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ENHANCED ORGANIC DECAY IN A STREAM RESULTING FROM EXPOSURE TO SUNLIGHT

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ABSTRACT: This experimental procedure was designed to test the hypothesis that streams which contain naturally colored water from swamp drainage exhibit a significantly enhanced degradation of organic constituents when exposed to sunlight. Mississippi Bayou is a small slowly flowing stream in southern Louisiana which receives a large part of its flow from swamp drainage. In two experiments replicate samples of water from Mississippi Bayou were placed in stoppered Pyrex glass containers, quartz glass containers, and, in the second experiment, also in BOD bottles. Control samples were placed in Pyrex glass containers and wrapped in foil to prevent light exposure. These containers were placed in a location which received sunlight in a pattern similar to the natural stream with periods of open shade and direct sunlight. Exposure to sunlight was for a period of seven days, after which the samples were incubated at 20 degrees centigrade for 20 days in the dark. This 20 day dark incubation was for the purpose of degrading a large portion of any organic carbon which might have accumulated in the light-bottles due to photosynthesis. Decrease in total organic carbon (TOC) after the complete 27 day period was found to be significantly greater ($n=4$ $p<0.05$) in the samples exposed to sunlight. The average change in TOC in the dark bottles was 2.68 and 0.47 mg/l in experiments 1 and 2 respectively. Change in quartz-light containers exceeded the change in dark containers by an average of 1.17 mg/l and 0.70 mg/l. Similarly, values for Pyrex light-bottles were 1.10 and 0.90; BOD bottle changes exceeded dark-bottle changes by 0.98 mg/l. Standard error of these means were near 0.1 mg/l.

KEY TERMS: Photooxidation; colored water; BOD; water quality modeling.

INTRODUCTION

It is frequently found that surface waters having high levels of color due to leaching of natural vegetation have unexpectedly low dissolved oxygen concentration (Miles and Brezonik, 1981; Roberts, 1983; Taylor and Adams, 1986). Such data suggest that the traditional mass balance approach to DO (dissolved oxygen concentration) analysis based on BOD, sediment oxygen demand, photosynthesis, and reaeration may prove to be an inadequate description of the mechanisms of DO dynamics in such waters. One possible explanation for this observed

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anomaly is that exposure to sunlight may result in the more rapid oxidation of some of the organic components in colored waters.

This paper reports the results of an experiment designed to test the hypothesis that streams which contain naturally colored water from swamp drainage exhibit a significantly enhanced degradation of organic constituents when exposed to sunlight. Enhanced degradation of organic materials could primarily result either from direct photochemical oxidation of organic material or, alternatively, from a photochemical reaction resulting in the transformation of an otherwise recalcitrant organic molecule or molecular fragment into a more easily decomposed product or isomer. The purpose of this experiment was not to decisively distinguish between these alternatives, but was designed to estimate the total enhancement of degradation due to both alternative mechanisms. This enhanced degradation of organic constituents could be significant in the analysis of dissolved oxygen budgets of surface waters containing colored waters, and in the determination of waste load allocations and permit limits for these waters.

The experiment was designed to simulate, as nearly as possible, the natural conditions in a stream. The nature of the hypothesis tested and simple experimental design obviates a need for chemical or physical sterilization or addition of a biological inhibitor in the samples exposed to sunlight. The effects of treatments with mercuric chloride, for example, may have caused some of the anomalous and contradictory results observed by Roberts(1983). Heat or filtration sterilization would similarly change the experimental conditions to conditions which are less analogous to the conditions which occur in natural streams.

It is well known that exposure to sunlight may result in the enhanced degradation of many naturally occurring (Nickerson, 1971, TeLang and Hodgson, 1983a, 1983b) and manmade chemical compounds (Zepp and Cline, 1977). These reactions may involve the photochemical production of singlet oxygen (Zepp and Cline, 1977, Baxter and Carey, 1982). Iron, suspended sediment, and algae concentrations may be significant mediating factors involved in the control or enhancement of the rate of light-induced degradation of organics (Oliver et al., 1979, Miles and Brezonik, 1981, Zepp and Schlotzhauer, 1983). Organic carbon concentration is found to increase with color (Hutchinson, 1957, Taylor and Adams, 1986). Hutchinson (1957) concludes that organic material associated with color represents the major fraction of the organic material in highly colored lakes, and that naturally occurring color in lakes largely results from organic material consisting of "the extractives of peat from the margins of the lake or from peat bogs and soils in the catchment area of the lake."

