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Influence of Autochthonous Dissolved Organic Carbon and Nutrient Limitation on Alachlor Biotransformation in Aerobic Aquatic Systems

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Much work has suggested that the rate of attenuation of water-soluble organic contaminants in aerobic aquatic systems is dependent on the level of secondary nutrients in the water column. For example, the decay rate of alachlor, a common herbicide, was over 10 times higher under hypereutrophic compared with oligotrophic water conditions. It has been presumed that higher water column nutrient levels produce larger microbial communities, resulting in higher rates of alachlor cometabolism. However, most earlier field studies only assessed alachlor fate in systems with full light exposure (FLE). Therefore, new experiments were performed to assess how variations in light level affect alachlor cometabolism in such systems. Twelve tank mesocosms were maintained using identical nitrogen (N) and phosphorus (P) supply conditions: four units with full light exposure (100% FLE), four with partial shading (19.3% FLE), and four with near complete shading (0.5% FLE). Alachlor half-lives were found to vary broadly, from 50 to 60 days in higher light units to >180 days in the 0.5% FLE units. Nutrient analysis indicated that the low light units were severely carbon (C)-limited for microbial decomposition, whereas the other units had excess C relative to N and P. Apparently, reduced light levels cause decreased production of bioavailable C for decomposition, which significantly reduces alachlor cometabolism. The data suggest that water column nutrient levels only correlate with the alachlor decay rate when light levels are high, and that the biodegradable carbon supply must be considered when the fate of water-soluble contaminants in aerobic aquatic systems is assessed.

Introduction

Photosynthetic activity by phytoplankton and phototrophic bacteria is a major source of autochthonous organic carbon in many aquatic systems. This organic carbon, in turn, fuels most microbial decomposition reactions and primes most other aquatic biological activity (*1*). Although much in situ heterotrophic microbial activity is dependent upon carbon supplied by primary production (e.g., the microbial loop (*2*)), little work has been done in assessing how this dependence might affect the biodegradation of water-soluble organic contaminants in aquatic systems. Aquatic systems receive many xenobiotic compounds that can be conditionally biotransformed (*3*); however, the mechanistic basis of in situ contaminant transformation is not always well understood (*4*). This is especially true for water-soluble contaminants that are biotransformed in the water column by cometabolic reactions. Such reactions require a primary carbon source to support microbial growth and secondary nutrients to retain elevated microbial activity.

This study was undertaken to assess relationships among light and carbon supply conditions, microbial decomposition, and the cometabolic transformation of a water-soluble contaminant in aquatic systems. Previous work has suggested that water column nutrient levels frequently correlate with contaminant transformation rates (*5*−*9*), with total phosphorus (TP) and total nitrogen (TN) levels often being positively linked with contaminant disappearance. The presumption has been that the secondary nutrient level influences the size of the microbial community, which in turn influences cometabolic biodegradation rates. However, most field studies assessing water-soluble contaminant fate have used systems with full light exposure (FLE); the influence of reduced light on cometabolic contaminant biotransformation has not been assessed.

The purpose of this project, therefore, was to examine how altering the light conditions might affect contaminant biotransformation in aerobic aquatic systems. To address this question, we monitored the fate of alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide), a common preemergence chloroacetinilide herbicide (*10*), in aquatic field mesocosms maintained under high, moderate, and very low light conditions. Previous evidence indicated that the major alachlor fate mechanism in aerobic systems is cometabolic biotransformation via nonspecific glutathine-*S*-transferase (GST)-mediated microbial pathways (*7*, *9*, *11*). This fate mechanism is quite different from those of many other organic contaminants (in aerobic aquatic systems) because it occurs primarily in the water column rather than in sediments or higher organisms (*5*−*8*).

This specific experiment assessed alachlor disappearance over time in field mesocosms, keeping TN and TP supply levels similar across treatments but varying the light conditions. Further, low (<1000; DOC_L) and high (>1000; DOC_H) molecular weight dissolved organic carbon (DOC) and water column TN and TP levels were measured over time to monitor how varying light levels affected relative nutritional conditions in each treatment. Our basic hypothesis was that reduced light would reduce the autochthonous carbon supply rate for microbial decomposition, which in turn would reduce the rate of cometabolic alachlor degradation.

