Session: Persistence & Biodegradation Assessment
Platform Presentation
Session Room B, Tuesday May 15th, 2018, 11:55 a.m., ID: 252

Relevance of photolysis for the fate of pendimethalin in deeper water layers - results of a scale-up approach according to OECD TG 309

Dieter Hennecke[1], Mike Kruse[1], Jan Hassink[2]

[1]Fraunhofer IME, Division Applied Ecology, Auf dem Aberg 1, 57392 Schmallenberg, Germany
[2]BASF SE, Crop Protection, 67117 Limburgerhof, Germany
E-mail contact: dieter.hennecke@ime.fraunhofer.de

1. Introduction

OECD TG 309 "Aerobic Mineralisation in Surface Water" [1] is currently used under different regulatory frameworks for the persistence assessment of chemicals in surface water. The test is performed in batch to measure biodegradation at defined standard conditions in the absence of light. Processes like direct and indirect photolysis, which might be relevant for the fate of a chemical in water, are not addressed. Since the assessment of degradation in surface water is triggered by the result of the OECD 309 study only, substances which are hydrolytically stable but sensitive to light might be falsely assessed persistent.

Within pesticide regulation direct photolysis studies are mandatory, indirect photolysis studies optional. However, rate constants determined in those studies are not considered in exposure assessment of the parent substance. Only purpose of the study is to get information on the occurance of potentially stable transformation products which have to be considered for registration.

Castro-Jiménez and de Meent (2011) [2] have reviewed the available literature on photolytic degradation of chemical substances under environmental conditions and concluded that light absorption in natural water is significantly lower than measured in laboratory water, with photo degradation about 30 times more slowly in typical fresh water. The relative importance of direct photolysis versus indirect photolysis varies and is dependent both on the substance and the media. Indirect photodegradation is stimulated in natural environmental waters by the presence of dissolved organic matter - which is not present in pure laboratory water. In natural waters, which have to be used for OECD 309, both processes can be relevant – but in the standard OECD 309 setup the influence of light on the degradation of the test item is not considered. Hence, beside direct photolysis in the upper layer of a water body, it is interesting to know until which water depth direct and indirect photolysis might contribute to degradation since the light intensity decreases with increasing water depth.

Figure 1: test system with simulated sunlight

2. Materials and methods

It requires a modified test system to measure the result of the biodegradation as well as photolysis processes in an integrative approach. Thus, simulation approach has been performed as a scale up OECD 309-like approach which enables the determination of the relevance of direct and indirect photolysis for the fate of the light sensitive test item pendimethalin within a water depth of up to 125 cm in natural surface water exposed to simulated sunlight.

Stainless steel containers with the shape of a vertically cut cylinder were filled with surface water taken from a natural lake and maintained at 20°C. The containers are 140 cm deep and the surface area is 0.70 m^2. Two of them were placed in an outer cylinder which could be temperature controlled (see figure 1).

The water body was exposed to simulated sunlight originated by an OSRAM HQI-TS lamp. The light spectrum behind the glass plate, that covers the container, was similar to natural sunlight with a cutoff at 290 nm. In contrast to the OECD 309 standard setup the water was not mixed by stirring or shaking because this would interfere with the determination of the degradation rate in different depths. Sampling was performed in five different water depths using permanently installed steel tubes of different length (figure 2) in order to avoid mechanical mixing of the water body during sampling.

A second container with the same test design, but covered by a stainless steel plate, served as dark control. The headspace between the water surface and the lids was actively sampled with gas traps to quantify losses of volatiles and $^{14}CO_2$ in order to establish a mass balance at the end of the incubation. The test was conducted with both options regarding the water quality, i.e. under pelagic conditions and with suspended-sediment.. Test substance was ^{14}C-pendimethalin, which is known to degrade rapidly in aqueous systems under the influence of light.

Figure 2: sampling system

3. Results and discussion

After application of the test substance dissolved in acetonitrile, the initial concentration was 0.09 mg/L in the water phase. Sampling in different depths proved the homogenous distribution of the substance. In the following samplings over 20 days significant differences in the pendimethalin concentration were observed in the irradiated container versus the dark control. In the dark control until 10 d the concentration was very constant in the upper water layer whereas the concentration in the container exposed to artificial sunlight dropped significantly (see figure 3). After 10 days a slow decrease was observed in the dark control as well.

Interestingly, the concentration decreased most rapid in the upper 5 cm layer of the irradiated container. In the other layers, the decrease observed was slower but still significantly faster compared to the dark control.

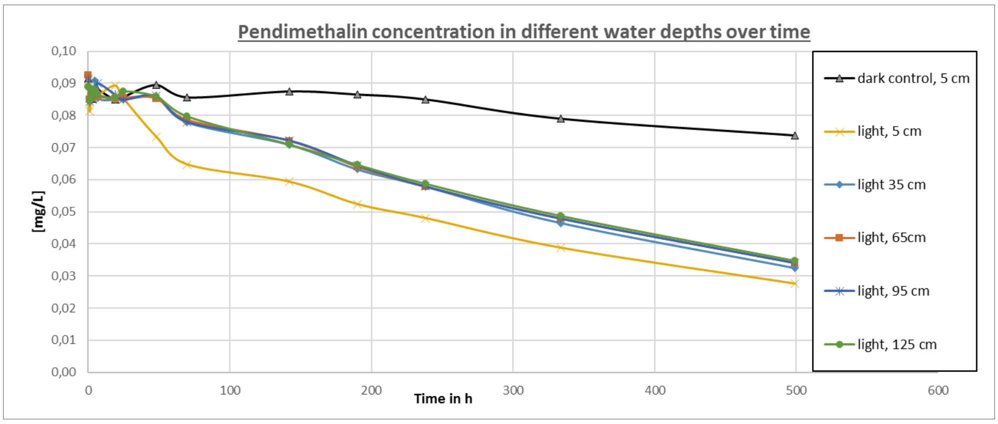


Figure 3: concentration of Pendimethalin in different water layers over time

4. Conclusions

It can be concluded that the so far observed differences in degradation are due to the exposure to simulated sunlight as all other parameters were identical. The concentration decreased – as expected – most rapidly close to the water surface, where direct photolysis should be most relevant.

No difference can be observed so far in all other water layers, hence, it can be concluded that indirect photolysis contributes at 35 cm depth in the same way as in 125 cm depth although the light intensity decreased rapidly with increasing water depth. Since the experiments are still running currently, the mass balance could not be established yet.

