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Oxalic, glyoxalic and pyruvic acids in eastern Pacific Ocean waters

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ABSTRACT

A sensitive high performance liquid chromatographic (HPLC) technique has been used to determine the concentration and distribution of several α-keto acids and oxalic acid in seawater samples from a station (28°29'N, 128°38'W) in the eastern Pacific Ocean. Glyoxalic, pyruvic and oxalic acids were found to be present. Although the pyruvic acid profile at this station was in general featureless, the profiles for glyoxalic and oxalic acids showed variations which could be attributed to both primary production and heterotropic activity. Surface waters were found to have a combined concentration of glyoxalic and oxalic acids of ~300 to 400 nm/liter which makes these two compounds some of the more abundant organic constituents of surface ocean waters.

1. Introduction

Low molecular weight α-keto acids and dicarboxylic acids are intermediates in many biological reactions, such as the tricarboxylic acid cycle, the catabolism and anabolism of amino acids, the fermentation of carbohydrates and glycolysis. Low molecular weight organic acids are also important algal exudates (Fogg, 1966; Hellebust, 1965). Profound increases in the concentrations of carbohydrates and amino acids have been shown to be associated with phytoplankton blooms in the ocean (Ittekkot, 1982) and the heterotropic utilization of these algal exudates should produce α-keto acids and dicarboxylic acids. Thus, measurements of the concentration of α-keto acids and dicarboxylic acids in oceanic waters could yield important information about the metabolic processes associated with primary production. In addition to biological sources, pyruvic and α-keto-butyric acids are intermediates in the nonbiological decomposition of the hydroxy-amino acids, serine and threonine, in seawater (Bada *et al.,* 1982; Bada and Hoopes, 1979).

Although a variety of low molecular weight organic acids have been investigated in marine sediments (Peltzer and Bada, 1981; Barcelona, 1980; Sasone and Martens, 1982) there have been few efforts to analyze for these compounds dissolved in

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seawater. Koyama and Thompson (1959) reported the presence of tricarboxylic acid cycle intermediates in seawater. However, because their analytical technique employed prolonged continuous extractions of seawater with chloroform or ether before chromatographic separation of the organic acids, the authors concluded that the organic acids detected likely resulted from the decomposition of other organic or biological components in the sample. Peltzer (1979) attempted to measure a suite of α-keto acids and dicarboxylic acids in a variety of seawater samples. However, this work was plagued by low recoveries and illustrates the difficulties involved in analytical procedures which require extensive concentration of the acids prior to analysis. Shah and Wright (1974) used a colorimetric procedure in order to measure glycolic acid in seawater. Because of the harsh chemical treatment required by this methodology, the specificity of the colorimetric response to glycolic acid may be questionable.

Previously we have reported (Steinberg and Bada, 1982) some initial measurements of α-keto acids and oxalic acid in some surface seawater samples using a reversed phase liquid chromatographic procedure. We report here the use of a modified and improved methodology using reversed phase and size exclusion chromatography to measure α-keto acids and oxalic acid. In addition we report results for a depth profile at a station located off the coast of southern California.

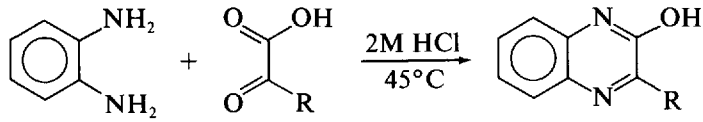
2. Experimental

a. Samples. Seawater was collected with a PVC niskin bottle and then immediately filtered through a precombusted GF/C filter in an all glass apparatus. The samples were shipped frozen back to the laboratory for analysis of combined amino acids (Bada *et al.*, 1982) and α-keto acids and oxalic acids.

b. Reagents. All reagents were as specified previously in Steinberg and Bada (1982). Various α-keto acids were purchased from Sigma; o-phenelene diamine (OPD; 98%) was obtained from Aldrich. Distilled in glass chloroform and acetonitrile and methanol were obtained from Burdich and Jackson. Triethylamine (analytical grade) was purchased from MLB and distilled before use. Analytical grade phosphoric acid was obtained from Mallinckrodt. AG50WX8, cation exchange resin was purchased from Bio-Rad and Sep-Pak C_{18} sample preparation cartridges were obtained from Waters. Deionized water was distilled twice in an all glass still before use. Hydrochloric acid (12 M) was diluted and subjected to two azeotropic distillations before use. Na_2SO_4 (Mallinckrodt analytical grade) was heated to 450°C for 24 hrs before use. All buffers were filtered through an 0.45μ Millipore HA filter. Zinc strips were obtained from Baker.

c. Sample preparation: α-keto acids. The various α-keto acids and oxalic acid were separated and quantified by reversed phase high pressure liquid chromatography

(HPLC) as their quinoxilinol derivatives. The quinoxilinols were synthesized according to the reaction shown in Eq. (1) using the method outlined in Steinberg and Bada (1982).

