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Marine Pollution Bulletin, Vol. 34, No. 9, pp. 739-744, 1997
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0025-326X/97 \$17.00 + 0.00
PII: S0025-326X(97)00042-8

The Distribution of Methyltin Species in Different Seas

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In recent decades, the worldwide production and use of organotin compounds as heat and light stabilizers, biocides, fungicides and antifoulants has increased significantly (UNEP, 1989). The known toxic potential of organotins together with the development of sensitive and precise analytical techniques for the quantitative speciation of organotin compounds at trace levels in environmental samples (Braman and Tompkins, 1979; Hodge *et al.*, 1979) has caused increasing concern about the distribution, fate and impact of methylated tins produced by biological processes, and of butyltins of anthropogenic origin. Such concern has generated increased study of biotic/abiotic methylation reactions, of degradation rates and of the ultimate products of man-made butyltins and phenyltin compounds under natural and simulated environmental conditions (UNEP, 1989; Oceans '87, 1987). However, only limited data for methyltin species in water, sediment and organisms are available in the literature, due to the low levels of methyltins in the aquatic environment.

It has been shown that the various oxidation states (0, II, IV) of tin and, in particular, individual methyltin compounds can be methylated by both abiotic and biotic pathways to yield a variety of methyltin compounds, depending on the redox potential of the studied environment (Ridley *et al.*, 1977; Guard *et al.*, 1981; Hallas *et al.*, 1982; Craig and Rapsomanikis, 1985; Rapsomanikis and Weber, 1985; Donard and Weber, 1988).

In 1988, UNEP initiated a monitoring study to determine the hot spots and the levels of butyltin compounds in the Mediterranean Sea, data from which

have been published elsewhere (Kubilay *et al.*, 1996). This study extends the research to the Marmara and Black Seas. The present paper discusses methyltin distributions in the physically and biochemically different Mediterranean, Marmara and Black Seas, and provides a brief evaluation of butyltin results from the same locations.

Water samples were collected from the locations shown in Fig. 1 and were acidified and kept cool until their analysis. Methyltin concentrations were determined by the hydride derivatization-AA-technique, after the pretreatment of the samples (Tuğrul *et al.*, 1983; Yemenicioğlu *et al.*, 1984).

Alkyltin concentrations of the waters sampled were measured without filtering the samples. Therefore, the data reported represent the total concentrations of hydride-reducible inorganic and organic tin compounds in the subsurface waters of the sites studied. The inorganic tin concentrations in the text represent the sum of Sn(II) and Sn(IV), since the method used is not capable of simultaneous speciation of Sn(II) and Sn(IV) in water (Brinckman *et al.*, 1981; Tuğrul *et al.*, 1983).

The Marmara Sea is connected to the Black Sea and the Aegean Sea by two narrow straits, the Bosphorus Strait to the north and the Dardanelles Strait to the south (Fig. 1). Thus, this sea has a permanently stratified water body with the less saline water of Black Sea origin in the upper layer (0-20 m) and the salty water of Mediterranean Sea origin in the lower layer (Beşiktepe *et al.*, 1994). As can be seen from the typical salinity and temperature profiles displayed in Fig. 2, the biochemical properties of this water body are dominated by the inflowing waters of the Aegean and Black Seas and their vertical mixing at the halocline. The depth profiles of organic carbon, nutrients and chlorophyll-a displayed in Fig. 2 demonstrate that algal production is always limited to the upper 20-30 m. Because of the presence of a permanent halocline at 20-25 m, the subhalocline waters have oxygen concentrations as little as 1-2 mg l⁻¹ throughout the year.