Materials and Methods

Experimental Program. *Mesocosm Setup*. The experiments were performed in late summer 2000 at the Nelson Environmental Study Area (NESA) located near the University of Kansas, Lawrence, KS. Twelve cylindrical 11.3 m^3 fiberglass tanks, 3.2 m in diameter and 1.4 m deep, were placed in two parallel "host" ponds (to minimize temperature fluctuations), as described previously (*5*−*7*). Furthermore, three 39 cm × 53 cm plastic sediment trays, containing fresh sediments from an adjacent uncontaminated pond, were placed on the bottom of the tanks to inoculate the units. The tanks were then filled with water from a protected source pond and fertilized with N and P to raise secondary nutrient levels.

Four tanks were left open, whereas eight of the twelve tanks were provided lids to either partially shade or com-

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pletely shade different units (four each). The lids for partial shading were made of black window screen, whereas the lids for "complete" shading were made of black vinyl plastic; both lid types were attached to PVC hoops that were hung using wire hangers about 10 cm below the tank rims above the water surface. A 15 cm square port with a flap door was cut into each lid for water sampling. The three functional treatments were (1) "open" (no lid) or 100% FLE, (2) "shaded" or 19.3% FLE, and (3) "dark" or 0.5% FLE, as measured using a LICOR (no. LI-185A) photon sensor. These treatment definitions were based on the geometric mean of all incident light measurements made at the top, middle, and bottom of the tank water columns.

Secondary Nutrient Supply Strategy. Secondary nutrients were provided to the tanks as HNO_3 and H_3PO_4 to raise baseline N and P levels and increase overall biological productivity in the units. The targeted water column N and P levels were 1200 μg/L TN and 40 μg/L TP, which were chosen on the basis of previous experience (*5*, *6*). As N and P were provided to the units, ambient water column TN and TP levels started to diverge among the treatments (after placement of lids); however, it was desired to retain the same mass nutrient loadings to all units. Therefore, the amount of nutrients added per week was determined by averaging the previous week's measured TN and TP levels across all 12 tanks, and then adding sufficient N and P to achieve overall averages of 1200 μg of TN/L and 40 μg of TP/L in the units. Although the actual amount of N and P added to the tanks varied each week, the overall nutrient input to all tanks was identical.

Mesocosm Experiment. Mesocosm water quality monitoring commenced immediately after the lids were placed in late July and continued through early September when conditions were sufficiently consistent among treatments to start the experiment. Alachlor was then added to each unit with tank water to a final concentration of 25 μg/L using commercial grade Lasso (Monsanto Corp., St. Louis, MO). Each unit was gently mixed with a paddle, initial water samples were collected, and sampling was continued for 42 days.

Weekly field monitoring included water temperature, pH, conductivity, and dissolved oxygen (DO) at three depths (at 0.25, 0.65, and 0.95 m below the water surface) using a Water Checker field monitor (Horiba Instruments). Additionally, two 500 mL composite water column samples were collected per tank using a 1.2 m long, 25 mm diameter PVC tube equipped with a check valve at the bottom (*6*). Laboratory analyses included TN, TP, total organic carbon (TOC), DOC, different molecular weight fractions of DOC (<1000, 1000−3000, 3000−10000, and >10000), total inorganic carbon (TIC), chlorophyll *a*, and alachlor. All water samples were collected in acid-rinsed amber glass bottles (using 5% H_2SO_4) that were also prerinsed with deionized water and tank water before use. All samples were maintained on ice in the dark prior to being returned to the laboratory for analysis.

Water samples for phytoplankton and bacteria enumeration were also collected with the PVC tube samplers. Typically, a 250 mL composite sample was drawn with the sampler; 100 mL volumes were then transferred to glass bottles and preserved with 1% Lugol's solution for phytoplankton analysis, and 30 mL volumes were transferred to sterile centrifuge tubes and preserved with gluteraldehyde (2% final concentration) for bacterial counts (*12*). Zooplankton samples were collected using a 10 cm diameter, 60 μm mesh Wisconsin vertical-haul net (Wildlife Supply Co.). The samples were resuspended in distilled water and preserved with ethanol (50% final concentration).

