

Photochemical degradation of phosphonates – what we know so far

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Chair Biotechnology of Water Treatment

01st October 2024

Photochemical degradation of ferric EDTMP

Matthijs et al. (1989), Water Res. 23, 845-851.

Measurement of o-PO₄³⁻ release

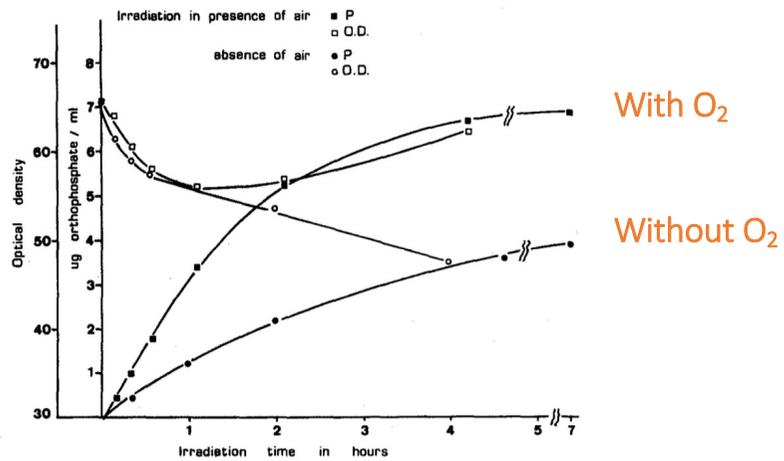


Fig. 4. Orthophosphate production and decrease in optical density of the photolysis of ferric EDTMP at 254 nm.

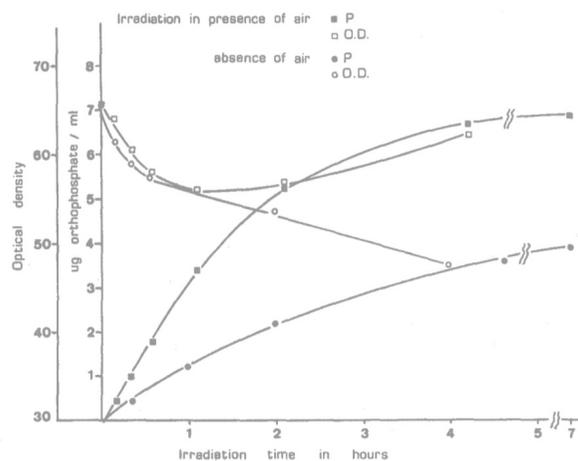
Photochemical degradation of ferric EDTMP

Matthijs et al. (1989), Water Res. 23, 845-851.

Measurement of o-PO_4^{3-} release



Postulated degradation mechanism



With O_2

Without O_2

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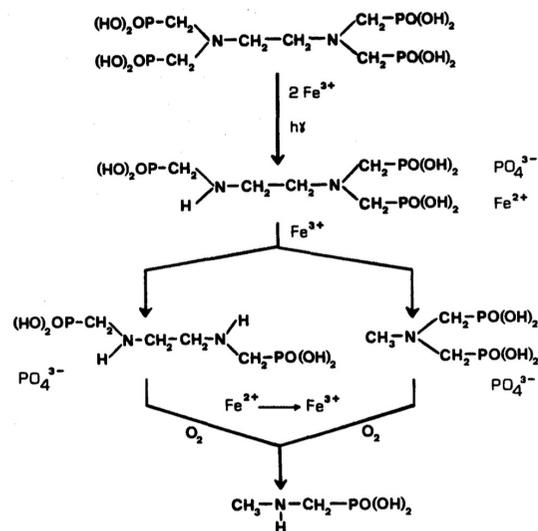


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Prediction environment

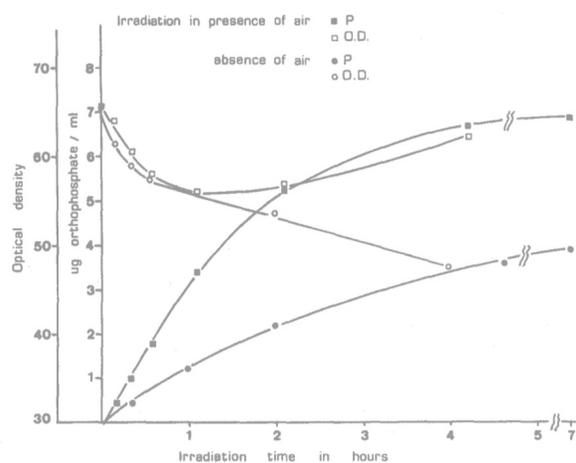


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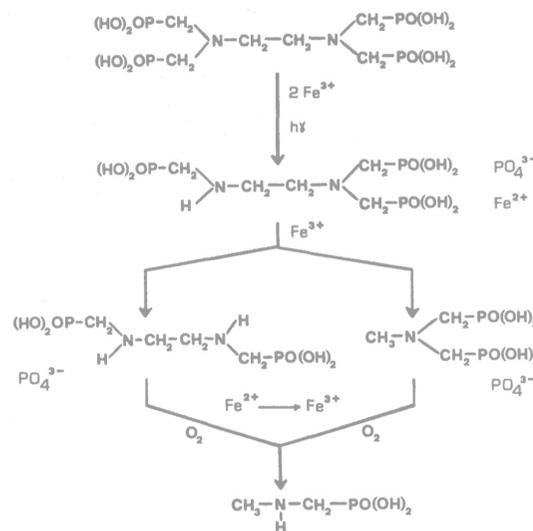


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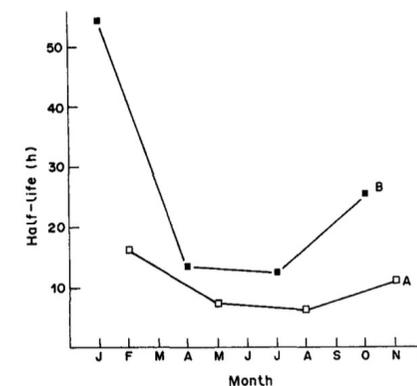
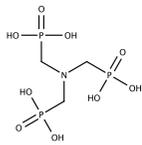


Fig. 7. Half lives for direct photolysis of ferric EDTMP in the top millimetres of a water body as a function of the time of year. A, average midseason, midday sunlight intensities/clear sky/40-50°N. B, average daily sunlight intensities/climatical situation at 50°N.

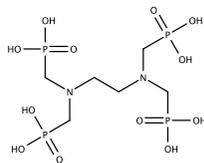
Photodegradation of phosphonates in water

Lesueur et al. (2005), Chemosphere 59, 685-691.

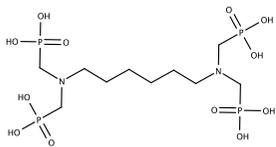
Investigated phosphonates



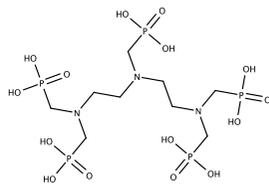
ATMP



EDTMP



HDTMP

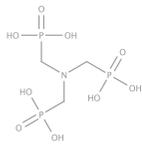


DTPMP

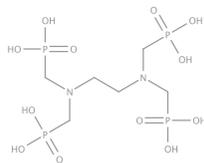
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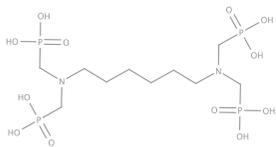
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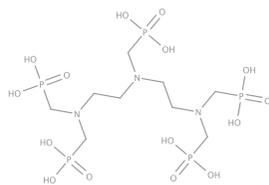
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HDTMP



DTPMP

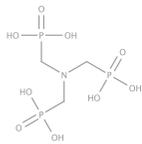
Investigated parameter

- Influence of pH values (3, 7 and 10)
- Influence of complexation with Fe(III)
- Release of $o\text{-PO}_4^{3-}$
- Release of AMPA

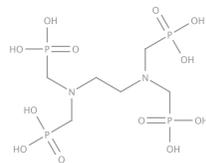
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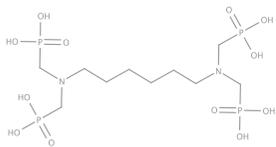
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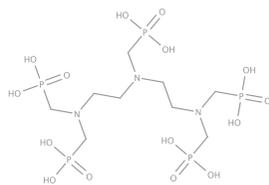
ATMP



EDTMP



HDTMP

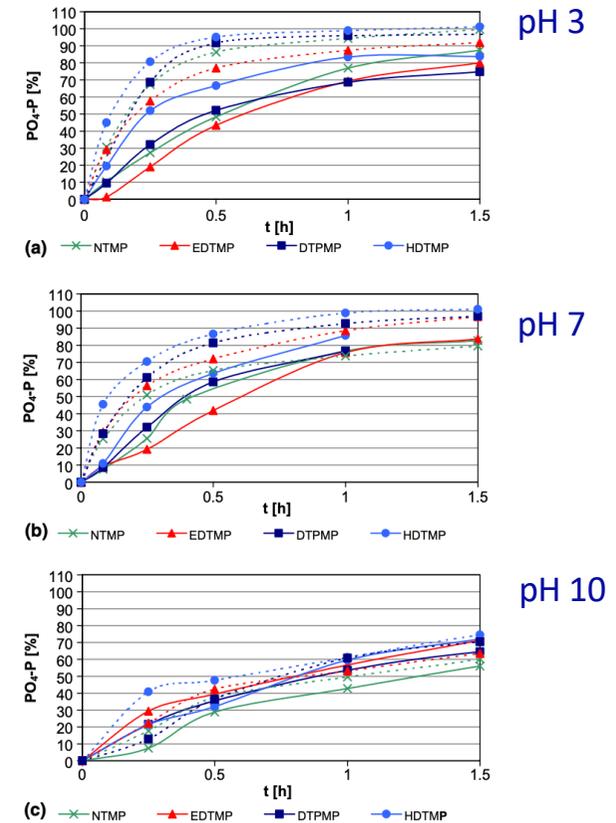


DTPMP

Investigated parameter

- Influence of pH values (3, 7 and 10)
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- Release of AMPA

Dashed line with Fe(III)
Solid line without Fe(III)



Photodegradation of phosphonates in water

Lesueur et al. (2005), Chemosphere 59, 685-691.

Table 3

Half-life times at different pH for the photodegradation (UV) and iron catalysed photodegradation (UV/Fe) of phosphonates

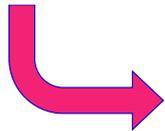
	NTMP		EDTMP		DTPMP		HDTMP	
	UV	UV/Fe	UV	UV/Fe	UV	UV/Fe	UV	UV/Fe
pH 3	30	10	35	12	30	11	15	6
pH 5–6	25	15	36	11	25	11	18	6
pH 10	75	60	50	50	55	45	50	35

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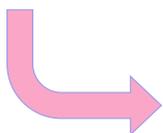
Half-lives based on o-PO_4^{3-} release reliable to predict degradation in aquatic environment?