5. References

[1] OECD Test Guideline 309: Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test, OECD, adopted 13th April 2004

[2] Castro Jiménez J and Van de Meent D (2011). Accounting for photodegradation in P-assessment of chemicals.

RELEVANCE OF PHOTOLYSIS FOR THE FATE OF PENDIMETHALIN IN DEEPER WATER LAYERS - RESULTS OF A SCALE-UP APPROACH ACCORDING TO OECD TG 309


Sampling of surface water (4 m^3)

Fraunhofer IME

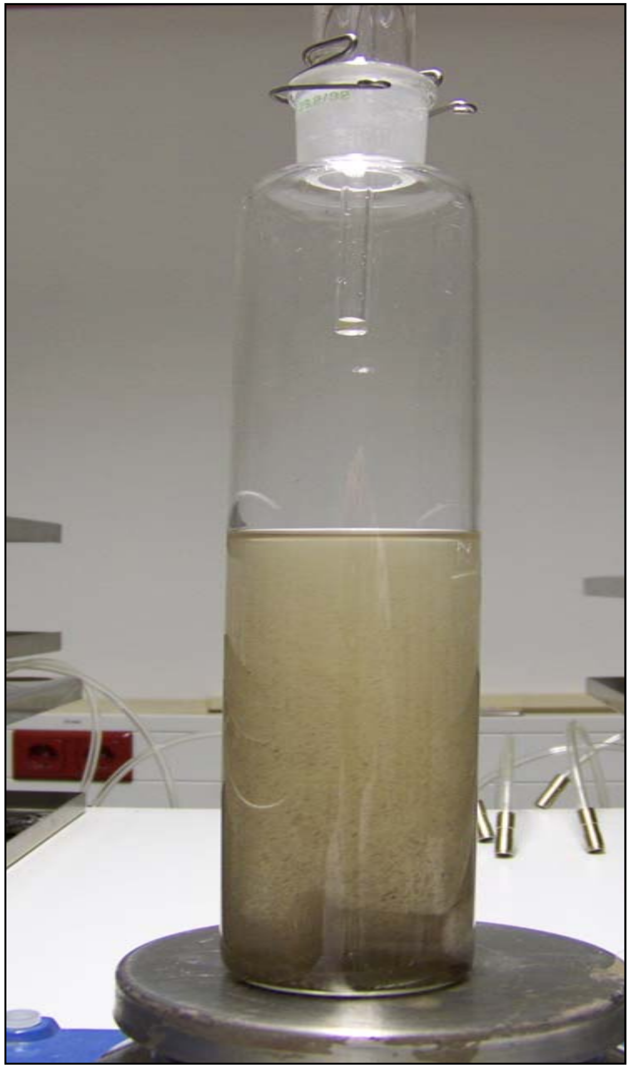
Jan Hassink, Dieter Hennecke, Mike Kruse

SETAC Rome, May 15th 2018

Background

OECD guideline 309

„Aerobic Mineralisation in Surface Water - *Simulation Biodegradation Test*"



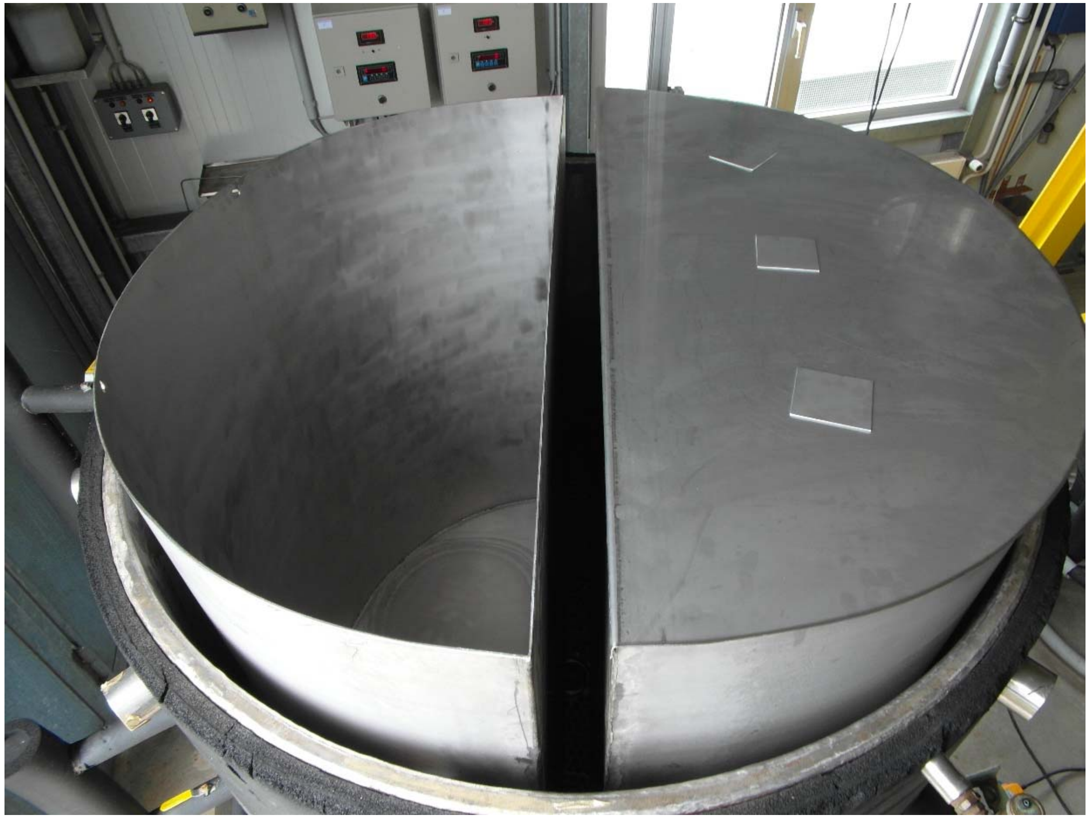
Idea of the guideline:

natural surface water (fresh, marine) is used in a batch experiment to determine the degradation of a test substance at a maximum starting concentration of 100 µg/L and a second concentration 5-10 times below, preferably < 1 µg/L

Standard test rather than **simulation test**! Laboratory batch test at controlled standard conditions.

