WATER RESOURCES RESEARCH GRANT PROPOSAL

Project ID: 2003IL22B

Title: Rapid Solar Transformation of Nutrients in Natural Waters

Project Type: Research

Focus Categories: Water Quality, Nutrients, Surface Water

Keywords: water quality, nutrients, non-point source, surface water, watershed, TMDL, BMP, geochemical, nitrate, ammonia, ammonification, organic nitrogen, solar, photochemistry, photolysis, radical, modeling, natural organic mater, NOM

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Federal Funds: $22,500

Non-Federal Matching Funds: $46,370

Congressional District: 15th

Principal Investigator:
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Abstract

There is a growing emphasis on the use of models to simulate the effect of various water and land management practices. It is expected that water quality models will be used in the process of setting water quality standards for nutrients, which will be used to develop TMDLs, which will, in turn, drive the selection of Best Management Practices. Current water quality models treat the nitrogen species at different levels of detail, but in most models, virtually all transformation of nitrogen species are considered to be biological processes. There is recent evidence, however, that solar-driven photochemical processes occur rapidly enough to also be significant in these transformations, as well as for in-stream degradation of natural organic matter (NOM). It was estimated in one recent study (Bushaw et al, 1996) that sufficient ammonia was photogenerated from aquatic NOM to add an additional 20% to the inorganic carbon loading of the stream as it reached the coastal area, and fractional conversion rates from organic nitrogen of 0.3 to 0.9% per hour were measured. In recent studies in this laboratory, a phenol which was spiked into various Illinois waters at about 3 mg/L was 95% removed from some waters after 3 hours of irradiation with artificial sunlight. Since fulvic material contains a high fraction of phenolic groups, this implies rapid transformation of the carbon in the organic material as

well. These rates are sufficiently high that these processes may be significant sources and sinks of nutrients. However, these pathways are not included in current water quality models, so that the conclusions drawn from the use of such models may be questionable or may attribute transformations to the wrong cause.

The proposed research effort would have 3 objectives: 1) To measure the photogeneration rates of ammonia and phototransformations of other nitrogen species that are induced by sunlight in several different Illinois waters, 2) Elucidate the important pathways of such transformations, by measuring the rates of reactive species generation, using established techniques, and estimating the reactivity of various functional groups in NOM with those active species by using the rate constants of similar type compounds in kinetic calculations to simulate the degradation processes, and 3) derive a kinetic model from the mechanistic model, and use it to develop the form of terms to be used in water quality models, should these processes need to be included in order to correctly describe nitrogen transformations.

Direct measurement of ammonia formation will be used to determine whether the generation rates are sufficiently high that they should be included in consideration as sources. The methods used to determine important pathways will be: kinetic analysis of the data; probe compound experiments in which the rate constant of a process is measured by comparing it with that of a model compound with known rate constant; use of model compounds to represent portions of the NOM macromolecule; and correlation of the rate of photogeneration of ammonia and other species with common water quality parameters, since DOC, nitrate, bicarbonate, etc. are known to be the precursors for the reactive radical species. A protocol for this correlation process has recently been developed in this laboratory and used to measure radical generation rates in different waters from the Calumet watershed in Northeastern Illinois.