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THE BIOGEOCHEMISTRY OF THE AIR-SEA INTERFACE

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INTRODUCTION

In recent years scientific investigators have evidenced a steadily growing interest in the interface between the atmosphere and the oceans. This region, termed the air-sea interface or surface microlayer, has been shown to have unique properties that may influence the geochemical cycles of many environmental pollutants. It is intuitively obvious that the air-sea interface must be traversed in the process of ocean-atmosphere exchanges. If, as the preponderance of evidence indicates, the interface has physical, chemical, and biological characteristics different from those of bulk seawater, it follows that those characteristics may influence the form and fate of materials that are introduced into the microlayer.

In this review the physical, chemical, and biological characteristics of the air-sea interface are described with particular emphasis on those features that may impact upon the form and/or fate of pollutants in the sea. There have been three major reviews that treat the air-sea interface (MacIntyre 1974a, Liss 1975, Duce & Hoffman 1976). Although these reviews consider biological and chemical interactions of toxic trace metals and organic pollutants at the air-sea interface, they are principally concerned with the process of chemical fractionation, particularly as it affects the exchange of materials between the oceans and the atmosphere. Emphasis in this review is placed on the composition of the surface microlayer and on the chemical and biological interactions that may ensue.

The air-sea interface is an extremely complex matrix. The discussion that follows is intended to provide the reader with an indication of the complexity of the interfacial solution and a sense of the possible interactions between trace metals and the other components of the interfacial

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matrix. The potential for such interactions is inherent in the occurrence of high interfacial concentrations of metals, organics, particulates, and microbiota.

TRACE METALS AT THE AIR-SEA INTERFACE

The surface microlayer of the ocean is a poorly defined region on both an operational and a conceptual basis. Operationally, the depth of the surface microlayer is often defined by the type of surface sampler employed. Consequently, the reported concentrations of trace metals at the air-sea interface reflect not only temporal and geographic variability but also—unfortunately—differences in the types of sampling devices used. The art of interfacial sampling is still developing and several devices have been applied, each of which varies in its efficiency or the effective depth sampled. Table 1 lists some of the interfacial samplers now employed and their reported sampling depths. The depths sampled have varied over more than four orders of magnitude, from 30 nm to 1 mm.

Table 1 Air-Sea interface sampling devices

Type	Depth sampled	Investigator
Screen	≈150 μm	Garrett 1965, 1972
Glass plate	60–100 μm	Harvey & Burzell 1972
Rotating drum	≈60 μm	Harvey 1966
V-shaped tube	qualitative for foams and collapsed films	Szekielda et al 1972
Teflon disk	?	Miget et al 1974
Teflon plate	50–100 μm	Larsson et al 1974
Bubble microtome	0.5–10 μm	MacIntyre 1968
Funnel	?	Morris 1974
Tray	1.0 mm	Parker & Wodehouse 1971
Prism	≈30 nm	Baier 1972

Conceptually, the "true" surface microlayer is often described as a monomolecular layer (Garrett 1967a, Duce et al 1972) which would extend to a few hundred angstroms in depth. However, calculations based on gas exchange and some thermal measurements indicate interfacial thicknesses of 30 to 100 μm (Liss 1975). The actual microlayer thickness may in fact vary with respect to the parameter of interest. That is, microlayer thicknesses of 100 μm for thermal gradients and 10 nm for chemical gradients are not necessarily mutually exclusive phenomena. These uncertainties in understanding microlayer thickness make equally uncertain the understanding of metal and ligand concentrations in the surface microlayer. Consequently, questions concerned with metal speciation, biological toxicity, and transport become very difficult to answer.

The relative sampling depths of some of the surface samplers in Table 1 have been compared by Roy et al (1970), Hatcher & Parker (1974), and Daumas et al (1976). The common feature of all interfacial samplers used, with the possible exception of those of MacIntyre (1968), Szekielda et al (1972), and Baier (1972), is that to varying degrees they dilute a sample from a monomolecular surface layer with bulk marine water. Thus, sample concentrations may need to be multiplied by a factor of up to 10^4 in order to reflect concentrations in a monomolecular microlayer.