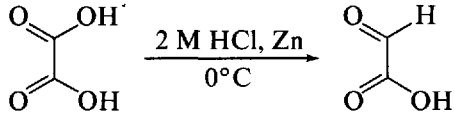


(1)

In a typical analysis, a 50 ml aliquot of seawater was acidified to pH 2–3 with 6 M HCl, and then spiked with an internal standard (α-keto caproic acid). A Sep-Pak C_{18} cartridge was prepared by rinsing with 50 ml of methanol and then 5 ml of water. The sample was then forced through the Sep-Pak using a disposable syringe, into a 125 ml erlenmeyer flask (with a ground glass stopper). The sample was then acidified by addition of 25 ml of 6 M HCl.

A 20 mg/ml solution of OPD in 2 M HCl was prepared fresh each day. A 3 ml aliquot of the OPD solution was added to the acidified sample which was then thoroughly mixed and covered with aluminum foil. The sample was then heated to 45°C for 3 hrs in an oven. At the end of the heating period, the sample was cooled to 0°C in a ice-water bath, and then neutralized with 15 ml of 10 M NaOH. Formic acid (88%, 5 ml) was added immediately and the sample pH adjusted to 2.5 with 10 M NaOH and 6 M HCl. The buffered sample was then extracted three times with 50 ml of $CHCl_3$. The extracts were combined, dried over Na_2SO_4 and then filtered through Whatman 1 filter paper. The sample was concentrated by rotary evaporation at 35°C to ~2 ml. The remaining $CHCl_3$ was removed under a stream of N_2, and the residue was dissolved in water for HPLC analysis.

d. Sample preparation: oxalic acid. Oxalic acid was analyzed following its reduction to glyoxalic acid according to the following reaction:



(2)

Seawater (100 ml) was acidified to pH 2–3 and treated with the Sep-Pak. A glass chromatography column (3 × 150 cm) was filled with 150 ml of AG50WX8. The resin was regenerated in the column by washing successfully with four column volumes of 2 M NaOH, water, 2 M HCl, and water. The seawater sample was passed through the column followed by 150 ml of water. The total eluant was collected. The eluant's volume was reduced to ~0.25 ml by rotary evaporation (in a pear shaped evaporation flask). HCl (2 ml of 2 M) was then added to the sample, which was then cooled to 0°C in an ice-water bath. A zinc strip (3 mm × 7 mm) was wrapped around a glass rod. The zinc strip was cleaned by dipping in 70% HNO_3 for ~2 sec and then rinsing with water

and 2 M HCl. The cold sample was exposed to the zinc for 15 minutes to reduce oxalic acid to glyoxalic [i.e., Eq. (2)].

At the end of the reduction period, 0.2 ml of OPD reagent was added to the sample. The sample was then heated to 45°C for 3 hrs in order to form the quinoxilinol. After 3 hrs the sample was again cooled to 0°C and neutralized with 0.5 ml of 10 M NaOH. Formic acid (0.02 ml of 88%) was added. The pH was then adjusted to 2.5 by addition of 6 M HCl or 10 M NaOH. The sample was extracted with two 5 ml portions of $CHCl_3$. The extracts were combined and filtered through Whatman 1 filter paper. The chloroform was removed under a stream of N_2, and the residue redissolved in 50 to 100 μl of water in preparation for analysis by HPLC.

It was found that this reduction procedure resulted in partial conversion (30%) of glyoxalic acid to glycolic acid. However, the extent of this reduction was highly reproducible. The fluorescence yield for oxalic acid with this procedure was highly linear in the range of 0–15 nmoles of oxalate (r^2 = 0.986). The oxalic acid concentration in the seawater samples was determined by comparing the glyoxalic acid concentrations in reduced and unreduced desalted seawater samples.

e. Chromatography. The liquid chromatograph was an Altec model 310, equipped with a Gilson Spectra Glo fluorimeter, with an excitation filter at 330–400 nm and an emission filter at 410–520 nm.