Analytical Procedures. *Sample Preparation for Water Chemistry.* Each 500 mL water sample was divided as follows. Approximately 150 mL was retained for TOC, TIC, TN, and TP analyses, and 250 mL was separated and filtered through prerinsed Whatman GF/F glass-fiber filters (particle retention of >0.70 μm) for chlorophyll *a* (captured particulates), DOC, and alachlor analyses. The filters were retained in the dark in aluminum foil at −10 °C prior to chlorophyll *a* analysis (<2 days), and the filtrate was divided into two 125 mL fractions for herbicide and DOC analysis. All filtration was performed under low light conditions to minimize degradation of the chlorophyll *a*. TN, TP, and TIC analyses were always performed immediately, whereas samples for TOC and DOC were acidified to ca. pH 2 with 85% H_2PO_4, stored at 4 °C, and processed within 72 h.

Samples for DOC molecular weight fraction analyses were processed the same as the DOC samples, except ultrafiltration was performed on the filtrates from glass-fiber filtration. Typically, three 100 mL aliquots of filtrate were passed through cellulose membranes (Millipore Corp., Bedford, MA) with molecular weight retentions of 10000, 3000, and 1000. The membranes were always prewashed with deionized water to remove residual carbon; 10.0 mL filtrate volumes were analyzed in duplicate.

Herbicide Analysis. Alachlor levels were determined using solid-phase extraction (*13*) followed by elution and detection using gas chromatography−mass spectroscopy (GC−MS) as reported previously (*11*). Sampling and analysis were performed in duplicate for each tank on each sample day. All reported alachlor values were corrected for both evaporative losses and/or rainfall inputs to the tanks over the duration of the experiment.

Other Chemical Analyses. DOC, DOC fractions, and TOC were determined using a Dohrmann organic carbon analyzer. TP was analyzed spectrophotometrically (Shimadzu UV-160) following wet digestion with potassium persulfate (*12*, *14*). TN also was measured spectrophotometrically following alkaline persulfate digestion (*12*, *15*). TIC was analyzed according to standard methods (*12*). Chlorophyll *a* was extracted with hot ethanol and then analyzed spectrophotometrically (*16*).

Microbiological Enumeration and Identification. Phytoplankton were enumerated and identified (at the genus level) using an Olympus inverted microscope at 400× by counting >30 randomly selected fields per sample. Zooplankton were also counted and identified using the inverted microscope, but enumeration used all fields at 100×. Total bacteria were quantified using acridine orange staining and fluorescence microscopy (Zeiss IIIRS) using 630/60m, 465/30x, and 505bs filters (Chroma Technology, Inc.). Thirty random fields per sample were counted at 400×; samples were prestained with acridine orange (0.01%) and filtered using black 2 μm polycarbonate filters (Osmonics).

Biovolumes were calculated as follows. For phytoplankton, 10 random cells per sample per genus were selected for estimation and their volumes calculated according to Hillebrand et al. (*17*). For zooplankton, the shapes of copepods and nauplii were assumed cylindrical, and cladocera and rotifers were assumed to be prolated spheres. Due to variability in body sizes, all zooplankton were measured two-dimensionally; however, appendages were excluded from all size measurements. All bacteria were assumed to be 1 μm^3 with specific gravities of 1.0.

Data Analysis. *Mean Water Chemistry Conditions in Each Treatment.* Mean physical and chemical conditions in each tank (post-alachlor addition) were estimated from seven measurements per tank for water temperature, pH, conductivity, and dissolved oxygen, and five sets of laboratory analysis for TN, TP, TIC, TOC, DOC, DOC fractions, chlorophyll *a*, and alachlor. Treatment means were calculated from the means from each tank under each treatment. All 95% confidence intervals were calculated using standard errors (using a two-tailed $P < 0.05$ value of t) associated with

