



## A hypothesis for the origin of perylene based on its low abundance in sediments of Green Bay, Wisconsin

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### Abstract

Perylene, a polycyclic aromatic hydrocarbon (PAH) that is common in sediments, is believed to originate principally from anaerobic diagenesis of organic matter, but its precursor material remains enigmatic. We have investigated the formation of perylene in a dated sediment core from Green Bay, WI. Comparisons of sedimentary profiles of perylene, anthropogenic PAHs, land-plant-derived hydrocarbons, and aquatic contributions of organic matter rule out a specific industrial, terrigenous, or aquatic precursor for perylene. Instead, perylene seems to be formed from any kind of organic matter as a consequence of a specific type of microbial activity in sub-bottom sediments. Despite an abundance of organic matter, the amount of perylene is low in Green Bay and in other organic-carbon-rich lake sediments. The abundant availability of organic matter that stimulates microbial activity in Green Bay sediments would seem to favor perylene formation in such sediments. We therefore hypothesize that the microorganisms responsible for perylene formation do not compete successfully with those that flourish in sediments rich in organic matter. Perylene formation consequently does not become significant until deeper in sediments after the more-reactive types of organic matter have been consumed. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous in sediments and soils, yet they are virtu-

ally absent in living organisms (Laflamme and Hites, 1978; Hites et al., 1980). Three processes produce distinctive suites of PAHs: (1) rapid, early diagenesis from reasonably well defined biogenic precursor molecules, (2) catagenetic alterations of biogenic precursor materials, and (3) high-temperature fragmentation and recombination of organic matter. Once formed, PAHs are considered to be robust molecules that resist alteration and degradation in sedimentary settings. The bulk of PAHs in modern settings originates from high-temperature anthropogenic processes (Gschwend and Hites, 1981; Heit et al., 1981; Tan

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and Heit, 1981; Helfrich and Armstrong, 1986; O'Malley et al., 1994; Smirnov et al., 1998), and their concentrations in sediments consequently record the history of fossil fuel combustion. Some originate from precursor substances liberated by other anthropogenic processes, such as logging (e.g., Wakeham et al., 1980). Because the extent and impact of human activities have progressively magnified over time, PAH concentrations are typically greater in younger sediments than in older deposits.

An important exception exists to the generalization that greater PAH concentrations occur in younger sediments. Perylene is a five-ring nuclear PAH that has been found widely in both marine and freshwater sediments, yet it is either absent, or present only in minor concentrations, in typical surface sediments. It is not found in plankton, and it is scarce in most soils (Wakeham et al., 1980). Important amounts of perylene are typically not encountered until deeper in sediments, a pattern that contrasts with those of anthropogenic PAHs.

Some amount of perylene can originate from human activities. It has been detected in municipal incinerator waste products (Davies et al., 1976), has been linked to automobile emissions (Blumer et al., 1977), and has been found sorbed onto aerosols (Lunde and Bjorseth, 1977). However, because of its widespread occurrence and particularly its distinctive sedimentary depth profiles, the major source of perylene appears to be natural in situ formation in subaqueous sediments (e.g., Gschwend et al., 1983). Furthermore, the pattern of increasing concentration with depth of subaqueous burial is circumstantial evidence that perylene formation requires anoxic conditions (Garrigues et al., 1988).

A number of PAH molecules are formed by early diagenesis in sediments, but their biological precursors are usually readily identifiable from structural affinities (e.g., Tan and Heit, 1981; Wakeham et al., 1980). Although a variety of precursor materials for perylene have been suggested, none have been confirmed. Venkatesan (1988) summarizes the inferential evidence that links perylene to aquatic precursor materials in some marine and freshwater sediments and to terrigenous precursors in others. Subsequently, Silliman et al. (1998) could find no relation between the amount of perylene and the availability of organic matter from terrigenous, aquatic, or an-

thropogenic sources in cores of Lake Ontario sediments. Because perylene concentrations correspond only to the concentration of total organic carbon in this setting and not to changes in the type of organic matter, it was hypothesized that the formation of perylene is primarily controlled by in situ microbial processing of non-specific organic matter rather than the availability of a specific precursor material. The nature of the processes that give rise to perylene remain unidentified, and hence the origin of perylene continues to be an organic geochemical enigma.

Most PAH molecules have fairly well known origins and therefore are useful indicators of their sources, delivery routes, and alteration conditions. The origin of perylene, in contrast, is obscure, even though it is found widely in sediments and often is one of the major PAHs. An improved understanding of the biogeochemical significance of this molecule is therefore likely to be important to paleoenvironmental interpretations. This paper describes our investigation of the relations of perylene to other organic matter components in the sediments of a freshwater setting that has experienced a succession of environmental changes. We compare our results to those from other lakes in order to explore how the formation of sedimentary perylene is affected by changes in organic matter delivery and depositional conditions.

