Experimental and modeled degradation and distribution of Metilox® in pond mesocosm

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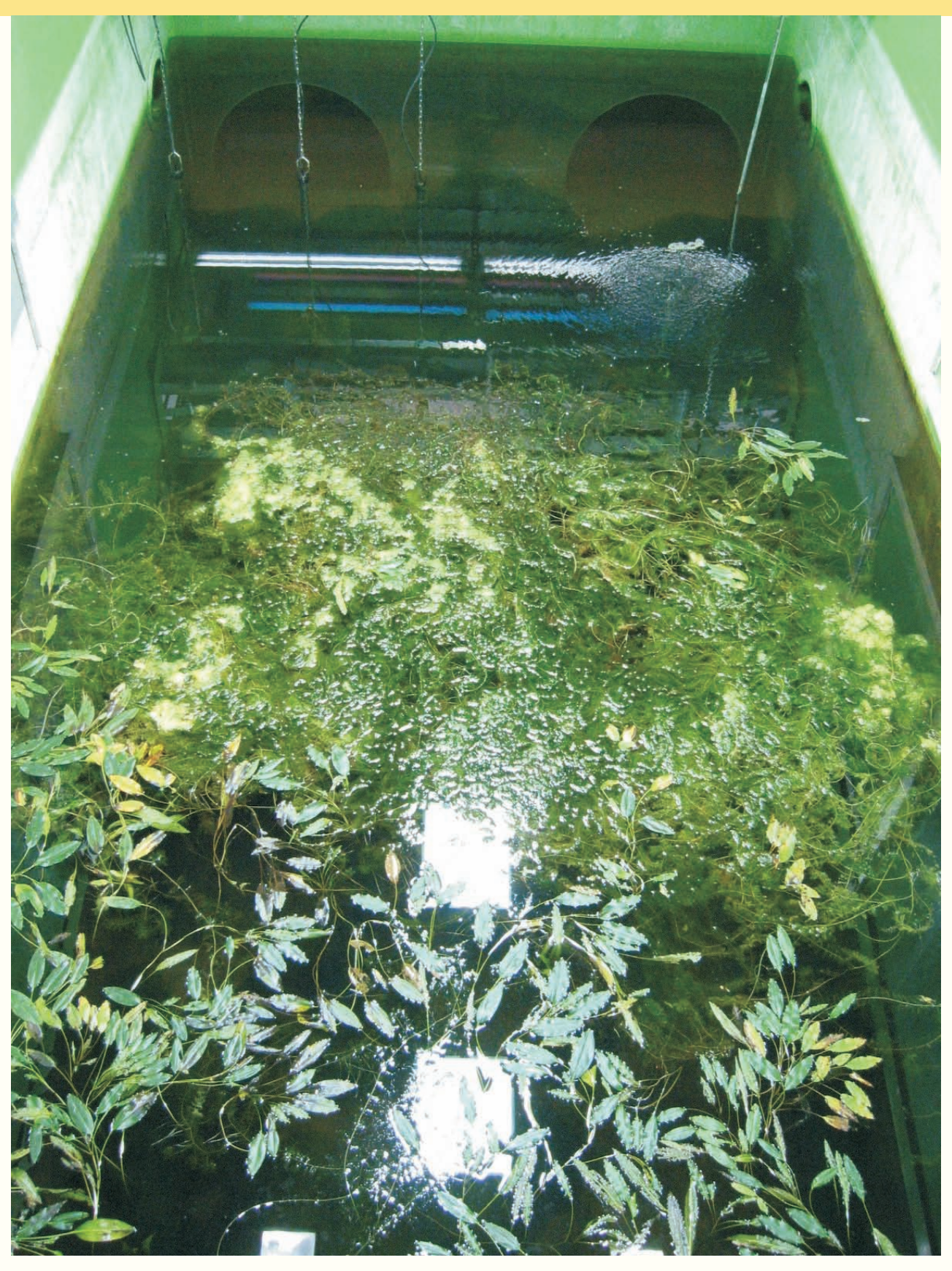

Fig. 1: Indoor pond with UV-lamps (indicated by blue reflexion), pond shown without dust protection