Decolorization of naturally colored water is of practical significance in maintaining suitable sources for domestic water supplies. It has long been recognized that exposure to sunlight has a decolorizing effect on colored waters (Whipple, et al. 1901). Stearns (1916) concluded that the reduction in color occurs as a first order process, and will continue to completion in both bottles and in large natural lakes. Stearns also reports that "by placing bottled water at different depths in a reservoir, the effective bleaching was

found to be confined to the upper few feet, while at a depth of 10 ft., in a reservoir water having a color of 40, no appreciable reduction was found after a month's exposure."

MATERIALS AND METHODS

Mississippi Bayou is a shallow bayou with a length of approximately 14.5 Km. It originates North of the natural levee of the Mississippi River, and flows generally in a northward direction away from the Mississippi River, toward Lake Maurepas, with flow into the lake passing through 4.5 Km of Dutch Bayou. A man-made levee on the Mississippi River prevents the flow of flood water from the river into the bayou drainage area. The drainage basin area is not well defined but is approximately 50 square Km, and is dominated by a cypress - tupelo swamp ecosystem. At times, urban drainage from communities built on the natural Mississippi River levee may also enter the headwaters of the bayou. Water samples for the experiments reported in this paper were taken from an interstate highway bridge which crosses the bayou approximately 9.3 Km above the confluence with Dutch Bayou.

A water sample from Mississippi Bayou was collected and stored overnight under refrigeration. Initial BOD, color, and TOC were measured. In order to measure the initial BOD of this sample, twenty-day nitrification suppressed and non-suppressed BOD analyses were also performed on this original sample. All TOC measurements were repeated in duplicate for each sample and recorded as an average value, or, if values differed by one mg/L or more, measurements were repeated to better define the value for the sample.

Six round-bottomed Pyrex flasks and six Quartz glass flasks were filled and stoppered with rubber stoppers. Six control Pyrex flasks were similarly prepared and wrapped with foil to serve as dark control samples. In the second experiment, BOD bottles were also included as a light - dark treatment. All flasks were then placed in a partially shaded outdoor location for a period of seven days. Diel temperature variations in these bottles may have been somewhat greater than that which occurred at the Mississippi Bayou sampling site, but would not have exceeded the variations which might naturally occur in shallow Louisiana streams. On the morning of the eighth day the samples were returned to the laboratory. One sample from each group was required for color determination, while another was used for TOC determination. These values are referred to as the seven day values in the following sections. Samples from the four remaining replicate flasks from each treatment were transferred to BOD bottles and incubated in a standard non-suppressed 20-day BOD incubation. BOD data from this incubation is referred to as the final BODs in the following sections. TOC analyses were performed on the samples following this final 20-day incubation. These TOC values are referred to as the final TOC values. The total change in TOC from the initial to the final TOC in each treatment is termed DTOC, and represents the total change in TOC of each treatment. This experiment was repeated on two occasions, with samples collected on July 6 and July 14, 1986 for the experiments 1 and 2 respectively.

RESULTS AND DISCUSSION

Results of these experiments are summarized in Table 1. Initial concentration of organic constituents was lower at the time of sampling for experiment 2. Initial twenty day BOD values were determined for each sampling date. Initial BOD values for experiment 1 were found to exceed those for experiment 2 by approximately 50% for both nitrification suppressed and non-suppressed BODs. Initial TOC values in the first experiment exceeded those in the second by 40%, and initial color in the first experiment exceeded that found in experiment 2 by 25%.

After the seven day exposure to sunlight, one sample bottle of each type was used for the analysis of TOC and color. A lower color value was found in all light bottles relative to the dark bottles. TOC values after seven days were not consistently lower in the light bottles. The variability between these light samples suggests that different levels of production of organic carbon through photosynthesis was occurring in the various treatments.

