Effects of the herbicide Metazachlor in lotic and lentic mesocosms I: Fate of Metazachlor and selected metabolites

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Umwelt Bundes Amt (i) für Mensch und Umwelt

Ponds:							
	Control		888	₹. ₹. ₹. ₹. ₹. ₹. ₹. ₹. ₹.	Control		
	5 μg/l		888	<u>***</u> **	5 μg/l		
	Control		10001	₹ <i>₹ ₹</i> <i>₹ ₹ ₹</i>	Control		
	80 µg/l		888	<u>****</u> *	80 µg/l		
	Control		888		Control		
	500 μg/l		888	* * * *	500 µg/l		
	20 µg/l		888	₩ ₩ ₩ # ₩ ₩ ₩ ₩	20 µg/l		
	200 µg/l				200 µg/l		

Introduction

In 2003 a mesocosm study was conducted in the new indoor pond and stream mesocosm system of the German Federal Environmental Agency (UBA 2004) in order to study fate and effects of the herbicide metazachlor.

This herbicide has been selected as a model substance because:

• It is used as a broad spectrum herbicide within 3 different plant protection products on cruciferian species especially canola (rape) (BBA 2004) in relevant amounts in Germany. Thus, it is the no. 3 of 'top 10 tonnage list' of active ingredients applied in **Brandenburg (LUA Brandenburg 2003)**





- Fig. 1: Scheme of the indoor pond and stream mesocosm system
- It is detected in surface as well as in groundwaters of different smaller catchments in different levels between <0,1 µg up to >100 µg/l (e.g. Germany LUA NRW 1997, Zullei-Seibert 1990, Sweden: Kreuger 1998)
- The lack of published fate and effect studies for the aquatic environment (e.g. Hindelang 1993).

Here, some results of Metazchlor and its main metabolites detected in the waterbodies of the indoor mesocosms are presented and compared with results from a similar designed outdoor study performed in 2002.



Fig. 2: Indoor ponds after application of metazachlor (Oct. 2003) - A: 200 µg/l dosage, B: control

Materials & Methods

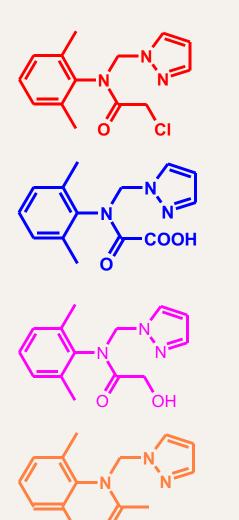
Mesocosms

8 indoor stream systems (c. 106 m length, c. 0.3 m depth, c. 33 m³ water volume) and 8 indoor pond systems (6.9 m length, 3.3 m width, c. 14 m³ water volume) were prepared by introducing sand, sediment, gravel, and macrophytes (for further details see Mohr et al. 2002, 2003, 2004) (Fig

Application

In June 2003 5 stream and 5 pond indoor mesocosm systems were dosed simultaneously by spraying and pouring carefully different solutions of metazachlor (nominal: 5, 20, 80, 200, 500 µg/l; methanolized stock solutions dissolved in water; ponds: 60 l, streams: 500 l) on the water surface of the mesocosm systems. Homogeneous dispersion of metazachlor was achieved by screw pumps (flow velocity: 0.12 m/s, stream systems) or by a 5 min operation of a battery driven outboard motor (pond systems) (Fig 1.).

Analytical procedures

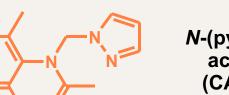


Metazachlor (CAS 67129-08-2) 2-Chloro-N-(pyrazol-1-ylm/z <u>209</u>, 211, 277 methyl)acet-2',6'-xylidide