Introduction

Identified and assumed PBT (**P**ersistent, **B**ioaccumulative, and **T**oxic) substances are in general highly lipophilic and may rapidly adsorp at organic particels and surface areas in aquatic systems. Hence, only a very small part of the corresponding chemical is dissolved in the water phase. Moreover, a sub-group of PBTs is instable in water due to abiotic hydrolysis and photodegradation as demonstrated in laboratory standard tests. Metilox® (methyl 3-(3,5-di-tert.-butyl 4 hydroxyphenyl) propionic acid) seems a suitable model substance of this sub-group. Metilox® is a synthesis intermediate, but by now it is also used as an antioxidant in plastics and oils. Metilox® is poorly soluble, has been classified by the manufacturer as persistent and was therefore temporarily suspected to be a PBT-candidate. However, it hydrolyses in water to 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid (Metilox® acid) and probably undergoes photodegradation in the air (DT_{50}:19 h calculated by AOPWIN).

The crucial question arises whether the adsorption at particles may slow down or hinder the abiotic degradation under semi-natural conditions. For that reason, fate of Metilox® was investigated in large pond mesocosm systems with and without particle-bound application and with and without UV-light.

The kinetic rate constants were calculated using a mathematical fate model, which had been designed for typical PB-substances (see also Poster TU 162). These rates were then compared to rate constants of photodegradation and hydrolysis data, which had been generated in laboratory studies of the IME.

