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Master of Science degree in Geological Sciences

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SEASONAL VARIATION IN THE BIOGEOCHEMICAL CYCLING OF SESTON AND ITS RELATIONSHIP TO PCB CONCENTRATIONS IN GRAND TRAVERSE BAY, LAKE MICHIGAN

By

Eileen Marie McGervey McCusker

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

1998

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ABSTRACT

SEASONAL VARIATION IN THE BIOGEOCHEMICAL CYCLING OF SESTON AND ITS RELATIONSHIP TO PCB CONCENTRATIONS IN GRAND TRAVERSE BAY, LAKE MICHIGAN

By

Eileen Marie McGervey McCusker

This study describes seasonal biogeochemical cycling of seston in Grand Traverse Bay, Lake Michigan and relates this to variation in total polychlorinated biphenyl concentrations (SPCB) in suspended solids. Seston was characterized by carbon and nitrogen elemental and isotopic abundances. Fluorescence, temperature, light transmittance, and concentrations of dissolved inorganic nitrogen were also determined. The vertical and seasonal trends in the δ^{13} C values of seston exhibited a broad range (-30.7 to -23.9%). Seasonal $\delta^{15}N$ values of seston were highest in the spring and subsequently declined. The $\delta^{15}N$ values of seston reflect a balance between fractionation during assimilation of NH_4^+ or NO_3^- and degradative processes. The seston ΣPCB and fluorescence were both high in the spring and subsequently declined suggesting that variation in PCB concentrations were associated with primary productivity. The strong seasonal trends in the organic geochemical characteristics of seston and concentrations of PCBs emphasize the complex nature of particle cycling in the bay.

DEDICATION

To my husband, Brent, whose encouragement and patience always keeps me going and to my family who always believes in me.

ACKNOWLEDGEMENTS

I would like to thank Peggy and Nathaniel Ostrom for both financial support of this research and their academic guidance.

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INTRODUCTION

Seston is a dynamic reservoir of organic matter in lakes and oceans that can change dramatically in composition on a seasonal and spatial basis. An understanding of the origin and cycling of seston has important ecosystem implications, as it is one of the pools of organic matter at the base of pelagic food webs and can facilitate the cycling of toxins in the environment. However, detailed studies of changes in the geochemical nature of seston on seasonal and spatial scales are limited, particularly in the Great Lakes where seston has been implicated in the role of contaminant transfers (Baker and Eisenreich, 1989; Baker et al., 1991; Axelman et al., 1997). Consequently, I characterized seasonal variation in the geochemical composition of seston in Grand Traverse Bay and used these data to assist in an interpretation of temporal changes in surface water PCB concentrations.

Seston is defined as the material collected on a filter with a pore size of 0.45 to 1.0 μ m (Riley, 1970; Parsons, 1975) and primarily consists of small particles which can have water column residence times on the order of several hundred years (McCave, 1975). Compositionally, seston can consist of mineral grains, phytoplankton cells and fragments, microzooplankton, amorphous inorganic and organic matter, charcoal fragments, bacteria, small fecal pellets, and fibers. In the Great Lakes, a seasonal progression of particle sources has been recognized with shoreline erosion predominating in winter, followed by biotic production in early spring and fall, and resuspension of bottom sediments prevailing in late fall following water column overturn (Eadie and Robbins, 1987;

Baker and Eisenreich, 1989). Although seston is often assumed to consist primarily of recently produced phytoplankton material, this is likely to be the case only during periods of high primary production and at other times of the year inorganic material or refractory organic matter may predominate. Consequently, the geochemical composition of seston is a complex interaction of changes in sources, in situ production, and microbial decay.

In this study, the geochemical composition of seston was characterized by deployments of a CTD equipped with a fluorometer and transmissometer, determinations of the elemental and isotopic composition of seston, and measurements of the total concentration of PCB congeners (Σ PCB) from April to September, 1997. Depth profiles of water column fluorescence and light transmission provide insight into relative concentrations of chlorophyll a, a labile constituent of phytoplankton (Furuya, 1990), and changes in particle concentrations, respectively. Carbon isotopes in aquatic systems can provide insight into the sources of CO_2 utilized by phytoplankton and changes in levels of primary productivity (Schelske and Hodell, 1991). In addition, stable carbon and nitrogen isotopes have been used to trace organic material in ecosystems (Minigawa and Wada, 1984; Peterson et al., 1985; Ostrom and Fry, 1993), to identify sources of sewage (Van Dover et al., 1992), to estimate trophic positions and to quantify bioaccumulation of contaminants in food web studies (Cabana and Rasmussen, 1994; Kidd et al., 1995; Kucklick et al., 1996). Organic contaminants in Great Lakes fish have been a concern for several decades and recent studies have proposed an efficient incorporation of these compounds in

food webs via an association with organic rich particles (Baker and Eisenreich, 1989; Baker et al., 1991; Swackhamer and Skoglund, 1993; Kucklick and Baker, 1998). In the present study, the biogeochemical transformations of seston were assessed using the water column characteristics of Grand Traverse Bay concurrently with the carbon and nitrogen elemental and isotopic abundance of seston. An understanding of the biogeochemical transformations of seston, will provide insight into the complex transformations that can affect contaminant concentrations on a temporal scale.

