

Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air–sea exchange

Xianliang Zhou ^{a,*}, Kenneth Mopper ^b

^a Brookhaven National Laboratory, Environmental Chemistry Division, Upton, NY 11973, USA

^b Department of Chemistry, Washington State University, Pullman, WA 99164, USA

Received 28 November 1994; accepted 6 August 1996

Abstract

Coastal and oceanic surface microlayer samples were collected using a stainless steel screen, along with subsurface bulk seawater, and were analyzed for low-molecular-weight (LMW) carbonyl compounds, including formaldehyde, acetaldehyde, propanal, glyoxal, methylglyoxal, glyoxylic acid and pyruvic acid. The enrichment factor in surface microlayer compared to corresponding subsurface seawater ranged from 1.2 to 21. A time-series measurement at a coastal site showed strong diurnal variations in concentrations of the LMW carbonyl compounds in the surface microlayer and in the enrichment factor, with maxima in the early afternoon and minima in the early morning. Exposure of samples to sunlight resulted in the higher yields of these compounds in the surface microlayer than in the bulk seawater, by a factor of 1.1–25, suggesting that the higher photoproduction rate of LMW carbonyl compounds in the surface microlayer accounts for the majority of the observed enrichment in these samples. Potential sinks include biological uptake and mixing. Air–sea exchange may be a source for soluble compounds and a sink for less soluble compounds. The enrichment of the LMW carbonyl in surface microlayer may alter their net air–sea exchange direction, e.g., from the ocean as a potential sink to a source for atmospheric acetaldehyde and acetone. The residence times of the LMW carbonyl compounds in the microlayer were estimated to be on the order of tens of seconds to minutes using a modified two-layer model. However, to maintain the observed microlayer enrichment factor, the residence time should be on the order of ~ 1 hour. This prolonged residence time may be due to organic enrichment in the surface microlayer ('organic film') which inhibited molecular transfer of carbonyl compounds into and out of the microlayer. The deviated behavior from model prediction may also be due to changes in the apparent partition coefficients of these species as a result of their physical and chemical interactions with organic matrix in the surface microlayer.

Keywords: carbonyl; photoproduction; surface microlayer; seawater; air–sea exchange

1. Introduction

Low-molecular-weight (LMW) carbonyl compounds are of special interest in the cycling of organic carbon in the ocean: They are produced

* Corresponding author. Present address: Wadsworth Center, Empire State Plaza/D514, Albany, NY 12201-0509, USA.

photochemically from the degradation of refractory dissolved organic matter (DOM), such as humic substances, in the ocean surface water (Kieber and Mopper, 1987; Kieber et al., 1990; Mopper et al., 1991); and they are biologically labile as they are taken up quickly by microorganisms (Kieber and Mopper, 1987; Kieber et al., 1989; Mopper et al., 1991). Coupling the two processes has been shown to be a major cycling pathway for the refractory marine DOM (Mopper et al., 1991) and riverine DOM (Kieber et al., 1990) in the ocean.

The surface microlayer is a unique environment in the ocean: It is enriched in DOM, including UV-absorbing humic substances and phenolic compounds, as well as trace metals, particulate matter and microorganisms (Liss, 1975; Carlson, 1982, 1983). It is exposed to the most intense solar radiation compared to the rest of water column. Upon absorbing sunlight, especially UV light, a series of photochemical reactions may occur in the microlayer, such as photoproduction of LMW carbonyl compounds, as has been shown to occur in the upper water column (Kieber and Mopper, 1987; Kieber et al., 1990). The compounds thus produced may be utilized by microorganisms in the microlayer, mixed down into the water column, and lost to the atmosphere by exchange across the interface (Thompson and Zafiriou, 1983; Conrad and Seiler, 1988).

In this paper, we present results of measurements of carbonyl compounds in surface microlayer and corresponding subsurface seawater samples collected in the open ocean and in coastal waters, demonstrate their photochemical production as a major source in the surface microlayer, and discuss the effect of surface microlayer enrichment of these compounds on their air–sea exchange.

2. Experimental

2.1. Materials

2,4-Dinitrophenylhydrazine (DNPH) was obtained from Sigma (St. Louis, MO) and was recrystallized twice from HPLC-grade acetonitrile. The DNPH reagent solution (20 mg DNPH in 15 ml of 2:5:1 concentrated HCl-water-acetonitrile) was further purified by three extractions with 2 ml carbon tetra-

chloride (CCl_4) to remove hydrazone impurities (Mopper and Stahovec, 1986; Kieber and Mopper, 1990). HPLC grade acetonitrile was from Baker (Phillipsburg, NJ) or Burdick and Jackson (Muskegon, MI). CCl_4 was Burdick and Jackson high purity solvent. Deionized water was obtained from a Millipore-Q-water system with an Organex attachment (Millipore, Milford, MA). Carbonyl compounds were obtained from Aldrich (Milwaukee, WI).

2.2. Samples

Surface microlayer and subsurface seawater samples were always collected at the same time. The surface microlayer samples were collected using a metal screen sampler (Garrett, 1965). The sampler was made of a 16-mesh stainless steel screen fitted into a 24 cm \times 24 cm chromium-plated wire frame. The sampler was dipped vertically into the water until completely submerged and drawn slowly and horizontally from the surface. The samples were drained into a 100-ml dark glass bottle via a glass funnel. A surface layer thickness of about 150 μm was sampled. Subsurface seawater samples were taken by hand with a glass bottle from a depth of 10–20 cm. Long polyethylene gloves were always worn during sampling. Glassware was cleaned by rinsing several times with 0.1 M HCl solution, acetonitrile, Millipore-Q-water and seawater samples. The metal screen sampler was cleaned by rinsing three times with acetonitrile and soaking in Q-water, and then dipping into seawater at least four times prior to microlayer collection.

Oceanic surface microlayer and subsurface seawater samples were collected in the south Sargasso Sea (~ 100 km east of the Bahamas), in March 1989, on a zodiac while steaming into the wind, about 1 km up-wind of the RV 'Columbus Iselin'. A diurnal study was carried out in Hatchet Bay, Eleuthera Island, Bahamas. During that study, the RV 'Columbus Iselin' was anchored ~ 3 km away and a zodiac was used for sampling. Coastal samples were taken from Biscayne Bay, FL, off the dock at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS), University of Miami.

Samples for carbonyl analysis were derivatized with DNPH within 1 hour after collection. Samples for irradiation experiments were kept in dark at 4°C

in glass bottles with Teflon-lined caps, and were used usually within 24 hours, but not longer than 2 weeks. Samples were not filtered to avoid contamination (Mopper and Stahovec, 1986). However, large particles in microlayer samples were allowed to settle out for ~30 min and the top portion of the sample was carefully decanted and used. Previous studies (Mopper and Stahovec, 1986; Kieber and Mopper, 1987) showed no difference between the carefully filtered and the unfiltered seawater samples from both coastal and oceanic regions with respect to both concentration measurement and photochemical production of LMW carbonyl compounds.