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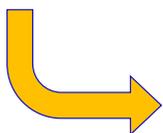
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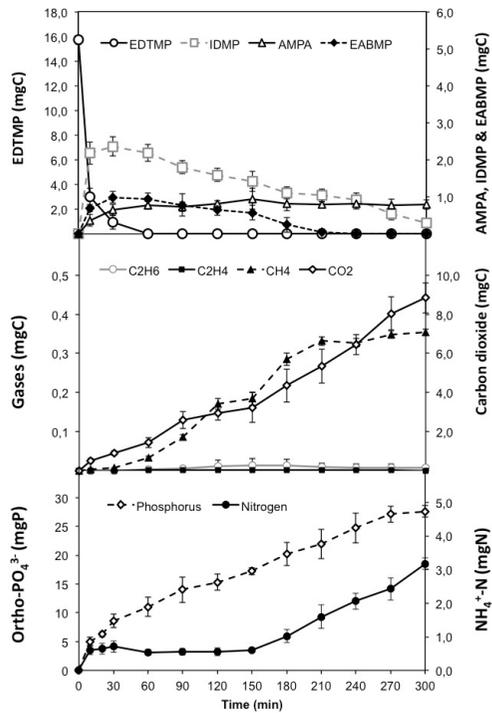
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Release of AMPA of all investigated phosphonates, not only by glyphosate!

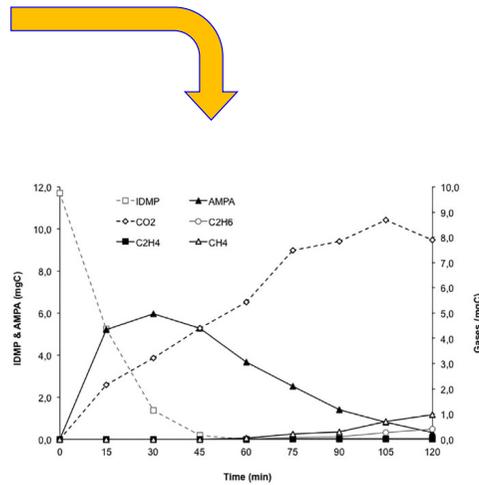
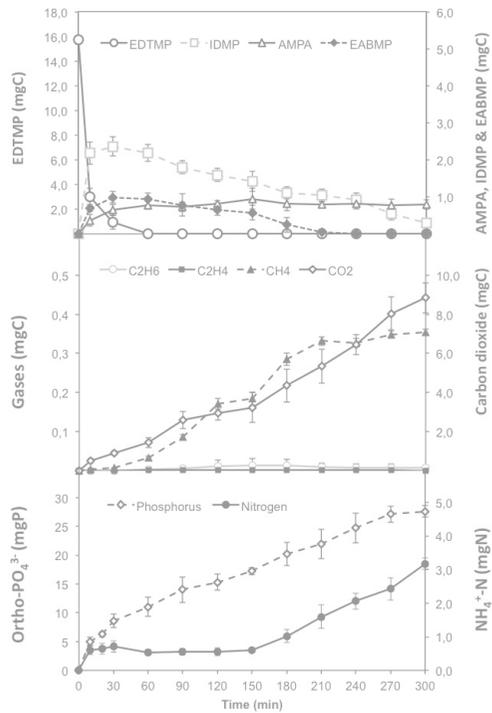
Photodegradation of uncomplexed EDTMP

Kuhn et al. (2017), Clean - Soil Air Water 45, 1500774.



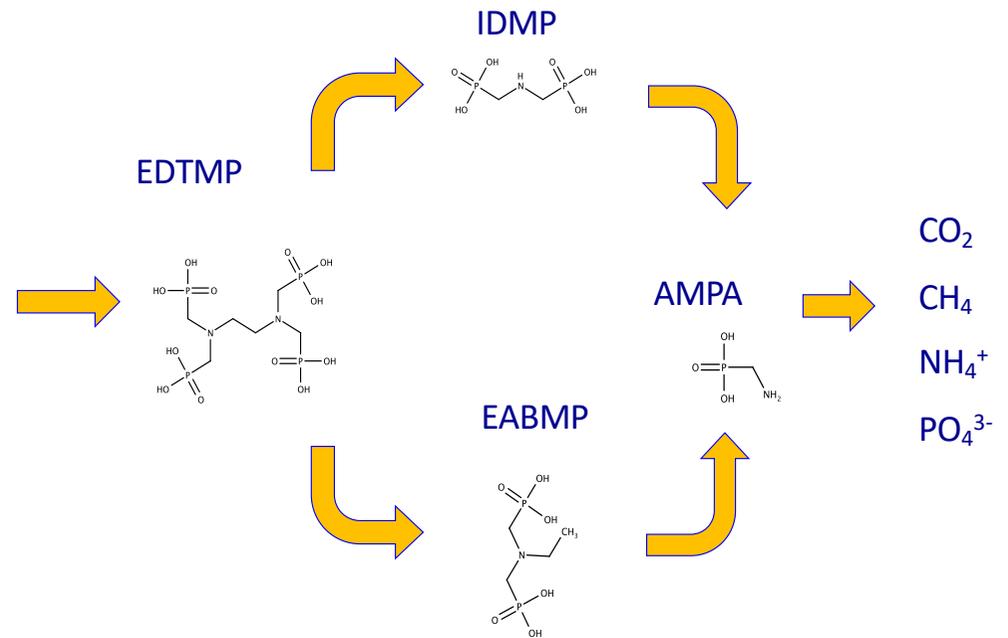
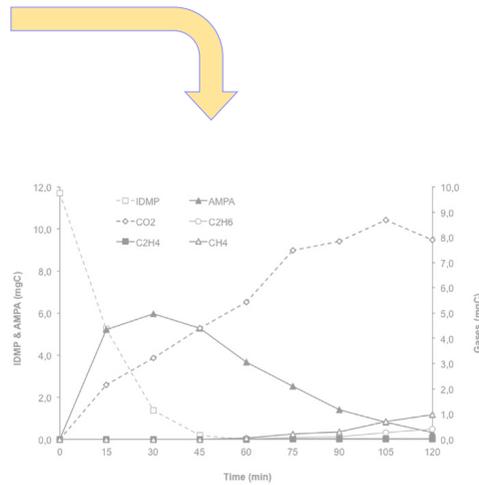
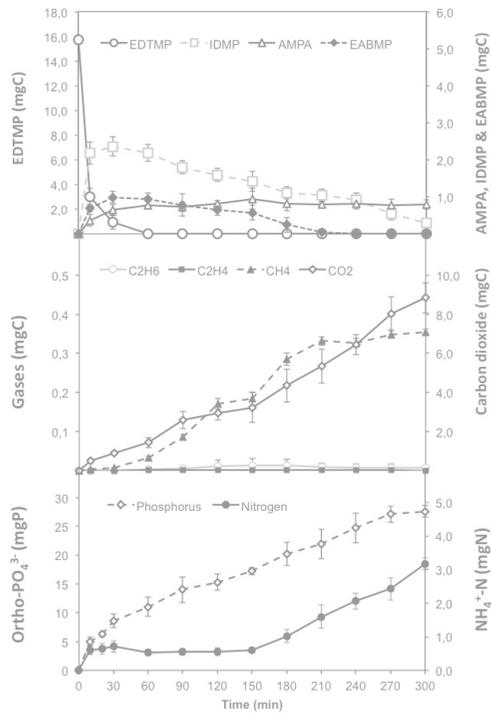
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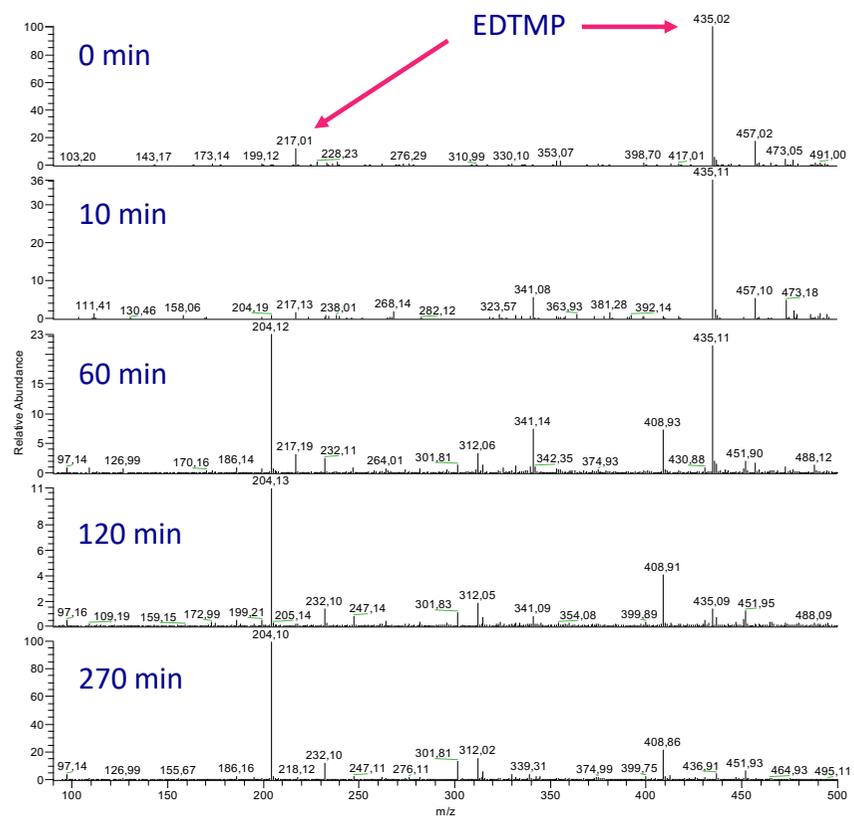
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Initially postulated but...