Aim of the study:
influence of simulated sunlight in a 309-like test setup with a photolytically sensitive substance

Test system



- Stainless steel container,
  140 cm depth,
  0.7 m^2 surface area (900 L)
- Outside container temperature controlled, (space filled with tap water)
- Dark: covered with a stainless steel lid (right side)
- Sunlight simulation: covered with special glass plate, light cut-off at 290 nm
  OSRAM HQI-TS lamp (2000 W)

At dark and sunlight simulation conditions:
- both, phelagic (< 100 µm) and suspended sediment (< 2 mm, 1 g/L),
- no active mixing of the water body during the test!

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On site sampling

Transport to test facility

100 µm sieve

Sampling:

December 1st, 2017

Hennesee
drinking water reservoir,
Germany,

51° 19′ 57″ N, 8° 15′ 48″ O

On site parameter:

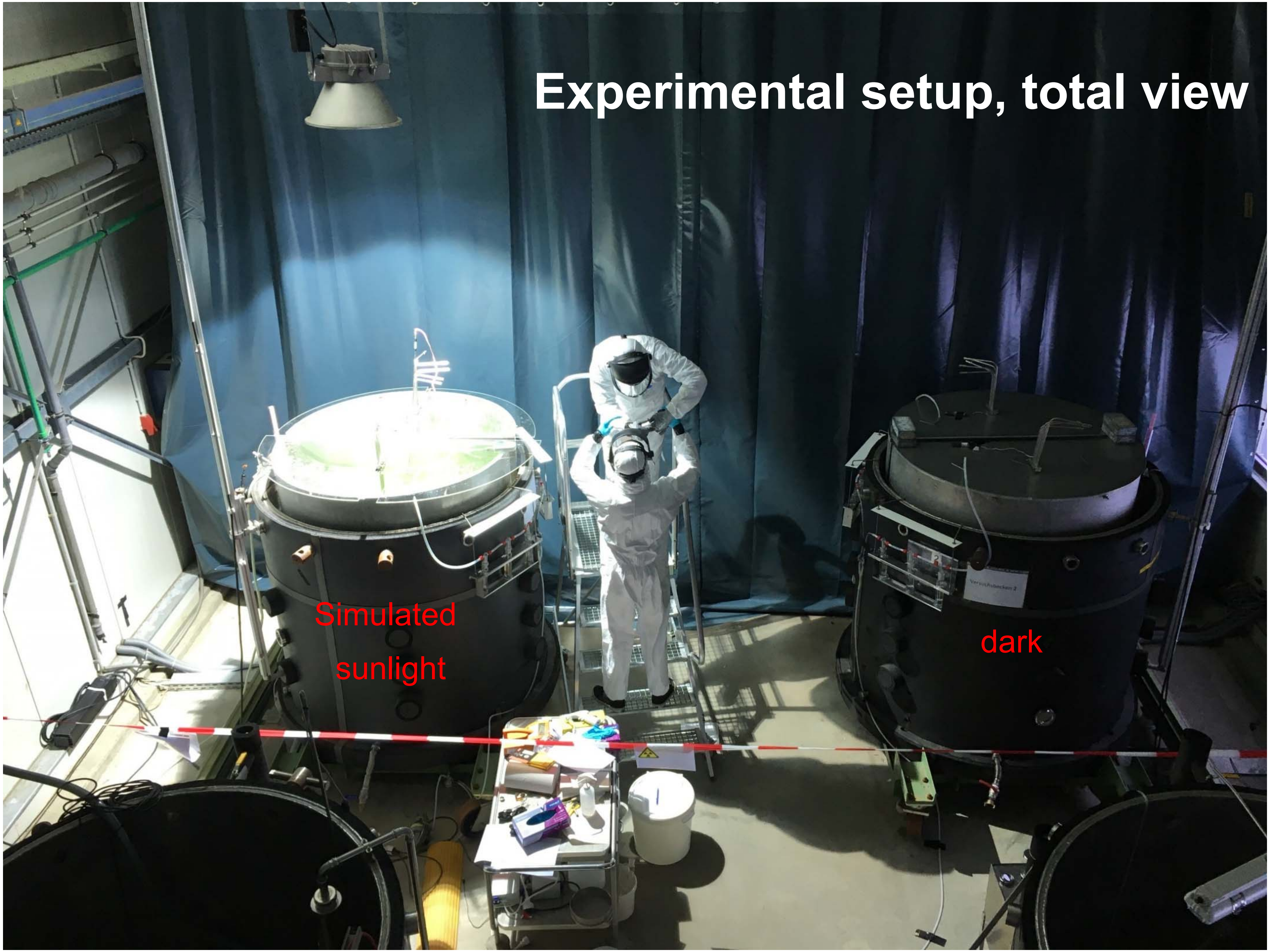
Redox: 292,6 mV

O_2: 10,49 mg/L

pH-Wert: 7,9

Temperatur: 7,9 °C

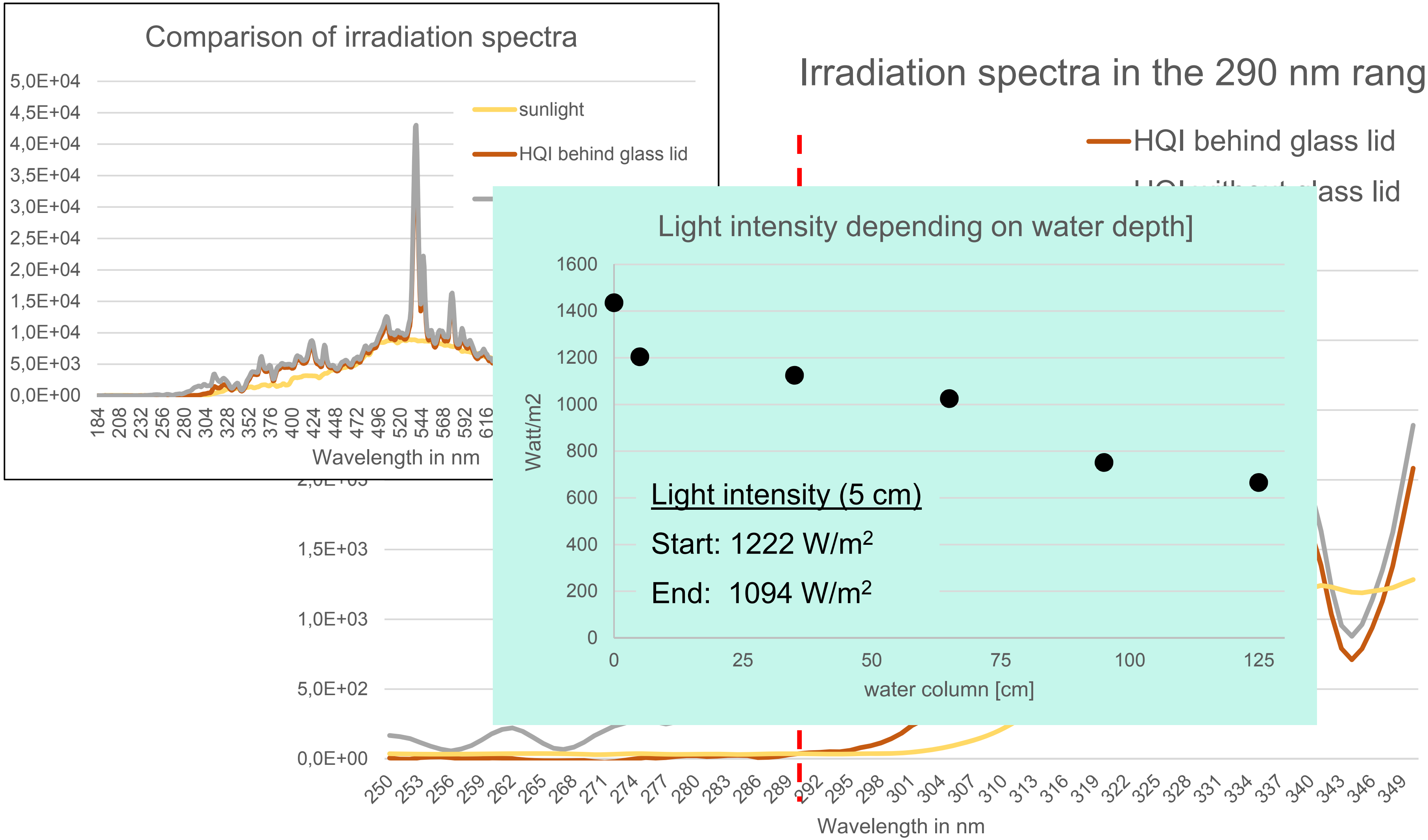
Fraunhofer IME


Experimental setup, total view
Simulated
sunlight
dark

Sampling

- Sampling at 5 different depths without disturbance of the system
- Sampling via vacuum, first 200 ml discarded
- Sediment sampling only at test end

Sunlight simulation



Results, mass balance ^{14}C