The quinoxilinol derivatives were separated by a two dimensional chromatographic procedure, involving both size-exclusion and reversed phase. Size exclusion chromatography was performed on a Lichrosorb Si-100 (10 μ, 0.46 × 25 cm) column. The column was protected with a guard column (0.2 × 5 cm) of Perisorb A (Merck, 35–40 μ). The exclusion limit of this column is 3×10^3 daltons. The reversed phase column was a Sperisorb 5-S (5 μ, 0.46 × 25 cm). The column was protected with a guard column (0.2 × 5 cm) of Co:pell ODS (Whatman, 35–40μ). The two columns were connected in series through a Reodyne 70–10 HPLC sample injection valve. The valve was plumbed so that when in the "load" position the size exclusion column effluent was vented to drain. When the reodyne valve was actuated to "inject" the size exclusion column effluent entered the reversed phase column.

A triethylamino phosphate (TEAP) buffer was used for chromatography. The buffer was prepared as follows. A reagent grade phosphoric acid solution (0.1 moles in 800 ml of H_2O) was titrated to pH 6 with triethylamine. The final volume was adjusted to 1 liter, and the buffer filtered through a 0.45 μ millipore filter before use. Acetonitrile was used as the organic modifier.

The chromatographic conditions were as follows. With the Reodyne valve in the "inject" position both columns were equilibrated with 10% acetonitrile/TEAP. Before beginning the analysis the Reodyne valve was moved to "load" and the flow rate adjusted to 0.5 ml/min. The sample (20–50 μl) was injected and after 7 minutes the

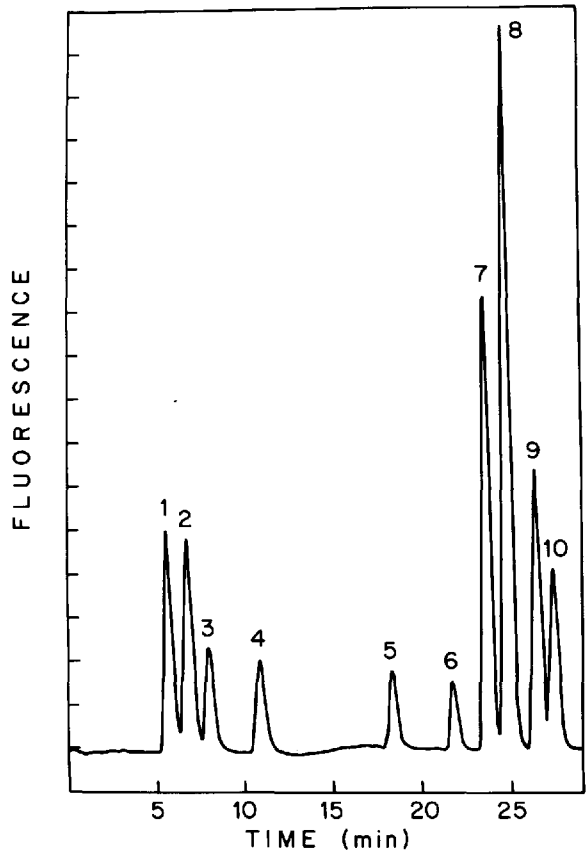


Figure 1. A standard chromatogram of 10 α-keto acid quinoxilinols. Chromatographic conditions are specified in the text. Peak identifications are as follows: (1) α-ketoglutaric; (2) α-ketoadeptic; (3) glyoxalic; (4) pyruvic; (5) α-ketobutyric; (6) α-ketovaleric; (7) α-ketoisovaleric; (8) α-keto-caproic; (9) α-ketoisocaproid; (10) β-methyl-α-ketovaleric. Time (min) starts when the size exclusion column effluent is switched to the reversed phase column.

Reodyne valve was actuated to "inject." At this time the flow rate was increased to 1 ml/min. At 8 minutes a 4 minute gradient to 0% acetonitrile was performed followed immediately by a 30 minute gradient to 50% acetonitrile. All 10 of the straight and branched chain quinoxilinols in the standard mixture were separated by this procedure (Fig. 1).

Standard responses for the various acids were determined by analyzing seawater samples that were spiked with 20 nmoles of each organic acid. These response factors correct for nonquantitative recovery. The analytical precision of the analyses was within 20%.

