OBTAINING PAST TRENDS IN MARINE ENVIRONMENTAL CONDITIONS WITH CONTEMPORARY DATA

CHEN: -TUNG A. CHEN
Institute of Marine Geology
National Sun Yat-Sen University
Kaohsiung, Taiwan
REPUBLIC OF CHINA

ABSTRACT. Two major approaches have traditionally been used to obtain secular variations of pollutant concentrations in the past. The direct approach is to compare current data with data collected at different times. This approach, however, is often unreliable because few earlier data exist. Furthermore, those that are available are sometimes of poor precision or with doubtful accuracy. As a result, comparing these unreliable data with current reliable data does not always give a meaningful trend. The indirect approach is to obtain samples of various ages. By analyzing and dating these samples, one obtains the past trend. Analyzing and dating seawater and sediment samples are notable examples in oceanography and geology. Another indirect approach is to analyze pollutant concentrations in banded corals. A case study for trace metals and radionuclides is presented.

### INTRODUCTION

With the establishment of the 200-mile Exclusive Economic Zone (EEZ), exploitation of marine resources within EEZ is bound to increase. And with increased activities, there comes increased pollution and the potential for conflicts regarding the use of EEZ. From the scientific point of view, it is important to know how these human activities change the marine environment. From the practical point of view, it is also desirable, or necessary, to know whether the activity of a certain industry (or even better, a specific company) has added significant amounts of pollutants into the marine environment. It is therefore, important to establish a baseline for pollutant concentrations. Even if the baseline has already been altered by previous activities, we must still find a way to obtain the past trends of pollutant concentrations.

Generally speaking, there are two major approaches to obtain the past trends in the marine environment. The first approach compares present data with data obtained from previous years. The difference represents the variation of pollutant concentrations with time. The method is straight forward but has a major drawback when applied to chemicals of trace amount, because early data are scarce and frequently

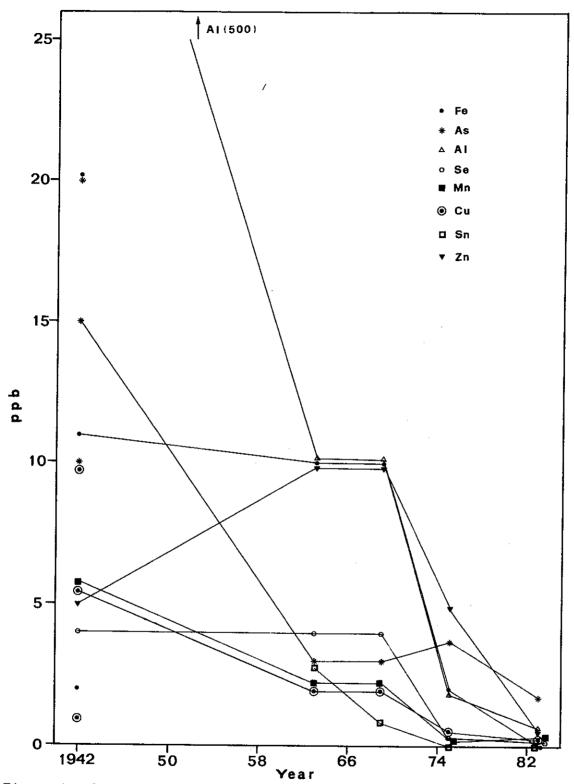


Figure 1. Concentrations of selected trace metals in seawater reported in different years (data from Goldberg, 1963; Horne, 1969; Brewer, 1975; Bruland, 1983).

