

Uptake and metabolism of the herbicide Metazachlor in macrophytes

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Introduction

Metazachlor (-chloroacetamide derivative) is a herbicide, which is commonly used in Europe for controlling weeds that invade rape and other brassicean fields. It inhibits the growth of vascular plants by an irreversible inhibition (covalent binding) of the enzyme which catalyses the long-chain fatty acid elongation. Since it is used as pre-emergence herbicide it may enter the aquatic environment in relevant amount by run-off or spray drift. In a previous mesocosm study of the German Federal Environmental Agency on fate and effects of Metazachlor results indicated that this herbicide may have a long-term effect

on the freshwater macrophyte *Myriophyllum spicatum* independent of the concentration in the water:

After single application, length growth of *M. spicatum* was not only inhibited at high concentrations but temporally shifted also at low concentrations even though concentrations in water went down to almost zero in the course of the 140 day study (Müller, 2003). Building on this finding, a microcosm study on the uptake and metabolism in macrophytes was conducted in order to further elucidate the case.

Materials and Methods



Fig. 1 : An indoor pond microcosm

Myriophyllum spicatum, *Elodea canadensis* and filamentous green algae were established in a 1.6m³ indoor pond (Fig.1). The system was contaminated once to a nominal concentration of 40 µg/L on 3 September 2004. The microcosm was illuminated by a 400 W HQI lamp and dosed with nutrients to low levels fortnightly.

Samples of macrophytes and filamentous algae were sampled on day 0, 17, 38, and 60. The material was treated in a spindrier at 2500 rpm and then frozen at -20 °C till analysis. For analyses of metazachlor and 3 of its metabolites (BH479-1, BH479-4, and BH479-6), modules of the well-established DFG (German Research Foundation) method S19, November 1999, for residue analyses in crops were modified (Fig. 2).

Water samples were taken at increasing intervals from 3 days to a fortnight at the end of the study and analysed according to the method described by Feibicke et al. (2004). In this method, 0.5 L of water sample, adjusted to pH2 and spiked with internal standards, is passed through the SPE column (Fig. 2). The column is freeze dried and then eluted as shown in Fig. 2. An aliquot of 1 mL is evaporated, the residue derivatised with pentafluorobenzyl bromide (PFB) and then dissolved in 1 mL of toluene (with 0.2 mg/L of DBOFB)

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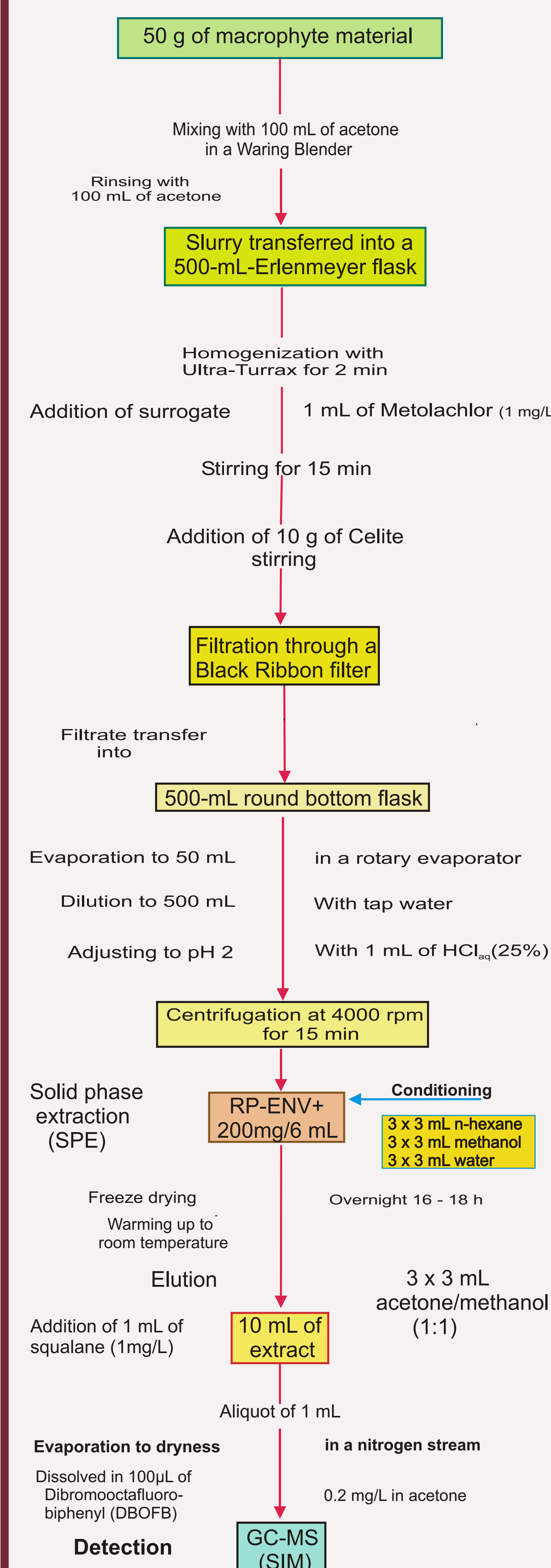