2.3. Irradiation conditions

Most irradiation experiments were carried out in 250-ml quartz flasks (with ground quartz stoppers) with natural sunlight (4-hour, solar noon, cloudless, 26°N). In addition, irradiation of Hatchet Bay samples was carried out using 80-ml quartz tubes (with ground quartz stoppers) in a merry-go-round irradiation system with a 450-W medium-pressure mercury lamp in a borosilica immersion well (about 290-nm wavelength cut-off) (Ace Glass, Vineland, NJ). The results from the irradiation system were normalized to natural sunlight by comparing formaldehyde production rate in Biscayne Bay seawater using the system and natural sunlight. Dark incubation was used as a control in every experiment to correct the photoproduction rate of carbonyl compounds.

2.4. Carbonyl analysis

LMW carbonyl compounds were determined by high performance liquid chromatography (HPLC) with UV-absorbance detection at 370 nm, after forming DNPH derivatives (Mopper and Stahovec, 1986; Kieber and Mopper, 1990). Briefly, derivatization was performed in a 7-ml Teflon vial by adding 50 μ l of purified DNPH solution to 5 ml sample. Solution was injected directly into the HPLC system after 1 hour reaction. A blank was obtained by injecting the sample solution immediately after reagent addition. To achieve a better detection limit, a few open ocean samples were pre-concentrated onto precleaned Sep-Pak C18 cartridges (Waters, Milford, MA) after 1-hour derivatization. Excess DNPH was immediately washed off the cartridge with 25-ml 13% aceto-

nitrile in water, and the hydrazone derivatives were eluted with 1 ml acetonitrile (Kieber and Mopper, 1990). In order to focus the DNPH-carbonyl derivatives at the top of the column, the eluates were diluted five times with Q-water immediately before injection into the HPLC system. A blank was obtained using a deep ocean water sample in an analogous fashion, except the sample was extracted immediately after DNPH addition to the seawater sample.

The HPLC system consisted of an E-Lab Model 2020 gradient programmer and data acquisition system (OMS Tech, Miami, FL) installed in an IBM-compatible PC, an Eldex Model AA-100S pump (Eldex Laboratories, Menlo Park, CA), and a six-port Valco injector (Valco Instruments, Houston, TX) with 2-ml sample loop. The mobile phase was generated by an inert solenoid valve placed on the low-pressure side and controlled by the E-Lab system. DNPH and carbonyl derivatives were separated on a reverse-phase C18 Radial-Pak column (Type 8NVC184, Waters), and detected by an ISCO Model V4 variable-wavelength absorbance detector (ISCO, Lincoln, NE).

Two mobile phases were used: 10% acetonitrile in water at pH 2.5 (A) and acetonitrile (B). A short gradient program was used for most of the analyses: isocratic at 36% B for 2 min, from 36% B to 53% B in 4 min, isocratic at 45% B for 8 min, and 45% B to 80% B in 8 min. The column was cleaned with 100% acetonitrile for 2 min before returning to the initial conditions. A long program was used for the analysis of higher aldehydes in the pre-concentrated samples. This program was the same as the short one except for the last two steps, i.e., from 45% B to 80% B in 10 min, and isocratic at 100% B for 20 min to elute the higher aldehydes. The flow rate was 1.5 ml/min, and the column was kept at ambient temperature.

3. Results and discussions

3.1. Photochemical production of carbonyl compounds

Surface microlayer and subsurface samples for photochemical experiments were collected at a pristine site in Hatchet Bay, Eleuthera Island, Bahamas during a cruise to the southern Sargasso Sea and

Bahamas, and in Biscayne Bay, FL, off the dock at RSMAS. Fig. 1 shows chromatograms of surface microlayer and bulk water samples before and after exposed to sunlight. Carbonyl compounds photochemically produced in the samples include formaldehyde, acetaldehyde, acetone, propanal, glyoxal, methylglyoxal, glyoxylic acid and pyruvic acid, as observed in earlier studies (Mopper and Stahovec, 1986; Kieber and Mopper, 1987; Kieber et al., 1990). Pyruvic acid is not used in the following discussions because its poor separation from the reagent peak made quantification difficult. The results from the photochemical experiments are summarized in Table

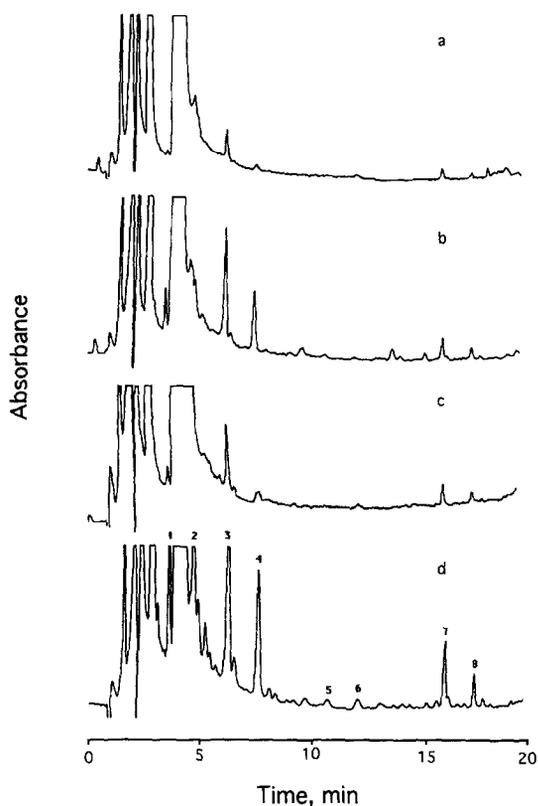


Fig. 1. Chromatograms of samples before and after 4-hour irradiation. (a) Bulk seawater before irradiation. (b) Bulk seawater after irradiation. (c) Microlayer sample before irradiation. (d) Microlayer sample after irradiation. Compound identifications: 1 = glyoxylic acid; 2 = pyruvic acid; 3 = formaldehyde; 4 = acetaldehyde; 5 = acetone; 6 = propanal; 7 = glyoxal; 8 = methylglyoxal.

