



Fig. 1: Boat hull which is prepared for the use of an antifouling paint

Introduction

The s-triazine Irgarol is an effective booster biocide to prevent fouling organisms on ship hulls (Fig. 1). It inhibits the electron transport chain of the Photosystem II and is therefore highly phytotoxic. For the Prymnesiophyta an effect concentration (EC_{50}) of $0.07 \mu\text{g/L}$ was attested for the endpoint 'photosynthetic pigments' (Readman et al. 2004). Until now, only very few data of effects and behaviour of Irgarol are available for freshwater sites and organisms. To close this gap of knowledge, impacts of Irgarol on freshwater periphyton communities (photosynthetic pigments and species composition) were investigated as part of a comprehensive 150 d indoor mesocosm study (Fig. 2 and 3).

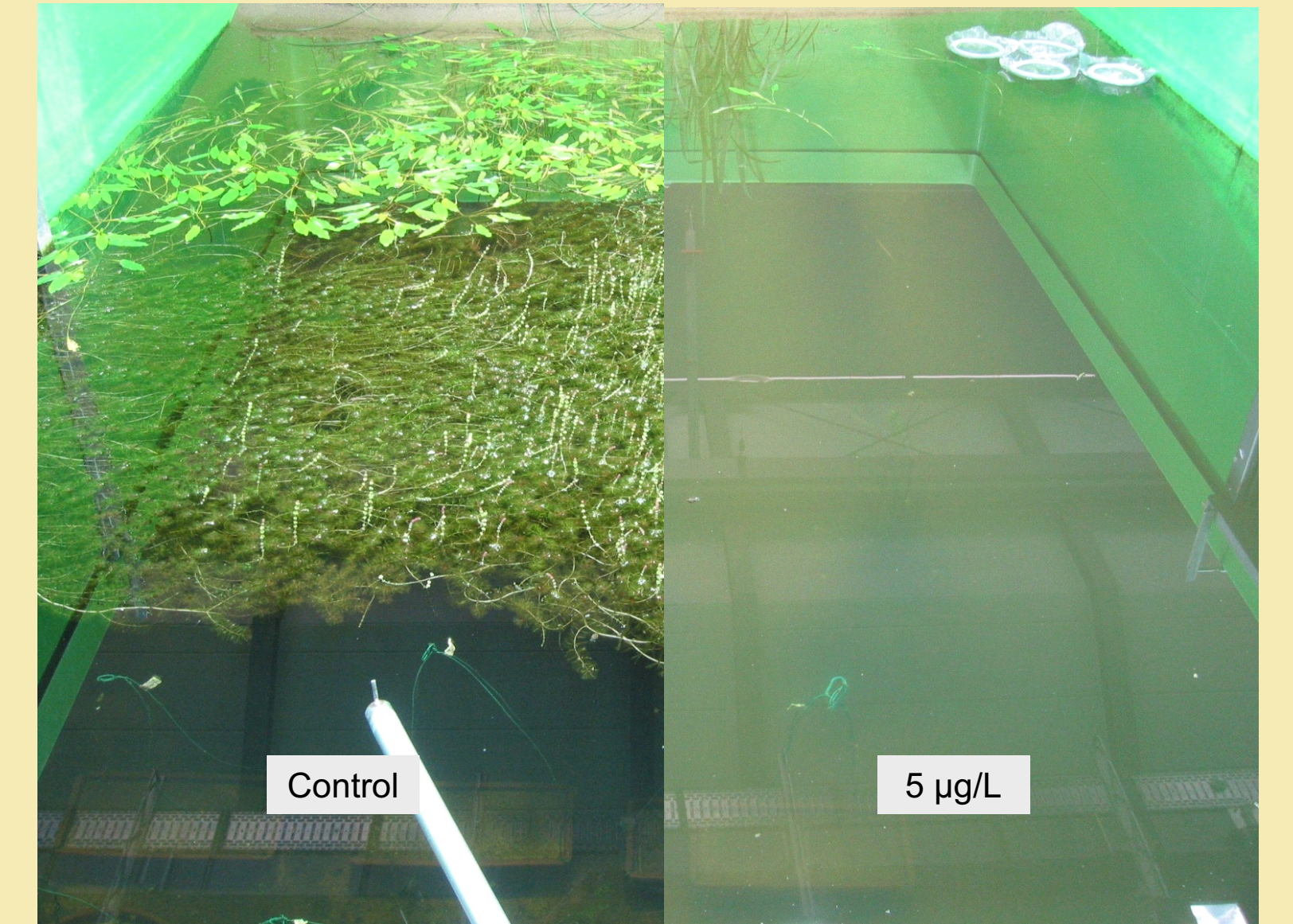


Fig. 2: Control pond and pond contaminated with $5 \mu\text{g/L}$ Irgarol (14.06.05)

Materials and Methods

Pond design

Size: length 690 x width 325 x height 250 cm

Water volume: 15 m^3

Artificial light: mean 13,000 lx

Nutrient regime: TP $>0.02 \text{ mg/L}$; TN $>0.7 \text{ mg/L}$

Biological establishing

Ground: Sand, natural fine sediment, shore area

Macrophytes: *Myriophyllum verticillatum* and *Potamogeton nodosus* had been planted in the littoral zone.

Stocking: Plankton from nearby mesotrophic lakes and ponds



Fig. 3: Photo of a pond mesocosm

Experimental design

- Single application of Irgarol (11-04-05) in 6 mesocosms at different concentrations (1 x $0.04/2 \times 0.2/1 \times 1/2 \times 5 \mu\text{g/L}$ nominal). Two systems served as controls.
- Exposition of 7 PP sheets each (IBICO DIN A 4, divided into equal strips, exposition at a depth of 0.3 m) per pond on 04-03-04
- Removal of one strip per exposed sheet (Fig. 4, 6 and 9; 7 per pond). All strips were scraped, suspended in de-ionised water and pooled for further treatment.
- Pigment analysis by HPLC (according to Woitke et al. 1994).
- EC_{50} calculation by Probit analysis (SPSS 11) and analysis of periphyton community response by principle response curve (PRC) analysis using CANOCO (version 4.5)



