

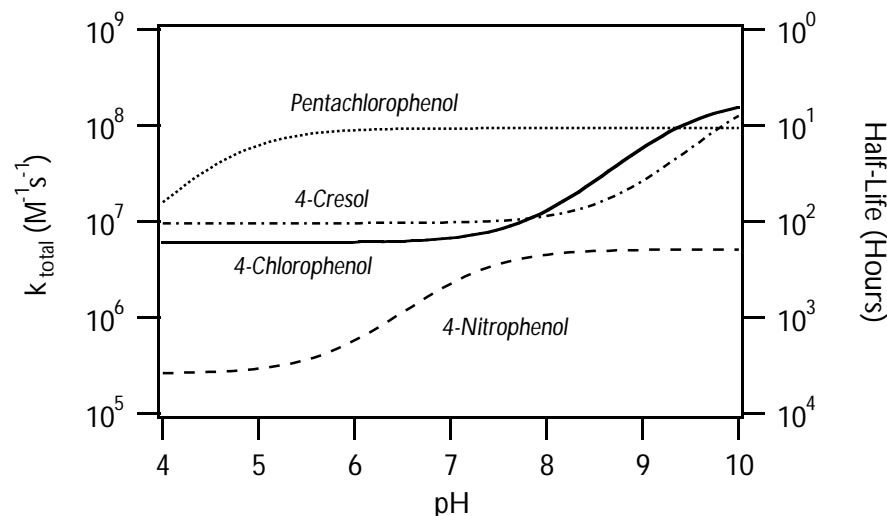
Associate Professor, Environmental Science and Engineering, Oregon Graduate Institute; B.A. Chemistry, Williams College, 1980; Ph.D. Applied Chemistry, Colorado School of Mines, 1987; National Research Council Research Associate, U.S. Environmental Protection Agency, Athens, GA, 1987-1988; Research Fellow, Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), Dübendorf, Switzerland, 1989-1991. (<http://www.es.eogi.edu/~tratnyek>, tratnyek@ese.eogi.edu)

Research Interests

DR. TRATNYEK'S research interests concern a wide range of oxidation-reduction reactions that occur in the environment, and the contribution of these reactions to the fate of organic pollutants. In most of his work, the focus is on pathways, kinetics, mechanisms, and other fundamental, molecular aspects of environmental organic chemistry. The goal is to understand these redox processes at a process level, and to use this knowledge to develop deterministic models of environmental systems and remediation technologies. In most cases, the research involves characterizing the reactivity of an organic pollutant or class of pollutants, and application of these results to environmental protection. However, environmental processes *per se* are also of interest. In these cases, organic "pollutants" may be employed, not so much as pollutants, but as probe substances with which to explore the geochemistry and microbiology of complex natural systems. Much of the research outlined below involves organic pollutants in this dual role as probe and substrate.

Oxidation Reactions in the Photic Zone

When surface waters absorb sunlight, a variety of transient oxidants are formed, including hydroxyl radical, superoxide anion, and singlet oxygen. These transient species are highly reactive and can have both beneficial and harmful effects. For example, singlet oxygen can oxidize organic substances such as phenols, polyaromatic hydrocarbons (PAHs), and pesticides, resulting in pollutant degradation. However, singlet oxygen can also attack cell constituents, resulting in phototoxicity. Dr. Tratnyek's research interests in this area include the kinetics of phenol photooxidation, the photodegradation of organic pollutants by singlet oxygen, and the unique photoprocesses that occur at the air-water and sediment-water interfaces.



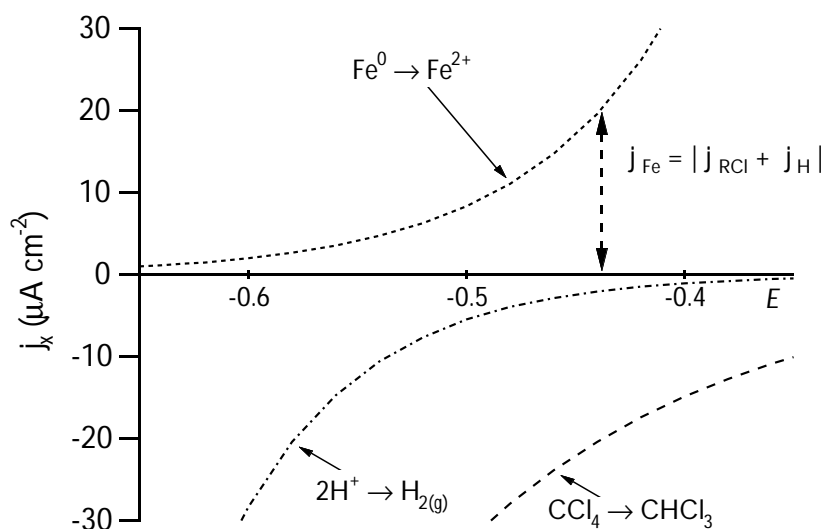
The effect of pH on the rate constant (left axis) for oxidation of several substituted phenols by singlet oxygen. The right axis gives the calculated half-life of this reaction in sunlit surface water, assuming a steady-state concentration of singlet oxygen equal to 2×10^{-13} M (Tratnyek and Hoigné, 1994). Similar effects are observed for other oxidants of environmental concern, such as chlorine dioxide and chromate (Tratnyek, 1998).