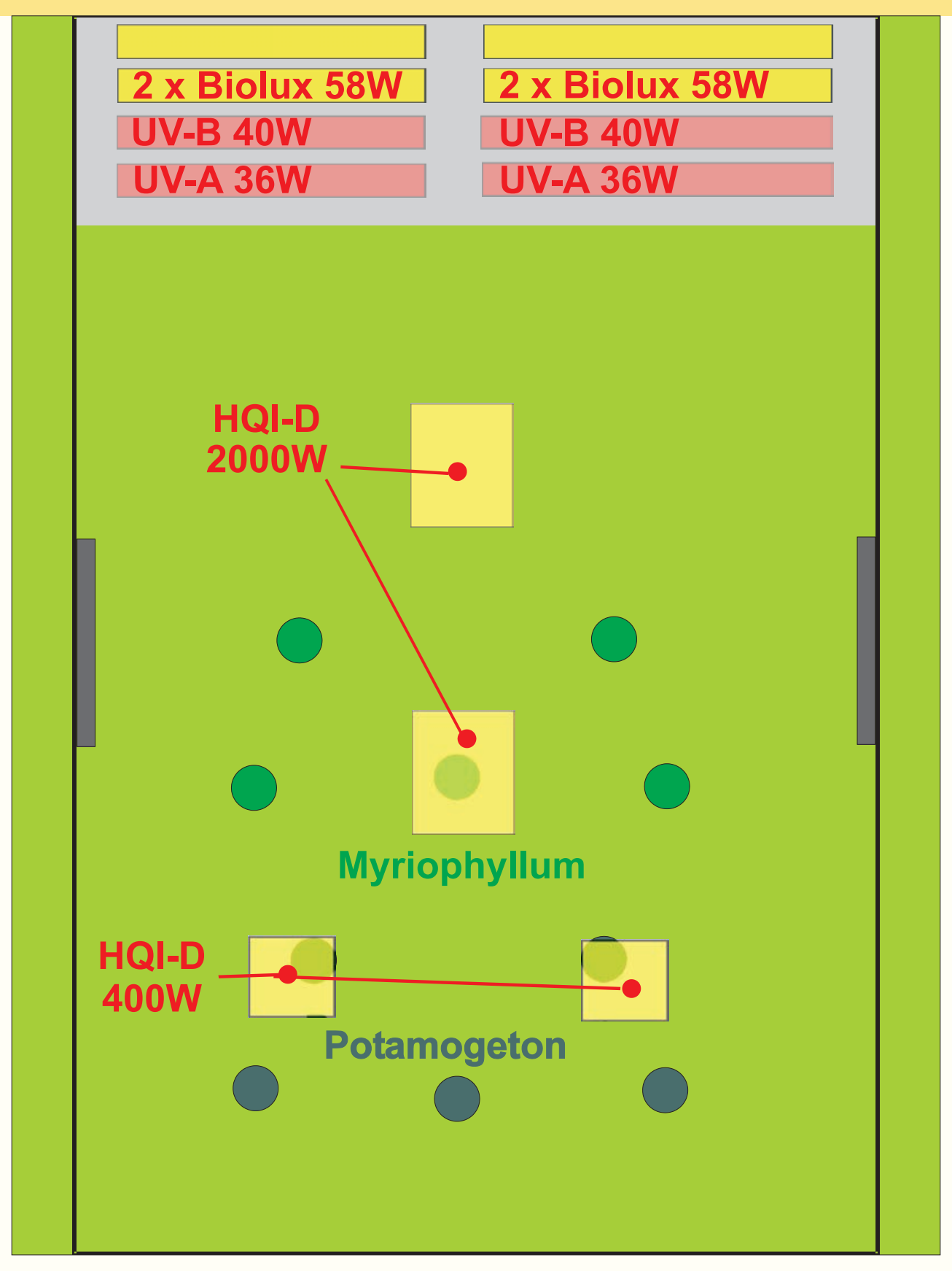

Fig. 2: Scheme of the artificial lighting and macrophyte planting (UV A/B tubes only in selected ponds)

Materials & Methods

Pond design

Size: length 690 x width 325 x height 250 cm
Water volume: 20-21 m^3
Artificial light: mean 13,000 lx, in one pond additional UV-fluorescent tubes (see Fig. 2)
Ground: sand covered with natural fine sediment
Macrophytes: *e.g. Myriophyllum verticillatum, Potamogeton nodosus*

Application

Liquid Application:
1 pond (marked as: -Celite), initial concentration 25 µg/L; Metilox® solved in ethanol/acetonitrile as solubilizer
Particle-bound application:
2 ponds (marked as: +Celite), initial concentration 25 µg/L and control; Metilox® 250 mg/750 g on inorganic carrier Celite 512 (diatomaceous earth), suspended in 200 L water.

