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Concentration of fulvic acid in the growth bands of hermatypic corals in relation to local precipitation

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Abstract. Coral growth rate and the concentrations of fulvic acid in the growth bands of the hermatypic coral *Porites lutea* Edwards & Haime and *Favia maxima* Veron were investigated in samples taken from 1986 to 1988 in the waters of southern Taiwan (22°05′ ∼ 36′N, 120°24′ ∼ 50′E). These were analyzed against the local annual precipitation, the locality of the sampling sites, the construction activity on nearby land and coral species. The results showed that the annual growth rate of *P. lutea* was 1.08 ± 0.12 cm while *F. maxima* was 0.83 ± 0.09 cm. The amount of fulvic acid incorporated in the growth band was positively correlated with the local annual precipitation. However, the correlation coefficient varied from as high as 0.9519 to as low as 0.0921 due to different topographies of the sampling sites, dilution factors from the ocean and construction activities along the coast. *F. maxima* was found to be more sensitive than *P. lutea* in terms of fulvic acid uptake from the surrounding waters. The study of fluorescence in the skeleton of hermatypic corals is a reasonable approach to biomonitor the environment after consideration of local factors.

Introduction

Annual growth banding in the skeleton of certain hermatypic corals can provide a record of previous environmental conditions. Analysis of bands has revealed information on changes in water chemistry and quality (Barnard 1974; Dodge et al. 1984; Cortes and Risk 1985; Chen et al. 1991), temperature variation (Ma 1937; Goreau 1977; Druffel 1982; Patzold 1984), and climatic fluctuations (Dodge and Vaisnys 1975). More recently, Isdale (1984) reported that fluorescent bands in the massive coral *Porites* sp. recorded coastal runoff and rainfall. Boto and Isdale (1985) further showed that fluorescent bands resulted from the input of terrestrial fulvic acid (FA).

In this study, FA in the annual growth bands of two different hermatypic corals, *Porites lutea* Edwards & Haime and *Favia maxima* Veron from different localities, were compared with local precipitation. The variation of the results was analyzed further to define other factors which might influence the correlation. It was found that when this method was applied to investigate the history of local rainfall, the correlation between FA concentration (FA) and the amount of precipitation was not always high. It appears that, as noticed by Scoffin et al. (1989), other undefined factors may be involved. These are discussed in this study.

Materials and methods

Specimen and sampling sites

Thirteen specimens ranging in size from 20 to 30 cm in diameter of living massive coral *P. lutea* and six of *F. maxima* were collected

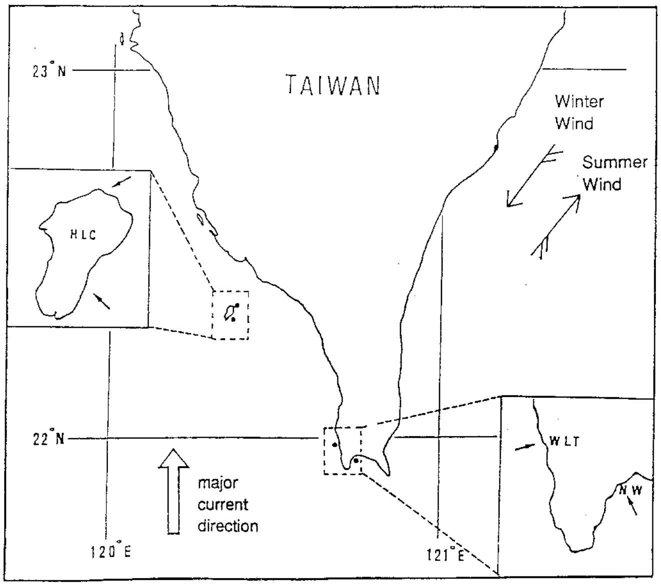

Fig. 1. Map of the sampling sites with indication of major current and seasonal wind direction

from inshore waters, 8 to 13 m deep from different localities of southern Taiwan. Collection locations were Nan-Wan (NW), a bay where a nuclear power plant was constructed during 1975 to 1985, Wan-Li-Tong (WLT), a coastal area with straight rocky shore, and two sites at Hsiao-Liu-Chiou (HLC), a coral island of 6.8 km^2 situated 13 km off the coast of Taiwan (Fig. 1).

