Fate of the antifouling biocide Irgarol 1051® in water and sediment of freshwater pond mesocosms

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FSA
Fließ- und Stillgewässer-
Simulationsanlage

Umwelt
Bundes
Amt
Für Mensch und Umwelt

Introduction

Irgarol 1051 (2-[tert-butylamino]-4-[cyclopropylamino]-6-methyltio-s-triazin) is an effective herbicidal booster biocide, commonly used as antifouling agent in coatings for hulls. Its usage in free-association antifouling paints leads to relevant release rates after boating (Fig. 1). For that reason, Irgarol has been detected in marine ports and marinas at concentrations up to 4.2 µg/L (Basheer et al. 2002). Compared to marine environmental concentrations, only few data on the exposition in freshwater are available. So far, maximum concentrations up to 0.23 µg/L Irgarol (Lake Mueritz, Mecklenburg-Western Pomerania, own analyses) have been found.

Fate of Irgarol after single dosing was studied under controlled conditions in the framework of a large-scale 150 d indoor mesocosm study employing 8 ponds (4 concentrations, 2 controls) since in the field its degradation and spreading behaviour is hard to determine. Besides Irgarol, the concentration of its toxic main metabolite M1 was analysed in water and sediment. Calculated degradation rates were compared to the rates determined from an outdoor stream mesocosm study of the UBA (Mailahn et al. 2005).

Fig. 1: Sampling station at Lake Mueritz, Mecklenburg-Western Pomerania, Germany

Fig. 2: One indoor pond of the artificial stream and pond system (FSA) of the UBA

Materials & Methods

Pond design
Size: length 690 x width 325 x height 250 cm
Water volume: 15 m³
Artificial light: mean 13,000 lx
Ground: Sand, natural fine sediment, littoral zone
Macrophytes: *Myriophyllum verticillatum* and *Potamogeton nodosus* (see: Berghahn et al. 2006 - SETAC)
Stocking: Plankton and makroinvertebrates from nearby mesotrophic lakes and ponds