## 2. Sampling and analysis

### 2.1. Study area

Green Bay is a partially enclosed, hypereutrophic, shallow basin that constitutes the west arm of Lake Michigan (Fig. 1). Even though Green Bay itself constitutes only a small portion of the surface area (7%) and volume (1.4%) of the Lake Michigan system, its catchment area represents more than 33% of the Lake Michigan drainage basin (Stoermer et al., 1991). The sediments of the bay consequently provide a sensitive record of land-use changes. Green Bay differs from most other parts of the Great Lakes in additional ways that are important to sediment studies. For example, the modern sedimentation rate at our study site in Green Bay (1 cm/year) is equivalent to the elevated sedimentation rates found

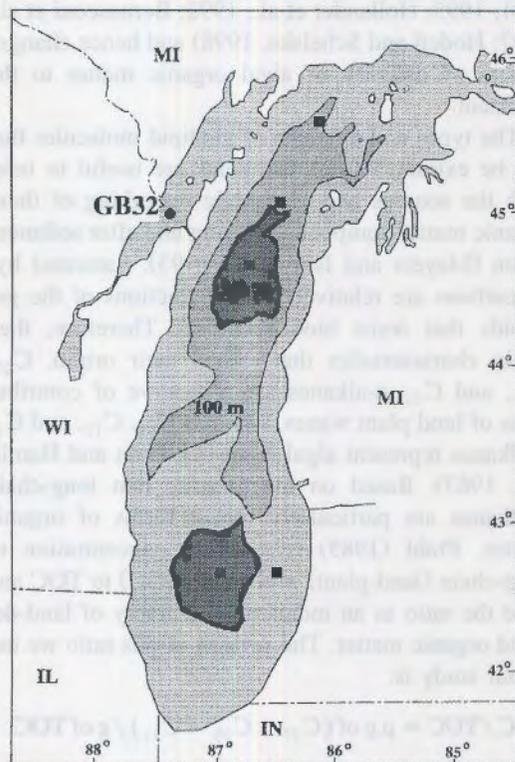


Fig. 1. Location of core site GB32 in Green Bay of Lake Michigan. The locations of the six core sites in Lake Michigan from which Simcik et al. (1996) report perylene data that are discussed in this report are shown as squares.

in eastern Lake Erie and is 3–4 times higher than the more typical Great Lakes rates found in Lake Ontario (e.g., Bourbonniere and Meyers, 1996). The elevated sedimentation rate yields a high-resolution history of the local paleoenvironment. Furthermore, the surface waters of Green Bay have greater phytoplankton productivity, and the sediments are consequently richer in organic matter.

The watershed of Green Bay began to be settled as part of the westward expansion of the U.S. during the early to mid 1800s (Stoermer et al., 1991). Following clear-cutting of forests during the 1880s to open land for agriculture, growth of cities and industry started (Smith et al., 1988). Soon after 1900, farmland runoff increased the nutrient load in Green Bay while the development of paper mills and communities along the lower Fox River contributed discharges of industrial wastes and sewage (Smith et

al., 1988). Increased organic wastes flowing into Green Bay from the Fox River and other tributaries led to eutrophication, which caused oxygen depletion in the southern half of the bay and produced periodic fish kills. Environmental deterioration persisted until passage of the Federal Clean Water Act in 1972. Because Green Bay has a history of large industrial and agricultural impacts, its sediments provide a good record to study changes in delivery of various possible precursors of perylene. In addition, we expected Green Bay sediments to contain plentiful perylene because of their organic matter richness.

## 2.2. Sediment coring and dating

Sediments used in this study were obtained from a 1-m gravity core that was collected in summer 1994 from site GB32 (44.93°N, 87.56°W) in 35 m of water (Fig. 1). This location is in a bathymetric low, where sediments are expected to accumulate at an elevated rate and thereby provide improved temporal resolution. The core was divided into 1-cm sections that were frozen within hours after collection. The sediment sections were freeze-dried and then stored at 4°C until analysis.