Table 2 summarizes some of the reported trace metal measurements made in the surface microlayer of both marine and fresh waters. For ease of comparison, the tabulated data show total trace metal concentrations (the sum of particulate and dissolved organic and inorganic concentrations where reported separately) averaged over the indicated number of independent samples. Concentrations of metals measured at the interface are seen to vary over a large range and, on the average, virtually all metals are found to be partitioned at the surface microlayer. It is worth noting the differences in microlayer sampling techniques when examining the data in Table 2. Samplers that select for foams or collapsed surface films, i.e. those of Szekielda et al (1972) and Pellenbarg (1976), provide sample metal concentrations up to 10^4 higher than those obtained from other surface-sampling devices, a factor roughly equivalent to the previously discussed dilution correction factor.

In some instances the authors cited here do not provide sufficient information to permit evaluation of the adequacy of their analytical procedures. The measurement of trace metals in the environment is, in fact, far from straightforward. Obtaining accurate, contaminant-free analyses of trace metals in environmental samples is now recognized as a major stumbling block by field investigators (Batley & Gardner 1977, Bruland et al 1978). In cases where discussion of analytical techniques is insufficient, we have assumed that the reported trace metal concentrations at the air-sea interface and their partitioning from bulk solution accurately reflect actual environmental concentrations. Although the results vary, some common features link many of the investigations: (*a*) the occurrence of measurable partitioning (surface excess) of trace metals is not a consistent phenomenon; the frequency of detectable partitioning increases with the presence of observable surface organic slicks (Piotrowicz et al 1972, Elzerman 1976); (*b*) the relative amount of organically associated (extractable) trace metals is higher at the surface microlayer than in bulk waters (Duce et al 1972, Barker & Zeitlin 1972); (*c*) particulate trace

Table 2 Summary of reported microlayer trace metal concentrations

Location	Type of sampler	Metal species	No. of samples	Microlayer concentration[a] (range and/or mean), ug/l	Mean partitioning[b]	Remarks	References
Narragansett Bay, Rhode Island	Screen	Pb	2	4.1, 9	1.7	Reported data differentiate between particulate (>0.45 μm) dissolved organic ($CHCl_3$ extractable), and dissolved inorganic metal species.	Duce et al 1972
		Cu	2	4.4, 16.2	3.5		
		Fe	2	57.1, 826.5	15.0		
		Ni	2	26.9, 39	1.9		
Narragansett Bay, Rhode Island	Screen	Pb	8	2.6–14 ($\bar{x} = 6.7$)	1.9	Reported data differentiate between particulate (>0.45 μm), dissolved organic ($CHCl_3$ extractable), and dissolved inorganic metal species.	Piotrowicz et al 1972
		Cu	8	4.1–16 ($\bar{x} = 6.6$)	2.3		
		Fe	8	3.7–830 ($\bar{x} = 149$)	5.1		
		Ni	8	12–40 ($\bar{x} - 25.5$)	1.3		
Delaware Bay (convergence zone)	V-shaped tube	Pb		10^5–5×10^5	$\simeq 10^7$	Microlayer values are for the analysis of the $CHCl_3$ extraction residue of a film sample. Enrichments are calculated from seawater values given by Goldberg (1965).	Szekielda et al 1972
		Cu		10^5–5×10^5	$\simeq 10^5$		
		Fe		2×10^6–10^7	$\simeq 5 \times 10^6$		
		Ni		10^5–5×10^5	$\simeq 10^5$		
		Zn	nr[c]	2×10^5–10^6	$\simeq 5 \times 10^4$		
		Hg		300	$\simeq 10^3$		
		Cr		10^5–5×10^5	$\simeq 5 \times 10^6$		
		Ag		10^4–5×10^4	$\simeq 10^5$		
		Co		5×10^4–2.5×10^5	$\simeq 10^5$		
		Mn		1×10^5–5×10^5	$\simeq 10^5$		