Fig. 4: A PP sheet divided into strips

Pigment analysis

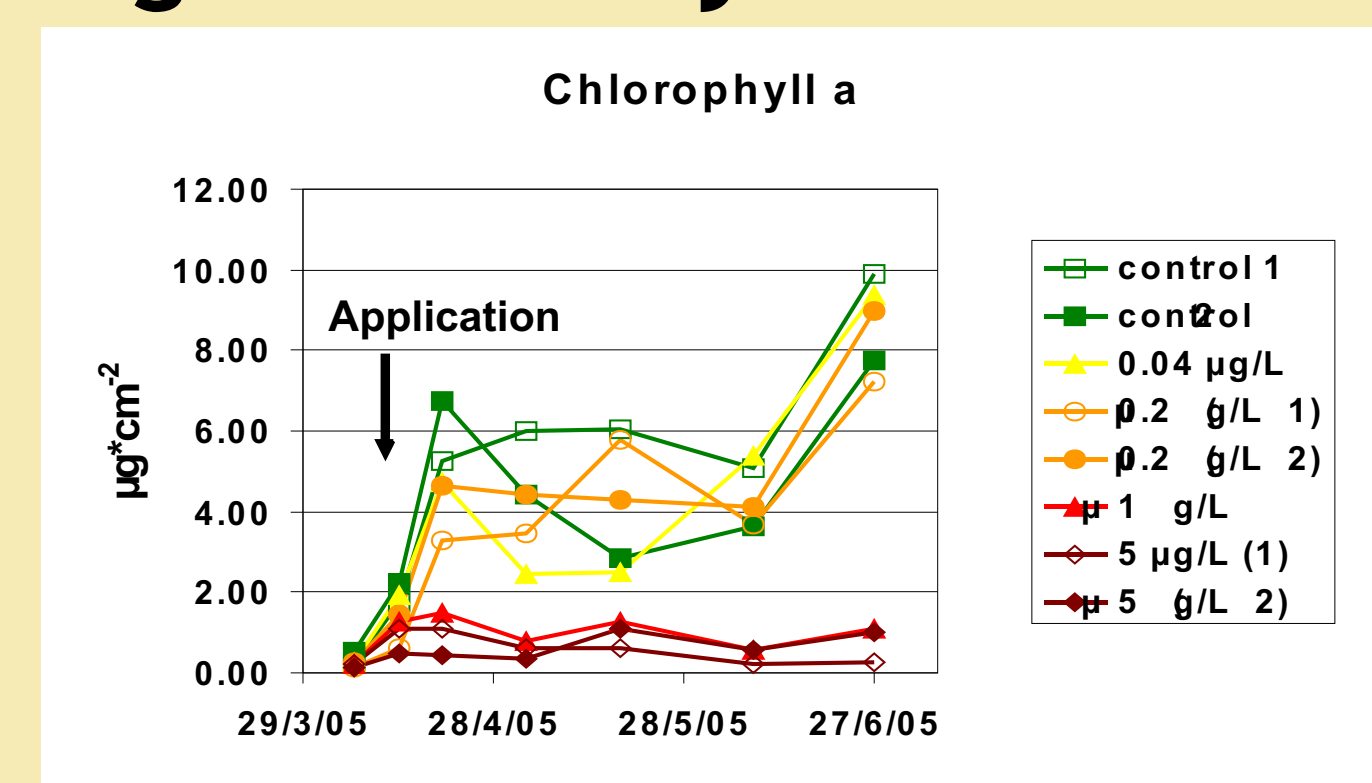


Fig. 5: Dynamics of chlorophyll-a on the substrates at the different Irgarol concentrations.

Species composition

- At any time diatoms dominated the pond systems (33 taxa) while green algae (9 taxa), cyanobacteria (5) and yellow green algae (1; Xanthophyceae) were only present to a lesser extent.
- The PRC analysis showed a strong concentration dependent response (Fig. 7) and underlined the results from the pigment analysis in which significant effects occurred at concentrations higher than $0.2 \mu\text{g/L}$ Irgarol.
- *Amorpha* spp. and *R. abbreviata* reacted with an decrease in abundance (positive species weights; Fig. 7 and 8) while the diatom *Centrales* reacted with an increase in abundance after Irgarol application. However, the genus occurred only in two samples at higher abundances in the highly contaminated ponds.