Table 1

Photoproduction rates ($nM h^{-1}$) of carbonyl compounds in surface microlayer and subsurface seawater samples. Acetone production rate $\leq 5 nM h^{-1}$

	C1	C2	C3	C4	GA	Glyox	MG
<i>(1) Hatchet Bay, Bahamas, 3/22/89:</i>							
BW	10.5	6.2	<0.5	<0.4	1.4	0.4	<0.4
SML1	46.5	27.0	2.1	1.5	24.0	5.0	1.3
R1	4.4	4.4	>2.6	>3.8	17	12.5	>6.5
SML2	54.3	32.8	2.4	1.7	34.3	5.8	2.5
R2	5.2	5.3	>4.2	>4.3	24.5	14	>13
<i>(2) Biscayne Bay, low tide, 4/12/89:</i>							
BW	10.6	8.1	0.7	<0.4	10.0	0.6	0.3
SML	24.3	17.0	1.3	<0.4	13.0	3.0	0.7
R	2.3	2.1	1.8	-	1.3	5.0	2.3
<i>(3) Biscayne Bay, low tide, foam on the surface, 4/13/89:</i>							
BW	11.4	7.9	0.8	<0.4	10.3	1.0	0.7
SML	93.2	58.4	7.4	4.2	73.1	15.5	9.4
R	8.2	7.4	9.3	>10.5	7.1	15.5	13.4
<i>(4) Biscayne Bay, low tide, 4/14/89:</i>							
BW	10.8	6.4	-	-	8.5	0.5	<0.3
SML	21.6	13.6	-	-	10.2	1.8	<0.3
R	2.0	2.1	-	-	1.2	3.6	-
<i>(5) Biscayne Bay, high tide, 4/18/89:</i>							
BW	5.5	2.6	-	-	1.3	0.7	<0.3
SML1	17.2	11.4	-	-	10.1	2.7	<0.3
R1	3.1	4.4	-	-	7.8	3.9	-
SML2	19.1	10.9	-	-	9.1	3.1	<0.3
R2	3.5	4.2	-	-	7.0	4.4	-
<i>(6) Biscayne Bay, high tide, 4/22/89:</i>							
BW	7.6	4.3	0.5	-	2.1	0.6	0.4
SML	21.9	10.6	1.3	-	8.8	3.9	2.1
R	2.9	2.5	2.6	-	4.2	6.5	5.3

Abbreviations: SML = surface microlayer sample; BW = subsurface bulk water; R = ratio of SML/BW; C1–C4 = C1–C4 aldehydes; GA = glyoxylic acid; Glyox = glyoxal; MG = methylglyoxal, - = not measured. The subtitles indicate the location and time of sample collection.

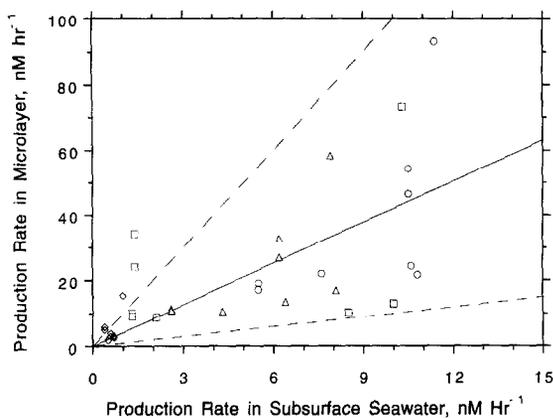


Fig. 2. Photoproduction rates of carbonyl compounds in microlayer samples versus those in bulk seawater. \circ = formaldehyde; \triangle = acetaldehyde; \square = glyoxylic acid; \diamond = glyoxal. Solid line represents the best fit of the data (slope = 4.3), and the lower and upper dash lines represent 1–1 and 1–10 ratio.

1. The photoproduction rates of formaldehyde, acetaldehyde, glyoxylic acid and glyoxal in the surface microlayer are plotted against those in bulk seawater (Fig. 2). The photoproduction rates of carbonyl compounds in surface microlayer samples were higher than those in the bulk water, however, the enhancement of the production (microlayer/bulk seawater) varies widely, e.g., from 1.2 in the Biscayne Bay samples collected at low tide to 25 in the Hatchet Bay samples for glyoxylic acid, with a composite mean enhancement factor of 4.3 for formaldehyde, acetaldehyde, glyoxylic acid and glyoxal (Fig. 2). DOM enrichment in the surface microlayer has been reported to be variable, from slightly less than 1 to about 8 (Carlson, 1983; Hardy, 1982). Since photoproduction rates of carbonyl compounds are proportional to the concentration of UV-absorbing DOM content in the water sample (Kieber et al., 1990), this large variation in the enhancement ratio may be explained in terms of the large variations in the enrichment factor of UV-absorbing DOM in the microlayer relative to bulk water. During the sampling, Hatchet Bay was calm and therefore a stable surface microlayer was probably present which, in turn, favored higher enrichment of UV-absorbing DOM (Carlson, 1983), while tidal currents generally caused turbulence around the RSMAS dock and thus inhibited the formation of a stable surface microlayer. The higher enhancement ratio of carbonyl

photoproduction in the Hatchet Bay samples relative to Biscayne Bay samples, except when foam was visible (Table 1), is consistent with the above explanation.

When foam was present on the sea surface (April 13, 1989, Biscayne Bay), photochemical production rates of carbonyl compounds in the surface microlayer sample were greatly enhanced (Table 1), e.g., increased by a factor of ~ 4 or more for all the compounds relative to those for the samples taken at the same site a day before and after when no foam was observed. Surface foams were found to be highly enriched in DOM as well as particulate organic matter (POM), by a factor of 8–40 and up to 6700, respectively, in freshwater samples (Eisenreich et al., 1978; Johnson et al., 1989). The higher DOM enrichment in our foam-rich microlayer sample probably resulted in higher production rates of LMW carbonyl compounds upon irradiation.

3.2. Field measurements of carbonyl concentration

Two surface microlayer samples and two corresponding subsurface samples were collected between 14:00 and 15:00 (local time) of March 29, 1989, at an open ocean station in the southwestern Sargasso

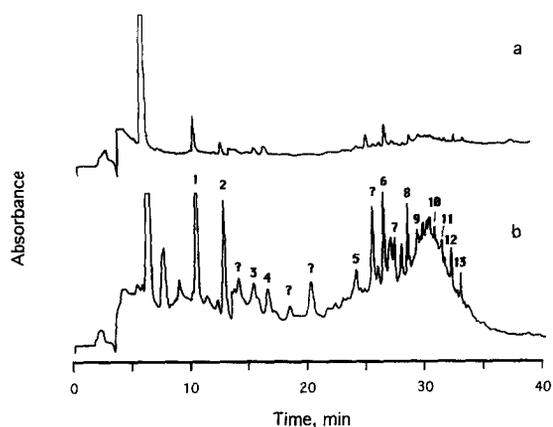


Fig. 3. Chromatograms of carbonyl compounds in a bulk water sample (a) and a surface microlayer sample (b) collected in the southern Sargasso Sea. Samples were preconcentrated by a factor of 50. Compound identification: 1 = formaldehyde; 2 = acetaldehyde; 3 = acetone; 4 = propanal; 5 = butyraldehyde; 6 = glyoxal; 7 = valeraldehyde; 8 = methylglyoxal; 9 = hexanal; 10 = heptanal; 11 = octanal; 12 = nonanal; 13 = decanal; ? = unidentified compounds. The baseline shift at ~ 13.5 min was a result of two-fold change in amplification.