Figures 2 and 3 show that in July 1988 and February 1989 the concentrations of methyltin compounds in the Marmara Sea were generally significant throughout the upper 150 m of water, mostly peaking at 50-150 m. In February 1989, the trimethyltin (TMT) species was ubiquitous and constituted the predominant form of

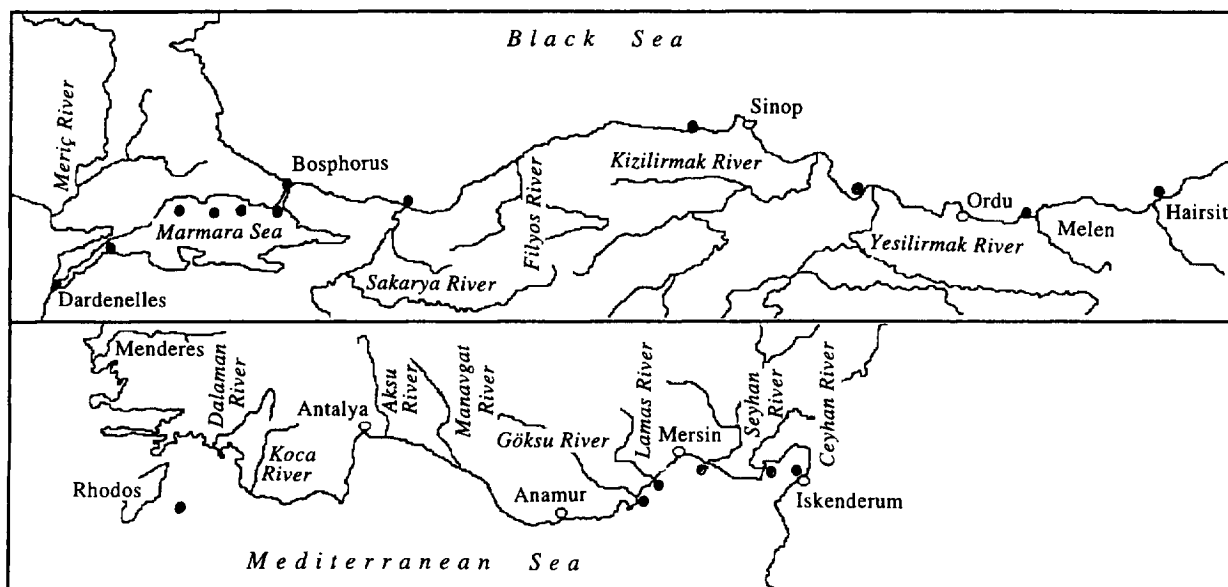


Fig. 1 Sampling locations.

methyltins in depths to 100 m (Fig. 2). This finding agrees with the methyltin results obtained in the coastal waters of the Black Sea and from the Rhodes Gyre in the Mediterranean Sea (Table 1). In July 1988, the salty waters of the Dardanelles Strait contained only monomethyltin (MMT) ranging in concentration from $10\text{--}20\text{ ng l}^{-1}$ while in the water column of the Bosphorus Strait, trimethyltin (TMT) predominated (Fig. 3), implying different occurrences and transformation pathways of methyltin species in these water masses.

The monobutyltin (MBT) concentrations both in the surface and deep waters of the Marmara Sea and in the two Straits were generally at trace levels. The patchy existence of methyltin species at depths of 30–150 m, which coincides with the presence of oxygen-deficient water masses, implies that the monomethyltin (MMT) and some fraction of the butyltin compounds observed at these depths originate from the dissolution and decomposition of sinking detritus, which carries butyltin and methyltin compounds from the productive surface layers to the sub-halocline waters.

In the water column of the Marmara Sea, no correlation has been observed between the vertical distributions of alkyltin concentrations and the chemical parameters measured simultaneously (fluorescing material; dissolved organic carbon; total mercury; and nutrients). Nevertheless, it is suggested that the conversion of methyltin to TMT may have proceeded at depths of 50–150 m where the majority of fast-sinking organic detritus is oxidized, or is dissolved by bacteria. Such bacteria are known to be capable of methylating inorganic tin in the ambient waters and to be associated with particulate matter. Moreover, measurable dissolved oxygen gradients observed in the subhalocline waters (Fig. 2) indicate the existence of very thin layers of redox gradient in the intermediate

waters of the Marmara Sea in which Sn(IV) could be reduced to Sn(II), this being the first step of abiotic/biotic methylation (Ridley *et al.*, 1977; Rapsomanikis and Weber, 1985; Donard and Weber, 1988). Furthermore, the existence of oxygen-depleted microzones associated with the surfaces of organic or inorganic aggregates has been shown by Paerl and Carlton (1988). This environment may be adequate for the production of both Sn(II) and methyltin species.