Sample preparation

After living tissue was removed by treating with 5% calcium hypochlorite and 15% hydrogen peroxide (Barnard et al. 1974), specimens were sectioned along the axis of maximum growth using a diamond rock saw. Slabs, 0.5 to 1 cm thick, were prepared for X-ray radiography (SOFTEX Model E-40, 30-40 KVP, 15–25 min exposure) to expose density banding. A couplet of high and low density bands was regarded as having been formed over a one-year period (Dodge et al. 1984). This banding pattern has been confirmed in massive corals from the study area using oxygen isotope records (Wang and Huang 1989). The growth rate of corals was determined by measuring the width from the top edge of one high density band to the lower edge of the next low density band on X-ray films.

Identification and measurement of fulvic acid

Fulvic acid in sea water could originate from either terrestrial or marine sources with different characteristics (Stuermer and Harvey 1974; Meyers-Schulte and Hedges 1986). In this study, we wanted to measure that which originated on land. Therefore, the characteristic fluorescence spectrum of FA extracted from coral banding was compared with that of a sample prepared from terrestrial soil. FA was further examined by the heavy metal quenching effect described by Boto and Isdale (1985), who demonstrated that the chelating characteristics of fulvic acid with metal ions lowered the intensity of the fluorescence of these molecules.

For soil sample preparation, 1 kg of sand near the beach was soaked in 3 l of 0.1N NaOH for 3 days. The supernatant was filtered, centrifuged (10,000 rpm, 20 min), refiltered through 0.45 µm cellulose nitrate filter paper, then dialyzed for 3 d in distilled water to eliminate small molecules.

After dialysis, 100 ml of 2N HNO_3 was added per liter of sample solution, lowering the pH to about pH 1. The solution was then centrifuged (10,000 rpm, 20 min) to obtain a supernatant. This was used as a standard FA solution and its fluorescent characteristics were obtained using a Hitachi F-3000 fluorometer with Xe lamp. The fluorescence intensity showed a linear relationship to the amount of FA in the solution and was used as an index of FA concentration.

The fluorescence spectrum of FA from coral was first determined and compared with that of the land FA. Then, Fe^{+3} or Cu^{+2} was applied to investigate its quenching effect for the further identification of these molecules (Boto and Isdale 1985).

The extraction and measurement of FA concentration in annual coral bands

An amount of skeleton encompassing a full annual growth band was cut from the slab year by year. Since a couplet of light-dark bands represented one year (Wang and Huang 1989), the year when the annual band was formed could be sequentially determined. In this study, bands representing 1985 to 1973 were examined with 3 gm of powdered coral from each year, soaked in 20 ml 0.05N HCl, filled with nitrogen gas, sealed in a glass tube, shaken for 24 hr, and centrifuged at 10,000 rpm for 10 min. The (FA) in the supernatant was measured with a fluorometer at 410 nm emission spectrum (Fig. 2). Concurrently, a 3 gm sample of pure $CaCO_3$ (Sigma Chem. USA) was processed similarly as a blank.

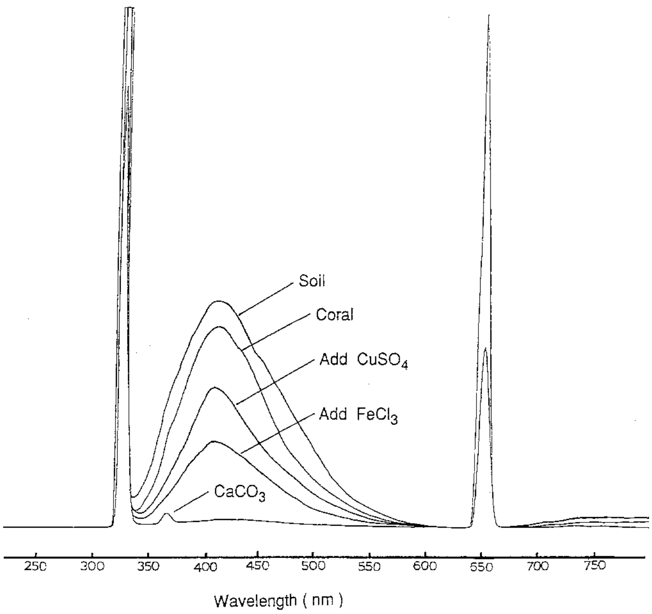

Fig. 2. The emission spectrum of fulvic acid from soil and coral. Excitation wave length was 350 nm. Spectrum of FA from coral was quenched after adding Cu^{+2} or Fe^{+3}

Table 1. The local precipitation record (mm/yr) of Nanwan, Wan-Li-Tong area (NW-WLT) and Hsiao-Liu-Chiou (HLC) island. Precipitation records at HLC were not available prior to 1974

Year	Precipitation (mm)	
	NW-WLT	HLC
1973	2506	
1974	3441	2059
1975	2072	2138
1976	1139	772
1977	2073	1747
1978	1925	1018
1979	2081	1497
1980	889	1126
1981	2328	1806
1982	1665	1279
1983	1772	1797
1984	2194	1458
1985	2419	876

Annual precipitation data were obtained from the National Central Weather Bureau, Republic of China (Table 1). Records from 1973 to 1985 were correlated with the year of coral band formation. The rainy season in southern Taiwan occurs in the summer months (usually May to September), which corresponds to when the high density bands formed (Wang and Huang 1987, 1989). Annual precipitation data matched yearly bands well.