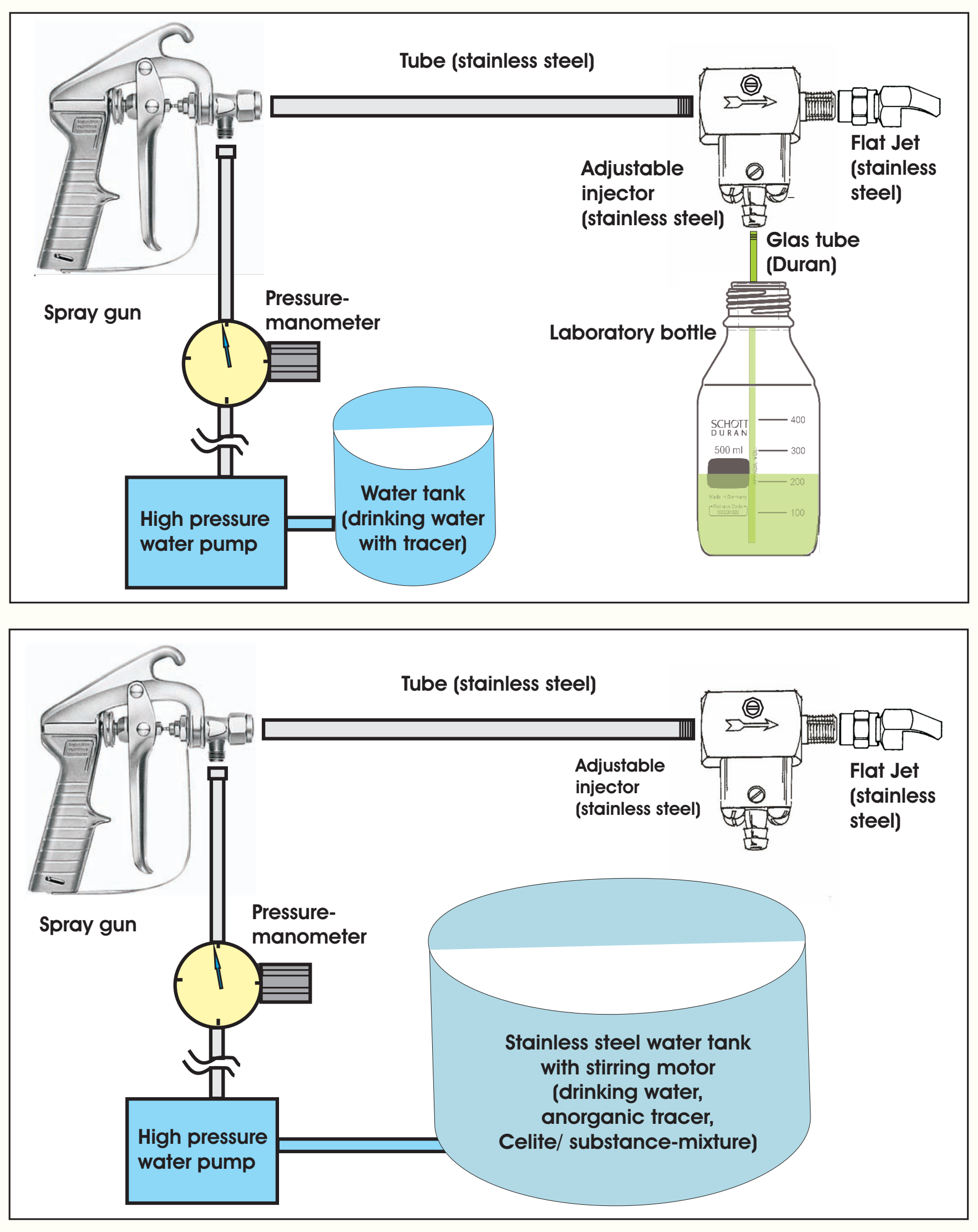

Fig. 3: Application: Liquid dosing of solved Metilox® (above), dosing of suspensed Metilox® (below)

Analysis

Analysis by GC-MS(SIM) after solid phase extraction (ENV) and derivatisation (PFB-Br).

