Geophysical Research Abstracts
Vol. 18, EGU2016-3494, 2016
EGU General Assembly 2016

Exposure of small water bodies to pesticides and their transformation products in a lowland catchment

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INTRODUCTION
Based on the European Directive 2009/128/EC (2009), all member states were obliged to set up National Action Plans for the sustainable use of pesticides. In the German National Action Plan (GNAP), the status of small water bodies (swb) defined as water bodies with a catchment <10km^2 was stressed among other issues. Since the GNAP stated that knowledge and data base of pesticide contamination of swbs is insufficient, a monitoring of 10 swbs in the catchment of the lowland river Kielstau was carried out in summer and autumn 2015 for selected herbicides and their transformation products (TP).

METHODS
Grab samples of the water phase were collected once at the end of the spring/summer application period and a screening was carried out for 102 pesticides and 6 TPs. During autumn application, the rape herbicide metazachlor and the winter grain herbicide flufenacet as well as their TPs oxalic acid (OA) and sulfonic acid (ESA) were in the focus of the study. The sampling was carried out event based after the first and second relevant rainfall events after application. The third sample was collected four weeks after the second sampling to observe the occurrence of the TPs. The target compounds were quantified by LC-MSMSMS.

RESULTS
For all swbs, the pesticide screening after the spring application showed pesticide/TP concentrations below the quantification limits (0.01-0.05 μg L-1) except of the corn herbicdes metolachlor, terbuthylazine and its TP desethylterbuthylazine. These findings were independent from the time elapsed since the last application of these compounds took place which was partly 4 years ago.
After autumn application, the samples were analyzed for the herbicides metazachlor, flufenacet and their TPs which were sprayed on the fields where the swb are located in. These results showed that TPs of both herbicides remained from the year before and reached concentrations up to 1.9 μg L-1 for metazachlor ESA, 0.55 μg L-1 for metazachlor OA, 0.16 μg L-1 for flufenacet OA and 0.04 μg L-1 for flufenacet ESA. After autumn application, maximum concentrations of the mother compounds were 0.62 μg L-1 for metazachlor after the second and 0.5 μg L-1 for flufenacet after the first relevant rainfall event. The TP concentrations after autumn application were up to 200 times higher than the mother compound (metazachlor and -ESA).

Key words: small water bodies, transformation products, metazachlor, flufenacet, -OA, -ESA