

Fractionation Studies of Aquatic Fatty Acids from Coastal & Off-Shore Marine Environments of Southern Florida

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ABSTRACT

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The nature, quantity, and distribution of dissolved and particulate-adsorbed fatty acids in seawater were studied in different coastal marine environments of southern Florida. The total fatty acid concentration increased in surface waters as sampling proceeded from off-shore to terrestrially-influenced areas. The overall degree of lipid unsaturation did not vary significantly with this transition, however, major changes in this parameter and in fatty acid speciation were apparent within different lipid fractions. Unsaturated fatty acids in particulate-adsorbed matter were found to fractionate primarily with neutral lipid suggesting an abundance of triacylglycerols and/or wax esters, whereas, unsaturated fatty acids in dissolved lipid were partitioned almost equally into both polar and neutral fractions. Monounsaturates ranged between 0 and 10.8% of total fatty acid while polyunsaturated fatty acids were negligible in all seawater samples (<1% of the total).

ADDITIONAL INDEX WORDS: *Marine Fatty Acids, Fractionation, Coastal, Offshore, Florida*



INTRODUCTION

Marine lipid biosynthesis and the subsequent deposition of lipid in ocean sediments is a subject of considerable interest to both marine biologists and to geochemists (ISHIWATARI & MACHIARA, 1982). From a biological standpoint, lipid is important as a high energy food source with a caloric content of approximately 9.3 kcal/g. Carbohydrate and protein, in contrast, contain only ca. 4.1 kcal/g (HOSHACHKA & SOMERO, 1973) although the oxygen requirement in utilization of the latter is significantly less than that for lipid. Lipid is also important as an essential nutrient to a wide variety of organisms including marine fish and zooplankton (D'ABRAMO, 1979; HILDITCH & WILLIAMS, 1964). Although many of these organisms can synthesize saturated, monounsaturated, and polyunsaturated fatty acids from non-lipid precursors, most fish and zooplankton are dependent on dietary lipid for optimal growth and development.

Fatty acids associated with neutral marine lipid comprise key components of triacylglycerols, alkydiacylglycerols, and wax esters. These substances have, not only an important role in biological energy storage, but also a role in buoyancy regulation and insulation. Fatty acids associated with the polar fraction of marine lipid (*e.g.*, nonesterified free fatty acids, phospho-lipids, and glyco-lipids) act perhaps most importantly in biological membrane formation and the maintenance of cellular integrity.

Numerous studies have been reported on lipid distributions in marine organisms (KATES & VOLCANI, 1966; LEWIS, 1967; MAYZAUD & MARTIN, 1975; ACKMAN *et al.*, 1980) coastal marine (FARRINGTON & QUINN, 1971 and 1973; BOON *et al.*, 1975; GILLAN & SANDSTROM, 1985) and lake sediments (MEYERS & TAKEUCHI, 1979; KAWAMURA & ISHIWATARI, 1984) and sea water (WILLIAMS, 1965; LISITSYN, *et al.*, 1971; ZSOLNAY, 1977; MEYERS, 1980; EHRHARDT *et al.*, 1980). Information is also available concerning the association of

different types of lipid within particulate and dissolved fractions of seawater (WAKEHAM 1985; MEYERS & QUINN, 1971; SUESS, 1970; WILLIAMS, 1965) and the fractionation of marine lipid into polar and neutral classes within different geographic regions (WAKEHAM, *et al.*, 1980). The currently reported investigation was undertaken in coastal southern Florida (*i.e.*, Florida and Biscayne Bays) and the adjacent off-shore oligotrophic waters of the Gulf Stream to determine changes in the nature and distribution of aquatic fatty acids within a limited geographic region and also to determine possible direct or indirect terrestrial influences on these parameters.

