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Fate of four herbicides in an irrigated field cropped with corn: lysimeter experiments

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Abstract

Lysimeter experiments were carried out to evaluate the applicability of compound-specific isotope analysis (CSIA) for assessing transport and fate of selected herbicides in two agricultural soils cropped with corn. Monitoring of target pesticides, metabolites and tracers in drainage water made apparent the significant role of preferential flow in the mobility of the studied compounds through the soil and the vadose zone during the first days after herbicides application. The detection of metabolites in drainage water confirmed herbicides degradation once higher residence times in the soil zone were achieved. An efficient preconcentration procedure was developed for 10-L drainage water samples to achieve enough analyte enrichment for C, N and Cl isotope ratios measurements. Methods for isotope analyses are currently being developed and the applicability of CSIA for assessing the in situ biodegradation of the target pesticides during transport in soil and vadose zone will be evaluated.

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1. Introduction

The contamination of soil, groundwater and surface waters by herbicides poses major environmental and health problems. Despite some pesticides have been banned or restricted in many countries, they are still detected in surface

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and groundwater. For fate assessment in soil and groundwater, detecting and observing concentration changes of the pesticides and their metabolites is often not conclusive. Compound-specific isotope analysis (CSIA) is a promising tool for assessing transport and fate in the environment of these compounds^{1,2}. CSIA is a well-established method to identify and quantify degradation pathways of priority pollutants such as chlorinated solvents and petroleum hydrocarbons³. For the extension of the CSIA approach to pesticides there are, however, two main analytical challenges: (1) pesticides and metabolites occur at very low levels and, as a consequence, large amounts of water are required to achieve enough analyte enrichment, which could lead to interferences from the aqueous matrix, and (2) some of these micropollutants are very polar which requires selective sorbent phases for solid-phase extraction (SPE) and, in some cases, derivatization prior to GC-IRMS analysis.

The main goal of this work was to assess if multi-element CSIA can be used to identify and quantify pesticide degradation in agricultural soils and vadose zone, where transformation and transport processes interact. We also evaluated the applicability of the CSIA approach for tracking transformation processes below the root zone, simulating high preferential pesticides flow. A field based lysimeter study was conducted focusing on some of the commonly worldwide used pesticides for control weed on corn. Although the commercial use of atrazine was forbidden in most of the European countries in the 90's, atrazine and its metabolites (like desethyl atrazine, DEA) are frequently detected in groundwater^{4,5}. The chloroacetanilide herbicides metolachlor and acetochlor are also widely used and both are also frequently detected in ground and surface water⁴. Their ionic ethane sulfonic acid and oxanilic acid derivatives are typically encountered at concentrations much higher than the parent herbicides⁵. Although chloridazon is not applied to corn, it was used in this work for assessing CSIA feasibility for tracking transformation processes below the root zone because its main metabolites, desphenyl chloridazon (DPC) and methyl-desphenyl chloridazon (M-DPC), are very polar substances that transport rapidly throughout the unsaturated zone. Both have been detected in groundwater exceeding the EU standard for groundwater of 0.1 µg/L⁴.

2. Materials and methods

2.1. Lysimeter experiments

Twelve weighing lysimeters (3.14 m² surface area, 2.5 m depth) from the Agroscope-Institute for Sustainability Sciences (ISS, Zurich, Switzerland) research station were used. Six of them are filled with a well-drained sandy loam cambisol developed from a stony alluvium ("gravel soil") whereas the other six are filled with a poorly-drained loam cambisol developed from moraine deposits ("moraine soil"). The two soil types are typical arable soils in Switzerland. Both soils were sown with corn on May 12th 2014. In four lysimeters atrazine, metolachlor and acetochlor were applied at the surface simulating the common scenario of pesticide application, whereas in other four lysimeters atrazine, metolachlor, acetochlor and chloridazon were injected at a depth of 40 cm to simulate high preferential transport of the herbicides through the topsoil. To ensure that sufficient mass for CSIA arrives at the drainage water, higher pesticide doses than normal were used, while respecting ecotoxicological criteria. Atrazine (2.1 kg/ha) was first applied at the 2- to 3-leaf stage. Metolachlor (6.4 kg/ha) and acetochlor (6.4 kg/ha) were sprayed at the 3- to 4-leaf stage. In addition to the pesticides, NaBr (500 kg/ha) and sodium fluorescein (1.3 kg/ha) were applied. Herbicides leaching was favored by maintaining high water content in the soil before pesticide application and by doing intense irrigation events (40-50 mm at 1 mm/min) just after application. The same application rates were used for depth injection of atrazine, metolachlor and acetochlor. Chloridazon at 6.4 kg/ha was also injected. The lysimeter facility was covered with a plastic tunnel and an irrigation system was installed to ensure full control of irrigation rates. Regular low-intensity irrigation events (5-20 mm once a week at 0.2 mm/min) were applied in addition to episodic intense irrigation events during the summer (30-40 mm at 1 mm/min). Drainage water was collected via Teflon tubes in 54L glass bottles placed on balances to record continuously the outflow.

