UNESCO-IWRA ONLINE CONFERENCE
17-19 JANUARY 2023
3RD IN THE IWRA ONLINE CONFERENCE SERIES

Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Quantum Chemical Computations Promote Understanding of Microbial Reductive Dehalogenation

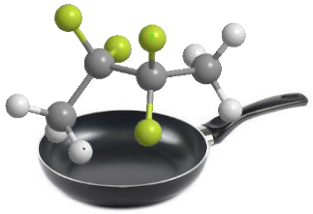
Shangwei Zhang, Xinghui Xia

18 January 2023, 13:00 CET

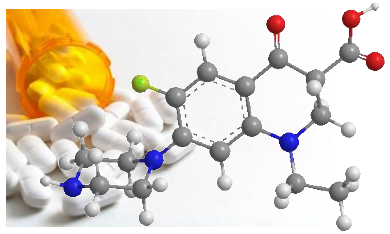
unesco
Programme hydrologique intergouvernemental

IWRA International Water Resources Association

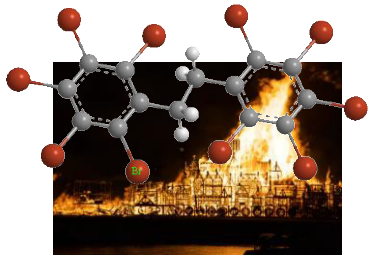
Old and Emerging Organohalides Imperil Health and Ecosystem