METHODS

Water column samples were collected from two stations within the western arm of Grand Traverse Bay, Lake Michigan, between April and September 1997 on the vessels M/V Northwestern and R/V Shenehon. Grand Traverse Bay is located in the northern part of Lake Michigan and covers a surface area of 681.6 km² (Figure 1). This Bay was chosen as a study site because it is an inland extension of Lake Michigan and many of its general characteristics, such as, morphometry, land use, nutrient concentration, and phosphorus limitation are similar to those of Lake Michigan (Auer, 1975). The southern portion of the Bay is divided into an eastern and a western arm, and most of the nutrient loading into Grand Traverse Bay enters through the Boardman River in the southern end of the western arm of the Bay (Auer, 1975). Our two sampling stations were located in the western arm, which has a maximum depth of 122 m. Station GT1 is located 7 km from the southern shore and has a depth of 98 m, and station GT 3 is 12 km from the southern shore with a maximum depth of 112 m (Figure 1). Prior to sampling, the water column at each station was characterized by deploying a SBE-25 conductivity temperature - depth profiler equipped with Sea Tech fluorometer and transmissometer sensors (SeaBird, Electronics Inc.). Water column samples were collected from several depths at each station using 5 L lever action Niskin bottles (General Oceanics), 8 L Go-Flo (General Oceanics), or an 8 L Niskin- X (General Oceanics). Depths were chosen such that samples were obtained above, within, and below the chlorophyll maximum and in close proximity to the

bottom.

For analysis of NH_4^+ and NO_3^- , an aliquot of water from each depth was transferred into acid-washed 1L Nalgene bottles and frozen. Seston samples were obtained by filtering 3 to 6 liters of water through a pre-combusted (500°C, 1 hour) and pre-weighed Whatman GF/F glass fiber filter. Seston samples were frozen prior to isotopic and elemental analysis.

Ammonium concentrations were determined using an Orion ion specific electrode (Garside et al., 1978). Nitrate concentrations were determined by suppressor based anion chromatography (Shipgun and Zolotov, 1988) on a high performance liquid chromatograph (Rainin Instruments) with conductivity detection (LDC Analytical). Separation of anions was achieved on a Dionex lonpac column (#AS4A-SC) with a suppressor using an eluent consisting of 2.4 mM NaHCO₃. The limit of detection and precision for the analysis of NO₃⁻ and NH₄⁺ by these methods is 0.1 μ M (Ostrom et al., in press).

In preparation for analysis, seston samples were dried at 40°C for approximately 12 hours and monofilament fibers and zooplankton were removed from the dry sample. The filters were weighed, acidified (10% HCl) to remove carbonate, and dried again at 40°C. The surface of the filter that contained the seston was placed in a precombusted (500°C, 1 hour) quartz tube with excess precombusted CuO and Cu (approximately 3 g of each). The tubes were evacuated, sealed, and combusted at 850°C. The combustion products were separated cryogenically on a vacuum line and the isotopic composition of the purified carbon dioxide and nitrogen gas was determined on a PRISM

(Micromass) mass spectrometer. Nitrogen and carbon isotope ratios are expressed in per mil notation (%):

$$\delta^{I}E = [(R_{sample}/R_{standard}) - 1] * 1000$$

where, I is the heavy isotope of element E and R is the abundance ratio of the heavy to light isotope. The internationally recognized standards for δ^{15} N and δ^{13} C are atmospheric nitrogen gas and V-Peedee Belemnite, respectively. The precision for this technique is 0.1‰ (Macko et al., 1987).

The concentration of organic carbon in seston samples was estimated using a calibrated baratron capacitance manometer (MKS Instruments) during gas separation. Organic nitrogen concentrations in the seston samples were determined based on a calibration of the ion beam (mass 28) produced from syringe injection of purified N₂ gas within a calibrated volume of the mass spectrometer.

Seasonal variation in the isotopic composition of seston for the entire water column was described with concentration weighted averages as detailed in Ostrom et al., (1997). Chlorophyll fluorescence was also integrated as relative fluorescence units (RFU) per square meter for the entire water column.

