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Synthesis

This chapter provides a summary of the main results and conclusions of this thesis, which examines the use of compound-specific stable isotope analysis (CSIA) in the analysis of sources and sinks of organic pollutants. Following this summary, it discusses the implications of the thesis results for the use of the presented methods and model concepts: it gives recommendations for potential applications of the SISS model, and the use of CSIA in the assessment of diffuse pesticide pollution. Moreover, this chapter presents an outlook for future research that might follow from the results of this research.

6.1 Summary

Previous studies have challenged the applicability of the Rayleigh equation approach and CSIA-based source apportionment in cases where isotope ratios change due to both contaminant degradation and mixing between contaminant sources. These cases were discussed in chapters **2** and **3**, which investigated the use of a CSIA-based mathematical model for the assessment of sources and sinks of organic contaminants (stable isotopes sources and sinks model; SISS model). The SISS model represents a combination of the Rayleigh equation (for degradation quantification) and the linear stable isotope mixing model (for source apportionment), and thus allows for combined source apportionment and quantification of in situ degradation. Chapter 2 presented a detailed derivation of the SISS model for a scenario with two sources and one reaction pathway. Chapter 3 provided a validation of the SISS model against reactive transport model simulations, and an example application to previously published CSIA data from a BTEX-contaminated aquifer.

Chapter 2 highlighted two major benefits of the SISS model. First, the SISS model accurately assesses the extent of degradation if contaminant transformation follows instantaneous mixing of two sources, and provides a conservative estimate of the extent of degradation otherwise. Second, the SISS model allows for an accurate estimate of source contributions even if degradation occurs prior to mixing between the two contaminant pools. It is thus, in general, possible to partition the dual-element isotope plot of a contaminant that originates from two sources according to the relative contributions of these sources. This finding contrasts with previous studies that challenge the use of CSIA-based source apportionment for situations where degradation-induced isotope fractionation occurs. Source apportionment (i.e., partitioning of the dual-element isotope plot) with the SISS model was illustrated by the example of CSIA data of perchlorate. The model showed little uncertainty in the calculated source contributions of natural and synthetic perchlorate sources.

The validation of the SISS model against the results of a reactive transport model that simulates isotope fractionation effects (**chapter 3**) illustrated the accuracy of the SISS model in source apportionment and quantification of contaminant degradation. However, a field application of the model to a benzene-contaminated aquifer revealed challenges in the use of the SISS model, which resulted from the inherent uncertainties in field CSIA data and heterogeneity of the field site. Despite these challenges, the SISS model illustrated that benzene contamination mainly stemmed from one of the two sources, and allowed for the assessment of the minimum and maximum extent of in-situ degradation at the field site. The

latter became especially beneficial in view of the contradictory estimates that the classical Rayleigh equation approach yielded for the investigated field site. The field application thus illustrated the role of the SISS model as a unique tool of CSIA-based source apportionment and quantification of contaminant degradation in systems with more than one contaminant source or reaction pathway (or both).

Whereas chapters 2 and 3 discussed CSIA-based methods that are independent of a specific environmental system or spatial scope, **chapter 4** narrowed the focus to the potential use of CSIA for diffuse pollutants at catchment scale. The aim was to analyze the evolution of CSIA data of diffuse pollutants under various hydrological conditions. To this end, virtual experiments of pesticide transport, degradation and isotope fractionation at hillslope scale were performed with a physically-based coupled subsurface-surface model (HydroGeoSphere). Pesticide concentrations and isotope ratios were simulated for steady-state hydrologic conditions, in response to an extreme rainfall event, and under transient hydrological conditions.