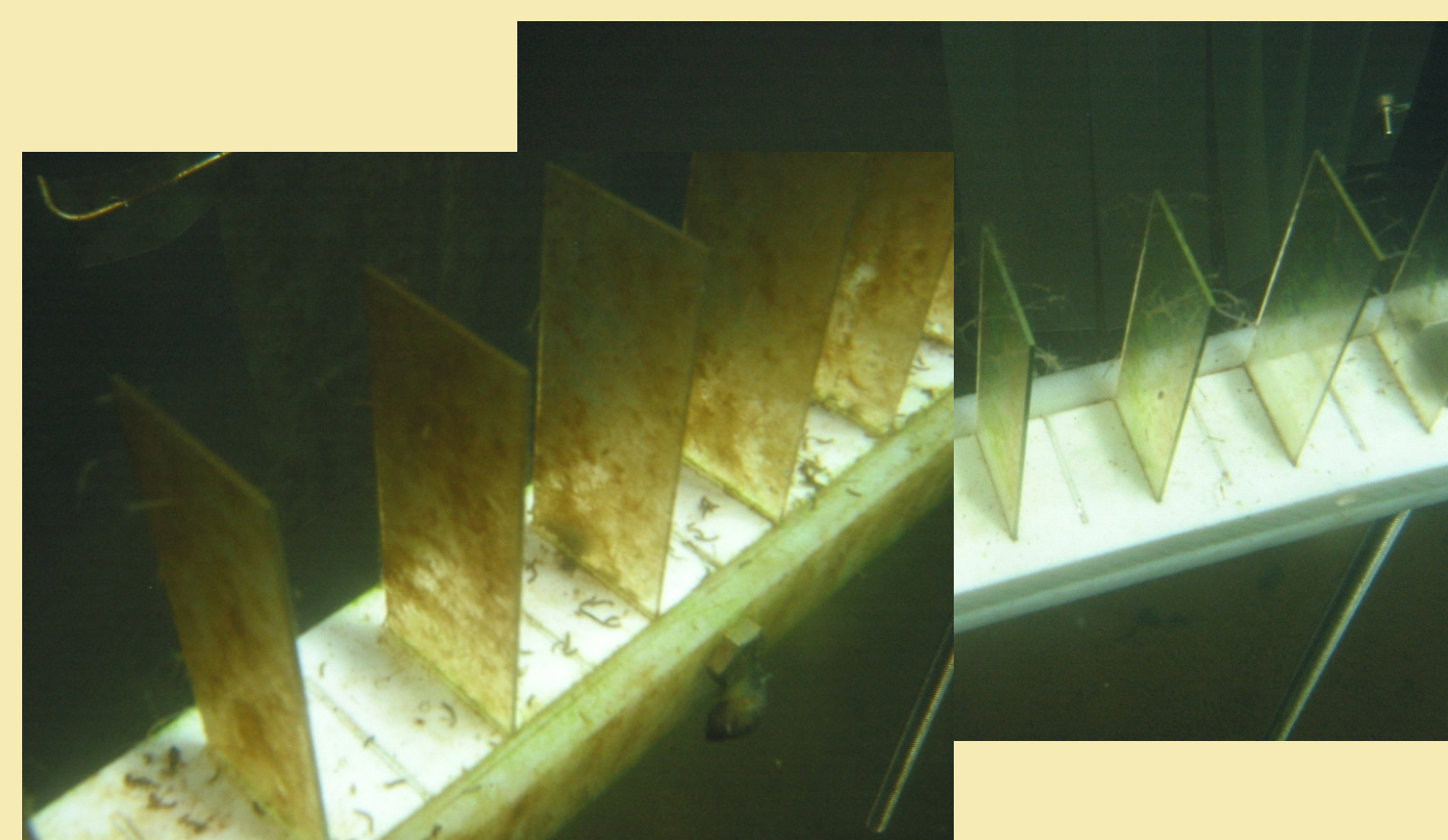


Fig. 9: Irgarol exposed periphyton slides. Left: control; right: $5 \mu\text{g/L}$

Discussion

As a photosystem II inhibitor, Irgarol may have an effect on all autotrophic organisms. However, in a microplate assay Bérard et al (2003) found for diatom species a higher variability in sensitivity (EC_{50} ranged from 0.5 to $253 \mu\text{g/L}$ Irgarol) than for green algae (0.5 to $5.1 \mu\text{g/L}$). Diatoms may be able to compensate the negative effects of Irgarol by switching to photosystem I. This may explain why the diatom *Centrales* reacted with an increase in abundance in this study.

References: Bérard et al. 2003, Chemosphere 53: 935-944. Readman et al. 2004, Mar. Environ. Res. 58 (2-5): 353-358. Woitke et al. 1994, Fresenius J. Anal. Chem. 348: 762-768.

Thanks to: M. Dewitz, A. Hawliczek, S. Pioch, R. Schmiediche, I. Schmiedling and FG IV 2.5

Results

- The pigment analysis revealed that all photosynthesis pigments found in the samples could be assigned to diatoms and green algae. Typical pigments of cyanobacteria were not detected.
- Already 10 days after Irgarol application, strong effects on the Chlorophyll-a concentrations in the highly contaminated systems (1 and $5 \mu\text{g/L}$) were notable and remained till the end of sampling (Fig. 5).
- For the parameter chlorophyll-a, an EC_{10} of $0.017 \mu\text{g/L}$ and an EC_{50} of $0.32 \mu\text{g/L}$ were calculated (10 d, nominal).

