

WATER QUALITY

Natural Photochemically Mediated Destruction of Contaminants in Rivers and Lakes of the Calumet Area

Final Report

The ability of sunlight to destroy pollutants in rivers and lakes is being investigated in order to determine how quickly this process takes place, identify what chemical processes are involved, and to relate this information to the specific composition of the particular water. If this can be done, a predictive model can be developed that could be used to estimate the ability of a water body to cleanse itself using solar energy. This information would be useful in identifying particularly sensitive waters and as a tool to help decision makers choose between alternative remediation methods for contaminated regions. In addition, if the processes are found to be fast enough, bankside treatment units may be practical, in which water would be pumped from a river or lake through a shallow pond, for better exposure, then returned to the water body. The cleansing process is the result of very reactive chemical species being formed when sunlight shines on natural water constituents. Experiments have therefore been conducted in which contaminants have been added to river and lake water in the laboratory, and the water illuminated with simulated sunlight. During this time, samples were taken and analyzed to determine the extent of disappearance of the contaminant. The water was also analyzed to determine the amounts of various natural constituents, in order to relate the ability to assimilate the contaminant upon illumination, to water composition. Model contaminants and methods were chosen so that the reactive chemical species could be identified, allowing generalization of the information to other contaminants and waters, by determining what kinds of pollutants react with which reactive species. It was found that even relatively high concentrations of some contaminants were 95% destroyed in 3 hours in some waters, indicating that removal of some contaminants in bankside reactors may be feasible. The results also indicated that chemical breakdown of dead plant and animal matter in water may be faster than anticipated, and implied that some of the ability of wetlands to assimilate pollutants may be due on part to these sunlight-driven processes. The predictive model is under development.

Major Goals and Objectives

Overall Goal: Evaluate the importance of pollutant transformation by solar-driven indirect photochemical processes in the water bodies of the Calumet Watershed (CWS). "Indirect" in this context means mediated by a solute in the natural water matrix, as opposed to direct photolysis of the contaminant.

Specific Objectives :1) identify specific radicals and other reactive species that are photochemically generated in CWS waters, 2) quantify the rates of generation of such species, 3) relate the rates of active species generation to the water composition, 4) develop a general protocol for carrying out such studies, 5) develop a predictive model for the observed phenomena, 6) identify implications and impacts of the findings.

Summary of Progress

Expected reactive species were identified from the literature and probe compounds (model pollutants) were selected for the measurement of individual reactive species. A general characterization protocol was developed, tested, refined, and used to measure reactive species production rates in various Calumet waters. A predictive kinetic model was developed and used to correlate the results with water composition. It was found that the majority of photochemical reactivity was not due to one of the expected active species, but was instead the result of an unidentified species. Several implications and impacts have been identified.

Accomplishments

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Narrative Report

Methods: Water samples were collected from 9 locations in the Calumet River watershed, from close (½ mile) to the entrance into the river from Lake Michigan, to well below the confluence of the Little Calumet with the Cal Sag Channel. Sampling sites included Calumet Lake, inside the mouths of the Grand Calumet and Little Calumet Rivers where they entered into the main channel, and above and below the large municipal wastewater treatment plant. Samples were brought back to the laboratory, filtered, and spiked with model contaminants (“probe compounds”) having known reactivity with various active species. These waters were irradiated with light similar to the solar spectrum, and the rate of active species generation calculated from the rate of disappearance of the probe compounds. Radical scavengers and other amendments were added to the water samples, in order to increase the selectivity of radical production or removal, and the results used in kinetic models to quantitate radical production. The active species initially considered included hydroxyl radical (OH), carbonate radical, singlet oxygen, hydrated electron, and peroxy radicals. The hydroxyl radical probe (PCBA = p-chlorobenzoic acid), which is very specific for hydroxyl radical and is unreactive with less powerful radicals, was used first to determine hydroxyl radical production. TMP is reactive with most radicals and singlet oxygen, and was used to determine total reactive species production. Removal of TMP by singlet oxygen was distinguished from other processes by adding deuterated water to some samples in order to amplify the portion of reaction due to singlet oxygen, since D₂O quenches singlet oxygen 13 times more slowly than does H₂O. The carbonate radical generation rate was calculated from the hydroxyl radical generation rate, the alkalinity of the water, and known reaction rate constants.

Results: The best known precursors of photogenerated active species in natural water are natural organic material (NOM) and nitrate ion. Both were present in waters from the Calumet area. It was found that removal of spiked PCBA from the water samples by hydroxyl radical was very slow, being statistically different from zero in only three of the 18 samples. The measured hydroxyl radical generation rates were one to two orders of magnitude smaller than the measured TMP disappearance rates, and were consistent in magnitude not only with OH generation rates calculated from the nitrate photolysis rates, but also with recent measurements by Vaughan and Blough (ES&T, 1998) for other waters, using a different method.

TMP removal was rapid in all samples. However, removal of TMP by OH is not an important mechanism relative to other processes, and accounted for only $4.0 \pm 1.5\%$ of the total observed TMP removal. Similarly, TMP removal by singlet oxygen was statistically significant in only three samples, accounting for 24, 12, and 10% of the observed TMP removal in those samples. Hydrated electron was shown by competition kinetic calculations to be unimportant because of its rapid reaction with oxygen. Even though carbonate radical is reactive with TMP, it was shown by calculation that the low OH radical generation rate and relatively low alkalinities produced carbonate radical too slowly to be important in TMP removal. Thus, the fraction of total TMP removal accounted for by OH radical, singlet oxygen, carbonate radical, and hydrated electron combined was less than 25% in all cases, and less than 5% in 14 of 18 cases. Similar results were found in samples from Homer and Clinton Lakes near Champaign, Illinois. The majority of TMP removal in all cases was due to unknown active species that could include peroxy radicals or, more likely, excited NOM molecules.