The eastern Mediterranean Sea (particularly its Levantine basin in the north-east) is known to be one of the most oligotrophic seas in the world due to the limited freshwater inflow, low precipitation and high evaporation rate. Only the surface waters of the Rhodes Gyre (formed permanently between the islands of Cyprus and Rhodes) are relatively productive, due to the continuous transport of nutrients to the euphotic zone by means of cyclonic circulation (Özsoy *et al.*, 1989; Salihoğlu *et al.*, 1990). The Black Sea receives significant amounts of freshwater from both rivers and precipitation. Thus, the wide coastal shelf regions are very productive when compared to the Mediterranean Sea and other oceans (Sorokin, 1983).

Table 1 shows the concentrations of methyltin and butyltin species measured in the subsurface waters of the Mediterranean, Marmara and Black Seas at the locations displayed in Fig. 1. As may be seen from Table 1, trimethyltin (TMT) predominates in the subsurface waters of the Black Sea, in the Rhodes Gyre and in the butyltin-containing waters of the Göksu River Estuary. Apart from the Marmara Sea the highest TMT concentration (267 ng l^{-1}) was measured in the waters of the Rhodes Gyre. In September 1988, TMT levels were observed to be as much as 80 ng l^{-1} in the brackish surface waters of the Black Sea and TMT was only detectable methyltin species in January, 1989. The