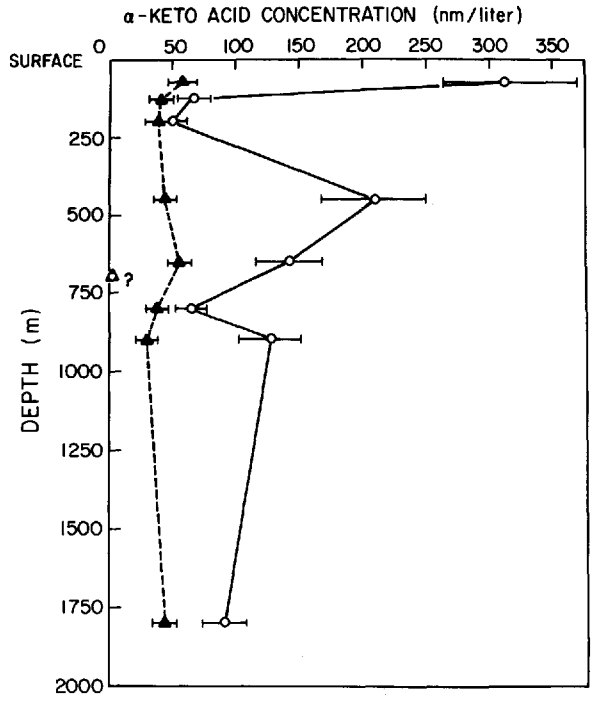


Figure 2. Vertical profile of glyoxalic (○) and pyruvic (▲) acids at 28°29′N and 121°38′W (Geosecs I station). The analytical blank concentrations are 25 nm/liter and 10 nm/liter for glyoxalic acid and pyruvic acid, respectively.

3. Results

This analytical scheme was used to determine the concentrations in the water column of several α-keto acids and oxalic acid at a station located at 28°29′N and 121°38′W (near the Geosecs I Station). Two α-keto acids, glyoxalic and pyruvic acids, as well as oxalic acid were found to be present in measurable concentrations. Other α-keto acids were not detectable. The concentrations of glyoxalic, pyruvic and oxalic acids with depth are given in Figs. 2 and 3.

Glyoxalic and oxalic acids both have high concentrations at 75 m and then decrease to a minimum at ~250 m. Both glyoxalic acid and oxalic acid increase to a subsurface maximum at 450 m and 650 m respectively. Below 1000 m oxalic acid apparently increases in concentration while glyoxalic acid remains approximately constant. The pyruvic acid profile is featureless within the analytical precision of these measurements. In all three profiles one point at 700 m was lower than 5 nm/liter. These measurements were suspect because they were far below blank levels for all three organic acids.

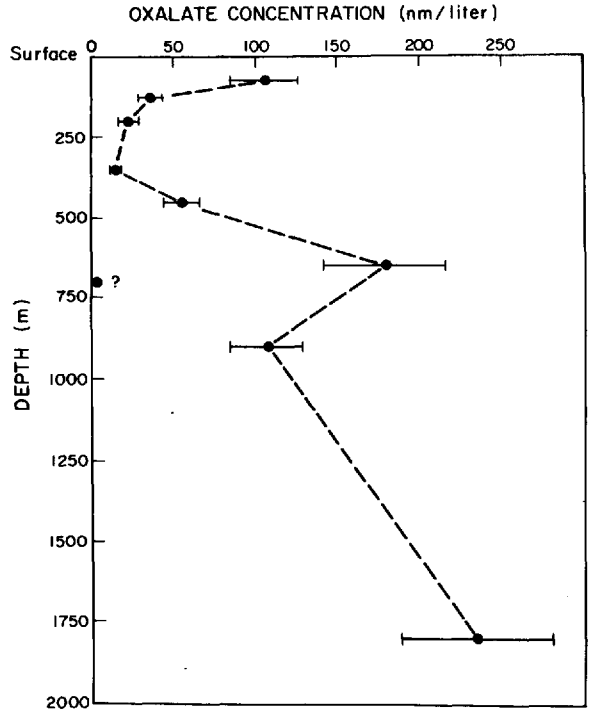


Figure 3. Vertical profile of oxalic acid concentration at 28°29'N and 121°38'W (Geosecs I station). The analytical blank concentration is 20 nm/liter.