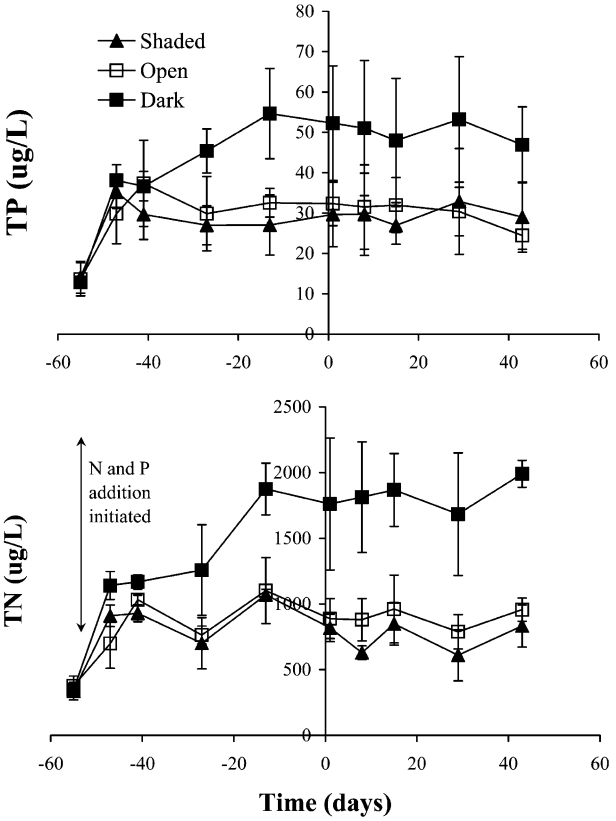

FIGURE 1. Development of water column TN and TP conditions in the three treatments. Time "zero" corresponds to the time when alachlor was added to the mesocosms; the time when N and P addition commenced is also noted. Each time point represents the mean of three or four samples. Error bars refer to 90% confidence intervals.

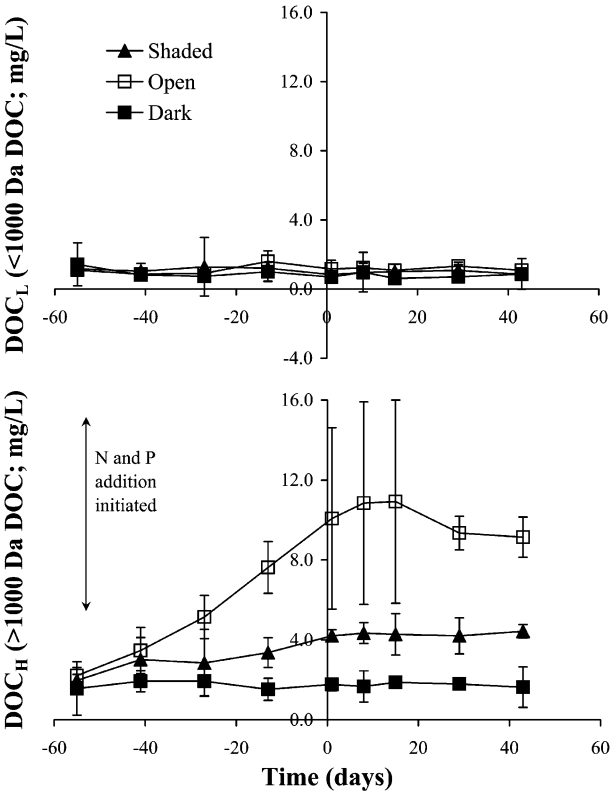

FIGURE 2. Development of water column low and high molecular weight DOC (DOC_L and DOC_H, respectively) conditions in the three treatments. Time zero corresponds to the time when alachlor was added to the mesocosms; the time when N and P addition commenced is also noted. Each time point represents the mean of three or four samples. Error bars refer to 90% confidence intervals.

the estimate of each mean. Data normality was tested using the Kolmogorov–Smirnov nonparametric test.

Estimation of Alachlor Decay Rates. The first-order model most closely fit alachlor disappearance patterns; therefore, first-order transformation rate coefficients were used to compare disappearance rates among treatments. Mean rate coefficients and 95% confidence intervals for each treatment were estimated on the basis of estimates from the individual tanks. Half-lives were calculated from the rate coefficients. All rate estimates were normalized to 20 °C using a previously determined rate versus temperature function developed from equivalent data (*18*).

