Quantum Mechanical Degradation Pathway Prediction for New and Emerging Contaminants

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Abstract. For many soil and groundwater contaminants, key properties that govern their fate in both natural environments and engineered remediation systems are unknown. The classical approach of conducting experimental degradation studies, however, is highly labor-intensive and costly. Thus, the objective of this study is to develop a predictive methodology that can be used to screen new and emerging contaminants such that natural attenuation processes, remediation approaches, degradation kinetics, and potential problem intermediates can be identified.
Several thermodynamic and kinetic parameters were calculated via quantum mechanical computations for the model contaminant in this study, hexamethylphosphoramide (HMPA), a mutagenic and carcinogenic solvent which is widely used in both science and industry. Redox mapping revealed that strong oxidants are needed in order to completely mineralize HMPA. Free energies of reaction show that oxidation at the nitrogen can be excluded, whereas oxidation of the methyl group can lead to multiple degradation pathways. Based on kinetic descriptors such as bond dissociation energies (a measure for covalent bond strength) and ionization potentials (a measure for susceptibility to oxidation), HMPA degradation rates are expected to slow down with increasing degree of demethylation. Using permanganate as an oxidant, the predicted pathways were confirmed experimentally via LC/ToF-MS and Ion-trap LC/MS/MS. Our ongoing research focuses on determining activation barriers computationally in order to predict degradation kinetics and consequently the dominant degradation pathway. The predictive methodology can ultimately be used to help assess the environmental fate for any new and emerging contaminant and its metabolites under both natural and engineered conditions.

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