



Insights into the origin of perylene from isotopic analyses of sediments from Saanich Inlet, British Columbia

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Abstract

Perylene is an abundant and common polycyclic aromatic hydrocarbon in sedimentary settings, yet its origin remains puzzling. We have investigated the relation of perylene to the amount and type of organic matter in the sediments of Saanich Inlet, a coastal marine anoxic basin. Organic matter is predominantly marine in origin, but the proportions of marine and land-derived components have varied. Perylene concentrations generally increase with sediment depth, relative to TOC, which indicates continued formation of this compound by microbially mediated diagenesis. Perylene $\delta^{13}\text{C}$ values range between -27.7 and -23.6‰ , whereas TOC $\delta^{13}\text{C}$ values vary narrowly from -21.7 to -21.2‰ over the same sediment depth interval. The variation in isotopic difference suggests that perylene originates from more than one precursor material, both aquatic and continental organic matter, different microbial processes, or some combination of these possibilities. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous in sediments and soils, yet are virtually absent in living organisms (Laflamme and Hites, 1978; Hites et al., 1980). The bulk of PAHs in most modern settings originates from high-temperature anthropogenic processes (Wakeham et al., 1980a; Gschwend and Hites, 1981; Heit et al., 1981; Tan and Heit, 1981; Helfrich and Armstrong, 1986; O'Malley et al., 1994; Smirnov et al., 1998), and their concentrations in sediments consequently correspond to the history of fossil fuel combustion (e.g., Simcik et al., 1996). Some PAHs originate from precursor substances liberated by other anthropogenic processes, such as

logging and deforestation (e.g. Wakeham et al., 1980b; Tan and Heit, 1981). Because the extent and impact of human activities have progressively increased over time, PAH concentrations are typically greater in younger sediments than in older deposits.

Perylene presents an important exception to the generalization of greater PAH concentrations in younger sediments. This five-ring nuclear PAH is found widely in marine and freshwater sediments, yet is rare in typical surface sediments. Furthermore, it is not found in plankton, and is scarce in most soils (Wakeham et al., 1980b). Significant amounts of perylene are typically not encountered until deeper in sediments, a pattern that contrasts with that of anthropogenic PAHs. 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) hypothesized that the formation of perylene is primarily

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controlled by in situ microbial processing of non-specific organic matter rather than the availability of a specific precursor material.

Because most PAH molecules have relatively well known origins and are considered to be long-lived, they can be useful biogeochemical indicators of sources, delivery routes, and alteration of organic matter in sediments. The origin of perylene, in contrast, is obscure, even though it is found widely and is one of the major PAHs in some settings. This paper describes our investigation of the relations of perylene to other organic matter components in the organic-carbon-rich sediments of Saanich Inlet, a coastal marine basin.

2. Study area and sampling

2.1. Selection of study area

Saanich Inlet is a fjord that extends southward into Vancouver Island, British Columbia, Canada. It is 26 km long and has a maximum depth of 236 m (German and Elderfield, 1989). Seawater exchange is limited by a sill that lies 70 m below the sea surface, at the northern end of the inlet (Fig. 1). Because water circulation within the inlet is restricted, anoxic conditions develop in its deep waters and especially below 200 m. Virtually permanent anoxia retards faunal bioturbation of sediment and allows accumulation of varved sediments (Gross et al., 1963). Holocene sediments contain well-developed annual laminae that consist of triplets of gray silty mud, olive diatomaceous ooze, and dark olive-gray diatomaceous mud (Shipboard Scientific Party, 1998). The two diatom-rich layers originate from phytoplankton blooms within the inlet during the spring and fall. In contrast, the silty muds originate principally from sources outside Saanich Inlet because of the absence of any significant rivers flowing into it (Gross et al., 1963; Gucluer and Gross, 1964).

Saanich Inlet has long been recognized as a model environment for studies of organic matter diagenesis in anoxic sediments (Gross et al., 1963; Gucluer and Gross, 1964; Kvenvolden et al., 1970; Brown et al., 1972; Nissenbaum et al., 1972). In particular, three features make this setting an attractive study area for organic geochemistry: (1) the sediments are relatively rich in organic carbon, (2) high sedimentation rates enable identification of the effects of early diagenesis, and (3) two distinctive sources of organic matter — marine algae and soil humus — contribute to the sediment contents. For these reasons and because significant amounts of perylene have been reported in Saanich Inlet sediments (Brown et al., 1972), we consider Saanich Inlet a good location to explore factors important to the origin of this curious and common component of organic matter in sediments.

