrial applications and released into the environment mainly via wastewater. Phototransformation was described to be the main transformation pathway in rivers [1]. Most transformation studies considered only the formation of CO_2, orthophosphate, and aminomethylphosphonic acid (AMPA). Further transformation products were rarely addressed due to analytical limitations.

In our research, we investigated the transformation of DTPMP across environmentally relevant processes, tracing its journey from application in laundry detergents through wastewater treatment plants (WWTPs) to receiving rivers. We identified and compared transformation products formed during the key stages of this entry pathway: in simulated laundry bleach, in sewage sludge from WWTPs, and during advanced oxidation processes like ozonation or UV advanced oxidation. Transformation products identified therein were also investigated in WWTP effluents. For corroboration of selected transformation products, we also studied DTPMP degradation in electrochemical cells. A suspect- and non-target screening approach using techniques such as capillary electrophoresis–mass spectrometry, high performance liquid chromatography–mass spectrometry, and ion chromatography-mass spectrometry/-amperometric detection was applied. This enabled us to detect and (tentatively) identify transformation products, partly aided by in-house synthesized reference standards and nuclear magnetic resonance spectroscopy to characterize structural isomers. Interestingly, DTPMP was found to be readily transformed under most conditions and gave rise to known but also a large number of transformation products not yet described, which varied depending on the process investigated. These included N-oxides, primary and secondary amines, carboxylic acids, methylated compounds and transformation products formylated and acetylated at the nitrogen atoms. Notably, compounds like iminodimethylenephosphonic acid, AMPA and glyphosate were detected. The observed cleavage of C-P- and C-N bonds, both in phosphonate groups and the central ethylenediamine chain, provided insights into the different transformation pathways.

References

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Martin Futterlieb (Talk 3)

Incipient $CaCO_3$-scaling detection for antiscalant free high recovery reverse osmosis operation

Martin Futterlieb[1,*] & Stefan Panglisch[1]

[1] Chair of Mechanical Process Engineering and Water Technology, University Duisburg-Essen, Germany; (*martin.futterlieb@uni-due.de)

Membrane scaling, i.e., the precipitation of sparingly soluble salts onto the membrane, is typically the limiting factor for the recovery of inland membrane desalination, i.e., reverse osmosis (RO) and nanofiltration (NF), plants [1]. The dosage of antiscalants, e.g., phosphonates and polyacrylic acids, is state of the art at to prevent membrane scaling [2,3]. Nevertheless, the application of antiscalants comes with several disadvantages. Discharge of brines containing antiscalants is disputed and subject to environmental concerns [4]. Moreover, in particular phosphorus-based antiscalants may increase the risk for biofouling [5,6]. Additionally, for some feedwater, the dosage of antiscalants may be ineffective [7]. Furthermore, traces of antiscalants can pass the membrane [8,9], which can, in combination with disinfection, lead to the formation of harmful disinfection by-products [10].

A straightforward approach reducing or even omitting the dosage of antiscalants is to detect incipient scaling for timely intervention, e.g., applying a forward flush. In this study, early detection of $CaCO_3$-scaling was investigated for conventional and upcoming discontinuous operation in semi-batch on a pilot and bench scale treating a real water matrix ($SI_{Calcite}$ ~ 0.4). The pilot plant has two 4″ spiral wound elements in series (~16 m^2), and the bench scale has one 2.5″ element (~2.5 m^2).

The concentrate-pH was the most reliable parameter for identifying incipient $CaCO_3$-scaling. A steady concentrate-pH decline was noticed before other parameters indicated $CaCO_3$-scaling, e.g., decreasing permeability, increasing pressure drop and salt passage. In a long-time test, the concentrate-pH was used as a primary control parameter to operate a plant on the edge to membrane scaling. In the case of decreasing concentrate pH, forward-flushing was initiated, effectively countering membrane scaling and enabling high recovery antiscalant-free operation.

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Ramona Riedel (Talk 4)

Photochemical degradation of phosphonates – what we know so far

Ramona Riedel[1,*] and Marion Martiessen[1]

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Due to the slow biodegradability, phosphonates are classified as persistent [1]. Like other chelating agents such as ethylenediaminetetraacetic acid (EDTA), phosphonates are also expected to accumulate over long periods of time in anthropogenically influenced streams and most rivers in industrialised countries [2]. A main degradation pathway assumed for the phosphonates is photolysis, as previously described for ferric iron complexes of EDTA [3]. The initial research into the photochemical degradation of synthetic aminophosphonates was initiated in 1989 [4]. The authors demonstrated the rapid degradation of ferric ethylenediaminetetra(methylenephosphonic acid) (EDTMP), with the release of 75 % of o-PO_4^{3-}. The formation of a photostable transformation product was confirmed and identified as N-methyl-aminomethylene-phosphonic acid. For long time, it was assumed that photochemical degradation of ferric phosphonates was the most significant degradation pathway in aquatic environments. In 2005, more than 15 years later, Lesueur et al. [5] demonstrated the influence of ferric iron at different pH values on the photochemical degradation of common phosphonates, including aminotris(methylenephosphonic acid) (ATMP), EDTMP, hexamethylenediaminetetra(methylene phos-phonic acid) (HDTMP) and diethylenetriamine penta(methylenephosphonic acid) (DTPMP). It was evident that AMPA was the major transformation product, thereby underscoring that the release of aminomethylphosphonate (AMPA) in aquatic environments is not solely attributable to the degradation of glyphosate. Another significant finding was that a low concentration of ferric iron, which is commonly found in aquatic environments at a level of 3.6 μM, was sufficient to facilitate the sunlight-induced transformation of phosphonates in natural waters.

A further decade elapsed before additional scientific findings on the photochemical and photocatalytic degradation of phosphonates were published. This delay was primarily attributable to the lack of suitable analytical methods. In the period between 2017 and 2024, at least 14 additional articles on the photolytic and photocatalytic degradation of HEDP, ATMP, EDTMP, and/or DTPMP have been published. However, only few studies reported the complete degradation pathways and kinetics of parent compounds as well as the release of transformation products and mineralisation products [6-8]. In most of these studies, it was found that a radical driven process was responsible for photochemical degradation of the treated compounds. Only recently, Mark et al. [9] showed that direct photodegradation of ATMP can take place at pH values higher than 10. Nevertheless, the relevance of this pH range in relation to aquatic ecosystems is somewhat constrained, given that such a pH range is not anticipated in the aquatic environment.