Table 2

Carbonyl concentrations (nM) in the surface microlayer and subsurface bulk water samples ($n = 2$ each) collected at an open ocean station (~100 km east of the Bahamas)

Compounds	Bulk water	Microlayer	Ratio
Formaldehyde	3.88 ± 0.26	34.4 ± 1.6	8.9
Acetaldehyde	1.38 ± 0.08	15.7 ± 2.2	11.4
Propional	0.40 ± 0.06	2.82 ± 0.4	7.1
Butyraldehyde	0.20 ± 0.06	2.40 ± 0.08	12
Valeraldehyde	0.11 ± 0.05	2.32 ± 0.06	21
Hexanal	< 0.05	0.54 ± 0.03	> 10.8
Heptanal	< 0.05	0.66 ± 0.05	> 13.2
Octanal	< 0.05	0.72 ± 0.05	> 14.4
Nonanal	0.09 ± 0.03	0.92 ± 0.04	10
Decanal	< 0.05	0.80 ± 0.02	> 16
Acetone	3.00 ± 0.23	54.8 ± 1.8	18.3
Methylethyl ketone	< 0.5	2.28 ± 0.4	> 4.6
Glyoxal	0.28 ± 0.03	5.92 ± 0.13	21.1
Methylglyoxal	0.20 ± 0.02	2.98 ± 0.15	14.9

Samples were pre-concentrated by a factor of 50 according to Kieber and Mopper (1990).

Table 3

Carbonyl concentrations (nM) in the surface microlayer and subsurface bulk water samples collected in coastal waters

	C1	C2	C3	GA	Glyox	MG
(1) Hatched Bay, Bahamas, 3/21/89, 14:45:						
BW	24.0	6.8	–	–	–	–
SML	171.7	37.4	75.6	37.5	8.8	–
R	7.2	5.5	–	–	–	–
(2) Hatched Bay, Bahamas, 3/22/89, 05:00:						
BW	15.5	2.8	–	–	–	–
SML	68.0	8.3	20.1	10.6	2.7	–
R	4.4	3.0	–	–	–	–
(3) Biscayne Bay, low tide, 4/12/89, 09:30:						
BW	42.2	12.1	~1	10.1	7.1	2.1
SML	103	24.6	3.4	15.2	7.6	5.1
R	2.4	2.0	~3.4	1.5	1.1	2.4
(4) Biscayne Bay, high tide, 4/18/89, 11:00:						
BW	16.7	1.3	< 0.5	0.8	2.4	0.7
SML	45.3	4.1	< 0.5	4.5	8.3	3.1
R	2.7	3.2	–	5.6	3.5	4.4

Abbreviations: same as in Table 1.

Sea. The sea was calm, no foam or slick was visible, and the sky was clear throughout the day. Samples were pre-concentrated by a factor of 50 according to the method of Kieber and Mopper (1990). Chromatograms of a surface microlayer sample and its corresponding subsurface seawater sample are shown in Fig. 3. The enrichment of carbonyl compounds in the surface microlayer relative to subsurface seawater is obvious. The results for these oceanic samples are summarized in Table 2, and for coastal samples collected in Hatched Bay, Bahamas, and in Biscayne Bay, FL, in Table 3.

In oceanic samples, carbonyl concentrations ranged from less than the detection limit of 0.05 nM for higher aldehydes to 3.8 nM for formaldehyde in subsurface seawater, and from ~0.5 nM for the hexanal to about 35 nM for formaldehyde and 55 nM for acetone in the surface microlayer. Concentrations in the coastal waters were significantly higher, e.g., 15–42 nM in bulk seawater and 45–172 nM in microlayer for formaldehyde. The enrichment factor ranged from 1.1 for glyoxal for Biscayne Bay samples collected in the early morning to 21 for glyoxal in the oceanic samples, with a composite mean enrichment factor of 4.2 for formaldehyde, acetaldehyde, glyoxylic acid and glyoxal (Fig. 4), similar to the enhancement factor of 4.3 in photoproduction rates of these compounds in microlayer samples relative to subsurface samples (Fig. 2). This

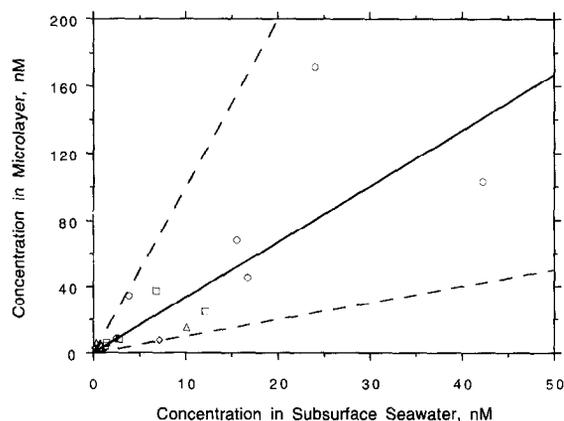


Fig. 4. Concentrations of carbonyl compounds in microlayer samples versus those in bulk seawater samples. Symbols are the same as Fig. 2.

similarity suggests that the enrichment of carbonyl compounds in the surface microlayer relative to subsurface water is at least in part due to higher photoproduction rate there. In fact, strong enrichment of DOM in the oceanic microlayer sample relative to the subsurface sample is obvious from their chromatograms in Fig. 3: The significantly higher elevation of the absorbance signal above solvent baseline for the microlayer sample compared to the subsurface water, with a large hump near the end of the run, is the result of elution of unseparated UV-absorbing DOM from the column. Since carbonyl photoproduction is directly proportional to the DOM content in the water sample (Kieber et al., 1990), the strong DOM enrichment in the surface microlayer will result in greater enhancement in carbonyl photoproduction there relative to the bulk water. In addition, action spectra show that carbonyl photoproduction occurs only in the UV-B region (Kieber et al., 1990). Because light in this region is attenuated quickly with depth, higher UV-B light intensity in the surface microlayer compared to the subsurface water may also contribute to a higher carbonyl photoproduction rate in the microlayer in situ. Two trends may be discerned from our data (Tables 2 and 3): First, the enrichment factor (R) was higher for afternoon samples than for early morning samples (see diurnal discussion below), and second, R increased from coastal waters to open waters, in the following orders: low tide coastal (Biscayne Bay) < high tide coastal (Biscayne Bay) < pristine coastal (Hatchet Bay, Eleuthera Island, Bahamas) < Oceanic (Sargasso Sea) (Tables 2 and 3). Although our data set was small, the apparent trend is in agreement with Carlson (1983) who found that DOM enrichment in the microlayer was highest in the oceanic samples, and diminished with increasing subsurface DOM content in coastal waters. The higher carbonyl enrichment in the oceanic samples relative to coastal samples may reflect this difference, suggesting that photochemical formation was a major source for carbonyl compounds in the microlayer.