Experimental design
Single application of Irgarol (11-04-05) in 6 mesocosms at different concentrations (1 x 0.04/ 2 x 0.2/ 1 x 1/ 2 x 5 µg/L nominal). Two systems served as controls. Application of LiBr as additional tracer.
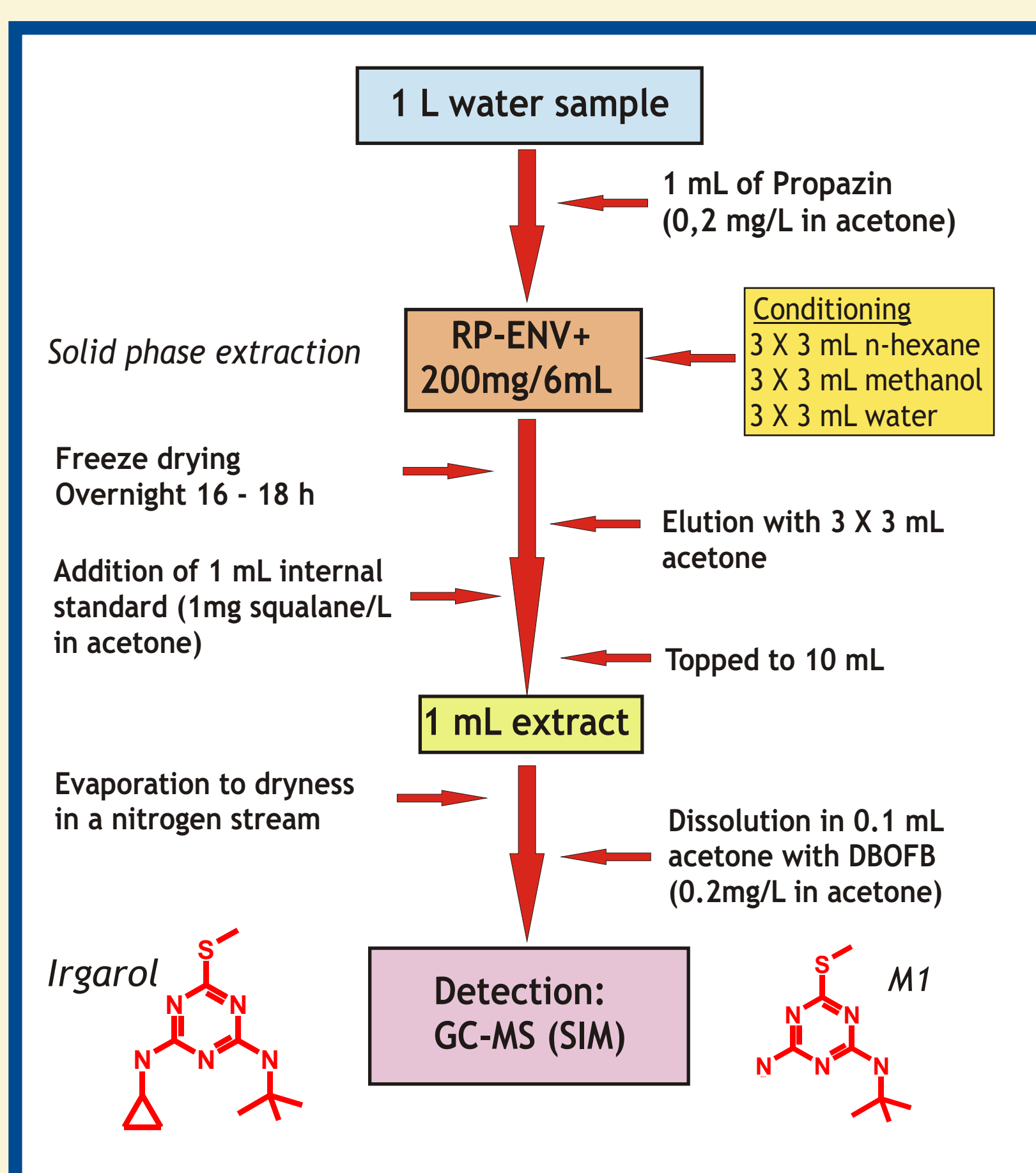
Analysis

1 L water sample
↓
1 mL of Propazin (0,2 mg/L in acetone)
↓
Solid phase extraction
RP-ENV+ 200mg/6mL
Conditioning
3 X 3 mL n-hexane
3 X 3 mL methanol
3 X 3 mL water
↓
Freeze drying Overnight 16 - 18 h
Elution with 3 X 3 mL acetone
↓
Addition of 1 mL internal standard (1mg squalane/L in acetone)
Topped to 10 mL
↓
1 mL extract
↓
Evaporation to dryness in a nitrogen stream
Dissolution in 0.1 mL acetone with DBOFB (0.2mg/L in acetone)
↓
Irgarol → Detection: GC-MS (SIM) → *M1*

