

Master Thesis Topics in Environmental Chemistry

Major in Biogeochemistry and Pollutant Dynamics, ETH Zürich

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Topic 1: Assessing the biodegradation of hexachlorocyclohexane isomers in contaminated soil

Hexachlorocyclohexanes (HCH), such as the insecticidal γ -HCH isomer, belong to the class of largely banned persistent organic pollutants (POP). Because HCHs only degrade over time-scales of decades and more, they are still found to contaminate soils at former production sites.¹

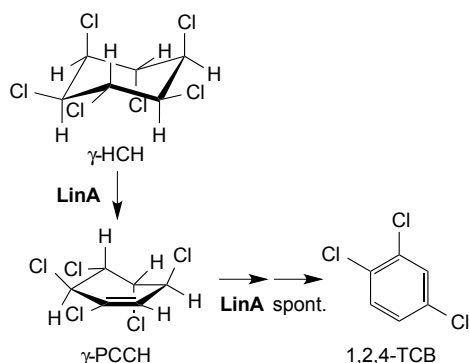


Figure 1 Initial steps of lindane (γ -HCH) biotransformation to a pentachloro-cyclohexene isomer (γ -PCCH). LinA catalyzes further dehydrochlorination, which can lead to the formation of equally problematic trichlorobenzene (TCB).

In our research, we develop new approaches to track biodegradation processes based on the stable isotope fractionation that can be measured in the remaining pollutant.² In this project, we aim at understanding the C and H isotope effects pertinent to the different enzymatic dechlorination mechanisms of several HCH isomers. An example of the most frequent reaction pathway is shown

in Scheme 1 for lindane (γ -HCH). The initial steps of for aerobic transformation is the HCl-elimination (β -elimination) and LinA stands for a dehydrochlorinase enzyme.

Students will learn (1) how to purify and work with LinA and LinB enzymes that are capable of transforming HCH isomers into less chlorinated compounds as well as (2) how to carry out compound-specific stable isotope analysis of H and C using gas chromatographs coupled to isotope ratio mass spectrometers.

Collaboration with Eawag Dept of Environmental Microbiology, Dr. Hans-Peter Kohler

Topic 2: Tracking the degradation of insecticides and industrial chemicals in contaminated groundwaters

In collaboration with environmental consultants and the chemical industry, we evaluate efforts to mitigate the pollution of groundwaters with organic chemicals.

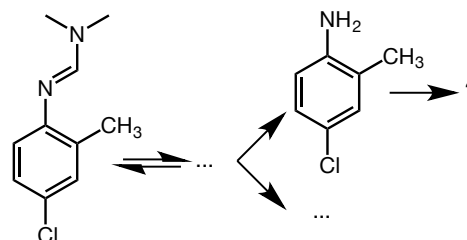


Figure 2 Unknown chemical transformation routes of the insecticide chlorodimeform to chloromethylaniline

In this project, we study the abiotic transformation of an insecticide

chlorodimeform to a toxic products such as substituted anilines as well as the biological degradation of the latter³ (Figure 2). Recent evidence from laboratory experiments, however, suggest a reversible first reaction, which implies that the original insecticide may be formed (!) in the environment. This study in environmental forensics involves the elucidation of reaction mechanisms with laboratory experiments as well as the use of modern stable isotope tools to track such processes in contaminated groundwaters.

Topic 3: Bioavailability of structural iron in smectites

Iron-bearing clay minerals are important redox buffers in the subsurface that can affect the biogeochemical cycling of elements and the fate, transport, and toxicity of pollutants. To assess the role that structural Fe in clay minerals plays in redox reactions in pristine and contaminated environments, we have recently developed electrochemistry-based

Suggested reading

(links to publications are [highlighted](#))

- [1] R. Lal, G. Pandey, P. Sharma, K. Kumari, S. Malhotra, R. Pandey, V. Raina, H. P. E. Kohler, C. Holliger, C. Jackson, and J. G. Oakeshott, "Biochemistry of microbial degradation of hexachlorocyclohexane and prospects for bioremediation," *Microbiol. Mol. Biol. Rev.*, vol. 74, no. 1, pp. 58–80, 2010 [doi:10.1128/Mmbr.00029-09](https://doi.org/10.1128/Mmbr.00029-09).
- [2] T. B. Hofstetter, J. Bolotin, S. G. Pati, M. Skarpeli-Liati, S. Spahr, and R. S. Wijker, "Isotope effects as new proxies for organic pollutant transformation," *CHIMIA*, vol. 68, no. 11, pp. 788–792, 2014 [doi:10.2533/chimia.2014.788](https://doi.org/10.2533/chimia.2014.788).
- [3] S. G. Pati, K. A. Shin, M. Skarpeli-Liati, J. Bolotin, S. N. Eustis, J. C. Spain, and T. B. Hofstetter, "Carbon and nitrogen isotope effects associated with the dioxygenation of aniline and diphenylamine," *Environ. Sci. Technol.*, vol. 46, no. 21, pp. 11844–11853, 2012 [doi:10.1021/es03043t](https://doi.org/10.1021/es03043t).
- [4] M. Sander, T. B. Hofstetter, and C. A. Gorski, "Electrochemical analyses of redox-active iron minerals: a review of nonmediated and mediated approaches.," *Environ. Sci. Technol.*, vol. 49, no. 10, pp. 5862–5878, 2015 [doi:10.1021/acs.est.5b00006](https://doi.org/10.1021/acs.est.5b00006).
- [5] C. A. Gorski, L. E. Klüpfel, A. Voegelin, M. Sander, and T. B. Hofstetter, "Redox properties of structural Fe in clay minerals: 3. Relationships between smectite redox and structural properties.," *Environ. Sci. Technol.*, vol. 47, no. 23, pp. 13477–13485, 2013 [10.1021/es403824x](https://doi.org/10.1021/es403824x).
- [6] C. A. Gorski, R. Edwards, M. Sander, T. B. Hofstetter, and S. M. Stewart, "Thermodynamic characterization of iron oxide-aqueous Fe²⁺ redox couples.," *Environ. Sci. Technol.*, vol. 50, no. 16, pp. 8538–8547, 2016 [10.1021/acs.est.6b02661](https://doi.org/10.1021/acs.est.6b02661).

approaches to derive thermodynamic parameters of such mineral phases.^{4–6}

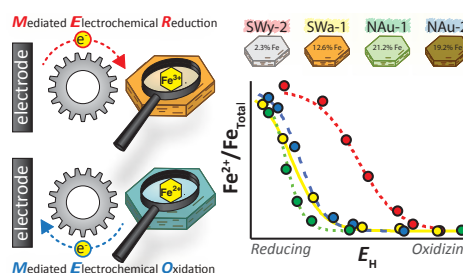


Figure 3 Mediated electrochemical analysis offers new avenues to quantify thermodynamics properties of redox active Fe in clay minerals.⁵

In this work, we explore whether the activity of iron-reducing bacteria (*Shewanella* and *Geobacter* species) is controlled by the thermodynamic properties of the mineral specimen. Students will have the opportunity to combine their knowledge on biogeochemistry and thermodynamics with new experience in electrochemical analyses.

Collaboration with Environmental Chemistry ETH Zürich, Dr. Michael Sander