3.3. Diurnal variations of carbonyl compounds

Diurnal variations of carbonyl compounds in the surface microlayer and in subsurface water in Hatchet Bay, Bahamas, were studied over a 30-h period. As

illustrated in Fig. 5, concentrations of all carbonyl compounds in both surface microlayer and subsurface water increased steadily in the morning and early afternoon to their maxima around 14:30 to 15:00 (local time), decreased through the late afternoon and evening and then remained relatively constant throughout the night and early morning. Similar diurnal variations have been observed in field and laboratory experiments for aldehydes (Mopper and Stahovec, 1986) and keto acids (Kieber and Mopper, 1987) in bulk seawater. The diurnal variation is due to the imbalance between sources and sinks. The enrichment factor (R) also varied diurnally: 7.2 and 5.5 for formaldehyde and acetaldehyde at their concentration maxima in the mid afternoon (14:45 local time) versus 4.4 and 3 in the early morning (Table 3). This diurnal variation in R may be due to greater sources and sinks of these compounds in the microlayer relative to subsurface water.

3.4. Processes in the surface microlayer

For LMW carbonyl compounds in subsurface water, photochemical production has been demonstrated to be the major source, i.e., as photodegradation products of humic substances and other UV-absorbing organic compounds (Kieber et al., 1990), and biological uptake the major sink (Kieber and Mopper, 1987). In the surface microlayer, photochemical production is probably the major source for these compounds, as discussed in the previous sections. However, additional sources and sinks must be considered. For example, exchange with the atmosphere may be a source for highly soluble compounds, such as formaldehyde, glyoxal and methylglyoxal, and a sink for less soluble compounds, such as acetaldehyde and acetone (see following section). Other sinks or sources for carbonyl compounds in the surface microlayer may include rising bubbles and microbial activity.

Rising gas bubbles adsorb dissolved organic matter, especially surface active materials (Blanchard, 1964; Garrett, 1967). This process may be important in bringing larger carbonyl compounds such as nonanal and decanal as well as carbonyl precursors, i.e., UV-absorbing DOM, to the surface microlayer. However, it is probably not a significant direct source for LMW carbonyl compounds such as formal-

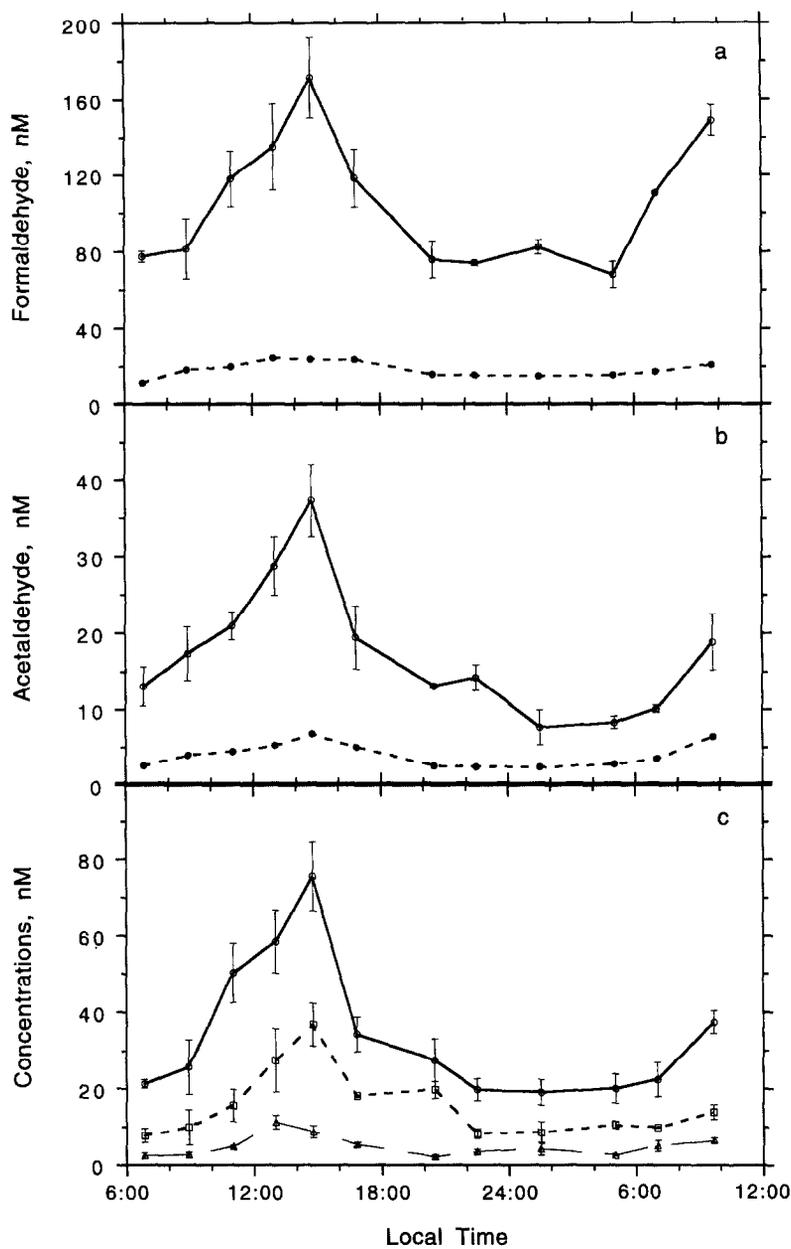


Fig. 5. Diurnal variations in carbonyl concentrations in surface microlayer (open symbols) and bulk seawater (closed symbols) in Hatchet Bay, Bahamas. (a) Formaldehyde. (b) Acetaldehyde. (c) Glyoxylic acid (○), glyoxal (□) and methylglyoxal (△).

dehyde and acetaldehyde in the microlayer, since they are not surface active. On the other hand, vigorous bubble activity tends to increase convection in the surface water and destabilize the surface microlayer, resulting in low enrichment in organic compounds there. During most of the sampling periods,

the sea surface was relatively calm, and therefore bubble activity may not have significantly affected the observed enrichment of carbonyl compounds in the surface microlayer.