The main conclusions to be drawn from the virtual experiments were that (i) the modeled isotope ratios allowed for the quantification of the extent of in-situ degradation and the relative contribution of two competing pathways to overall degradation; (ii) the decrease in isotopic signatures during extreme rainfall events can be used as an indicator of pesticide transport via surface runoff; (iii) the modeled extent of isotope fractionation was large enough to be measured by current analytical methods; and (iv) the inherent underestimation of the extent of degradation by the Rayleigh equation approach remained small even under transient conditions. The virtual experiments thus indicate the usefulness and feasibility of CSIA in the analysis of diffuse pollution, especially given that concentration data alone would not allow for analyses such as mentioned under points (i) and (ii). Nonetheless, these promising results need to be confirmed in experimental studies of CSIA of diffuse pollutants. Such an experimental study was presented in chapter 5.

Chapter 5 illustrated a combined measurement and modeling approach of concentrations and carbon isotope ratios of two herbicides (i.e., S-metolachlor and acetochlor) aimed at examining the added value of CSIA data in monitoring and modeling of pesticide transport and degradation. These field data were collected in a 47-ha agricultural catchment in Alsace (France; Alteckendorf catchment), and represent the first systematically measured CSIA data of pesticides at catchment scale. Concentrations at the catchment outlet ranged from the low ng L^{-1} level before the application period to $65 \mu\text{g L}^{-1}$ following an extreme rainfall event in the first month after herbicide application. While concentrations show several peaks associated with rainfall events, carbon isotope ratios gradually increased during the study period, leading to an enrichment of more than 2 ‰ within two months. Consequently, whereas concentrations did not provide clear evidence of transformation processes, the increase in isotope ratios indicates the occurrence of herbicide degradation in the soil and during transport to the catchment outlet. This illustrates the added value of CSIA in the analysis of pesticide pollution at catchment scale.

To underpin and extend the analysis of the field CSIA data, pesticide concentrations and isotope ratios at the catchment outlet were simulated in a conceptual (parsimonious) model (chapter 5). This model is based on the description of flow and

transport by travel time distributions, and is able to simulate transient hydrological conditions, pesticide degradation, and pesticide transport to the stream via overland flow and groundwater discharge. The model was calibrated against discharge, pesticide concentration, and CSIA data. The calibration results demonstrated that incorporation of CSIA data into model calibration can reduce model uncertainty by restricting the range of parameter values and constraining the simulated extent of degradation. Model results were used to assess the isotopic enrichment factor (ε_C), and to specify the extent of degradation, which could not be derived from the measured CSIA data only. At the same time, the field data informed the modeling, as measured concentration and CSIA data illustrated which processes had to be included in the model. For example, the best model fit to the field data was achieved by assuming inhibition of degradation in the topsoil for sorbed pesticide, and a decreasing rate of pesticide degradation with increasing depth.

6.2 Implications and Outlook

6.2.1 Assessment of contaminant sources and sinks with the SISS model

Despite the detailed field site characterization, the application of the SISS model in **chapter 3** was complicated by uncertainties in the field CSIA data. Consequently, there is still considerable room for additional model testing, which might indicate how to address and minimize these complications. Chapter 3 mentions several factors that facilitate the application of the SISS model: (i) small analytical uncertainties in CSIA data, (ii) clearly distinct source signatures, (iii) a single reaction process or a combination of reaction processes with known relative contributions to overall degradation, and, ideally, (iv) a perpendicular mixing line between the sources with respect to the degradation trajectories in the dual-element isotope plot. As the SISS model has also been outlined for more than two sources and one reaction pathway, respectively, future research might aim for application of the model to a combination of multiple emission sources and reaction pathways. In addition, it might be interesting to evaluate the performance of the SISS model in the characterization of diffuse pollution, as studied in **chapters 4** and **5**. These systems involve different flowpaths and a larger degree of heterogeneity than aquifers. Validation of the SISS model for these systems would thus require virtual experiments with a more complex coupled subsurface-surface model that incorporates isotope fractionation effects. If the SISS model proves applicable for such systems, it might support the identification and quantification of pesticide sources and sinks, especially in catchments with detailed information about applied pesticide products, corresponding isotope ratios, and isotope fractionation effects of the considered pesticide.

