

Assessing pesticide dynamics in soil and vadose zone using compound-specific isotope analysis (CSIA): A lysimeter study

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Summary

For evaluating pesticide/metabolite transformation under complex environmental conditions new compound-specific isotope analysis (CSIA) methods were developed and tested in lysimeter experiments. Selected herbicides and metabolites commonly detected in groundwater were applied either at the surface or through artificially created preferential flow paths in two agricultural soils (moraine and gravel) cropped with corn or sugar beet. With both surface application and depth injection, pesticide breakthrough was observed. In the moraine soil, a rapid preferential breakthrough within two days occurred followed by a slower arrival during several months likely due to matrix flow, while in the gravel soil only the latter occurred. Metabolites from all the applied parent compounds were detected in the leachates. Over a period of one year a steady enrichment of ¹³C over ¹²C was observed for acetochlor and metolachlor, even if injected below the root zone, indicating that transformation also occurred at depth. These results highlight the potential of CSIA to provide evidence of slow transformation of pesticides/metabolites under complex environmental conditions, which is difficult to achieve with other methods.

Keywords: herbicides, degradation, metabolites, preferential flow, tracers

Introduction

Herbicides are extensively used in agriculture for plant protection against weeds. After pesticide application, vertical movement out of and below the root zone can result in groundwater contamination. Sorption of solutes into soil particles and degradation processes can mitigate pesticide migration through the matrix soil. Pesticides can also infiltrate rapidly by preferential flow, which could be caused by the presence of macropores (such as cracks, soil fauna channels or root holes) or by heterogeneity in soil hydraulic properties (Flury et al. 1994). Preferential flow is often a rule rather than an exception (Vogel et al. 2006). Due to an accelerated transport, pesticide residence time might be too short for degradation and therefore it might pose a threat to groundwater. While pesticide degradation in top-soil has been extensively studied, there is

limited knowledge about pesticide degradation below the root-zone and about the fate of pesticide-metabolites. A main reason is that transformation processes are difficult to track in soil and vadose zone as concentrations tend to fluctuate strongly due to highly transient hydrological conditions. Compound-specific isotope analysis (CSIA) is a promising tool for assessing transformations of these compounds. For priority pollutants such as chlorinated and petroleum hydrocarbons, this approach has become a well-established method to identify and quantify degradation pathways (Elsner et al. 2012). For micropollutants, however, CSIA application is still emerging as several analytical challenges associated with the low concentrations and the high polarity of these compounds are encountered (Elsner and Imfeld 2016). Recently, the feasibility of CSIA at low concentrations has been documented for some pesticides using optimized pre-concentrations and new analytical methods (Schreglmann et al. 2013, Elsayed et al. 2014). Nonetheless, CSIA data of pesticides and metabolites in environmental or near-natural systems remain extremely scarce (Milosevic et al. 2013, Schreglmann et al. 2013, Bashir et al. 2015, Schürner et al. 2016). The main goal of this work was to evaluate if CSIA can be used to assess the fate of selected herbicides and metabolites in agricultural soils and vadose zone, where transformation and transport processes interact. A multi-element (C, N, Cl) CSIA approach is being tested not only for demonstrating transformation but also identifying underlying mechanisms.

In the present study, selected herbicides were applied not only at the surface but also through artificially created preferential flow paths for evaluating degradation below the root zone. The study focused on some commonly and worldwide used herbicides for weed control on corn and sugar beet with (relatively) high leaching potential, which are frequently detected in groundwater: atrazine, acetochlor, metolachlor and chloridazon (Loos et al. 2010). Some of their transformation products are even more frequently detected in groundwater than their parent molecules (Kolpin et al. 2000). Taken together, knowledge about the degradation of pesticides and the environmental fate of their metabolites is, therefore, crucial to assess possible effects on human health and the environment.

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Material and methods

A field-based lysimeter study was conducted using twelve weighing lysimeters (3.14 m² surface area and 2.5 m depth) from Agroscope. These large outdoor lysimeters were constructed in 1979 when six of them were mechanically filled with a well-drained sandy loam cambisol developed from a stony alluvium (“gravel soil”) and the other six were filled with a poorly-drained loam cambisol developed from moraine deposits (“moraine soil”) (Troxler et al. 1998). The two soil types are typical arable soils in Switzerland.

The lysimeters were planted with corn in spring of 2014 and with sugar beet in spring of 2015. In four lysimeters atrazine, metolachlor, acetochlor and chloridazon 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 preferential transport of the pesticides through the topsoil. In the last four lysimeters selected metabolites (desethylatrazine, DEA, desphenylchloridazon, DPC, and 2,6-Dichlorobenzamide, BAM) were applied at the surface. To ensure that sufficient mass for CSIA arrives at the drainage water, in some cases higher pesticide doses than normal were used, while respecting ecotoxicological criteria. Pesticide leaching was favored by maintaining high water content in the soil before application and by applying intense irrigation events just after application. Sodium bromide was applied as a water conservative tracer, whereas uranine was applied as “surrogate” tracer for mimicking pesticide transport. The lysimeter facility was covered with a plastic tunnel and an irrigation system was installed to ensure full control of irrigation rates. Frequency capacitance sensors were installed in two of the lysimeters (one for each type of soil) for measurement of the soil-water content at different soil depths. Drainage water was collected via Teflon tubes in 54 L glass bottles placed on balances to record continuously the outflow.