simulated sunlight, phelagic

sampling	water phase	CO_2 dissolved	CO_2 trapped	total recovery
0d	100.0			100.0
1d	100.5		0.0	100.5
3d	100.3		0.0	100.3
7d	96.9		0.0	96.9
10d	94.2		0.0	94.2
14d	79.0	12.9	0.1	92.0
22d	72.0	13.7	0.1	85.9
30d	63.3	17.9	0.2	81.3
58d	43.3	26.6	0.3	70.2

simulated sunlight, suspended sediment

sampling	water phase	CO_2 dissolved	CO_2 trapped	total recovery
0d	100.0			100.0
1d	101.2		0.0	101.2
3d	86.1		0.0	86.2
7d	82.5		0.0	82.5
10d	85.3	4.5	0.1	89.9
14d	73.2	13.9	0.1	87.2
22d	68.5	16.1	0.2	84.8
30d	61.1	20.4	0.2	81.7
58d	42.3	28.2	0.2	70.6*

*+ 4.2% at sediment

dark, phelagic

sampling	water phase	total recovery
0d	100.0	100.0
1d	100.0	100.0
3d	97.2	97.2
7d	96.8	96.8
10d	83.2	83.2
14d	78.4	78.4
22d	74.7	74.7
30d	73.0	73.0
58d	92.6	92.6

Sunlight simulation:

Recovery only ~70% at 58d

Significant CO_2-poduction

Dark:

Good recovery at 58d

No CO_2-production observed

dark, suspended sediment

sampling	water phase	total recovery
0d	100.0	100.0
1d	104.8	104.8
3d	92.2	92.2
7d	73.1	73.1
10d	87.2	87.2
14d	90.3	90.3
22d	94.6	94.6
30d	96.6	96.6
58d	90.6	98.3*

*+ 7.7% at sediment

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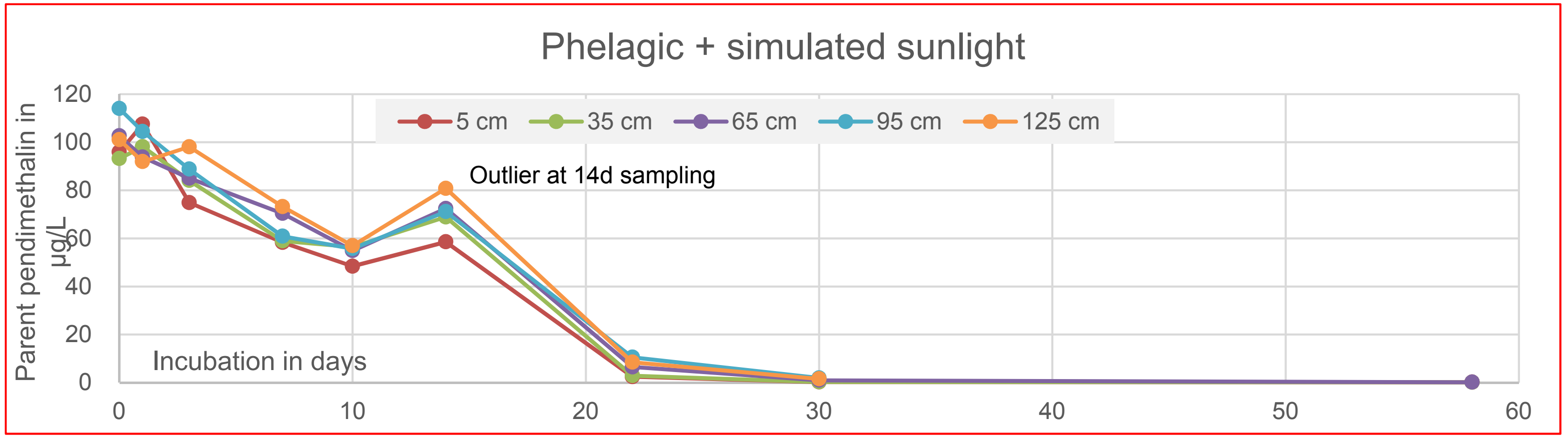
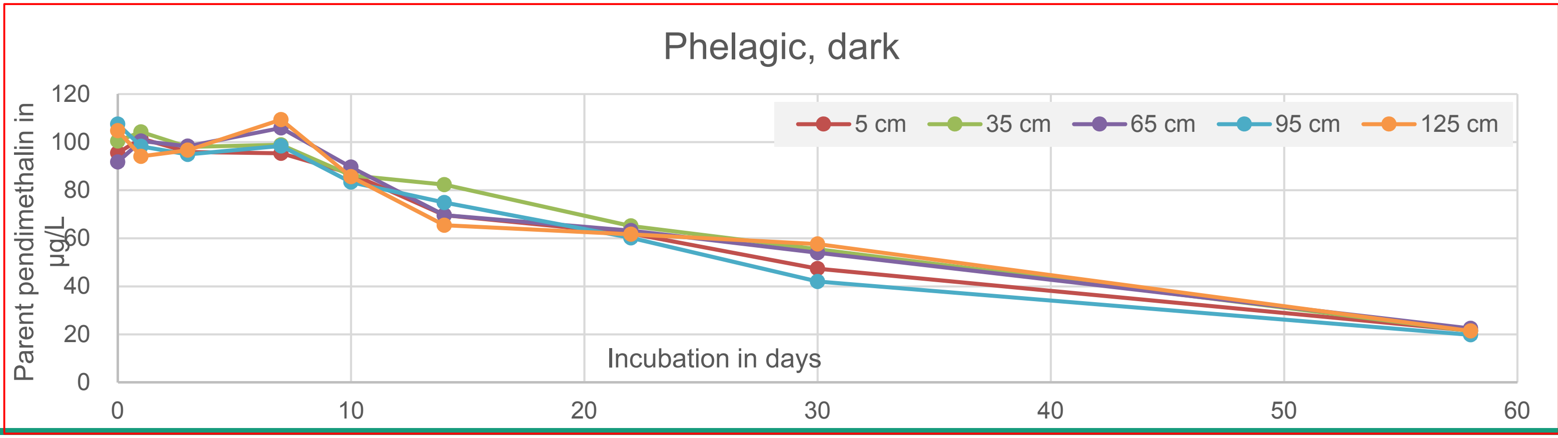
Results LC-MS/MS, phelagic

