How can we use compound-specific isotope data to model organic contaminants in catchments?



source: Fenner (2013)

Stefanie Lutz 3rd MASSTWIN Exploratory Workshop November 14th – 16th 2018 Helmholtz Centre for Environmental Research in Halle, Germany

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### **Organic pollution**







source: André Künzelmann/UFZ

Widespread organic pollution in aquifers ("legacy contaminants", e.g., benzene, chloroethenes) and catchments ("micropollutants", e.g., pesticides)

Common issues:

- identify emission sources
- provide evidence and quantification of transformation
- identify transformation pathway

#### **Key questions**





Common issues:

- identify emission sources
- provide evidence and quantification of transformation
- transformation pathway

How to extract this information?

- compound-specific isotope analysis (CSIA)
- mathematical and hydrological isotope models



# **1.1) CSIA FOR ORGANIC POLLUTANTS**



#### **Dilution vs. degradation of organic contaminants**



# **The Rayleigh equation**



### **Advantages of CSIA: degradation**

Evidence and quantification of degradation because

- degradation alters isotopic composition
- dilution has no impact
- physical processes (sorption, dispersion...): generally limited impact on isotopic composition





#### **Advantages of CSIA: sources**

Source fingerprinting: isotopic composition can depend on manufacturer or source of raw material

Lorax Striker Bladex Fieldstar Aatrex Herbicides		
<b>Fertilizer</b> (Skitmore, 1997)		
Michigan & Appalachian Formation Waters (Drimmie and Frape, 1996)	Product name	Active ingredient
Sewage Sludge (Skitmore, 1997)	Aatrex Nine-O Striker Fieldstar	Atrazine Clopyralid, flumetsulam, 2,4-D Clopyralid, flumetsutlam
Road Salts (Rosen, 1999)	Bladex Nine-T Lorox DF	Cyanazine Linuron
(Desaulniers et al., 1986) Lambton & Sarnia Regional Groundwaters		
Chlorinated Solvents TCA   (van Warmerdam et al., 1995) TCE		
-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 $\delta^{37}$ Cl % (SMOC)		<b>HELMHOLTZ</b> ZENTRUM FÜR UMWELTFORSCHUNG
source: Annable (2007)		UFZ

#### **Advantages of CSIA: sources**

Source apportionment: what is the contribution of each source to the sample mixture?



isotope mixing model:

contribution of source A

$$f_A = \frac{\delta^{13}C_S - \delta^{13}C_B}{\delta^{13}C_A - \delta^{13}C_B}$$



# **1.2) DUAL-ELEMENT ISOTOPE DATA**



### Source identification with 2D isotope data



 main source: coal combustion at low temperatures

# Differentiation between transformation pathways with 2D isotope data



characteristic slopes ( $\epsilon_{\rm H}/\epsilon_{\rm C}$ ) for different transformation pathways

# 2) FIELD CSIA DATA OF ORGANIC GROUNDWATER POLLUTANTS





# Calculating degradation in the field

#### **CSIA in the field: heterogeneous systems**



#### **CSIA in the field: heterogeneous systems**



source: Kopinke (2005) ES&T

#### 3) COMBINED SOURCE APPORTIONMENT AND DEGRADATION QUANTIFICATION



#### **Mixing and degradation**

CSIA applied either for degradation quantification or source apportionment

→ What if isotopic composition changes due to source mixing and degradation?



### **SISS model: approach**

Mathematical model for two mixing sources and degradation via one reaction pathway

 $\rightarrow$  the <u>Stable Isotope Sources and Sinks Model</u>



### SISS model: mixing followed by degradation

- 1. calculate mixing line (green)
- 2. set up equation for degradation trajectory (red)
- 3. calculate intersection point
- 4. calculate source contributions and extent of degradation



traditional isotope mixing model:  $f_A = \frac{\delta^{13}C_M - \delta^{13}C_B}{\delta^{13}C_A - \delta^{13}C_B}$ 

from Rayleigh equation:

$$B[\%] = (1 - f_{deg}) \cdot 100$$
$$= \left[1 - \left(\frac{\delta^{13}C_S + 1000}{\delta^{13}C_M + 1000}\right)^{1000/\varepsilon_C}\right] \cdot 100$$

#### SISS model: unequivocal source partitioning

• Relative source contributions defined by 2D-isotope signature



 $\rightarrow$  It is possible to divide the 2D-isotope plot into areas of certain source contributions

#### **SISS model: field application**

degradation [%]

3.2ª-3.3b

7.1-7.3

4.0-6.9

20.1-82.8

9.7-15.6

15.7-26.2

<sup>a</sup> conservative estimate (scenario 1)

W9F2

W13F2

W15F2

W18F2

W18F3

W18F4

<sup>b</sup> maximum estimate

of source A

0.37

0.57

0.04

0.05

0.09

0.13



degradation [%]

3.6-3.8

8.1-8.4

4.6-13.5

n.d.