Results and Discussion

The measurement of the annual growth bands (Table 2) showed that the average growth rate of *P. lutea* was 1.08 ± 0.12 cm per year while that of *F. maxima* was 0.83 ± 0.09 per year. There was little variation within one species of coral from the three sampling sites, suggesting

Table 2. The estimation of annual growth rate of *Porites lutea* and *Favia maxima* from different sampling sites. Individual specimens were marked with a sample number. Growth rate was the average width of growth bands in each individual

Sampling site	*Porites lutea*			*Favia maxima*		
	Sample no.	Growth rate (cm/year)	No. of growth bands	Sample no.	Growth rate (cm/year)	No. of growth bands
Nan-Wan	1	1.10±0.06	8	1	0.78±0.03	13
	2	1.05±0.08	10	2	0.87±0.06	8
	3	1.07±0.10	8	3	0.88±0.02	10
	4	1.05±0.07	12			
	5	1.07±0.11	9			
	6	0.92±0.07	12			
	Mean	1.04±0.10		Mean	0.84±0.06	
Wan-Li-Tong	1	0.82±0.01	12	1	0.79±0.01	11
	2	1.05±0.05	14			
	3	1.21±0.07	16			
	4	1.07±0.05	21			
	5	1.21±0.12	17			
	Mean	1.07±0.13		Mean	0.79±0.01	
Hsiao-Liu-Chiou	1	1.09±0.05	18	1	0.98±0.04	11
	2	1.17±0.13	13	2	0.67±0.04	11
	Mean	1.13±0.11		Mean	0.82±0.11	
Total from 3 sites	No. of samples:	13		No. of samples:	6	
	Mean	1.08±0.12		Mean	0.83±0.09	

Table 3. The linear regression correlation coefficient of fulvic acid in the annual growth band of *P. lutea* and *F. maxima* with local precipitation in different sampling localities

Location	Correlation coefficient between [FA] in coral bands and local precipitation	Sample size	
		Individuals	No. of annual bands used to correspond with precipitation
Nan-Wan Bay (NW)	0.9519	7	8
Wan-Li-Tong (WLT)	0.3723	4	12
Hsiao-Liu-Chio (HLC)	0.0921	3	8
Data pooled from three locations	0.3078		

that growth conditions of corals at the sites were similiar, making further comparisons of (FA) in annual growth bands possible.

On the other hand, the (FA) in the growth bands of corals from the three localities revealed different degrees of linear regression correlating with annual precipitation (Table 3). This FA most likely originated on land as determined by its fluorescence spectrum characteristics and by the 70% and 40% quenching effect in the presence of Fe^{+3} or Cu^{+2}, respectively (Fig. 2) (Boto and Isdale 1985). When a correlation coefficient was calculated based upon all the coral band (FA) values and all the precipitation data for all sites and all years, a correlation coefficient of $r=0.3078$ was obtained (Table 3). However, if the data from the three different localities were analyzed separately against local precipitation, more meaningful information was extracted. In this analysis, coral samples collected from each site were treated as coming from a homogeneous group. Therefore, (FA) values in coral years of different samples by site were averaged and then compared to the years of precipitation at each site. The NW area, a bay with nuclear power plant and semi-closed circulatory current pattern, showed a very high correlation coefficient of $r=0.9519$ (Table 3) while the WLT area, an open rocky coastal line, had a coefficient of $r=0.3723$. The HLC area, an isolated coral island, had a correlation coefficient of $r=0.0921$. Since there is no major river runoff in these 2 areas, the results may indicate that the accumulation of (FA) in the coral bands was influenced by other factors such as local topography, construction activity on adjacent land areas, dilution by the seawater, and residence time of seawater in the bay.