Swedish West Coast	Teflon disk	Zn	nr	≃100 ppm	bulk water metal concentration not reported	Metal concentration is ppm of $CHCl_3$-MeOH (2:1 v/v) extractable lipid weight.	Larsson et al 1974
		Ni		≃100 ppm			
Canary Creek Salt Marsh, Delaware	V-shaped tube	Cu		$1.48 \times 10^4 \pm 3.4 \times 10^3$	10.1	Averages for flood tide over three seasons (Pilottown Station). Data also available for other stations and for ebb tides.	Pellenbarg 1976, Pellenbarg & Church 1979
		Fe		$1.39 \times 10^7 \pm 1.8 \times 10^4$	15.5		
		Zn		$1.03 \times 10^5 \pm 6.1 \times 10^4$	17.5		
Lake Michigan	Screen	Cu	51	0.74–85 $(\bar{x} = 4.85)$	2.6	Data also available for dissolved and particulate (>0.4 um) metals and for lakes Ontario and Mendota	Elzerman 1976, Elzerman & Armstrong 1979
		Pb	62	0.9–190 $(\bar{x} = 11.0)$	4.8		
		Zn	62	1.0–88 $(\bar{x} = 16.8)$	2.8		
		Cd	62	0.05–4.7 $(\bar{x} = 0.44)$	3.0		
Openocean	Glass plate	Cu	nr	11.5 ± 3.7	3.1	Reported data differentiate between total and $CHCl_3$ extractable trace metals.	Barker & Zeitlin 1972
		Fe		56.8 ± 8.0	4.2		
		Zn		39.7 ± 13.7	2.8		
Lake Mendota	Foam	Cu	30	140–1410 $(\bar{x} = 900)$	448	Microlayer analysis performed on acid-digested foam samples.	Eisenreich et al 1978
		Fe	30	7,500–12,900 $(\bar{x} = 11,300)$	240		
		Pb	30	20–5,910 $(\bar{x} = 2,210)$	1,110		
		Zn	30	20–2,260 $(\bar{x} = 880)$	293		
		Cd	30	0.1–340 $(\bar{x} = 110)$	544		
Northwest Atlantic	Screen	Hg	6	0.005 to 0.01	no surface enrichment observed	Analysis for reactive and total Hg; range of values shown does not include analysis from coastal stations.	Fitzgerald 1976, Fitzgerald & Hunt 1974

Table 2 *(continued)*

Location	Type of sampler	Metal species	No. of samples	Microlayer concentration[a] (range and/or mean), ug/l	Mean partitioning[b]	Remarks	References
Open ocean, California current	Screen	Cd	13	0.015–0.060 ($\bar{x} = 0.030$)	3.7	Partitioning calculated vs. 0.3 m bulkwater samples. Average values shown do not include analysis from coastal stations.	Martin et al 1976
Lake foam	Screen	Fe	1	1,920	190		Pojasek & Zajicek 1978
		Mn	1	190	3.8		
South San Francisco estuary—salt marsh border	Screen	Pb	18	1.1–48 ($\bar{x} = 13.1$)	11.6	Data averaged over two separate tidal cycles. Total metal represents sum of dissolved and particulate (>0.4 μm) forms.	Lion 1980
		Cu	18	5.6–181 ($x = 37.8$)	4.8		
		Cd	18	0.36–2.31 ($\bar{x} = 0.80$)	1.7		
North Sea coastal waters		Pb	15	1.5–10.7 ($\bar{x} = 3.8$)	1.7	Data shown are for particulate trace metal concentrations.	Hunter 1980
		Cu	15	0.38–5.3 ($\bar{x} = 1.7$)	2.3		
		Fe	15	156–854 ($\bar{x} = 415$)	0.84		
		Ni	15	<0.35–36.0	—		
		Zn	15	2.0–13.2 ($x = 5.3$)	1.5		
		Cd	15	<0.06–0.92	—		
		Mn	15	3.0–20.3 ($\bar{x} = 8.1$)	0.74		

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[a] Uncorrected for dilution effects.