Metilox® & light spectra

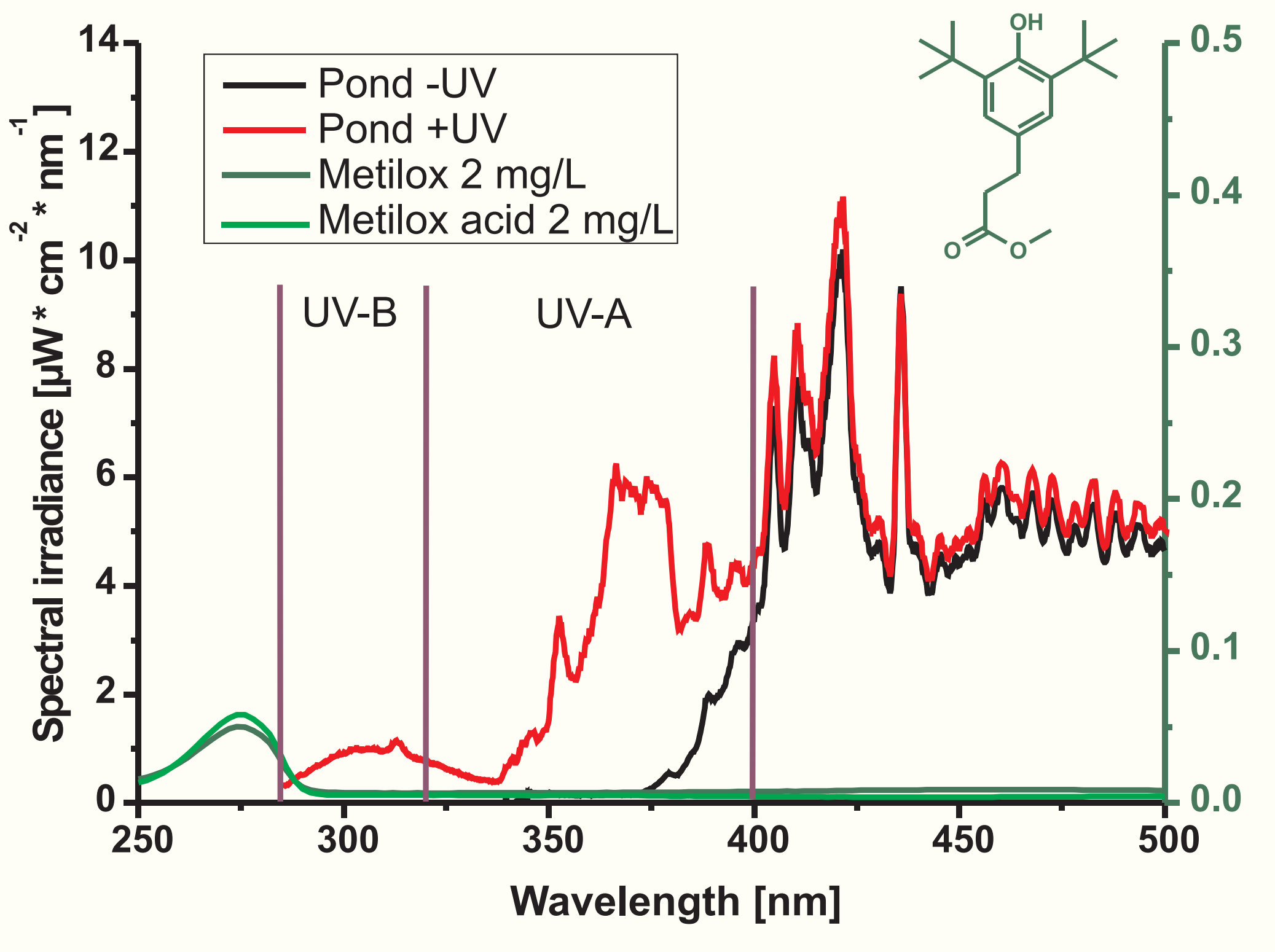

Fig. 4: Absorbance spectrum of Metilox® (green) and light spectrum of the pond illumination (water surface) with and without additional UV A/B-fluorescent tubes (red, black, resp.). Wave length classification acc. DIN 5031 T7) (below)