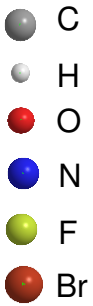
non-stick coatings

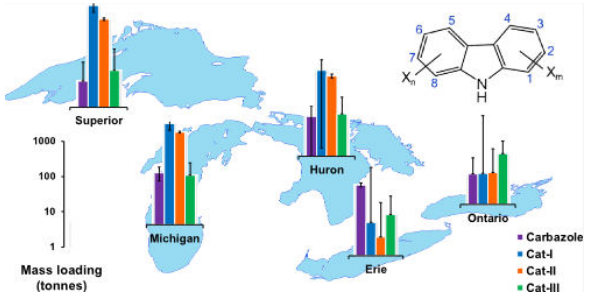


antibiotics



flame retardants





naturally; emerging; conc. increasing

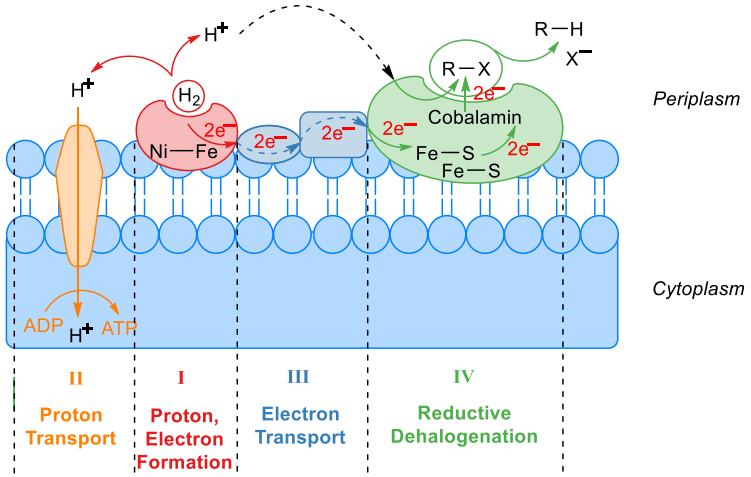
kill whale, global pop. decline, PCBs

chloracne on the ear & neck

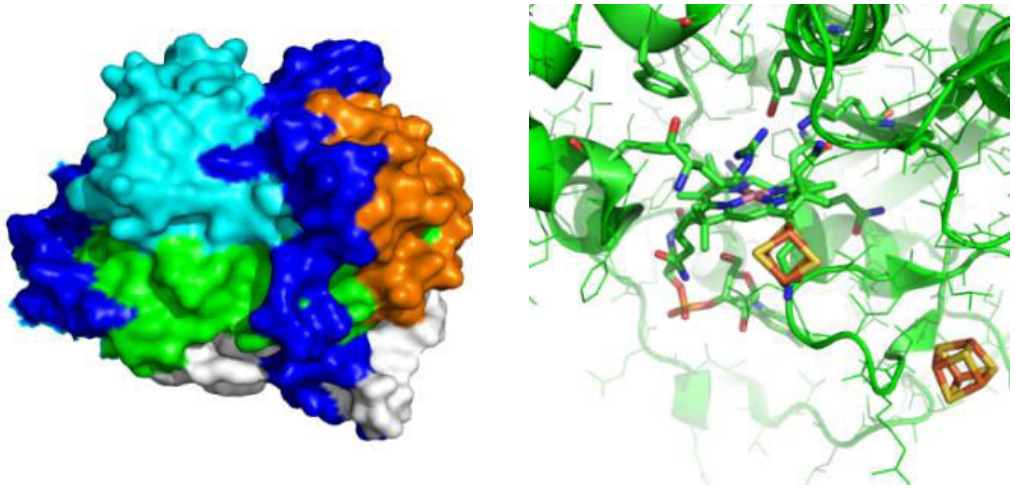
including organohalides

Desforges, J.-P.; Hall, A.; McConnell, B.; Rosing-Asvid, A.; Barber, J. L.; Brownlow, A.; De Guise, S.; Eulaers, I.; Jepson, P. D.; Letcher, R. J.; Levin, M.; Ross, P. S.; Samarra, F.; Víkingson, G.; Sonne, C.; Dietz, R.. *Science* **2018,** *361*, (6409), 1373-1376.
Li, A.; Zhou, S.; He, H.; Guo, J.; Rockne, K. J.; Sturchio, N. C.; Giesy, J. P. *ACS ES&T Water* **2022,** *2*, (9), 1544-1554.
Malaj, E.; von der Ohe, P. C.; Grote, M.; Kühne, R.; Mondy, C. P.; Usseglio-Polatera, P.; Brack, W.; Schäfer, R. B.. *Proc. Natl. Acad. Sci.* **2014,** *111*, (26), 9549-9554.

Microbial Reductive Dehalogenation
A Highly Desirable Approach Targeting Organohalide Pollution



biochemical process of dehalogenation



reductive dehalogenase and its catalytic site

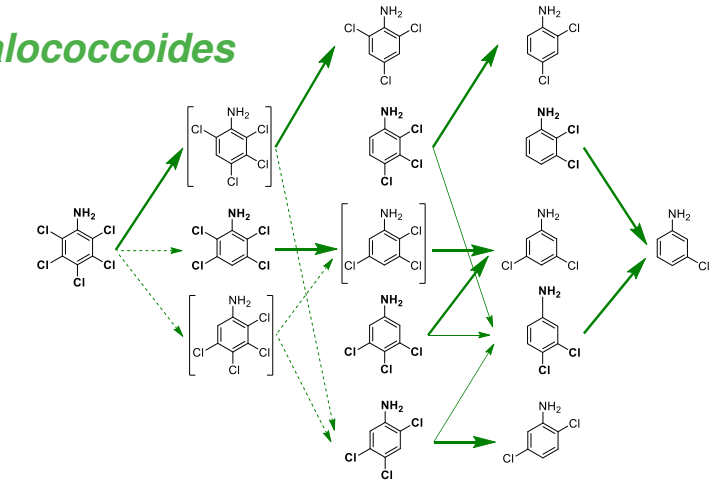
experimental demonstration: cob(I)alamin catalyzes dehalogenation