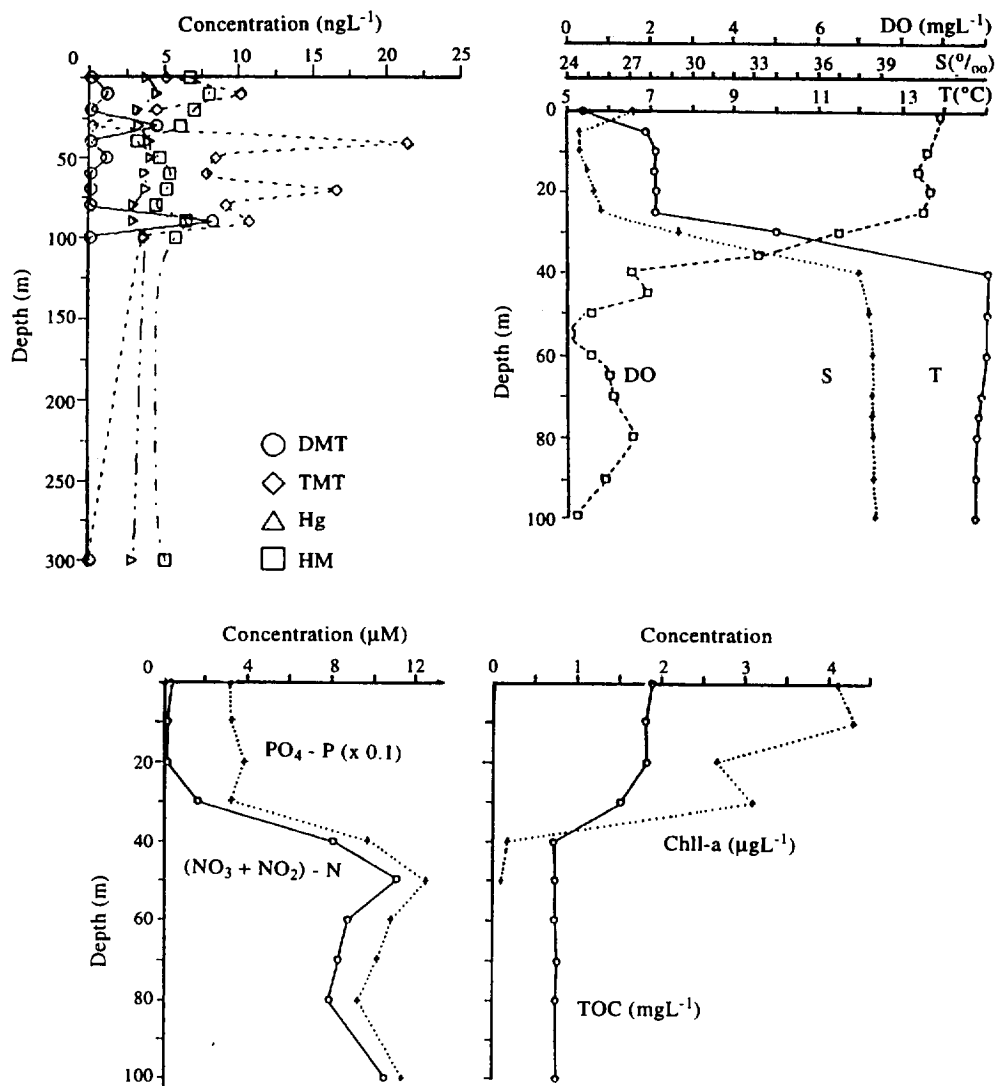
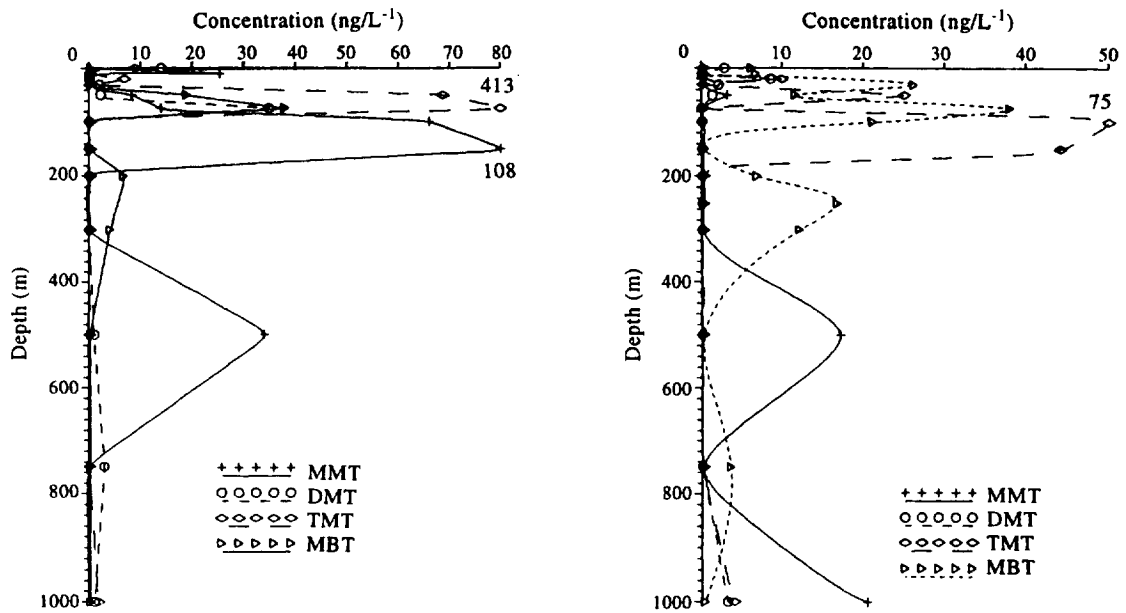


Fig. 2 Vertical distributions of DMT, TMT, total mercury (Hg), fluorescing material (HM), dissolved oxygen (DO), temperature (T), salinity (S), nutrients (PO₄-P, NO₃ + NO₂-N), chlorophyll-a, and total dissolved organic carbon (TOC) in the basin water of the Marmara Sea, February, 1989.