Reduction Reactions in Anaerobic Environments

Some organic compounds undergo reduction reactions in anaerobic sediments, soils, and groundwaters. Examples of this reaction type include nitro reduction of the pesticide parathion, and dehalogenation of DDT or chlorinated hydrocarbon solvents like trichloroethylene (TCE). These reactions can be important contributors to the environmental fate of pollutants, but little is known about the reducing agents that cause them or the factors that control their rates. One specific issue that is central to understanding reduction of organic pollutants is the role of substances that can mediate electron-transfer, like certain enzymes, porphyrins, and quinonoid compounds. We are currently studying the role of these mediators by treating them as reactive transients that are present at low steady-state concentration and that can (only) be assayed by their rate of reaction with selective probe substances. Steep gradients in these and other biogeochemical properties of sediments are expected near the sediment-water interface, which we are investigating using solid-state microelectrodes.

Despite our general lack of knowledge regarding the mechanisms of environmental reduction reactions, research in this area has already led to some important practical applications, particularly with respect to the remediation of contaminated aquifers. For example, fine-grained zero-valent iron metal is very effective at dechlorinating halogenated hydrocarbon solvents like carbon tetrachloride (CCl_4) and TCE. Laboratory tests have shown that complete mineralization of the contaminants is possible, and recent field-scale tests have shown that groundwater remediation technologies based on this process may have practical value. We are currently investigating the mechanism of contaminant reduction by iron, and the geochemical and microbiological processes that might affect the performance of this technique in the field. Our work should help provide a sound scientific basis for designing, operating, and enhancing such technologies.

Since the iron-water interface will consist of a partially-passivating oxide film under environmental conditions, the film must mediate dechlorination of halocarbons in solution. To probe the halocarbon-oxide surface interaction, we are studying the effect of a variety of ligands on iron dissolution and CCl_4 dechlorination. Since the oxide film must mediate the transfer of electrons from the bulk donor (Fe^0) to the adsorbed halocarbon, the role of the oxide in the charge transfer process is also under investigation. The role of the oxide can be interpreted as a semiconductor, as a coordinating surface, and electrochemical cell.



Partial current density curves for the Fe^0 - CCl_4 - H_2O system. Curves were generated from the Tafel equation using data obtained with an iron rotating disk electrode (Scherer, et al. 1997). Note that hydrogen evolution is minor compared to dechlorination at the corrosion potential (arrow). From this study, we also found that charge transfer is rate limiting on bare iron. This result may apply to oxide-coated iron, based on correlations we are developing for C1 and C2 halocarbons. To determine the effect of oxide composition on this analysis, further investigation is underway.

Correlation Analysis

Quantitative structure-activity relationships (QSARs) are correlations between an important property for a series of related compounds (e.g., oxidation or reduction rate constants) and one or several more convenient independent variables. QSARs are of enormous importance in environmental chemistry and toxicology because of their predictive power, but they also reveal a great deal about reaction mechanisms and the nature of substituent effects. QSARs are frequently tools in, and products of, the studies of environmental redox reactions described above.

Selected Publications

- P. G. Tratnyek. "Correlation analysis of environmental reactivity of organic substances" In: D. L. Macalady (Ed.) *Perspectives in Environmental Chemistry*. Oxford, 1998, pp. 167-194.
- M. M. Scherer, J. C. Westall, M. Ziomek-Moroz, and P. G. Tratnyek. "Kinetics of carbon tetrachloride reduction at an oxide-free iron electrode" *Environ. Sci. Technol.* 1997, *31*, 2385-2391.
- T. L. Johnson, M. M. Scherer, and P. G. Tratnyek. "Kinetics of halogenated organic compound degradation by iron metal" *Environ. Sci. Technol.* 1996, *30*, 2634-2640.
- A. Agrawal and P. G. Tratnyek. "Reduction of nitro aromatic compounds by zero-valent iron metal" *Environ. Sci. Technol.* 1996, *30*, 153-160.
- P. G. Tratnyek and J. Hoigné. "Photooxidation of 2,4,6-trimethylphenol in natural waters and laboratory systems: Kinetics of reaction with singlet oxygen" *J. Photochem. Photobiol. A: Chem.*, 1994, *84*, 153-160.
- P.G. Tratnyek, M. S. Elovitz, and P. Colverson. "Photoeffects of textile dye waste waters: Sensitization of singlet oxygen formation, oxidation of phenols, and toxicity to bacteria" *Environ. Toxicol. Chem.* 1994, *13*, 27-33.