Further Mechanism: Unknown, experimental bottleneck

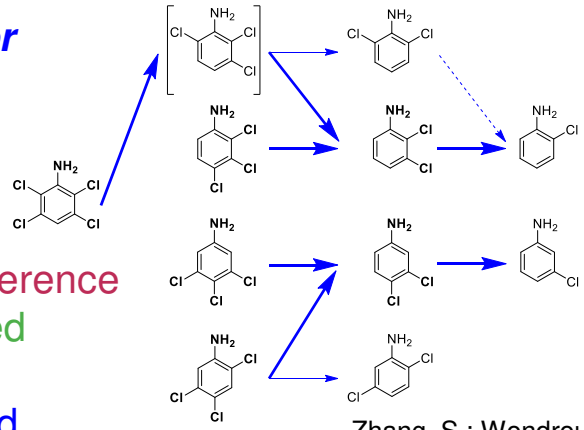
Bommer, M.; Kunze, C.; Fesseler, J.; Schubert, T.; Diekert, G.; Dobbek, H. *Science* **2014**, 346, (6208), 455-458.
Payne, K. A.; Quezada, C. P.; Fisher, K.; Dunstan, M. S.; Collins, F. A.; Sjuts, H.; Levy, C.; Hay, S.; Rigby, S. E.; Leys, D. *Nature* **2015**, 517, (7535), 513-516.

Quantum Chemical Study I
Electron Density Unravels Distinct Electron Transfer in Bacteria

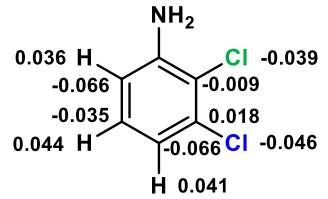
Dehalococcoides

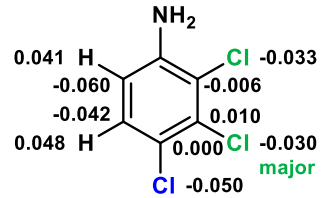


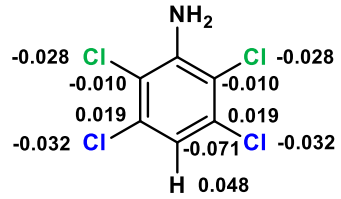
Dehalobacter



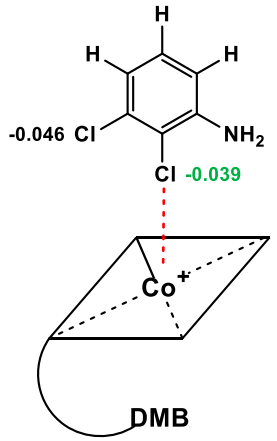
Cl abstraction preference
doubly-flanked
vs.
singly-flanked