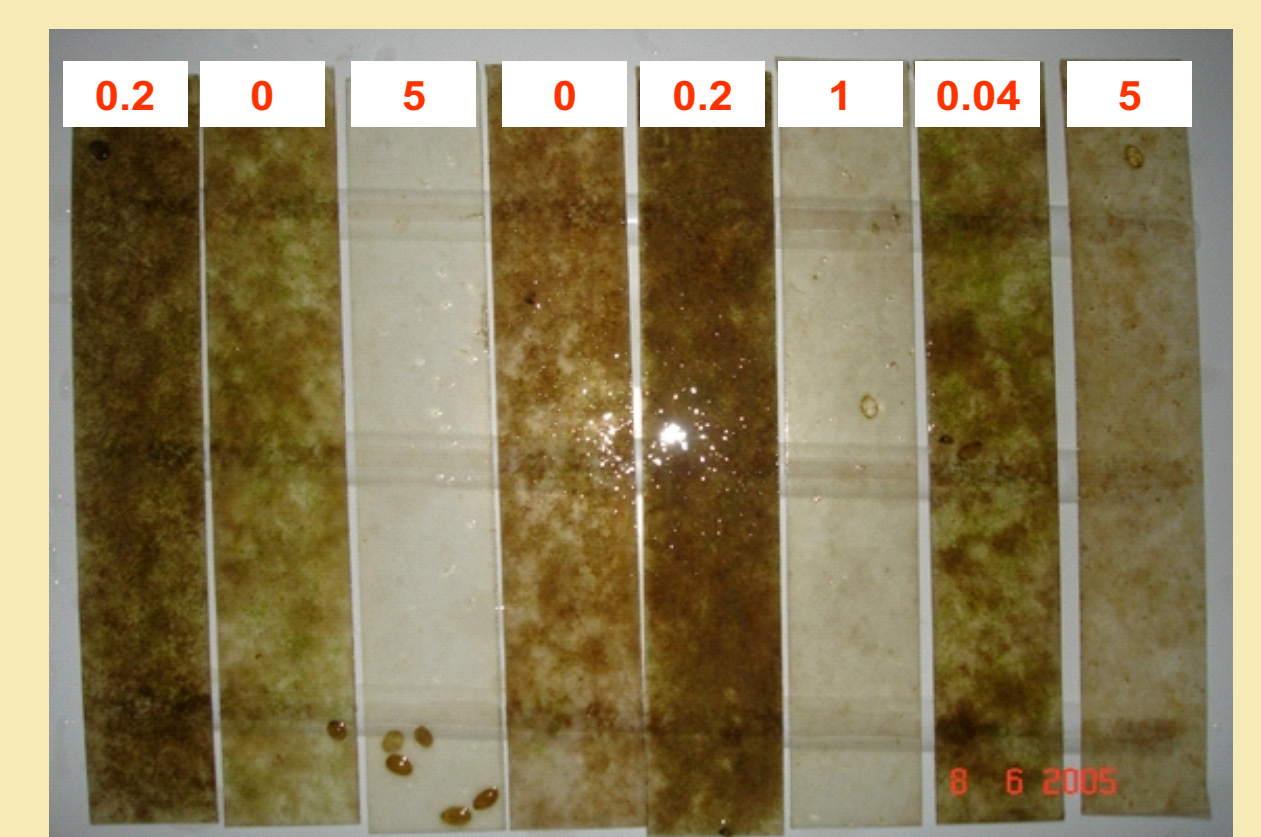


Fig. 6: Strips from the ponds 1-8, from left to right (08-06-2005). Numbers: nominal concentration in $\mu\text{g/L}$