The core was dated using the  $^{210}\text{Pb}$  method developed by Robbins and Edgington (1975). Excess  $^{210}\text{Pb}$  amounts in the sediments were applied to a steady-state mixing model in order to calculate a mean sediment mass accumulation rate (MAR) of 0.15 g/cm<sup>2</sup> year. Surface sediments were affected by bioturbation, which indicates the presence of bottom-water oxygen. The  $^{210}\text{Pb}$  specific activity, shown in Fig. 2 with the age–depth profile, fairly consistently increases from the bottom of the core up to 8–9 cm subsurface. From 8 cm to the surface, the specific activity decreases from 13.7 to 9.5 dpm/g. The subsurface activity peak is not likely to result from bioturbation, because such mixing typically homogenizes  $^{210}\text{Pb}$  activity profiles in upper horizons of cores. A more probable explanation for the unusual  $^{210}\text{Pb}$  pattern is that older sediments were displaced from a shallower region of the bay during a stormy period and were then redeposited at our site by sediment focusing. This explanation is supported by field evidence that sediment resuspension occurred widely in Green Bay during the winter prior to our core collection. Because of the unusual  $^{210}\text{Pb}$

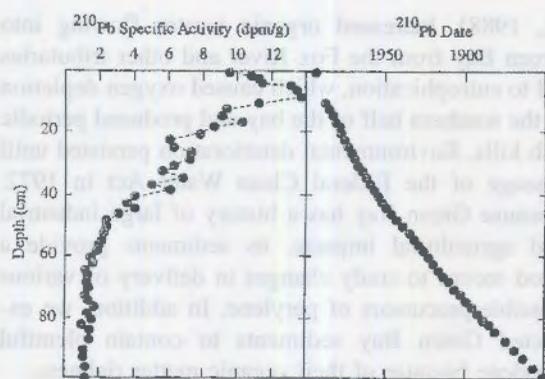


Fig. 2. Specific  $^{210}\text{Pb}$  activity and age–depth profiles for sediment core GB32 from Green Bay. Sediment ages above the  $^{210}\text{Pb}$  activity peak at 8–9 cm are extrapolated from ages of deeper sediments.

distribution, the dates of deposition of sediments above 8 cm are extrapolated from the measured ages of deeper sediments.

### 2.3. Analytical strategy

We have utilized a variety of geochemical measurements to study the relations between perylene and changes in the amounts and types of organic matter in Green Bay sediment. Calcium carbonate contents can help to identify changes in delivery of lake sediment components from their various sources. Total organic carbon (TOC) concentrations represent the summation of organic matter inputs from aquatic production, riverine transport and atmospheric deposition, and TOC MARs record the rates of organic matter delivery, independent from dilution by other sediment components. Organic carbon/total nitrogen (C/N) ratios can be used to distinguish between aquatic and terrigenous sources of organic matter. C/N ratios less than 10 are characteristic of lacustrine algae, whereas vascular land plants have C/N ratios greater than 20 (Meyers, 1994; Meyers and Lallier-Vergès, 1999). Organic  $\delta^{13}\text{C}$  values of Great Lakes algae are the same as in local land plants (Meyers and Lallier-Vergès, 1999) and therefore are not useful in distinguishing between aquatic and terrigenous sources of organic matter in Green Bay sediment. However, these values are sensitive to changes in algal productivity (Schelske and Hodell,

1991, 1995; Hollander et al., 1992; Bernasconi et al., 1997; Hodell and Schelske, 1998) and hence changes in rate of delivery of algal organic matter to the sediment.

The types and amounts of geolipid molecules that can be extracted from sediments are useful to infer both the sources and diagenetic reworking of these organic matter components during and after sedimentation (Meyers and Ishiwatari, 1993). Saturated hydrocarbons are relatively robust fractions of the geolipids that resist biodegradation. Therefore, they retain characteristics that reflect their origin.  $\text{C}_{27}$ ,  $\text{C}_{29}$ , and  $\text{C}_{31}$  *n*-alkanes are indicative of contributions of land plant waxes, whereas  $\text{C}_{15}$ ,  $\text{C}_{17}$ , and  $\text{C}_{19}$  *n*-alkanes represent algal input (Eglinton and Hamilton, 1963). Based on the premise that long-chain *n*-alkanes are particularly robust forms of organic matter, Prahl (1985) related the concentration of long-chain (land-plant) *n*-alkanes (LHC) to TOC and used the ratio as an indicator of delivery of land-derived organic matter. The version of this ratio we use in our study is:

$$\text{LHC/TOC} = \mu\text{g of } (\text{C}_{27} + \text{C}_{29} + \text{C}_{31}) / \text{g of TOC}.$$

We employ two other ratios involving *n*-alkanes to help identify changes in the delivery or preservation of terrigenous and aquatic geolipid components of sedimentary organic matter. The terrigenous/aquatic ratios of *n*-alkane hydrocarbons (HC) that are used in this study to infer the origins of geolipid components are defined as:

Terrigenous/Aquatic Ratio ( $\text{TAR}_{\text{HC}}$ )

$$= (\text{C}_{27} + \text{C}_{29} + \text{C}_{31}) / (\text{C}_{15} + \text{C}_{17} + \text{C}_{19})$$

where  $\text{C}_{27}$ ,  $\text{C}_{29}$ , etc., represent the concentration of the *n*-alkane.