Comparison of the Rate Coefficients and Tank Conditions among Treatments. The Kruskall–Wallis test was used to compare and contrast alachlor disappearance rates among the three treatments. This is a nonparametric test for determining whether the groups of data come from the same or different parent populations (*19*). Pearson's bivariate correlation analysis was used to assess directional trends between transformation rate coefficients and the various measured parameters. All statistical analyses were performed using SPSS (*20*).

Results

Development of TN, TP, and DOC Conditions under the Different Treatments. All treatments achieved relatively steady water column nutrient levels before alachlor was added, although nutrient conditions in each treatment differed significantly (Figures 1 and 2). The two light-exposed treatments had similar TN and TP levels throughout the entire experiment; however, the level of DOC_H increased over time in both treatments. In contrast, water column TN and TP levels progressively increased in the dark treatment, and DOC_H levels were nearly constant. DOC_L levels were low and quite similar among the treatments. The segregation of DOC according to DOC_H and DOC_L fractions is based upon the Amon and Benner (*21*, *22*) definition of more and less bioavailable DOC for microbial decomposition reactions, respectively. Table 1 shows significant differences in mean DOC levels among the treatments, and those differences were apparent in measured DOC_L and DOC_H fractions, which were used for all comparisons.

Mean Physical and Chemical Water Conditions in the Mesocosms. Tables 1 and 2 summarize the mean water column physical and chemical conditions under the three treatments after alachlor was added. In general, the open tanks had high pH, DO, DOC_H, and TOC levels and low TIC and conductivity levels, suggesting they were dominated by photosynthesis relative to microbial decomposition. In contrast, the dark tanks had low relative levels of photosynthesis as indicated by lower pH, DO, DOC_H, and TOC levels and higher TIC and conductivity levels. The shaded tanks were similar to the open tanks, although reflective parameters were less extreme than those for the open units.

The proportional levels of DOC_H, TN, and TP differed among the treatments. In particular, the DOC_H:TN and DOC_H:TP ratios were much lower in the dark units compared with the open units; i.e., average DOC_H:TN:TP ratios were 34:0.9:1, 140:5.6:1, and 350:12:1 in the dark, shaded, and open units, respectively. In contrast, TN:TP ratios were similar among all three treatments (~25:1 to 36:1 by mass). In summary, P was generally deficient compared to N and C in the open units, whereas both N and P were deficient relative to C in the dark units.

TABLE 1. Mean Chemical and Nutritional Conditions under the Three Mesocosm Treatments

treatment	TN (mg/L)	TP (mg/ L)	TIC (mg/L)	TOC (mg/L)	DOC (mg/L)	DOC < 1000 (mg/L)	1000 < DOC < 3000 (mg/ L)	3000 < DOC < 10000 (mg/L)	DOC > 10000 (mg/L)
open	0.90[a]	0.030	13.1	14.2	11.9	1.2	0.7	1.5	8.5
	(0.13)	(0.008)	(2.4)	(5.9)	(5.1)	(0.2)	(0.1)	(0.5)	(4.5)
shaded	0.75	0.030	17.3	6.0	5.2	1.0	0.6	0.9	2.9
	(0.11)	(0.012)	(1.9)	(0.7)	(0.5)	(0.1)	(0.1)	(0.2)	(0.4)
dark	1.82	0.050	22.8	2.8	2.5	0.8	0.4	0.5	0.9
	(0.35)	(0.017)	(1.8)	(0.2)	(0.4)	(0.3)	(0.1)	(0.1)	(0.2)

[a] Mean estimated or measured parameter for each treatment with 95% confidence intervals provided in parentheses.