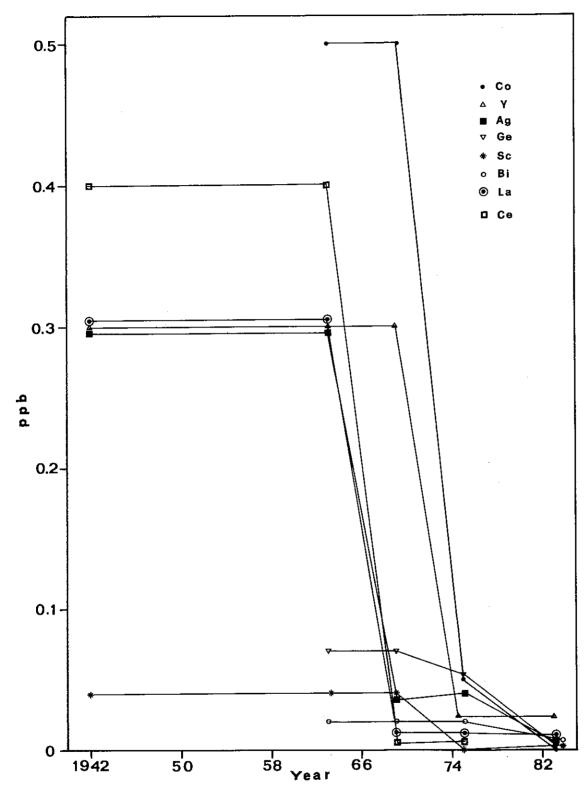


Figure 1. Continued.

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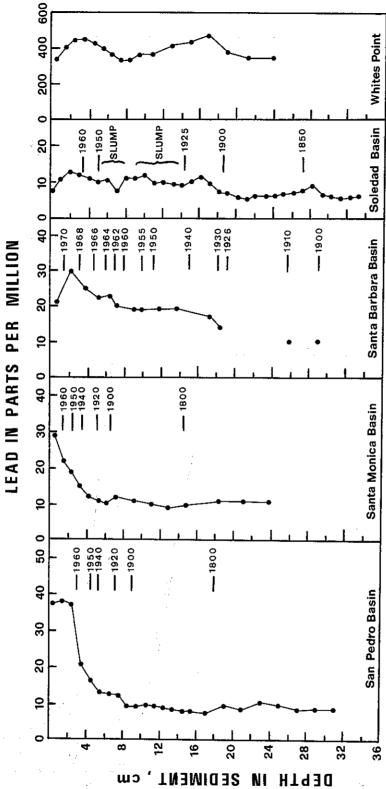


Figure 2. Vertical profiles of lead in sediments at San Pedro, Santa Monica, Santa Barbara Basins and Whites Point off southern California, and at Soledad Basin off Baja California (taken from Goldberg, 1975).

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unreliable. As a result, direct comparison of the present data with early data which have large uncertainties does not always give a meaningful trend.

Take heavy metals as an example, early samples were often contaminated during sampling, making the measured values artificially high. I have plotted seawater trace metal concentrations taken from text books published in different years (Fig. 1). The aluminium concentration reported in 1983 was only a quarter of the 1975 value. In other words, it was believed in 1983 that the aluminium concentration reported only eight years ago was a factor of four too high. Many other trace metals were also found to be much higher in 1975 than in 1983, and even higher in 1969 or 1963. If one took these results at face value, then one would arrive at the conclusion that trace metal concentrations in the marine environment are decreasing, which is almost certainly an erroneous conclusion.

The second major approach to obtain the past trends of pollutant concentrations in the marine environment is to use sediments. The vertical profiles of lead in sediments collected near southern California are plotted in Fig. 2 as an example. In general, the deeper the sediment, the older it is. It is obvious that the lead content is the highest near surface in the San Pedro, Santa Monica and Santa Barbara Basins. The values approach a constant, representing a baseline, for deep sediments deposited prior to 1900. The Soledad Basin off Baja California is away from major pollution areas and the lead concentration is relatively low throughout the sediment column. On the other hand, the Whites Point, which receives the Los Angeles area sewage outflow, has very high lead concentration in the sediments, as indicated clearly in the figure.