Contributions of land-derived organic matter typically contain higher proportions of *n*-alkanes than do those from aquatic algae, and consequently parameters like the  $\text{TAR}_{\text{HC}}$  may exaggerate the absolute amount of terrigenous organic matter (cf. Cranwell et al., 1987; Goosens et al., 1989; Meyers and Ishiwatari, 1993). This ratio nonetheless is valuable for determining relative changes in contributions of organic matter from land and lake flora.

Because short-chain (algal) *n*-alkanes are sensitive to post-depositional degradation (e.g., Meyers

and Ishiwatari, 1993), we use the ratio of short-chain components (SHC) to TOC to assess the magnitude of microbial reworking of organic matter. This ratio is given as:

$$\text{SHC/TOC} = \mu\text{g of } (C_{15} + C_{17} + C_{19}) / \text{g of TOC.}$$

In addition to the ratios involving *n*-alkane compositions, concentrations of pyrene have been compared to those of perylene to identify different sources of high-temperature anthropogenic PAHs (Venkatesan, 1988). We use the pyrene/perylene ratio in this study to evaluate possible relations between perylene in Green Bay sediments and combustion sources.

#### 2.4. Analyses of organic carbon, total nitrogen, and CaCO<sub>3</sub> concentrations

Amounts of organic carbon and total nitrogen were measured in subsamples of the freeze-dried sediment that had been treated with 3 N HCl to remove carbonate minerals using a Perkin Elmer 240 CHN analyzer. This procedure involves heating the sample at 950°C and analyzing the combustion products by gas chromatography (e.g., Verardo et al., 1990). Known amounts of acetanilide (C<sub>8</sub>H<sub>9</sub>NO) were used to calibrate the instrument and to calculate the quantities of C and N released from the samples. TOC concentrations were then calculated on a whole-sediment basis, adjusting for carbonate loss from the acid pre-treatment. TOC/total N values were calculated on an atomic basis.

Calcium carbonate concentrations were determined by analyzing intact sediment with the same high temperature procedure as for TOC. The difference in carbon contents of the intact and acid-treated samples was taken as the carbonate carbon. These values were converted to CaCO<sub>3</sub> concentrations assuming that all the carbonate was present as calcite.

#### 2.5. Organic carbon isotopic values

Organic <sup>13</sup>C/<sup>12</sup>C ratios were measured on the carbonate-free samples using a VG Isogas Prism mass spectrometer calibrated with the NBS-20 (carbonate) standard. The samples were combusted at 850°C in sealed Vycor tubes in the presence of Cu

and CuO for 2 h. Data are expressed in the conventional δ<sup>13</sup>C notation relative to the PDB standard.

#### 2.6. Geolipid extraction and analysis

The geolipid contents of the sediment were extracted with dichloromethane from freeze-dried samples by immersion in a sonic bath for 1 h. The extracts were concentrated to 3–5 ml by rotary evaporation and then the remaining dichloromethane was replaced by petroleum ether. Following the solvent exchange, extracts were heated to 100°C in the presence of 0.5 N potassium hydroxide in methanol to hydrolyze bound geolipids and then heated again with 14% methanolic boron trifluoride to convert the fatty acids to their methyl ester derivatives (FAMES). Extracts were then separated into three fractions using a 1 × 10 cm column containing 2.5 g of 5% deactivated silica gel and eluting with petroleum ether (*n*-alkanes), 60:40 petroleum ether:toluene (aromatics), and toluene (FAMES).

The contents of the hydrocarbon fractions were analyzed using a Hewlett Packard 5890 Series II gas chromatograph equipped with on-column injection, a 20-m SPB-1 capillary column, and flame ionization detector. Identifications of hydrocarbon components were made by comparison of retention times to those of authentic standards. Quantities of individual components were determined from electronic integration of their respective peak areas and those of known amounts of internal standards (10 μg each 5α-cholestane and 1,2:3,4-dibenzanthracene) that had been added to the sediment samples prior to extraction. Detector response corrections were employed. In addition, the data have been corrected for the small amounts of procedural contaminants determined by blank analyses.