The half-life for removal of TMP was found to be longest (about 5 hours) for the relatively “clean” water that had just entered the Calumet River from Lake Michigan, and was considerably shorter ($t_{1/2} = 0.6$ to 1.3 hours) at and below the confluence with the Grand Calumet River, just below the O’Brien Lock and Dam, indicating a significant difference in the ability of upstream and downstream water components to promote photochemical activity. These rates correspond to removal at the water surface. The rate of TMP removal in various waters correlated with both DOC (dissolved organic carbon, the quantification of NOM) and nitrate concentration. However, NOM is probably the precursor responsible for TMP removal, because of the low photolysis rates for nitrate. The rate constant for TMP removal from these (filtered) samples appears to also correlate with the chlorophyll A content in the unfiltered samples. An effect of algal exudates has previously been reported in the literature.

Discussion: The high rate of removal for the general probe TMP, coupled with the low rates of generation of hydroxyl radical, indicate that rapid removal of contaminants by photochemical processes will only occur for some contaminant types. Since the exact active species responsible for TMP removal is not yet known, definitive statements cannot be made at this time, but some conclusions can be drawn. Easily oxidized contaminants, such as phenols and sulfides should be removed quickly, as was seen in the results for TMP. At the other end of the scale, refractory compounds that require hydroxyl radical, which is generated approximately one to two orders of magnitude more slowly than the TMP removal rate, would be expected to exhibit half lives of 10 to 100 hours of full-sun irradiation, or approximately 2 to 20 days at the water surface. Removal throughout a well-mixed water column would be slower by, to a first approximation, the ratio of the water depth to half the thickness of the photic zone. Contaminants of intermediate reactivity, e.g., polynuclear aromatic hydrocarbons, should exhibit intermediate reaction rates, affected also by the extent of their partitioning to suspended sediments. The few contaminants such as heavily chlorinated organics that are quite unreactive with hydroxyl radicals, tend to be more easily reduced than oxidized, and would probably undergo reduction in the sediments before solar driven reactions could affect them.

Problems Encountered: 1) Removal of PCBA by OH radical was so slow that it was difficult to quantitate. Improvement in the test method increased the ability to quantitate removal by OH, verifying the low removal rate. 2) The active species responsible for most of the TMP removal in Calumet waters was not among those expected, or for which probe compounds have been developed, and has not been identified. Further work is needed to identify the active species and develop a more precise predictive model.

Impacts: A preliminary screening protocol and the theoretical framework to interpret the results have been developed, tested, and used to characterize waters from the Calumet watershed with respect to hydroxyl and carbonate radicals, hydrated electron and singlet oxygen generation. In all cases, the importance of these species was found to be low, but the rapid production of an unidentified reactive species means that some classes of pollutants, including phenols, will be rapidly destroyed by solar-mediated processes in Calumet and other Illinois waters. A preliminary calculation indicates that bankside treatment may be feasible. About 50% removal of TMP could occur during the 1-hour transit of the water through a SEPA (Sidestream Elevated Pool Aeration) station like those located on the Calumet Rivers and the Cal Sag Channel.

Other potential applications of these results include the addition of indirect photochemical processes to existing contaminant fate and transport and mass balance models, and use as a decision tool for evaluating the assimilative ability of a water body following remediative actions like dredging, which will disturb the sediments. However, for these uses, a more detailed predictive model is needed, requiring further development. In addition to the above impacts, preliminary calculations indicate that very rapid transformation of natural organic matter should be occurring within a period of a few hours, which impacts our view of the rate of transformations between various forms of both nitrogen and carbon in natural waters.

Brief Summary

The ability of sunlight to destroy pollutants in rivers and lakes was investigated in order to determine how quickly this process takes place, identify what chemical processes are involved, and to relate this information to the specific composition of the particular water. The cleansing process is the result of very reactive chemical species being formed when sunlight shines on natural water constituents, particularly nitrate ion and the products of plant decay. Experiments were therefore conducted in which model contaminants were added to river and lake water samples in the laboratory, and the water illuminated with simulated sunlight. During this time, samples were taken and analyzed to determine the extent of disappearance of the contaminant. The water was also analyzed to determine the amounts of various natural constituents, in order to relate the ability to assimilate the contaminant, to water composition. Model contaminants and methods were chosen to include compounds that were removed by most kinds of radicals, as well as one that was destroyed only by the most powerful radicals so that the range of effectiveness of the cleansing process could be investigated. It was found that even at relatively high concentrations, some contaminants were 95% destroyed in 3 hours in some waters, indicating that rapid removal of some contaminants occurs, while contaminants requiring the most powerful radicals for their degradation disappeared much more slowly. The results also indicate that 1) shallow bankside reactors may be practical for the removal of some pollutants, 2) chemical breakdown of dissolved organic matter in water by solar processes may be faster than anticipated, and 3) some of the ability of wetlands to assimilate pollutants may be due in part to these sunlight-driven processes.

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