TABLE 2. Mean Physical Conditions and Alachlor Transformation Rate Coefficients under the Three Treatments

treatment	k_{20}[a] (day^{-1})	half-life (days)	pH	conductivity (mS/cm)	DO (mg/L)	temperature (°C)	light intensity[c] ($\mu E/m^2/s$)
open	0.012[b]	58.1	9.5	0.230	13.0	16.6	1200
	(0.004)	(21.2)	(0.4)	(0.003)	(3.1)	(0.1)	(330)
shaded	0.013	52.8	8.9	0.236	12.5	16.4	240
	(0.002)	(8.3)	(0.2)	(0.014)	(2.2)	(0.1)	(50)
dark	0.004	185.4	7.6	0.270	6.1	16.7	7.2
	(0.003)	(116.6)	(0.1)	(0.016)	(1.3)	(0.2)	(2.7)

[a] First-order alachlor transformation rate coefficient normalized to 20 °C. [b] Mean estimated or measured parameter for each treatment with 95% confidence intervals provided in parentheses. [c] Individual light intensities represent the geometric mean of midday readings recorded at the top, middle, and bottom of the water column. These light levels correspond to 100% FLE (open), 19.3% FLE (shaded), and 0.5% FLE (dark) conditions.

TABLE 3. Biological Characteristics of the Three Treatments

treatment	algae[a] (μg/L)	zooplankton (μg/L)	cyanobacteria (μg/L)	other bacteria (μg/L)	chlorophyll *a* (μg/L)
open	10700[b]	323	4.37	1980	13
	(8020)	(196)	(8.56)	(430)	(20)
shaded	3470	710	96.4	1170	6
	(1370)	(774)	(109)	(144)	(6)
dark	29.7	125	32.7	834	1
	(14.5)	(142)	(59.5)	(255)	(1)

[a] Calculated biovolumes of each respective group of organisms. Converted to units of equivalent mass concentration for the different groups. [b] Mean estimated or measured parameter for each treatment with 95% confidence intervals provided in parentheses.

Mean Biological Conditions in Mesocosm Waters. Microbiological results were consistent with the physical and chemical water quality observations. Table 3 shows that the photosynthetic community (algae plus cyanobacteria) in the open tanks was large compared with those in the dark (i.e., ~160× greater) and shaded (~3× greater) tanks, which is consistent with the dominance of photosynthesis in the open units. The bacterial community size was also larger in the open units, although the proportional difference in bacterial community size was smaller (~2 times) than that in photosynthetic community size.

Figure 3 summarizes log-transformed quantitative relationships between total biovolume and relative light level, and photosynthetic community biovolume and chlorophyll *a* level. Both relationships are highly correlated ($r^2 > 0.99$, $P < 0.01$), suggesting that the light supply controlled biological productivity in the mesocosms; however, Table 3 suggests that the microbial community composition within each treatment was quite variable (i.e., large 95% confidence intervals).

Specific algae observed in the open units were primarily chlorophytes (usually >96% by biovolume, typically, *Chlamydomonas*, *Golenkia*, and *Oocystis* spp.), whereas the shaded units were dominated by *Cryptomonas* and *Rhodomonas* spp. (up to 99% per tank). Observed cyanobacteria largely consisted of *Oscillatoria* and *Anabaena* spp. Zooplankton in the open tanks were mostly rotifers (~58%) and ciliates (~27%). In contrast, the shaded tanks had fewer rotifers (only ~4.3%), and had much larger adult copepod (~79%) and cladoceran (~13%) populations. The dominant zooplankton and phytoplankon in the dark units were cladocerans and small chlorophytes (<3 μm diameter), respectively.

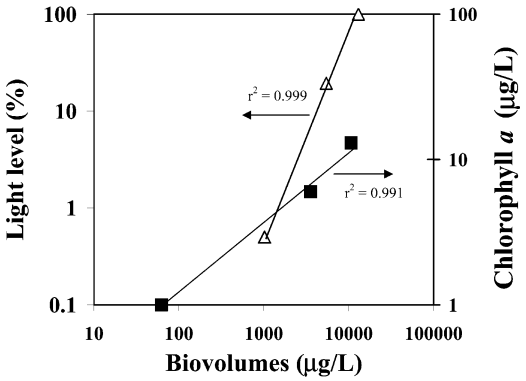

FIGURE 3. Relationships between the algal biovolume and chlorophyll *a* level (■), and the total biovolume and relative light level (△) in the three mesocosm treatments. All data were log-transformed. It was assumed that the percent light level was equivalent to the absolute light level because the mesocosms were in close proximity to each other.