All photochemical studies have in common that they identified the major transformation products. Wang et al. [10], Pan et al. [11] and Marks et al. [9] confirmed independent the release of IDMP and AMPA of ATMP. Despite, Kuhn et al. [6-8] showed that beside AMPA, also iminodi(methylenephosphonic acid) (IDMP) and ethyl-amino(bismethylphosphonic acid) (EABMP), and dimethylamino(methylenephosphonic acid) (DAMP) are common transformation products of EDTMP, HDTMP and DTPMP. The objective of photochemical degradation studies is to simulate potential degradation processes that predominantly occur in aquatic environments. In most cases, most experiments on phosphonates were conducted with artificial light sources, which do not fully reflect the spectrum of natural sunlight. For that reason, the degradation pattern and kinetics might be different between artificial UV treatment and natural sunlight treatment. To date, only one study has investigated and compared the degradation pathway and kinetics of DTPMP treated with artificial irradiation and sunlight [12]. It has been demonstrated that the phosphonate DTPMP is also susceptible to degradation in sunlight, resulting in release IDMP, AMPA and EABMP as major transformation products.

In conclusion, the results all photochemical studies in the past four decades have demonstrated that phosphonates are susceptible to photochemical degradation, regardless of whether metal ions are present. The formation of a range of transformation products including AMPA and at least IDMP has been evidenced and are also to be expected in the aquatic environment. The degradation pathway investigated with artificial irradiation is transferable to natural sunlight irradiation. Therefore, it may be reasonably assumed that photochemical degradation of synthetic phosphonates in the aquatic environment will also occur.

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Julia Schowarte (Talk 5)

Photocatalytic degradation of EDTMP by nano-sized Au/TiO_2 nano particles modified with sodium, yttrium and potassium

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Ethylenediaminetetra(methylenephosphonic acid) (EDTMP) is an important anti-scaling and bleach stabilising additive in detergents [1]. In general, phosphonates are often applied as dispersing agents in paper and textile industry stabilizing peroxide bleaching baths [2]. They are easy to formulate and provide noticeable benefits to the user even at very low application concentrations. Along with steadily increasing consumption it is not very surprising that their release into the aquatic environment has also increased [3,4].

Photochemical degradation has been proposed as advanced oxidation process to easily break down phosphonates in process waters and wastewaters. With regard to EDTMP, the complete degradation pathway via ultra-violet (UV) irradiation has been recently reported [5]. Photocatalytic treatments were also recently proposed to further enhance the degradation of persistent substances such as glyphosate [6]. Only few studies, however, report the use of photocatalysts for the degradation of other phosphonates and therefore only little is known on their potential to further enhance their degradation. Thus, the objective of the presented study was to investigate the influence of nanoparticles (NP) based on the TiO_2 benchmark P25 with gold (Au) doped either with sodium (Na), potassium (K) or yttrium (Y). To ascertain the optimal ratio of cations on the NP carrier material (TiO_2/Au) for photocatalytic degradation, all NPs were doped with 2 %, 5 %, and 10 % of the cation, respectively.

TiO_2 benchmark P25 was used in a facile synthesis, consisting of metal doping (wet impregnation, [7]) and Au-doping through direct anion exchange [8]. The synthesized photocatalysts were characterized via TEM, XRF, XRD, UV-Vis DRS (band gap estimation) and N_2-physisorption. In the initial pre-screening stage, the impact of the three pH values (3, 7 and 10) was evaluated during the photocatalytic treatment of EDTMP. The most effective EDTMP degradation based on o-PO_4^{3-} release was observed at pH 7 and 10 for NP doped with either K or Y. For further investigation, it was decided to run all experiments at pH 7, as this is closer to the common pH values expected in wastewater treatment. The results of LC/MS analysis showed that the NPs doped with 5 % Y (TiO_2/Au/5Y) resulted in the fastest degradation kinetics of EDTMP and highest release of o-PO_4^{3-}. EDTMP was completely degraded within 60 minutes, 4 times faster than photochemical treatment of unadulterated EDTMP. The release of major transformation products indicated an enhanced effect on the release of ethylamino(bismethylphosphonic acid) (EABMP), iminodi(methylenephosphonic acid) (IDMP), and aminomethylphosphonate (AMPA) by NP doped with 10 % K followed by 5 % Y. Scavenger experiments were conducted to determine the domination degradation mechanism based of reactive oxygen species (ROS). It was found that hydroxyl radicals and electron holes (h^+) at the surface of the NP catalyst are mainly responsible for the enhanced photocatalytic degradation of EDTMP.

The study demonstrates that the catalytic efficiency of TiO_2 nanocomposites is significantly influenced by the choice of dopants, which affect particle size, band gap, and photocatalytic activity. Yttrium at low concentrations (i.e., 5 wt.% Y) doping emerged as particularly effective, enhancing both the visible light absorption and electron-hole separation, leading to superior photocatalytic performance in the degradation of EDTMP. The Au content also plays a crucial role in enhancing the photocatalytic efficiency. However, the combination of Au and Na doping was found to be less effective for this photocatalysis in aqueous media, potentially due to larger particle sizes and insufficient dopant contents. In conclusion, the findings emphasise the necessity of optimising both the selection of dopants and the design of catalysts to enhance photocatalytic applications.

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Anna M. Röhnelt (Talk 6)

DTPMP oxidation by MnO_2 leads to glyphosate as a minor transformation product

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Recent research revealed municipal wastewaters as previously overlooked source of the widely used broad-spectrum herbicide glyphosate in European surface waters [1,2]. As potential precursor compounds, aminopolyphosphonate (APPs) chelating agents have been proposed [2]. Although glyphosate and APPs are structurally related, dedicated studies on the formation of glyphosate during the transformation of APPs under environmentally relevant conditions are missing.

Our laboratory batch study shows for the first time that glyphosate is formed during manganese-driven oxidation of diethylenetriamine penta(methylenephosphonate) (DTPMP), the commercially most relevant APP. Glyphosate formation was observed at pH 6 (i) in the presence of MnO_2 (with and without dissolved O_2) as well as (ii) in the presence of Mn^{2+} and O_2. Maximum glyphosate yields varied with reaction conditions and ranged from 0.06 to 0.16 mol-%. Given the ubiquitous presence of manganese both in natural settings and wastewater systems [3,4], the investigated transformation processes likely contribute to glyphosate formation from DTPMP in the environment. Our findings offer a new perspective on the sources of glyphosate in the environment and lay the foundation for further detailed investigations of manganese-driven oxidation of APPs in environmental and technical systems.

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Vojtěch Kubíček (Talk 7)

Metal complexes of aminophosphonates in solution - stability constants and speciation

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Polyphosphonates are important class of compounds used in large quantities in industry and in daily life and, thus, they are released to the environment and could enter wastewater, river water and body liquids of various organisms. Polyphosphonates are strong complexing agents – ligands – and, thus, they effectively bind metal ions present in any aqueous solution. Formation of complexes changes charge and polarity of the species and, therefore, it must be carefully considered when evaluating environmental and in vivo behaviour of polyphosphonates.

