Rapid Solar Transformation of Nutrients in Natural Waters

Basic Information

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Problem and Research Objectives

Solar phototransformation of nitrogen nutrients between forms such as organic nitrogen, nitrate, and ammonia can provide significant sources and sinks for the individual nutrient forms, and generate reactive species including free radicals, that can drive other transformations. One example of such phototransformations is the now well-established generation of ammonia by photolysis of aquatic NOM. Recognition of these contributions to the concentration of various nutrient species may impact the setting of water quality standards and best management practices for nutrients, as well as their modeling. The objectives of the project are to 1) measure the photogeneration of ammonia in several Illinois waters, 2) identify important transformation pathways for nitrogen nutrients, and 3) derive models for the process rates in terms of water quality parameters, for adaptation into water quality models.

Methodology

Photoammonification rates are being measured in water samples brought to the laboratory, using simulated solar light and standard methods for ammonia measurement (phenate) and other important water quality parameters. Natural organic material (NOM) that makes up dissolved organic carbon (DOC) is not a mixture of compounds, but rather is primarily a mixture of similar but nonidentical macromolecules; therefore, chemical change in DOC can not be followed by measuring specific compounds, and the development of "surrogate" methods is necessary. The photo- and free-radical chemistry of nitrogen functional groups that occur in NOM is being investigated in this study using model compounds for which individual byproducts can be measured, in order to determine the types of products that are formed in these reactions. This may allow the development of surrogate characterization tests that can be used to measure the extent of reaction of various functional groups without having to rely on quantification of individual compounds for mass balance. Recent work [Vairavamurthy and Wang, ES&T, 36(2002)3050-56] indicates that amides and pyridine groups represent a significant portion of the organic nitrogen present In humic and fulvic material, but the technique (XANES spectroscopy) used by those authors was unable to quantify the relative amount of amine functional groups present. We therefore chose monomeric and polymeric model compounds containing these functional groups (discussed below) for our studies. Specific radicals will be produced in water samples by known reactions, to determine which radicals are primarily responsible for ammonia production. Specific radical "probe" compounds will be used to measure radical production in the natural waters upon irradiation with simulated sunlight in several spectral regions. This information will be compared for various waters, and, along with the solar emission and water absorbance spectra, may be used to develop simple mechanistic/kinetic models for prediction of ammonia photoproduction.

Principal Findings and Significance

In addition to considerable effort spent on the development of an investigation strategy, progress to date has been made in four areas:
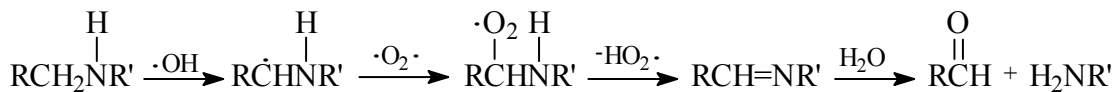
1) *Measurement of Photoammonification in Natural Waters* – Experiments were carried out on six local Illinois waters last fall, sampled from Clinton Lake, Salt Creek below Clinton Lake, Homer Lake, Collins Pond (Homer Lake Park), Salt Fork of the Vermillion River, and Windsor Creek. The increase in ammonia in these samples ranged from 10% in Clinton Lake to 220% in Collins Pond. It is too early to draw conclusions concerning the effect of DOC source from these results; however, it is obvious that the photoproduction of ammonia can vary widely from one water to the next within a small geographic region. In addition, the shape of the ammonia evolution curves varied, ranging from rapid initial increase and early plateau, to continuous accumulation, to induction period followed by increase followed by plateau of ammonia concentrations. These widely different curve shapes imply differences in the photoactivity and amount of precursor present, as well as whether precursor is initially present (immediate ammonia production) or needs to be produced from other substances through intermediate reactions (induction period). QA/QC experiments using replicate samples indicated an analytical precision of about 2.5% on ammonia analyses of triplicate samples (not triplicate analyses of a single sample), and a point-to-point variation of about 6% for samples from successive time points taken periodically from a single experiment after a plateau in ammonia production. Each of these curve shapes can be fit

with simple kinetic models, which will be made more specific after more is known about the NOM functional groups that are involved. Sampling of additional waters is now beginning for spring.

2) *Development of Analytical Procedures for Model Compounds and for Surrogate Functional Group Measurement* – The primary analytical tool being used is HPLC with UV/visible detection, because gas chromatography requires thermal volatilization of the sample, which would not occur with macromolecular NOM. Use of a derivatization method that increase the sensitivity of detection of a particular function group (e.g., aldehydes) relative to the rest of the NOM spectrum (by introducing a chromophore) minimizes interferences, so that it may be possible to use these methods on substances of unknown structure to quantitate the formation or destruction of particular functional groups, even though analysis of individual compounds is not possible. We have adapted previously developed methods for quantifying aldehydes (as the corresponding dinitrophenylhydrazones) and amines (as the substituted phenylthiourea) suspected to be intermediates in the mechanism previously postulated for ammonia production from diethylamine by hydroxyl radical attack, and are using those methods to verify or refute the proposed mechanism (see below). We will investigate the value of these "surrogate" methods in tracking the progress of reactions in DOC, first by the use of nitrogen-containing polymeric model compounds polyvinylpyrrolidone, polyacrylamide, and polyethyleneimine, then with actual water samples. We are still looking for a way to make polyvinylpyridine sufficiently water-soluble to use it as a model macromolecule for the pyridine functionality. Polyvinylphenol can be used to simulate the carbon backbone of NOM.

