

high pH levels caused by increases in photosynthesis.

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Submitted: 18 June 1975

Accepted: 20 October 1975

Dissolved fatty acids in seawater from a fringing reef and a barrier reef at Grand Cayman¹

Abstract—The concentration of dissolved fatty acids decreased in seawater as it flowed across a windward barrier reef at Grand Cayman. No comparable changes were observed over a leeward fringing reef although an increasingly enriched organic surface layer could be detected as distance from shore increased.

Several oceanographers have worked on the biological productivity of coral reef communities. A common approach has been to measure changes in concentration of various chemical properties as seawater flows

across reefs (e.g. Johannes et al. 1972). Here I report observations on changes in dissolved fatty acids in water crossing a Caribbean barrier reef, with measurements from water collected over a fringing reef for comparison.

I thank J. W. Porter and J. S. Patton for comments on this manuscript.

Samples were taken during March 1974 at Grand Cayman in the British West Indies. A barrier reef off the northwest tip of the island and a fringing reef off the western shore were selected (Fig. 1). Prevailing winds were from the northeast, resulting in an onshore wind over the barrier reef area and an offshore wind over the fringing reef

¹ This investigation was supported by funds from the American Philosophical Society and from the Rackham School of The University of Michigan.

area. This wind pattern caused a steady 1-knot current to flow over the barrier reef into the flat between the reef and shore. Strong water motion was not observed at the fringing reef site, although a net offshore transport of surface water was likely. The influence of land runoff was judged negligible because Grand Cayman has no rivers.

The barrier reef transect consisted of five stations, from 200 m windward to 150 m leeward of the reef. One of these stations was on the reef crest, immediately behind the breaker zone, and another was 15 cm from a large colony of *Acropora palmata* in the backreef area. All water samples in this transect were collected 20 cm below the surface.

The transect of the fringing reef contained three stations, at 30, 1,000, and 2,000 m from shore: Water depths were 3, 8, and 600 m. Samples were collected at depths of 0.5 cm and 20 cm at each of these stations.

Water sampling was done using 1-liter screwcap Teflon bottles. The samples were stored at 4°C until analytical preparations began, usually within 12 h. Single samples were taken at all stations unless otherwise noted.

The extraction scheme of Quinn and Meyers (1971) for total dissolved fatty acids was followed, using 20 µg of heptadecanoic acid as an internal standard, extracting three times with 50-ml volumes of chloroform, combining the extracts, and storing them at 4°C until shipment to Michigan for analysis.

The extracted fatty acids were saponified with methanolic KOH and then converted to their methyl esters with $\text{BF}_3\text{-MeOH}$. Thin-layer chromatography was used to isolate the fatty acid methyl esters (Meyers et al. 1974). Gas-liquid chromatography was performed using a Varian Aerograph 1526-C F.I.D. gas chromatograph equipped with 1.5-m × 2.1-mm I.D. stainless steel columns packed with 10% SP-216-PS on 100/120 mesh Supelcoport. The instrument was operated isothermally at 175°C with a nitrogen carrier gas flow rate of 20 ml min⁻¹.

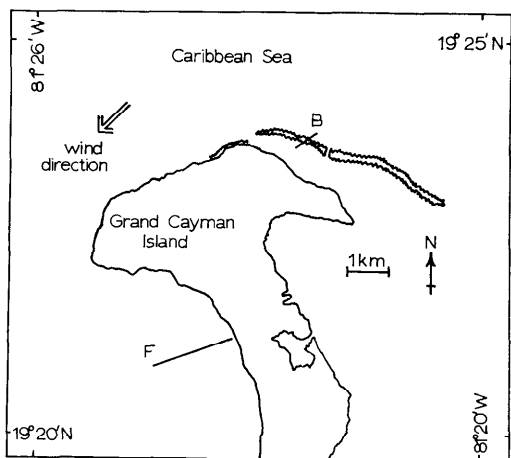


Fig. 1. Northwest tip of Grand Cayman, showing sampling locations. Transect B crosses the barrier reef; transect F the fringing reef.

Individual fatty acid esters were identified by comparison of retention times of authentic standard methyl esters and by coinjection of standard methyl esters.

All glassware involved in fatty acid analysis was rinsed with 1% HCl, distilled MeOH, and distilled CHCl_3 before use. Blanks for all procedures showed only small amounts of contamination; the results reported have been corrected accordingly.

Three 1-liter samples were collected in rapid succession at a depth of 20 cm below the surface at one station in the fringing reef transect. Analysis of these samples showed a relative standard deviation of 19.3% for total acids and relative standard deviations ranging from 2.6% to 36.0% for the major fatty acids detected. Since the extraction is essentially quantitative (Quinn and Meyers 1971) and the analytical procedure is capable of a relative standard deviation of about 3% on repetitive samples (Meyers and Quinn 1971), the scatter found may represent natural inhomogeneity in the water samples.