2.2. Pesticides extraction and analytical methods

For the extraction of the target micropollutants for concentration and isotopic analysis a combination of hydrophilic (Septra ZT, Phenomenex) and hydrophobic (Bakerbond SDB-1, J.T. Baker) polymer-based sorbents with high specific surface area was used. Both sorbents show high adsorption capacity for highly polar micropollutants^{6,7}.

For concentration measurements, 20-mL samples were extracted using 6-mL cartridges packed with 0.2 g of each of the selected sorbents. Ethyl acetate was used for elution and after solvent evaporation, dried contents were redissolved in methanol:MilliQ (70:30 v/v) for determination of pesticides and metabolites concentration by using UHPLC-QTOF-MS. For isotope analyses large volume samples (10 L) were extracted after filtration with 0.7 μm glass fiber filters. 60-mL cartridges packed with 8 g of each sorbent were used. The cartridges were eluted with 8 \times 15 mL ethyl acetate. The combined eluates were evaporated until dryness and stored frozen until isotope analyses. Methods for C, N and Cl isotope analysis of the target micropollutants are under development by using GC-IRMS for C and N, and GC-qMS for Cl isotope ratios.

3. Results and discussion

Over the study period (27 May 2014 -10 March 2015), the total amount of water applied by sprinkler irrigation was 750 mm with regular 5-20 mm and occasional 30-50 mm intense events as shown on Fig. 1. Cumulative drainage over the study period was 245-300 mm from the gravel soil and 270-325 mm from the moraine soil, which corresponds to around 40% of total irrigation.

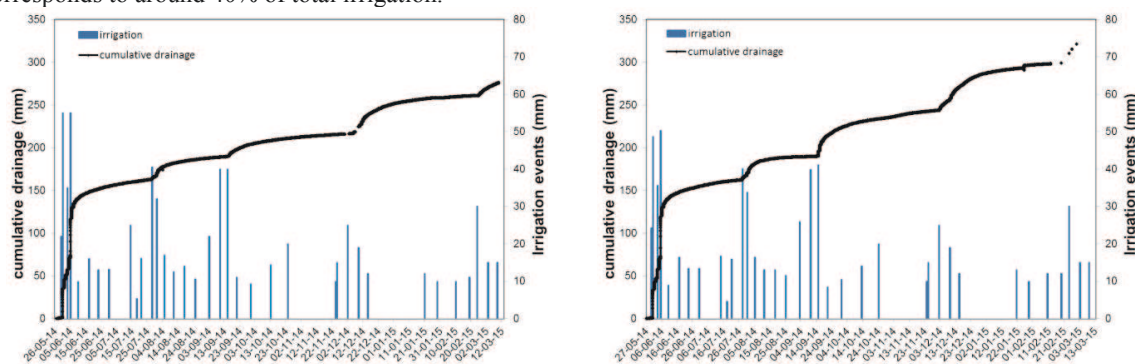


Fig. 1. Irrigation and cumulative drainage during the study period in one of the lysimeters in the gravel soil (left) and in the moraine soil (right).

Preliminary bromide results show a first peak starting in the beginning of August, after 170 mm of cumulative drainage. In few of the lysimeters, an early secondary bromide peak was detected few hours or days after herbicides application, after only 100 mm of cumulative drainage, which indicates that some preferential flow occurred just after herbicides application. Fluorescein peaks coincided with this secondary bromide pulse.

In the lysimeters with surface application, a rapid breakthrough (few hours) of the applied herbicides, with concentrations of up to 30 $\mu\text{g/L}$ for atrazine and up to 5 $\mu\text{g/L}$ for acetochlor and metolachlor, was observed in moraine soil but not in gravel soil (Fig. 2). In gravel soil only small concentration of atrazine (up to 0.1 $\mu\text{g/L}$) was detected after 200 days. Shortly after herbicide application, high irrigation with relatively low evapotranspiration could result in preferential flow along soil macropores (e.g. soil fauna channels, root holes)⁸. The faster transport of the pesticides compared to bromide indicates that higher mass fractions of pesticide than bromide was transported via preferential flow paths. Nevertheless, the concentrations of acetochlor and metolachlor in this early pulse were lower than that of atrazine, although the former were applied at a higher rate, suggesting herbicides movement through probably not only macropores but also soil matrix. These peaks coincided in time with the fluorescein peaks.

In the lysimeters with injection below the root zone, higher concentrations were detected (up to 120 $\mu\text{g/L}$ for atrazine, up to 290 $\mu\text{g/L}$ for acetochlor and metolachlor and up to 230 $\mu\text{g/L}$ for chloridazon) and maximum concentrations occurred within few days (gravel soil) or few hours (moraine soil) after pesticides injection and persisted longer than in the experiments with surface application (Fig. 2). No significant differences were observed between the two soil types.