The values referred to as final in Table 1 were measured following a 20 day dark incubation in a BOD incubator. In every treatment, final TOC values were significantly less in the light treatments than in the dark treatments, but no significant difference was found between the Pyrex bottles, quartz bottles, and the BOD bottles ($n=4$, $p<0.05$). Assuming rates of decay observed in typical BOD incubations, approximately 90% (at a decay rate of 0.12 per day) of the biologically degradable organic matter would have decayed after 20 days. Thus the final TOC and BOD values should exclude 90% of any organic material produced by photosynthesis during the seven day light exposure period, and, similarly, should not include 90% of any organics which were phototransformed from a recalcitrant form into a degradable form during the light exposure. The difference between the initial TOC and final TOC is labeled DTOC in Table 1.

Under the assumption that photosynthetically produced and phototransformed organic materials were degraded during the twenty day incubation, and that the degradable organic fraction of the initial sample degraded over the total 27 days of incubation, the final TOC represents the recalcitrant organic carbon which remained after treatment, and the DTOC represents the part of the initial TOC which degraded over the period of the experiments. In each treatment, the DTOC of the light exposed samples exceeds that of the corresponding dark samples. The overall average difference between the light DTOC and corresponding dark DTOC is 1.0 mg/L.

TABLE 1. SUMMARY OF RESULTS.

	Experiment 1			Experiment 2			
	Dark Pyrex	Quartz		Dark Pyrex	Quartz	BOD- Bottle	
Initial BOD20							
N-suppressed (S.E., n=10)			5.37 (0.16)				3.65 (0.08)
non-suppressed (S.E., n=10) (S.E., n=8)			12.53 (0.21)				8.40 (0.16)
Initial color			100				80
Initial TOC (mg/l)			17.8				12.7
7-day color	100	60	60	100	50	60	50
7-day TOC (mg/l)	16.60	16.00	15.80	12.20	12.70	12.40	11.50
final TOC (mg/l) (S.E., n=4)	15.13 (0.08)	14.03 (0.11)	13.95 (0.13)	12.23 (0.11)	11.33 (0.09)	11.53 (0.09)	11.25 (0.09)
DTOC (mg/l)	2.60	3.70	3.05	0.47	1.37	1.17	1.45
Final BOD20 (S.E., n=4)	5.09 (0.53)	6.46 (0.52)	5.75 (0.33)	3.41 (0.22)	6.04 (0.44)	6.59 (0.47)	9.98 (0.42)

A first estimate of the influence of this increased organic degradation on oxygen demand within a stream may be obtained by assuming that during microbial degradation that each organic carbon atom reacts with two oxygen atoms to form carbon dioxide. Under this assumption, a ratio of 2.7 (32/12) would be predicted between BOD and TOC. Thus, the 1.0 mg/L increase in degraded TOC corresponds to an added load of 2.7 mg/L of oxygen demand per week in the bayou. With such a value, light enhanced degradation of otherwise recalcitrant organic materials is clearly a major oxygen sink and is possibly the major oxygen demanding load in Mississippi Bayou.

CONCLUSION

Development of water quality standards and waste load allocations for streams depends on an understanding of the mechanisms of organic material decay within the water body. In streams which are

significantly impacted by naturally colored drainage, it appears that a significant part of this transformation may be enhanced by sunlight. Traditional BOD determinations on such waters may therefore greatly underestimate in-stream oxygen loads.

Quantification of these light related mechanisms may resolve apparently anomalous DO values observed in colored waters. Further research is required to distinguish between photo-oxidation of recalcitrant organics as a direct DO sink, and phototransformation of recalcitrant materials into biologically degradable organic materials. Separation of these mechanisms in an experiment of design similar to the one reported here would require a quantitative evaluation of the level of photosynthetic production within the light bottles. Photosynthesis could be quantified by either measurement of primary production, or through controlling production by inhibition or sterilization which would result in zero production.

Future research in this area should also attempt to quantify the rates of light induced transformation in water bodies impacted by runoff from various natural and agricultural ecosystems and from industries such as paper mills which are known to release highly colored effluents. Identification and quantification of these mechanisms will allow the appropriate extension of water quality models commonly used in water quality management.

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