The transect across the barrier reef showed changes in the concentrations of dissolved fatty acids in seawater as stations progressed from outside the reef over the reef crest and into the backreef area. Total dissolved fatty acids were lowest over the

Table 1. Dissolved fatty acids from barrier reef transect. Samples collected at a depth of 20 cm. Concentrations given in micrograms per liter. Weight percent compositions are in parentheses.

Location	Fatty Acid*					total
	12:0	14:0	16:0	18:0	18:1	
200 m windward of reef crest	13.6 (20.7)	14.1 (21.4)	21.4 (32.4)	12.5 (19.1)	4.0 (6.2)	66
reef crest	6.4 (18.3)	9.1 (26.1)	10.3 (29.5)	7.4 (21.0)	1.8 (5.1)	35
backreef, 20 m from crest†	10.3 (22.8)	12.1 (26.9)	14.8 (32.8)	5.3 (11.8)	2.6 (5.8)	45
backreef, 100 m from crest	11.0 (26.8)	7.6 (18.6)	13.8 (33.7)	5.3 (13.0)	3.2 (7.9)	41
backreef, 150 m from crest	11.0 (26.1)	8.7 (20.6)	12.9 (30.8)	4.7 (11.1)	4.8 (11.4)	42

* Represented as carbon chain length: number of double bonds.

† Collected 15 cm from *Acropora palmata* colony.

reef crest and somewhat lower in the backreef area than seaward of the reef. However, if the 19% relative standard deviation given above is applicable to all the samples, the only significant differences in total acids were between the open ocean and reef crest samples. The concentration at the crest was about half that of the water which had not yet flowed through the surf area at the reef crest. This decrease was accompanied by increases in total and dissolved organic carbon (Westrum and Meyers in prep.), suggesting that fatty acids are selectively removed from water over the reef crest relative to total organic matter. Alternatively, the increase in organic carbon may be due to a contribution of lipid-poor material from the reef crest community. If the source of the added dissolved organic carbon is coral mucus, then a conflict may exist with the work of Benson and Muscatine (1974) who found that coral mucus is rich in fatty acid waxes. It is possible that while much of the mucus may dissolve, the fatty acid portions do not. However, the level of particulate fatty acids remained consistently low and essentially not measurable over the entire transect (Meyers unpublished). Therefore the fate of the fatty acids lost from the dissolved matter and from any mucus contribution is not clear. Dissolved fatty acids may be removed from water and used by reef crest

organisms at a rate exceeding their contribution to the water.

Comparison of the weight percent composition of the dissolved fatty acids of the stations involved in the barrier reef transect reveals several trends. The major fatty acids and their contributions to the total dissolved acids at each location are listed in Table 1. Although the absolute amounts are different, the percent compositions of the prereef and reef crest stations are similar, except for a small increase in myristic acid (14:0). This similarity supports the suggestion that material containing soluble fatty acids is not added at the reef crest, but is removed.

The first backreef location in the transect was close to a large colony of *A. palmata* to see whether measurable amounts of fatty acids are contributed to seawater by this coral. Concentrations of lauric acid (12:0), myristic acid, and palmitic acid (16:0) did increase. The dominant fatty acid in *A. palmata* is palmitic acid; but since stearic acid (18:0) is the second-most abundant (Meyers et al. 1974) and no increase in the level of stearic acid was detected, this coral is apparently not a major source of dissolved fatty acids in the reef waters.

The other two backreef stations in the transect have nearly identical fatty acid compositions different from any of the others, having lower levels of myristic acid and showing a trend toward increasing

Table 2. Dissolved fatty acids from fringing reef transect. Concentrations given in micrograms per liter. Weight compositions are in parentheses.

Distance from shore (m)	Water Depth (cm)	Fatty Acid*						Total
		12:0	14:0	16:0	16:1	18:0	18:1	
30	0.5	1.7 (5.4)	10.4 (32.5)	9.6 (29.9)	2.2 (6.9)	6.0 (18.9)	2.0 (6.3)	32
30	20	1.5 (5.7)	8.5 (31.3)	8.5 (31.5)	1.0 (3.8)	6.6 (24.5)	0.9 (3.2)	27
1000	0.5	2.7 (5.2)	9.0 (17.6)	20.6 (40.3)	3.7 (7.2)	12.5 (24.6)	2.6 (5.1)	51
1000	20	0.8 (3.6)	3.3 (14.9)	8.3 (37.6)	2.3 (10.3)	5.9 (26.4)	1.6 (7.2)	22
1000	20	2.1 (6.5)	5.6 (17.2)	12.3 (37.3)	2.0 (6.2)	9.1 (27.6)	1.7 (5.3)	33
1000	20	1.1 (3.7)	5.2 (17.7)	10.4 (35.8)	2.2 (7.7)	7.3 (25.2)	2.9 (10.0)	29
2000	0.5	3.5 (4.6)	12.4 (16.5)	25.8 (34.4)	1.4 (1.9)	31.2 (41.6)	0.8 (1.1)	75
2000	20	2.3 (6.8)	11.5 (33.7)	11.5 (33.9)	0 (0)	7.5 (22.1)	1.2 (3.6)	34
2000	20	1.8 (6.7)	9.7 (35.9)	8.9 (32.9)	0.2 (0.6)	5.0 (18.7)	1.4 (5.2)	27