Formation of complexes and abundance of various species in the solutions reflect protonation constants of ligands and stability constants of their complexes. The data published in the literature are incomplete and often inconsistent, because corresponding measurements were performed under various conditions. Thus, we have determined a large set of protonation and stability constants by combination of potentiometry and spectral techniques. We have included industrial polyphosphonates – HEDP, ATMP, ATMP-*N*-oxide, EDTMP, DTPMP, HMDTMP, BHMT and HEBMP – and studied their complexes with divalent transition metals Cu(II), Zn(II), Ni(II), Co(II), alkaline earth metals Ca(II), Mg(II), alkali metals Na(I), K(I) and trivalent Fe(III).

The complexes of divalent and trivalent metals are formed along a broad pH range, whereas alkaline metal complexes are formed mostly only in the strongly alkaline solution. Data treatment and evaluation of results was highly challenging due to the high number of species present in solutions. The polyphosphonate ligands form typically complexes with 1:1, 1:2 and 2:1 metal-to-ligands ratio and all complexes are present as a mixture of species in various protonation degree in which protons are bound to non-coordinated amino groups or phosphonate oxygen atoms. In addition, mixed hydroxido complexes are often formed in alkaline solutions.

The results were used to simulate specie's distribution of the studied polyphosphonates in model test media, water, and blood. Three groups of metals could be identified considering the extent of metal scavenging:

1) Transition metals Fe, Cu, Zn, Co. These transition metals form strong complexes with all studied ligands. Thus, the complexes are formed quantitatively in the simulated pH region and the extent of scavenging is only function of ligand concentration. As far as ligand concentration exceeds the metal concentration, the metal is bound quantitatively. All these metal ions are present in media in low concentrations, thus, only at low ligand concentration abundance of the complexes is higher or comparable to those of Ca and Mg complexes. The highest stabilities were found for Fe and Cu. Thus, Fe and Cu complexes are often the most abundant species at low ligand concentrations. The order of conditional stabilities and scavenging extent of Fe and Cu differs for each ligand as it is function of ligand geometry.

2) Alkaline earth metals Ca and Mg. Alkaline earth metals form complexes of intermediate stability. Thus, their abundance and extent of metal scavenging changes from ligand to ligand and from media to media. Abundances of these complexes reflect differences in the complexing abilities

of individual ligands. Despite that complexes are formed in high quantities in all the media due to the high concentrations of alkaline earth metal ions, which typically exceed ligand concentration. Thus, Ca and Mg complexes are typical ligand-containing species being present at the high phosphonate concentration.

3) Alkaline metals Na, K. Alkaline earth metals form weak complexes. All studied ligands except EDTMP form the complexes only in the strongly alkaline solution and, thus, no complexation was observed under the simulated conditions. The number of donor atoms and their geometry results in the increased stability of EDTMP complexes with alkaline earth metal ions. However, the reasonable extent of Na and K scavenging could be observed only at high EDTMP concentrations (> 1 mM).

Graciela Gonzalez-Gil (Talk 8)

Antiscalant Secrets: Unravelling their impact on microbial growth in seawater

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Water desalination removes salts and impurities from seawater, making it suitable for drinking and industrial purposes. Reverse osmosis (RO), a widely used membrane-based desalination technology, filters water by allowing it to pass through the membrane while rejecting salts and other solutes. Although RO is a well-established process, it faces significant challenges, particularly membrane fouling. Fouling reduces both the quality and flow of the treated water (permeate), which in turn requires higher operating pressures, increases energy consumption, and raises overall costs [1,2].

During seawater desalination, sparingly soluble salts can accumulate and exceed their solubility limits. This leads to the formation of scale on the RO membrane, causing blockages and reducing the membrane's performance [3]. To mitigate scale formation, antiscalants are typically added to the seawater before it enters the RO system [4]. However, these chemicals can serve as sources of phosphorus or carbon, promoting microbial growth and leading to membrane biofouling issues [5].

Selecting a proper antiscalant is a complex task because there are various antiscalants in the market, combined with the lack of information regarding to what extent those antiscalants promote bacterial growth. Previous tests assessing the potential of antiscalants to promote bacterial growth were conducted in drinking water or seawater inoculated with model bacterial species [6,7]. Unfortunately, such conditions do not accurately represent the diverse bacterial communities and conditions found in natural seawater. To reflect better on the conditions of desalination systems, we recently developed a new sensitive test method to determine the bacterial growth potential of antiscalants in natural seawater applying the autochthonous bacterial population as inoculum [8].

We researched a set of chemically diverse antiscalants as applied in desalination systems to determine their impact on bacterial growth in natural seawater. The antiscalants ranged from phosphonates, polymers, and blends. Results show that our approach in combination with nuclear magnetic resonance (NMR) characterization of antiscalants allows an accurate determination of antiscalants' bacterial growth potential under relevant conditions. This work significantly contributes to our understanding of how antiscalants, based on their chemical composition, influence biological responses. Moreover, our research has potential to address the challenges faced by the industry in choosing the most effective antiscalants, thereby contributing to the enhanced efficiency of seawater desalination.

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Gerd Braun (Talk 9)

Considerations for the selection and dosing of inhibitors for $CaCO_3$-scaling in reverse osmosis and nanofiltration plants

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Since phosphonates are often used as antiscalants (AS) to prevent membrane scaling and are discharged into the environment with the concentrate, determining the minimum required dosage is crucial. The formation of $CaCO_3$ scale on reverse osmosis (RO) and nanofiltration (NF) membrane surfaces involves complex phenomena, including both crystallization and transport mechanisms. Crystallization becomes feasible when the solution is supersaturated, as indicated by the Langelier Saturation Index (LSI) of the water. The extent of the membrane scaling is primarily determined by the kinetics of precipitation, which must be carefully considered.

Scale formation in membrane systems results from a combination of surface crystallization and bulk crystallization, both of which are influenced by membrane properties and process conditions [1-6]. The induction time, or the time required for nucleation crystals to form is crucial for scale formation on RO membranes. To assess the risk of scaling, the induction time must be compared with the residence time of the water in the membrane modules. The typical average residence time of the feed water, or the concentrate, in the membrane modules is around 1 to 2 minutes. However, due to the presence of the feed-spacers, there are dead zones that locally increase the residence time significantly and also elevate the local supersaturation.

The addition of AS disrupts one or more mechanisms of the scaling process. Generally, AS do not completely eliminate the scaling tendency but rather delay the onset of crystallization (nucleation phase), inhibit crystal growth (growth phase) [7], or disperse the precipitates and disrupt the crystal lattice.