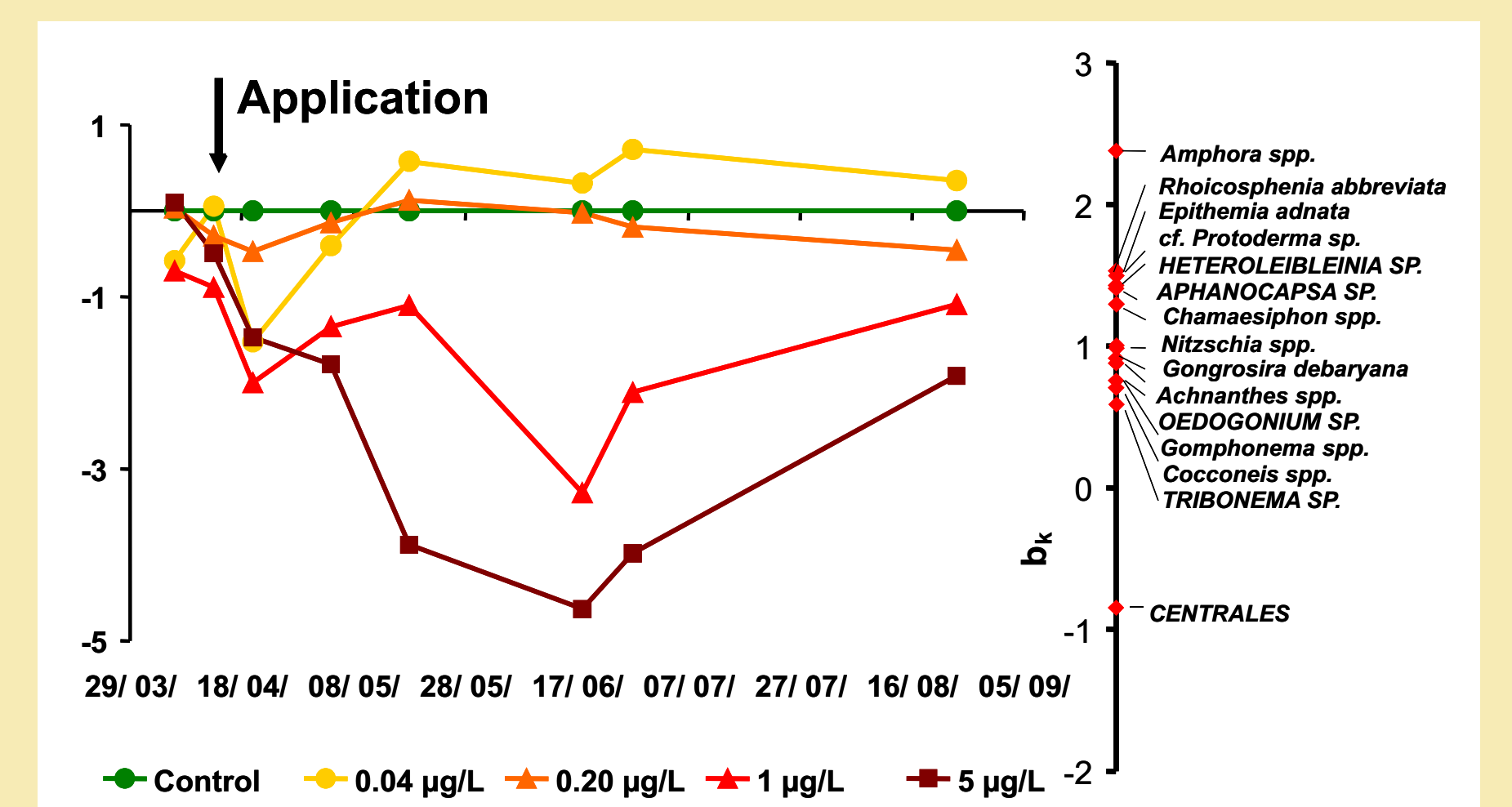


Fig. 7: PRC-analysis of the periphyton data set (strips) in the pond mesocosms. Bk value = species weight, arrow = date of application