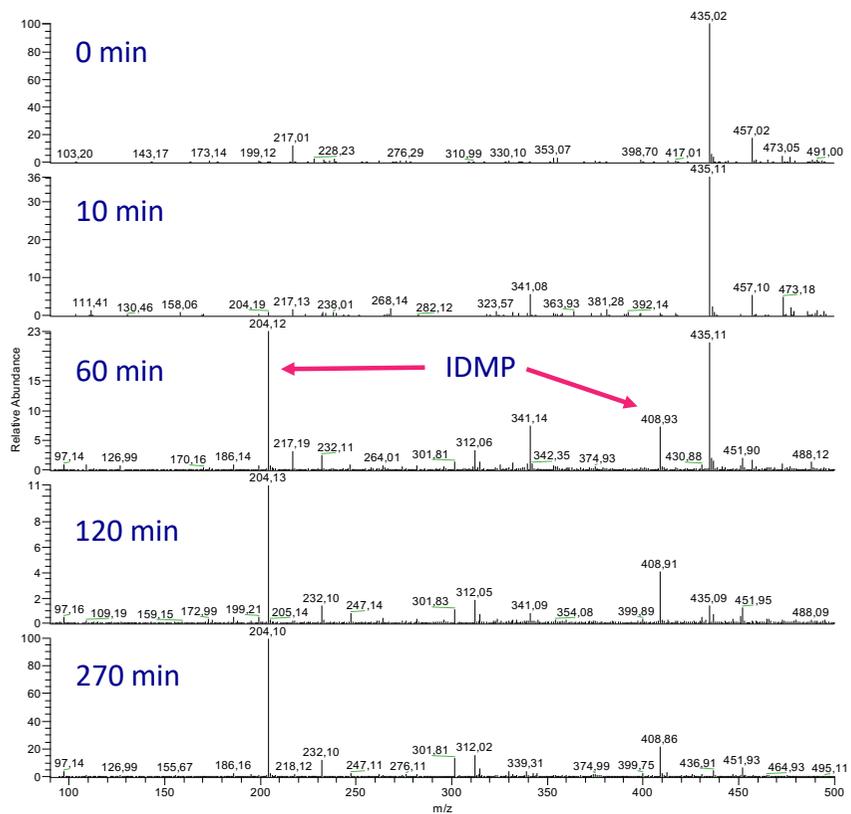
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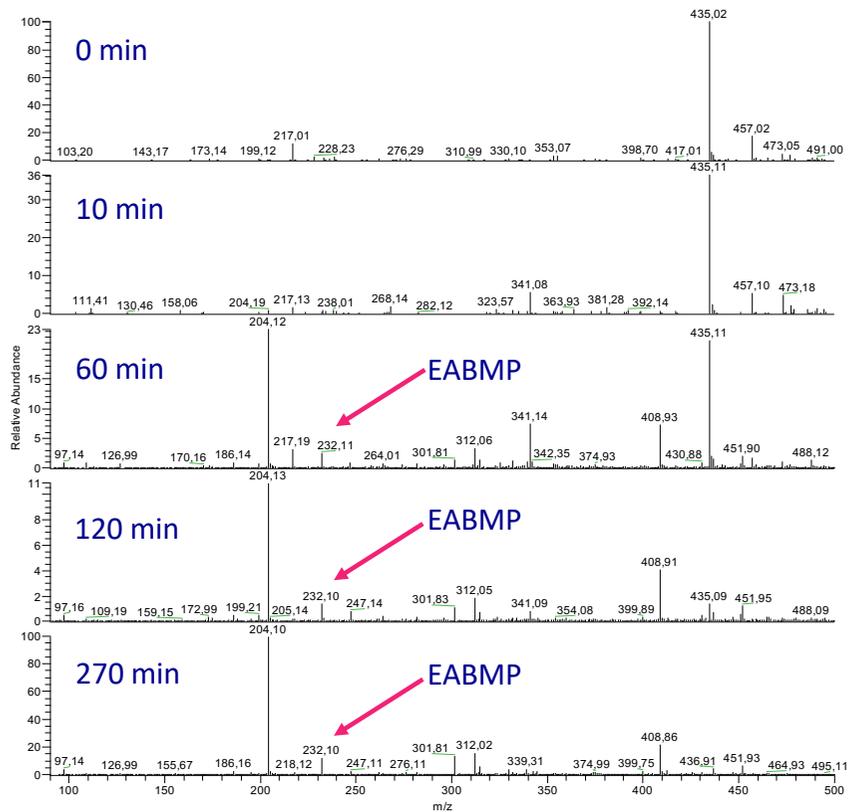
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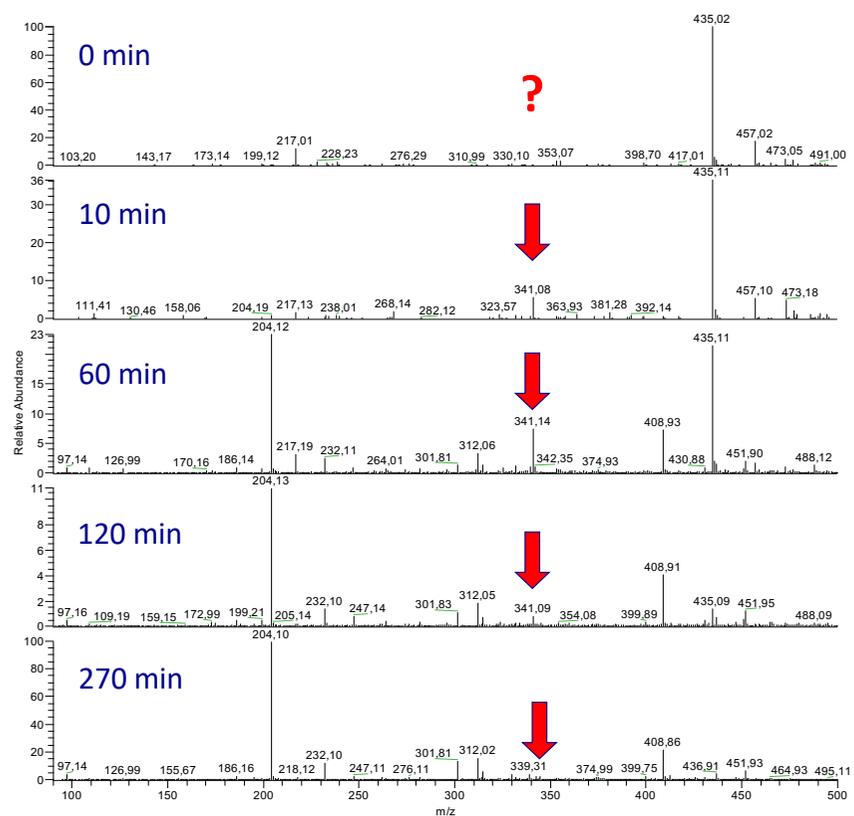
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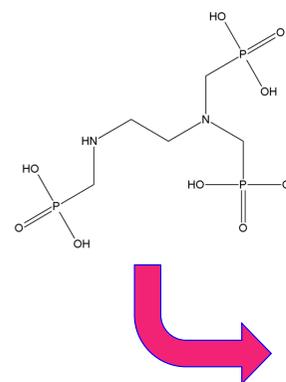


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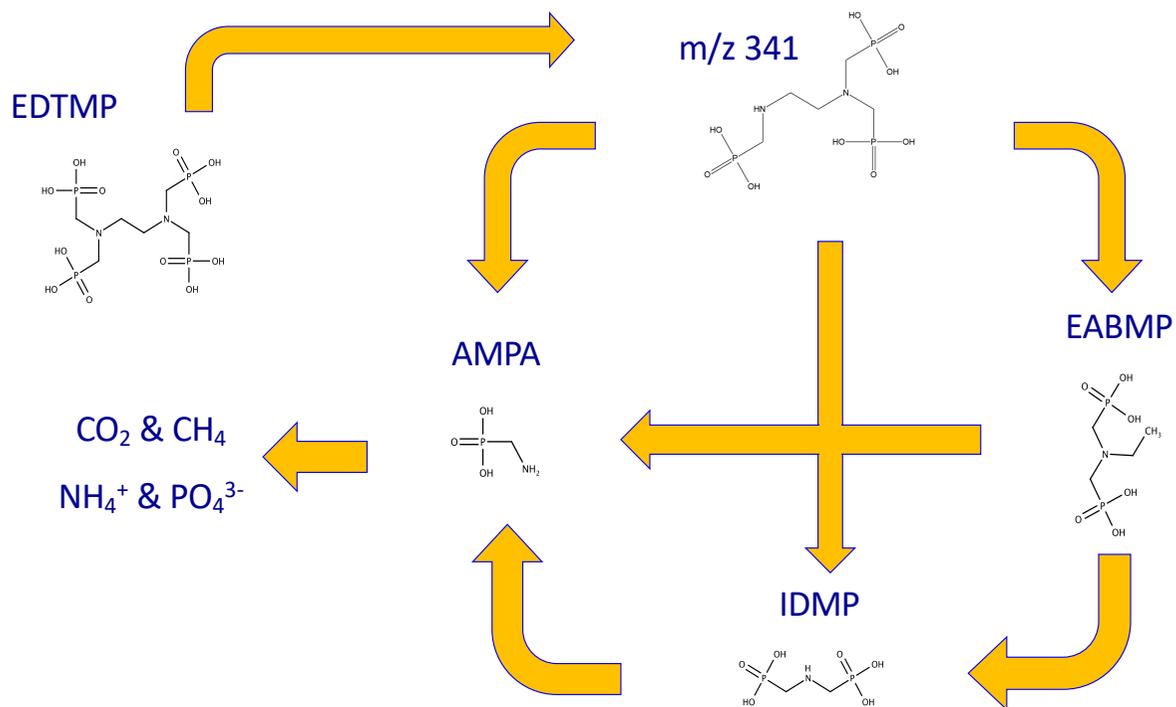
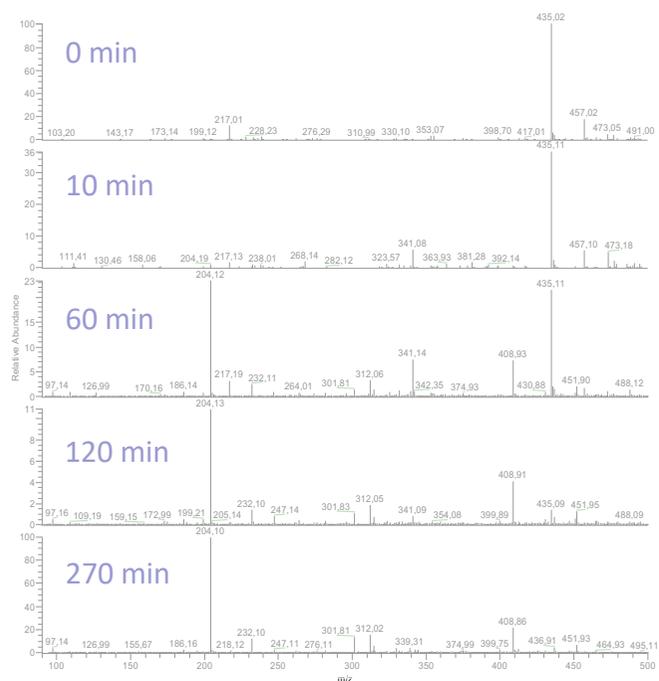
m/z 341