### 3. Results and discussion

#### 3.1. CaCO<sub>3</sub> and organic carbon in Green Bay sediments

Concentrations of CaCO<sub>3</sub> vary narrowly between 12.1% and 21.1% over the 130-year record of accumulation provided by the sediment core (Table 1) and have an average of 16.0 ± 2.5%. The linear

Table 1  
Concentrations of CaCO<sub>3</sub>, total organic carbon (TOC), and PAHs in sediment sections from Green Bay core GB32

Depth (cm)	Date ( <sup>210</sup> Pb)	CaCO <sub>3</sub> (%)	TOC (mg/g)	Per (ng/g)	Phen (ng/g)	Fl (ng/g)	Pyr (ng/g)	BaP (ng/g)	Pyr/Per
2–3	1993	15.2	74.2	68	118	177	159	160	2.3
8–9	1989	16.0	68.7	67	124	188	166	117	2.5
18–19	1980	21.1	56.2	50	143	258	211	162	4.3
26–27	1972	13.8	65.9	47	150	230	183	128	3.9
34–35	1963	12.1	59.6	96	220	360	311	174	3.2
42–43	1953	16.1	51.9	98	227	430	325	205	3.3
50–51	1939	16.0	50.4	159	147	264	211	154	1.3
58–59	1927	16.7	52.9	105	47	71	49	52	0.5
72–73	1904	14.5	46.9	84	17	33	22	16	0.3
82–83	1885	20.4	41.2	75	14	20	12	20	0.2
90–91	1869	15.6	52.3	114	15	18	14	20	0.1
96–97	1857	15.1	46.9	95	bd	bd	bd	bd	–

Dates for the top two depths are extrapolated from <sup>210</sup>Pb-measured ages of deeper sediment. PAH components: Per = Perylene, Phen = Phenanthrene, Fl = Fluoranthene, Pyr = Pyrene, and BaP = Benzo(a)pyrene. bd = Below detection.

sedimentation rate decreases gradually beneath the <sup>210</sup>Pb peak at 8–9 cm (Fig. 2), which reflects progressive decrease in sediment porosity with increase of depth-related compaction. Mass accumulation rates of CaCO<sub>3</sub> change little over the extent of the core (Fig. 3). The overall impression given by these sedimentary parameters is one of uniform deposition, with the probable exception of the storm-disturbed top 8 cm, over the period of time represented by nearly this entire core.

Against this backdrop of uniform sedimentation, changes exist in the accumulation of organic matter.

TOC concentrations decrease from 74.2 mg/g at 2–3 cm to 46.9 mg/g at 96–97 cm (Table 1). The decrease with depth in organic carbon content is relatively smooth, as illustrated by the TOC mass accumulation rates in Fig. 3. Two perturbations in the decrease appear at depths of 18–19 and 82–83 cm, where higher concentrations of CaCO<sub>3</sub> dilute the organic matter. Changes in the type of organic matter that was delivered to the sediments of Green Bay are evident between 59 cm (~1927) and 18 cm (~1980). C/N ratios increase from 9–10 in older and younger sediment to values of 11–12 in this interval

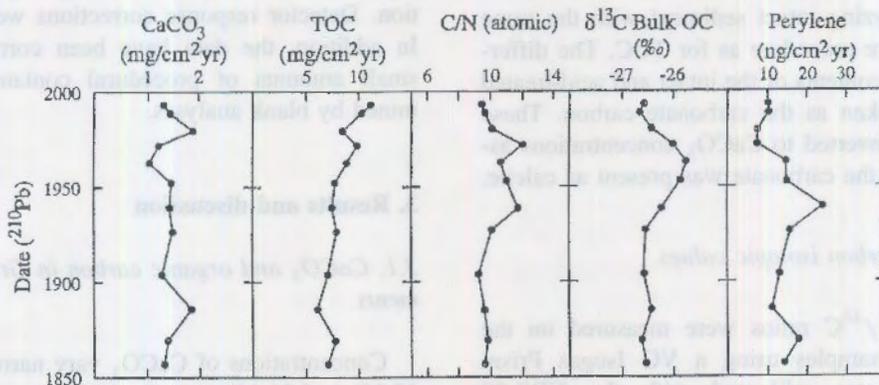


Fig. 3. Mass accumulation rates of CaCO<sub>3</sub>, total organic matter (TOC), and perylene in sediment from Green Bay core GB32. Organic C/total N and organic carbon δ<sup>13</sup>C values reveal that the type of organic matter that was delivered to Green Bay sediments changed between 1927 and 1980.

(Fig. 3). These values indicate that most of the organic matter ( $\sim 90\%$ ) in pre-1927 sediments originates from algal production and that the proportion of land-plant-derived organic matter temporarily increased to  $\sim 20\%$  between 1927 and 1980. At the same time as the excursion in C/N values, organic  $\delta^{13}\text{C}$  values increase from a background of  $-26.6\text{‰}$  to reach  $-25.8\text{‰}$  in sediment deposited  $\sim 1963$  before returning to values around  $-26.6\text{‰}$  in shallower sediment (Fig. 3). The isotopic excursion mimics similar patterns found in sediment from Lakes Erie and Ontario (Schelske and Hodell, 1991, 1995; Hodell and Schelske, 1998; Ostrom et al., 1998) that record maxima of cultural eutrophication between 1965 and 1975. The isotopic shifts record elevated algal productivity and consequent diminished isotopic discrimination in favor of  $^{12}\text{C}$  (e.g., Hollander et al., 1992; Schelske and Hodell, 1995; Bernasconi et al., 1997). The simultaneous excursions in C/N and  $\delta^{13}\text{C}$  values indicate that delivery of organic matter to Green Bay sediment from both land and aquatic sources temporarily increased for several decades and has subsequently returned to earlier levels. Because the increased delivery is recorded neither in TOC concentrations (Table 1) nor in TOC mass accumulation rates (Fig. 3), the rate of microbial degradation of organic matter must have increased as well during this interval.