4. Discussion

Few data are available on low molecular weight organic acids in seawater. This is partially due to the lack of sensitive analytical techniques and the high volatility of the compounds, which makes their concentration from large volumes of seawater impractical (Peltzer, 1979). Thus, the concentration and distribution of biologically important organic compounds (i.e., formate, acetate, lactate, pyruvate, glycolate, glyoxalate, succinate, and oxalate) in the ocean is effectively unknown. Since algae may exude a large proportion of photoassimilated carbon as glycolate this compound has attracted some attention (Watt, 1966; Fogg, 1966; Wright, 1970). Shah and Wright (1974) measured 0–800 μg/liter (0–11 μM) of glycolic acid in coastal seawater, using a colorimetric procedure, which they attributed to an algal source. The concentrations that are reported here for oxalic, glyoxalic and pyruvic acids at the Geosecs I station indicate that these compounds are present in seawater at levels comparable to glycolic acid.

The possible role of low molecular weight organic acids in the organic carbon cycle

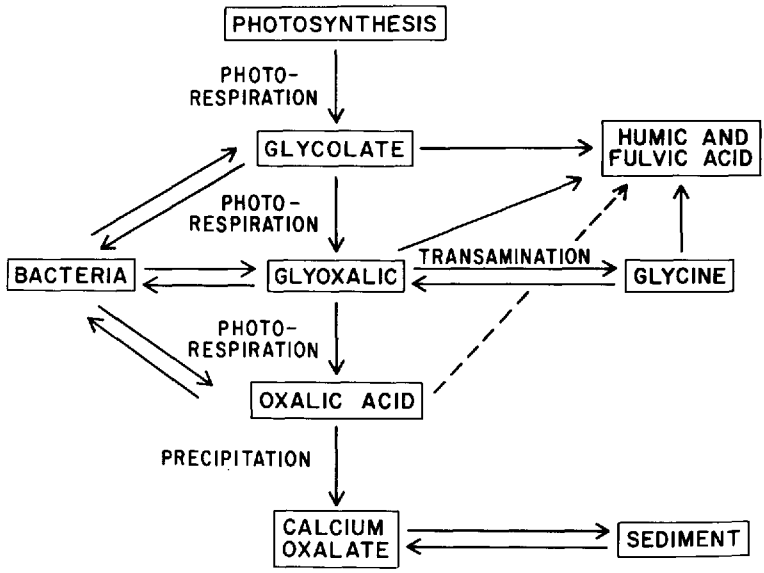


Figure 4. Proposed model of the physical and biological processes involving various low molecular weight organic constituents (glycine, glycolic acid, glyoxalic acid and oxalic acid) in seawater.

of seawater is illustrated in Figure 4. As is shown, the presence of glycolic acid, glyoxalic acid and oxalic acid in surface seawater may be a result of photorespiration. Glycolic acid is produced by photooxidation of ribulose diphosphate. Further enzymatic oxidation of glycolic acid produces glyoxalic acid which may, in turn, be oxidized to oxalic acid (Tolbert, 1980). Glyoxalic acid produced in this way may enter the glyoxalic acid cycle or be transaminated to glycine. Glycine may be hydroxymethylated to form serine. Glycine and serine are both important by-products of photorespiration. Lee (1975) found that serine is one of the most concentrated free amino acids in coastal seawater. Mopper and Lindroth (1982) have also found relatively (to other amino acids) high concentrations of serine and glycine in the Baltic Sea. Thus, glycine, serine, glycolic acid, glyoxalic acid and oxalic acid in surface waters of the ocean may all be products of photorespiration.

Oxalic acid is a common constituent of forest soils where it is produced by soil fungi (Graustein and Cranack, 1977). In addition, calcium oxalate crystals are found in the vacuoles of certain marine algae (Friedman *et al.*, 1972). Oxalic acid has also been found to be the most concentrated low molecular weight dicarboxylic acid in the surface sediments of the Santa Barbara Basin and the Cariaco Trench (Peltzer and Bada, 1981). Diffusion from these anaerobic sediments may be a possible source of oxalic acid in the overlying water column.

α-Keto acids and oxalic acid are products and substrates of marine bacteria and

other heterotrophs capable of assimilating dissolved organic compounds. The concentration profiles of Figures 2 and 3 show a subsurface maximum for both glyoxalic and oxalic acid. Both maxima are in the region of the O_2 minimum for this station (Craig and Weiss, 1970). Maxima in other chemical and biological features have also been noted to occur in the region of the O_2 minimum. For example, Liebeziet *et al.* (1980) observed a broad maximum in total dissolved carbohydrates, in the Sargasso Sea, at ~200–500 m, where O_2 depletion is just beginning. Menzel and Spaeth (1962) observed a similar maximum in vitamin B-12, in the Sargasso Sea, at a station located off Bermuda. The ATP measurements of Karl *et al.* (1976), in waters located off southern California indicated that a maximum in bacterial biomass commonly occurs between 500–800 m which is approximately the depth of the O_2 minimum. Significantly the phosphate and the nitrate maxima also occur at this depth.