Fate model

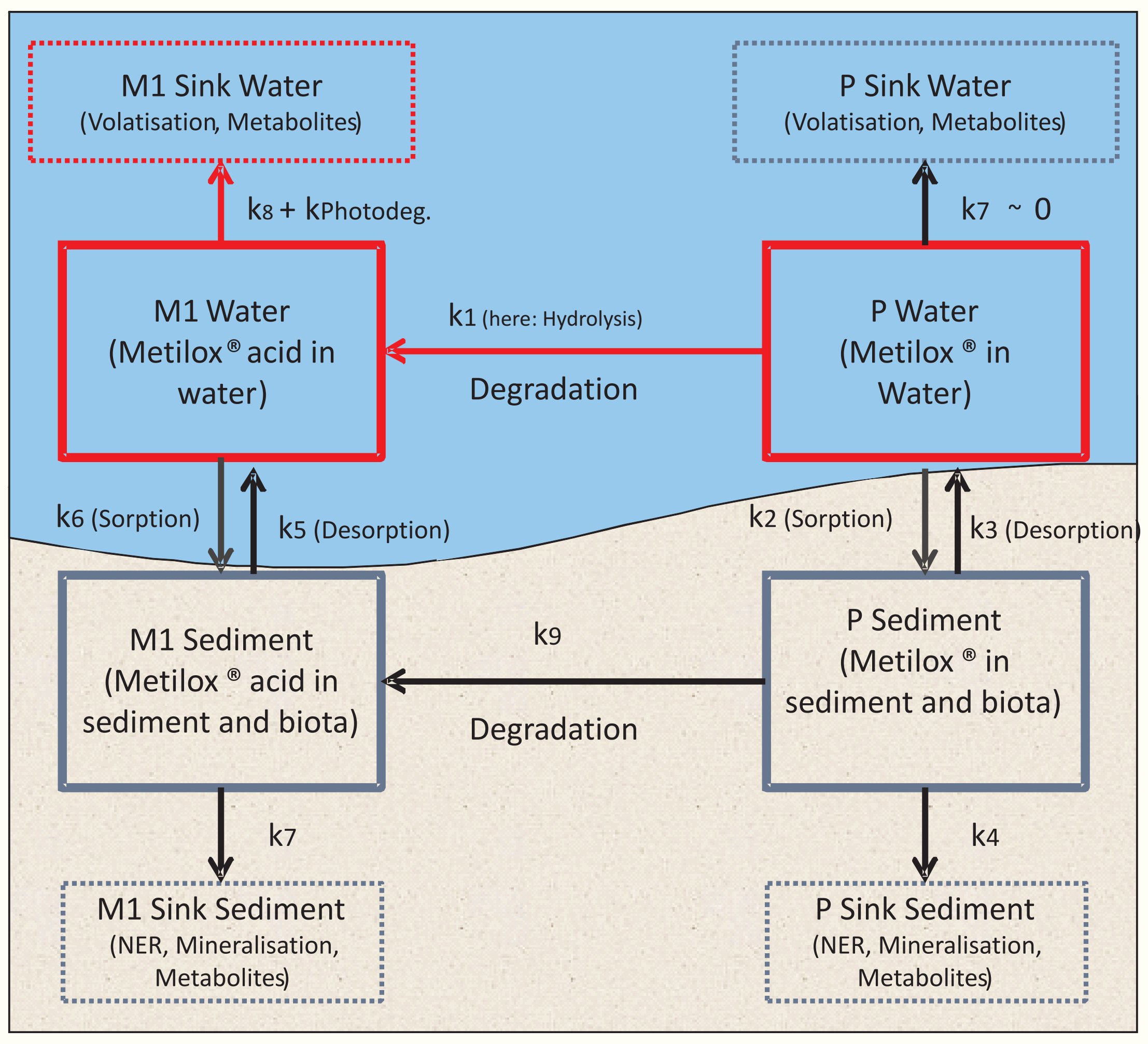

Fig. 5: Scheme of the fate model used for the calculation of kinetic rate constants. The red marked flows are the main processes of dissipation of Metilox®