High enrichment factors for microorganisms in the surface microlayer have been reported (Liss,

1975, and references therein), and thus microbial activity may strongly influence the concentrations of carbonyl compounds in the microlayer. Microorganisms may either take up LMW carbonyl compounds (Mopper and Stahovec, 1986; Kieber and Mopper, 1987) or release them, the latter occurring under anaerobic conditions (Eberhardt and Sieburth, 1985; Mopper and Kieber, 1991). Since the sea surface is well oxygenated, anaerobic activity is inhibited, and therefore microbial activity probably represents a net sink rather than a source for the carbonyl compounds in the surface microlayer. The turn-over time for LMW carbonyl compounds via microbial metabolism is on the order of a few hours to a few days in bulk subsurface seawater (Mopper and Stahovec, 1986; Kieber and Mopper, 1987; Mopper and Kieber, 1991). Since the number of microorganisms and thus the microbial activity in the surface microlayer is higher than in the bulk seawater (Garabetian, 1991), the carbonyl uptake rate may be higher in the microlayer.

3.5. Air–sea exchange of carbonyl compounds

From the atmospheric concentrations and the apparent partition coefficients of carbonyl compounds

between gas and aqueous phases, we can predict their equilibrium concentrations in seawater and thus their net exchange directions (Table 4). The predicted formaldehyde concentration of 1.5 μM is far greater than 1–40 nM in the bulk seawater and 34–171 nM in surface microlayer observed in this study. Therefore, its net exchange flux is from the air to the sea. For acetaldehyde and acetone, the predicted equilibrium concentrations are 4 and 10 nM, respectively, within the ranges observed of 1–15 and 2–15 nM in the seawater in the surface mixed layer. However, the concentrations in the surface microlayer are 16–38 nM for acetaldehyde and 55 nM for acetone, higher than the predicted values, meaning that the net exchange flux is from the sea surface to the air. No calculations were attempted for other LMW carbonyl compounds because of the lack of reliable atmospheric concentrations in the clean marine boundary layer. For soluble compounds like glyoxal, methylglyoxal, glyoxylic acid and pyruvic acid, whose apparent partition coefficients (K^* , in M atm^{-1}) were measured to be $\geq 3 \times 10^6$, 4.1×10^4 , $\geq 3 \times 10^6$ and 1.7×10^5 , respectively (Zhou and Lee, 1994), the net exchange direction is expected to be from air to sea. On other hand, a flux from water to air is expected for the aldehydes with

Table 4
Exchange directions and constants for formaldehyde, acetaldehyde and acetone across the air–sea interface

Compounds	p^a (ppb)	$K^*{}^b$ (M atm^{-1})	C_{pred}^c (nM)	C_{SML}^d (nM)	C_{BSW}^e (nM)	Dir ^f	H^g ($\times 10^3$)	k_g^h (cm s^{-1})	k_l^i (cm s^{-1})	α^j	K_1^k (cm s^{-1})	r_g/r_l^k	F^l ($\text{nmol cm}^{-2} \text{ s}^{-1}$)
Formaldehyde	0.4	3700	1500	34–171	2–40	+	26	0.64	0.0056	7.3	0.012	2.5	7.6×10^{-6}
Acetaldehyde	0.3	13	4	16–38	1–15	–	7.5	0.53	0.0056	2.0	0.0029	2.8	-2.0×10^{-5}
Acetone	0.3	31	10	55	3–15	–	1.3	0.46	0.0056	1	0.00054	9.4	-2.7×10^{-5}

^a Atmospheric concentrations are from Zhou and Mopper (1993).

^b Partition coefficients K^* are taken from Zhou and Mopper (1990) for 25°C.

^c Predicted equilibrium concentrations were calculated according to: $C = K^* \times p$.

^d Measured concentrations in surface microlayer.

^e Measured concentrations in bulk seawater.

^f Directions of net exchange across air–sea interface, + is from air to sea and – is from sea to air.

^g Dimensionless intrinsic Henry's Law constant defined as $H = C_g/C_l$, calculated from Zhou and Mopper (1990). Hydration constants were 2.3×10^3 for formaldehyde and 1.4 for acetaldehyde (Bell and Avans, 1966).

^h $k_g = 0.83\sqrt{(\text{MW}/18)} \text{ cm s}^{-1}$, where MW is the molecular weight of the carbonyl compound considered.

ⁱ From Liss and Slater (1974).

^j Enhancement factor calculated according to Hoover and Berkshire (1969) and Liss and Slater (1974). Hydration rate and equilibrium constants are from Schecker and Schultz (1969) and Bell and Avans (1966).

^k Overall exchange constant K_1 is defined by Eq. (4): $1/K_1 = 1/Hk_g + 1/\alpha k_l = r_g + r_l$, where r_g and r_l are gas phase resistance and liquid phase resistance, respectively.

^l Flux from air into sea.

3 or more carbon atoms, which have $K^* \leq 10 \text{ M atm}^{-1}$ (Zhou and Mopper, 1990).

The transfer of a gas across a clean air–water interface is illustrated by a classical two-layer model (Liss and Slater, 1974) in Fig. 6a, which has been used to study air–sea exchange of various gases (e.g., Liss and Slater, 1974; Thompson and Zafiriou, 1983), including formaldehyde (Thompson, 1980; Zafiriou et al., 1980). At steady state, the flux of a gas across the interface (F , in $\text{mol cm}^{-2} \text{ s}^{-1}$) can be expressed as:

$$F = k_g(C_g - C_{sg}) = k_l(C_{sl} - C_l) \quad (1)$$

where k_g and k_l are the exchange constants for the gas and liquid phases (in m s^{-1}), respectively, and C_g , C_{sg} , C_{sl} and C_l the concentrations in the bulk

gas phase, gas phase at interface, liquid phase at interface and bulk liquid phase, respectively, all in mol cm^{-3} . C_{sg} and C_{sl} can be related by Henry's Law:

$$C_{sg} = HC_{sl} \quad (2)$$

where H is the dimensionless Henry's Law constant. Eliminating C_{sg} and C_{sl} from Eq. (1), we have:

$$F = K_1(C_g/H - C_l) \quad (3)$$

K_1 is the overall exchange constant, defined as:

$$1/K_1 = 1/\alpha k_l + 1/Hk_g \quad (4)$$

where α is the enhancement factor by chemical reactions, such as hydration of carbonyl compounds (Liss and Slater, 1974; Thompson and Zafiriou, 1983). The first term ($1/\alpha k_l$) in Eq. (4) is also called the liquid phase resistance (r_l) and the second term ($1/Hk_g$) the gas phase resistance (r_g).