MATERIALS AND METHODS

Seawater Collection and Lipid Fractionation

Figure 1 illustrates the geographic distribution of sampling locations. Marco Island is the site closest to the southern Florida mainland (< 1 nautical mile). This area has substantial ter-

restrial input of organic material from the neighboring Florida Everglades (DADDIO & van de KREEKE, 1979). Other sites, listed in order of decreasing terrestrial influence are Biscayne Bay (< 2 nautical miles from the mainland), Central Florida Bay near Islamorada (approximately 15 nautical miles from the mainland), Key West (approximately 50 nautical miles from the mainland), and a Gulf Stream sampling site (approximately 20 nautical miles from the southern Florida mainland but with almost no influence from it).

Seawater samples from these locations were collected at the surface (0–15 cm) on an outgoing tide in methylene chloride, methanol-aqueous ammonia (9.35:0.65 v/v) and acid-washed (0.01 M HCl) 20 L glass carboys from small vessels off-shore. Samples from the Marco Island site, however, were collected from a rock jetty near shore. All locations except the Gulf Stream site were in waters approximately 3–5 meters in depth (each area had a sandy bottom and was virtually devoid of both seagrasses and corals). Seasonal sampling times were chosen randomly and ranged generally from December to June (1980–1981). Sea-state was light to moderate at all collection sites.

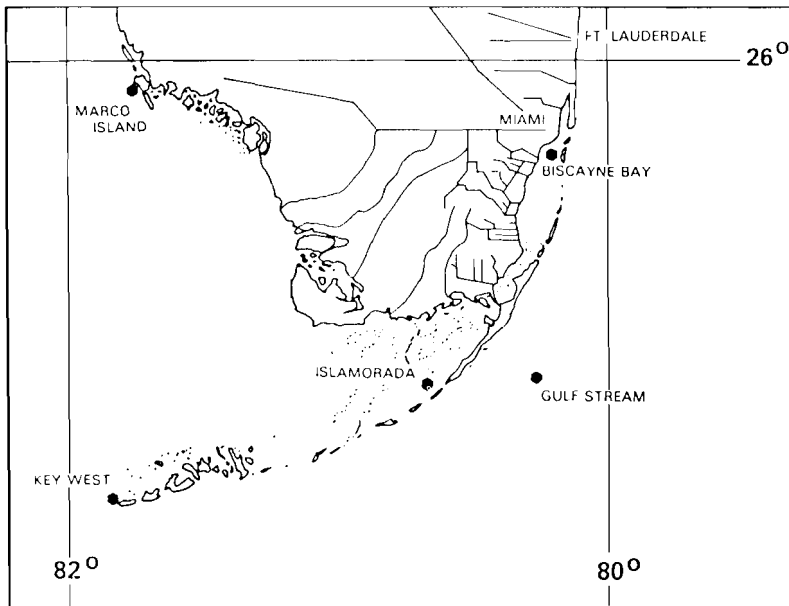


Figure 1. Geographic location of selected sampling sites in marine coastal waters of southern Florida.

"Dissolved" and "particulate-adsorbed"¹ fractions were separated and *operationally defined* as such after partitioning of coarse particulates and associated adsorbed lipid using entrapment in a glass fiber matrix² and subsequent extraction of dissolved lipid and other organic substances on Amberlite XAD-2 resin (procedure analogous to that for humic substances described in MANTOURA & RILEY, 1975). Resin was washed extensively with acetonitrile, benzene, methanol-aqueous ammonia (1:1 v/v), deionized water and 0.01 M HCl before use. Seawater was similarly acidified to pH 2.0 by addition of 6 M HCl before sample filtration and resin extraction. Containers were washed thoroughly after sample filtration with 0.01 M HCl and these washings were then also filtered through columns. Subsequent refiltration of particulate-extracted water on Whatman GLC glass fiber filters yielded no additional particulate materials.

Fatty acids associated with polar lipid, later identified by gas chromatography, were defined as those fatty acids found to elute from the glass fiber matrix (*i.e.*, particulate-adsorbed fraction) or Amberlite XAD-2 resin (dissolved fraction) with a solution containing methanol and concentrated aqueous ammonia (9.35:0.65 v/v) and subsequently extracting with methylene chloride. Fatty acids associated with neutral lipid were operationally defined as those fatty acids (presumably in complexed form) not eluting from the glass matrix or XAD-2 resin with methanol-ammonia but subsequently eluting with methylene chloride.