For contaminant and lipid analysis, monthly epilimnetic water samples were collected by pumping water directly through pre-combusted (550° C, 24 hrs), 293 mm diameter glass fiber filters (GFFs, Schleicher and Schuell, 0.7 mm) from depth (5 to 35 m) using a submersible pump (March Mfg, model

5CMD) to collect the operationally defined particulate phase. Filter samples typically ranged from 400 to 740 L. Lipid analysis was done on 2 to 4 L of water from the Niskin or Go-Flo bottles. Water was filtered on 47 mm diameter GFF filters and lipids analyzed by the method of Bligh and Dyer (1959).

Suspended solids were extracted and analyzed for PCB congeners using methods similar to those previously published by Ko and Baker (1995) and Kucklick et al. (1996). The samples were extracted with a 50:50 mixture of acetone and hexane for 24 hours. Prior to extraction, a PCB surrogate consisting of 3,5 dichlorobiphenyl, (PCB 14); 2,3,5,6 tetrachlorbiphenyl (PCB 65); and 2,3,4,4', 5,6 hexachlorobiphenyl (PCB 166) were added to each sample. Following extraction, back-extraction using water and hexane removed acetone. The sample was reduced in volume by rotary evaporation and fractionated using Florisil (Norstrom et al., 1988). The purified extract was reduced in volume to 1-2 mL and 2,4,6 trichlorobiphenyl (PCB 30) and 2,2', 3,4,4', 5,6,6' octachlorobiphenyl (PCB 204) were added as internal standards. The samples were further reduced in volume to < 100 μ L under a gentle stream of purified nitrogen prior to analysis. All samples were analyzed for polychlorinated biphenyl congeners by gas chromatography with a ⁶³Ni electron-capture detection (GC-ECD) using a Hewlett-Packard 5890 series II GC equipped with a 0.32 mm x 60 m DB-5 capillary column (J&W Scientific). The carrier gas was H₂ at a flow rate of 35 cm/s; the injector and detector temperatures were 250°C and 320°C, respectively. PCBs were quantified by the method of Mullin (1985), that uses a calibration mixture of Aroclors 1232:1248:1260 in a ratio of 25:18:18. In

the present study, 69 PCB congeners or congener groups were quantified by dividing the chromatogram in half based on retention time and quantifying the first half against PCB 30 and the second half against PCB 204. The Σ PCB for seston was calculated by summing all of the congeners quantified in each sample.

RESULTS

Changes in thermal structure and primary production were clearly evident in temperature and fluorescence profiles throughout the season in Grand Traverse Bay. Generally, the uniform temperature, fluorescence, and transmittance depth profiles in April and May reflected vertical mixing throughout the water column at GT 1 and GT 3 (Figures 2 and 3). The cold and protracted spring of 1997 was indicated by a lack of density stratification at either station and maximum temperatures less than 5°C until early June. After this time, density stratification became more distinct and surface temperatures gradually rose from 4°C to approximately 22°C in August. The water column remained thermally stratified through mid September.

Prior to stratification, April through early June, the majority of the water column was characterized by chlorophyll fluorescence greater than or equal to 0.5 relative fluorescence units (RFU) at both stations (Figures 2 and 3). With the onset of stratification in mid June at GT 1, and in July at GT 3, a maximum in RFU was observed in the mid water column (15 to 40 m) through September (Figures 2 and 3). These mid water column maximums occurred below the thermocline at both stations. Another salient feature of the fluorescence data are distinct peaks that are prevalent in the mid water column at 40 m in July at GT 1 and 20 m in September at both stations (Figures 2 and 3). These peaks are associated with a decrease in light transmittance. Light transmittance reached a minimum near the bottom between June and July at both stations, suggesting the presence of a benthic nepheloid layer (Figures 2 and 3), a

localized region of high total suspended matter that is a common feature of the Great Lakes during stratified periods (Bell et al., 1980; Eadie et al., 1983; Sandilands and Mudroch, 1983). A slight increase in integrated chlorophyll fluorescence in September may indicate a fall bloom at both stations (Figure 4). Integrated water column fluorescence was high between May and June at both stations (between 68.1 and 73.3 RFU/m² at GT1 and between 66.3 and 69.9 RFU/m² at GT3), and suggested that productivity was highest in the early spring (Figure 4).

Concentrations of particulate organic carbon (POC) ranged from 3.7 to 10.0 μ M at GT 1, and 3.0 to 8.7 μ M at GT 3, while concentrations of particulate organic nitrogen (PON) ranged from 0.2 to 1.3 μ M at GT 1, and 0.2 to 1.0 μ M at GT 3 (Figures 2 and 3). Average C/N values for seston were 10.8 \pm 3.0 and 10.2 \pm 3.4 for GT 1 and GT 3, respectively.