Results

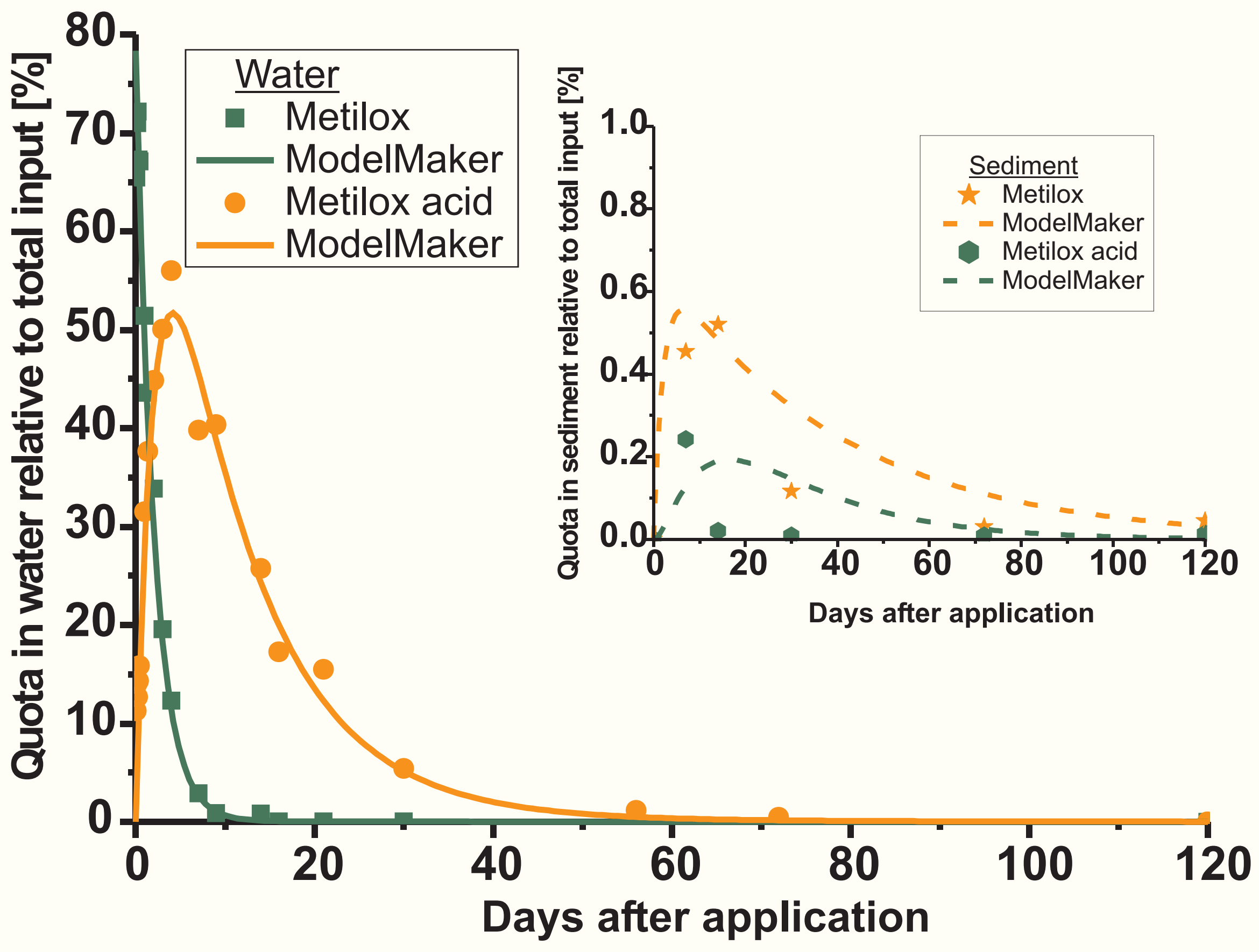

Fig. 6: Results of the model calculations (lines) and experimental data; pond with UV-light and particle-bound application of Metilox

Tab. 1: Results of the mesocosm and laboratory studies in comparison ($DT_{50\ system}$ = DT_{50} of Metilox® and Metilox®-Acid in water, sediment and biota relative to the start concentration); * DT_{50} calculated for annual mean natural sunlight irradiation

System	$DT_{50Hydrolysis}$	$DT_{50Photodeg.}$	$DT_{50System}$
Pond 1, 21°C -Celite, -UV	1,1 d	-	16 d
Pond 2, 21°C +Celite, -UV	1,3 d	-	14 d
Pond 3, 21°C +Celite, +UV	1,7 d	15,2 d	8,2 d
Pond 4, 11°C +Celite, -UV	5,5 d	-	38 d
OECD 111 25°C,Hydrolysis	2,9 d (pH 9)	-	-
OECD 316 Photodeg.	9,7 d	2,7 d 77 d *	2,1 d

- Metilox® hydrolyses rapidly under semi-natural conditions. The hydrolysis rate is in the range of the laboratory study (Tab.1).
- Metilox® and Metilox® acid were not persistent at room temperature.
- Negligible concentrations of Metilox® + Metilox® acid were detected in sediment and macrophytes (<0,5 % of initial concentration).
- Low concentrations of Metilox® occurred in periphyton (<2% of initial concentration).
- Besides Metilox® acid most probably further smaller, polar metabolites were formed, but not quantified for the mesocosm systems until now.
- Under additional UV-light the dissipation of Metilox® acid in water was accelerated.
- The calculated $k_{photodeg}$ (Fig. 5) is higher in comparison to the laboratory test result, if converted to natural sunlight irradiation.
- The mathematical model describes the measured data very well (Fig 6).
- Metilox behaved like a water soluble substance. Thus, the model can be simplified accordingly Fig.5 (red marked).