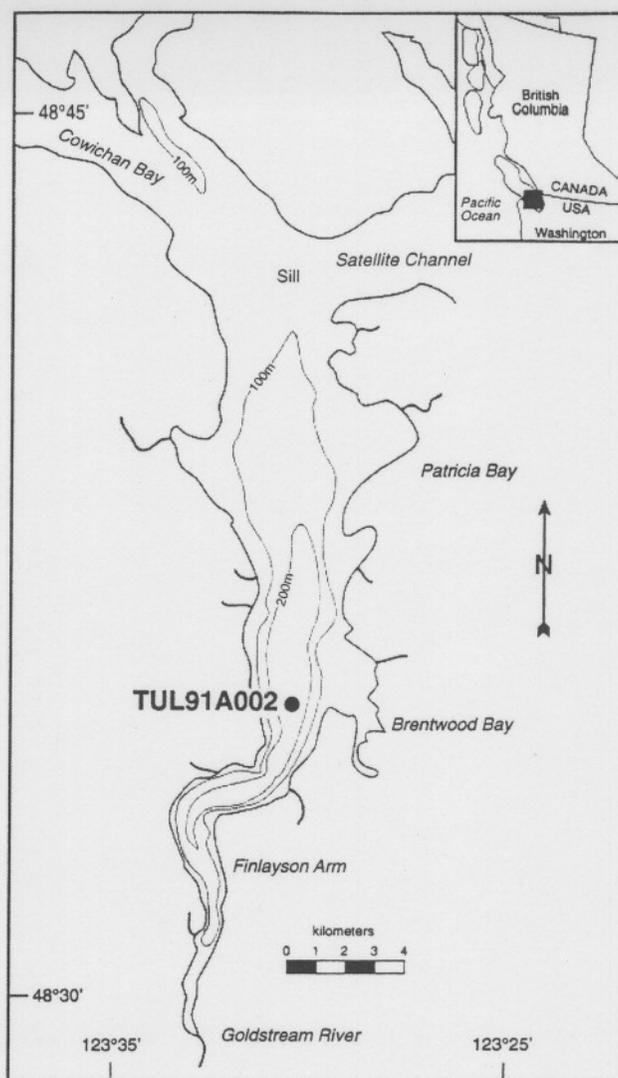


Fig. 1. Location of Site TUL91A002 in Saanich Inlet on Vancouver Island, BC, from which the freeze-core and piston core of sediment for this study were collected. Water depth at this location is approximately 235 m.

2.2. Sediment coring

Sediments for this study were obtained from a freeze-core (~125 cm deep) and a piston core (>7.1 m deep) that were collected during the summer of 1991 from the same location in Saanich Inlet (Site TUL91A002, Fig. 1). The freeze-core was frozen in place at the sampling site in order to preserve fine sediment features (i.e. sediment-water interface, varves, etc.). Freeze-core samples were kept frozen and piston core sediments were stored under refrigeration until analysis started in April 1998.

Reliable dating has not been done on either the freeze-core or the piston core, but sedimentation rates in Saanich Inlet are great. The thickness of Holocene sediments varies from 35 to 70 m in the deep parts of the inlet (Nissenbaum et al., 1972; Shipboard Scientific Party, 1998), which corresponds to average sedimentation rates that

range between 3.5 and 7 m/ky. On this basis, sediment at the base of the piston core was deposited between 1 and 2 ka. Varve-counting gives an approximate age of about 110 years for the base of the freeze-core. None of these age estimates has been verified by accepted means of age determination. Because of the lack of reliable ages for the freeze-core and piston core horizons, meaningful sediment mass accumulation rates could not be calculated.

3. Methods

3.1. Analytical strategy

A variety of analyses were used to determine the amount and type of organic matter present in the cored horizons of Saanich Inlet sediment and to infer the sources that contributed this material. The amounts of perylene were then determined, both as absolute concentrations and relative to sediment organic matter, and the carbon isotopic composition of the perylene was measured to relate this PAH to possible precursor material.

3.2. Organic carbon and nitrogen concentrations

Amounts of organic carbon and residual nitrogen in carbonate free residues were determined using a Carlo Erba EA1108 CHNS-O analyzer. This procedure involves heating the sample at 1020°C and measuring the combustion products by gas chromatography (Verardo et al., 1990). Known amounts of sulfanilamide (C₆H₈N₂O₂S) were used to calibrate the instrument and to calculate the quantities of C and N released from the samples. Total organic carbon (TOC) concentrations were then calculated on a whole-sediment basis, adjusting for carbonate loss from pre-treatment involving sample acidification. Organic carbon/total nitrogen (C/N) ratios were calculated on an atomic basis.

3.3. Bulk organic carbon isotopic values

Isotopic contents of organic matter were determined from analyses carried out in the Stable Isotope Laboratory at The University of Michigan. The ¹³C/¹²C ratios of carbonate-free residual carbon were determined with a Finnigan Delta S mass spectrometer calibrated with the NBS-21 (graphite) standard. Combustion of the carbonate-free organic matter was performed at 800°C in sealed Vycor tubes in the presence of CuO and Cu. Data are corrected for ¹⁷O (Craig, 1957) and expressed in conventional δ¹³C notation relative to the PDB standard.