Fig. 3: Analysis scheme of water samples

60 g of wet sediment
-50 g dry mass
↓
Addition of 70 mL of acetone
Treatment in a sonic bath (30 min)
Settling (10 min)
Centrifugation (15 min, 4000 rpm)
3 times repeated
↓
Supernatant
Settable residue
↓
Combined extracts
↓
Evaporation to 10 mL in a rotary evaporator
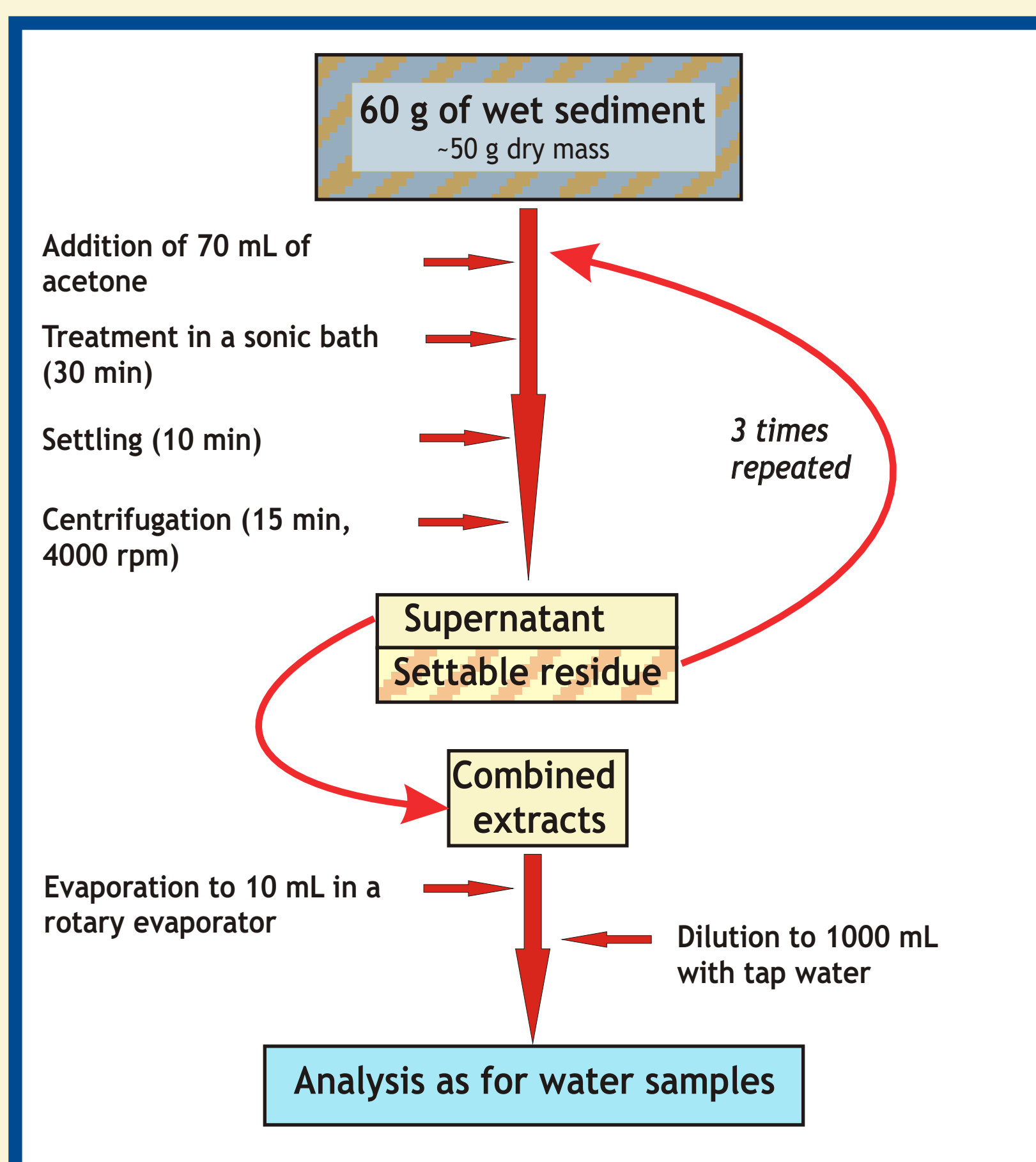Dilution to 1000 mL with tap water
↓
Analysis as for water samples