Fig. 2 : Analytical method for Metazachlor and 3 metabolites in macrophytes

Results and Discussion

The decrease of the metazachlor concentration in the water column could be fitted to a first-order degradation curve with a DT50 of 51 days (Fig. 3, 4). The metabolite with the highest concentration in the water column was BH479-4 with continuously increasing concentration up to 4.3 µg/L at the end of the study (Fig. 3, 5). The metabolite BH479-6 remained rather constant at concentrations around 0.6 µg/L (Fig. 3, 6). The concentration of the metabolite BH479-1 slightly increased from 0.25 µg/L to 0.45 µg/L (Fig. 3, 7).

Metazachlor could also be detected in the plants, however at low concentrations and in different patterns for the 3 species (Fig. 4). Uptake of metazachlor corresponded well with plant growth which was documented on photos taken before every plant harvest of the experiment: Growth of *Elodea canadensis* was already heavily effected by metazachlor after the first harvest (day 17) while *Myriophyllum spicatum* ceased to grow after the second harvest (day 38). Filamentous algae were inhibited at the start of the experiment. However, they started to grow at the end of the study when the metazachlor concentration in the water was below 20 µg/L and they could among other things benefit from the higher amount of remaining resources (space, light, and nutrients).

Concentrations of metabolites increased as well in the plants (Fig. 5-7). The fact that this increase exceeded the concentration in water for BH479-6 indicates that water plants were actively involved in the degradation process of metazachlor. However for the macrophytes, this role decreased over the time since they had been impaired by the herbicide. This interpretation is in line with the reduced length growth independent of the metazachlor concentration which had been found in the previous mesocosm study.