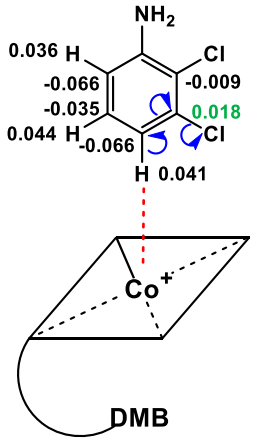




atomic charge



Dehalococcoides CBDB1

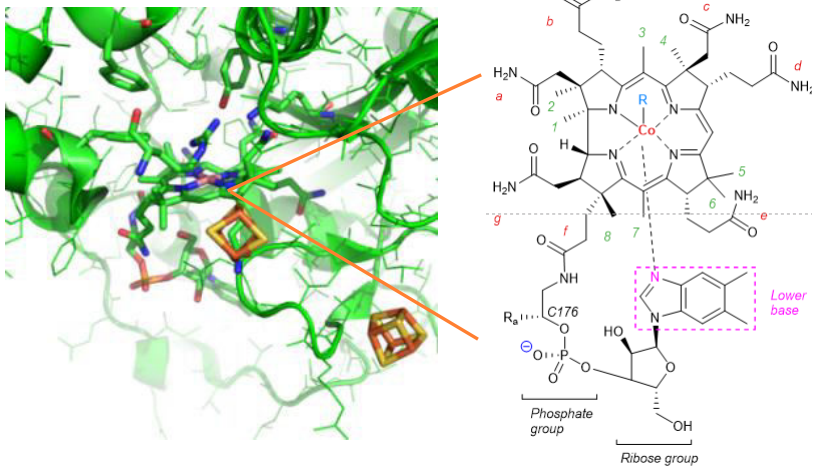


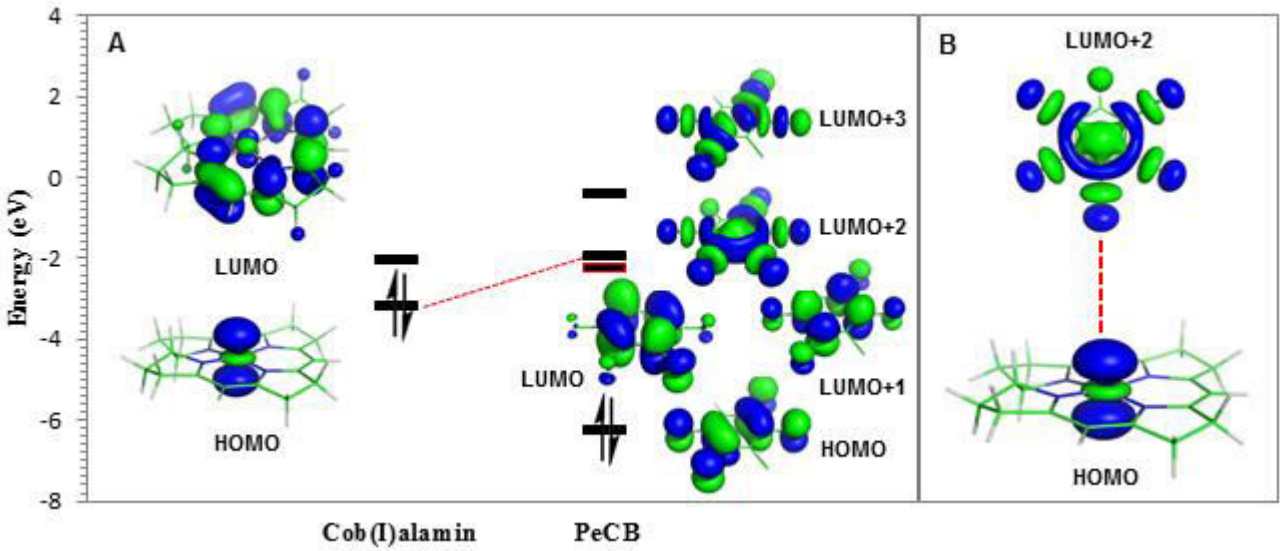
***Dehalobacter* 14DCB1**

Distinct ET Mechanisms Unraveled

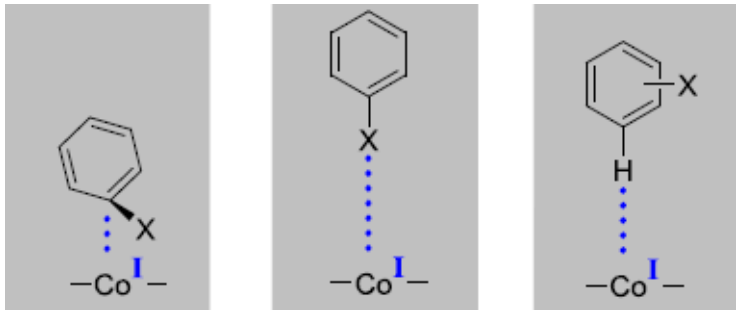
Zhang, S.; Wondrousch, D.; Cooper, M.; Zinder, S. H.; Schüürmann, G.; Adrian, L. Anaerobic *Environ. Sci. Technol.* **2017,** *51*, (7), 3714-3724.

Quantum Chemical Study II
Interaction Mode Between Organohalides and Cofactor of RDase





?

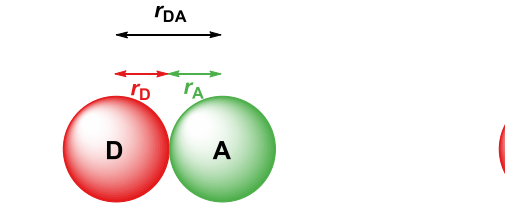


93 chemicals, 5 compound classes, validated by experimental pathways with *Dehalococcoides*

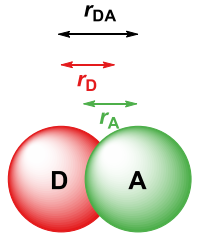
Electron Transfer: $3dz^2 \cdots \sigma^*_{C\text{-}X}$

Zhang, S.; Adrian, L.; Schüürmann, G. *Environ. Sci. Technol.* **2018,** *52*, (4), 1834-1843.