3.4. Extraction and separation of geolipid fractions

Thawed sediment samples were extracted in dichloromethane using a one-hour sonication procedure. Anhy-

drous sodium sulfate was mixed with the wet samples just before extraction to absorb most of the water. Internal standards were added to the solvent at levels of 10 µg each prior to extraction. The internal standards used were 5α-cholestane, 1,2:3,4-dibenzanthracene, and *n*-heptadecanoic acid for the aliphatic, aromatic, and fatty acid fractions, respectively.

Saponification and esterification were carried out in order to convert all fatty acids present in the extracts to their methyl ester derivatives. Extracts were concentrated to 3–5 ml by roto-evaporation and then transferred to 12 ml graduated conical tubes. Before starting the saponification step, the extracts were solvent-exchanged to petroleum ether (a more suitable solvent for saponification inasmuch as dichloromethane poisons the reaction). The saponification procedure was carried out by adding 1 ml of 0.5 N potassium hydroxide in methanol to each tube and then heating at 100°C for 5 min. Esterification was accomplished by adding 14% boron trifluoride in methanol to each extract and heating again at 100°C for 5 min. The organic phase was then collected from each tube and stored under refrigeration for isolation.

Column chromatography was used to separate compounds of interest from the total extract. Glass columns (29 × 1 cm) were filled with 2.5 g of 5% deactivated silica gel overlying 1 cm of activated copper to trap sulfur. Extracts were concentrated to 1 ml via nitrogen blow down and added to the top of the silica gel. Three fractions of interest were collected for analysis using a modified version of the procedure found in Leenheer et al. (1984). The *n*-alkane fraction was eluted with 15 ml of petroleum ether, aromatic hydrocarbons with 13 ml of a 60:40 mixture of petroleum ether:toluene, and the fatty acid methyl esters with 15 ml of toluene.

3.5. Gas chromatography

A Hewlett-Packard 5890 Series II gas chromatograph was used to analyze for organic compounds. It was equipped with on-column injection, a 20 meter SPB-1 (polydimethylsiloxane) capillary column, and an FID (flame ionization detector). The injection port temperature was set at 280°C, the oven had an initial temperature of 70°C, and the FID was run at 280°C. Good separation of compounds was accomplished by the oven temperature program which raised the initial temperature from 70 to 150°C at a rate of 30°C/min, followed by a rate of 4°C/min to 270°C. The oven was kept at 270°C for 20 min until the end of each run. Qualitative results were obtained by determining retention times for all compounds of interest from composite solutions. Quantitative analysis was determined by measuring compounds with respect to the internal standards that were added to the samples just before extraction. Data have been corrected for any procedural contaminants determined by blank analyses.

3.6. Compound specific isotopic analysis

Stable carbon isotope ratios of perylene were carried out on a Micromass Isochrom GC/IRMS system consisting of a Hewlett-Packard 5890 Series II gas chromatograph coupled to a PRISM isotope-ratio mass spectrometer through a combustion furnace/water trap (Bakel et al., 1994). A 60 m DB-1 (polydimethylsiloxane) column was installed on the gas chromatograph in which the same temperature program previously described was used. The aromatic fractions, containing perylene and the 1,2:3,4-dibenzanthracene internal standard, were solvent exchanged to dichloromethane and divided into three quantitatively equivalent portions. Each portion was concentrated down to 10 μL from which a 1 μL aliquot was injected into the GC/IRMS. The $\delta^{13}\text{C}$ value of 1,2:3,4-dibenzanthracene was consistently measured at -26.1‰ ($\pm 0.3\text{‰}$) from fraction to fraction. Duplicates run on two out of the six perylene samples differed by 0.1 and 0.3 ‰ , respectively. Stable carbon isotope values of perylene were obtained only from the piston core extracts because the frozen core sediment samples were too small to give reliable measurements from their low perylene yields.

4. Results and discussion

Because loss of a variable amount of surficial sediment (0.2–1 m) is common during piston-coring, we have not attempted to splice together the depth profiles of the results from the two cores. Indeed, it is likely that some indeterminate gap in sedimentation record exists between the base of the freeze-core and the top of the piston core even though the data appear to overlap. Progressively deeper sediment horizons are nonetheless assumed to have increasingly greater age, and our discussion of the results of our organic geochemical analyses will be in terms of these age relations.