Fig. 4: Analysis scheme of sediment samples

Results
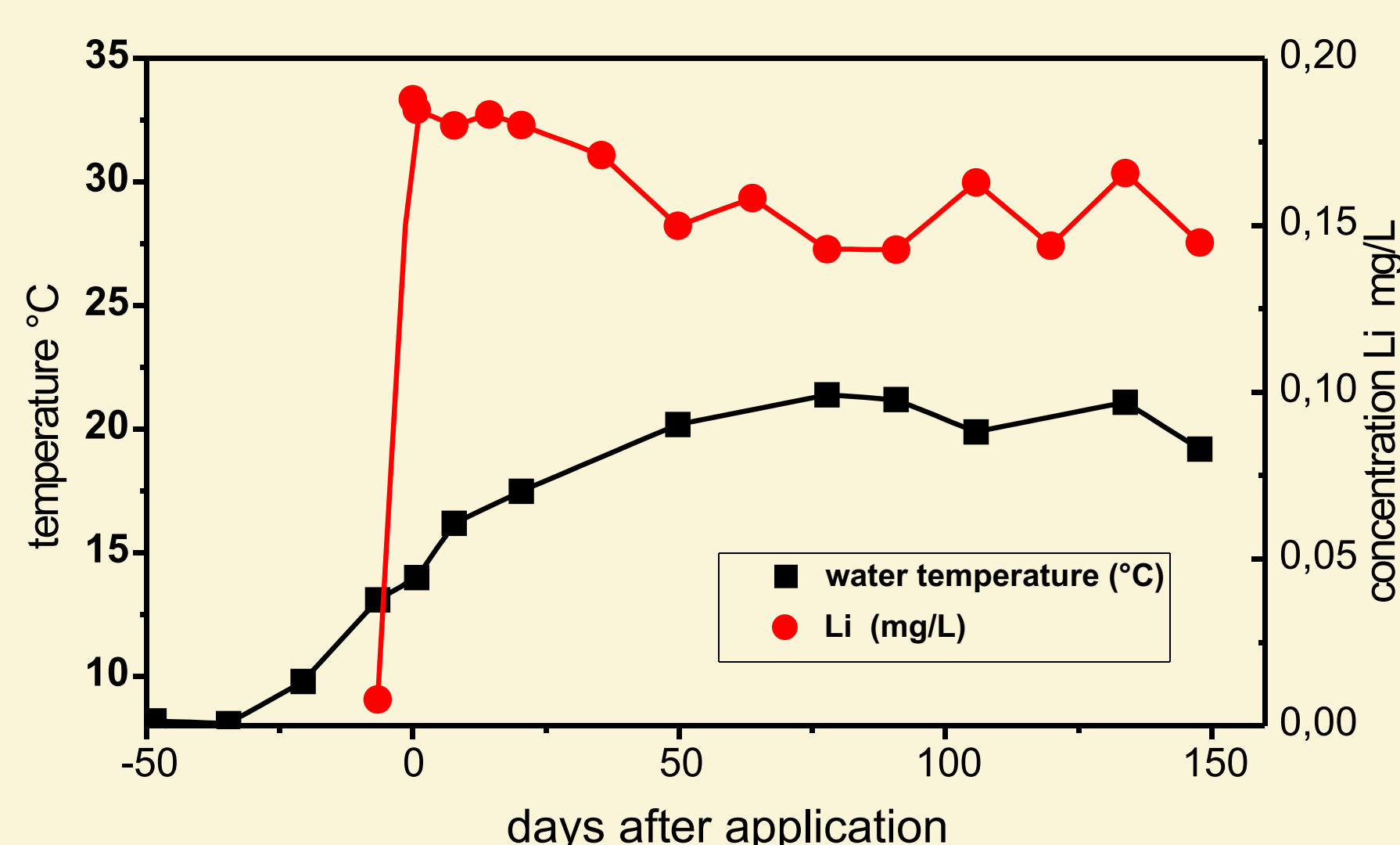
Fig. 5: Water temperature and Li-concentration (Tracer) in one of the pond systems

- Degradation kinetics are concentration-dependent.

- A strong decrease of Irgarol in the water body was already detected in the first 2-3 weeks after application. In a second phase between day 20 and day 120 the decrease of Irgarol continued at a slower rate. At lower initial concentrations (<=1 µg/L) degradation went on in a third phase at even much slower rates (Fig. 8).