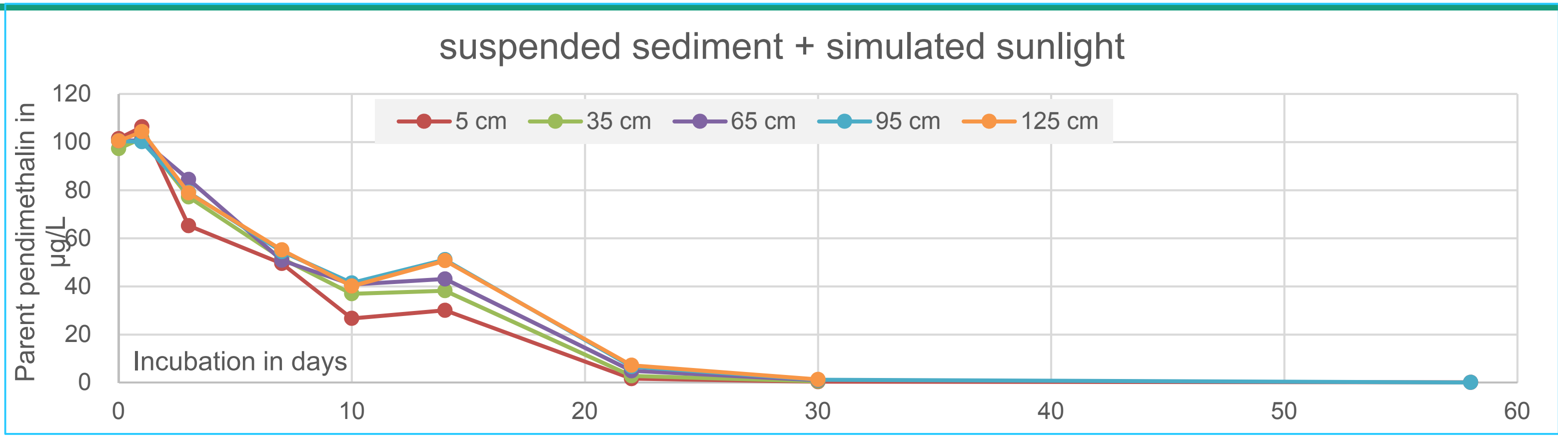


Sunlight simulation: fastest at 5 cm, slowest at 125 cm, at 30d no parent Pendimethalin remaining