4.1. Bulk properties of organic matter in Saanich Inlet sediments

The TOC concentration is a proxy for the summed inputs of organic matter from aquatic production, riverine transport, and atmospheric deposition in different sediment horizons, and is also affected by the degree of organic matter preservation. TOC concentrations range between 2.25 and 3.13% sediment dry weight (Table 1) and are high relative to most marine sediments. Concentrations

Table 1
Concentrations of total organic carbon (TOC), organic carbon/total nitrogen (C/N) atomic ratios, organic $\delta^{13}\text{C}$ values (PDB), *n*-alkane (HC) and *n*-alkanoic acid (FA) terrigenous/aquatic ratios (TAR), concentrations of perylene relative to sediment dry weight (ng/g) and TOC (ng/mg), and $\delta^{13}\text{C}$ values (PDB) of perylene in sections from two cores of sediment from Site TUL91A002 in Saanich Inlet (Fig. 1)

Depth (cm)	TOC (%)	C/N (atomic)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TAR (HC)	TAR (FA)	Perylene (ng/g)	Per/TOC (ng/mg)	$\delta^{13}\text{C}_{\text{perylene}}$ (‰)
<i>Freeze-Core</i>								
0–3	3.05	8.6	-21.7	4.52	0.08	0	0	nd ^a
18–21.5	2.55	8.8	-22.5	4.53	0.32	105	4.1	nd
31–34	2.68	8.9	-22.9	5.00	0.61	137	5.1	nd
44–46	2.82	8.9	-22.4	5.47	0.76	233	8.3	nd
57–60	2.39	8.9	-22.6	5.32	0.78	195	8.2	nd
73–74.5	3.13	8.9	-22.1	5.34	0.87	769	24.5	nd
83–84.5	2.90	8.7	-21.9	5.39	0.55	346	12.0	nd
94–95.5	2.69	7.9	-22.1	3.96	0.28	528	19.7	nd
106–108	2.66	7.9	-21.9	4.10	0.33	422	15.8	nd
115–117	2.70	7.8	-22.0	3.14	0.26	483	18.0	nd
124–125	2.62	7.8	-21.9	4.35	0.34	725	27.7	nd
<i>Piston Core</i>								
101–103	2.95	8.6	-21.8	4.31	0.74	111	3.8	nd
254–256	2.30	7.9	-21.7	2.00	0.74	412	17.9	-26.4
308–310	2.47	7.9	-21.0	7.19	0.37	481	19.5	nd
349–351	2.52	7.9	-21.9	2.39	0.35	694	27.6	-27.4, -27.3
477–479	2.46	7.1	-21.1	1.59	0.48	528	21.5	-27.7
556–558	2.25	6.7	-21.3	4.06	0.73	487	21.6	-23.6
641–643	2.33	6.8	-21.1	2.22	0.57	894	38.4	-24.3, -24.6
710–712	2.37	7.4	-21.2	3.23	0.63	596	25.1	-26.1

^a nd, not determined.

are somewhat greater (2.5–3.1%) in the freeze-core that captured the upper 1 m of sediment (Fig. 2) than in the piston corer (2.2–2.5%) that yielded the deeper 2–7 m of sediment (Fig. 3). The pattern of lesser TOC concentrations with greater sediment depth agrees with a similar pattern found in Holocene sediments from nearby Ocean Drilling Program Sites 1033 and 1034 (Shipboard Scientific Party, 1998). Because the presence of annual varves in these sediment sequences precludes an active benthic faunal community and its associated metabolism of organic matter, the change in TOC concentration probably reflects a progressive increase in delivery of organic matter to the sediments towards modern

time. However, the abundance of microbial gases in Holocene sediments of Sites 1033 and 1034 indicates the presence of active microbial communities to sub-bottom depths as great as 70 m (Shipboard Scientific Party, 1998). Microbial metabolism could result in progressively larger amounts of remineralization of organic matter with depth in the sediment and thereby contribute to the pattern of decreasing TOC concentrations.

C/N values of organic material can be used to distinguish between aquatic and continental sources; ratios less than 10 are characteristic of algae, whereas vascular land plants have ratios greater than 20 (Meyers and Ishiwatari, 1993; Meyers, 1994). Organic C/total N