- The metabolite M1 increased at a nearly constant rate until day 100 and the degradation rate of M1 was significantly lower compared to Irgarol (Fig. 6).

- The concentration of Irgarol and M1 in sediment increased in the first 2 weeks up to 4 µg Irgarol/kg. The maximum concentration of Irgarol (6 µg/kg) was detected at day 47 and of M1 (1 µg/L) at day 90 (Fig. 7).

- Physical parameters like temperature, exchange of water body with interstitial water (Li was used as tracer) and water level were monitored (Fig. 5).

Kinetics

Single first order models (SFO) do not provide an acceptable description of the degradation of Irgarol. The fast degradation in the first phase is attributed to sorption effects, the second phase mainly to biodegradation. The third phase cannot be well-defined due to the lack of data after more than 150 days, so only trend information was derived.

In accordance with the recommendations of the FOCUS Working Group, the "1st + 1st" order model 'Double First Order in Parallel' (DFOP) was used. The quality of the fit was checked with the Chi²- and R²-Test.

By use of the bi-exponential model the half-live (DT_{50}) increased with time. For that reason, two half-lives were calculated for each concentration (Tab. 1).

Modell: ExpDecay 1and 1
c=A1*exp(k1*t) + A2*exp(k2*t)

Chi^2: 0.0459   R^2: 0.97708
A1: 1.2394   k1: -0.37383
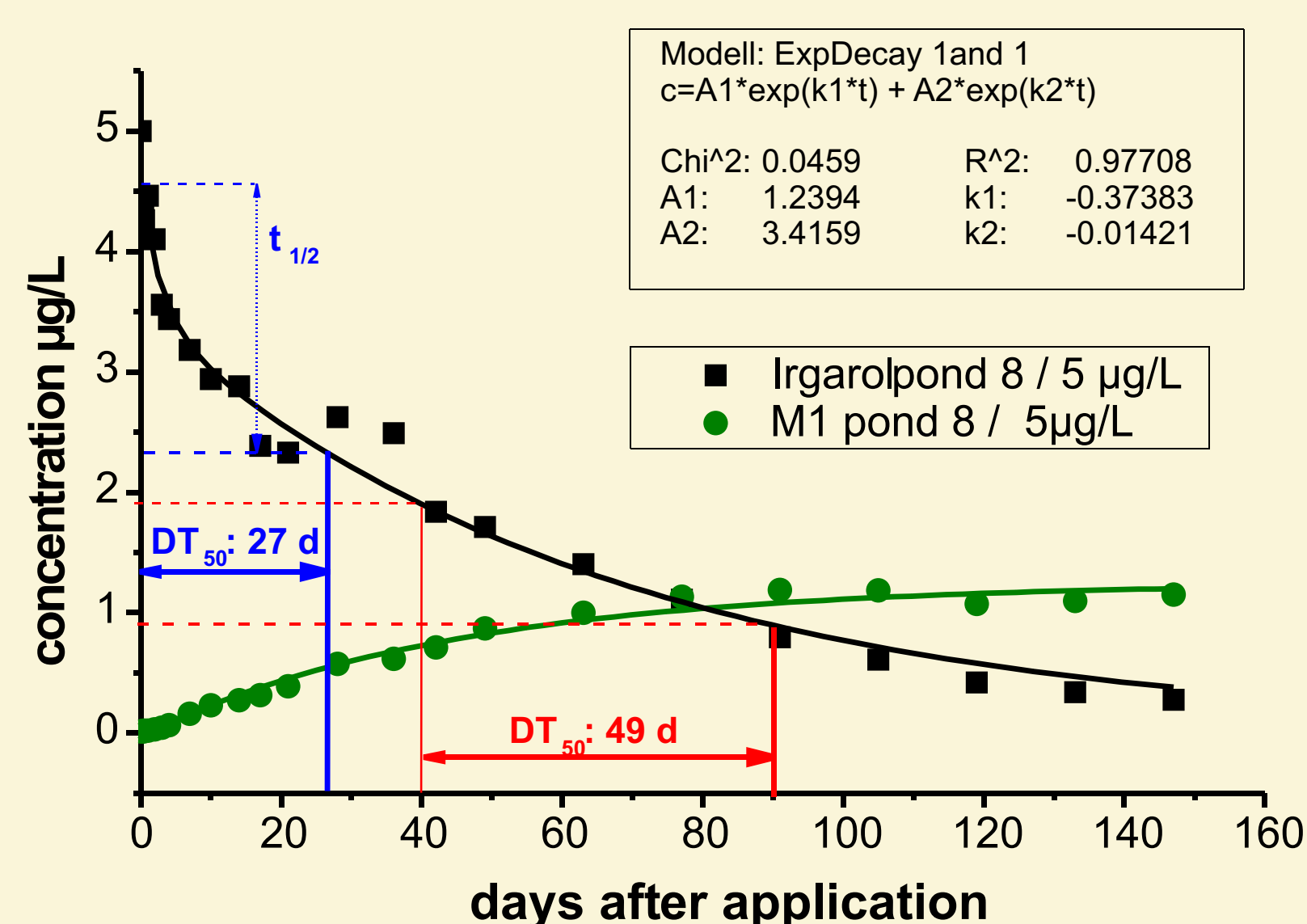A2: 3.4159   k2: -0.01421