### 3.2. Perylene in Green Bay sediment

The concentrations of perylene vary with depth in sediments of Green Bay, yet they are uniformly smaller in upper sediments than deeper in the core. Concentrations vary between 47 and 68 ng/g in sediment deposited since 1972 (Table 1). The maximum concentration (159 ng/g) occurs in sediment deposited in 1939, and the next higher concentration (114 ng/g) appears in the 1869 sediment horizon. The change from low-to-higher concentrations with increasing depth in the sediment is similar to patterns reported in other lake sediments, although the change is not as dramatic as is found elsewhere (e.g. Wakeham et al., 1980; Gschwend and Hites, 1981; Tan and Heit, 1981; Silliman et al., 1998). In particular, concentrations in the surface sediments of most lakes are less than those present in Green Bay. However,

as suggested by the curious  $^{210}\text{Pb}$  profile (Fig. 2), the upper  $\sim 10$  cm of sediment in Green Bay may be redeposited older sediment, in which case the higher-than-expected perylene concentrations in the upper sediment could be explained by the upper sediment being older than its estimated age. In addition, it is likely that some proportion of anthropogenic contributions exists in the perylene that is present in the upper sediment horizons.

Perylene concentrations in Green Bay sediments are markedly lower than those in sediments from Sites E30 and G32 in the Rochester Basin of Lake Ontario, where maximum values of 1098 and 834 ng/g were found (Silliman et al., 1998). This contrast is surprising for two reasons. First, the ecosystems in and around Green Bay and Lake Ontario have similar types of aquatic and land flora, so the mixtures of organic matter delivered to sediments in both settings should be similar. Second, sediment TOC concentration at peak perylene concentration in Green Bay is greater (50 mg/g) than at either Lake Ontario location (both 22 mg/g), so it would seem that in situ formation of perylene would produce more of this PAH in the Green Bay setting. Comparison of the peak perylene concentrations to the TOC concentrations magnifies the difference between these lake settings: the perylene/TOC value in Green Bay is 3.3 ng/mg, whereas it is 49.9 ng/mg at Site E30 and 34.5 ng/mg at Site G32. However, in situ formation may be influenced by the rates of delivery and burial as well as by the abundance of precursor material. If this is true, then some of the contrast in perylene concentrations may stem from the fact that sedimentation rates in Green Bay are greater than those in Lake Ontario. Nonetheless, comparison of the MARs, which for perylene is more correctly the appearance rate rather than the accumulation rate, at the three sites diminishes, but does not erase, the contrast in perylene occurrence at these locations: the maximum MAR for perylene is 24 ng/cm<sup>2</sup> year in Green Bay (Fig. 3), but it is 44 ng/cm<sup>2</sup> year for Site E30 and 75 ng/cm<sup>2</sup> year for Site G32 (Silliman et al., 1998).

To seek an explanation of what seem to be unexpectedly low perylene concentrations in the sediments of Green Bay, we will explore possible relations between contributions of organic matter from aquatic and terrigenous sources and the appearance

of perylene. An essential first step in this journey to understand more about this curious PAH is to evaluate the importance of anthropogenic contributions of perylene to the sediments of Green Bay.

### 3.3. Relation of perylene in Green Bay sediments to anthropogenic contributions of PAHs

Perylene is known to have anthropogenic origins. Venkatesan (1988) summarizes a number of examples where sources of perylene to sediments appear to be from street runoff, steel smelting, coke production, incineration of municipal waste, oil refining, and fossil fuel combustion. Simcik et al. (1996) concluded from strong similarities in the depth profiles of perylene and 27 other PAHs in sediment cores from five locations in Lake Michigan (Fig. 1) that these compounds had the same general origin and that airborne transport was probably important in their delivery to the lake. The molecular distributions of PAHs in sediments from Lake Michigan and Green Bay suggest that high-temperature combustion is their principal origin (Helfrich and Armstrong, 1986; Zhang et al., 1993). Consequently, contributions of pyrogenic perylene from human activities should be anticipated in sediments of the Great Lakes.