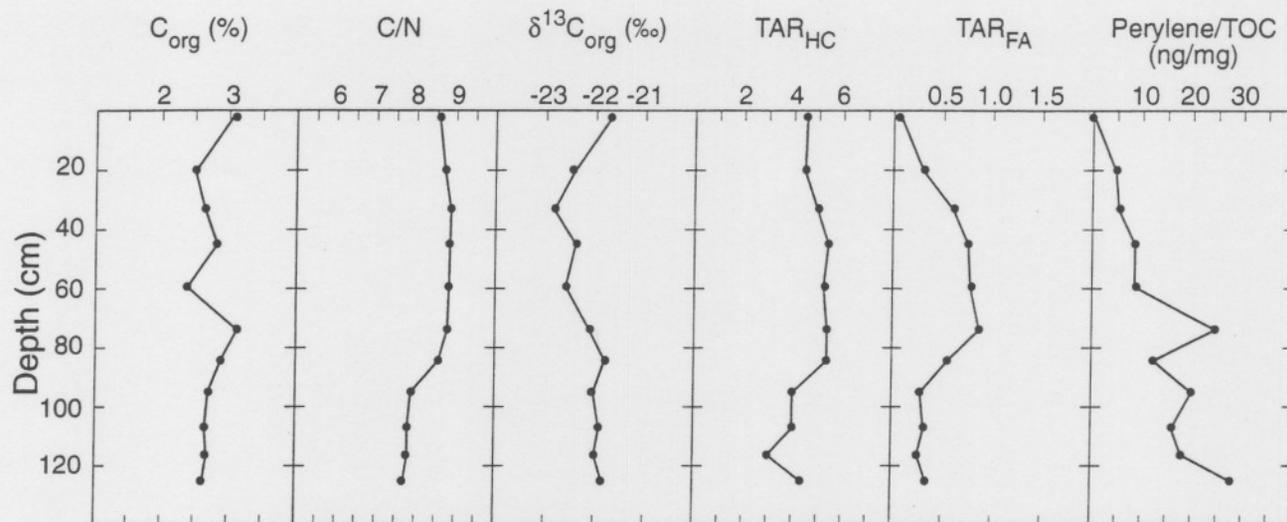


Fig. 2. Concentrations of organic carbon, organic C/total N atomic ratios, organic $\delta^{13}\text{C}$ values, terrigenous/aquatic n -alkane (TAR_{HC}) and n -alkanoic acid ratios (TAR_{FA}), and perylene concentrations relative to total organic carbon in samples from the freeze-core of Saanich Inlet sediment.

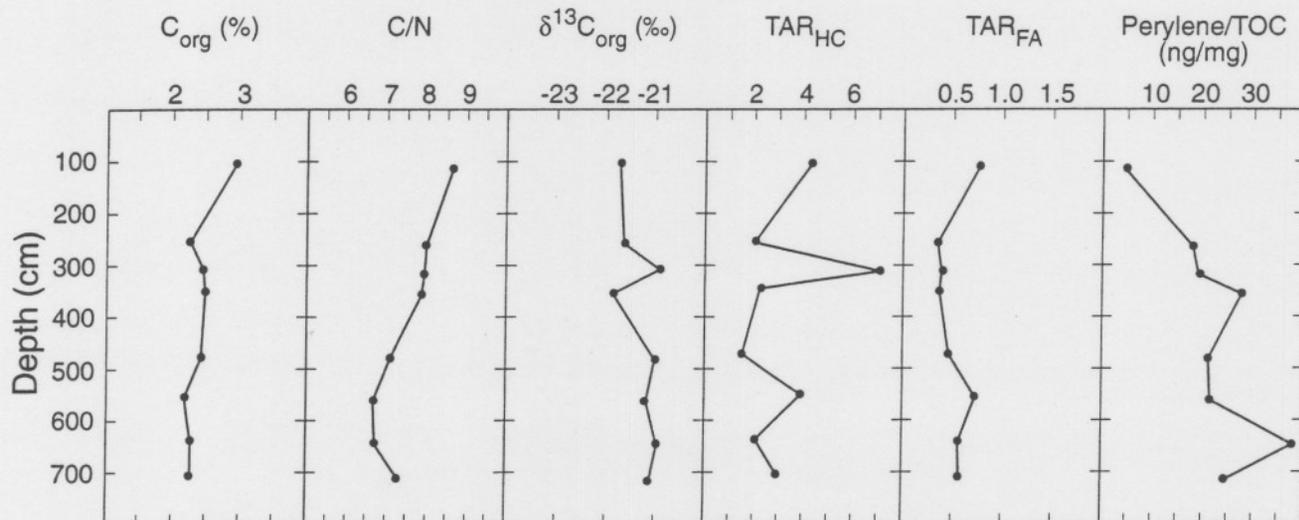


Fig. 3. Concentrations of organic carbon, organic C/total N atomic ratios, organic $\delta^{13}\text{C}$ values, terrigenous/aquatic n -alkane (TAR_{HC}) and n -alkanoic acid ratios (TAR_{FA}), and perylene concentrations relative to total organic carbon in samples from the piston core of Saanich Inlet sediment.

values that range between 6.8 and 8.9 (Table 1) indicate that the majority of the organic matter has originated from marine production.