The effectiveness of an AS is often assessed through laboratory tests such as the NACE Standard Test Method 03-74 for calcium carbonate and calcium sulphate [8, 9]. In these tests, the AS is added to the sample, which is then allowed to react for a defined period before scale settling. The concentration of Ca ions in the solution is used to evaluate the efficiency of the inhibitor.

While these test methods are advantageous due to their ease of application, they neglect interactions with membranes under real operating conditions: The results can be significantly influenced by the relatively long reaction and settling times, during which crystal morphologies may develop that differ from those in actual RO or NF plants. Consequently, these test methods provide only limited insights into membrane blocking under practical conditions.

To address this issue, a membrane-based method was developed and applied to investigate the performance of AS in preventing calcium carbonate scale. In addition to the membrane-based method, a separate method was tested and validated for determining the induction time in beaker experiments, serving as a measure of AS effectiveness. The results of these studies are presented for both phosphorus-containing and phosphorus-free AS, highlighting the impact of dosage on effectiveness. Additionally, the morphology of the scaling layer and the risk associated with overdosing are discussed in detail.

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Stephan Liebsch (Talk 10)

The benefits of phosphonates for everyone - property profile and applications of this substance class

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Since the early 1980s, various organic phosphonic acids have conquered and permanently expanded their place in many industrial applications due to their complex and unbeatable property profile. It is widely known that phosphonates are frequently used in detergents and cleaning agents as complexing agents, incrustation inhibitors and dispersing additives [1]. Of particular importance are diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) and hydroxyethylidene(diphosphonic acid) (HEDP) and, to a lesser extent, aminotris(methylenephosphonic acid) (ATMP) and its N-oxide.

The above-mentioned substances and other important industrial phosphonates, such as ethylenediaminetetra(methylenephosphonic acid) (EDTMP), hexamethylenediaminetetra(methylene-phosphonic acid) (HMDTMP) hydroxyethylaminobis(methylenephosphonic acid) (HEBMP) or 2-phos-phonobutane-1,2,4-tricarboxylic acid (PBTC), also play an important role in predominantly aqueous applications in many other industrial sectors by preventing or minimizing undesirable side effects caused by substances contained in the water. For many forms of industrial water treatment and drinking water production (e.g. conditioning of cooling circuits, water treatment by reverse osmosis), phosphonates are an indispensable component of formulations, as they inhibit the crystallization and precipitation of poorly soluble alkaline earth salts in highly substoichiometric application concen-trations of a few ppm, thus ensuring excellent heat transfer at heat exchangers and long process stability [2,3].

In the production of textiles, phosphonates are almost indispensable for the processing of raw cotton to remove interfering alkaline earth ions and as a complexing stabilizer in alkaline hydrogen peroxide bleaching [4]. The same applies to the production of pulp and paper in the pulping of wood to obtain cellulose and in its bleaching [5,6]. Different phosphonates are also often used to prevent incrustations such as $CaCO_3$, $CaSO_4$ and $BaSO_4$ in technical systems for oil and gas production [7]. The specific product selection depends on the temperatures and pressures prevailing in the application area as well as the saline conditions [8]. Phosphonates also perform similar tasks in the use of geothermal energy [9].

In addition to their technical applications, bisphosphonates such as HEDP have also proven their usefulness in pharmaceutical applications [10]. Special forms of EDTMP are used, for example, for the palliative treatment of osteosarcoma [11].

It becomes evident that phosphonates (often unrecognized by the user) make a decisive contribution to improve the efficiency of processes in many industrial and consumer-related areas. Due to the complex property profile of phosphonates, their substitution is very difficult and would require in the best case the use of several other additives, often in much higher quantities, in order to achieve a similar performance of the corresponding formulations.

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Werner Nader (Talk 11)

Phosphonic acid in organic food and feed – residue, contaminant or natural metabolite?

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Analysis of 30,793 samples of organic food and feed since 2013 by Eurofins pesticide laboratories in Germany revealed that 27 % contained phosphonic acid in concentrations above 0.01 mg kg^{-1}. Particularly legumes and tree nuts are highly affected, e.g. 50.7 %, 68.6 % and 84.3 % of all organic lentil, peanut and almond samples, respectively. This causes serious challenges for the production and trade with products from ecological agriculture, as the sodium and potassium salts of phosphonic acid and its ester fosetyl are listed as fungicides in the EU MRL regulation 396/2005. Their use in organic agriculture is not permitted and even traces are considered by control bodies as potential violations of EU organic regulation 2018/848. Even more troublesome are such traces for the baby food industry, as EU legislation (2016/127) defines a default maximum level of 0.01 mg kg^{-1}for most pesticides. We doubt that agricultural applications of phosphonate products can be the only explanation for the frequent occurrence of phosphonic acid in organic food and feed [1,2]. New evidence from basic research reveals that phosphonic acid occurs ubiquitously in the environment and is produced naturally by microorganisms by reduction of phosphoric acid, which was until recently considered impossible due to the high redox potential of -0.69 V. Further evidence reveals that phosphonic acid can be a by-product during the degradation of organophosphonates, which can be of natural or anthropogenic origin. Plants accumulate inorganic phosphonate, as they assimilate it like as phosphate, but cannot metabolize it. Phosphonic acid is no real fungicide and has at most fungistatic efficacy. Instead, it activates the natural defence system of the plants against fungus infections. Accordingly, the ban to use phosphonic acid in organic agriculture can be questioned. Also, for infant nutrition the compound is not a threat due to its low toxicity.

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Marion Martienssen (Talk 12)

Effect of iron and aluminium flocculants on the adsorption of phosphonates to activated sludge

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In this study three different aminophosphonates, namely aminotri(methylenephosphonic acid) (ATMP), ethylenediaminetetra(methylenephosphonic acid) (EDTMP) and diethylenetriaminepenta(methylene-phosphonic acid) (DTPMP) were studied regarding to its capability to adsorb to the activated sludge during the sewage treatment process.

Due to its efficient metal complexing properties, aminophosphonates have a wide range of industrial and household applications. In household applications they are frequently used as a sequestrant in toilet cleaning and laundry products or in dishwasher detergents. As a result, increasing concentrations have been measured in the influents of German and Swiss WWTPs [1] as a part of dissolved and particulate organic phosphorus. Due to its structure and the high P/C ratio, it is not to be expected that they are biodegraded in sewage treatment plants [2]. However, several studies found a significant elimination between 40 % and > 90 % due to sludge adsorption [3]. The high discrepancies between different measurements may be caused by differences in the treatment process. Therefore, we studied the effect of different iron and aluminium contents to the adsorption of phosphonates to the activated sludge. Our results demonstrate that the adsorption of the three aminophosphonates studied was strongly correlated with the Fe^{3+} content of the sludge. The maximum phosphonate loadings were 5.94 mmol g^{-1} Fe^{3+} for ATMP, 4.94 mmol g^{-1} Fe^{3+} for EDTMP and 4.74 mmol g^{-1} Fe^{3+} for DTPMP. Activated sludge with low Fe^{3+} contents did not adsorb significant amounts of any of the phosphonates. The adsorption of aminophosphonates on sludge containing iron and aluminium ions was comparable to samples containing Fe^{3+} only. Apparently, aluminium salts had no significant effect on adsorption.