Table 4 summarizes the calculated exchange constants for formaldehyde, acetaldehyde and acetone. For these three compounds, the resistance to molecular transfer across the interface is greater in the gas film than in the liquid film, with r_g/r_l values at 2.5, 2.8 and 9.4, respectively. Using an atmospheric formaldehyde concentration of 0.4 ppb and a K_1 of 0.012 cm s^{-1} , its flux from the atmosphere to the sea is $7.6 \times 10^{-6} \text{ nmol cm}^{-2} \text{ s}^{-1}$, i.e., $0.07 \text{ g m}^{-2} \text{ yr}^{-1}$, in good agreement with $0.06 \text{ g m}^{-2} \text{ yr}^{-1}$ estimated by Zafiriou et al. (1980). For acetaldehyde and acetone, however, because of their enrichment in the surface microlayer, the molecular transfer would go in both directions, i.e., into bulk seawater and into air (Fig. 6b). If photochemical production is the dominant source, the maximum concentration is likely to occur near the air/sea interface within the surface microlayer as the result of higher precursor concentration. Using the first part of Eq. (1) and substituting C_{sg} with $C_{sl}H$, assuming $C_{sl} \sim C_{sm1}$ of 6.7 nM for acetaldehyde (total concentration of 16 nM) and 55 nM for acetone (Table 2), we estimate their flux from the ocean surface to the atmosphere to be $\sim 2.0 \times 10^{-5} \text{ nmol cm}^{-2} \text{ s}^{-1}$ and $\sim 2.7 \times 10^{-5} \text{ nmol cm}^{-2} \text{ s}^{-1}$, respectively. Thus, the residence time in the microlayer via air–sea exchange is ~ 1.2 minutes for formaldehyde with the atmosphere as a source, 12 and 30 seconds for acetaldehyde and acetone with the atmosphere as a sink.

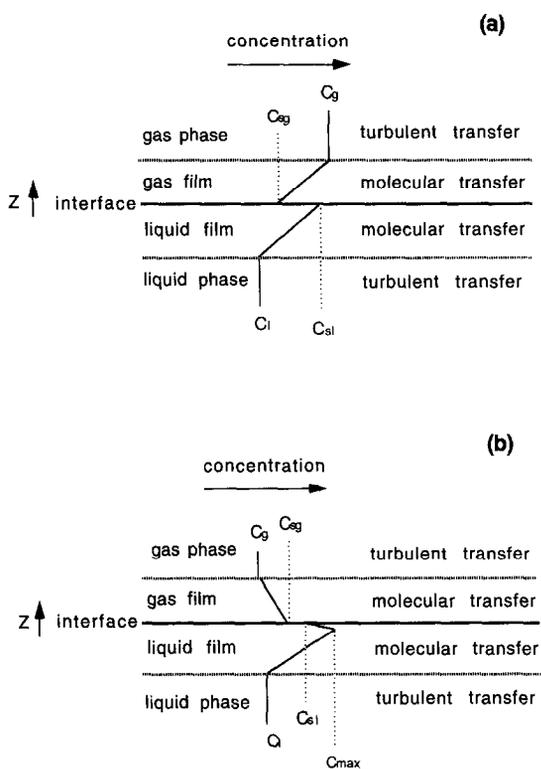


Fig. 6. (a) A classical two-layer model of a gas–liquid interface (Liss and Slater, 1974) and (b) a modified two-layer model with a maximum solute concentration in the liquid film. C_g , C_{sg} , C_{sl} , C_l and C_{max} are solute concentrations in the well mixed gas phase, at the gas side of interface, at the liquid side of interface, in the well-mixed liquid phase and at the maximum within the liquid film, respectively. C_{sg} and C_{sl} are in equilibrium according to Henry's Law: $C_{sg} = HC_{sl}$.

The high molecular transfer rate and short residence time of LMW carbonyl compounds in the surface microlayer is not consistent with the observed enrichment of these compounds there. The enrichment factors in the microlayer relative to subsurface water (Tables 2 and 3) and the diurnal variation patterns (Fig. 5) are actually similar for formaldehyde and acetaldehyde, even though exchange with the atmosphere has opposing effects on their concentrations. Carbonyl compounds photochemically produced in the microlayer have a replacement time ($= C_{\text{smi}}/\text{photoproduction rate}$) of ~ 1 hour, much greater than the calculated residence times of seconds to minutes via air–sea exchange. If the predicted exchange rates are correct, acetaldehyde photochemically produced in the microlayer would escape into the atmosphere too quickly to allow any significant accumulation there, while formaldehyde input from the atmosphere would overwhelm its photoproduction in the microlayer by 1–2 orders of magnitude and thus should show a more significant enrichment relative to subsurface water. In order to maintain the observed enrichments of carbonyl compounds in the surface microlayer, sink and source terms must be roughly in balance, i.e., molecular diffusion must be greatly inhibited, and/or additional sources must exist to speed up the replacement for the loss due to diffusional transfer. Alternately or additionally, the apparent partition coefficients of these species among the surface microlayer, bulk seawater and air must be significantly altered so that microlayer enrichment relative to bulk seawater is always maintained even in equilibrium.

The unique chemistry of the surface microlayer may play a critical role in prolonging the residence times and/or changing the apparent partition coefficients. Hardy et al. (1985) measured residence times for trace metals, which are mostly associated with particles, in the surface microlayer and found them ranging from 1.5 to 15 hours, instead of minutes predicted by a gravitational settling model. They attributed the prolonged residence times to the stabilizing effects on microparticles by the organic film at the interface. Similarly, organics enriched in the surface microlayer may inhibit molecular transfer of carbonyl compounds there by changing physical characteristics of the microlayer, e.g., increasing viscosity. In addition, physical and chemical interac-

tions, such as hydrophobic bonding (Schautman and Morgan, 1993), between these species and organic matrix in the microlayer may lower their effective concentrations or activities, and thus change their apparent partition coefficients among surface microlayer, subsurface water and air, resulting in higher apparent concentrations in the microlayer than in bulk water even in or close to equilibrium.

4. Conclusions

Low-molecular-weight carbonyl compounds were significantly enriched in oceanic and coastal surface microlayers compared to the corresponding subsurface waters, by a factor ranging from 1.2 to 21 with a composite average of 4.2. Photochemical production probably was the major source for these compounds in microlayer as in subsurface water. The carbonyl enrichment in the microlayer may be mainly attributed to the significantly enhanced photoproduction rate there relative to subsurface water, by a factor of 1.1 to 25 with a composite average of 4.3. The short predicted residence times of LMW carbonyl compounds using a two-layer model, which were on the order of tens of seconds to minutes, were not consistent with the observed enrichment of all these compounds in the surface microlayer regardless of the net exchange direction. Air–sea exchange of these compounds was probably slowed down by the presence of an organic-rich surface microlayer which inhibited molecular transfer of carbonyl compounds into and out of the microlayer. In addition, physical and chemical interactions between these species and organic matrix in the microlayer may change their apparent partition coefficients among surface microlayer, subsurface water and air, resulting in higher apparent concentrations in the microlayer than in bulk water even in or close to equilibrium.

Our results, along with some earlier observations (e.g., Conrad and Seiler, 1988), clearly indicate that classical exchange models are inadequate to describe the behavior of species that are produced or destroyed and/or participate in physicochemical interactions in the surface microlayer that affect their transport rates or apparent partition coefficients. It is possible that surface potential or film pressure mea-

surements (Van Vleet and Williams, 1983) may be useful in estimating the latter behavior.