Sediments, however, only record what settles down, either as particles or as material absorbed on the surface. Sediments are also frequently re-worked or undergo diagenesis, thus disturbing the original signal. Further, dating sediments is not a trivial matter and it is difficult to obtain annual bands. Two other approaches have recently been used to obtain the past trends of pollutant concentration. The first approach is used to trace back pollutant concentrations in the water column, and the second provides accurate dates.

# 2. ANTHROPOGENIC SIGNAL IN SEAWATER

Deep and Bottom Waters are mainly formed in the polar regions. Once they sink below the air-sea interface, it may take hundreds of years before the water returns to the surface and contacts the atmosphere again. Consequently, subsurface waters of various ages record certain pollutant concentrations in the atmosphere when the water were last in contact with the atmosphere. Thus tracing waters of various ages provides a trend of pollutant variations especially if the pollutant remains in the dissolved phase and moves with water.

Figure 3 provides an example of the distribution of bomb-produced tritium in the Atlantic Ocean (Ostlund et al, 1976). Tritium penetrates all the way to the seafloor in the northern North Atlantic.

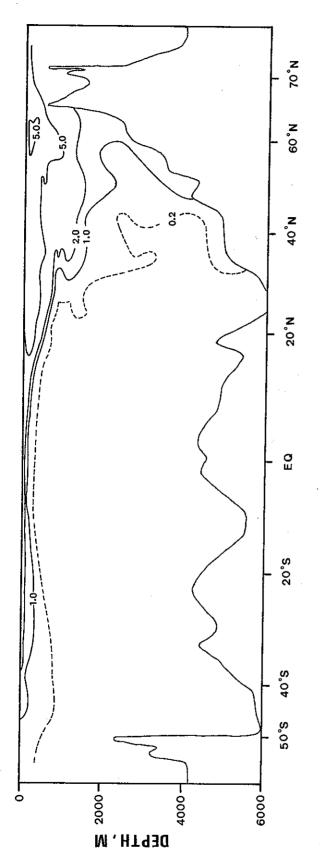


Figure 3. Cross-section of tritium in the Atlantic Ocean (taken from Ostland et al, 1976).

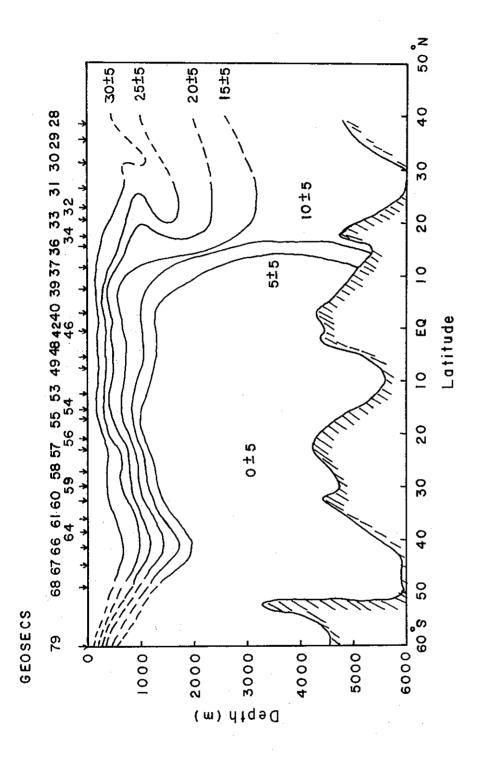


Figure 4. Cross-section of anthropogenic  ${\rm CO_2}$  in the Atlantic Ocean (taken from Chen and Drake, 1986).

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Further, there is a tritium minimum (older water) at an intermediate depth where remnant Antarctic Intermediate Water (AAIW) can be found. Tritium moves freely with water masses and does not undergo chemical reactions except by radioactive decay. Some chemicals, such as C-13 and  $\rm CO_2$ , however, are altered by the production and decomposition of organic material and calcium carbonate. (Chen and Millero, 1979; Chen, 1982; Kroopnick, 1985). Once these alterations are subtracted from the observed values, the contribution of the anthropogenic activities appears.