Experiments were done to test this classification scheme with two lipid tracers, trinodecanoin (neutral triglyceride) and nonadecanoic acid (polar free fatty acid). Results of this analysis indicate that approximately 93% of the free nonadecanoic acid recovered was found, as expected in the polar fraction while approximately 91% of the trinodecanoin was found as neutral lipid. The remaining 7–9% represented loss or cross-over into the other fraction. It should be emphasized, therefore, that this is an operational definition.

1. This term is used throughout to designate both particulate fatty acids and fatty acids subsequently adsorbed to this fraction in seawater.

2. Three cm of compacted glass-wool previously washed with methylene chloride, methanol-aqueous ammonia (9.35:0.65 v/v), and 0.01 M HCl.

Methylation and Analysis of Fatty Acids

Free and esterified fatty acids (*e.g.*, triglycerides, alkyldiacylglycerides, *etc.*) were methylated in 2–5 ml of BF₃-methanol (2 hours at 100–110°C). Fatty acid methyl esters were then extracted 3 X with an equal volume of hexane. These fractions were pooled and residual water removed from samples with anhydrous sodium sulfate (0.5 g). The resulting samples were dried under nitrogen and redissolved in 200 µl of hexane. Fatty acid methyl esters were then purified from hydrocarbons, aromatic compounds, and sterols by a silica-alumina column procedure cited in HARVEY *et al.* (1979).

After preliminary purification, fatty acid methyl esters were transferred into hexane and analyzed on a Tracor 550 gas chromatograph equipped with a 15 m SE-52 glass-capillary column. The column temperature was programmed to increase from 50 to 270°C at a constant rate of 20°C per minute and remain at final temperature for sufficient time to elute long-chain (C-22 to C-28) fatty acids. Running times normally averaged 15 minutes although chromatograms were also monitored over periods as long as 40 minutes. Peak retention times and areas for each compound were compared with known standards for identification and quantitation of unknowns.

Within each experimental run, tracers (nonadecanoic acid or trinodecanoin) were added to samples and procedural blanks to determine an estimate of efficiency for the purification procedure. These recoveries were included in calculations. Blanks from each run were subtracted from results where applicable, however, blank percentages were negligible in most determinations.

RESULTS AND DISCUSSION

The concentrations of total particulate-adsorbed fatty acids in Florida and Biscayne Bay samples varied substantially among regions. Fatty acid levels in this fraction were approximately 4- to 5-fold higher in waters off Marco Island compared with other areas examined although it is difficult to discern a consistent gradient in the concentration of these substances within other coastal regions varying in distance from the mainland (Table 1) There were, however, very clear differences in dis-

Table 2. Fatty acid composition of the dissolved lipid fraction from seawater samples of selected southern Florida coastal regions.