Concentrations of POC and PON in April and May at both stations exhibited little variation with depth at either station, consistent with a well-mixed water column, as indicated by uniform fluorescence and transmittance depth profiles (Figures 2 and 3). A peak in POC and PON occurred on June 4 at GT 1 at 20 m that was not observed at GT 3 (Figure 2). Increases in fluorescence coincident with high concentrations of POC and/or PON between 20 and 60 m occurred between mid June and August at GT 1 and GT 3. The depth at which this trend was observed varied among months. From mid June through September, an increase in particle concentration in the lower water column coincident with decreases in light transmittance further suggests the

development of a benthic nepheloid layer.

Dissolved inorganic nitrogen concentrations varied throughout the season at both stations. Concentrations of NO₃⁻ ranged from 12.6 to 18.7 μ M at GT 1 and from 17.4 to 12.8 μ M at GT 3. The concentration of NH₄⁺ ranged from the detection limit at both stations to 2.4 μ M at GT 1 and 1.1 μ M at GT 3 and was always less than the concentrations of NO₃⁻. From April to June at GT 1, and May to June at GT 3, NO₃⁻ concentrations were uniform with depth but decreased with time (Figures 2 and 3). With the exception of April and May, NH₄⁺ concentrations throughout the water column were consistently above 0.5 μ M at either station. The highest NH₄⁺ concentration of the season was seen at GT 1 on June 4 concurrent with peaks in POC and δ^{13} C at a water depth of 20 m (Figure 2).

Carbon isotope values for seston ranged from -23.9 to -30.6‰ at GT 1 and -24.9 to -30.7‰ at GT 3. There was little variation in δ^{13} C values with depth in April and May and values were low at both stations (Figures 2 and 3). Between mid June and August, seston δ^{13} C values were higher at the surface (5 to 10 m) relative to the hypolimnion (between 15 and 60 m) at both stations (Figures 2 and 3). The low δ^{13} C values in the mid water column at this time and on September 16 at GT 1 were associated with peaks in chlorophyll fluorescence. Lower depths (below 60 m) showed an increase in seston δ^{13} C values at GT 1 and GT 3 from mid June through September that was often coincident with a decrease in light transmittance.

The water column concentration weighted average δ^{13} C values for seston

were low in April and May (-29.9‰ in April at GT 1, and -29.7‰ and -28.9‰ in May at GT 1 and GT 3, respectively) (Figure 5). The δ^{13} C value at GT 1 increased by approximately 1.5‰ in early June, and decreased to -29.3‰ in July, while the δ^{13} C concentration weighted average concentrations at GT 3 declined steadily from May to July. After July the concentration weighted δ^{13} C values increased steadily at both stations and reached a maximum in September (-25.3‰ and -27.0‰ at GT1 and GT 3 respectively).

Nitrogen isotope values for seston in Grand Traverse Bay ranged from 2.5 to 8.7‰ at GT 1, and 1.7 to 11.6‰ at GT 3. In April and May, high seston δ^{15} N values (> 5‰) were observed at GT 1 above 20 m. At GT 3 in May, a maximum in the δ^{15} N value of seston of 9.7‰ occurred at 30 m (Figure 3). In June, July, and August, there was a tendency for minimum δ^{15} N values to occur in the mid water column (20 to 60 m) at both stations. The water column concentration weighted average δ^{15} N values for seston at GT 1 and GT 3 exhibited a decline from approximately 6‰ in April to approximately 2‰ in August (Figure 6). From August to mid September, the concentration weighted average for GT 3 remained relatively constant, while it exhibited an increase to 3.3‰ at GT 1.

Seasonal trends in the Σ PCB of surface seston (5 to 10 m) were evident at GT 1. The PCB concentrations ranged from a maximum of 44.2 ng/g dry weight in April to a minimum of 9.3 ng/g dry weight in September (Figure 7). The concentration of PCBs in the seston of the surface waters was highest in the spring, and showed a steady decline throughout the season. This trend was concurrent with a general decline in integrated fluorescence with time.



















‰^{v N∂t} δ bətdgiəW



PCB concentration (ng/g)

DISCUSSION

The biogeochemical cycling of suspended particles in Grand Traverse Bay is characterized by variation in seasonal and depth profiles of fluorescence, concentrations of POC and PON, δ^{13} C, and δ^{15} N and seasonal Σ PCB. Temporal and spatial changes in these geochemical characteristics reflect the complex and dynamic nature of seston. Fluorescence, concentrations of NH₄⁺ and NO₃⁻, and the δ^{13} C and δ^{15} N values of seston characterize temporal and spatial changes in productivity, nutrient uptake, and microbial activity. Temporal trends in these data can be related to variation in seasonal Σ PCB of seston in the water column of the Bay.