11.1-28.1

17.8-54.7

source A

0.36

0.54

0.02

n.d.

0.06

0.07

$\varepsilon_{H}$ =-79‰ and $\varepsilon_{C}$ =-3.6‰
(sulphate reducing)

 $\varepsilon_{H}$ =-60‰ and  $\varepsilon_{C}$ =-1.9‰ (methanogenic)

<u>Lutz</u> (2014b)

# 4) ISOTOPE MODELLING FOR DIFFUSE ORGANIC POLLUTANTS



#### **Modelling of CSIA data**

- IF-RTMs (isotope fractionation reactive transport models) for groundwater systems
  - $\rightarrow$ analyse isotope ratios in contaminant plumes
  - $\rightarrow$ test performance of Rayleigh equation in open systems



source: Prommer (2009)

- Novelty: simulation for diffuse pollutants
  - $\rightarrow$  include groundwater, unsaturated zone and surface runoff

#### **Diffuse pollutants on catchment scale**

- challenges:
  - extrapolating from lab to field conditions
  - low environmental concentrations
- → hydrological models help explore the use of CSIA for diffuse organic contaminants



# 4.1) VIRTUAL EXPERIMENTS FOR A HILLSLOPE



#### **Example I: hillslope model**

- Can CSIA be used in river monitoring to analyse diffuse pesticide pollution?
- → performance of "virtual experiments" with flow and solute transport model (HydroGeoSphere)



# Hillslope model: results



#### concentrations

 decreasing concentrations with increasing depth and distance from the source



#### carbon isotope ratios

- isotope enrichment with growing distance from the emission source
- enrichment > analytical uncertainty

source: Lutz (2013)

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# Hillslope model: results



#### underestimation by Rayleigh equation

 comparison to modelled concentrations of conservative solute

extreme rainfall event

- isotope ratios drop to the source values → emission via surface runoff
- use in source identification



# **Insights from the virtual experiments**

- magnitude of enrichment >> analytical uncertainties → can be detected by CSIA
- CSIA can be used for detection of pesticide transport via surface runoff
- good accuracy of Rayleigh equation approach

How does this work in a real catchment with field data?



# 4.2) FIELD CSIA DATA FROM AN AGRICULTURAL CATCHMENT



#### **Catchment-scale modelling of pesticide CSIA**

What does **CSIA** tell us about pesticide transport and degradation?

concentration + carbon CSIA of S-metolachlor during a growing season



collaboration with G. Imfeld, O. Elsayed, M. Lefrancq, S. Payraudeau (University of Strasbourg)



32

\_source: Lutz (2017)

#### Field CSIA data – catchment scale



#### **Concentrations:**

Highest outlet concentrations after extreme rainfall event in May

#### **CSIA:**

- evidence of degradation: 2.5% enrichment vs. 0.5‰ analytical uncertainty
- challenge of low environmental ٠ concentrations for CSIA
- degradation at catchment outlet via ٠ Rayleigh equation: 94.1%





#### Model results: concentrations and $\delta^{13}C$ of S-met



- calibrated against discharge, concentrations and CSIA in multiple runs (grey area)
- underestimation of peaks
- mobilisation of sorbed and thus non-degraded pesticide in the source zone following
- calibrated  $\varepsilon_{\rm C}$ =-1.13‰ (best fit) and  $\varepsilon_{c}$ =-0.9±0.3‰ (mean)

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### Model results: mass balance



### Monitoring and modelling: feedbacks

benefits of modelling

- mass balance: extent of degradation, transport, retention
- calibration of enrichment factor
- testing of alternative model setups (no erosion, first-order kinetics everywhere etc.)