In contrast to what is found in Lake Michigan, the depth profiles of the concentrations of perylene and four combustion-derived PAHs in the sediments of Green Bay exhibit important differences (Fig. 4). Surface concentrations of perylene are lower than

those of benzo(a)pyrene, pyrene, fluoranthene, and phenanthrene, whereas deeper concentrations of perylene exceed those of the pyrogenic compounds. Concentrations of the four anthropogenic PAHs have maxima in the 1953 sediment horizon, but the perylene peak occurs in older sediments. Simcik et al. (1996) note a close similarity between the history of coal use in Illinois and the concentrations of combustion-derived PAHs in sediments of Lake Michigan and conclude that the principal origin of the pyrogenic PAHs is from the coke and steel production. In addition, Karls and Christensen (1998) conclude that coal combustion has been the dominant source of most of the PAHs in Green Bay since the early 1950s, a finding that agrees with the concentration profiles of the four combustion-derived PAHs in Fig. 4. Given the generally assumed durability of PAHs in sediments, the differences between these profiles and the perylene profile suggest that most of the perylene in the sediments of Green Bay has an origin other than high-temperature combustion.

Further evidence that perylene does not originate largely from industrial sources is provided by pyrene/perylene ratios. These ratios vary between 4.3 and 1.3 in sediments deposited since ~1950 and are below 0.5 in older sediments (Table 1). Even in the upper sediments, these values are substantially lower than the pyrene/perylene ratios of between 9 and 15 that are diagnostic indicators of PAH contributions from combustion emissions (Venkatesan, 1988). The low values therefore substantiate that most of the perylene in the sediments of Green Bay is not anthropogenic.

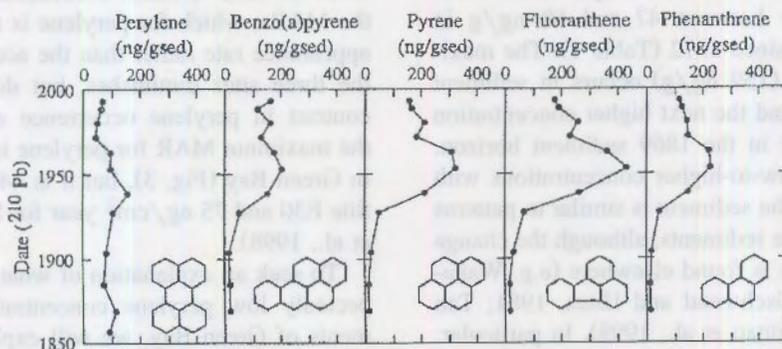


Fig. 4. Concentrations of perylene and four combustion-derived polycyclic aromatic hydrocarbons in Green Bay sediments. Ring structures of the five compounds are shown.

### 3.4. Aquatic sources of perylene

Some investigators have postulated that perylene is formed in sediments principally from aquatic precursor materials. Orr and Grady (1967) linked the formation of perylene in sediments under the upwelling system along the California margin to algal organic matter that was deposited rapidly, thereby retarding its degradation and creating anoxic conditions in near-surface sediments. Similarly, Wakeham et al. (1979) found high concentrations of perylene in sediments under the upwelling system along the southwest Africa margin. The organic matter in these sediments is predominantly derived from algal productivity, hence implicating an aquatic precursor for perylene. The results of other studies have shown a correspondence between diatom-rich marine sediments and elevated perylene concentrations (Hites et al., 1980; Louda and Baker, 1984; Venkatesan and Kaplan, 1987; Venkatesan, 1988). Fluctuations in perylene concentrations with depth in the sediments of Lake Washington, Lake Lucerne, Lake Zurich, and Greifensee have been interpreted as reflecting variations in precursor input and/or depositional conditions (Wakeham et al., 1980). In particular, the concentrations of perylene in Greifensee sediments increase during periods of dominance of lake-derived organic matter and decrease when land-derived organic matter becomes dominant (Wakeham et al., 1980).

The sediments of Green Bay provide a good test of the significance of the availability of aquatic organic matter to the abundance of perylene. The TOC concentrations in Core GB32 are relatively high, averaging 56 mg/g. C/N values between 9 and 12 indicate that most of the organic matter is from algal production. Moreover,  $\delta^{13}\text{C}$  values record a period of elevated aquatic productivity from ~1925 to ~1980 (Fig. 3). If the availability of algal organic matter is important to the appearance of perylene, then the sediments deposited during this interval in particular should contain abundant perylene. However, neither the concentrations (Table 1) nor the MARs (Fig. 3) of perylene are conspicuously elevated in these sediments. On the contrary, both parameters are lower than sediments of equivalent age and lower TOC concentrations from Lake Ontario (Silliman et al., 1998). Therefore, the Green

Bay results reinforce the conclusion reached by Silliman et al. (1998) from their Lake Ontario results that the availability of aquatic organic matter is not important to the appearance of perylene in sediments of the Great Lakes.