* Represented as carbon chain length: number of double bonds.

amounts of oleic acid (18:1). Evidently the backreef community contributes fatty acids to the water which dominate the total acid composition and differ from contributions from the open ocean or reef crest communities.

In the fringing reef transect, evidence of an increasingly greater concentration of organic matter at the surface with greater distance from shore is given by the total fatty acid concentrations (Table 2). Surface levels of fatty acids increase with distance from shore, and the ratios of surface to subsurface acids progress from 1.2 to 1.8 to 2.5 for the three distances at which samples were collected. It appears that as surface water flows away from shore due to wind stress, fatty acids produced by underlying communities accumulate at the sea surface due to their hydrophobic character. Similar surface concentrations have been described before (e.g. Garrett 1967), but a gradient such as reported here has not appeared in the literature.

The fatty acid compositions of the station closest to shore are about the same at the two sampling depths. The water here was only 3 m deep; wave action would mix the entire water column. Similarly, essentially no difference in percentage composition

exists between the surface and subsurface samples at the intermediate station. Wave mixing should be less effective here because of the greater depth. Another factor besides mixing may also be important: the proximity of the source of the acids. If the coral reef benthic community is the primary source of fatty acids in reef waters, then these materials must migrate through the water column to the sea surface. As long as the area being sampled is over a benthic area which is producing acids, the compositions of the surface and subsurface waters will probably be similar, even though the absolute concentrations may be higher at the surface. When a benthic fatty acid source is no longer present, fractionation of the acids according to solubility and biochemical stability can begin.

Indications of such fractionation can be observed in the samples collected farthest from shore, beyond the edge of the fringing reef in water about 600 m deep. The concentrations of palmitic and stearic acids are substantially higher in surface water than in water collected at 20 cm. This is not true for the shorter chain acids. The surface: subsurface ratios change from 1.2 for myristic acid to 2.5 for palmitic acid to 5.0 for stearic acid. This trend follows the order of

decreasing water solubility of these acids as carbon chain length increases (Ralston and Hoerr 1942) and indicates the importance of solubility in establishing organic surface films.

Unsaturated acids are present in small amounts in the offshore samples relative to the samples closer to shore. Palmitoleic is virtually absent in the subsurface water. The fact that unsaturated acids are prone to oxidation and therefore less stable than saturated acids may explain this observation and suggests that the nearness of the source of acids is important in determining the composition in the water.

Comparison of the overall fatty acid compositions of the two transects reveals distinct differences. Lauric acid was a major component of the acids from the barrier reef waters, but only a minor one in the fringing reef samples. Palmitoleic acid is found in significant amounts in most of the fringing reef waters but not far from shore nor near the barrier reef. These and other less obvious differences suggest different sources for the fatty acids in these two locations. The fringing reef site was a low-energy environment having no obvious currents and little wave activity, while the barrier reef location was a high energy environment having breaking waves at the reef crest and a longshore current of about 1 knot in the backreef area. Different benthic and pelagic communities in these two

sampling areas could explain the fatty acid differences.

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Submitted: 8 April 1975

Accepted: 20 October 1975

Influence of sampling method on the chemical composition of water surface film

Abstract—The composition of the surface microlayer was compared at two sites, having different degrees of water pollution, near the northern Mediterranean coast. Harvey (rotating drum device) and Garrett (screen) samplers were used and their effectiveness compared; the enrichment factor shown was greater with the former.

Eutrophication due to river runoff and hydrocarbon pollution from refinery effluents may contribute to an increase in the enrichment factor. Differences in chlorophyll, ATP, and pheophytin content between the two sampling methods suggest stratification of the living and inert planktonic material.

The surface film of fresh- and seawater has physical and chemical properties quite different from those of the water underneath. Investigations in fresh- and seawater have shown the accumulation in the surface film of organic matter such as alcohols and fatty acids (Jarvis et al. 1967; Wheeler 1972; Larsson et al. 1974), hydrocarbons (Garrett 1967), nutrient salts (Goering and Menzel 1965; Goering and Wallen 1967; Williams 1967), metallic elements associated with dissolved or particulate organic matter