Figure 4 shows a cross-section of excess, anthropogenic CO<sub>2</sub> in the Atlantic Ocean (Chen and Drake, 1986). Deep waters south of 10°S do not contain any excess CO<sub>2</sub> because these waters were formed prior to industrialization and has not contacted fossil-fuel CO<sub>2</sub>. Near-surface waters and deep waters in the North Atlantic Ocean, however, were formed more recently, thus contain excess CO<sub>2</sub>. The highest amount of excess CO<sub>2</sub> is found in the surface waters now in contact with the atmosphere. An excess CO<sub>2</sub> minimum is found at the tritium minimum.

When fossil fuels are burned, the CO<sub>2</sub> released contains more C-12 relative to C-13 as compared to the atmosphere. As a result, the C-13C-12 ratio in the atmosphere has gradually decreased, and this signal can be traced in the oceans. Fig. 5 shows the preformed C-13 concentration for the Antarctic Intermediate Water in the Atlantic, Indian and Pacific Oceans (Chen and Chen, 1988). The AAIW is formed near the Subtropical Front and then spreads northward. Fig. 5 indicates that when older AAIW waters near the equator were formed, they contained more C-13 than more recently formed waters further south.

## 3. ANTHROPOGENIC SIGNAL IN CORALS

Several orders of corals form annual growth bands which can be used to study the environmental perturbations in both contemporary and paleocommunities. For example, patterns of annual banding has been used to assess the impact of long-term changes involving sedimentation, temperature and nutrients (Knutson et al, 1972; Hudson et al, 1976; Dodge et al, 1984). Several investigators have also attempted recently, to varying degrees of success, to use banded coral skeletons to document the chronology of coastal pollution (Dodge and Gilbert, 1984; Chen et al, 1986, 1988; Shen and Boyle, 1987, 1988; Shen et al, 1987). For instance, annual variations of several metals have been detected for samples collected in Southern Taiwan.

Figure 6 shows the variation of zinc and cadmium, both used heavily in industry (Chen et al, 1986; Cheng, 1988). Zinc shows the clearest increase with time and the values are higher for samples collected at Hsiao-Liu-Chiu near the heavily polluted industrial city of Kaohsiung. Local fishermen have complained that the dumping of slags from the China Steel Corp. off Kaohsiung starting in 1985 has increased the trace metal content, especially zinc, in seawater. Our data, however, indicate that the zinc concentration has started to increase at least 20 years ago. China Steel Corp., therefore, could not have been the culprit. Samples collected at the Third Nuclear