- Initial cleavage at C-N bond
- Radical attack though $\cdot\text{OH}$
- Superoxide radical also involved

Photodegradation of uncomplexed EDTMP

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Photodegradation of uncomplexed EDTMP

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Postulated degradation mechanism

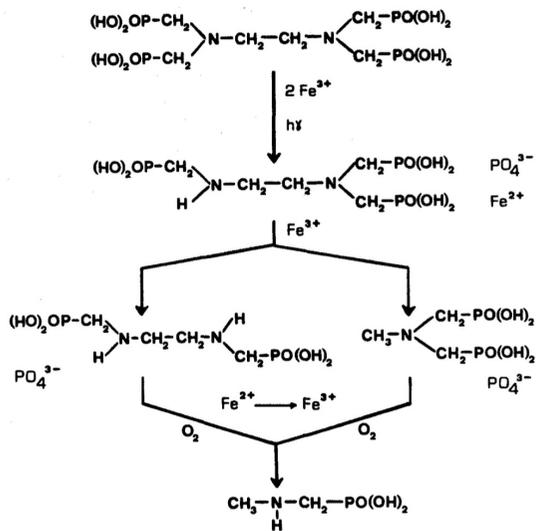
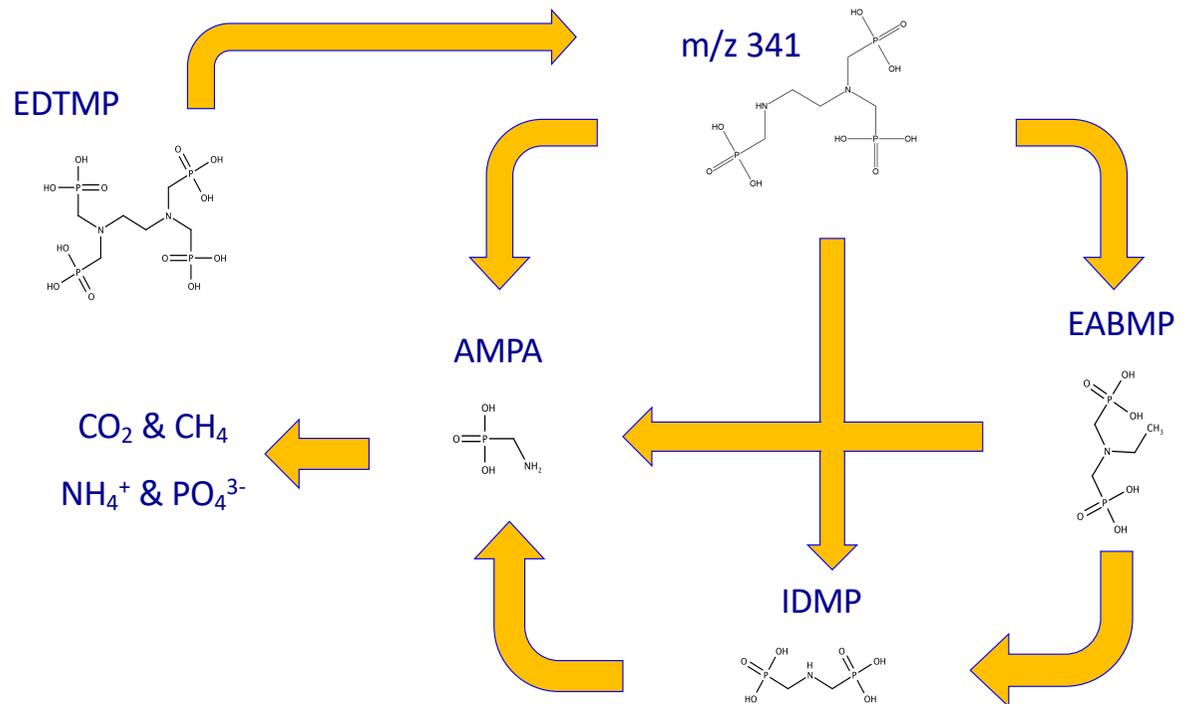


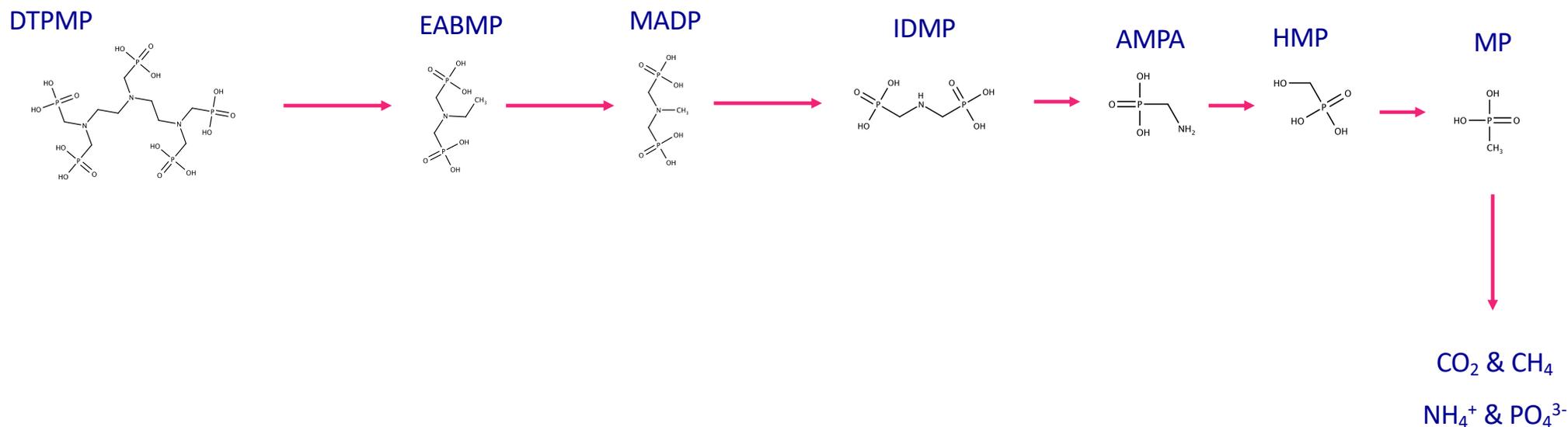
Fig. 6. Proposed photodegradation scheme of ferric EDTMP.



Is the photochemical and sunlight degradation of phosphonates the same?

