Investigating airborne pesticide deposition using trace analysis in precipitation, soil, and agricultural plants

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Introduction and aim of the study

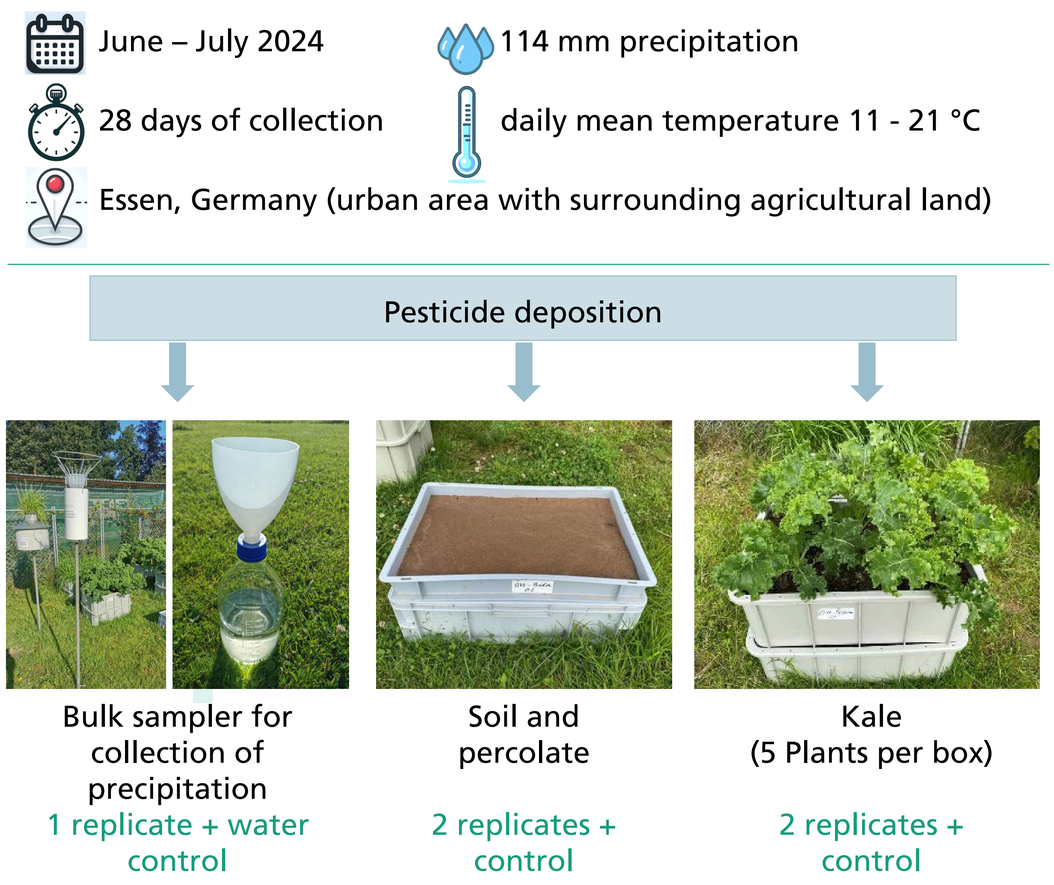
Airborne pesticide transport and deposition, e.g. from agricultural applications, is an underinvestigated source of environmental contamination. This study investigated the airborne deposition of relevant pesticides or pesticide metabolites on plants and soil, as well as in rain precipitation, with the aim of comparing the amounts of these substances deposited in the respective compartments. This study further intended to solve possible practical problems for a planned nationwide monitoring of airborne pesticide transport in Germany.

Experimental setup for deposition collection

The experimental setup consisted of three test systems (Figure 1):

- Bulk sampler to capture rainfall and dust
- A test soil with collection of percolation water
- Pre-grown kale plants

Figure 1: Experimental setup for collecting the deposition of airborne pesticides



Trace analysis of pesticides / metabolites

The target analytes were selected based on findings in bulk collectors in a pre-study or based on typical application during the time of study performance. Analyses were performed by U(H)PLC-MS/MS including isotope-dilution analysis. A multi-method was developed for 9/10 analytes. Propamocarb was analysed by a separate method due to its high polarity. The samples were prepared as follows:

- Aqueous samples: samples were stabilized with acetonitrile and measured directly
- Soil and kale samples (multi-method): QuEChERS extraction with ethyl acetate as solvent and a dispersive SPE clean-up
- Soil and kale samples (Propamocarb): direct extraction using a QuPPe method

Validation results

The methods were successfully validated following SANTE 2020/12830 rev. 2 guideline, except for Pendimethalin in kale, which failed validation. Blank values were subtracted from the validation samples, where necessary. Limits of quantification (LOQ) were in the low ppt range, respectively (Table 1). The major limitation with the LOQs was ubiquitous background values of the blank matrices used for validation.