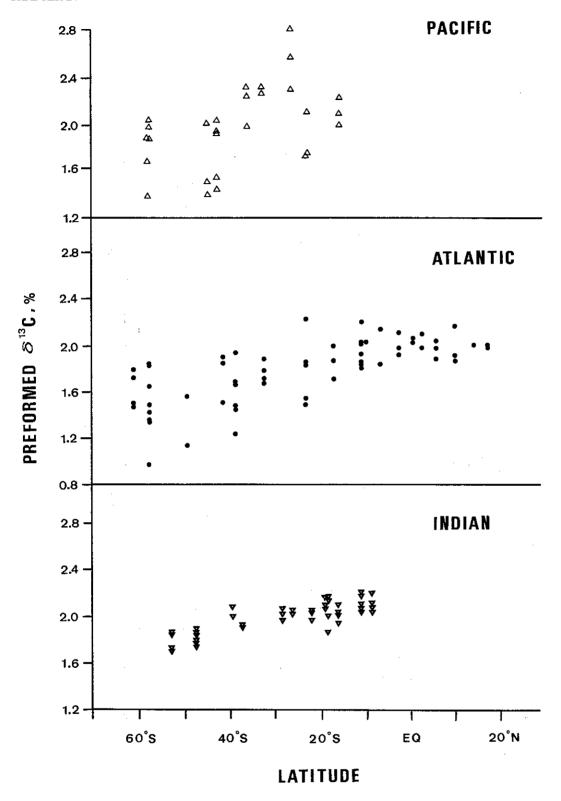
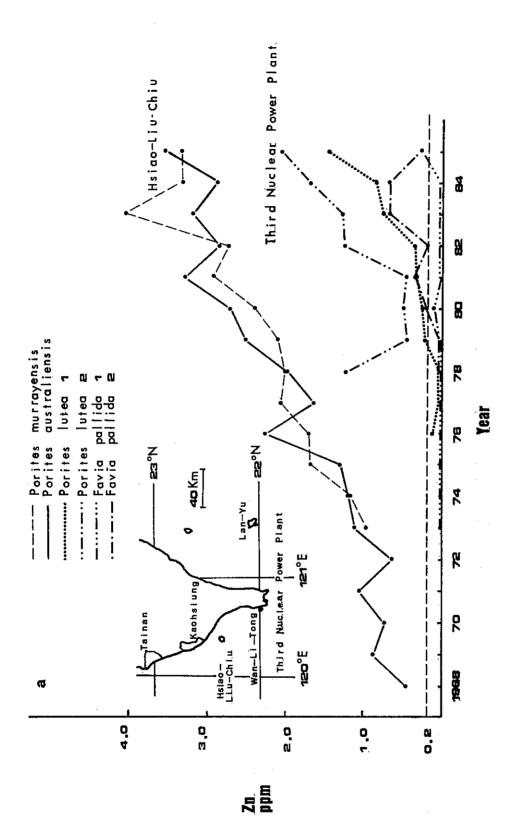


Figure 5. Preformed &C-13 concentrations for the Antarctic Intermediate Water.



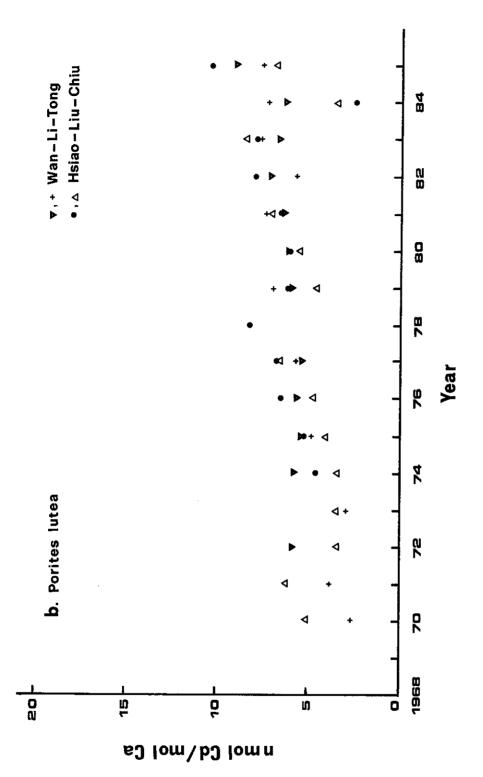


Figure 6. Annual variation of (a) zinc and (b) cadmium in corals collected in Southern Taiwan (taken from (a) Chen et al, 1986; and (b) Cheng, 1988)