#### For you to take home

Field CSIA data

Evidence and quantification of degradation (Rayleigh) Source delineation for local pollution

Modelling

Low-cost complementary approach Mass-balance based quantification of degradation Simulation of scenarios and virtual experiments

#### $\rightarrow$ Field CSIA data and modelling can inform each other

#### Outlook

Advances in analytical methods to allow for higher resolution in CSIA data of diffuse organic pollutants

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#### **References (I)**

- Alvarez-Zaldívar, P., Payraudeau, S., Meite, F., Masbou, J., and Imfeld, G. (2018) Pesticide degradation and export losses at the catchment scale: Insights from compound-specific isotope analysis (CSIA), Water Research, 139, 198-207, https://doi.org/10.1016/j.watres.2018.03.061.
- Annable, W. K., Frape, S. K., Shouakar-Stash, O., Shanoff, T., Drimmie, R. J., and Harvey, F. E. (2007) 37CI, 15N, 13C isotopic analysis of common agro-chemicals for identifying non-point source agricultural contaminants, Applied Geochemistry, 22, 1530-1536, https://doi.org/10.1016/j.apgeochem.2007.03.049.
- Bosch, C., Andersson, A., Kruså, M., Bandh, C., Hovorková, I., Klánová, J., Knowles, T. D. J., Pancost, R. D., Evershed, R. P., and Gustafsson, Ö. (2015) Source Apportionment of Polycyclic Aromatic Hydrocarbons in Central European Soils with Compound-Specific Triple Isotopes (δ13C, Δ14C, and δ2H), Environmental Science & Technology, 49, 7657-7665, 10.1021/acs.est.5b01190.
- Braeckevelt, M., Fischer, A., and Kästner, M. (2012) Field applicability of Compound-Specific Isotope Analysis (CSIA) for characterization and quantification of in situ contaminant degradation in aquifers, Applied Microbiology and Biotechnology, 94, 1401-1421, 10.1007/s00253-012-4077-1.
- Burt, T. P. and Pinay, G. (2005) Linking hydrology and biogeochemistry in complex landscapes. Progress in Physical Geography, 29(3):297–316.
- Elsayed, O. F., Maillard, E., Vuilleumier, S., Nijenhuis, I., Richnow, H. H., and Imfeld, G. (2014) Using compound-specific isotope analysis to assess the degradation of chloroacetanilide herbicides in lab-scale wetlands, Chemosphere, 99, 89-95, https://doi.org/10.1016/j.chemosphere.2013.10.027
- Elsner, M. (2010) Stable isotope fractionation to investigate natural transformation mechanisms of organic contaminants: principles, prospects and limitations, Journal of Environmental Monitoring, 12, 2005-2031, 10.1039/C0EM00277A.
- Lutz, S. R., Velde, Y. V. D., Elsayed, O. F., Imfeld, G., Lefrancq, M., Payraudeau, S., van Breukelen, B. M. (2017) Pesticide fate on catchment scale: conceptual modelling of stream CSIA data. Hydrol. Earth Syst. Sci., 21(10), 5243-5261. doi:10.5194/hess-21-5243-2017.

#### **References (II)**

- Lutz, S. R., Van Breukelen, B. M. (2014a) Combined Source Apportionment and Degradation Quantification of Organic Pollutants with CSIA: 1. Model Derivation. Environmental Science & Technology 48, (11), 6220-6228.
- Lutz, S. R., Van Breukelen, B. M. (2014b) Combined Source Apportionment and Degradation Quantification of Organic Pollutants with CSIA: 2. Model Validation and Application. Environmental Science & Technology 48, (11), 6229-6236.
- Lutz, S. R., van Meerveld, H. J., Waterloo, M. J., Broers, H. P., van Breukelen, B. M. (2013) A modelbased assessment of the potential use of compound-specific stable isotope analysis in river monitoring of diffuse pesticide pollution. Hydrol. Earth Syst. Sci., 17, 4505-4524, doi:10.5194/hess-17-4505-2013
- Penning, H., Sørensen, S.R., Meyer, A.H., Aamand, J., Elsner, M. (2010) C, N, and H Isotope Fractionation of the Herbicide Isoproturon Reflects Different Microbial Transformation Pathways, Environmental Science & Technology 44 (7), 2372-2378, DOI: 10.1021/es9031858
- Prommer, H., Anneser, B., Rolle, M., Einsiedl, F., and Griebler, C. (2009) Biogeochemical and Isotopic Gradients in a BTEX/PAH Contaminant Plume: Model-Based Interpretation of a High-Resolution Field Data Set, Environmental Science & Technology, 43, 8206-8212, 10.1021/es901142a.
- Van Breukelen, B. M. (2007) Quantifying the Degradation and Dilution Contribution to Natural Attenuation of Contaminants by Means of an Open System Rayleigh Equation, Environmental Science & Technology, 41, 4980-4985, 10.1021/es062846u.
- Van Keer, I., Bronders, J., Verhack, J., Schwarzbauer, J., Swennen, R. (2012) Limitations in the use of compound-specific stable isotope analysis to understand the behaviour of a complex BTEX groundwater contamination near Brussels (Belgium). Environ. Earth Sci., 66 (2), 457–470.