3) *Verification of One Postulated Mechanism for Photoammonification* – In recent experiments, we have subjected aqueous diethylamine (DEA) solutions (1 mM) to hydroxyl radical generated by UV (254 nm) photolysis of hydrogen peroxide, to determine whether the byproducts and kinetics are consistent with the mechanism hypothesized in scheme I in the proposal.

scheme I

$$RCH_2NR' \xrightarrow{\cdot OH} R\overset{H}{\underset{|}{\dot{C}}}HNR' \xrightarrow{\cdot O_2\cdot} R\overset{\cdot O_2 \; H}{\underset{| \quad |}{C}}HNR' \xrightarrow{-HO_2\cdot} RCH=NR' \xrightarrow{H_2O} R\overset{O}{\overset{||}{C}H} + H_2NR'$$

For DEA, the stable products for these steps should be acetaldehyde and ethylamine, while a similar attack on ethylamine should yield another molecule of acetaldehyde and one of ammonia. Control experiments showed that neither UV photolysis nor peroxide treatment alone causes significant decomposition of DEA., so that DEA removal observed in the combined UV/H$_2$O$_2$ experiment is due to hydroxyl radical, and ceases when the peroxide is exhausted. Byproducts identified during the DEA degradation were ethylamine, acetaldehyde, and ammonia, consistent with the mechanism shown in Scheme I. This result supports the proposed mechanism for DEA degradation and suggests that a similar mechanism may be operative for primary and secondary amines in NOM, since ethylamine degradation was observed as well. Since the precursor for ammonia (ethylamine) must be produced before ammonia can be generated, a lag time (induction period) in ammonia is expected.

4) *Development of a Screening Procedure for Ammonia Precursors* - Mechanisms other than OH radical must be considered as well. For example, In a recent study of photactivity of waters from the Calumet River watershed, OH radical was shown to be of secondary importance in photo-removal of the general probe compound 2,4,6-trimethylphenol from various Calumet area waters. In addition, the NO$_2$X produced (along with HOX radical) by the photolysis of nitrate is also a strong but more selective oxidizing agent than OH radical. Amines are also known to be vulnerable to photosensitization, and NOM has been shown to be a good photosensitizer for some reactions, so this pathway will be investigated as well, by adding DEA to natural waters and/or purified water containing NOM that has been previously isolated from natural water. "Standard" humic and fulvic acids isolated from the Suwannee River are available from the

International Humic Substances Society and are used by many investigators to allow direct comparison of their work.

The following reactive species have been reported to be photochemically formed from NOM, nitrate, or nitrite: XOH, RO_2X (peroxyl radicals), NO_2X, NOX, $^1O_2$ (singlet oxygen), e^-_{aq} (hydrated electron), CO_3^-X (carbonate radical) and NOM* (excited state of NOM, i.e., photosensitization). Of these, hydrated electron is sufficiently reactive with oxygen in surface water, that significant reaction would be expected only with the most reactive of compounds, i.e., halogen compounds that are 2-4 orders of magnitude more reactive with e^-_{aq} than are amines. Hydroxyl radical, carbonate radical, peroxyl radicals, and nitrogen dioxide are all one-electron oxidants or add to the ring in aromatics, with OH radical being equal to or a stronger oxidizer than carbonate radical, peroxyl radicals, or NO_2 for virtually all substrates. Therefore, for screening model compounds for ammonia production, reaction with hydroxyl radical will identify possible reactions for all four oxidizing radicals, or, conversely, if a compound does not produce ammonia when reacting with OH, it probably won't produce ammonia through the action of the other three oxidizing radical types either, and only OH need be tried if it fails to produce ammonia. Screening for singlet oxygen and sensitizers is a little more complicated, since singlet oxygen is usually made by using a sensitizer. We are still considering conditions to discriminate between these two cases. The intended screening strategy will be to check for photoammonification from amines, amides, pyridines, oxypyridines, and NOM by reaction with excited NOM* and with OH radical. Reaction with OH will be carried out as described above for diethylamine, while reaction with NOM* will be evaluated by adding the model compound to natural water and comparing any ammonia formation to that from the water alone and that formed in the model compound photolysis blank. Subsequent in-depth studies will focus on processes that caused photoammonification in the screening experiments.

Work for the next reporting period will follow the strategy described above, including 1) the extension of these methods to other forms of nitrogen (amides, pyridines) thought to occur in NOM, using the model compounds acetamide and ethylacetamide, and pyridine or a substituted pyridine, as well as the corresponding polymeric model compounds; 2) evaluation of the surrogate methods for characterization of NOM reactivity; 3) continuation of ammonia production measurement in Illinois waters; and 4) correlation of ammonia production with water quality parameters such as bicarbonate (alkalinity), DOC, DON, nitrate and nitrite content of the water.