Fig. 6: Concentration of Irgarol and the metabolite M1 in the waterbody of the ponds with highest start concentration (pond 8: 5 µg/L)

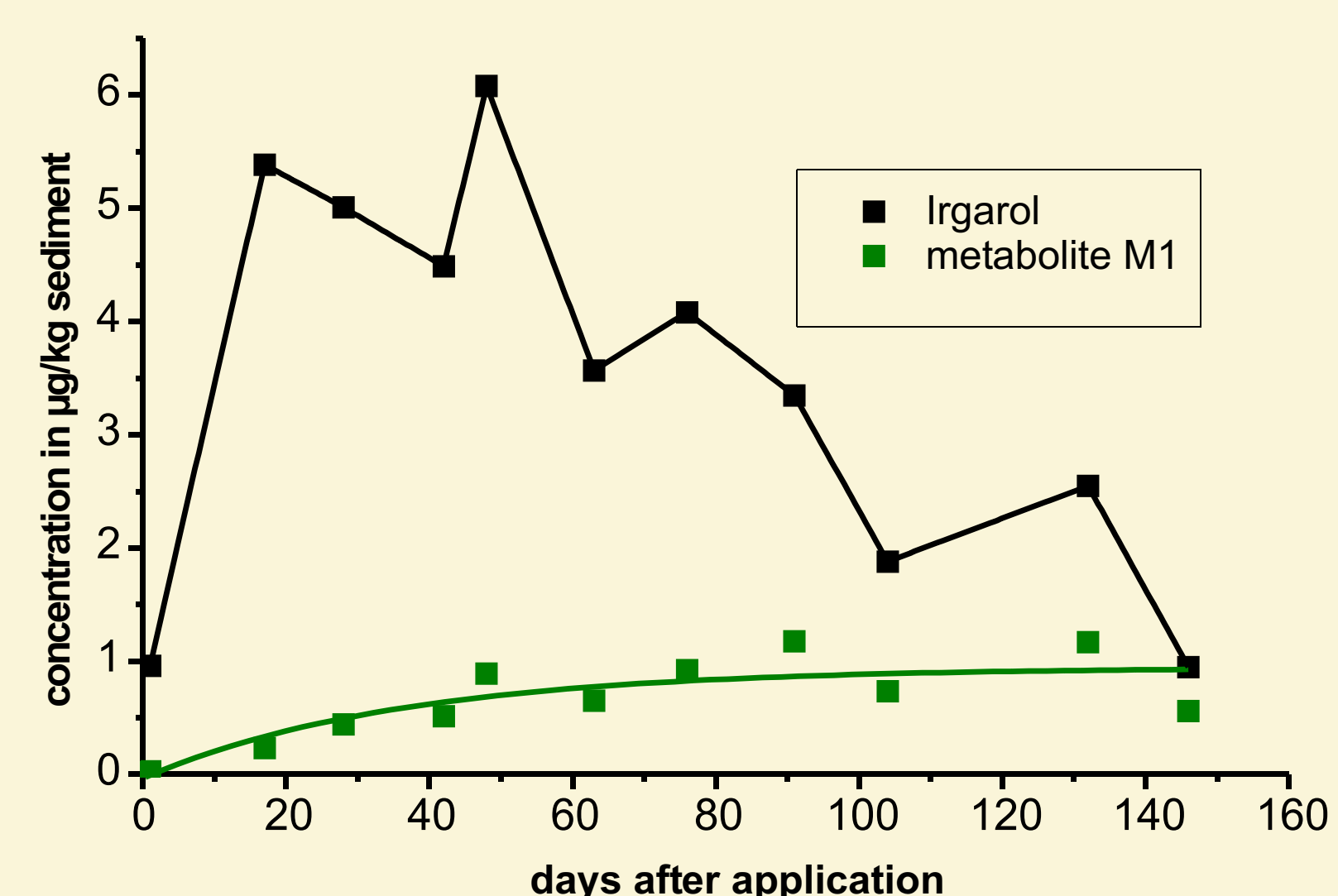