One of the main challenges in calculating the adsorption of phosphonates to metal flocculants was the chelating effect of the aminophosphonates to the metals. A portion of the adsorbent itself (mainly $Fe(OH)_3$ flocs) became more and more dissolved depending on the concentration of the aminophosphonates due to the complexing activity. As a result, the adsorption capacity of the activated sludge is reduced with increasing phosphonate concentrations. Taking this into account, the adsorption of EDTMP and ATMP could be described by the Langmuir model up to a maximum concentration of about 1.0 mmol L^{-1}. With DTPMP, the Fe^{3+} adsorbent was significantly disturbed at concentration above 0.3 mmol L^{-1}.

In summary, we conclude that three aminophosphonates commonly used in domestic applications can be efficiently adsorbed to activated sludge when iron salts are used for chemical phosphorus removal. Aluminium salts are much less efficient, and in treatment plants without chemical phosphorus removal, we assume that only a very low level of phosphonate removal is achieved.

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Ramona Riedel (Talk 13, Lecture)

Overview on enzymatic mechanisms to break down phosphonates

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In order to gain a deeper insight into the fate of phosphonates in the environment, it is essential to gain an understanding of the mechanisms and pathways involved in the biodegradation of phosphonates. In recent years, the biodegradability of glyphosate (GS) has been investigated in detail and was demonstrated for a range of bacterial strains originating from diverse sources, including activated sludge [1], lakes [2], soil [3], and sediments [4]. In contrast to GS, studies on the biodegradation of other commercially available phosphonates such as aminotris(methylenephosphonic acid) (ATMP), ethylene-diaminetetra(methylenephosphonic acid) (EDTMP), hexamethylenediaminetetra(methylene phos-phonic acid) (HDTMP) and diethylenetriamine penta(methylenephosphonic acid) (DTPMP) and others have long been difficult due to the lack of adequate detection methods and insufficient test conditions [5]. Therefore, not much is known about potential biodegradation of such industrially relevant phosphonates.

In recent years, a significant number of studies have been conducted to investigate the enzymatic mechanism of how the C-P bond of phosphonates is cleaved, particularly in the absence of an amino group. It has been demonstrated that the induction of phosphonate-cleaving enzymes is dependent on extracellular inorganic orthophosphate (P_i) uptake and/or P_i starvation in a number of cases (i.e., direct control by the PhoR/PhoB two-component system). It can be surmised, therefore, that biodegradation of synthetic phosphonates like ATMP, EDTMP, HDTMP and DTPMP is contingent upon the presence of a specific condition that induces the Pho regulon.

At least three distinct enzymatic cleavage mechanisms for phosphonates have been recently documented, including: (i) the hydrolytic cleavage catalysed by the enzymes phosphonoacetate hydrolase (PhnA), phosphonopyruvate hydrolase (PalH) and phosphonoacetaldehyde hydrolase (PhnX). (ii) the oxidative cleavage mediated by enzymes designated as phosphonatase (PhnY and PhnZ); and (iii) the radical-mediated cleavage conducted by the multienzyme complex designated as C-P lyase (PhnCDEFGHIJKLMNOP) [6]. Both the hydrolytic and oxidative pathways exhibit a narrow substrate-specific spectrum, which is particularly prevalent for organophosphonates such as 2-aminoethyl-phosphonate (2-AEP). Independent of the narrow substrate spectrum, the hydrolytic pathway is widespread in the environment and is mainly observed in marine ecosystems [7]. In the hydrolytic pathway mediated by PhnX requires an initial enzymatic step before final C-P cleavage by PhnX. This specific substrate activation is commonly mediated by PhnW yielding phosphonoacetaldehyde (PnAA). Recently, the three putative FAD-dependent oxidoreductases phosphonate breakdown factors (Pbf) PbfB, PbfC and PbfD [8] have been identified and suggested to replace *phnW*. This demonstrates that the biochemical possibilities were evidently comprehended in their fundamental aspects, yet not fully elucidated.

In contrast, the C-P lyase catabolism exhibits a broad substrate specificity, enabling bacteria to degrade phosphonates also other than GS. This multi-enzyme complex is encoded by the *phnCDEFGHIJKLMNOP* operon, of which the PhnGHIJKLM component is essential for its cleavage activity. The PhnI is responsible for the activation of the phosphonate. The catalytic activity of PhnI is contingent upon the multi-subunit protein complex (PhnGHIJK), which is responsible for the generation of 5'-triphosphoribosyl-1'-phosphonate [9]. The final C-P cleavage is then mediated by PhnJ, resulting in the formation of 5-phospho-d-ribosyl-α-1-diphosphate (PRPP) and either sarcosine, glyoxylate or methane for GS, amino(methylphosphonic acid) (AMPA) or methylphosphonate (MP), respectively.

The mechanism of the C-P lyase was first discovered in *Escherichia coli* designated as tolerance mechanism as the strain cannot use GS as direct P source [10]. However, the direct use of P from industrially relevant phosphonates such as EDTMP via the C-P lyase pathway has been demonstrated and confirmed by genomic and proteomic analyses for strain *Ochrobactrum* sp. BTU1 [11]. And more recently, the degradation of ATMP, EDTMP and IDMP was shown for new strain *Delftia* sp. UMB14 isolated from a laundry biofilm applying the PhnX pathway [12]. In both instances, the microorganisms employed were observed to utilise pre-existing enzymatic degradation pathways to facilitate the degradation of phosphonates. It is evident that the potential for their biodegradation has been hitherto underestimated, as the majority of bacteria appear to possess the requisite enzymatic arsenal for this process via horizontal gene transfer.

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Karsten Meißner (Talk 14)

Phosphonate degradation by laundry isolate *Delftia* sp. UMB14

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Phosphonates such as ethylenediaminetetra (methylenephosphonic acid) (EDTMP) and aminotris (methylenephosphonic acid) (ATMP) are used every day in water treatment processes or in household products. Their consumption is still increasing, regardless of the debates on their environmental impact.