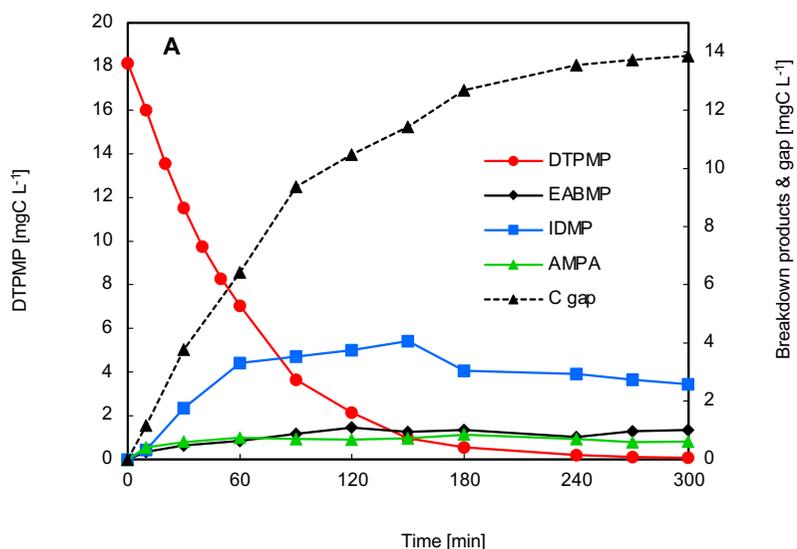
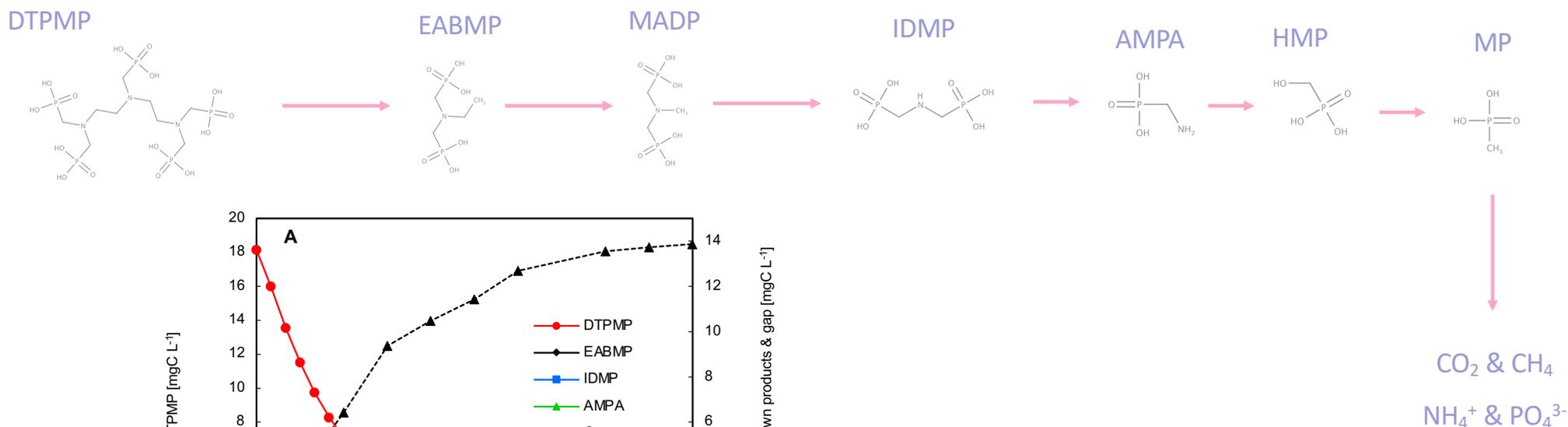
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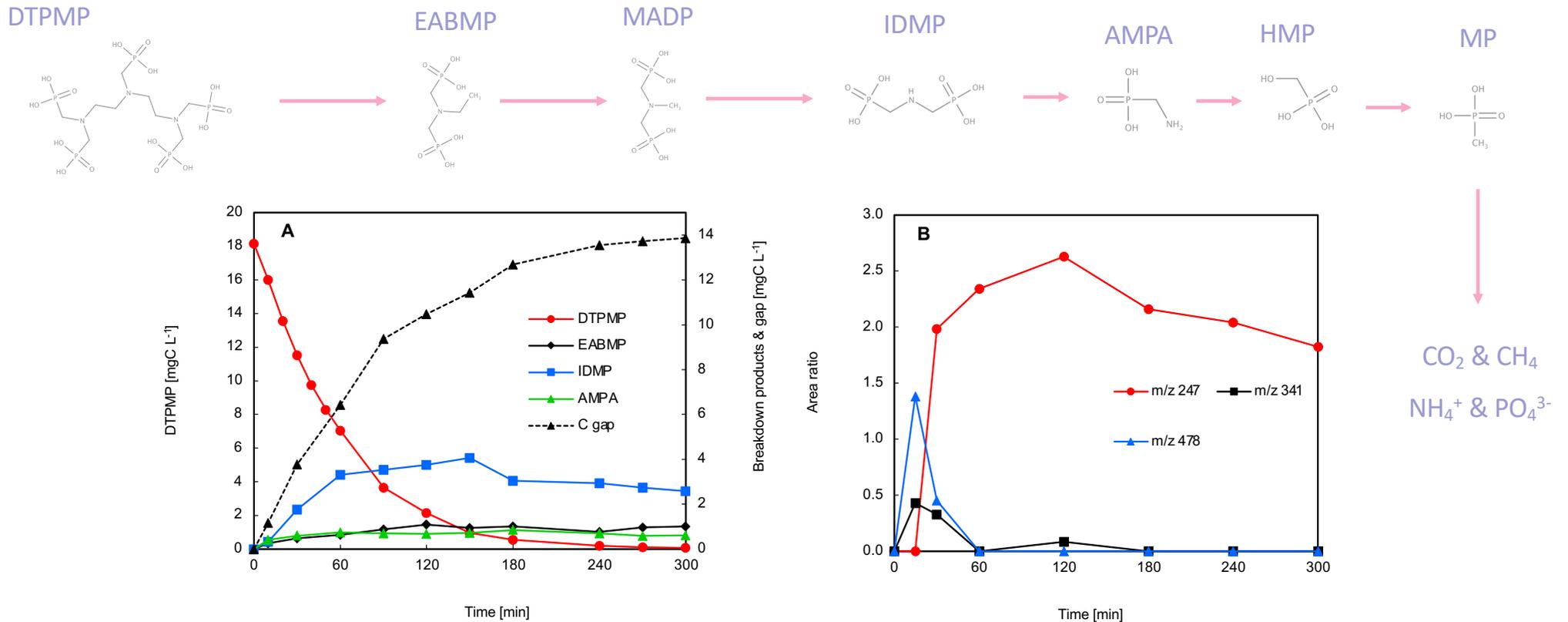
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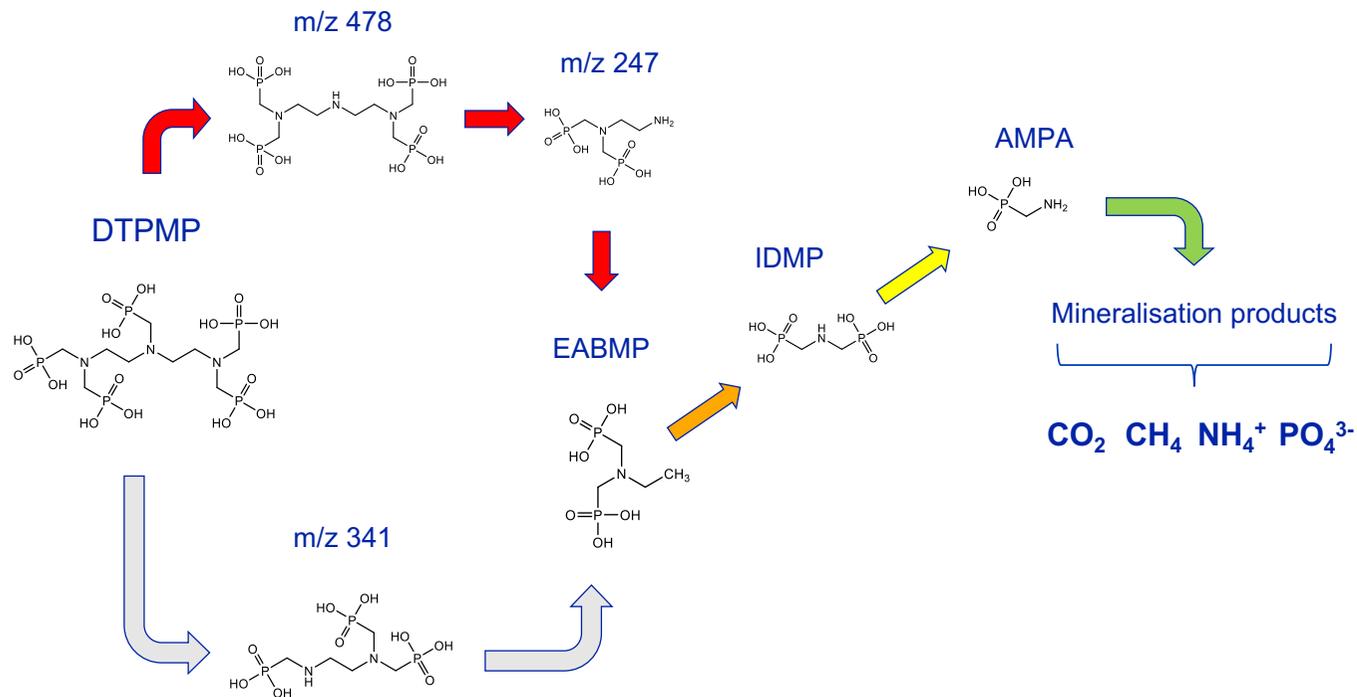
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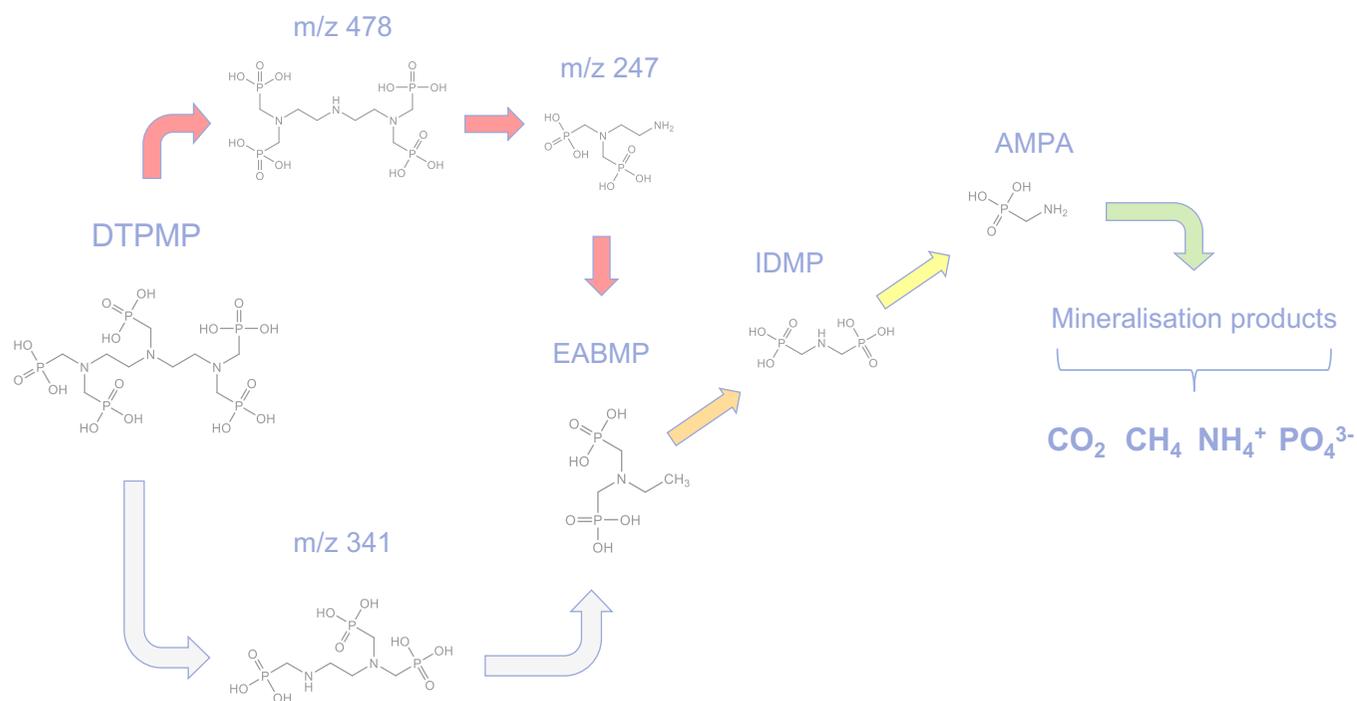
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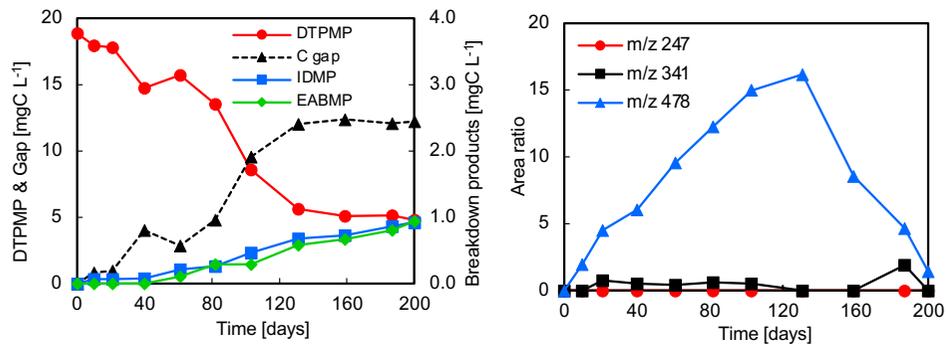
Conditions in sunlight?