Metabolites, especially DEA and DPC (where chloridazon was applied), were detected in the leachates of all the experiments. Low DEA to atrazine ratio (DAR) values⁹ were observed just after the atrazine application due to the early fast preferential flow. Higher DAR values were detected with time, indicating longer residence time of atrazine

in the soil zone and considerable degradation to DEA. After 200 days, DAR values up to 1.1 were measured in the lysimeters with depth injection, whereas higher values were found in the lysimeters with surface application (up to 1.7 in the moraine soil and higher than 10 in the gravel soil). These results confirmed that the role of the preferential flow on the pesticides movement decreased with time and that under the common scenario of surface application slower atrazine infiltration through the soil occurred in the gravel soil compared to the moraine soil.

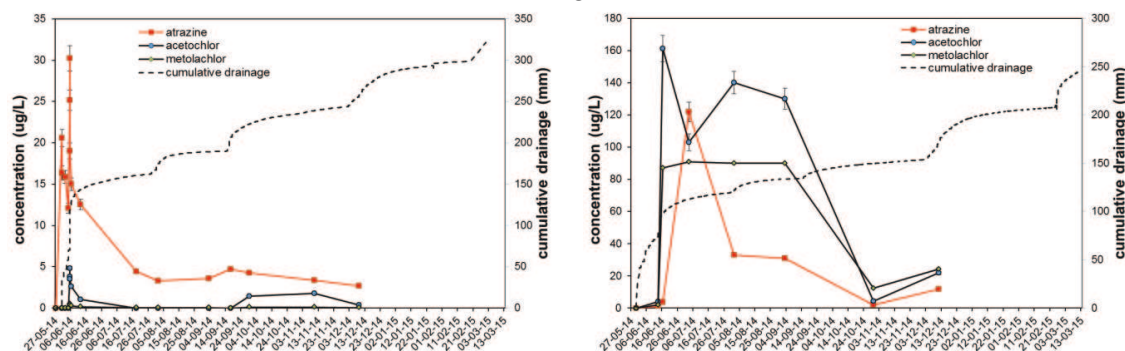


Fig. 2. Pesticides breakthrough curves. Left: one of the lysimeters with surface application in gravel soil. Right: one of the lysimeters with depth injection in gravel soil.

4. Conclusions

Few days after herbicides application, significant infiltration of the target compounds took place by preferential flow, bypassing the sorption and degradation capacity of the soil matrix. Once this effect decreased, degradation processes took place as evidenced by the detection of metabolites in the leachates. An efficient SPE approach for 10-L drainage water samples was developed. The observed high drainage water pesticide concentrations, especially in the lysimeters in which the pesticides were injected at depth, provide enough micropollutants mass for multi-element CSIA, which is currently being carried out. The applicability of CSIA for assessing in situ biodegradation of the target pesticides during transport in a complex and dynamic environmental system will be evaluated.

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References

- Schreglmann K, Hoeche M, Steinbeiss S, Reinicke S, Elsner M. Carbon and nitrogen isotope analysis of atrazine and desethylatrazine at sub-microgram per liter concentrations in groundwater. *Anal Bioanal Chem* 2013;**405**: 2857-2867.
- Elsayed OF, Maillard E, Vuilleumier S, Nijenhuis I, Richnow HH, Imfeld G. Using compound-specific isotope analysis to assess the degradation of chloroacetanilide herbicides in lab-scale wetland. *Chemosphere* 2014;**99**: 89-95.
- Elsner M, Jochmann A, Hofstetter TB, Hunkeler D, Bernstein A, Schmidt TC, Schimmelmann A. Current challenges in compound-specific stable isotope analysis of environmental organic contaminants. *Anal Bioanal Chem* 2012;**403**: 2471-2491.
- Loos R, Locoro G, Comero S, Contini S, Schwesig D, Werres F, Balsaa P, Gans O, Weiss S, Blaha L, Bolchi M, Gawlik BM. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res* 2010;**44**: 4115-4126.
- Kolpin DW, Thurman EM, Linhart SM. Finding minimal herbicide concentrations in ground water? Try looking for their degradates. *Sci Total Environ* 2000;**248**: 115-122.
- Weigel S, Bester K, Hühnerfuss H. New method for rapid solid-phase extraction of large-volume water samples and its application to non-target screening of North Sea water for organic contaminants by gas chromatography-mass spectrometry. *J Chromatogr A* 2001;**912**: 151-161.
- D'Archivio AA, Fanelli M, Mazzeo P, Ruggieri F. Comparison of different sorbents for multiresidue solid-phase extraction of 16 pesticides from groundwater coupled with high-performance liquid chromatography. *Talanta* 2007;**71**: 25-30.
- Germann P, Beven K. Water flow in soil macropores I. An experimental approach. *J Soil Sci* 1981;**32**: 1-13.
- Adams CD, Thurman EM. Formation and transport of deethylatrazine in the soil and vadose zone. *J Environ Qual* 1991;**20**: 540-547.