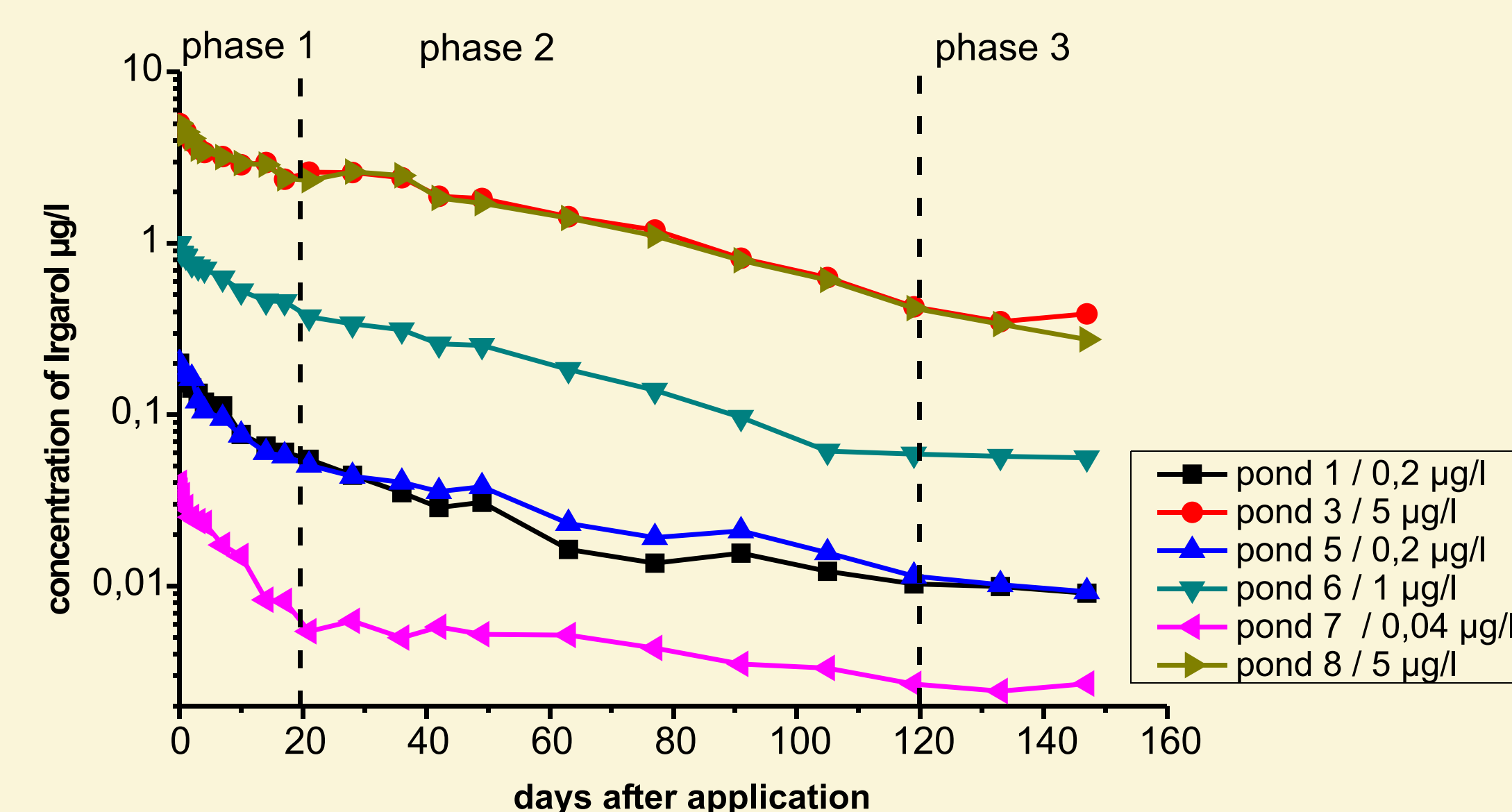Fig. 7: Concentration of Irgarol and the metabolite M1 in the sediments of the ponds with highest start concentration (pond 8 - 5 µg/L)