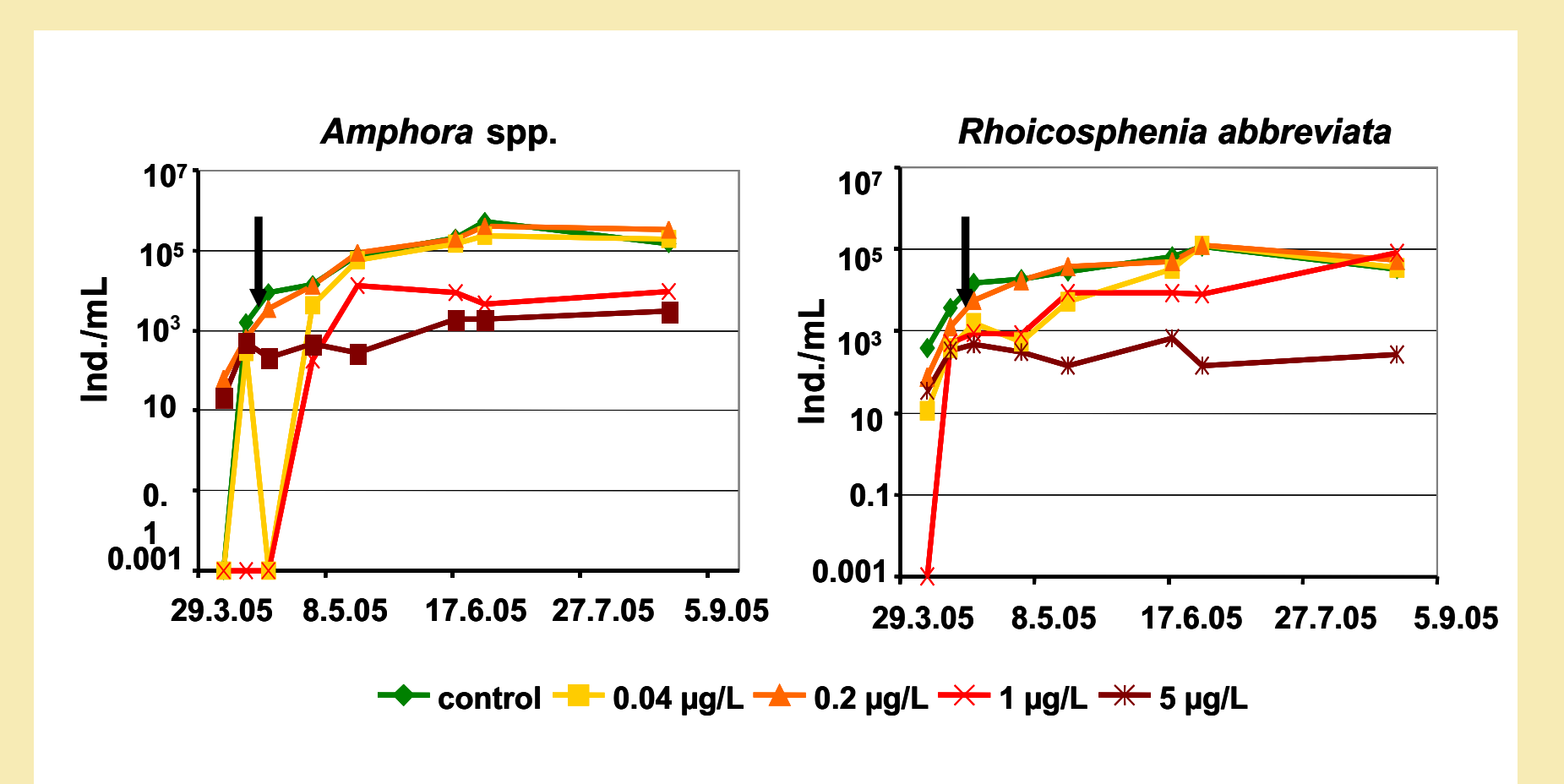


Fig. 8: Dynamics of two periphyton species in the pond mesocosms. Arrow: day of application

Conclusions

- A single application of Irgarol in the pond mesocosms had strong effects on the periphyton community at concentrations higher than $0.2 \mu\text{g/L}$ Irgarol (Fig. 2, 6, 9).
- Under natural conditions, there is a continuous release of Irgarol from ship hulls. Therefore, the effects detected in this best-case study (single-application) are likely to be underestimated.
- Environmental concentrations are in the range of the EC_{50} value ($0.32 \mu\text{g/L}$) for periphyton. Potential hazard for periphyton community on natural substrates can not be excluded.