

# Photochemical effects on the interaction of enzymes and dissolved organic matter in natural waters

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ABSTRACT: Extracellular enzymes such as phosphatase ($P_{ase}$) and glucosidase ($G_{ase}$) can be inactivated in natural waters through photochemical processes. In this study, we examined the mechanisms involved in enzyme inactivation. We first explored the possibility of direct photoinactivation. The quantum yield spectrum ($\Phi_\lambda$) for the direct photoinactivation of $P_{ase}$ increased exponentially with decreasing wavelength, with a much steeper slope relative to other $\Phi_\lambda$. This, combined with modeled half-life values for direct photoinactivation in excess of 5 d, indicates that direct photoinactivation of $P_{ase}$ by natural sunlight in lakes is negligible. Nonetheless, photoinactivation of enzymes occurred rapidly in light-exposed natural waters and suggested an indirect mechanism. The pH of natural waters greatly affected photoinactivation. In acid humic lake water exposed to ultraviolet radiation, the half-lives of both $P_{ase}$ and $G_{ase}$ were 4 h. The half-life of these enzymes under the same conditions were twofold higher for lake waters obtained from a limed humic lake (8 h). The higher rate of inactivation in acid water was likely caused by a pH-mediated increase in Fe photoreduction and enzyme binding. Solutions of $P_{ase}$ with Fe(II) and $H_2O_2$ resulted in rapid inactivation (half-life 7 min at 8.9 μmol $L^{-1}$ Fe). There was no significant inactivation of controls without $H_2O_2$, indicating that enzymes are inactivated through Fe(III)/enzyme binding, which is enabled through the oxidation of Fe(II) by H2O2 to Fe(III). Direct inactivation by reactive oxygen species (ROS) was ruled out by tests with ROS scavengers.