Fig. 8: Degradation curve of Irgarol in water of the pond mesocosms (logarithmic scale)

Nominal concentration	R^2	Chi^2	Half-live DT_{50} (days)		
			Phase 1	Phase 2	Phase 3
5 µg/l - Stream outdoor	0,978	0,068	8,5	35	+
5 µg/l - Pond 3 indoor	0,985	0,034	24,5	48	+
5 µg/l - Pond 8 indoor	0,977	0,046	27	49	o
1 µg/l - Pond 6 indoor	0,994	0,0006	14	36	+
0,2 µg/l - Pond 1 indoor	0,983	<0,0001	8,5	38	+
0,2 µg/l - Pond 5 indoor	0,989	<0,0001	5,5	47	o
0,04 µg/l - Pond 7 indoor	0,984	<0,0001	6	109	+

Tab. 1: Fitting Quality and Half-lives (DT_{50}) of Irgarol; phase 1: lost after application; Phase 2: loss between day 20-120 after application, phase 3: loss after day 120 (o = no change to phase 2; + tendency of increase of Dt_{50})

Discussion

- In this study the degradation of Irgarol after single application was simulated. The degradation of Irgarol is a complex process of sorption/desorption, biodegradation and bioaccumulation.

- The degradation can be adequately described with an bi-exponenial model. The half-lives calculated for primary degradation are concentration depend between 36 and 109 days (valid until day 120 after dosing).

- The degradation in the outdoor stream was slightly faster (at lower temperature), but could be explained by the favourable surface to water ratio; direct photolysis seems to be not important.

- Analysis of accumulation in plants are still in progress.

References:
Basheer *et al.* 2002, Mar. Pollut. Bull. 44 (7): 697-703. FOCUS Work group on Degradation Kinetics 2004 http://www.epa.gov/oppelfed1/models/water/recommend_kinetics.htm. Mailahn *et al.* 2005, SETAC Basel.
Schmidt *et al.* 1985, Appl. Environ. Microbiol.Vol.50(No. 2): 323-331.