- Direct sunlight
- Diffuse sunlight
- Diffuse sunlight + Ca^{2+}
- Diffuse sunlight + Mg^{2+}
- Diffuse sunlight + tap water
- All at pH value of 7.0
- All treatments sterile

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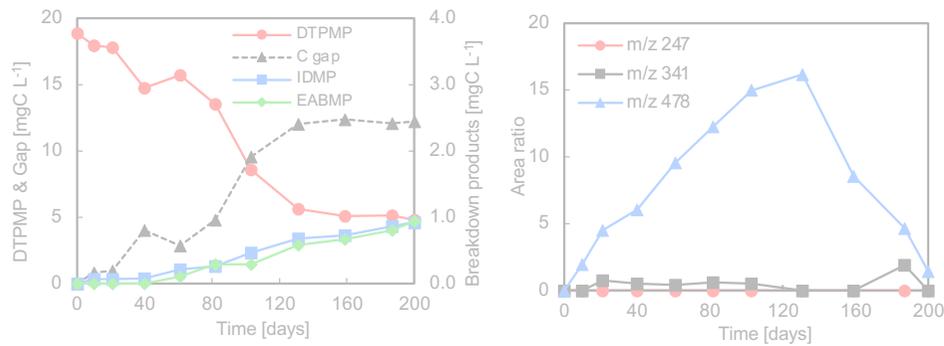
Direct sunlight



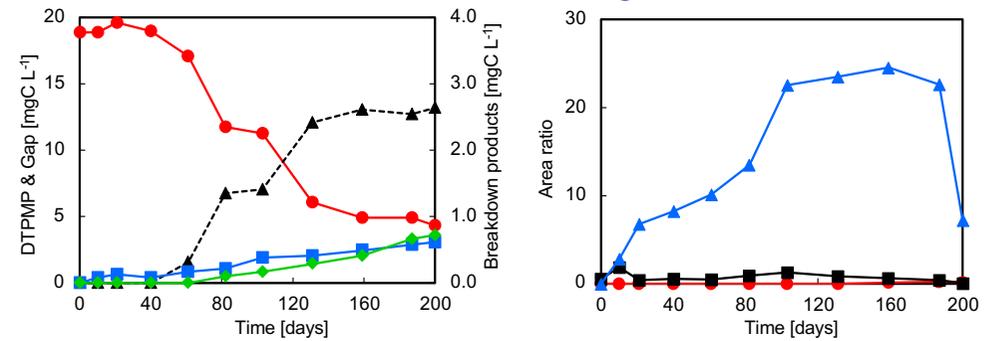
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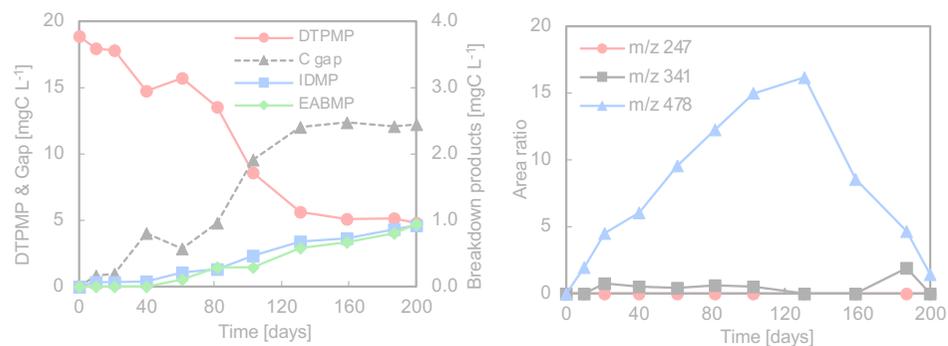
Diffuse sunlight



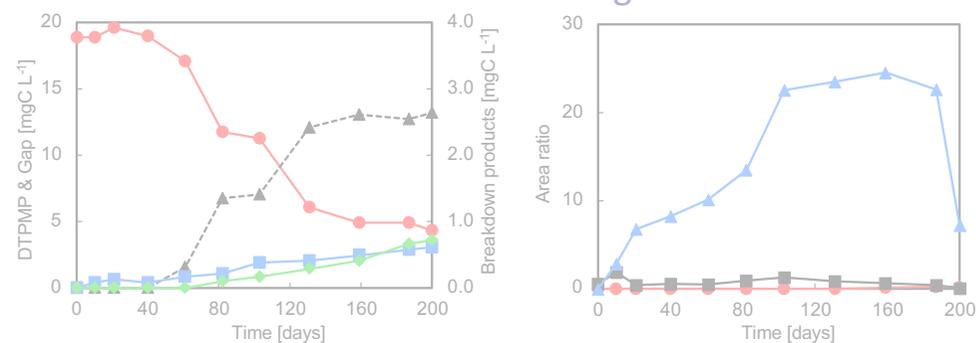
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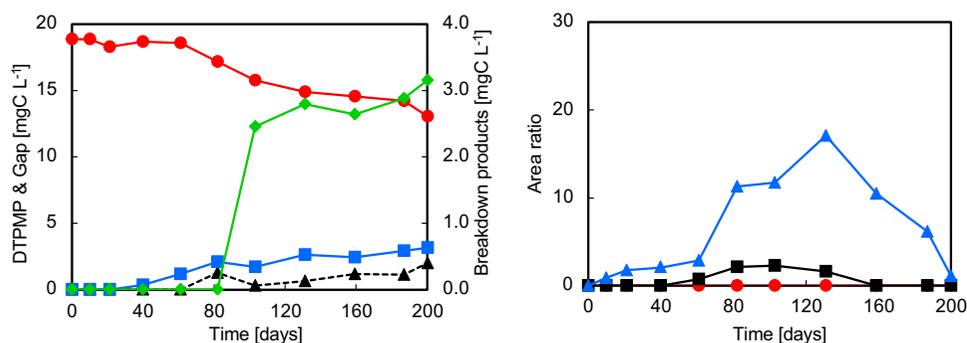
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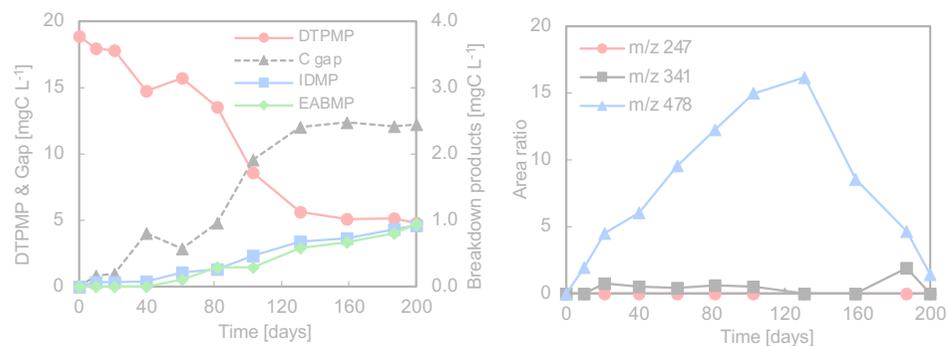
Diffuse sunlight & Mg²⁺



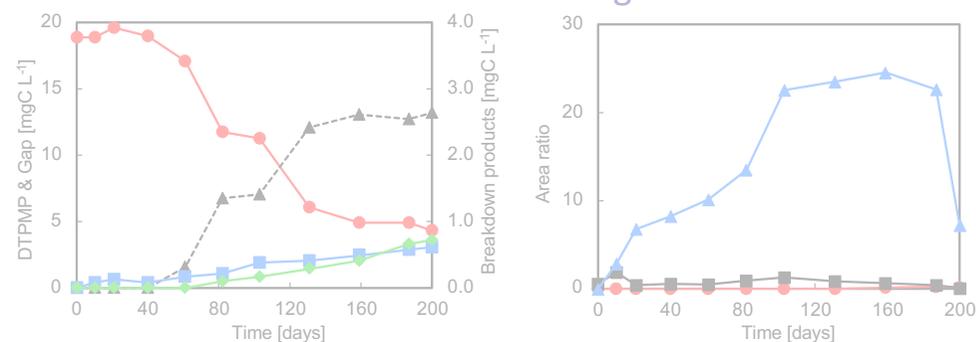
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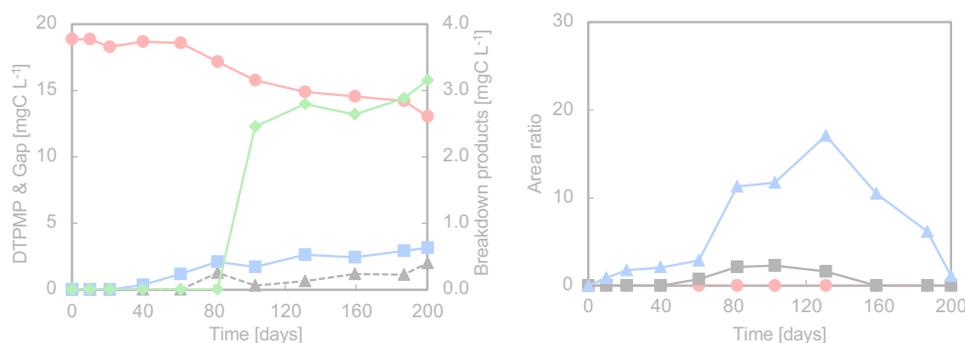
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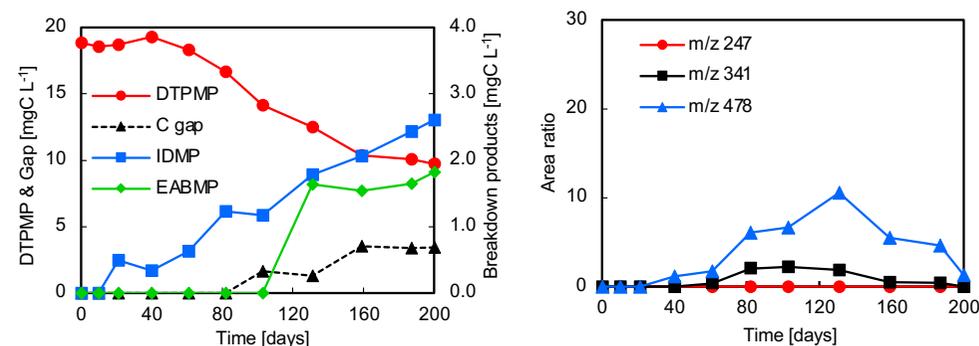
Diffuse sunlight



