TIME-DEPENDENT TRANSFORMATION OF VARYING CONCENTRATION OF THE HYDROXAMIC ACID METABOLITES MBOA AND BOA IN SOIL

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INTRODUCTION

When hydroxamic acids from Graminae species, including rye, Triticale, wheat and corn, are leached to the soil, a chemical and microbial transformation of the compounds will take place. The identification and quantification of the transformation products is crucial, if the properties of these compounds for suppressing weeds and soil-borne diseases are going to be exploited and if the non-target effects of the compounds are going to be elucidated (1). The most abundant hydroxamic acid in wheat is 2,4-dihydroxy-7-methoxy- 1,4-benzoxazin-3(4H)-one (DIMBOA) and the most abundant hydroxamic acid in rye is 2,4-dihydroxy-1,4-benzoxazin-3(4H)-one (DIBOA). When DIMBOA and DIBOA leaches out into the soil they are chemically transformed to MBOA and BOA respectively. A number of transformation products from BOA, formed by microorganisms in growth media have been reported in the literature and reviewed by Fomsgaard et al (1). Little knowledge however exist about the transformation in soil. The purpose of this study was to investigate the transformation of MBOA and BOA in soil in varying concentrations.

MATERIALS AND METHODS

2-benzoxazolinone (BOA) and 6-methoxy-2-benzoxazolinone (MBOA) (obtained commercially) was added to a number of individual replicates of soil. BOA degradation studies were performed at the concentrations levels 400 ng g^{-1}, 400 μg g^{-1} and 4000 μg g^{-1}. MBOA studies were performed at the concentrations 400 ng g^{-1}, 400 μg g^{-1} . The samples were incubated in the dark at 15°C. During a period of up to 90 days, the incubation was interrupted succesively. Each soil sample was extracted with accelerated solvent extraction and analyzed in LCMSMS (2), (3). The identification and quantification of metabolites focused on the compounds 2-amino-3H-phenoxazin-3-one (APO), 2-acetylamino-3H-phenoxazin-3-one (AAPO), 2-amino-7-methoxy-3H-phenoxazin-3-one (AMPO) and 2-acetylamino-7-methoxy-3H-phenoxazin-3-one (AAMPO). APO and AAPO were synthesized as described in Gents et al (2) and AMPO and AAMPO were synthesized by Macías et al (4).

RESULTS AND DISCUSSION

The degradation of both BOA and MBOA in the lowest concentration (400 ng g^{-1}) occurred fast with a half life below 1 day. None of the metabolites APO, AAPO, AMPO or AAMPO were detected. The result from the degradation studies MBOA 400 μg g-1; BOA 400 μg g^{-1} and BOA 4000 μg g^{-1} are shown in Figure 1, 2 and 3 respectively.

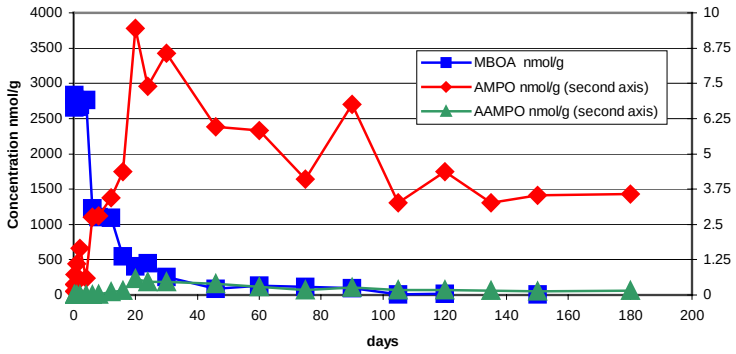

Figure 1. Degradation of MBOA (400 μg g^{-1}) in soil and formation of AMPO and AAMPO

Gagliardo and Chilton (5) and Kumar et al (6) showed that the formation of APO from BOA and AMPO from MBOA took place in soil. A further acetylation of both APO and AMPO in the soil environment is now shown for the first time. The structure of the compounds is shown in Figure 4.

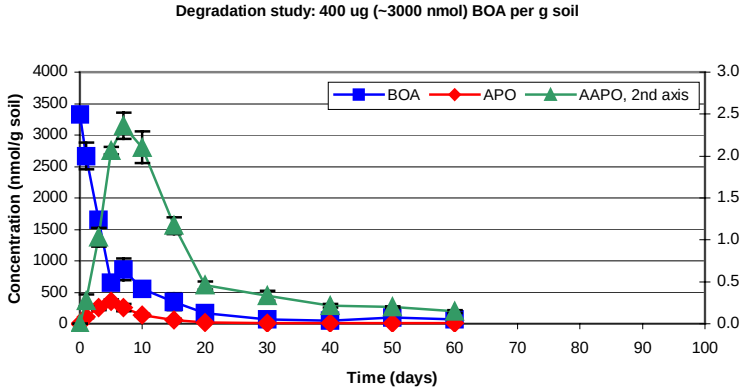

Figure 2. Degradation of BOA (400 μg g^{-1}) in soil and formation of APO and AAPO

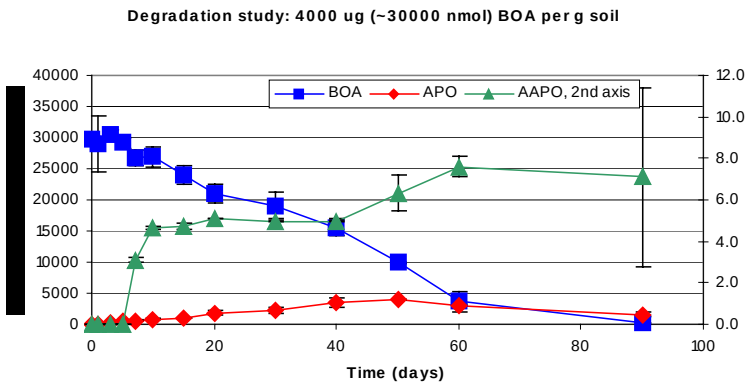

Figure 3. Degradation of BOA (4000 μg g^{-1}) in soil and formation of APO and AAPO

The biological activity of APO generally is higher than of BOA and AAPO (7). Similarly the biological activity of AMPO is higher than the activity of of MBOA and AAMPO (7). Thus a focus on the time and concentration dependency is needed if a biological effect on target weed species is looked for. The transformation from the benzoxazolinone structure to aminophenoxazinone and later to the acetylated aminophenoxazinone increases the hydrofobicity and the sorption to soil substantially, which will reduce the bioavailability of the compounds. In spite of the high sorption of the compounds the half life is still below 90 days, which is the limit that is set for half-live for synthetic pesticides in the European registration procedure.

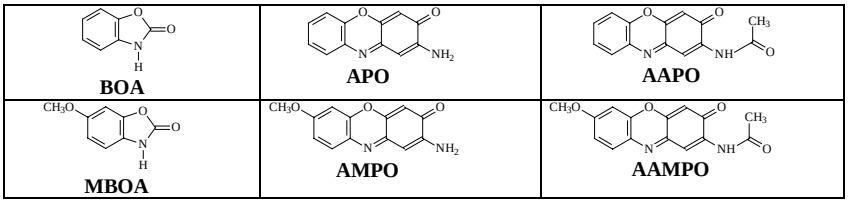

Figure 4. Molecular structure of parent compounds, BOA and MBOA and of transformation products, APO, AAPO, AMPO and AAMPO

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