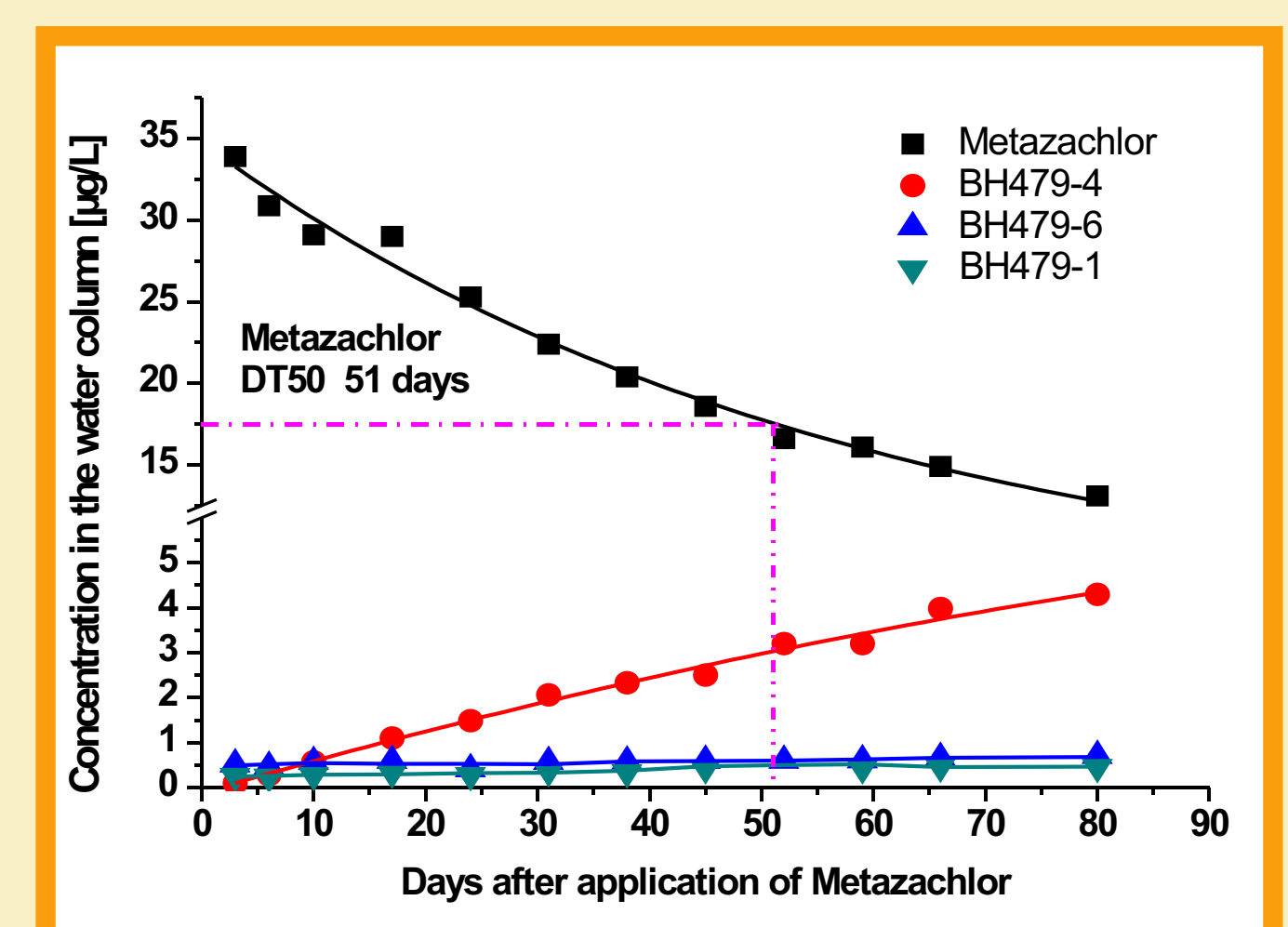


Fig. 3: Degradation of metazachlor and formation of metabolites in the water column

