

Networking people, sites, ideas and data for Earth's Critical Zone: www.CZEN.org

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The Critical Zone Exploration Network (CZEN, <http://www.czen.org>) is a network of people, sites, tools, and ideas to investigate processes within the Critical Zone (CZ). This Zone supports all life on Earth, and is defined to encompass all fluid, mineral, gaseous, and biotic components from the outer envelope of vegetation down to the lower limits of groundwater.

CZEN grew from an international initiative for scientists interested in the CZ. The U.S. National Science Foundation (NSF) has recognized the importance of CZ research with support for eight seed sites within CZEN and three Critical Zone Observatories (CZO). The CZEN community includes representatives of the CZOs, CZEN seed sites, the CZEN steering committee, NSF, cyberinfrastructure specialists, students and others. An ongoing effort exists to fund and incorporate new seed sites both internationally and within the U.S.

The CZEN website aims to unite CZ groups and facilitate discovery. The website is built with a community management system which allows groups to self-organize and share privately within groups, across groups and/or publicly. Group members can share announcements, publications, events, images, links, and datasets. The goal of the site is to invite geoscientists to post data online for private use with the intention long-term of enabling that data to become a community resource. So far, published data are being collated online.

CZEN has unique challenges. In order to shed sufficient light on the CZ, databases will need to be constructed that relate disparate data types collected on a multitude of temporal frequencies across many experimental designs. These CZEN databases will need to interoperate seamlessly with existing databases and networks. In many ways, CZEN is tasked with building a network of networks.

Assessing redox reactions and light-induced transformations of organic water contaminants using multi-element kinetic isotope effects

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Analysis of stable isotope fractionation in individual organic water contaminants such as fuel constituents, solvents, pesticides, and explosives provides important information for identifying degradation pathways and assessing the extent of transformation. The applicability of isotopic analysis to many important redox reactions and light-induced transformations, however, is hampered, as the knowledge of the extent and variability of isotope fractionation is limited and the underlying reaction mechanisms are not well understood. Investigating multiple isotopic elements offers a promising avenue to elucidate the isotopic elementary reactions in greater detail and, thus, to contribute to a more reliable interpretation of the isotope fractionation observed in the environment.

We explored the isotope fractionation during typical enzymatic and abiotic transformation processes of nitroaromatic groundwater contaminants (NACs) and during light-induced reactions of triazine herbicides such as atrazine. While different biodegradation pathways of NACs can occur in the presence of oxygen and exhibit ¹³C- and ¹⁵N-kinetic isotope effects (KIEs) that are typical for dioxygenation and partial reduction mechanisms, respectively, abiotic reactions are confined to reductions under anoxic conditions. Regardless of the type of mineral-bound reductant, apparent ¹⁵N-KIEs were large (1.040) and virtually identical for a series of different NACs. Combination of experimental evidence and computations using density functional theory suggests that the cleavage of N-O bonds from the dehydration of substituted *N,N*-dihydroxyanilines to nitroso intermediates is responsible for ¹⁵N fractionation. During reduction in homogeneous solution, however, the e⁻ and H⁺-transfer reactions preceding the N-O bond cleavage modulate apparent ¹⁵N-KIEs so that they become as small as 1.010 owing to a shift in rate-limiting step.

Direct photolysis of triazine herbicides is accompanied by a significant inverse ¹³C- and ¹⁵N-fractionation while shifts in ²H-signatures are absent. This unusual isotope fractionation is presumably associated with magnetic isotope effects (MIE) of excited radical pair intermediates and could be key to distinguish between photochemical and microbial triazine degradation.