Distinctive organic $\delta^{13}\text{C}$ values of soil humus and marine algae generally exist. Balesdent et al. (1993) report $\delta^{13}\text{C}_{\text{org}}$ measurements from the soil of a temperate forest that vary between -29.8 and -24.3% . Temperate marine algae typically have $\delta^{13}\text{C}_{\text{org}}$ values between -22 and -20% (Meyers, 1994). The carbon isotope compositions of the land-derived and marine organic matter delivered to Saanich Inlet conform to these generalizations; humus-rich soil from the shore has a $\delta^{13}\text{C}_{\text{org}}$ value of -26.6% , and a mixed plankton sample has a value of -19.2% (Brown et al., 1972). Organic $\delta^{13}\text{C}$ values of sediments from the two cores that we studied range narrowly between -21.1 and -22.9% (Table 1). These results are similar to those of Brown et al. (1972), who report values between -20.1 and -22.5% in four cores from Saanich Inlet. The $\delta^{13}\text{C}_{\text{org}}$ values are consistent with a dominance of marine-derived organic matter in these sediments as indicated by the low C/N values (Table 1). Excursions to slightly smaller $\delta^{13}\text{C}_{\text{org}}$ and slightly higher C/N values in the upper 85 cm of sediment (Fig. 2) suggest that some increase in delivery of land-derived organic matter may have occurred since ca. 1920, which is the approximate varve-count age of this sediment horizon.

4.2. TAR indicators of organic matter source and preservation

Terrigenous/aquatic ratios (TARs) of *n*-alkanes and *n*-alkanoic acids can be useful for distinguishing differences in the contributions of land-derived and marine components to the geolipid contents of different sediment horizons. The short-chain *n*-alkanes (C_{15} , C_{17} , and C_{19}) are representative of algal material while their long-chain counterparts (C_{27} , C_{29} , and C_{31}) originate from land plants (Eglinton and Hamilton, 1963). Long-chain *n*-alkanoic acids (C_{24} , C_{26} , and C_{28}) are characteristic of land plants, pollen, and flowers (Rieley et al., 1991) whereas the short-chain versions (C_{12} , C_{14} , and C_{16}) are more abundant in algae (Cranwell et al., 1987). The TARs for both hydrocarbons (HC) and fatty acids (FA) were calculated using the expressions:

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

$$\text{TAR}_{\text{FA}} = (\text{C}_{24} + \text{C}_{26} + \text{C}_{28}) / (\text{C}_{12} + \text{C}_{14} + \text{C}_{16})$$

in which C_{27} , C_{29} , etc., represent the concentration of each component in the sediment.

The *n*-alkane TARs range between 1.59 in the 477–479 cm sediment horizon and 7.19 in the 308–310 cm horizon (Table 1) and indicate that land-derived components dominate the hydrocarbon contents of Saanich

Inlet sediments. In contrast, *n*-alkanoic acid TARs are consistently below one and indicate that the fatty acid fraction of the sediments is dominated by algal or microbial components. Part of the disagreement between the source indications of the *n*-alkane and *n*-alkanoic TARs is explained by the observation that land plants typically contain higher proportions of *n*-alkanes than do algae (e.g. Cranwell et al., 1987; Goosens et al., 1989). The relative richness in waxy hydrocarbons in land-derived organic matter also helps to explain how the organic matter that C/N and $\delta^{13}\text{C}$ values indicate to be predominantly marine in origin also has relatively high *n*-alkane TAR values; the proportion of land-derived organic matter is over-represented by these values in the sediments of Saanich Inlet. Another factor that is likely to contribute to the TAR disparity is a difference in the degree of preservation of the hydrocarbon and fatty acid components of the sediments. Meyers and Eadie (1993) estimate that fatty acid degradation during settling of organic particles in Lake Michigan. Comparison of both *n*-alkane and *n*-alkanoic distributions in the sediments of four Japanese lakes has indicated that microbial utilization of the original alkanolic acids and their replacement by microbial lipids occurs (Kawamura and Ishiwatari, 1985). Similar facile microbial alteration of the original biomarker compositions of a coastal marine sediment has been documented by Canuel and Martens (1993).

The TAR values nonetheless indicate that a change in the nature of the organic matter that has been deposited in the sediments of Saanich Inlet has occurred since ca. 1920. Both the TAR_{HC} and the TAR_{FA} values increase slightly between 85 and 33 cm (Fig. 2), which is the interval in which C/N and $\delta^{13}\text{C}$ values indicate some increase in delivery of land-derived organic matter. The higher TAR values agree with the greater terrigenous contribution evidenced by the bulk parameters. The increased delivery of organic matter from land, which is not large ($\sim 10\%$), probably records settlement and forest harvesting around Saanich Inlet. Moreover, the relatively high TAR_{HC} values are evidence that delivery of land-derived lipid components to the sediments of Saanich Inlet occurs. These components or other land-derived components associated with them may contribute to the formation of perylene.