[b] Partitioning = $\frac{\text{microlayer concentration}}{\text{bulkwater concentration}}$ [Note: In some cases the mean partitioning indicated represents an average of observed values from different stations or over a time series of measurements which were reported separately by the cited authors.]

[c] nr = not reported.

metals (especially lead) occur at higher levels in the surface microlayer (Piotrowicz et al 1972, Elzerman et al 1979).

These general conclusions suggest several possible processes for trace metal transport to the air-sea interface. Processes to be considered would be those that would preferentially transport organically bound metals or particulate metals. Such processes include rising bubbles from bulk solution (Lemlich 1972a) or airborne deposition of particulates. An alternative (not necessarily exclusive of the other processes) is that metals delivered to the microlayer react there to form organic complexes or are adsorbed at the surface microlayer onto particulates. In the sections that follow, the chemical and biological nature of the surface microlayer and the possibilities for transport processes and reactions in the microlayer are considered in further detail.

ORGANICS AT THE AIR-SEA INTERFACE

In this section the enrichment of organic compounds at the air-sea interface is reviewed. Organic enrichment is seen to be predictable based on simple thermodynamic considerations. Classes of organics that may be partitioned are described qualitatively and compared to available field data. The possible effects of organic surface films are reviewed and shown to include damping of capillary waves, perturbations in gas transfer efficiencies, stabilization of bubbles, and generation of particulate organic aggregates. The formation of organic aggregates may influence the form and fate of trace metals. Metal complexation by surface-active organics is also discussed.

Thermodynamics of Surface Adsorption and Classes of Surface-Active Organics

There is a large body of literature on the physical-chemical nature of the air-solution interface for aqueous systems. The information available from that literature is of significant use in establishing a framework for discussion of the behavior of organic solutes at the surface microlayer and to give a basis for comparison.

The Gibbs adsorption isotherm, which describes the basic thermodynamic relationships for interfacial phenomena, can be represented as

$$-\mathrm{d}\gamma = \sum_{i=1}^{n} \Gamma_i \mathrm{d}\mu_i, \tag{1}$$

where γ is the surface tension, Γ_i is the surface excess (as moles/cm^2), and μ_i is the chemical potential of species i.

Also,

$$\mu_i = \mu_i^0 + RT \ln a_i,$$

where a_i is the activity of species i, R is the universal gas constant, and T is the absolute temperature.

Equation (1) predicts that positive adsorption or creation of a surface excess will result in a decrease in the surface tension of a given bulk liquid. At constant temperature and pressure and considering the surface as occupying zero volume, the free energy, G, of a system and surface tension are related by

$$dG = \gamma\, dA + \sum_{i=1}^{n} \mu_i\, dn_i, \tag{2}$$

where n_i is the moles of species i at the surface, and dA is the differential change in surface area.

A solute species, i, which decreases surface tension, will positively adsorb at the air-solution interface [Equation (1)] and this reaction will occur spontaneously [Equation (2)]. Most organic solutes decrease the surface tension of water (National Research Council 1928) and would therefore be expected to positively adsorb at the air-solution interface. Conversely, most inorganic electrolytes raise the surface tension of water (Osipow 1977) and therefore will tend to be negatively adsorbed (excluded) at the surface.

These simple relationships lead to some rather important conclusions. The principal one of interest for this discussion is that all naturally occurring air-water interfaces will exist with chemical constituents that differ either in chemical nature or in concentration from those of the bulk liquid. Such predictions have been dramatically confirmed by results of field sampling and analysis performed by Garrett (1967a, 1970) and Baier (1972). Surface-active organic materials are consistently found at all natural air-water and air-sea interfaces sampled regardless of the absence of observable slicks.

The formation of aquatic surface films preferentially occurs with certain types of molecules, which have been categorized by Gaines (1966) as (*a*) nonpolymeric substances, which are essentially insoluble but whose molecules have sufficient attraction for the aqueous phase to permit dispersion, and (*b*) polymeric materials, including certain proteins. The long-chain fatty acids and alcohols, which have a nonpolar hydrophobic hydrocarbon tail and a polar hydrophilic functional "head" group, such as $-COOH$ or $-OH$, are a typical example of molecules in category (*a*).