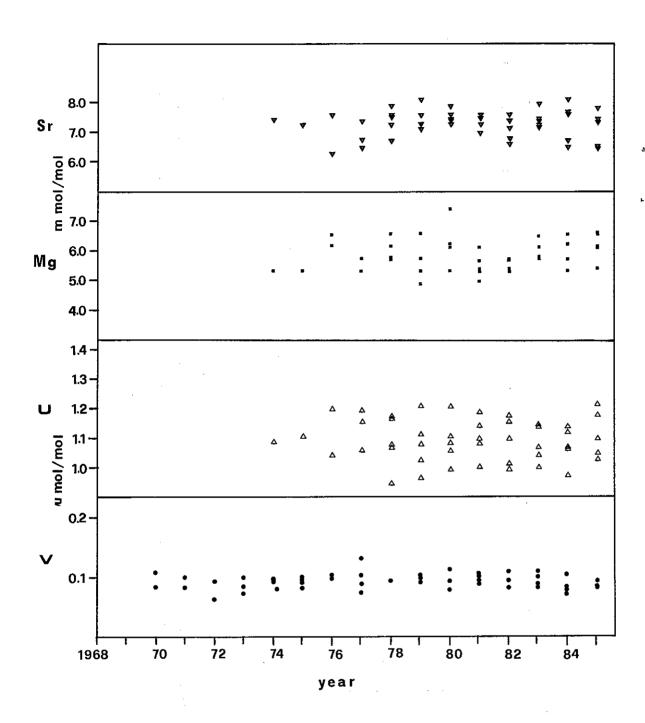


Figure 7. Annual variation of strontium, magnesium, uranium and vanadium in corals collected in Southern Taiwan (taken from Chen, unpublished results, 1986; and Cheng, 1988).

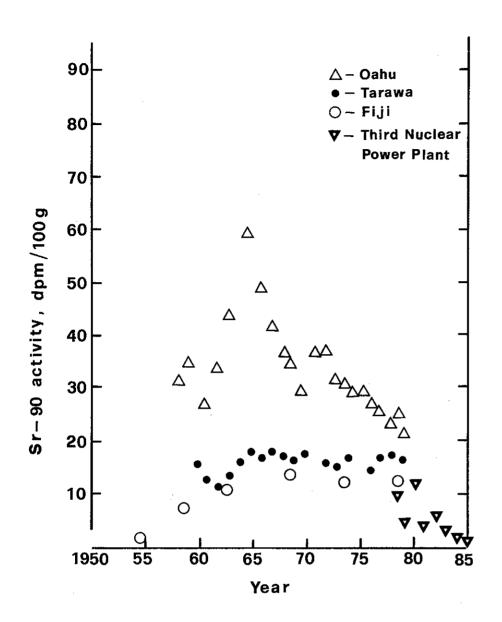


Figure 8. Annual variation of Sr-90 in corals (taken from Chen et al, 1988).

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Power Plant contain lower amount of zinc because the sampling site is far from any industrial activities except for the power plant. Cadmium shows a less clear trend but the concentration is also increasing.

Figure 7 shows the concentrations of strontium, magnesium, uranium and vanadium that we did not expect to detect annual variations because the anthropogenic inputs are swamped by the much higher natural background. Indeed we did not see any annual variations for these metals. Sr-90, on the other hand, was produced by a large amount relative to the natural environment during the atmospheric nuclear bomb tests which peaked in the early 1960s. The concentrations started to decrease since then and our samples collected near the Third Nuclear Power Plant confirm the decreasing trend reported elsewhere (Toggweiler and Trumbore, 1985). Since other artificial nuclides commonly discharged by a nuclear power plant, such as Mn-54, Co-60, Zn-65, Sb-125 and I-131, are undetectable in our samples, we believe that the Sr-90 comes mainly from the atmospheric fallout and the level is decreasing (Fig. 8).

#### 4. CONCLUSION

Certain anthropogenic signals can be detected in seawater and in corals. These signals can be used to establish past base-lines and to reveal the pollution history of the marine environment.

## 5. ACKNOWLEDGEMENT

I acknowledge the support of the National Science Council and the Nuclear Regulatory Committee of the Republic of China.

#### 6. REFERENCES

- Brewer, P.G. (1975) 'Minor elements in sea water', in Chemical Oceanography, V.1, 2nd ed., J.P. Riley and G. Skirrow, eds., Academic Press, London, pp.415-496.
- Bruland, K.W. (1983) 'Trace elements in sea-water', in Chemical Oceanography, V.8, 2nd ed., J.P. Riley and R. Chester eds., Academic Press, London, pp.157-220.
- Chen, C.T. (1982) 'On the distribution of anthropogenic CO<sub>2</sub> in the Atlantic and Southern Oceans', Deep-Sea Research 29, pp.563-580.