Diffuse sunlight & Mg²⁺

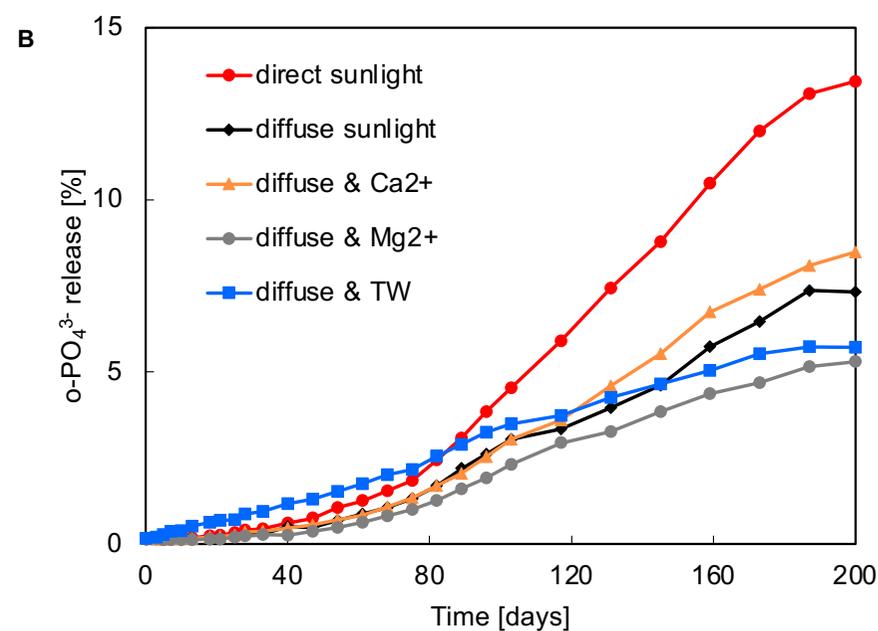
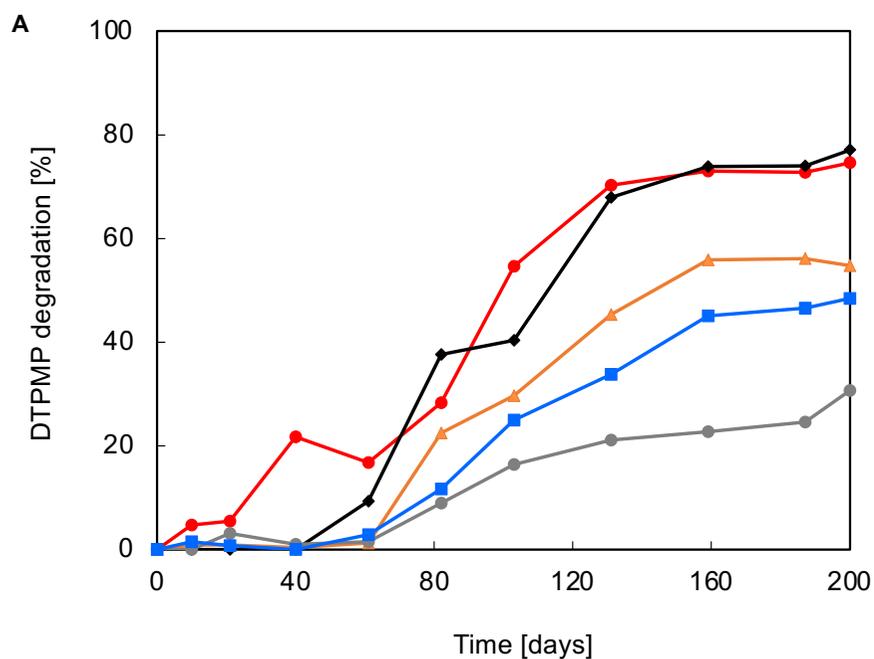


Diffuse sunlight & TW



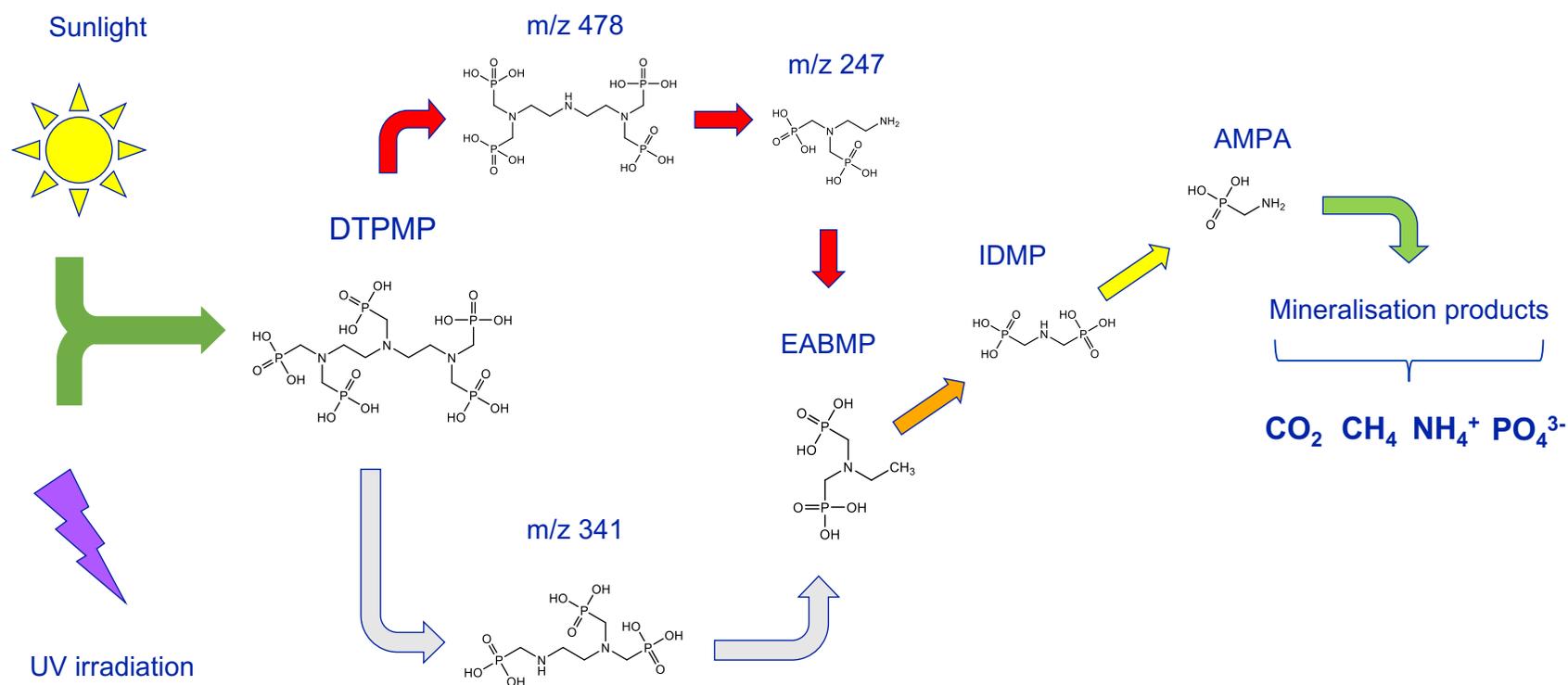
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- Smaller phosphonates, i.e., like ATMP or EDTMP release mainly IDMP and AMPA as major TP

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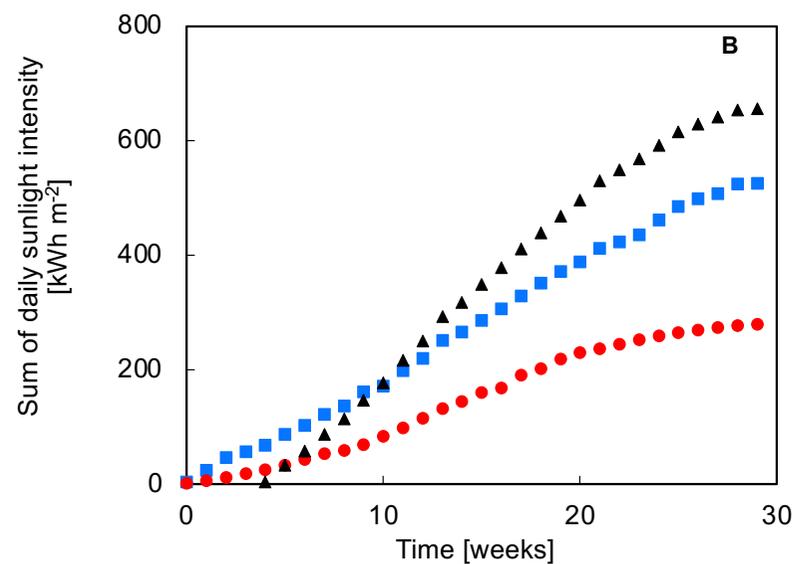
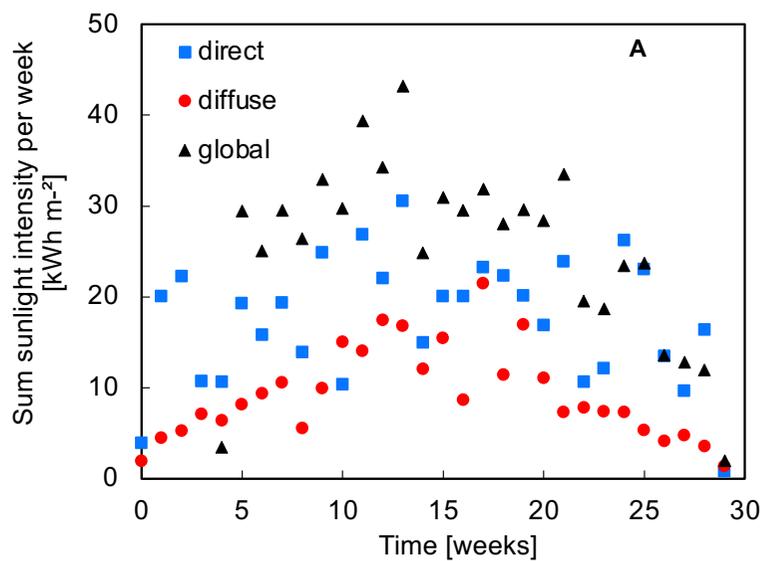
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- Photochemical degradation mechanism is the same as in sunlight
- Photochemistry can predict behaviour in the aquatic environment

Questions?