4.3. Perylene in sediments of Saanich Inlet

Perylene is absent from surficial sediments of Saanich Inlet, and its concentration generally increases with depth to reach values of 600–900 ng/g in the two cores that we studied (Table 1). The increase continues deeper into the sediment; Brown et al. (1972) report concentrations of 1700 ng/g at 17.2 m and 2400 ng/g at 34.7 m. Perylene is the sole detectable PAH in Saanich Inlet

sediments, whereas most modern sediments contain a wide array of pyrogenic and diagenetic PAHs (e.g. Laflamme and Hites, 1978; Prahl and Carpenter, 1979; Wakeham et al., 1980a,b; Gschwend and Hites, 1981; Heit et al., 1981; Tan and Heit, 1981; Gschwend et al., 1983; Helfrich and Armstrong, 1986; O'Malley et al., 1994; Lipiatou et al., 1996; Smirnov et al., 1998; Silliman et al., 2000). The origin of most of this variety of PAHs is attributed to a combination of industrial combustion (Hites et al., 1977; Gschwend and Hites, 1981; Heit et al., 1981; Simcik et al., 1996), combustion of land plant organic matter (Lipiatou et al., 1996), in situ formation from land-plant precursors (Wakeham et al., 1980b; Tan and Heit, 1981), and wash-in of soil organic matter (Prahl and Carpenter, 1979). The PAH contents of most sedimentary settings diminishes with depth and essentially disappears in sediment horizons deposited prior to a century ago. This pattern is commonly interpreted to record the history of contributions of PAHs from human activities, inasmuch as the compounds are generally considered to be robust and to resist degradation after deposition in sediments (e.g. Hites et al., 1977; Gschwend and Hites, 1981; Heit et al., 1981). The absence of the usual variety of PAHs throughout the sediment record in Saanich Inlet indicates that this setting has not received the burden of anthropogenic contaminants that typify most locations.

The region surrounding Saanich Inlet is relatively unpolluted. The main source of pollution around Vancouver Island and along the coast of mainland British Columbia has been municipal sewage (Nix et al., 1994). The cities of Vancouver and Victoria have reportedly dumped so much sewage in the past that the coastal waters of the state of Washington have been adversely affected (Davey, 1995). However, industrial (i.e. pulp and paper mills) and agricultural impacts seem to have been relatively minor. An oil spill from a tanker that occurred in 1988 polluted shorelines along the coasts of Vancouver Island and the mainland of British Columbia (Obee, 1989). The hydrographic isolation of Saanich Inlet evidently minimized introduction of oil from this spill into the inlet and its sediments, and other sources of anthropogenic contaminants have been minor. Moreover, the location of Saanich Inlet at the western extreme of North America minimizes delivery of the airborne contaminants, including pyrogenic PAHs, that are common to most continental sites.

Because perylene is the only PAH present in Saanich Inlet sediments, its origin is likely to be from local, natural sources. Its absence in the topmost sediment layer indicates that erosion and delivery of preformed perylene from nearby land areas, as suggested to explain the abundance of this PAH in sediment trap material in Dabob Bay, Washington (Prahl and Carpenter, 1979), cannot be occurring. Instead, perylene is evidently being formed after the sedimentation of organic matter in

Saanich Inlet. The lack of accurate sediment ages precludes calculation of perylene mass accumulation rates, or more correctly mass appearance rates, to evaluate the depth-dependence of the rate of perylene formation in these sediments. However, the amount of perylene that is formed relative to the amount of organic matter can be evaluated using the ratio of perylene and TOC concentrations. This ratio is less than 10 ng/mg in sediment shallower than 40 cm, rises to 10–20 ng/mg between 40 and 125 cm depth (Fig. 2), and is 20–40 ng/mg between 300 and 710 cm depth (Fig. 3). The ratios for the deeper perylene concentrations reported by Brown et al. (1972) are 60 ng/mg at 17.2 m and 95 ng/mg at 34.7 m. Either perylene formation continues deep in these sediments or the amount of the still-unidentified but ubiquitous precursor material for perylene has been a larger proportion of the sedimentary organic matter earlier in the Holocene.

4.3.1. Perylene $\delta^{13}\text{C}$ values

The formation of aromatic compounds does not appear to be accompanied by large systematic shifts from the carbon isotopic compositions of precursor materials (Simoneit et al., 1993; Freeman et al., 1994; O'Malley et al., 1994; Schoell et al., 1994). Compound-specific isotope analyses (CSIA) are therefore potentially useful to search for product-precursor relationships, and we employed these analyses to explore the origin of perylene in the sediments of Saanich Inlet. Our CSIA results show that (1) perylene $\delta^{13}\text{C}$ values are consistently less than those of TOC (Fig. 4) and (2) the offset between perylene and TOC $\delta^{13}\text{C}$ values varies from 2.3 to 6.6‰ (Table 1). Because the $\delta^{13}\text{C}$ values of the extractable hydrocarbons and fatty acids from plankton, sediment, and soil at Saanich Inlet are consistently less than those of bulk organic matter (Brown et al., 1972), perylene may originate from a component