Carbon Isotopes

Variation in the δ^{13} C values of seston can be controlled by many factors, including variation in the relative contribution of different types of seston, degree of isotopic fractionation during carbon fixation, variation in phytoplankton species composition, pH, temperature, isotopic composition of dissolved inorganic carbon (DIC), degree of lipid production, and changes in water masses (Wong and Sacket, 1978; Fontugne and Duplessy, 1978; Farquhar et al., 1982; Guy et al., 1986; Rau et al., 1989; Rau et al., 1991; Nakatsuka et al., 1992; Fogel and Cifuentes, 1993). With regard to variation in the composition of seston, the two primary sources of organic matter to lacustrine environments are autochthonous (algal) and allochthonous (terrestrial) production, which may differ in isotopic composition. Therefore, variation in the relative contribution of each of these

reservoirs influences the isotopic composition of seston. Given that the proportion of terrestrial and aquatic inputs may change spatially and seasonally, variation in the δ^{13} C of seston can be expected. Within Lake Michigan and the other Great Lakes more than 90% of the organic matter is of an aquatic origin (Andren and Strand, 1981; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993). Average C/N values for seston in Grand Traverse Bay (10.8±3.0 and 10.2±3.4 for GT 1 and GT 3, respectively) are similar to those found in other Great Lake environments and are indicative of an algal origin (Muller, 1977; Prahl et al., 1980; Meyers et al., 1984). Therefore, terrestrial inputs into Grand Traverse Bay are expected to be quite low.

Among the processes that can affect the δ^{13} C composition of seston, strong evidence suggests that variance in the growth rate of phytoplankton and intracellular and extracellular CO₂ concentrations predominate (Fogel and Cifuentes, 1993;Laws et al., 1995). In the process of photosynthesis, discrimination against ¹³C occurs during diffusion of CO₂ into the phytoplankton cell and, to a greater extent during fixation by the enzyme RuBP carboxylase (O'Leary, 1981). When DIC concentrations are high, the isotope effect associated with RuBP carboxylase is more fully expressed, resulting in larger isotope fractionation between the phytoplankton and DIC (Fogel and Cifuentes, 1993). In aqueous systems, the rate of the enzymatic reaction often exceeds the rate of CO₂ transport into the cell, allowing diffusion to become the rate limiting process (O'Leary, 1981; Raven et al., 1987; Cifuentes et al., 1988). When diffusion of CO₂ into the cell is limiting, the δ^{13} C value for the photosynthetic

tissue is primarily determined by the smaller isotope effect associated with this process (Fogel and Cifuentes, 1993). Some phytoplankton species have concentrating mechanisms that can actively transport bicarbonate, which is enriched in ¹³C relative to dissolved CO₂, into the cell during periods of low DIC concentration (Lucas, 1983; Fogel and Cifuentes, 1993). When the processes of diffusion and active transport of bicarbonate dominate, the result is a heightened degree of ¹³C assimilation and an increase in the δ^{13} C values of phytoplankton (Fogel and Cifuentes, 1993).

Seston collected during April and May in Grand Traverse Bay was characterized by low δ^{13} C values (less than -29.0‰) and showed little variation with depth. Although integrated water column fluorescence suggests that productivity was high at this time relative to later in the summer, the low δ^{13} C values suggest that CO₂ was not limiting (Figures 2 and 3). Diatoms have been observed to predominate in the water column of Lake Michigan in the early spring (Gala and Giesy, 1991) and accumulate large amounts of lipid (Jacobson et al., 1970). Given that the δ^{13} C of lipids is lower than that of the material from which they are derived (Abelson and Hoering, 1961), low δ^{13} C values of seston in the spring may be a consequence of a high lipid content in diatoms at that time.

Variation in δ^{13} C with depth was evident beginning in June prior to stratification (Figures 2 and 3). On June 4 at GT 1, there was an increase in the δ^{13} C of seston from -28.4‰ at the surface to -26.2‰ at 20 m (Figure 3). This trend is concomitant with an increase in the concentration of POC, PON, and NH₄⁺ at the same depth. Integrated water column fluorescence was still

relatively high in June. The high particulate elemental concentrations and fluorescence data suggest that high δ^{13} C values at 20 m may be related to a reduction in isotopic discrimination resulting from decreases in the aqueous CO₂ reservoir during photosynthesis.