3

- Chen, C.T. (1987) 'Obtaining past trends in pollutant concentrations with contemporary data', Bulletin of Marine Science and Technology, 2, pp.38-48 (in Chinese).
- Chen, C.T.A. and Millero, F.J. (1979) 'Gradual increase of oceanic CO<sub>2</sub>', Nature 277, pp.305-307.

307

- Chen, C.T. and Drake, E. (1986) 'Carbon dioxide increase in the atmosphere and oceans and possible effects on climate', Ann. Rev. Earth Planet, Sci. 14, pp.201-235.
- Chen, C.T., Fang, L.S., Chang, K.H., Chou, E.C. and Hwang, J.C. (1986) 'Annual variation of heavy metals and radio-isotopes in corals in recent years', Proceedings, symposium on Marine Sciences, Kaohsiung, Taiwan, Republic of China, August, pp.141-147 (in Chinese).
- Chen, C.T.A., Chang, K.H. and Fang, L.S. (1988) 'Recent changes of trace metals and radionuclides in banded corals in southern Taiwan', Environmental Protection, in press.
- Chen, D.W. and Chen, C.T.A. (1988) 'The anthropogenic CO<sub>2</sub> signal in the Indian Ocean', Environmental Protection, submitted.
- Cheng, K.L. (1988) 'Method of trace metal pre-concentration and analysis in seawater and corals', thesis, Sun Yat-Sen Univ., Kaohsiung, Taiwan, 97pp.
- Dodge, R.E. and Gilbert, T.R. (1984) 'Chronology of lead pollution contained in banded coral skeletons', Mar. Biol., 82, pp.9-13.
- Dodge, R.E., Jickells, T.D., Knap, A.H. and Bak, R.P.M. (1984) 'Reef-building coral skeletons as chemical pollution (phosphorus) indicators', Mar. Pollut. Bull., 15, pp.178-187.
- Goldberg, E.D. (1963) 'The oceans as a chemical system', in The Sea. Vol. 2. M.N. Hill ed., Interscience, New York, pp.3-25.
- Goldberg, E.D. (1975) 'Marine pollution', in Chemical Oceanography, J.P. Riley and G. Skirrow, eds., Academic Press, London, pp.39-89.
- Horne, R.A. (1969) 'Marine Chemistry', Wiley-Interscience, New York, 568 pp.
- Hudson, J.H., Shinn, E.A., Halley, R.B. and Lidz, B. (1976) 'Sclerochronology, a tool for interpreting past environments', Geology, 4, pp.361-364.
- Knutson, D.W., Buddemeier, R.W. and Smith, S.V. (1972) 'Coral chronometers: seasonal growth bands in reef corals', Science., 177, pp.270-272.
- Kroopnick, P.M. (1985) 'The distribution of  $^{13}$ C and  ${\rm CO}_2$  in the world oceans', Deep-Sea Res. 32, pp.57-84.
- Ostlund, H.G., Dorsev, H.G. and Brescher, R. (1976) 'Tritium Laboratory Report No. 5, Univ. Miami, 192 pp.

308

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- Shen, G.T. and Boyle, E.A. (1987) 'Lead in corals: reconstruction of historical industrial fluxes to the surface ocean', Earth Planet Sci. Lett. 82, pp.289-304.
- Shen, G.T. and Boyle, E.A. (1988) 'Determination of lead, cadmium and other trace metals in annually-banded corals', Chem. Geol. 67, pp.47-62.
- Shen, G.T., Boyle, E.A. and Lea, D.W. (1987) 'Cadmium in corals as a tracer of historical upwelling and industrial fallout', Nature, 328, pp.794-796.
- Toggweiler, J.R. and Trumbore, S. (1985) 'Bomb-test Sr-90 in Pacific and Indian ocean surface water as recorded by banded corals', Earth Planet Sci. Lett. 74, pp.306-314.