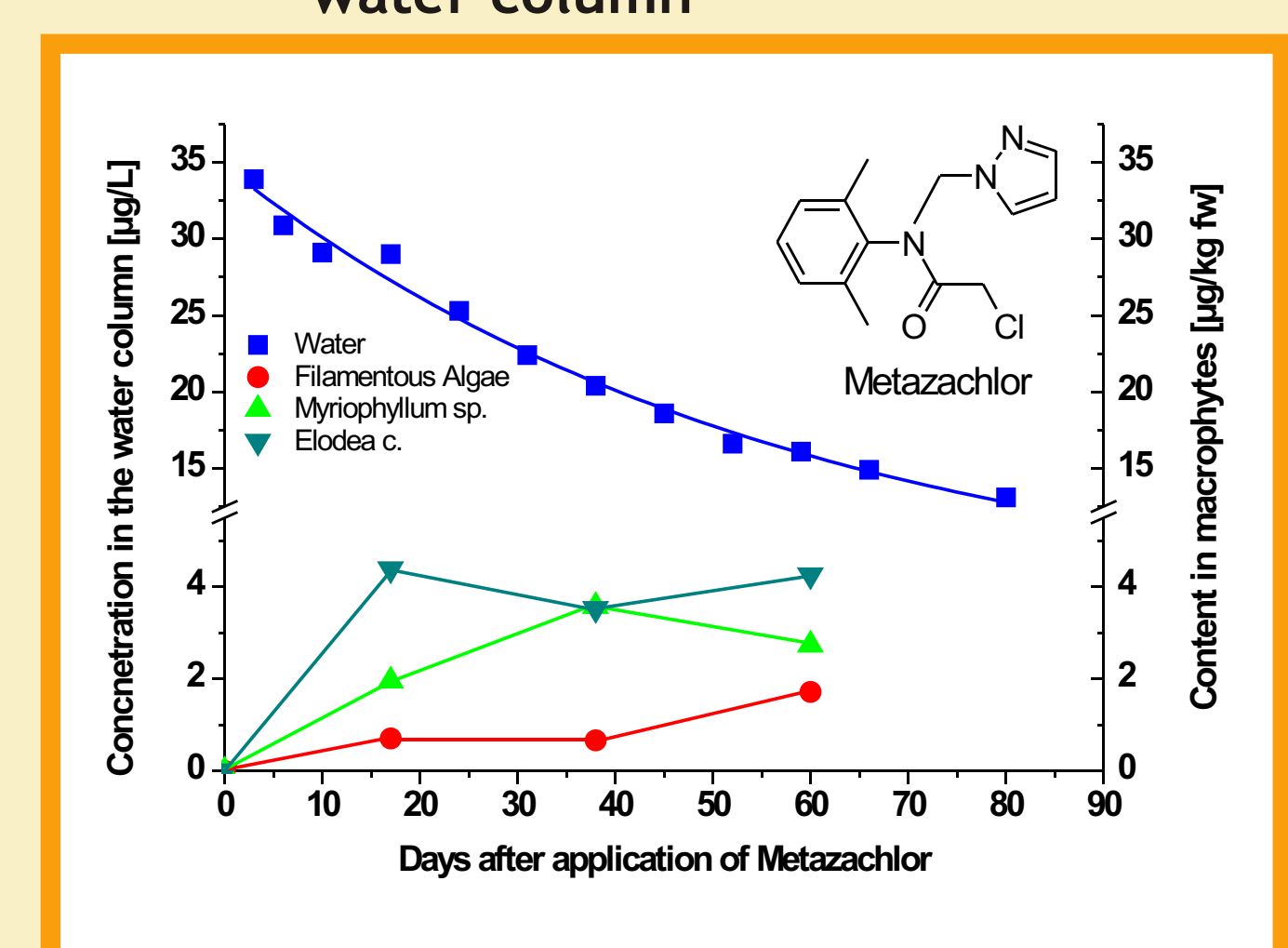


Fig. 4: Metazachlor in the water column and the content in macrophytes

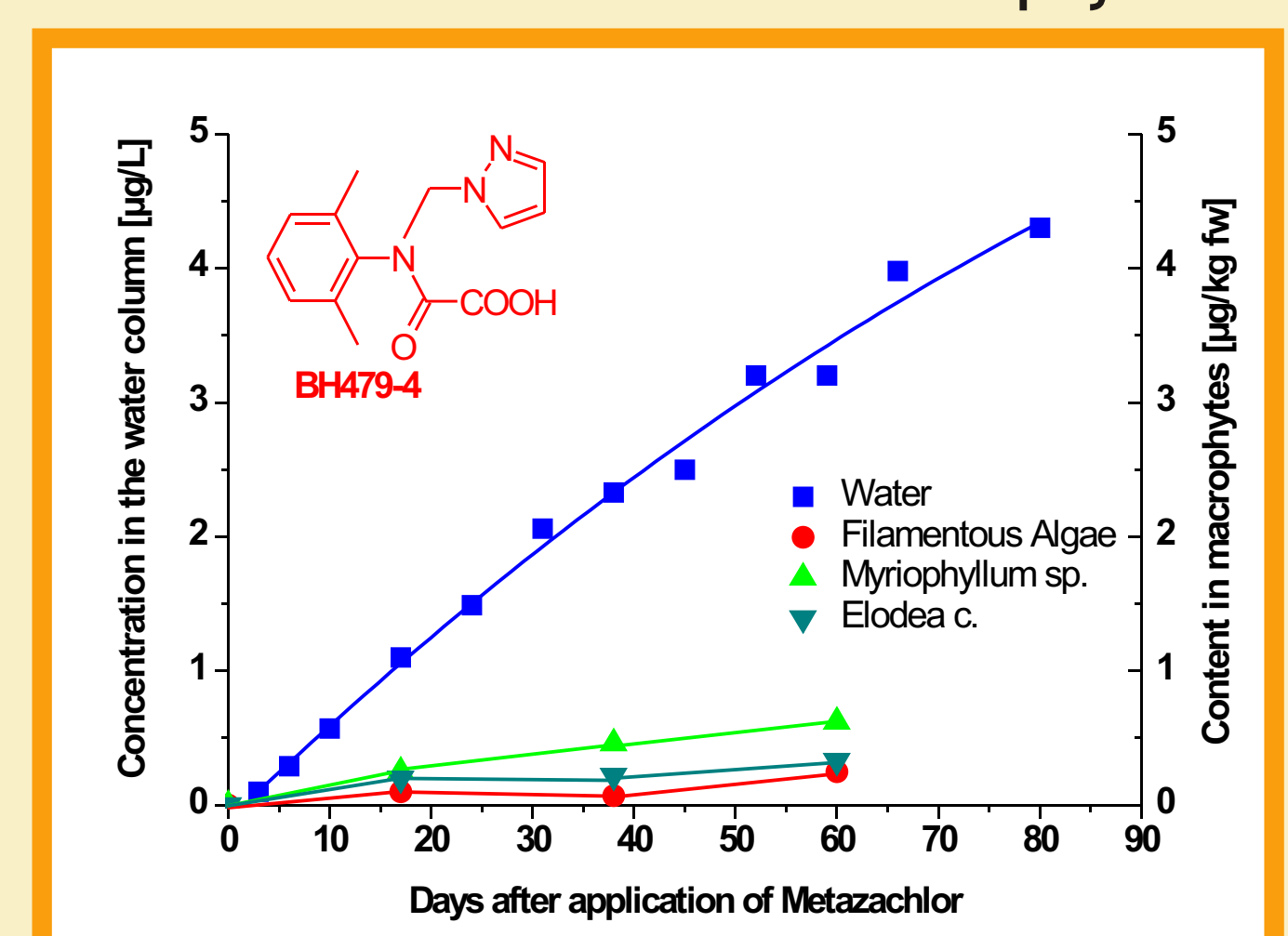