chlorophyll-a concentrations measured in January 1989 were significantly higher than in September 1988, indicating an early spring bloom in January, 1989. However, the total concentrations of methyltin species recorded in September 1988 were much greater than those in January 1989, when the samples contained no detectable MMT or dimethyltin (DMT; see Table 1). The results of the tin speciation studies which have appeared in the literature and include both inorganic tin and methyltin species in the same sample are also compiled in Table 1. These data indicate that, in tin-polluted waters, methylation reactions proceed to yield predominantly MMT and DMT. The Bay of Iskenderun receives continuous inorganic tin inputs from an iron and steel factory and from a fertilizer factory located on its eastern shoreline (Yemenicioğlu *et al.*, 1987). The inorganic tin concentration in the waste-

water of these industries ranged between 15 and 1100 ng l⁻¹. According to Rapsomanikis and Weber (1985), Sn(II) is methylated abiotically mainly to MMT and DMT under reducing conditions, depending upon the availability of carbonium/carbanion ions. Considering the methyltin products of these model experiments, it may be suggested that in the polluted surface waters of Iskenderun Bay, Sn is reduced to the Sn(II) form and is then methylated by biomediated chemical reactions to produce MMT and DMT. The occasional disappearance of MMT in the polluted subsurface waters of Iskenderun Bay can be attributed to the tendency of this chemical species to be strongly adsorbed onto sinking particulate matter of various origins (Hodge *et al.*, 1979; Tuğrul *et al.*, 1983; Donard and Weber, 1985), as well as to changes in the biomediated reaction mechanisms.



In Marmara Basin

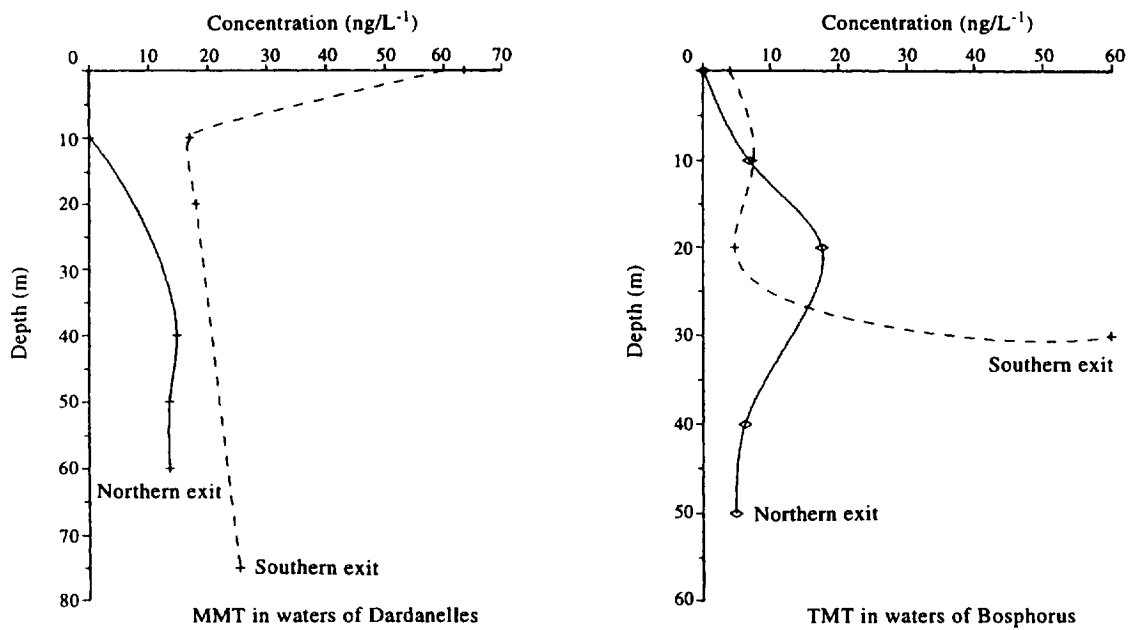


Fig. 3 Vertical distributions of methyltins and monobutyltin in the Marmara Sea and straits (Dardanelles Strait and Bosphorus Strait), July, 1988.