Here, the microbial characterisation and determination of the biodegradation potential of selected industrially relevant phosphonates for the isolate *Delftia* sp. UMB14 (Accession no: PP980724) is reported [1]. The opportunistic strain was isolated from a biofilm that was derived from a conventional washing machine using conventional detergents containing phosphonates. Here, phosphonate degrading isolates were enriched by suspending biofilm samples from different locations of standard washing machines in liquid media spiked with final concentrations of 50 mg L^{-1} HEDP, 100 mg L^{-1} EDTMP or 100 mg L^{-1} DTPMP as sole source of phosphorus [2]. Strain UMB14 was obtained from HEDP enrichment. In antimicrobial susceptibility testing, the strain was only susceptible to sulfonamide, tetracycline, and chloramphenicol. Physiological and biochemical characteristics were determined using the BIOLOG EcoPlate assay. Most importantly, the strain was shown to convert D-malic acid and D-mannitol, as confirmed for strains of *Delftia lacustris* [3], and thus the new isolate could be closely related. Biodegradation tests with different phosphonates showed that the strain preferentially degrades ATMP and EDTMP but does not degrade glyphosate (GS) and amino (methylphosphonic acid) (AMPA). A specific gene amplification confirmed the presence of *phnX* (phosphonoacetaldehyde hydrolase) and the absence of *phnJ* (the gene for the core component of C–P lyase) [4,5]. The presence of PhnCDE is strongly suggested for the strain, as it is common in *Delftia lacustris* species.

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Dirk Benndorf (Talk 15)

Proteome based elucidation of phosphonate biodegradation

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Biodegradation of pollutants such as aminophosphonates can be catalyzed by multiple enzymes. Whereas genome-based analysis shows the genetic potential to degrade organic pollutants, the presence of respective enzymes confirms the usage of the proposed pathways.

Proteomics targets the whole set of cellular proteins and gives a comprehensive overview on the present functions. The experimental workflow of proteomics consists of protein extraction, protein determination, tryptic digestion, nanoHPLC coupled to mass spectrometry and bioinformatic data analysis using the corresponding genome as a database for protein identification. Recently this workflow was applied first to the new isolate *Ochrobactrum* sp. BTU 1 [1]. The strain was capable to degrade the selected aminophosphonates glyphosate (GS), ethylenediaminetetra(methylene-phosphonic acid) (EDTMP), aminomethylphosphonic acid (AMPA), iminodi(methylenephosphonic) (IDMP) and ethylaminobis(methylenephosphonic) acid (EABMP). The strain used all phosphonates served predominately as sole phosphorus source during phosphorus starvation. The highest growth rate was achieved for the smallest phosphonate AMPA, while the largest phosphonate EDTMP and GS were least supportive for growth. The proteomic analysis revealed different levels of key enzyme expression of the C-P lyase pathway for GS and the other aminophosphonates. The workflow, above mentioned, has also been applied to the second isolates, *Ochrobactrum* sp. BTU2, which is also capable to degrade phosphonates. The results are showing different utilization profiles of aminophosphonates between the two strains.

Proteomics of both *Ochrobactrum* sp. BTU 1 and *Ochrobactrum* sp. BTU 2 revealed that the protein composition correlates with the complexity of the phosphonate provided as single P-source. Besides a clear response to phosphate starvation, the presence of different C-P lyases was detected. Further enzymes including oxygenases were differently expressed. Comparative data of the proteomes of both isolates is still ongoing. It is expected that the comparison enables the identification of genes involved in the substrate specifity and degradation pathways of aminophosphonates, respectively. Potential candidates should be confirmed by overexpression or knockout of the corresponding genes.

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Lisa Engelbart (Talk 16)

DTPMP transformation in sewage sludge yields AMPA and glyphosate

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The most important aminopolyphosphonate in terms of sales numbers is of diethylenetriamine penta(methylenephosphonic acid) (DTPMP) [1]. It is present at elevated concentrations of up to 5 mg kg^{-1} in river sediments and 100-250 mg kg^{-1} in wastewater treatment plant (WWTP) influent particle [2]. Although elimination rates of up to 95 % for different phosphonates have been demonstrated, large quantities of these chemicals are constantly released into our waterways. [3]. Aminomethyl phosphonic acid (AMPA) is a major transformation product from aminopolyphosphonates [4-6], and the only one monitored in surface waters due to its formation also from the herbicide glyphosate. In a large meta-study, we demonstrated that AMPA and glyphosate dominantly enter European surface waters via WWTP [7]. In addition, negative elimination rates in WWTPs were observed for AMPA and glyphosate [8,9]. This triggered the hypothesis that both, glyphosate and AMPA, may be transformation products of DTPMP.

We conducted several incubation experiments with DTPMP spiked to fresh sewage sludge but also followed the OECD 302b test on biodegradability. The formation of glyphosate and AMPA in samples spiked with DTPMP was clearly visible in all experiments. Rates of glyphosate and AMPA formation differed between experiments conducted under different conditions, e.g. sludge from summer or winter sampling. Phosphonates are generally considered to be poorly biodegradable, thus we considered abiotic reaction conditions after sodium azide treatment and indeed, similar formation rates were observed, prompting further investigation with metal-based transformation. As a final proof and to exclude possible desorption of glyphosate and AMPA present in the raw sewage sludge by competition with DTPMP for sorption sites, we synthesized $^{13}C_5$-labeled DTPMP. We clearly observed the formation of ^{13}C-labeled glyphosate and AMPA.

In conclusion this study proves the *de novo* formation of glyphosate and AMPA from DTPMP in sewage sludges and can aid explaining surface water contamination.

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ABSTRACT COLLECTION OF POSTER PRESENTATION

Lisa Engelbart (Poster 1)

The possible role of aminopolyphosphonates for glyphosate contamination of European rivers

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Glyphosate is the most widely used herbicide and, together with its main transformation product aminomethylphosphonic acid (AMPA), contaminates surface waters around the globe. Agricultural and urban applications of glyphosate are commonly discussed as sources.

AMPA is also a major transformation product of aminopolyphosphonates, which are widely used as antiscalants and bleach stabilizers, but the relevance of this source is not well understood. We therefore conducted a large meta-analysis of about 100 sites in the USA and Europe with long time series of data going back to 1997.

We show that data from the USA show pulses of glyphosate and AMPA during periods of high river discharge, indicating rainfall-induced mobilization after herbicide application, as expected for a dominant agricultural input.