Alachlor Transformation Rates. Figure 4 and Table 2 present alachlor disappearance curves, transformation rate coefficients, and half-lives. Rate coefficients differed significantly between the dark treatment and the open and shaded treatments (ANOVA, $F_{2,9} = 31.45$, $P < 0.01$), whereas coef-

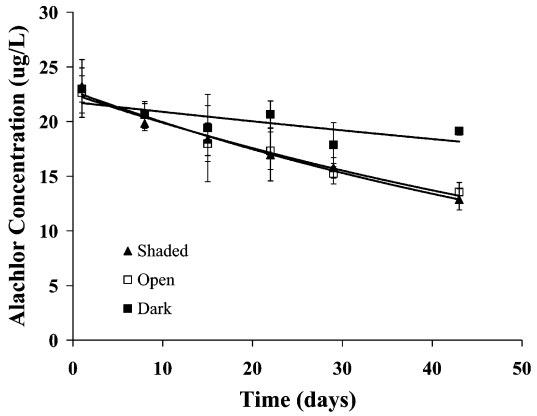

FIGURE 4. Mean alachlor disappearance curves for the shaded (▲), open (□), and dark (■) mesocosm treatments. Each time point represents the mean herbicide level based on four samples. Error bars refer to 95% confidence intervals. Trendlines for each treatment are provided.

TABLE 4. Summary of Parameters Correlated[a] with the Alachlor First-Order Transformation Coefficient, k_{20}

positive correlation with k_{20}	negative correlation with k_{20}
DO (0.892)* [b]	TN (−0.943)*
pH (0.871)*	conductivity (−0.842)*
DOC_L (0.778)*	TIC (−0.752)*
total bacteria[c] (0.590)*	TP (−0.730)*
DOC (0.588)	
DOC_H (0.572)	
TOC (0.572)	
other bacteria (0.563)	
zooplankton (0.545)	
total eukarya[d] (0.512)	

[a] Significant defined as $P < 0.1$. Values in parentheses refer to the r^2 of each parameter's correlation coefficient. [b] The asterisk indicates a significant correlation ($P < 0.05$) [c] Refers to the sum of "other bacteria" plus cyanobacteria as indicated by biovolume estimates (see Table 3). [d] Refers to the sum of zooplankton plus algae as indicated by biovolume estimates.

ficients from the open and shaded units were statistically similar (*t*-test, $t = 0.81$, $P = 0.45$). Rate coefficients ranged from 0.004 to 0.013 day^{-1}, and half-lives ranged from about 50 days to 185 days in the different units.

Trend Analysis in Water Conditions and Transformation Rates. Most water column parameters correlated with the alachlor transformation rate coefficients in the experiment (see Table 4); however, many relationships were nonlinear. Therefore, linear bivariate correlation analysis was only used to assess directional trends, such as increasing, decreasing, or constant, among measured parameters and rate coefficients. pH, DO, DOC_L, and the biovolume of the bacterial community ("other bacteria" plus cyanobacteria) were most positively correlated with k_{20} ($P < 0.05$), whereas TN, TP, conductivity, and TIC were all negatively correlated with k_{20}. Table 4 shows that other measures of organic carbon and biological community size also correlated with decay rate, although the correlations were weaker. It should be noted that DOC_H was less linearly correlated than DOC_L with k_{20}, which appears to contradict our assumption of "bioavailable" DOC. However, this anomaly results from excessive DOC_H production in the open tanks, which causes any linear correlation between DOC_H and k_{20} to be weak when N or P are growth limiting.

Discussion

Previous work has suggested that the rate of attenuation of water-soluble organic contaminants, such as alachlor, is positively correlated with water column secondary nutrient conditions (*5*−*7*, *11*, *18*); however, our results suggest that this is not always true and that the alachlor biotransformation rate can vary significantly under different light conditions. Table 4 shows a strong, statistically significant inverse relationship between decay rate and water column TN and TP, which is different from previous data. The practical question is, why?