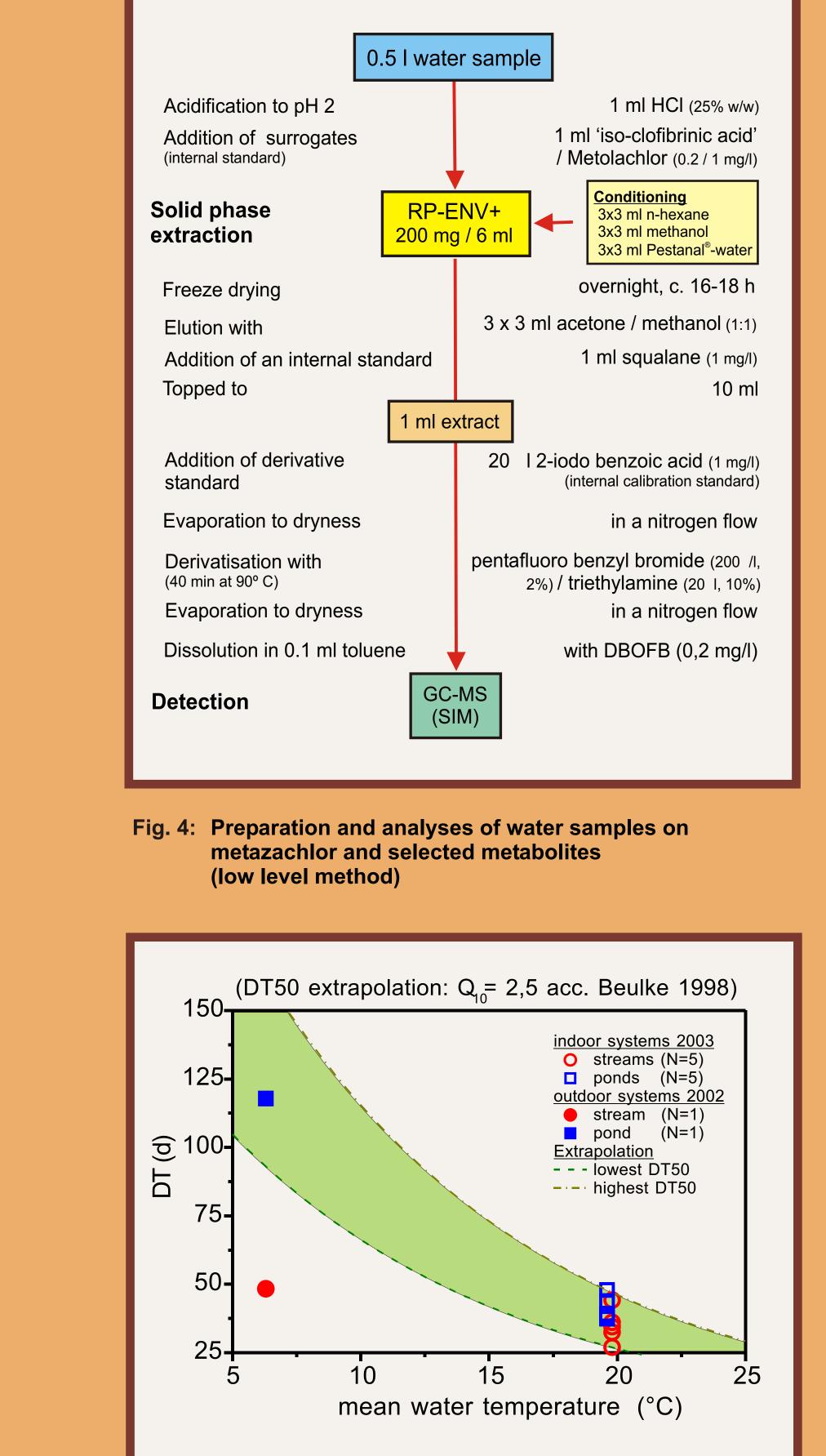
N-(Pyrazol-1-ylmethyl)oxm/z 160, 228, >453< 2',6'-xylidic acid - >PFB<



2-Hydroxy-N-(pyrazol-1-ylmethyl)acet-2',6'-xylidide m/z <u>191,</u> 133, 228 (CAS 125709-81-1)



N-(pyrazol-1-yl-methyl) acet-2',6'-xylidide m/z 243, 175, 133 (CAS 75972-11-1)



Monitoring

Metazachlor and its metabolites were monitored mostly in weekly interval whereas additional parameters (field parameters, nutrients, macro and micro constituents, plankton etc.) were sampled biweekly.