In contrast, glyphosate and AMPA concentration data from Europe show a distinct seasonal pattern inversely related to river discharge and a high correlation with wastewater markers such as pharmaceuticals, but not with other herbicides. This suggests a dominant input from point sources such as wastewater treatment plants (WWTPs) over decades, which is well supported by their detection in WWTP effluents. Additionally, rather high and constant base mass fluxes of glyphosate and AMPA are observed in Europe. Consequently, we searched for a hidden source of glyphosate that is commonly used in Europe but not in the U.S. Based on the low use of aminopolyphosphonate in detergents in the USA and the similarity of the European concentration patterns of glyphosate and AMPA, we hypothesize that aminopolyphosphonates may acts as an important source of glyphosate in European rivers.

Tomáš Bakalár (Poster 2)

Phosphonates in Phosphorus Management: A Comprehensive Overview

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Phosphonates, a versatile group of organophosphorus compounds, are increasingly used across industries, agriculture, and environmental management due to their unique properties and effectiveness in phosphorus control. Their distinctive chemical properties and ability to control phosphorus levels have made them valuable assets. The chemistry, benefits, risks, and future of phosphonates are examined, focusing on their role in phosphorus management, environmental impact, and the potential benefits and risks associated with their use [1,2].

Phosphorus is vital for life, but its finite supply and environmental impact pose challenges. With their stable C-P bond, phosphonates offer promising solutions for efficient phosphorus use and management [3]. They are resistant to degradation, making them effective chelating agents and scale inhibitors, widely used in industry. In agriculture, phosphonates act as controlled-release fertilizers and plant protection agents, improving phosphorus uptake and reducing environmental leaching. They also serve as corrosion inhibitors in water treatment and detergents [4]. While their stability is beneficial, it raises concerns about environmental persistence. Research focuses on developing biodegradable phosphonates, understanding their ecological impact, and engineering microorganisms for their degradation.

Innovation in phosphonate derivatives aims to enhance their efficacy and reduce toxicity, promoting sustainable agriculture and industry [5]. Phosphonates are crucial in phosphorus management across various sectors, offering benefits such as improved phosphorus utilization, crop protection, and industrial efficiency. However, their environmental persistence necessitates careful management and continued research into biodegradable alternatives and effective remediation techniques. As the demand for sustainable phosphorus management grows, phosphonates will likely remain a key component in achieving this goal.

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Ruoning Guo (Poster 3)

Phosphate quantification by molybdenum blue is impaired by the presence of polyphosphonates (PPs)

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Polyphosphonates (PPs) are organophosphorus compounds widely applied as chelating agents in households & industry and thus are detected in wastewater treatment plants [1,2]. Although classified as stable, PPs are transformed via various processes (e.g., during photolysis [3-5] or at MnO$_2$ [6-8]) with phosphate as a major transformation product. Therefore, PO$_4^{3-}$ was used in multiple studies to prove and quantify PPs transformation. UV/Vis spectroscopy, especially the molybdenum blue (MB) method, is widely applied for phosphate quantification due to its sensitivity and ease of operation [9]. However, unlike the well-documented interference of inorganic ions [10], the influence of PPs remains unexplored, despite their prevalent coexistence in transformation processes.

In this study we investigated the effects of glyphosate and five PPs on the quantification of PO$_4^{3-}$ by MB, namely iminodi(methylene phosphonate) (IDMP), aminotris(methylphosphonic acid) (ATMP), ethylenediaminetetra(methylene phosphonic acid) (EDTMP), diethylenetriaminepenta-(methylene phosphonic acid) (DTPMP), and 1-hydroxyethylidene(1,1-diphosphonic acid) (HEDP). We compared the spectra of single PO$_4^{3-}$ standards and different phosphonate-PO$_4^{3-}$ mixed solutions across the wavelength range of 400 nm to 1100 nm. The spectra of single PO$_4^{3-}$ standards showed two distinct absorbance peaks at 710 nm and 880 nm, commonly used for phosphate quantification. When PPs were present, a new absorbance peak at approximately 760 nm emerged, indicating the formation of a new coloured species. This new absorbance peak was dependent on both phosphate and phos-phonate concentrations. Additionally, the absorbance at 710 nm and 880 nm was also enhanced in the presence of phosphonates, leading to an overestimation of phosphate concentration, especially relevant at 710 nm. Among the phosphonates tested, DTPMP exhibited the most substantial impact (up to 340 % overestimation), whereas glyphosate caused in minimal interference (generally within 20 %). The effects were most significant when phosphonates exceed the equivalent molar amount of PO$_4^{3-}$.

These findings highlight the limitations of the MB method for phosphate quantification in the presence of phosphonates. Therefore, careful validation of the results using complementary analytical methods is necessary to ensure accurate phosphate measurements, especially in PP transformation studies where phosphonates are initially present at significant concentrations.

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Oliver Happel (Poster 4)
Transformation of phosphonates during activated carbon filtration

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Some phosphonates undergo chemical transformation during activated carbon filtration. This recent observation has hitherto not been described in literature. It is commonly assumed that phosphonates are persistent and cannot be retained by sorption on activated carbon due to their ionic nature.

During the recent KonTriSol research project, concentrates of RO membrane filtration plants as well as concentrate treatment procedures were investigated. Depletion of diethylenetriaminepenta-(methylenephosphonic acid) (DTPMP) was observed after a granular activated carbon filtration step applied by a water supplier. Throughout multiple samplings, it was demonstrated that the DTPMP concentration in the filter effluent was strongly reduced, while the orthophosphate concentration simultaneously increased. It was also possible to detect increased levels of iminodi(methylenephosphonic acid) (IDMP) and aminomethylphosphonic acid (AMPA) in the filter effluent.

Comparative measurements in the laboratory showed rapid transformation of the nitrogen-containing phosphonates DTPMP and aminotris(methylphosphonic acid) (ATMP). The tests showed that this was not a biological transformation. Chemical and thermal sterilization of the activated carbon which was used in the waterworks filter had no effect. The reactions were further confirmed with a set of virgin commercial activated carbons (charcoals derived from stone coal, coconut, synthetic polymer, and sugar) and particle sizes, whereby variations in the rate of conversion were found. We are currently testing the correlations with e. g. the particle size, the ash content and the element composition of the activated carbons to explain the different reactivity. For 1-hydroxyethylidene(1,1-diphosphonic acid) (HEDP) and 2-phosphonobutane-1,2,4,-tricarboxylic Acid (PBTC) there were no clear transformations found under the selected test conditions.

These new findings on the reaction of aminopolyphosphonates on activated carbon are surprising and indicate the need for a more refined definition of the term “persistence”. Publications dealing with the subject of "phosphonates and activated carbon" should be critically re-read, as elimination or sorption measurements were often based on total phosphorus measurements due to the lack of single-substance analysis. In technical treatment processes, these findings should also be taken into account, as reactions are to be expected during concentrate treatment or purification steps in wastewater treatment plants involving activated carbon.