The logical answer is that alachlor is actually being transformed by direct photocatalyzed or other reactions, and not biotransformation; however, all evidence suggests that this is not the case for alachlor. Knapp et al. (*11*) found that high alachlor transformation rates only occur in aerobic aquatic systems when both decomposing and photosynthetic organisms are metabolically active in the system, and that alachlor photooxidation and other abiotic processes were minimal in these aquatic systems. Further, the only biological parameter that consistently correlated with k_{20} is the water column eubacterial community size (*5*, *6*, *11*)—the presumed microbial domain responsible for aquatic decomposition reactions. Finally, "signature" alachlor biotransformation products, such as alachlor oxanilic acid, were consistently found where the alachlor degradation rate was high (*6*). The question, therefore, is, why does altering the light supply alter the decay rate so dramatically for alachlor?

The answer becomes apparent when one examines nutrient-limitation conditions for microbial decomposition under different light conditions. Previous evidence indicated that alachlor biotransformation in aerobic systems primarily occurs via GST-mediated cometabolic pathways associated with decomposition reactions (*6*, *8*, *11*). Therefore, using DOC_H as the presumed bioavailable carbon for decomposition (*21*, *22*), a comparison of DOC_H:TN:TP ratios under the different treatments shows that the removal of light causes a significant shift from N and/or P limitation to C limitation for decomposition (assuming balanced microbial growth requires a C:N:P ratio of about 41:7.5:1 by mass (*23*)). The mean DOC_H:TN:TP ratio in the dark tanks was 34:0.9:1, whereas the open and shaded tanks had much higher DOC_H levels relative to N and P. The apparent "overproduction" of DOC_H in the well-lit tanks is exemplified by the rapid accumulation of DOC_H in those units prior to alachlor addition, whereas the relative deficiency of DOC_H compared with N and P in the dark tanks is indicated by progressively increasing TN and TP levels (see Figures 1 and 2). Therefore, our general mechanism is supported by the data: i.e., when the light supply is high, the autochthonous carbon supply is also high and carbon is not limiting for decomposition; larger bacterial communities result, and high alachlor degradation rates prevail. When light is restricted, the opposite is true.

The above model is consistent with chemical and biological results (Tables 1−3). Ambient nutrient data indicate that when N and P are supplied to the well-lit tanks, the supplied nutrients clearly contribute to elevated photosynthesis and larger algae communities (Figure 3), which in turn produces higher levels of DOC_H. Excess DOC_H accumulates because the decomposition rate is limited by the secondary nutrient supply and some DOC_H that is less degradable, which in turn results in the uncoupling of the alachlor decay rate and water column nutrient level. The presumption that alachlor cometabolism is largely eubacterial (as opposed to algal) is suggested by the large difference in algal versus bacterial community size in the open tanks. If algae rather than bacteria were responsible for alachlor cometabolism, one would expect alachlor degradation to be the greatest in the open tanks; however, this was not the case. In fact, the highest rates of alachlor degradation were seen in shaded units that had the most "balanced" levels of DOC_H, TN, and TP among the three treatments.

The relationship between photosynthesis and decomposition and its affect on C versus P limitation for decomposition has been known for many years (*1*, *4*, *21*, *24*, *25*); however, this relationship has not been examined relative to the cometabolic degradation of water-soluble contaminants. Relationships between eutrophication and organic contaminant fate are becoming understood better (*4*), but much of the current emphasis is on less soluble compounds. Our data suggest that the fate of alachlor, a more water-soluble contaminant, is strongly impacted by the eubacterial decomposition (*5*, *6*, *11*) of autochthonous carbon. Background organic carbon level and type clearly influences the fate of most organic contaminants in aquatic systems; however, the influence of carbon on alachlor is different than for more hydrophobic compounds. With alachlor, background DOC appears to be a source of carbon for growth and cometabolism, and not just a "surface" for adsorption and settling reactions (*4*). In summary, the link between eutrophication and the fate of organic contaminants varies for different compounds; however, we feel that our new mechanism for contaminants such as alachlor should provide a more complete picture of factors that affect contaminant fate and help refine future modeling efforts.

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