In the butyltin-polluted San Diego Bay, only MMT and DMT were detected in low concentrations by Hodge *et al.* (1979). However, Braman and Tompkins (1979) found all three forms of methyltins in this location, DMT being the predominant form. Furthermore, the concentrations of methyltins did not relate to the butyltin levels in the studied areas. The methylated forms of tin in estuarine waters are predominantly

DMT, and to a lesser extent MMT. The relatively low concentrations of MMT in these shallow waters may again be the result of its fast removal by particulate matter of terrigenous origin. Donard and Weber (1985) have observed that MMT (and to a lesser extent, DMT) are precipitated by particulate matter under simulated estuarine environments, whilst TMT remains in solution. Thus, the TMT determined occasionally in surface

TABLE 1

Concentrations of monobutyltin, methyltins and inorganic tin (ng l^{-1} as chlorides) in the coastal waters of the Mediterranean, Marmara and Black Seas.

Location	S. Date	MBT	MMT	DMT	TMT	Sn ⁺⁴	Source
Marmara Sea	July 1988	<0.4-38	<0.3-108	<0.15-35	<0.25-413	—	This work
	Sept. 1988	<0.4-14	<0.3-30	<0.15-56	<0.25-77	—	This work
	Dec. 1988	<0.4-64	<0.3-16	<0.15-7	<0.25-5	—	This work
	Feb. 1989	<0.4-20	<0.3-26	<0.15-8.3	<0.25-21	—	This work
Black Sea	Sept. 1988	<0.4-36	<0.3	<0.15-5.1	<0.25-80	—	This work
	Jan. 1989	<0.4	<0.3	<0.15	<0.25-12	—	This work
Mediterranean Sea Rhodes Gyre	July 1988	<0.4	<0.3	7.5	267	—	This work
	Oct. 1988	<0.4	<0.3	18	129.2	—	This work
Estuaries							
Lamas River	1982-1983	—	<0.3-2.2	<0.15-3.6	<0.25	4.1-15	Yemenicioğlu <i>et al.</i> (1984); Tuğrul <i>et al.</i> (1983)
Göksu River	1982-1983	—	<0.3-4.8	0.6-20.5	<0.25-1.5	3.2-49	Yemenicioğlu <i>et al.</i> (1984)
	Oct. 1988	212	<0.3	<0.15	27.5	—	Kubilay <i>et al.</i> (1996)
	Feb. 1989	268	<0.3	<0.15	<0.25	—	Kubilay <i>et al.</i> (1996)
Ceyhan River	1982-1983	—	12-16	13-21	<0.25	24-123	Yemenicioğlu <i>et al.</i> (1984)
Iskenderun Bay	Jul. 1982	—	6.0-83	4-18.3	<0.25	11-175	Yemenicioğlu <i>et al.</i> (1984)
Iskenderun Bay	Aug. 1982	—	5.5-10	5-12	<0.25	26-7710	Yemenicioğlu <i>et al.</i> (1984)
Iskenderun Bay	Sep. 1982	—	<0.3	9-12.5	<0.25	219-237	Yemenicioğlu <i>et al.</i> (1984); Tuğrul <i>et al.</i> (1983)
Iskenderun Bay	Nov. 1982	—	<0.3	0.5-1.4	<0.25	13-207	Yemenicioğlu <i>et al.</i> (1984); Tuğrul <i>et al.</i> (1983)

—, Not measured.

waters might be produced in the water column itself, or be released from the underlying sediments.

It may be concluded that in the productive waters of the Marmara and the Black Seas, the methylation of Sn proceeds to yield predominantly TMT. However, in the Mediterranean Sea, TMT predominates only in the estuarine waters at the mouth of the Göksu River and in the productive waters of the Rhodes Gyre. MMT and DMT species appear to predominate in the tin-polluted Iskenderun Bay waters and in most estuarine waters of the Mediterranean Sea. This is similar to the relative distributions of methyltins in model studies, and is indicative of a sequential methylation mechanism for Sn. However, no model study exists so far to support and describe the formation of TMT as the predominant chemical species in productive open seawaters. Trimethyltin (and to a lesser extent DMT) produced in marine environments is of great importance in the large-scale transport of Sn in the oceans. The present and previous Sn speciation studies have revealed that the occurrence and fate of methyltins in the marine environment is dominated not only by the inorganic/organic Sn input, but also by other abiotic and biotic processes.