The construction of the power plant along the coast of NW lasted for 10 years (1975–1985) and caused a great amount of land-derived humic substances to be washed into the bay area by rainfall. These humic acids subsequently accumulated in hermatypic corals and may explain the high correlation between (FA) and precipitation. FA from runoff in WLT was also incorporated in the local corals. Since this area is much more open to dilution with open ocean waters than NW bay, the effect of local rainfall is much less. Therefore, only a moderate correlation was revealed between (FA) and precipitation with an r value similar to that of the pooled data (Table 3). Another extreme case was the coral island of HLC. Land-originated materials washed into the coastal waters by rainfall were greatly diluted by the open ocean around HLC. Hence, little FA would be available to be incorporated into the corals there, resulting in the low correlation between the (FA) and local precipitation. However, other factors, such as discrete water bodies

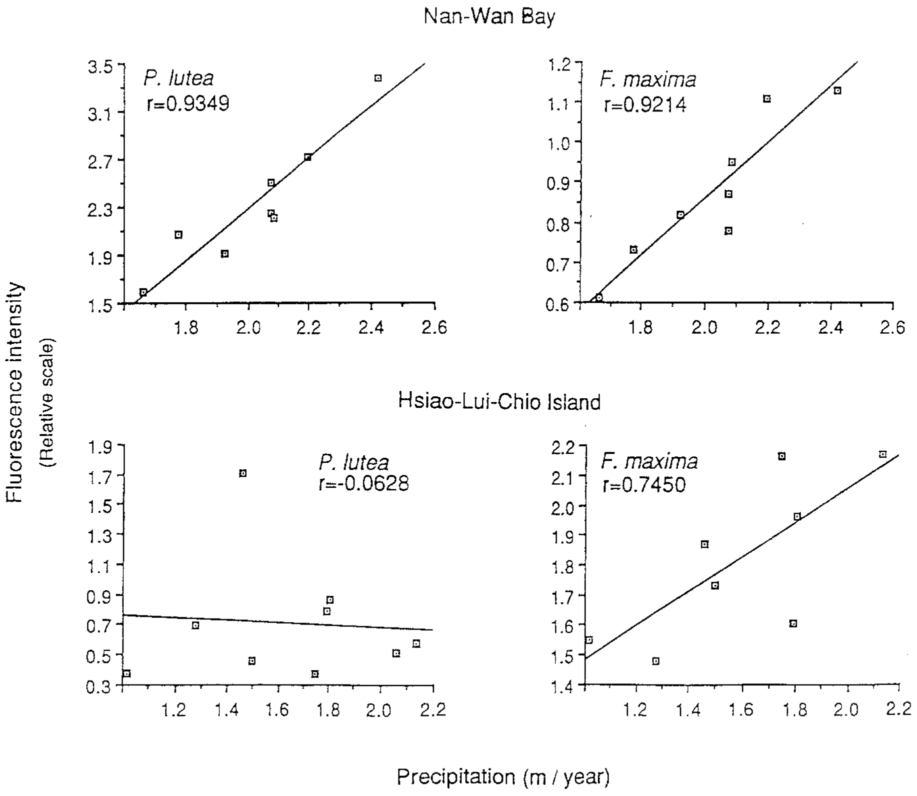

Fig. 3. The linear regression and correlation of average fulvic acid concentration in the annual growth bands of *P. lutea* and *F. maxima* with local precipitation in Nan-Wan bay and Hsiao-Liu-Chiou island

carrying different sources of terrestrial organic compounds, could have influenced these empirical data (Scoffin et al. 1989). These factors were not considered in this study.

Further studies on the ability of the two different species to accumulate FA are shown in Fig. 3. It was noticed that (FA) in both *P. lutea* and *F. maxima* gave good correlations ($r = 0.9349$ and 0.9214) with annual precipitation in NW bay. Yet that of the *P. lutea* from HLC showed a very low correlation ($r = -0.0628$) while that of the *F. maxima* gave a higher result ($r = 0.7450$). This suggests that when there was abundant (FA) in the water, both *P. lutea* and *F. maxima* could accumulate it in their skeletons. But if the (FA) is low, *F. maxima* is a much better biological monitor than is *P. lutea*. As there is little information about the mechanism of FA accumulation in different coral species, these results could prove important in choosing a proper species for biomonitoring purposes.

The use of fluorescent bands from FA in the skeleton of massive corals could be a powerful tool to detect the strength and periodicity of terrestrial rainfall and coastal runoff (Isdale 1988). Before the application of this method, as well as the application of other studies to use banded coral skeleton to monitor environmental changes, e.g. heavy metals, isotopes, organic pollutants, temperature, even biological activities (Chen et al. 1991; Druffel 1982; Dodge et al. 1984; Cortes and Risk 1985; Hudson et al. 1976; Flor and More 1977; Bak and Laane 1987), it is worth noting that important factors to be considered are the local topography of the sampling site, the ocean or current conditions nearby, and the sensitivity of the chosen coral species.

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