Table 1: Limits of quantification for trace analysis of pesticides analyzed for this study

	Water	Soil	Kale
Analyte	LOQ [ng/L]	LOQ [ng/kg dw]	LOQ [ng/kg fw]
Flufenacet	5	5	5
Fluopyram	5	5	5
Pendimethalin	20	100	-
Prosulfocarb	5	5	5
Prothioconazol-desthio	5	5	5
Tebuconazol	5	5	5
Terbuthylazin	5	5	5
Terbuthylazin-desethyl	20	5	20
Azoxystrobin	20	20	20
Propamocarb	5	5	20

LOQ = limit of quantification; dw = dry weight; fw = fresh weight

Results of the test samples

- For comparison the measured values were normalized to the surface area of the compartment → area-normalized deposition values in ng/m²
- For the soil samples, the results of the control soil were subtracted from the exposed soils. Deposition from percolation water was added. Kale controls could not be subtracted due to unpreventable contact with outdoor air.

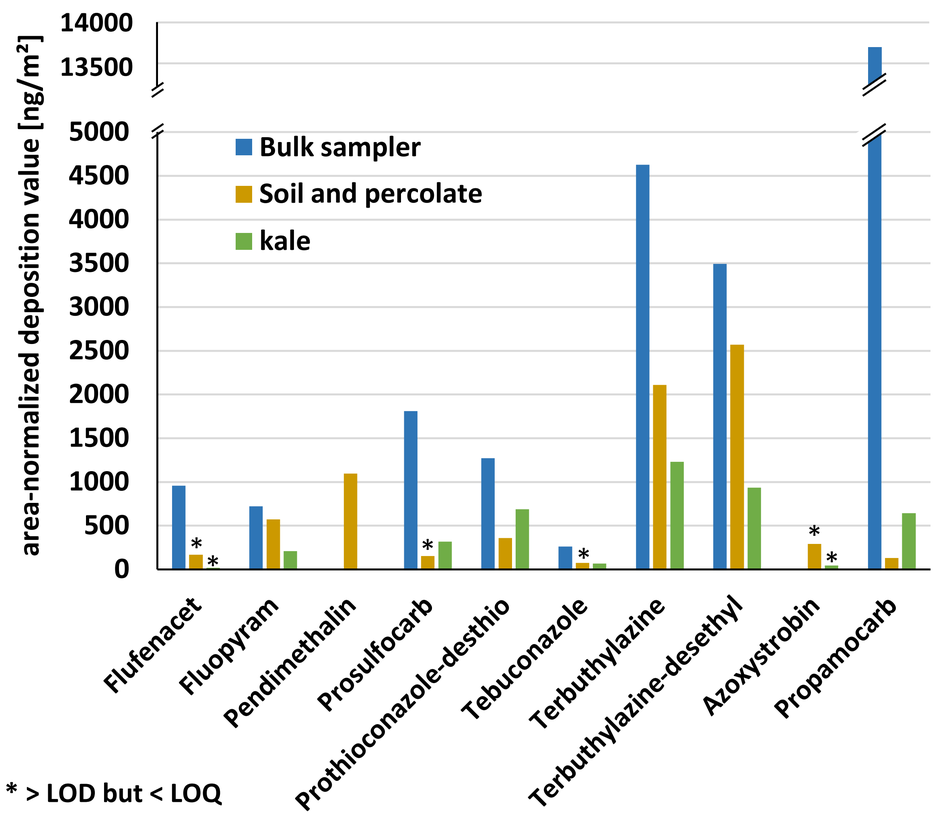
➢ For 8 / 10 substances, significantly higher substance quantities were measured in the bulk collector than in the other test system (up to 100 times higher)

➢ Pendimethalin values in soil were subject to errors due to the high background values in the control soil.

➢ Trace analysis in soil and kale required more effort for method development and validation due to the complex matrix and background contamination in the blank matrices used for validation

➢ Trace analysis of aqueous samples was less time-consuming and more robust.

Figure 2: Comparison of deposition on the test systems



Conclusion

- Trace analysis in the ppt range allowed to quantify airborne pesticide deposition
- The bulk sampler enabled a conservative estimate of airborne pesticide deposition.
- The selected analytes in this study covered a large range of physical-chemical-properties of approved pesticides
- The bulk sampler is suitable for estimating the deposition of airborne pesticides within the framework of a future national monitoring

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