The drainage water samples were analyzed for bromide by anion chromatography and for uranine by fluorescence spectrometry. For the preconcentration and extraction of the target herbicides 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. Pesticide and metabolite concentrations in the solid phase extraction (SPE) eluates were determined by using ultra-performance liquid chromatography quadrupole time of flight mass spectrometry (UHPLC-QTOF-MS). C and N isotope ratios were determined by gas chromatography isotope ratio mass spectrometry (GC/IRMS), whereas gas chromatograph coupled to quadrupole mass spectrometry (GC/qMS) was used for measuring Cl isotope ratios.

Results and discussion

Over the study period (January 2014 to December 2016), the total amount of water applied in each lysimeter by sprinkler irrigation was about 2460 mm, by regular 5-20 mm and occasional 30-50 mm intense events. About 930 mm were applied during 2014, 845 mm during 2015 and 685 mm during 2016. Cumulative drainage over the study period was between 700 and 970 mm. In relation to water input, these amounts constituted 30-40% of total irrigation.

Drainage increases coincided with periods with high volume of irrigation and high soil water content. The existence of preferential flow paths was evident from the soil moisture readings. In the moraine soil, rapid soil moisture content increases were observed at 16 cm depth after any irrigation event, whereas at 56 cm depth only intense irrigation events lead to quickly significant soil moisture rises. Fluctuations in the soil water content were less significant for the gravel soil, especially for the deeper points, suggesting fewer contributions of preferential paths in water movement through the soil.

With surface application, the total amount of bromide that leached 20 months after application was equivalent to 30-55% of the mass applied. In the moraine soil, bromide peak concentration reached 80-110 mg L⁻¹ within 12 months, after approx. 400-450 mm of accumulated leachate, followed by a steady decrease. This leaching pattern indicates that only a small fraction of the tracer was transported along preferential flow paths and points to main transport through the porous matrix. In the gravel soil, bromide peak (120-180 mg L⁻¹) was more rapidly reached, after 9-11 months and 300-350 mm of accumulated seepage. This is consistent with the higher water retention capacity of the moraine compare to the gravel soil. In the experiments with depth injection, higher amounts of bromide were recovered (70% and 90% of the applied mass for moraine and gravel soil, respectively), and the peak was reached after 180-220 mm of accumulated seepage. The removal of bromide by plant uptake and harvesting was low: 10-13% and 5-7% of the applied bromide at surface and depth, respectively, for corn (3 months after application) and less than 1% for sugar beet (17 months after application).

Uranine leaching pattern was different than for bromide, with concentration peaks detected few hours after application. With surface application, uranine peaks were detected 1-2 days after application and less than 100 mm of accumulated seepage. The maximum concentration was higher in moraine (13 µg L⁻¹) than in gravel soil (2.6 µg L⁻¹). With depth injection, uranine peaks were observed also within 24 hours and after approximately 100 mm of accumulated seepage. Maximum concentrations were higher than with surface application (40 and 22 µg L⁻¹ for moraine and gravel soil, respectively). The considerably small amount of accumulated leachate needed for uranine peak to occur suggests that uranine was mainly transported through preferential flow, bypassing large fractions of the soil matrix. A very small amount of the applied mass (less than 1.5%) actually reached the seepage water.

With both surface application and depth injection, pesticide breakthrough was observed, however, with a distinct difference among the two soil types. As observed for the tracers, the transport consisted of two components: flow through the porous matrix vs. preferential rapid flow through macropores. Shortly after surface herbicide application and due to the heavy irrigation and low evapotranspiration, a rapid preferential breakthrough took place in the moraine soil, but not in the gravel soil. In the moraine soil likely more macropores occurred and were better preserved due to the clayey matrix. In contrast, in the lysimeters with depth injection preferential breakthrough was observed in both soil types. The faster transport of the pesticides compared

to bromide indicates that higher mass fractions of pesticide than bromide were transported via preferential flow paths, similar to the observations for uranine.

A slower pesticide arrival during several months, likely due to matrix flow, was observed thereafter. During this period, a second solute pulse occurred 10-11 months after application, once the cumulative drainage water volume was higher than 300-350 mm. This peak lasted for 1-2 months (cumulative drainage to approximately 400-500 mm) followed by a long period with small and slow arrivals coincident with very slow seepage rate. In the case of depth application, higher concentrations were measured and before the occurrence of this second peak, additional pulses were observed after intense irrigation events, which involved herbicide movement through probably both matrix and macropores. Peak concentrations were considerably lower in these new pulses, probably because of degradation and longer contact times, allowing the herbicides to diffuse into the less-mobile pore water. As occurred with surface application, slight pesticide breakthrough occurred during the period with very slow seepage rate.