In addition to research purposes, CSIA has also attracted the interest of consultants and regulators for the assessment of, e.g., groundwater pollution beneath industrial sites. In this context, the SISS model might improve the CSIA-based assessment of contaminant degradation, as it helps in distinguishing degradation-induced isotope fractionation from changes in isotope ratios due to mixing of sources. Future applications of the SISS model might, therefore, also include commercial purposes

that focus on monitored natural attenuation. Finally, the SISS model is not restricted to applications in contaminant hydrology, but it might also be employed in other disciplines such as atmospheric pollution.

6.2.2 Applicability of CSIA for diffuse pollutants

CSIA of pesticides in the study catchment (**chapter 5**) was only feasible for samples with relatively high pesticide concentrations (in the $\mu\text{g L}^{-1}$ range except for one sample) due to analytical detection limits. The interpretation of the CSIA data was, therefore, solely based on six data points. A higher temporal resolution might have allowed for a more detailed interpretation, including the analysis of isotope ratios before the application period and during baseflow periods, and multiple samples during single rainfall events. However, the low concentrations of these samples did not allow for CSIA. Similarly, additional CSIA data points might have been beneficial for the calibration of the parsimonious pesticide model. CSIA-based studies of pesticide transport and degradation as presented in chapter 5 should, therefore, aim at a fine temporal resolution of CSIA data, and, preferably, also include isotope ratios during baseflow conditions. The latter is, however, challenged by current detection limits of CSIA, as baseflow conditions usually imply low pesticide concentrations. At present, CSIA of environmental samples requires large sample volumes, and special extraction and preconcentration techniques (Elsner et al., 2012). By employing these techniques, it has, nonetheless, been possible to determine carbon isotope ratios of organic contaminants (including one pesticide) at concentrations below 100 ng L^{-1} (Jochmann et al., 2006; Schreglmann et al., 2013). In view of in-stream concentrations of pesticides commonly reaching a few $\mu\text{g L}^{-1}$ (Kreuger, 1998; Müller et al., 2002; Fenner et al., 2013), concentrations of pesticides can be expected to frequently exceed these limits.

Although **chapters 4** and **5** both suggest the applicability of CSIA in the analysis of diffuse pollutants, the studied hydrological systems show fundamental differences: whereas hillslope discharge was dominated by groundwater (chapter 4), the agricultural study catchment was characterized by a high responsiveness to rainfall via overland flow (chapter 5). Accordingly, pesticide transport was governed by groundwater in the virtual hillslope model, and by overland flow in the Alteckendorf catchment. Therefore, simulated isotope ratios show a highly fluctuating pattern in the Alteckendorf catchment, whereas seasonal variations in isotope ratios were small in the virtual hillslope model. These contrasting results suggest that the detail needed in CSIA sampling is dependent on the characteristics of the hydrological system. Catchments with well-drained soils and long response times will dampen variations in the isotope ratios, and thus yield a stable CSIA pattern as seen for the simulated hillslope. For these systems, application of the Rayleigh equation to one CSIA data point might, therefore, already give an accurate estimate of pesticide degradation in the catchment (see chapter 4). In contrast, extreme events or highly responsive systems that are prone to the generation of overland flow and erosion (such as the Alteckendorf catchment in chapter 5) might require a fine temporal resolution of CSIA samples, as the sampled pesticide might have undergone a different extent of degradation depending on which flowpath dominates stream discharge.