From mid June to August at both stations and on September 16 at GT1, minimum δ^{13} C values were present in the mid water column (15 to 60 m), usually coincident with the chlorophyll maximum and high POC or PON concentrations (Figures 2 and 3). This trend could be associated with the accumulation of isotopically depleted lipids or uptake of respiratory CO₂ by phytoplankton. Lipid data, particularly in August at GT 1 and GT 3, indicate increases in lipid concentration coincident with decreases in δ^{13} C values. Lipid concentrations at GT 1 during August increased from 15.4 μ g/L at 5 m to a maximum of 33.5 μ g/L at 35 m concomitant with a decline in δ^{13} C values between the surface and 35 m. We suggest that assimilation of respiratory CO_2 is also likely because the peak of primary production, as indicated by the chlorophyll fluorescence profiles. appears below the thermocline where active respiration occurs. This suggestion is supported by preliminary data indicating that the δ^{13} C values of DIC in the hypolimnion of Grand Traverse Bay are low in July and August (average = $-1.1 \pm 0.3\%$ in July and average = $-2.4 \pm 1.0\%$ in August), and previous observations that respiratory CO_2 is ¹³C depleted (Jacobson et al., 1970; Peterson and Fry, 1989). In addition, there is evidence of intense microbial respiration at the base of the chlorophyll maximum (Ostrom et al., 1997).

In addition to the mid water column minima in the δ^{13} C values of seston,

depth profiles of δ^{13} C are characterized by high values in the water column below 60 m in late summer. Decreases in light transmittance at these depths suggest the presence of a benthic nepheloid layer. The low δ^{13} C values for seston below 60 m could result from isotopic discrimination during microbial degradation. Active bacterial cycling is a common feature of the benthic nepheloid layer (Hicks and Owen, 1991).

An overview of seasonal variation in the δ^{13} C composition of seston is facilitated by an assessment of the concentration weighted average data (Ostrom et al., 1997). These data are also useful in that they serve to emphasize the primary factors that control the carbon isotopic composition of the entire reservoir of seston in the water column. The concentration weighted average δ^{13} C of secton in early spring (April and May) exhibited low values (< -28.5‰) at both stations indicating production without CO₂ limitation (Figure 5). The increase in the concentration weighted average (1.5%) between May 7 and June 4 at GT 1 occurred at a point when POC was high, and CO₂ may have been limiting (Figure 2 and 5). The weighted δ^{13} C values attained a low value in July at both GT 1 and GT 3 (-29.3‰ and -30.7‰ respectively). Peak fluorescence at this time was below the thermocline. Utilization of a large pool of ¹³C depleted respiratory CO₂ in the hypolimnion is the most likely cause of this substantial decrease in the carbon isotope ratios in July. Weighted average δ^{13} C values for seston reached a maximum in September at both stations. Fluorescence profiles indicate the presence of a fall phytoplankton bloom at this time. Thus, decreases in the size of the CO₂ pool may have

resulted in less isotopic discrimination and an increase in δ^{13} C value of seston. Both down water column δ^{13} C values and seasonal weighted δ^{13} C averages suggest that, in Grand Traverse Bay, lipid production and assimilation of respiratory CO₂ are the predominant controls on the carbon isotopic composition of seston in Grand Traverse Bay.

Nitrogen Isotopes

Variation in the δ^{15} N values of seston can be attributed to many factors, including changes in (1) the relative contribution of different nutrient sources, (2) types of particulate matter, (3) the degree of isotopic fractionation during nutrient uptake and/or diagenetic transformation (e.g. ammonification). In Grand Traverse Bay, where autochthonous material predominates the seston, fractionation during nutrient uptake and subsequent fractionation during biogeochemical cycling are the primary controls the δ^{15} N of sector. Variation in the δ^{15} N value of algal derived seston has traditionally been interpreted to be a consequence of the isotope effect associated with nutrient uptake and assimilation (Saino and Hattori, 1980, 1987; Altabet and McCarthy, 1986; Altabet 1988; Nakatsuka et al., 1992; Ostrom et al., 1997). Low δ^{15} N values for seston have been attributed to isotopic fractionation during nutrient uptake (Saino and Hattori, 1980,1987). In this case, inorganic nitrogen that is enriched in ¹⁴N is preferentially utilized when nitrogen is not limiting to primary production (Altabet and Deuser, 1991; Altabet and McCarthy, 1985, Saino and Hattori, 1980, 1987). Under nutrient depleted conditions, the degree of isotopic discrimination

decreases, resulting in an increase in δ^{15} N values for sector. If the isotope effect associated with nutrient assimilation is the major control on δ^{15} N variation of seston, then the δ^{15} N value of seston should be less than or equal that of the inorganic nitrogen source (Ostrom et al., 1997). In many oligotrophic systems, such as Grand Traverse Bay, where NO₃ is abundant it is considered an important source of nitrogen for phytoplankton growth (Dugdale and Goering, 1967; Eppley and Peterson, 1979). In Grand Traverse Bay, δ^{15} N values for NO₃⁻ were characterized by an average of 2.6 \pm 0.9‰ for 33 samples. Although phytoplankton in Lake Michigan are not nitrogen limited, seston in Grand Traverse Bay was enriched in ¹⁵N relative to NO₃ values. Similar ¹⁵N enrichments in seston relative to NO₃ have been found in Lake Michigan, Lake Superior, and Conception Bay, Newfoundland (Ostrom et al., 1997; and Ostrom et al., in press). The observation that the δ^{15} N values of seston are higher than those of NO₃ suggests that phytoplankton may be utilizing ¹⁵N enriched NH₄⁺, or that other processes in addition to the isotope effect associated with assimilation of NO₃ are controlling the δ^{15} N value of seston (Ostrom et al., 1997).