Matej Šuránek (Poster 5)

Recent advances and future perspectives on adsorbents in removal of polyphosphonates

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Widely used in various industrial applications such as water treatment, detergents, and corrosion inhibitors, polyphosphonates pose significant environmental challenges, particularly in water bodies, due to their strong chelating ability and resistance to biodegradation. Conventional water treatment methods often fall short in effectively removing these compounds, necessitating the development of more advanced and efficient technologies. Adsorption has emerged as a promising technique for the removal of polyphosphonates, given its high efficiency, versatility, and potential for regeneration [1,2].

Recent advances in adsorbent materials have significantly improved adsorption capacity, selectivity, and reusability in the removal of polyphosphonates. Novel materials, such as modified activated carbons, metal-organic frameworks (MOFs), biochar, and nanocomposites, have demonstrated remarkable performance in capturing polyphosphonates from aqueous solutions. The functionalization of adsorbents with various chemical groups, such as amines, thiols, and carboxylates, has further increased their affinity for polyphosphonates, enabling more efficient removal processes [3,4].

Furthermore, recent studies have focused on optimizing adsorption conditions, such as pH, temperature, and contact time, to maximize the removal efficiency. The integration of adsorption with other treatment processes, such as membrane filtration and advanced oxidation, has also been explored to increase the overall treatment efficiency. However, challenges such as the high cost of advanced adsorbents, potential secondary pollution, and the need for regeneration methods remain areas of concern [4].

The development of cost-effective, environmentally friendly, and easily regenerable adsorbents is crucial for the sustainable removal of polyphosphonates. The integration of machine learning and computational modeling in the design of new adsorbents offers promising future directions. Continued research in this field will be pivotal in addressing the global challenge of polyphosphonate pollution in water systems.

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Burga Braun (Poster 6)

Biodegradation of phosphonates by *Bosea thiooxidans* UMB21

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Phosphonates are organic complexing agents that are widely used in various technical and industrial processes, especially in detergents and cleaning agents to reduce water hardness. This study focused on the utilization of selected phosphonates, namely hydroxyethylidenedi(phosphonic acid) (HEDP), aminotris(methylenephosphonic acid) (ATMP), ethylenediaminetetra(methylenephosphonic acid) (EDTMP) and diethylenetriaminepenta(methylenephosphonic acid) (DTPMP), butylendiamintetra-(methylenephosphonic acid) (BDTMP), hexamethylenediamintetra(methylenephosphonic acid) (HDTMP), dodecanmethylenediamintetra(methylenephosphonic acid) (DDTMP), and methylaminbis-(methylenephosphonic acid) (MADP). For this, phosphonate degrading isolates were enriched by suspending biofilm samples from different locations of standard washing machines in liquid media spiked with final concentrations of 50 mg L^{-1} HEDP, 100 mg L^{-1} EDTMP or 100 mg L^{-1} DTPMP as sole source of phosphorus, respectively. Strain UMB21 (Accession no: PP980723) obtained from the EDTMP enrichment could be assigned to *Bosea thiooxidans* by microbiological and molecular methods.

As *Bosea* is stated to be auxotrophic for glutamate and also requires trace amounts of yeast extract as a growth factor [1,2], the standard biodegradation test for synthetic phosphonates developed by Riedel et al. [3] was not applicable and the minimal medium composition for degradation test was optimized. Here, it could be shown that strain UMB21 grew in the standard biodegradation media [3] by adding glutamate and replacement of yeast by nicotinic acid.

For the biodegradation tests in optimized mineral media, the resulting phosphorous concentration were the following: DTPMP (33.4 mgP L^{-1}), EDTMP (17.5 mgP L^{-1}), ATMP (19.4 mgP L^{-1}), HEDP (18.8 mgP L^{-1}) and KH_2PO_4 (11.4 mgP L^{-1}). BDTMP, HDTMP, DDTMP, MADP and Glyphosate were used with phosphorous concentrations of 20 mgP L^{-1}. Strain UMB21 preferentially degraded DTPMP, EDTPM and ATMP, but did not degrade HEDP. Specific gene amplification confirmed the presence of the core gene *phnJ* for the C–P lyase pathway and the absence of *phnX* (phosphonoacetaldehyde hydrolase). So, strain UMB21 possesses the genetic basis for the formation of the catalytic core enzyme of the C-P lyase pathway PhnJ, involved in C-P bond cleavage.

Antimicrobial susceptibility testing revealed strain UMB 21 as resistant to Lincomycin. The minimal inhibition concentrations (MIC) were as follows: Ampicillin 512 µg mL^{-1}, Doxycycline 0.5-1 µg mL^{-1}, Gentamicin 8-16 µg mL^{-1}, Kanamycin 2-4 µg mL^{-1}, Polymyxin B 64 µg mL^{-1}.

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Kleanthi Kourtaki (Poster 7)

Effect of organophosphonates as alternative P-sources on the bacterial transformation of glyphosate

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Research on glyphosate biotransformation has demonstrated that various bacterial strains have the potential to scavenge phosphorus (P) from glyphosate under P-deficiency conditions [1,2]. However, the ubiquitous abundance of other biogenic as well as of synthetic organophosphonates (OPs) in the environment reduces the chances that bacterial isolates -the main drivers of glyphosate breakdown- will face conditions where glyphosate is the sole P-containing compound [3,4].

The presence of co-existing OPs, which can serve as alternative P-sources, can likely affect the efficiency of glyphosate biotransformation in the environment. In this study, we conducted cultivation experiments in a carbon and nitrogen-rich medium, where glyphosate and an additional OP were simultaneously supplied as P-sources. The bacterial strains *Achromobacter isolitu*s strain Kg 19 (B-3295) and *Ochrobactrum pituitosum* strain GPr1-13 grow efficiently and transform glyphosate as well as the other OPs that were used. Experiments with glyphosate and one additional monophosphonate (aminomethylphosphonate) (AMPA), 2-aminoethylphosphonate (2-AEP), or phenylphosphonate (PPA) showed that glyphosate was the least preferred P-source. The presence of the tested monophosphonates retarded or even completely inhibited glyphosate transformation. Conversely, when a diphosphonate iminodi(methylene phosphonate) (IDMP) or 1-hydroxyethane 1,1-diphosphonic acid (HEDP) was the second P-source, both strains primarily utilized glyphosate and the diphosphonate was either transformed sequentially (IDMP) or remained untouched (HEDP). These results demonstrate that glyphosate biotransformation can be adversely impacted by the presence of OPs with one C–P bond. Therefore, the co-existence of OPs must be considered as a key factor when assessing the bacterial transformation dynamics of glyphosate in environmentally relevant conditions, where OPs such as AMPA are often detected alongside glyphosate.

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