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Marine Pollution Bulletin, Vol. 34, No. 9, pp. 744–749, 1997
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 0025-326X/97 \$17.00 + 0.00
 PII: S0025-326X(97)00026-X

An Estimate of the Annual Input of Natural Petroleum Hydrocarbons to Seafloor Sediments in Prince William Sound, Alaska

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Natural seepage is an important contributor to the petroleum baseline of the marine environment at many locations (NRC, 1985). For areas known to be influenced by natural petroleum seepage, this source of hydrocarbons can be an important part of the baseline. The actual annual input of petroleum from natural seepage is uncertain, with estimates of total worldwide annual seep inputs ranging from 0.025×10^6 to 6×10^6 t yr⁻¹ (Wilson *et al.*, 1973, 1974; Kvenvolden and Harbaugh, 1983; Miller, 1992). One reason for this uncertainty is that observations of seeps often lack sufficient geographic sampling density over an adequate period of time to allow accurate estimates of inputs to a given geographical area to be made. Further complicating the estimation of oil seepage rates is the fact that, for a given location, the rate of seepage can vary considerably over time (Wilson *et al.*, 1973). For example, variable seepage rates of 7–10 t day⁻¹ have been estimated for the Coal Oil Point (California) offshore seeps by slick area/thickness measurements and by direct collection of oil from submarine seeps made at different times (Allen *et al.*, 1970). Where conditions permitted the actual visualization of surface oil slicks by remote sensing, estimates of regional seepage rates of

ca. 17 100 t yr⁻¹ were made for a seep area in the Gulf of Mexico offshore of Louisiana (MacDonald *et al.*, 1993). There are also reports of flow estimates for individual seeps based on direct observation (Wilson *et al.*, 1973, 1974; Kvenvolden and Harbaugh, 1983).

As part of the scientific studies following the *Exxon Valdez* oil spill of 24 March 1989 in Prince William Sound (PWS), Alaska, a number of deep subtidal sediment chemistry studies were completed within PWS and outside the spill zone in the Gulf of Alaska (Rapp *et al.*, 1990; Kvenvolden *et al.*, 1991; Page *et al.*, 1995, 1996). Analysis of the distributions of polycyclic aromatic hydrocarbons from nearshore and offshore 1989 and 1990 subtidal sediment samples from PWS identified two major types of petrogenic sources (Fig. 1): *Exxon Valdez* (Alaska North Slope) petroleum with a high relative alkyl dibenzothiophene content, and natural oil seep petroleum with a low relative alkyl dibenzothiophene content (Page *et al.*, 1995). Chemical analyses of age-dated sediment core samples from PWS (Page *et al.*, 1995, 1996) showed that this natural oil seep petroleum has been a feature of the PWS hydrocarbon baseline for at least 160 years. Saturate biomarker analyses of deep subtidal sediment samples collected in 1989 in PWS and offshore of the Kenai Peninsula *ca.* 70 km south of Seward, Alaska, found hopanes indicative of mature petroleum hydrocarbons (Rapp *et al.*, 1990) and oleanane, a saturate biomarker indicative of post-latest Cretaceous petroleum terrigenous sources (Peters and Moldowan, 1993). In the present study, oleanane is a specific indicator for seep-derived petrogenic background. Oleanane is not present in Alaska North Slope crude oils in general (Kvenvolden *et al.*, 1985), and was specifically absent from the cargo oil of the *Exxon Valdez* (Bence and Douglas, 1993; Page *et al.*, 1996).

While oil seeps have not been found within PWS, numerous active petroleum seeps have been reported along the coast of the Gulf of Alaska east of PWS from the Copper River delta almost to Juneau (Miller, 1951; McGee, 1972; Rosenberg, 1974; Wilson *et al.*, 1974; Blasko, 1976; Becker and Manen, 1989). The widespread occurrence of oil seepage along the coast of the eastern Gulf of Alaska makes this a potentially important source of background petrogenic hydrocarbons on suspended sediment matter in Alaskan coastal waters. Westward sediment transport (see Fig. 2) is carried out by the Alaskan Coastal Current from