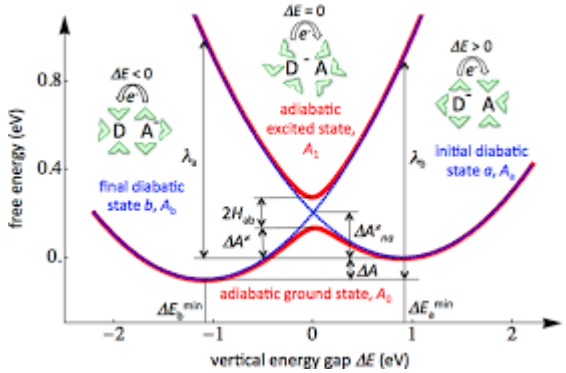
Quantum Chemical Study III
Outer-Sphere ET Does Not Underpin Microbial Dehalogenation

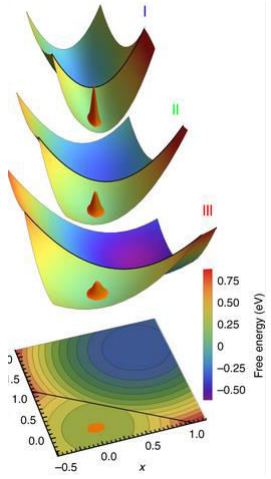


Outer-Sphere Electron transfer

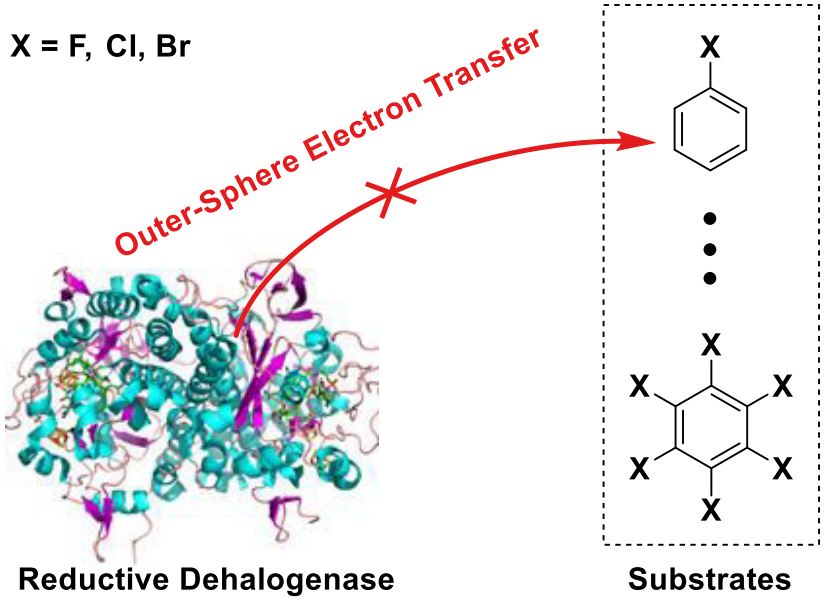


Inner-Sphere Electron transfer





X = F, Cl, Br



Reductive Dehalogenase

Substrates

cover
36 representative substrates

all OS-ET mechanism

336 reaction routes

Free Energy Barriers: 334 reactions > 20 kcal/mol
The Rest 2 Reactions: no ET

Zhang, S.; Adrian, L.; Schüürmann, G. *Environ. Sci. Technol.* **2020,** *54*, (24), 15751-15758.

Environmental Significance

- **Guide Dehalogenation Experiments** (e.g., dehalogenation potential and pathway prediction, substrate selection and cell cultivation)
- **Provide Theoretical Basis for Respective Bioremediation** (e.g., feasibility assessment, strain selection, remediation strategy optimization)

Quantum Chemical Computations Facilitate

Emerging Pollutant Control and Management

&

Green Chemical Synthesis

Acknowledgements

国家自然科学基金委员会 NSFC

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北京師範大學 BEIJING NORMAL UNIVERSITY

ADIIEE

环境与生态前沿交叉研究院
Advanced Interdisciplinary Institute of Environment and Ecology

Thank You So Much !

Contact:
zhangshangwei@bnu.edu.cn