Dark: no difference in depths, after 58d still around 20% Pendimethalin

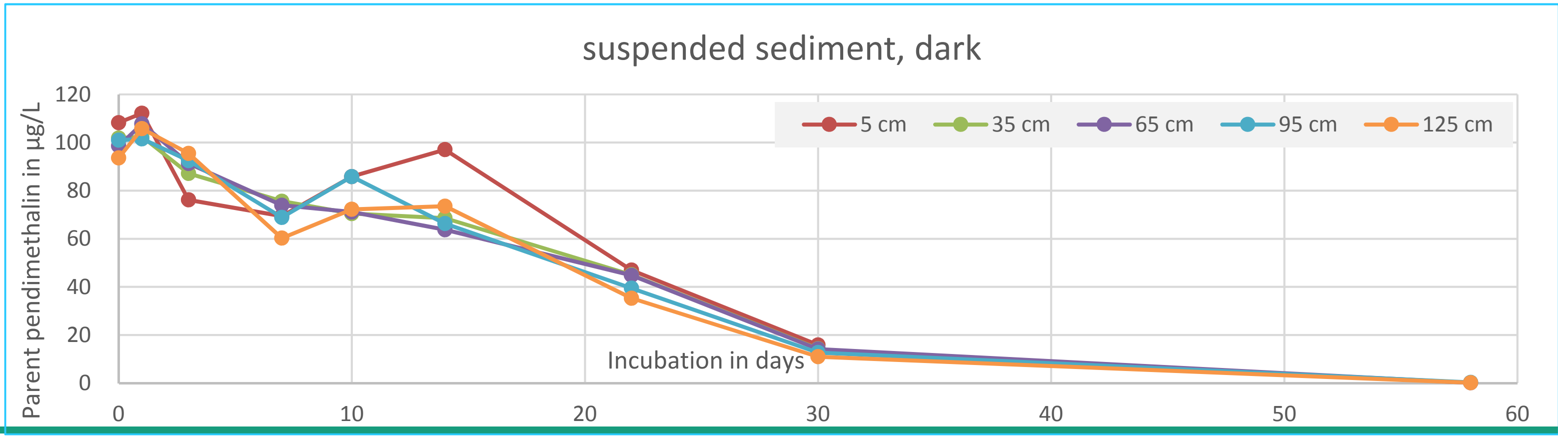


Results LC-MS/MS, suspended sediment

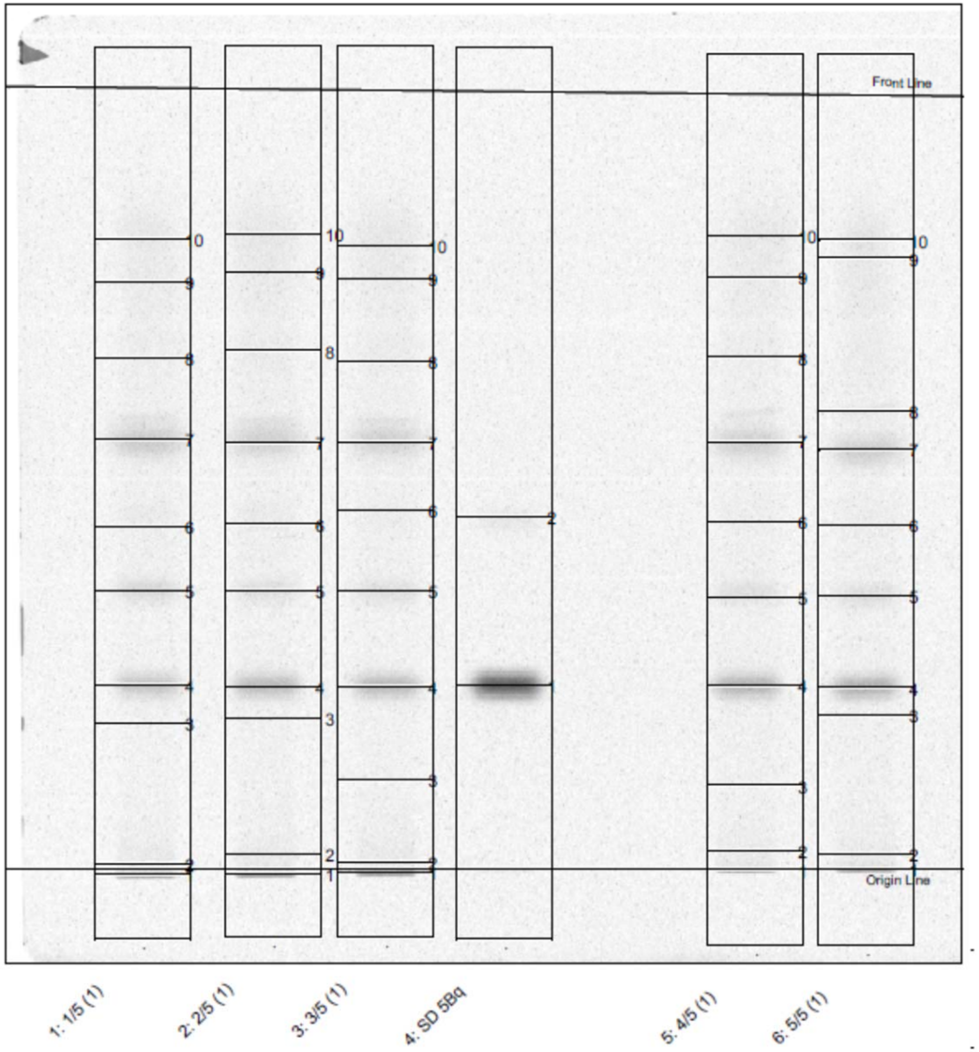


Sunlight simulation: fastest at 5 cm, slowest at 125 cm, at 22d only Pendimethalin almost gone

Dark: no trend in depths, after 58d no parent Pendimethalin remaining



Results radio TLC (simulated sunlight)



Homogenous distribution of degradation products in sampled water layers

Influence of light not visible in vertical water profile!

Example:

Simulated sunlight, suspended sediment, 14d sampling:

1/5 = 5 cm sampling depth

2/5 = 35 cm

3/5 = 65 cm

4/5 = 95 cm

5/5 = 125 cm

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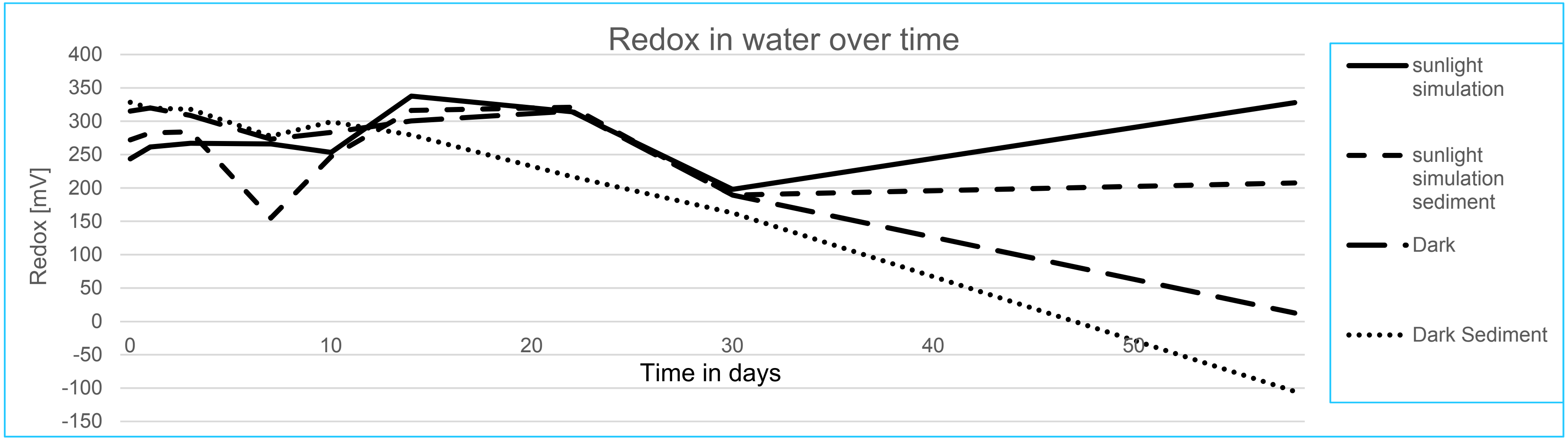
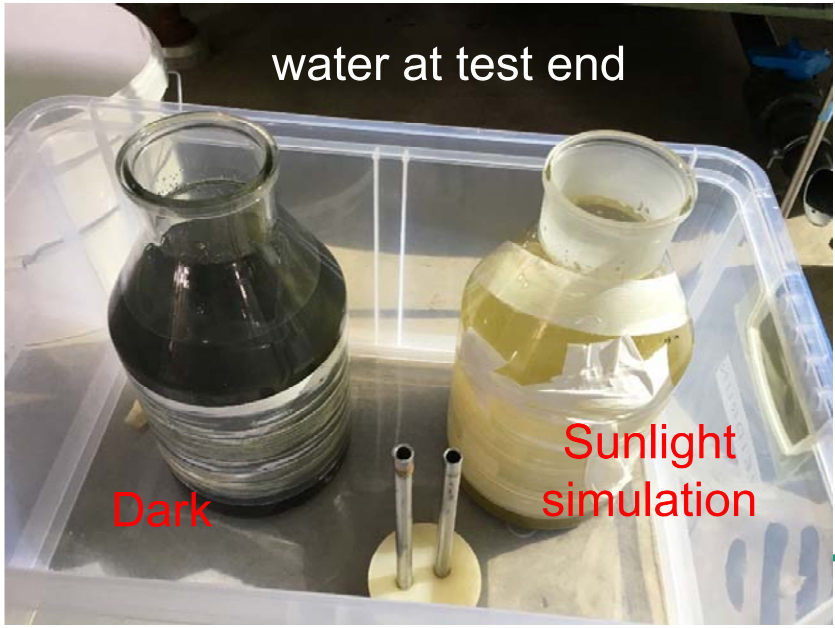
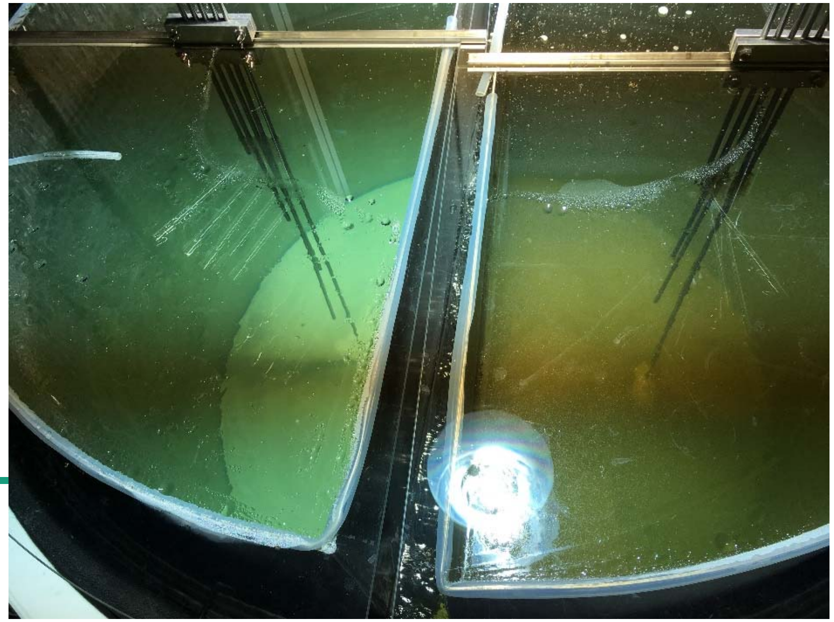
Results, further observations