Previous studies suggest that phytoplankton prefer NH_4^+ to NO_3^- (McCarthy, 1980), and in the Pacific Ocean concentrations of NH_4^+ as low as 0.3 μ M were observed to cause inhibition of NO_3^- uptake (Wheeler and Kokkinakis, 1990). In Grand Traverse Bay, NH_4^+ concentrations were typically higher than 0.3 μ M, suggesting that NH_4^+ may be an important source of inorganic nitrogen to phytoplankton despite NO_3^- being the most abundant

nutrient. Preliminary measurements of the isotopic composition of NH₄⁺ in Grand Traverse Bay indicate that NH₄⁺ can be extremely enriched in ¹⁵N (average = $12.3 \pm 3.0\%$, n = 16) and this is consistent with high values for seston, especially in the early spring. Alternatively, high δ^{15} N values for the suspended particulate matter in the spring may be related to isotopic fractionation during biogeochemical cycling of this particulate pool. The long residence time of seston increases the potential for its transformation in the water column (McCave, 1975). Processes other than nutrient assimilation that can cause an increase in the δ^{15} N values of seston include microbial cycling, microzooplankton grazing, peptide bond hydrolysis, and the formation of dissolved organic nitrogen (DON) (Saino and Hattori, 1987; Altabet, 1988; Checkley and Miller, 1989; Silfer et al., 1991,1992; Ostrom and Macko, 1992; Hoch et al., 1996; Feuerstein et al., 1997).

Although the high δ^{15} N values for seston in the spring may indicate utilization of NH₄⁺, decreases of ca. 3 µM in NO₃⁻ concentrations in the upper water column from April through August at both stations (Figures 2 and 3) suggest that phytoplankton may have also been utilizing ¹⁵N depleted NO₃⁻. Relative to earlier in the season, lower δ^{15} N values for seston between 20 and 60 m during June, July and August at GT 1, and in June and August at GT 3 suggest utilization of isotopically light NO₃⁻ or discrimination against ¹⁵N during uptake (Figures 2 and 3). The temporal decline in the δ^{15} N weighted average of seston and decrease in NO₃⁻ concentration with time is indicative of increased utilization of NO₃⁻ as the season progresses.

The vertical water column trends for the nitrogen isotopic composition of seston reflect a balance between discrimination against ¹⁵N during assimilation of NO₃⁻ and NH₄⁺, and ¹⁵N enrichment resulting from the uptake of enriched NH_4^+ , and microbial degradation. Despite large variation in $\delta^{15}N$ depth profiles throughout the season, there are specific cases where subsets of these processes appear to predominate. When δ^{15} N values for secton are high, the uptake of ¹⁵N enriched NH_4^+ appears to be an influential process. For example, high δ^{15} N values (> 5‰) in the surface 20 m of the water column at GT 1 combined with a decrease in NH4⁺ concentrations from April to May are consistent with uptake of NH4⁺ by phytoplankton (Figure 2). A sharp increase from 4.0 to 9.7‰ at 30 m depth in May at GT 3 is concurrent with a decrease in the NH4⁺ concentrations at the same depth and also suggests uptake of ¹⁵N enriched NH₄⁺ (Figure 3). In contrast, the high δ^{15} N value (9.4‰) in the hypolimnion (60 m) on July 2 at GT 3 is indicative of loss of ¹⁴N during degradation. High δ^{15} N values for seston are also observed within the benthic nepheloid layer (Figures 2 and 3). This layer is believed to originate from near shore erosion and resuspension (Eadie et al., 1983). The material comprising the nepheloid layer in these profiles is not likely to be recently produced material since there is no corresponding increase in chlorophyll fluorescence. In addition, it is enriched in ¹³C and ¹⁵N at both stations relative to seston in the upper water column, and this observation is consistent with more heavily degraded material.

Seasonal trends in concentration weighted average δ^{15} N values for seston

are similar at both stations. The most salient feature of these data is that $\delta^{15}N$ weighted averages peak in May, and decrease steadily through August (Figure 6). The high values in the spring are consistent with the utilization of NH4⁺ with an elevated $\delta^{15}N$ or loss of ¹⁴N during degradation, while the decrease with time can be caused by preferential assimilation of ¹⁴N during nutrient uptake or increase in the uptake of ¹⁵N depleted NO₃⁻. Declines in NO₃⁻ concentration support an increased utilization over the season. Both the temporal and spatial trends in this study suggest that $\delta^{15}N$ values for seston in Grand Traverse Bay are controlled by a balance between depletions in ¹⁵N associated with fractionation during uptake of NH4⁺ and NO₃⁻ and depletions caused by degradative processes in the water column.

