Quantum Chemical Degradation Pathway Prediction for New and Emerging Contaminants

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Abstract. For many groundwater contaminants, key properties that govern their fate in natural and engineered environments 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 pathways, and persistent intermediates can be identified.

The oxidation of the model compound hexamethylphosphoramide (HMPA), a widely used solvent and potential groundwater contaminant, was estimated to require at least iron-reducing conditions at low to neutral pH and nitrate-reducing conditions at high pH. The transformation of HMPA by the common remediation agent permanganate was predicted to proceed through sequential *N*-demethylation. Experimental validation confirmed that HMPA is oxidized to phosphoramide via the formation of less methylated as well as singly and multiply oxygenated reaction intermediates. Other potential degradation pathways were excluded based on thermodynamic or kinetic constraints.

Our ongoing research focuses on the computational determination of activation barriers in order to predict degradation kinetics and, consequently, the primary degradation pathway. The predictive methodology can ultimately be used to assess the environmental fate for any new and emerging contaminant and its degradation products.

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