Fig. 5: BH479-4 in the water column and the content in macrophytes

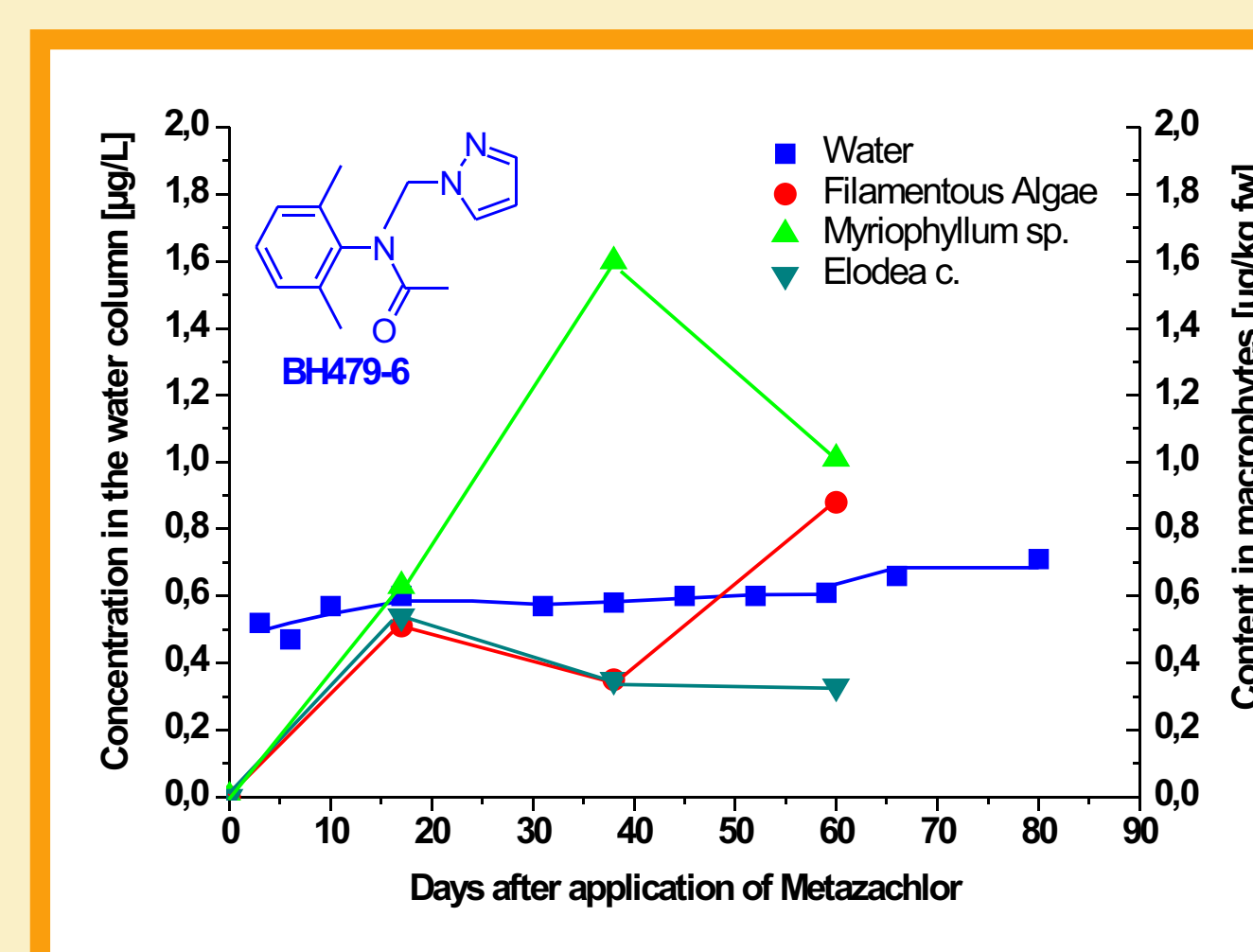


Fig. 6: BH479-6 in the water column and the content in macrophytes