Contaminants

PCBs have persisted in the Great Lakes for several decades, despite regulations reducing their use and manufacture. These hydrophobic compounds tend to degrade slowly and bioaccumulate (Thomann and Connolly, 1984; Swackhamer and Skoglund, 1993), and can be transported great distances in the atmosphere before they enter surface waters via wet or dry deposition (Eisenreich et al., 1981; Swackhamer and Armstrong, 1986; McVeety and Hites, 1988). Following atmospheric deposition PCBs are known to partition into organic rich particles, thus subsequent cycling of PCBs is closely related to the production, physical transport, and loss of particles within the water column (Baker et al., 1991). Although sedimentation and burial has been cited as a

mechanism of contaminant removal of PCBs (Eadie and Robbins, 1987), only small amounts of these contaminants were found to be incorporated into surficial sediment in Lake Superior (Baker et al., 1991;Jeremiason et al., 1994). This suggests that PCBs are being recycled in the water column (Baker et al., 1985; Jeremiason et al., 1988; Stow et al., 1995) or transported into the food chain via zooplankton grazing (Swackamer and Skoglund, 1993; Stange and Swackhamer, 1994).

Phytoplankton play a significant role in the incorporation of contaminants into the aquatic food web (Swackamer and Skoglund, 1993; Stange and Swackhamer, 1994; Skoglund et al., 1996). Our data show that Σ PCB of surface seston decline throughout the season from a maximum in the spring (44.20 ng/g dry weight) and appear to be correlated with integrated water column fluorescence (R² = 0.71) (Figures 4 and 7). This trend is indicative of high concentrations of labile phytoplankton material in the spring that decreases as the season progresses. If these hydrophobic compounds partition into the lipid fraction or organic carbon of phytoplankton, then the observed trend in Σ PCB may result from a decrease in labile phytoplankton material. Specifically, our data suggests that PCBs preferentially associate with the labile fraction of the phytoplankton reservoir.

In addition to new production, high Σ PCB in the spring may be a result of the resuspension of sediment or the benthic nepheloid layer. Although C/N ratios indicate that seston is comprised mainly of algal material, a small contribution of refractory resuspended material may be significant if it is enriched

in PCBs. Particulate matter from the benthic nepheloid layer has been implicated as an important source of contaminants to the food web (Baker and Eisenreich, 1989; Baker et al., 1985,1991). The benthic nepheloid layer, as seen by decreases in transmittance, developed following stratification in mid June at both stations (Figures 2 and 3). In April, prior to stratification and the formation of the nepheloid layer, Σ PCB in the surface waters (5 to 10 m) at GT 1 were at the highest of the season. Later, when the benthic nepheloid layer begins to form, Σ PCB at the surface decrease. The high concentration of PCBs in the surface waters of GT 1 in the spring may result from mixing of nepheloid material rich in organic contaminants throughout the water column. As the water temperature rises, and stratification sets in, resuspended benthic nepheloid layer material may settle out from the surface waters, resulting in a decrease in the concentrations of PCBs in the surface seston. However, the δ^{13} C values of spring surface seston (-29.7‰ for both April and May,) differ from that of the benthic nepheloid layer (average = $-25.9 \pm 1.7\%$, n = 9 for August to September) and sediment from several locations in the western arm of Grand Traverse Bay (average = $-24.8 \pm 1.1\%$, n = 8), suggesting that resuspension is not the major contributor to the seston. In this case, a large contribution of PCBs from resuspension would necessitate that resuspended material is enriched in PCBs. Quantifying the relative contribution of PCBs from phytoplankton and resuspended material is problematic owing to the difficulty in isolating phytoplankton from other suspended particles.

CONCLUSIONS

Carbon and nitrogen isotopes, coupled with other water column data such as temperature and fluorescence, can be used to provide a better understanding of the dynamics of the cycling and the transformations of suspended particulate matter in a lake system. Biogeochemical analysis of suspended particle dynamics is critical for characterizing the base of the pelagic food web and understanding the cycling of contaminants within food webs. The carbon isotopic composition of seston in Grand Traverse Bay was largely affected by that of the source of CO₂, and the lipid content of the phytoplankton. The nitrogen isotopic composition of seston, however, appeared to reflect a balance between fractionation during uptake of ¹⁵N enriched NH₄⁺ or ¹⁵N depleted NO₃⁻, and other degradative processes that cause δ^{15} N enrichments. High Σ PCB in surface seston appears to be associated with increases in the labile fraction of phytoplankton in the spring.

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