Acknowledgements

We dedicate this paper to Dr. Peter J. Wangersky whose significant contribution to marine chemistry has been a great inspiration to our studies.

We thank R.J. Kieber and G.M. Vaughan for valuable discussions and technical assistance, and the captain and crew of the RV 'Columbus Iselin' for their skillful assistance during sampling. We also thank X. Chen for critical comments on the manuscript. This work was supported by the U.S. National Science Foundation's Chemical Oceanography Program, OCE-9315821 and OCE-9096314.

References

- Bell, R.P. and Avans, P.G., 1966. Kinetics of the dehydration of methylene glycol in aqueous solution. *Proc. R. Soc. London, Ser. A*, 291: 297–321.
- Blanchard, D.C., 1964. Sea-to-air transport of surface active material. *Science*, 146: 396–397.
- Carlson, D.J., 1982. Surface microlayer phenolic enrichments indicate sea surface slicks. *Nature (London)*, 296: 426–429.
- Carlson, D.J., 1983. Dissolved organic materials in surface microlayers: Temporal and spatial variability and relation to sea state. *Limnol. Oceanogr.*, 28: 415–431.
- Conrad, R. and Seiler, W., 1988. Influence of the surface microlayer on the flux of nonconservative trace gases (CO, H₂, CH₄, N₂O) across the ocean–atmosphere interface. *J. Atmos. Chem.*, 6: 83–94.
- Eberhardt, M.A. and Sieburth, J.McN., 1985. A colorimetric procedure for the determination of aldehydes in seawater and in cultures of methylotrophic bacteria. *Mar. Chem.*, 17: 199–212.
- Eisenreich, S.J., Elzerman, A.W. and Armstrong, D.E., 1978. Enrichment of micronutrients, heavy metals, and chlorinated hydrocarbons in wind-generated lake foam. *Environ. Sci. Technol.*, 12: 413–417.
- Garabetian, F., 1991. ¹⁴C-glucose uptake and ¹⁴C-CO₂ production in surface microlayer and surface-water samples: Influence of UV and visible radiation. *Mar. Ecol. Prog. Ser.*, 77: 21–26.
- Garrett, W.D., 1965. Collection of slick-forming materials from the sea surface. *Limnol. Oceanogr.*, 10: 602–604.
- Garrett, W.D., 1967. Stabilization of air bubbles at the air–sea interface by surface-active material. *Deep-Sea Res.*, 14: 661–672.
- Hardy, J.T., 1982. The sea surface microlayer: Biology, chemistry and anthropogenic enrichment. *Prog. Oceanogr.*, 11: 307–328.
- Hardy, J.T., Apts, C.W., Crecelius, E.A. and Fellingham, G.W., 1985. The sea-surface microlayer: Fate and residence times of atmospheric metals. *Limnol. Oceanogr.*, 30: 93–101.
- Hoover, T.E. and Berkshire, D.C., 1969. Effects of hydration on carbon dioxide exchange across an air–water interface. *J. Geophys. Res.*, 74: 456–464.
- Johnson, B.D., Zhou, X., Parrish, C.C., Wangersky, P.J. and Kerman, B.R., 1989. Fractionation of particulate matter, the trace metals Cu, Cd, and Zn, and lipids in foam and water below Niagara Falls. *J. Great Lakes Res.*, 15: 189–196.
- Kieber, D.J. and Mopper, K., 1987. Photochemical formation of glyoxylic and pyruvic acids in seawater. *Mar. Chem.*, 21: 135–149.
- Kieber, R.J. and Mopper, K., 1990. Determination of picomolar concentrations of carbonyl compounds in natural waters, including seawater, by liquid chromatography. *Environ. Sci. Technol.*, 24: 1477–1481.
- Kieber, D.J., McDaniel, J.A. and Mopper, K., 1989. Photochemical source of biological substrates in seawater: Implications for carbon cycling. *Nature (London)*, 341: 637–639.
- Kieber, R.J., Zhou, X. and Mopper, K., 1990. Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. *Limnol. Oceanogr.*, 35: 1503–1515.
- Liss, P.S., 1975. Chemistry of the sea-surface microlayer. In: J.P. Riley and G. Skirrow (Editors), *Chemical Oceanography*. Academic Press, London, 2nd ed.
- Liss, P.S. and Slater, P.G., 1974. Flux of gases across the air–sea interface. *Nature (London)*, 247: 181–185.
- Mopper, K. and Kieber, D.J., 1991. Distribution and biological turnover of dissolved organic compounds in the water column of the Black Sea. *Deep-Sea Res.*, 38: 1021–1047.
- Mopper, K. and Stahovec, W.L., 1986. Photochemical production of low molecular weight organic carbonyl compounds in seawater. *Mar. Chem.*, 19: 305–321.
- Mopper, K., Zhou, X., Kieber, R.J., Kieber, D.J., Sikorski, R.J. and Jones, R.D., 1991. Role of photochemical degradation in the cycling of oceanic dissolved organic carbon. *Nature (London)*, 353: 60–62.
- Schautman, M.A. and Morgan, J.J., 1993. Effects of aqueous chemistry on the binding of polycyclic aromatic hydrocarbons by dissolved humic materials. *Environ. Sci. Technol.*, 27: 961–969.
- Schecker, H. and Schultz, G., 1969. Untersuchungen hydrationskinetik von formaldehyde in wässriger Lösung. *Z. Phys. Chem., Neue Folge*, 65: 221–224.
- Thompson, A.M., 1980. Wet and dry removal of tropospheric formaldehyde at a coastal site. *Tellus*, 32: 376–383.
- Thompson, A.M. and Zafiriou, O.C., 1983. Air–sea fluxes of transient atmospheric species. *J. Geophys. Res.*, 88C: 6696–6708.
- Van Vleet, E. and Williams, P.M., 1983. Surface potential and film pressure measurements in seawater systems. *Limnol. Oceanogr.*, 28: 401–414.
- Zafiriou, O.C., Alford, J., Herrera, M., Peltzer, E.T., Gagosian,

- R.B. and Liu, S.C., 1980. Formaldehyde in remote marine air and rain: Flux measurements and estimates. *Geophys. Res. Lett.*, 7: 341–344.
- Zhou, X. and Lee, Y.-N., 1994. Henry's Law solubilities of some multiple-oxygenated carbonyl compounds. *J. Phys. Chem.*, submitted.
- Zhou, X. and Mopper, K., 1990. Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater: Implications for air–sea exchange. *Environ. Sci. Technol.*, 24: 1864–1869.
- Zhou, X. and Mopper, K., 1993. Carbonyl compounds in the lower marine troposphere over the Caribbean Sea and Bahamas. *J. Geophys. Res.*, 98C: 2385–2392.