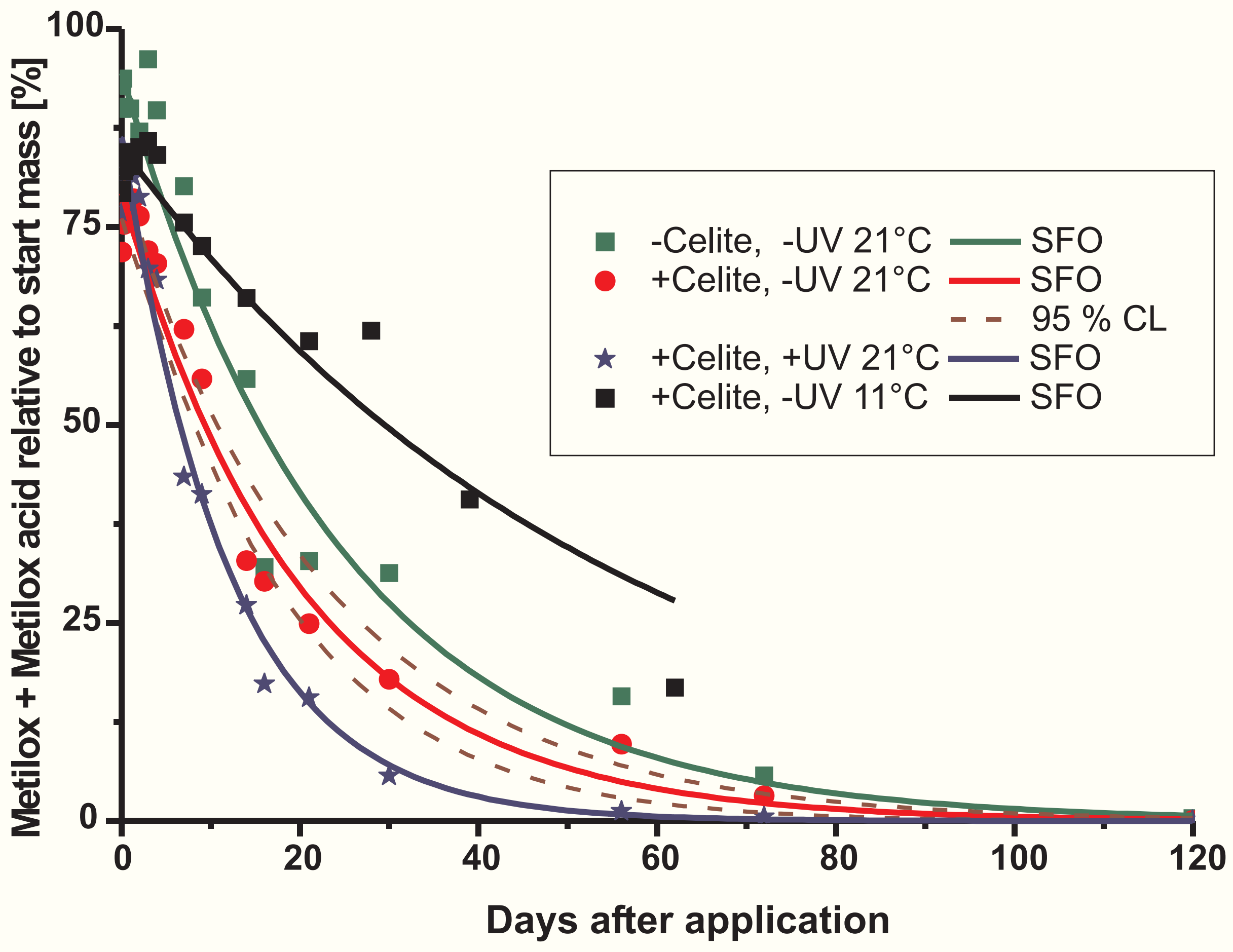

Fig. 8: Fate of Metilox® and metabolites in the whole system (water, sediment, biofilm, and macrophytes)

Discussion

- No influence of mode of application on hydrolysis of Metilox® was found.
- In comparison to the laboratory results no inhibiton of direct photolysis by particles could be observed. However, the inhibition may have been superimposed by other processes (e.g. indirect photolysis) and may be differ with the trophic status of the corresponding surface water.
- Abiotic degradation of Metilox® may be a relevant process in the environment.
- Only low concentrations of Metilox® and Metilox® acid were detected in sediment and biota.
- Further metabolites have to be quantified.
- In contrast to the literature, Metilox was degradable in this study.
- Mathematical kinetic models may provide useful indications for kinetic processes in fate studies even without the use of radiolabelling (no full mass balance feasible).

Literature:

[1] PBT-Working Group des ECB:
http://ecb.jrc.ec.europa.eu/DOCUMENTS/PBT_EVALUATON/PBT_sum065_CAS_6386-38-5.pdf
[2] OECD SIDS: Metilox 2001 UNIEP Publications
http://www.inchem.org/documents/sids/sids/Metilox.pdf

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