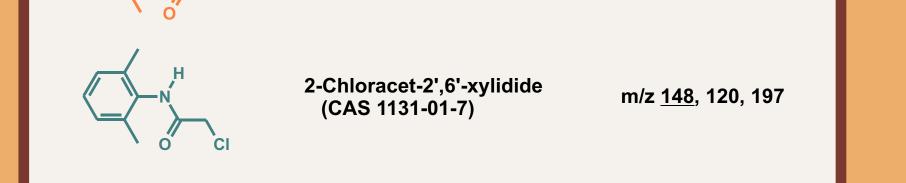


Fig. 3: Metazachlor and analyzed metabolites

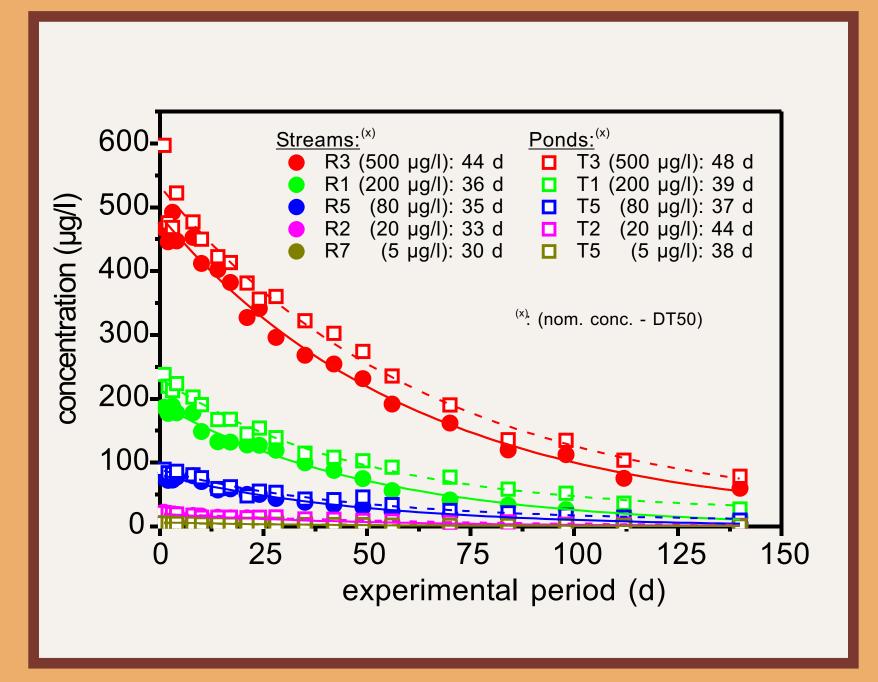


Fig. 5: Concentration of Metazachlor in the waterbodies of streams and ponds



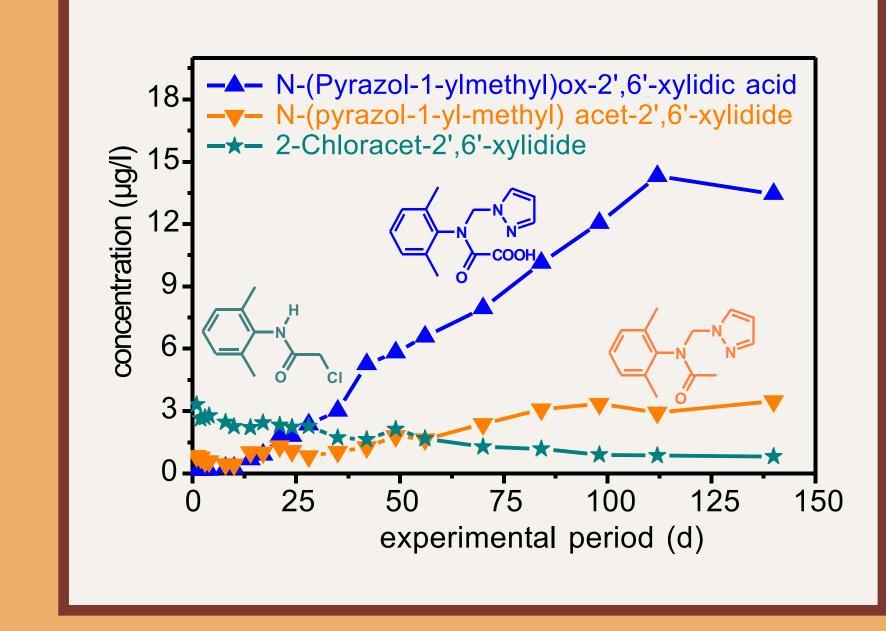


Fig. 6: Selectecd metabolites of Metazachlor in the waterbody of a pond (200 µg/l nom.)

Fig. 7: DT50 - temperature relationship (indoor and outdoor mesocosm systems)

Results & Discussion

- Losses of metazachlor in the water bodies followed a first order kinetic (R²: 96 - 99% in streams and ponds, Fig. 5).
- DT50s of metazachlor in the ponds (mean 41 d) indicated a slightly prolonged primary degradation compared to the streams (mean 35 d), propably caused by the different water turbulence regime (flowing vs. stagnant conditions) and the different 'surface area to water volume ratio' being relevant for a biofilm based degradation (ratio c. 4 for stream and 2.2 for pond mesocosms) (Fig. 5).
- Typical concentration time response curves of identified main metabolites are given in Fig. 6. The main metabolite

References

BBA2004: http://www.bvl.bund.de/pflanzenschutz/psmdb/fr_ob_be.htm Beulke, S. 1998: Thesis, Shaker. ISBN-3-8265-3941-9 Feibicke et al. 2003: Fate study of metazachlor in lotic and lentic mesocosms. -Poster SETAC Europe, 2003, Hamburg Hindelang, D. 1993: Thesis, TU München, Fakultät für Landwirtschaft und Gartenbau.

was N-(Pyrazol-1-ylmethyl)ox-2',6'-xylidic acid reaching 4 -5% of the start concentration of metazachlor in the streams and 7 - 14% in the ponds in maximum.

Indoor data from summer 2003 (this study) compared with outdoor data from autumn winter 2002 (Fig. 7) (Feibicke et al. 2003) indicate that the high DT50 of the outdoor pond (118 d) was within the expected range extrapolated from indoor data by using an Arrhenius function, whereas the low DT50 in the outdoor stream (48 d) seemed to be rather unaffected by low water temperature (mean: 7°C). As a working hypothesis, photolysis could have acted as an additional relevant loss process especially in the outdoor stream system because of its different light exposition (day light with UV), geometrical dimensions (water depth, insolated surface area) and water turbulence regime.

• Specific photolytic tests (by using day light incubators) are in preparation. Analysis of sediments samples are still running and will be published soon.



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