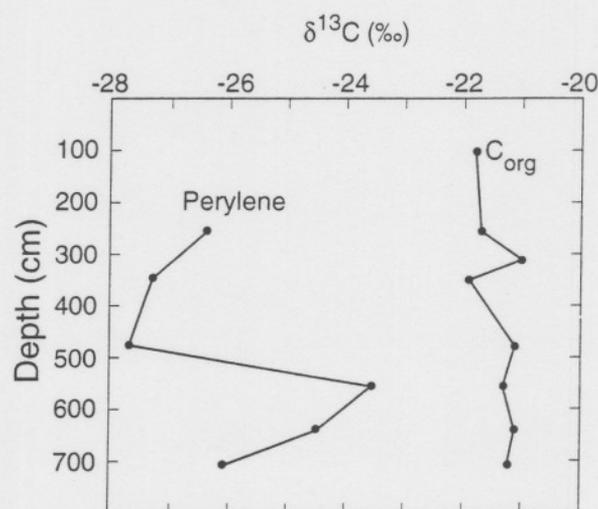


Fig. 4. $\delta^{13}\text{C}$ values (PDB) of perylene and bulk organic carbon in sediment from the piston core from Saanich Inlet.

of the lipid fraction of sediment organic matter. As indicated by its C/N and $\delta^{13}\text{C}$ values (Table 1), this organic matter is principally derived from marine production.

However, results of CSIA analyses of other investigators complicate simplistic product-precursor relations for PAHs. Freeman et al. (1994) conclude that aromatized molecules are generally depleted in ^{13}C by about 1‰ relative to their presumed precursors, yet they find that some compounds are enriched compared to their parent molecules. Similarly, Schoell et al. (1994) report that some types of PAH are enriched whereas others are depleted by 1–2‰ relative to total organic matter. Whether the shift is positive or negative, both studies conclude that the isotopic difference between the product and its precursor is usually small because most of the carbon atoms are preserved during the molecular transformation. In light of these studies, the variation in the extent of the isotopic depletion with respect to TOC $\delta^{13}\text{C}$ values that we find in the Saanich Inlet sediments is perplexing. Even though the excursions in perylene $\delta^{13}\text{C}$ values in Fig. 4 are not random, they cannot be explained in terms of related fluctuations in any of the organic geochemical parameters shown in Fig. 3. A straightforward product-precursor isotopic relation does not appear to exist in these results.

The variable offset between perylene and TOC $\delta^{13}\text{C}$ values that exists in the sediments of Saanich Inlet (Fig. 4) suggests that perylene can originate from different precursors at different times in one setting. This possibility is reminiscent of the results of Radke et al. (1998), who found that the isotopic values of alkylphenanthrenes from continental sequences are larger (–24.3 to –26.0‰) than those from marine sequences (–28.8 to –30.5‰). Assuming that the isotopic differences between products and precursors are small, these findings similarly suggest that a given PAH can be formed from different precursors in different settings.

Our CSIA results suggest three possible scenarios for perylene formation: (1) perylene is formed from a single compound that has variable carbon isotopic composition and can originate from both aquatic and continental sources, (2) perylene is formed from more than one precursor, each one having a different $\delta^{13}\text{C}$ value, and (3) perylene is formed by microbial transformations that variably modify the isotopic compositions of the parent material, depending on how many carbon atoms are removed or added during the transformation. Furthermore, it is quite conceivable that several of these scenarios could occur in sequence and possibly even simultaneously as depositional conditions allowed. The integrated results of our study do not point to a specific type of organic matter that is the prerequisite for the origin of perylene and instead suggest that diagenetic processes are the major determinants in the formation of this PAH.

5. Summary

The absence of anthropogenic PAHs in the sediments of Saanich Inlet indicates that perylene is formed by *in situ* diagenesis in this depositional setting. Perylene abundance does not relate to C/N ratios, organic carbon concentrations, $\delta^{13}\text{C}$ values of bulk organic carbon, or terrigenous/aquatic ratios of *n*-alkanes and *n*-alkanoic acids. Therefore, no relation between the appearance of perylene and the amount or type of organic matter is evident. Perylene/TOC ratios generally increase with sediment depth, indicating that perylene formation in this marine setting is continuous over time.

Perylene $\delta^{13}\text{C}$ values vary from –27.7 to –23.6‰ and are less than the bulk organic carbon $\delta^{13}\text{C}$ values that remain between –21.7 and –21.1‰ in the same sediment interval. The variable isotopic composition of perylene is unlikely to be caused by diagenesis alone, but it could result if perylene were derived from multiple components of sedimentary organic matter. It is probable that perylene originates from microbial aromatization of constituents from both aquatic and terrigenous organic matter in the sediments of Saanich Inlet. These results point to diagenetic conditions as the main control on perylene formation, rather than a specific source of organic matter. Consequently, the particular route of perylene formation may differ for different sedimentary settings. In light of these findings, it is not surprising that previous studies have linked perylene to both terrigenous and aquatic sources of organic matter.

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