Annex

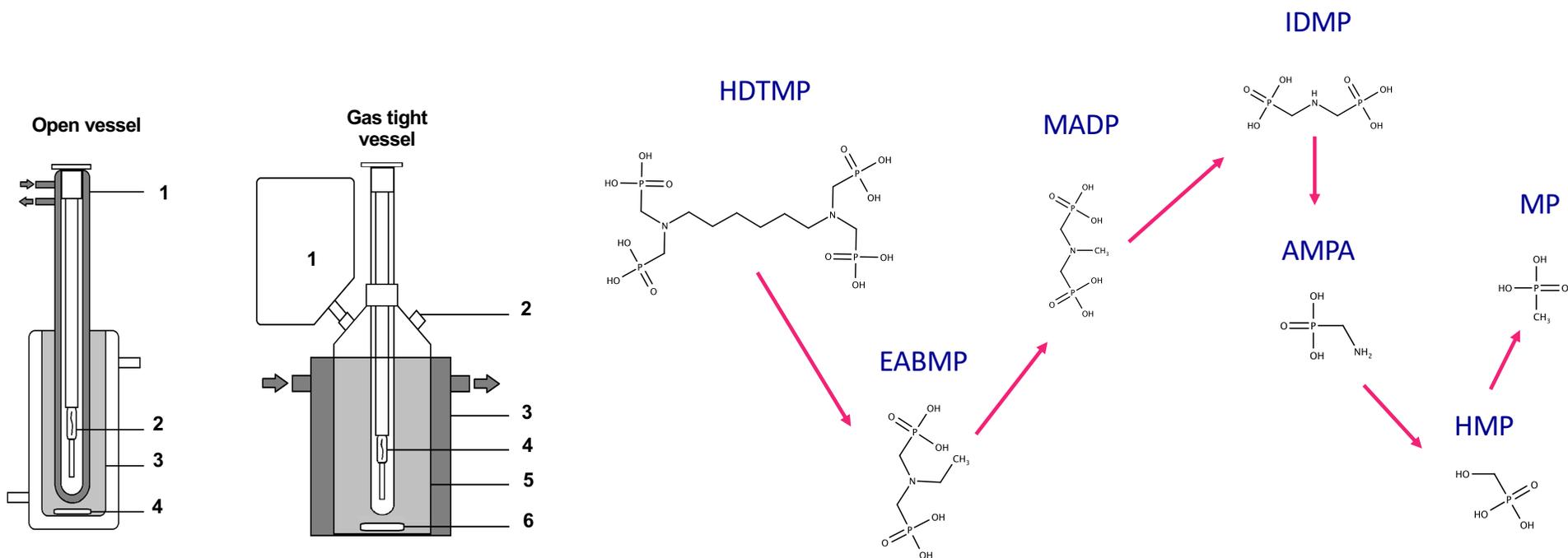
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Photodegradation of HDTMP with H₂O₂ and/or Mn²⁺

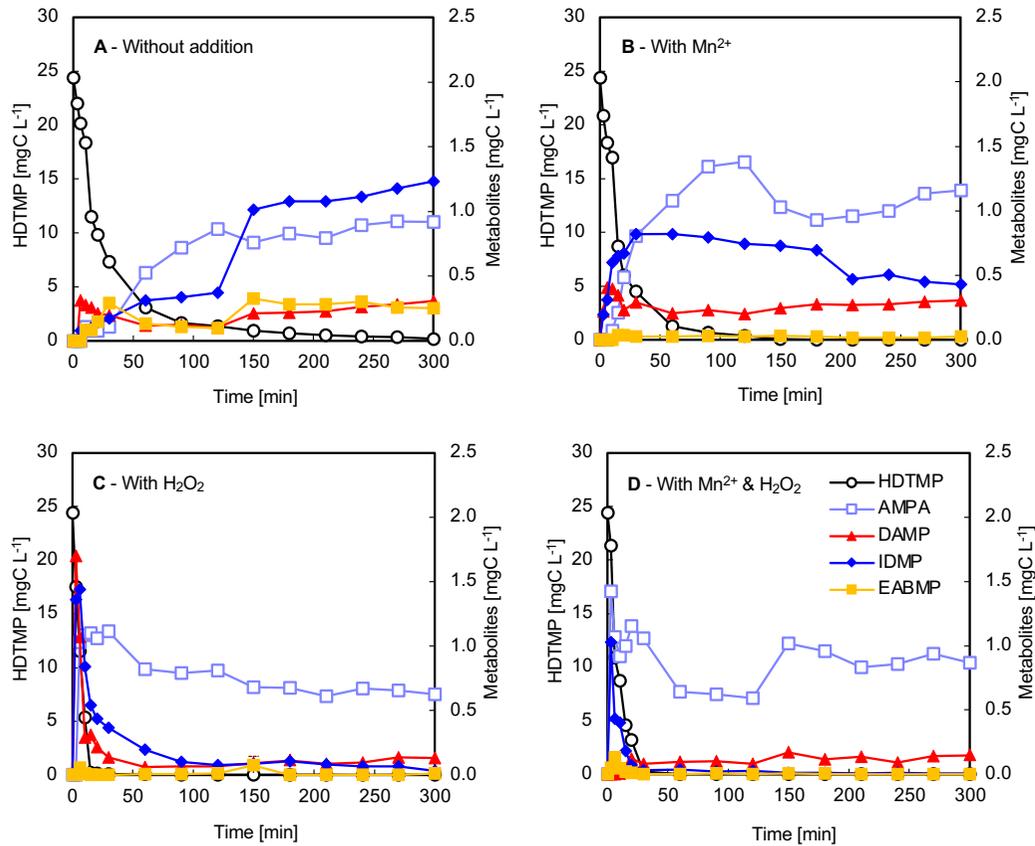
Kuhn et al. (2020), Emerging Contaminants 6, 10-19.



We expected different pathways, but...

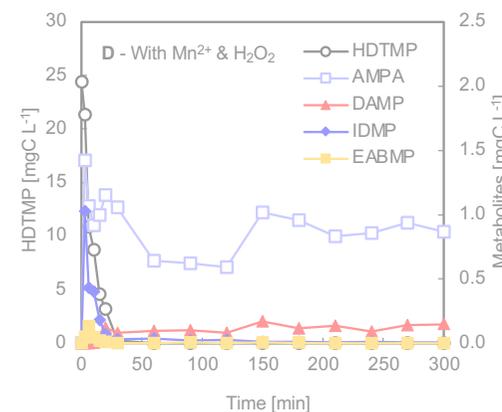
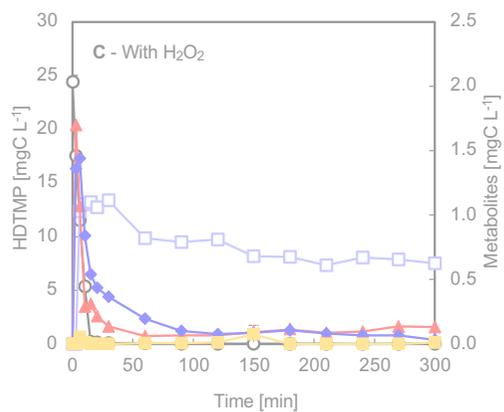
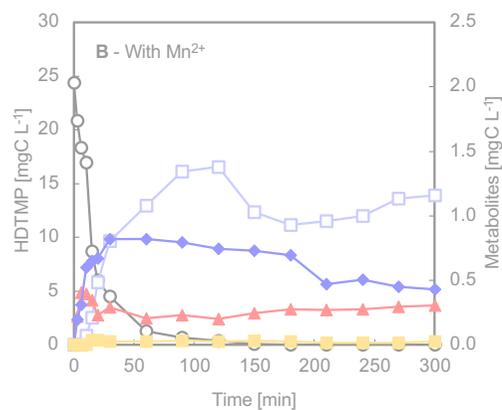
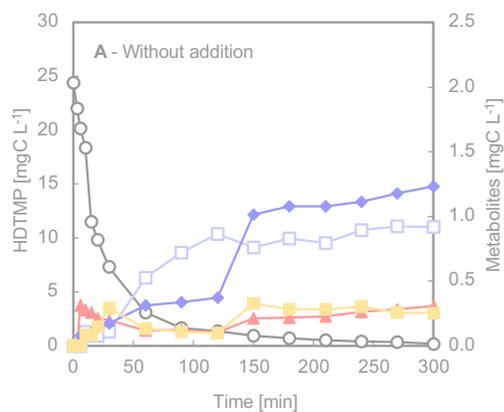
Photodegradation of HDTMP with H₂O₂ and/or Mn²⁺

Kuhn et al. (2020), Emerging Contaminants 6, 10-19.



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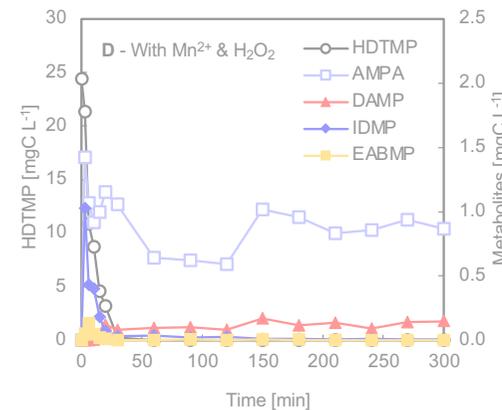
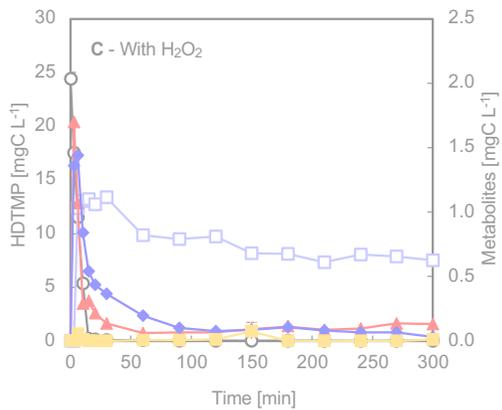
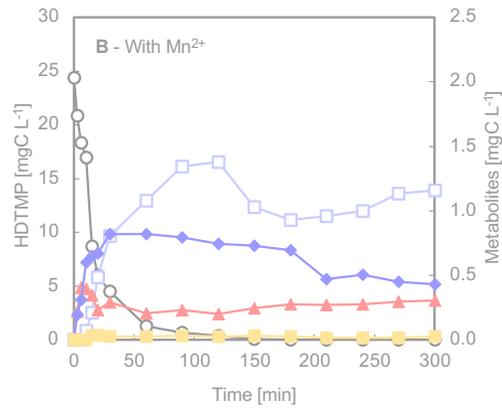
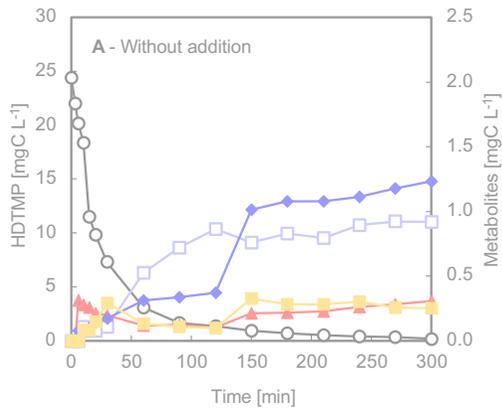
Kuhn et al. (2020), Emerging Contaminants 6, 10-19.



	$k_{\text{obs}} [\text{s}^{-1}]$	Half-life [min]
No addition	$6.34 \cdot 10^{-4} \pm 9.51 \times 10^{-5}$	18.52 ± 3.04
Mn ²⁺	$9.59 \cdot 10^{-4} \pm 7.23 \times 10^{-5}$	12.10 ± 0.95
H ₂ O ₂	$2.40 \cdot 10^{-3} \pm 8.39 \times 10^{-5}$	4.81 ± 0.17
Mn ²⁺ & H ₂ O ₂	$1.76 \cdot 10^{-3} \pm 9.17 \times 10^{-5}$	6.59 ± 0.34

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- The same pathway, but different kinetics
- Initial cleavage at C-P bond
- Mn²⁺ similar catalytic effect as Fe²⁺