In the case of the Alteckendorf catchment, CSIA could only be applied to samples with high pesticide concentrations, which were associated with the occurrence of pesticide transport via overland flow and erosion. This restriction might affect the CSIA-based assessment of degradation in opposing ways. Pesticides that are transported via surface runoff stem from the microbially active upper soil layers, and might thus show a larger extent of degradation than pesticides that have quickly percolated to groundwater. However, the model results suggest that pesticides in surface runoff are associated with less degradation compared to pesticides in groundwater discharge. This might be the case if sorption in the upper soil layers limits bioavailability of the pesticide and thus results in reduced pesticide degradation (as assumed in the model in chapter 5); or if pesticides discharged via groundwater also stem from applications in previous years, and have thus undergone significantly more degradation than recently applied pesticide emitted via surface runoff (as in the virtual hillslope system in chapter 4). In other cases, redox conditions in groundwater might be more favorable to pesticide degradation than those in the soil, which would also result in a larger extent of degradation for pesticide in groundwater discharge compared to pesticide in surface runoff.

Regardless of the type of hydrological system, model results and field data from **chapters 4 and 5** suggest that the isotopic enrichment between the applied pesticide product and a river sample is large enough to be detected by CSIA (given instrumental uncertainties of about 0.5 ‰ for carbon and 5 ‰ for hydrogen isotope analysis, respectively; Sherwood Lollar et al., 2007). Moreover, although more than 90% of the total mass export in the Alteckendorf catchment occurred within two weeks after the main pesticide application, enough pesticide was retained in the catchment to allow for CSIA several weeks later. This indicates the applicability of CSIA for diffuse pollutants even in highly responsive catchments.

6.2.3 Recommendations for modeling of CSIA of diffuse pollutants

Chapter 5 demonstrates the usefulness of a combined measurement and modeling approach for CSIA data, as the model gave further insight into pesticide transport and degradation in comparison to the measurements alone. However, it is crucial that such a modeling approach includes all important pesticide transfer processes. For example, in chapter 5, pesticide application was modeled as a homogeneous input into the shallow reservoir. This representation was sufficient in view of the purpose of this study and the limited CSIA data. For other applications, however, it might prove useful to apply a spatially-distributed model instead, as this would allow simulation of the hydrologic connectivity between agricultural fields and the catchment outlet, and thus help in identifying areas that pose a high risk of surface water contamination. Similarly, spatially-distributed models might assist in source identification of pesticide pollution. Moreover, more complex models than the one in chapter 5 might be able to incorporate additional processes affecting pesticide fate at catchment scale (such as in-stream degradation), or explicitly simulate soil erosion and associated particulate pesticide transport. Nonetheless, distributed models, and especially physically-based models, are computationally intensive and

require many input data and parameters (Holvoet et al., 2007; Kampf and Burges, 2007). In general, the choice between different models of pesticide pollution greatly depends on the objectives and scope of the modeling approach (Payraudeau and Gregoire, 2012). As seen in chapter 5, it can prove advantageous to begin with a very simple model concept, and gradually increase its complexity by updating the model with information gained from the analysis of field data. Hence, it is inadvisable to favor, a priori, a certain model type for the interpretation of CSIA data.

The model validation and calibration in chapter 5 was challenged by a lack of information about isotope fractionation associated with S-metolachlor transformation. Isotopic enrichment factors were only available for other chloroacetanilide pesticides (Elsayed et al., 2014), and it is unknown to what extent these laboratory values are representative of processes occurring at catchment scale. Hence, there is a clear need for additional studies that determine isotope fractionation effects specifically for the considered compound. As shown in chapter 5, the determination of appropriate enrichment factors can also be assisted by modeling of field CSIA data. However, this can only yield accurate estimates in combination with sufficient CSIA data, which restrict equifinality of model parameters.

In summary, this thesis presents novel CSIA-based methods in the analysis of sources and sinks of organic pollutants. **Chapters 2** and **3** illustrated how source apportionment and degradation quantification with CSIA can be combined and refined by employing the SISS model. **Chapters 4** and **5** illustrated the unprecedented use of CSIA in the characterization of transport and transformation of diffuse pollutants, which was underpinned by analysis and modeling of field CSIA data. While the discussed CSIA-based methods are not free of limitations, the presented example applications clearly demonstrate how these methods allow for an improved assessment of sources and sinks of organic pollutants.