### 3.5. Terrigenous sources of perylene

The results of some studies suggest that land-derived organic matter may provide the major precursor material for perylene. Aizenshtat (1973) found that concentrations of perylene in sediments along the California margin increased in the presence of the long-chain *n*-alkanes and more negative organic  $\delta^{13}\text{C}$  values indicative of land-plant organic matter. Wakeham (1977) proposed a terrigenous precursor for perylene in sediments of Lake Washington because of the relatively short transport time to the lake bottom, rapid sedimentation rate, and anoxic conditions present in the bottom sediments. Ishiwatari et al. (1980) reported a correspondence between greater perylene concentrations and increases in C/N values that record larger proportions of terrigenous organic matter in sediments of Lake Haruna. Finally, high concentrations of perylene have been found in peat bogs, adding strong support to the importance of land-plant organic matter to the origin of this enigmatic PAH (Bergmann et al., 1964; Aizenshtat, 1973; Venkatesan, 1988).

Based on the C/N values (Fig. 3), approximately 10% of the organic matter in the sediments of Green Bay originates from land plants. Elevated C/N ratios in sediments deposited between ~1925 and ~1980 (Fig. 3) indicate that the proportion of land-plant organic matter increases to 20% during this period. Perylene MARs are at their lowest in the more recent part of this interval and at their highest near its onset (Fig. 3). The formation of perylene in sediments has been hypothesized to be a first-order reaction (Gschwend et al., 1983), meaning that the amount of perylene at different sediment horizons depends on both the availability of precursor material and time. A consequence of the time-dependence is that a delay should be expected between the deposition of the perylene precursor material and the appearance of this PAH. A pattern of this type is typical of most sediment records, and this time-dependence may be a possible reason why perylene

of Green Bay is not anomalously low; instead, the concentrations reported by Silliman et al. (1998) in Lake Ontario are in reality elevated relative to the organic matter contents in other lakes.

An additional factor that may impact the perylene abundance in sediments of Lake Ontario and Green Bay is the general maturity of their sedimentary organic matter. Sites E30 and G32 in Lake Ontario are located in the deepest basin of the lake where organic matter must settle through a water column that is 4 to 6 times deeper than that which is present at the Green Bay core site. As a result, organic matter deposited in Lake Ontario sediments is older and more oxidized than that which is deposited in sediments of Green Bay. If perylene formation is mediated by microbes that can metabolize recalcitrant forms of organic matter, then higher perylene MARs would be expected in Lake Ontario sediments. That is exactly what is found. Perylene MARs are 44 ng/cm<sup>2</sup> year at Site E30 and 75 ng/cm<sup>2</sup> year at Site G32 in Lake Ontario (Silliman et al., 1998), whereas the MAR is 24 ng/cm<sup>2</sup> year in Green Bay. These results suggest a possible relation between rate of perylene formation and the maturity of sedimentary organic matter.

#### 4. Conclusions

The origin of perylene remains enigmatic. Our investigation of the occurrence of perylene in relation to other organic matter components in the sediments of Green Bay has not identified a specific precursor compound, nor has it found a clear link to either aquatic or terrigenous organic matter. We note, instead, that the appearance of perylene in these sediments appears to be independent of changes in delivery of organic matter and that it is limited to deeper sediment layers. Our observations can be summarized as:

1. Deliveries of both aquatic and land-derived organic matter increased between 1925 and 1980, but increased rates of degradation compensated for the increases and held mass accumulation rates virtually constant.
2. Preferential degradation of *n*-alkanes indicative of algal production biases the sedimentary record

of land-plant/algal hydrocarbon delivery and implies substantial microbial activity in these sediments.

3. The amounts of perylene relative to organic matter are low in these sediments, yet they are also low in sediments of other lakes in which organic matter is abundant.
4. Anthropogenic contributions of perylene to the sediments of Green Bay are low. Natural in situ processes are principally responsible for the occurrence of this PAH in this depositional environment.

Our observations lead us to hypothesize that the formation of perylene in sediments is mediated by microbes that compete poorly with other microbes in subaqueous environments in which metabolizable organic matter is readily available. As a consequence, perylene concentrations do not generally increase until deeper in sediments and after most of the easily metabolized organic matter has been consumed. An exception to this generalization exists in situations where the organic matter that is deposited in surface sediments is mostly recalcitrant material. Perylene-producing microorganisms would encounter less competition, and perylene concentrations would be larger relative to the available organic matter. Our hypothesis suggests that the biogeochemical significance of perylene is not as an indicator of organic matter origins, but instead as an indicator of the degree of organic matter preservation and the nature of consequent microbial activity.

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