The microbial population of the O_2 minimum are likely maintained by the sinking of particulate organic carbon (POC) from the eutrophic zone (Karl *et al.*, 1976; Liebezeit *et al.*, 1980). The rate of descent of POC may be retarded or arrested at density discontinuities in the water column (Leman, 1979), where the O_2 minimum is found. Local increases in POC, at density discontinuities, should stimulate heterotropic activity. This metabolic activity is responsible for the phosphate and nitrate maxima and may also lead to maxima in the concentration of bacterial metabolites, such as low molecular weight α-keto acids. This process is indicated in Figure 4 by the bacterial contribution.

Oxalic acid may possibly be removed from the water column as a calcium salt. For example, the calcium oxalate mineral weddelite has been isolated from sediments of the Weddell Sea (Bannister and Hey, 1936) but there have been no observations of this mineral in other marine sediments. The possibility of nonbiological precipitation of calcium oxalate from seawater can be addressed by estimating the degree of saturation of seawater with respect to this mineral. This estimate can be made using the ion solubility product for calcium oxalate in 0.7 M NaCl; e.g., $K_{sp} = 2.5 \times 10^{-8}$ at 0°C and 5×10^{-8} at 20°C, (Linke, 1958). For the oxalate concentrations which we report here, the calculated degree of saturation was found to be <0.1. These calculations indicate that precipitation of calcium oxalate is unlikely in the ocean. However, coprecipitation of oxalate with other mineral phases or the scavenging of calcium oxalate ion pairs on marine particulates may be a viable mechanism for removal of oxalate from the water column (Okamura *et al.*, 1983). Arrhenius (1963) has suggested that weddelite was an artifact generated by inadequate preservation of Antarctic cores. The microbial mediated decomposition of the organic matter during storage of the core may result in the production of enough oxalic acid for the precipitation of weddelite. Also, in the highly productive waters of the Weddel Sea, the oxalate concentrations could be considerably higher than we have measured at the Geosecs I station and thus these waters might be more highly saturated with respect to calcium oxalate.

The concentrations of oxalic acid and α-keto acids that are reported here are of the

same order of magnitude in concentration as other labile organic compounds in seawater. Amino acids have been found in seawater in both the free and the combined (peptides and marine humics) form. Free amino acids have been observed in the equatorial Pacific and in the Sargasso Sea, at total concentrations less than 100 nM, in surface water, with concentrations decreasing rapidly with depth (Lee and Bada, 1975, 1977). Recently, Liebezeit *et al.* (1980) observed that free amino acids and carbohydrates are concentrated at pycnoclines, where concentrations 2–3 times that of surface waters are achieved. Free amino acid concentrations may be highly variable in both time and depth, as a result of phytoplankton variabilities and variations in zooplankton grazing. Hammer and Eberlein (1981) demonstrated that algal blooms may cause profound increases in free amino acid concentrations in outdoor plastic tanks (increase of 0.2 μM to 1 μM). A similar phenomenon has been reported by Dawson and Pritchard (1978). Mopper and Lindroth (1982) studied diel and depth variability in free amino acid concentrations in the Baltic Sea. They found low concentrations early in the day (~40 nM) with 5 to 10 fold increases in concentration by late evening. Total and combined carbohydrates have been studied in the North Sea during a phytoplankton bloom, by Ittekkot *et al.* (1981). Concentrations were found to vary from 40–400 μg/liter (0.2 to 2 μm). Maximum release of carbohydrate occurred during the peak of the bloom. Mechanisms similar to those involving these other organic compounds may be responsible for determining the distribution of oxalic and glyoxalic acids in the oceans.

5. Conclusion

Some preliminary results on the concentration and distribution of oxalic, glyoxalic and pyruvic acids, in seawater, indicate that investigations of these low molecular weight organic acids could provide a greater understanding of biological oceanographic processes such as energy transduction in the marine food web and the organic carbon cycle. In addition, these results indicate that a sizable fraction of the DOC may be comprised of these low molecular weight organic acids.

In the future, measurements of these compounds should be made in conjunction with detailed hydrological and biological studies, as well as the simultaneous measurement of other classes of organic compounds. Such detailed investigations will clarify the role of low molecular weight organic acids in the organic chemistry of seawater.

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