| Station* | % of Total Dissolved Fatty Acids | | | | | | | |
|--------------|----------------------------------|------------|-----------|-------------|-----------|-------------|-------------|-----------|
| | 12:0 | 14:0 | 16:1 | 16:0 | 18:1 | 18:0 | 20:0 | 22:0 |
| Gulf Stream | | | | | | | | |
| Polar | 15.5 ± 7.4 | 18.2 ± 4.4 | 4.1 ± 1.6 | 39.7 ± 9.5 | 1.2 ± 1.2 | 15.1 ± 1.5 | 5.7 ± 4.3 | 0.8 ± 0.8 |
| Neutral | 1.6 ± 0.5 | 19.6 ± 1.0 | 0.8 ± 0.8 | 50.1 ± 2.7 | 7.9 ± 1.9 | 15.5 ± 2.8 | 0.5 ± 0.4 | 4.3 ± 1.0 |
| Key West | | | | | | | | |
| Polar | 0.4 ± 0.4 | 12.1 ± 1.6 | 3.3 ± 0.2 | 31.5 ± 14.3 | 0.8 ± 0.7 | 17.6 ± 0.1 | 33.0 ± 14.9 | 1.5 ± 0.2 |
| Neutral | 0.6 ± 0.3 | 14.0 ± 3.0 | 2.7 ± 0.3 | 46.0 ± 5.4 | 1.5 ± 1.1 | 19.6 ± 2.1 | 12.2 ± 6.1 | 3.5 ± 1.6 |
| Islamorada | | | | | | | | |
| Polar | 5.4 | 8.4 | 0.3 | 23.0 | 0.3 | 10.3 | 32.5 | 19.8 |
| Neutral | 3.6 ± 3.6 | 7.0 ± 5.2 | 1.5 ± 0.7 | 36.0 ± 13.9 | 0.6 ± 0.6 | 29.8 ± 14.1 | 15.0 ± 13.0 | 6.7 ± 3.2 |
| Biscayne Bay | | | | | | | | |
| Polar | 5.6 ± 5.6 | 24.9 ± 2.2 | 4.3 ± 0.0 | 40.2 ± 4.4 | 3.4 ± 0.3 | 15.8 ± 3.8 | 3.7 ± 3.1 | 2.3 ± 2.2 |
| Neutral | 1.8 ± 0.9 | 18.6 ± 3.0 | 3.5 ± 0.5 | 50.6 ± 0.2 | 2.8 ± 0.4 | 13.5 ± 2.1 | 3.9 ± 0.7 | 5.3 ± 0.1 |
| Marco Island | | | | | | | | |
| Polar | 24.4 ± 0.7 | 16.0 ± 0.6 | 1.2 ± 0.3 | 40.8 ± 0.3 | 0.2 ± 0.2 | 10.5 ± 1.8 | 7.1 ± 1.0 | 0.0 ± 0.0 |
| Neutral | 1.2 ± 0.9 | 15.6 ± 1.8 | 0.7 ± 0.1 | 64.8 ± 0.1 | 0.8 ± 0.6 | 10.8 ± 0.1 | 4.3 ± 2.3 | 2.1 ± 0.1 |

Variations within each fraction represent the range or S.E. of the means of 2–6 determinations except for the dissolved lipid analysis from a single Islamorada sampling. Collection and analysis procedures are described in the Materials and Methods section.

* Stations are shown in order of increasing terrestrial influence.

Table 1. Fatty acid concentrations in seawater samples from selected southern Florida coastal regions.

| Station* | Particulate-Adsorbed Form µg/l | Dissolved Form µg/l | Ratio Part/Diss. | Total Lipid µg/l |
|--------------|--------------------------------|---------------------|------------------|------------------|
| Gulf Stream | 0.84 ± 0.02 | 0.73 ± 0.17 | 1.2 | 1.56 ± 0.15 |
| Key West | 0.91 ± 0.02 | 1.23 ± 0.35 | 0.7 | 2.14 ± 0.33 |
| Islamorada | 0.71 ± 0.15 | 1.28 | 0.6 | 1.99 |
| Biscayne Bay | 0.84 ± 0.27 | 1.69 ± 0.35 | 0.5 | 2.53 ± 0.05 |
| Marco Island | 3.68 ± 0.18 | 2.15 ± 0.24 | 1.7 | 5.83 ± 0.06 |

Variations within each fraction represent the range or S.E. of means of 2–6 determinations except for the dissolved lipid analysis from a single Islamorada sampling.

* Stations are shown in order of increasing terrestrial influence.

solved fatty acid concentrations that declined in relatively consistent manner from near-shore (*i.e.*, Marco Island) to progressively more off-shore oligotrophic environments (*e.g.*, the Key West and Gulf Stream sampling sites, in particular).

The dominant fatty acid associated with all fractions of aquatic lipid was palmitic acid (16:0), which in one instance accounted for as much as 75% of those fatty acids identified (Tables 2 and 3). Stearic acid (18:0) was also detected in relatively high concentrations and accounted for as much as 33% of particulate-adsorbed neutral fatty acid. The two dominant

unsaturated fatty acids in these studies were palmitoleic acid (16:1) and oleic acid (18:1), which accounted for as much as 6.3% and 7.9%, respectively, of total fatty acids in some fractions.