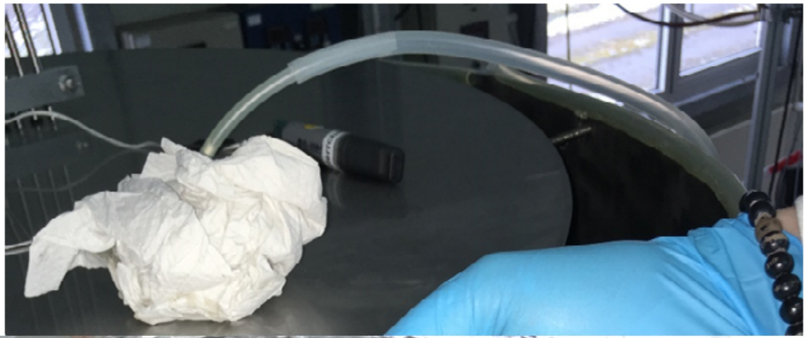
Sunlight simulation at test end

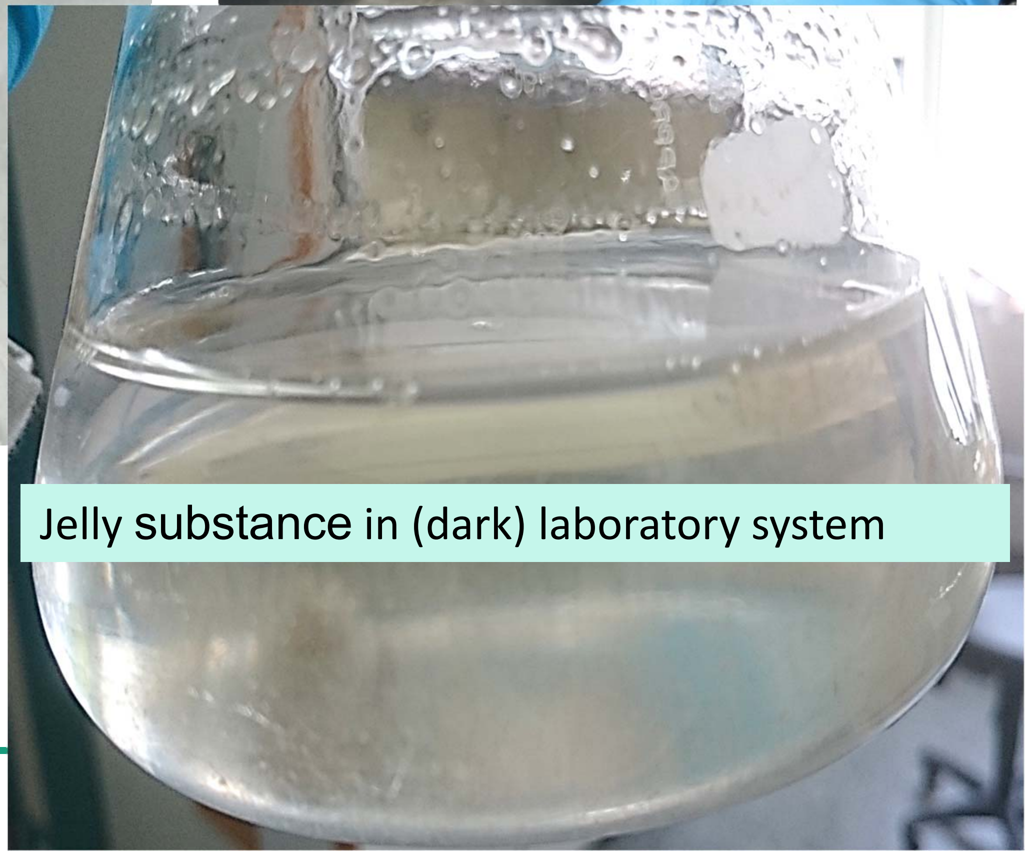


Results, further observations

„Dark“ at test end:

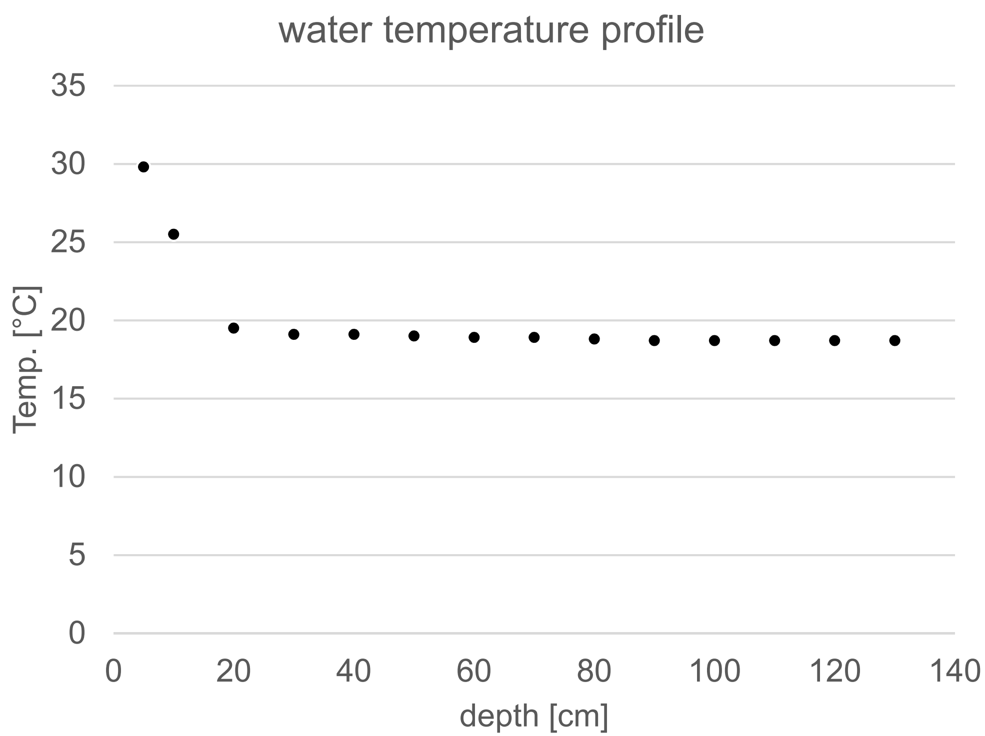
- strong smell (anaerobic)
- jelly layer on top (2-3 cm)
- observed in lab setup as well!





Results, further observations

Temperature profile in simulated sunlight setup:



<u>Temperature in 5 cm: 27°C</u>

below 20 cm: 20°C

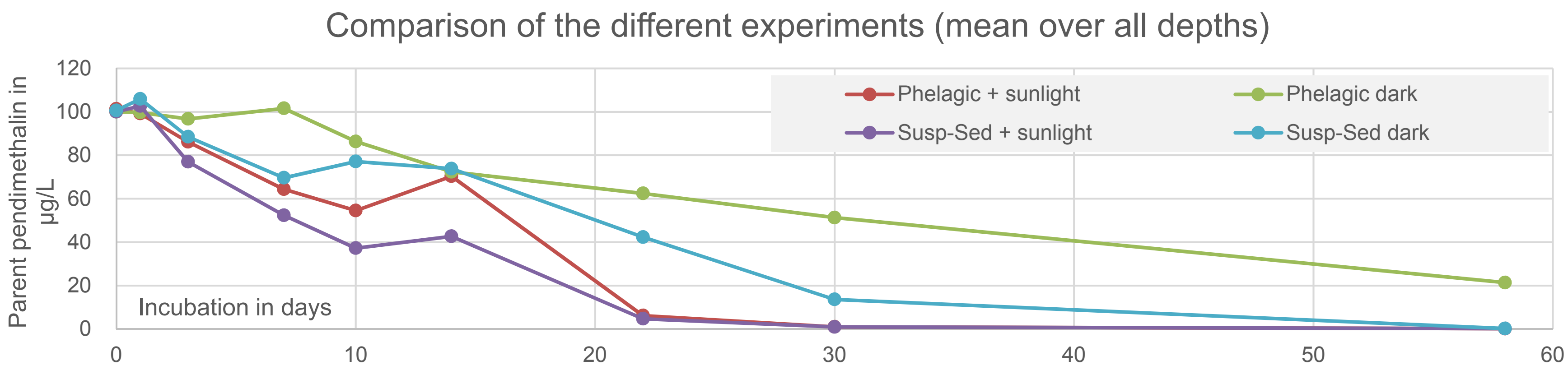
No mixing of layers:

energy of HQI-Lamp heats the upper water layer

but similar process in natural lakes

Summary of results

- ➢ Pendimethalin degrades in all test setups, but significant differences between the setups are observed. The degradation speed increases in the following order: dark phelagic < dark sediment < sunlight phelagic < sunlight sediment



- ➢ Degradation of pendimethalin on the water surface by direct photolysis as well as by indirect photolysis in deeper water depth.
- ➢ Decreasing light intensity in deeper water layers does not lead to different degradation products.
- ➢ The standard OECD 309 test should not be applied for the P-assessment of hydrolytically stable compounds which are sensitive for degradation under light in the aqueous phase, by direct and/or indirect photolysis.

Acknowledgements

The study was financed by BASF