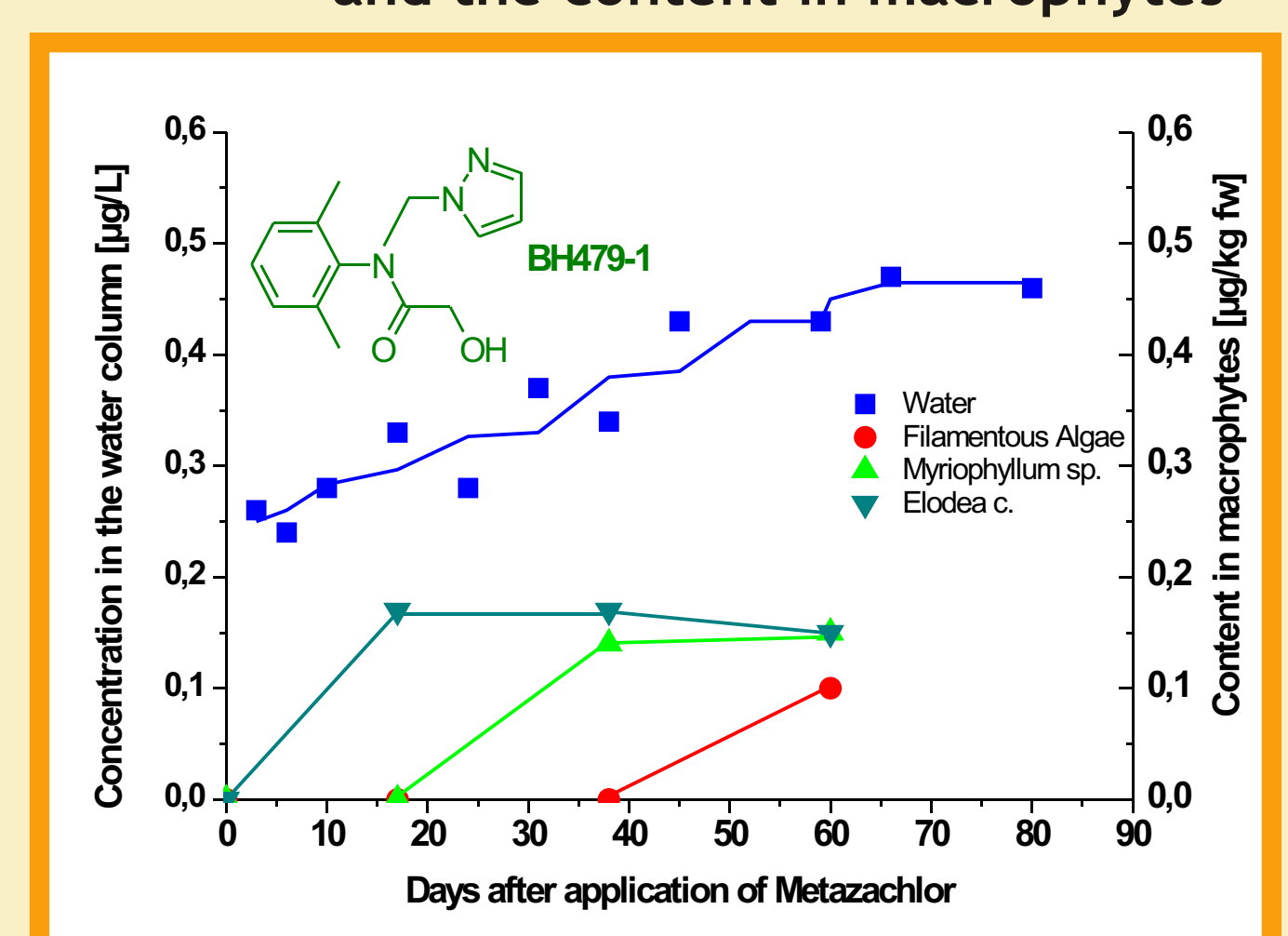


Fig. 7: BH479-1 in the water column and the content in macrophytes

References

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