Although minute quantities of 16 and 18 carbon polyunsaturates were also observed in a small number of coastal seawater samples, they typically constituted a negligible fraction of total lipid. These results were not unexpected as prior studies have shown polyunsaturated lipid to be highly unstable in aqueous solutions due to free radical and peroxide formation around double bonds (BAKER & WILSON, 1966; and SCHAUENSTEIN, 1967). Recently HARVEY *et al.* (1984) have demonstrated that marine fulvic materials may in fact be derived from polyunsaturated lipid.

In comparative studies, fatty acid distributions in cultures from a selected algal species (*i.e.*, *Thalassiosira weissflogii*) and samples of concentrated zooplankton from the Sargasso Sea were found to contain approximately 5–7% of total fatty acid as 16 and 18 carbon polyunsaturates (Unpublished Data). The abundance of monounsaturates was also found to be relatively high in such samples (*i.e.*, 42–50% w/w). Findings of this nature support previously published results which have shown that polyunsaturates may occur at significant concentra-

Table 3. Fatty acid composition of the particulate-adsorbed lipid fraction from seawater samples of selected southern Florida coastal regions.

| Station* | % of Total Particulate-Adsorbed Fatty Acids | | | | | | | |
|--------------|---|------------|-----------|-------------|-----------|-------------|-----------|-------------|
| | 12:0 | 14:0 | 16:1 | 16:0 | 18:1 | 18:0 | 20:0 | 22:0 |
| Gulf Stream | | | | | | | | |
| Polar | 0.8 ± 0.4 | 12.1 ± 0.7 | 0.2 ± 0.2 | 56.9 ± 0.6 | 0.8 ± 0.5 | 24.3 ± 1.0 | 1.9 ± 0.2 | 3.1 ± 0.6 |
| Neutral | 0.0 ± 0.0 | 6.0 ± 2.5 | 5.0 ± 0.6 | 33.5 ± 20.4 | 0.3 ± 0.2 | 33.4 ± 12.2 | 5.6 ± 1.7 | 16.8 ± 3.2 |
| Key West | | | | | | | | |
| Polar | 0.4 ± 0.2 | 18.1 ± 0.7 | 0.1 ± 0.1 | 50.8 ± 15.3 | 0.2 ± 0.1 | 12.7 ± 0.2 | 1.2 ± 0.1 | 2.0 ± 0.0 |
| Neutral | 0.0 ± 0.0 | 8.1 ± 2.3 | 4.8 ± 0.2 | 66.7 ± 0.0 | 0.0 ± 0.0 | 17.6 ± 1.6 | 0.8 ± 0.8 | 1.8 ± 1.5 |
| Islamorada | | | | | | | | |
| Polar | 0.7 ± 0.7 | 7.5 ± 0.5 | 6.3 ± 0.1 | 53.4 ± 0.2 | 4.5 ± 4.5 | 18.0 ± 1.6 | 7.9 ± 4.8 | 1.8 ± 0.9 |
| Neutral | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 74.8 ± 2.1 | 0.0 ± 0.0 | 12.6 ± 1.0 | 0.0 ± 0.0 | 12.5 ± 1.0 |
| Biscayne Bay | | | | | | | | |
| Polar | 1.5 ± 0.2 | 21.3 ± 1.7 | 1.3 ± 1.3 | 54.8 ± 1.3 | 1.2 ± 1.0 | 15.3 ± 2.2 | 1.8 ± 0.4 | 3.0 ± 0.8 |
| Neutral | 0.1 ± 0.1 | 7.7 ± 0.5 | 4.7 ± 1.2 | 55.7 ± 11.0 | 0.0 ± 0.0 | 18.4 ± 1.9 | 0.6 ± 0.6 | 12.9 ± 12.9 |
| Marco Island | | | | | | | | |
| Polar | 1.4 ± 0.2 | 17.7 ± 2.7 | 0.6 ± 0.2 | 68.9 ± 2.7 | 0.9 ± 0.1 | 8.7 ± 5.3 | 0.6 ± 0.1 | 1.3 ± 0.2 |
| Neutral | 0.0 ± 0.0 | 11.2 ± 2.7 | 5.5 ± 3.0 | 48.4 ± 20.7 | 0.0 ± 0.0 | 19.1 ± 6.5 | 0.0 ± 0.0 | 16.0 ± 14.0 |

Variations within each fraction represent the range or S.E. of the means of 2–6 determinations. Collection and analysis procedures are described in the Materials and Methods section.