2.5 years after application (20 months in the case of surface chloridazon application) an average of 0.3% and 2.1% of the applied mass after surface application and depth injection, respectively, was recovered in the drainage water for all the substances, similarly to what was observed for uranine (up to 0.3% and 1.2%, respectively). No residues of atrazine, acetochlor, metolachlor or chloridazon were detected in the 0- to 10- cm soil layer two years after application.

Metabolites for all the applied herbicides (DEA and desisopropylatrazine, DIA, from atrazine, tertiary ethane sulfonate, ESA, and oxanilic acid, OXA, metabolites from the chloroacetanilides, and DPC from chloridazon) were detected in the leachates of all the experiments. Low metabolite to parent compound ratio values were observed shortly after application due to rapid preferential flow. Although several fluctuations were observed, higher ratio values were detected with time, indicating longer pesticide residence time in the soil zone and considerable degradation. A significant increase in the arrival of the metabolites was observed after 10-11 months, coincident with the rebound in the parent compounds. Residues of DPC (up to 0.13 mg kg⁻¹) were found in the 0- to 10-cm soil layer one year after surface chloridazon application, which correspond to approximately 5 and 10% of the chloridazon applied mass in gravel and moraine soil, respectively.

In the experiments with metabolite application, breakthrough occurred for the three applied substances. Breakthrough of BAM was faster and higher than for DEA and DPC. Eighteen months after application, an average of 3% and 15% of the BAM applied mass was recovered in the moraine and gravel soil, respectively, whereas less than 1% of DEA and DPC was leached. Movement of the applied metabolites was mainly by matrix flow, with a steady increase in concentrations with time, although fluctuations were observed, especially for DEA. Residues of DPC (up to 0.19 mg kg⁻¹) were found in the 0- to 10- cm soil layer one year after application, which correspond to approximately 4 and 9% of the applied mass in gravel and moraine soil, respectively. Up to 0.09 mg kg⁻¹ of BAM were detected in the moraine soil, which equals to approximately 4% of the applied mass.

Thanks to the successful development of large-volume (up to 40L) pre-concentration and clean-up methods, it was possible to perform CSIA at environmentally relevant concentration levels (as low as 0.2 µg L⁻¹). In the experiments with surface application, although only few samples have been already analyzed for δ¹³C and δ¹⁵N, preliminary results of a moraine soil lysimeter show a substantial enrichment in ¹³C for both acetochlor (up to approximately 6 ‰) and metolachlor (up to approximately 5 ‰) five months after application. Ten months after application, when the significant rebound in acetochlor and metolachlor was observed, carbon isotope ratios returned to the initial composition of the applied substances, suggesting that no degradation occurred during that time and that the observed increases in concentration of both parent compounds and metabolites were related to leaching of significant amounts of bound residues sorbed to the soil matrix. No significant changes were observed, however, neither in δ¹³C of atrazine nor in δ¹⁵N of atrazine and chloroacetanilides. In an experiment with depth injection, a significant steady enrichment in ¹³C with time was observed for acetochlor (up to approximately 10 ‰ after 9 months) and metolachlor (up to approximately 5 ‰ after 10 months). Atrazine, however, did not show significant ¹³C enrichment after 10 months. No changes in δ¹⁵N for any of the analyzed herbicides were observed. Regarding isotope ratios in metabolites, preliminary results show enrichment in ¹³C-DEA for both atrazine surface and depth application 11 months after application (up to approximately 5 ‰ and 2.5 ‰, respectively) and in ¹³C-DPC for chloridazon depth injection 22 months after application (up to 3.5 ‰), although fluctuations were observed. These results suggest that further degradation of DEA and DPC is also taking place. Preliminary isotope results for the lysimeters with metabolites application showed an increase in δ¹³C of DPC up to 3 ‰ one year after application.

Conclusions

Monitoring recovery of applied herbicides, their metabolites, as well as uranine and bromide ions in lysimeters drainage water made the significant role of preferential flow apparent in the mobility of the studied compounds through the soil and the vadose zone within few days after application. Uranine was a more realistic marker than bromide for the early preferential transport of the applied pesticides. Rapid preferential breakthrough of the applied solutes was more significant for the moraine than for the gravel soil and, as expected, more evident after depth injection. This movement bypassed large fractions of the soil matrix and thus the degradation potential was reduced and high contents of the parent compounds were detected in the drainage water. A slower herbicide arrival during several months, likely by matrix flow, was observed thereafter. Bromide was a good marker for this slow pesticide transport through the soil matrix, although it overestimated pesticide leaching. Recoveries of bromide were 40 and 150 times as high as pesticides/uranine for surface and depth application, respectively. Pesticide concentrations during leaching via matrix flow are greatly reduced by sorption and degradation. The detection of metabolites of all the applied compounds in the drainage water suggested the occurrence of herbicide degradation once higher residence times in the soil zone were achieved. For some compounds, a steady

enrichment of ^{13}C over a period of one year was observed even if injected below the root zone confirming that transformation also occurs at depth. These preliminary results highlight the potential of CSIA to gain insight into slow transformation of pesticides/metabolites under complex environmental conditions, which is difficult to achieve with other methods. Results obtained in the lysimeters might readily be expanded to large-scale studies.

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