* Stations are shown in order of increasing terrestrial influence.

tions in cultured phytoplankton and zooplankton (LEWIS, 1969) but are often low or absent in seawater (MEYERS, 1980) although some laboratories have reported polyunsaturated fatty acids (*e.g.*, 20:5 and 20:6) in marine environments at concentrations representing as much as 20% of total particulate fatty acid (WAKEHAM *et al.*, 1980).

It should be noted that the quantity and nature of lipid in marine plankton has been found to vary substantially under altering environmental parameters. Changes in light and temperature, for example, appear to be particularly important. Under certain conditions, it has been shown that polyunsaturate synthesis may in fact account for a major fraction of primary productivity (SMITH & MORRIS, 1980 a,b). While seasonal sampling times ranged in these studies from December to June there are currently too few data to compare variations within each region to season.

In most instances lauric acid (12:0) was discerned at significant concentrations (as much as 24% of fatty acid) in southern Florida coastal waters in the dissolved polar fraction but was usually much lower in particulate-adsorbed neutral lipid (0–0.1%). The level of arachidic acid (20:0) also varied substantially (0–33.0%). Typically, the highest concentrations of this substance occurred in dissolved polar and dissolved neutral form.

Myristic acid (14:0) was found consistently to be lowest in particulate-adsorbed neutral lipid (0–11.2% of the total) while the highest levels of behenic acid (22:0) were generally seen in this fraction. It should be noted that long chain fatty acids (*i.e.*, predominantly C-22 to C-28) have been previously shown by CRANWELL (1974) to be suggestive of terrestrial organic influences while short chain fatty acids (C-12 to C-18) are reportedly dominant in aquatic lipid sources. The data in Tables 2 and 3, however, show no clear or consistent changes between near-shore and off-shore samplings in regard to fatty acid chain-length and virtually no fatty acid chains longer than C-22 were observed. It is possible that increased levels of fatty acids near shore were not derived from, but only influenced by their proximity to land. An explanation for such differences might involve the modulation of coastal marine productivity and subsequent in-situ lipid biosynthesis by the terrestrial runoff of mainland-derived non-lipid materials. Such influences might indirectly cause an elevation of lipid concentrations in near-shore coastal waters by serving as nutrients or biological regulatory agents for plankton growth. Further studies would be needed, however, to confirm or refute this hypothesis.

It is apparent from data presented in Table 4 that the polar to neutral fatty acid ratio was

Table 4. Polar to neutral partitioning ratio of particulate-adsorbed and dissolved fatty acids from seawater samples of selected southern Florida coastal regions.

| Station* | Particulate-Adsorbed Fraction | | Polar/Neutral Ratio | Dissolved Fraction | | Polar/Neutral Ratio |
|--------------|-------------------------------|-------------|---------------------|--------------------|-------------|---------------------|
| | Polar | Neutral | | Polar | Neutral | |
| | μg/l | | | μg/l | | |
| Gulf Stream | 0.78 ± 0.02 | 0.05 ± 0.00 | 16 | 0.32 ± 0.03 | 0.41 ± 0.14 | 0.8 |
| Key West | 0.84 ± 0.00 | 0.07 ± 0.01 | 12 | 0.70 ± 0.33 | 0.52 ± 0.01 | 1.3 |
| Islamorada | 0.69 ± 0.16 | 0.02 ± 0.00 | 35 | 0.63 | 0.64 ± 0.13 | 1.0 |
| Biscayne Bay | 0.77 ± 0.26 | 0.08 ± 0.01 | 10 | 0.94 ± 0.13 | 0.74 ± 0.21 | 1.3 |
| Marco Island | 3.43 ± 0.38 | 0.25 ± 0.20 | 14 | 0.66 ± 0.16 | 1.49 ± 0.40 | 0.4 |

Variations within each fraction represent the range or S.E. of the means of 2–6 determinations except for the dissolved polar lipid analysis from a single Islamorada sampling.

* Stations are shown in order of increasing terrestrial influence.

always higher in southern Florida coastal waters in the particulate-adsorbed lipid fraction (*i.e.*, 10 to 35 compared to 0.4 to 1.3 for the dissolved fraction).

If this result were artefactual and unrelated to biological or geochemical processes, one would expect the overall degree of saturation in samples to be roughly equivalent in both dissolved and particulate-adsorbed polar lipid fractions since saturation would not be expected to affect partitioning to any great extent.³ The data in Table 5 indicate that there were in fact substantial differences. Particulate-adsorbed polar lipid unsaturation values at four of five stations were indeed quite different from those of dissolved polar lipid. Unfortunately, the chemical association of fatty acid in the polar fraction was not further analyzed in these studies. As mentioned earlier, however, it is known that fatty acids associated with polar lipid typically comprise key components of phospho- and glyco-lipid and exist also in the nonesterified free polar form.

In summary, elevations in both dissolved and particulate-adsorbed lipid fractions were observed between various off-shore and near-shore, terrestrially-influenced marine environments, however, present data show no clear or consistent variations in the ratio of particulate-adsorbed to dissolved fatty acid or fatty acid chain length with this transition. There were, however, distinct differences in the degree of fatty acid saturation in particulate-adsorbed and dissolved lipid fractions. With only one

exception, unsaturated fatty acids in particulate-adsorbed matter were found to fractionate primarily with neutral lipid, suggesting an abundance of triacylglycerols and/or wax esters (WAKEHAM, 1985), whereas, unsaturated fatty acids in dissolved lipid were partitioned almost equally into both polar and neutral forms. This trend was observed in both off-shore and near-shore marine environments. Therefore, while most fatty acids in particulate-adsorbed matter were polar, the dominant fraction of unsaturated fatty acids in particulate-adsorbed matter was neutral. This finding may, in part, represent differences in the stability of particulate-adsorbed polar and neutral lipid containing unsaturated fatty acids although differences in the biosynthesis and release of these compounds are also possible.

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3. Unsaturated fatty acids should in fact have slightly higher dipoles and behave, therefore, marginally more polar than saturated fatty acids. The neutral fraction of particulate-adsorbed lipid, however, was found to have the highest percentage of unsaturates at most sites.

Table 5. Unsaturates as a percentage of particulate-adsorbed and dissolved fatty acid in seawater samples of selected southern Florida coastal regions.

| Station* | % Unsaturates Particulate-Adsorbed Form | | % Unsaturates Dissolved Form | |
|--------------|--|------------------|---------------------------------|------------------|
| | Polar Fraction | Neutral Fraction | Polar Fraction | Neutral Fraction |
| Gulf Stream | 1.0 ± 0.3 | 5.3 ± 0.7 | 5.3 ± 2.7 | 8.7 ± 1.2 |
| Key West | 0.3 ± 0.0 | 4.8 ± 0.2 | 4.1 ± 0.5 | 4.2 ± 1.4 |
| Islamorada | 10.8 ± 4.5 | 0.0 ± 0.0 | 0.6 | 2.1 ± 1.2 |
| Biscayne Bay | 2.5 ± 0.3 | 4.7 ± 1.2 | 7.7 ± 0.3 | 6.3 ± 0.9 |
| Marco Island | 1.5 ± 0.3 | 5.5 ± 3.0 | 1.4 ± 0.5 | 1.5 ± 0.5 |

Variations within each fraction represent the range or S.E. of the means of 2–6 determinations except for the dissolved polar lipid analysis from a single Islamorada sampling.

* Stations are shown in order of increasing terrestrial influence.

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