The metabolic by-products of phytoplankton and algae are additional potential sources of surface-active materials in the marine environment.

Wilson & Collier (1972) have shown that marine diatoms produce organics capable of forming stable foams. Hoyt (1970) reports phytoplankton and algal exudates to be high molecular weight ($>50{,}000$) polysaccharides which can form surface slicks.

Within the first surface-active organic category (fatty acids, alcohols, and their esters) it is generally a safe simplification to consider that polar groups confer water solubility and hydrophobic groups tend to prevent it. In the absence of a polar group, long-chain hydrocarbon molecules such as decane ($C_{10}H_{22}$) will not form monolayers but merely float as drops or lenses on a water surface. As the length of a hydrocarbon chain increases, the solubility of molecules decreases. Solubility of a given chain length is controlled by its functional groups. The "effectiveness" of functional groups in providing attraction to water has been listed qualitatively by Gaines (1966). Alkylhalides and hydrocarbon functional groups do not form films. Typically, organic acids, alcohols, and amino groups all produce stable films with C_{16} hydrocarbon chains.

For some simple solutions with one adsorbate, the Langmuir isotherm [Equation (3)] may be used to predict adsorption behavior in a quantitative manner:

$$\Gamma_i = \frac{\Gamma_{\max} K a_i}{a_w + K a_i}, \tag{3}$$

where K is the equilibrium constant for the adsorption reaction $a_i(\text{aq}) +$ surface site $(S) = a_iS$, $\Gamma_{\max}$ is the maximum surface adsorption capacity, a_i is the activity of adsorbate, and a_w is the activity of water.

The free energy and the equilibrium constant for the adsorption reaction are related by

$$\Delta G^\circ = -RT \ln K. \tag{4}$$

(It should be noted that the symbol ΔG° may be misleading since an established convention for standard states for adsorption reactions has not been agreed upon.)

Szyszkowski (1908) described the surface adsorption reactions of unionized aliphatic acids using a variable that reflected the free energy contribution from Van der Waals interactions of the hydrophobic tails (which increase in proportion to chain length). Davies & Rideal (1963) show that these data may be expressed in the form of a Langmuir isotherm as

$$\Gamma = \frac{K(C/K')}{1 + C/K'} = \text{moles/cm}^2, \tag{5}$$

where C is the solute concentration (moles/liter), K' equals 1.9 exp $(-710\ m/RT)$, m is the number of CH_2 groups in the organic acid, and K is 5.28×10^{-10}.

From this approximation, qualitative estimations can be made of the relative surface excess for acids of differing chain lengths. However, such approximations must remain crude because in aquatic environments there exist a large number of surface-active materials that compete for the relatively few surface sites. Competitive adsorption phenomena and other complexities of the marine environment, such as ionic strength effects and turbulence (which minimizes the probability of adsorbates existing as simple monolayers), make realistic quantitative predictions of actual adsorption densities unlikely. Results by Garrett (1967b) indicate that competitive adsorption phenomena do indeed occur in the marine environment. In the presence of a compressed monolayer (sea slick), high molecular weight fatty acids and alcohols are thought to force lower molecular weight (more soluble) constituents out of the surface environment.

Field Observations of Surface-Active Organics

The results of analysis of field samples for surface organic constituents are summarized in Table 3. It is not surprising that the organics observed at the microlayer fall into the two surface-active categories described above, i.e. (*a*) fatty acids, alcohols, and lipids, and (*b*) proteinaceous materials. Also represented at the air-sea interface are carbohydrates and insoluble hydrocarbons from pollutant and natural sources and chlorinated hydrocarbon pollutants.

Measured organic concentrations at the air-sea interface are generally elevated above those of the bulk liquid in the sea. The reported enrichments for total organic carbon (TOC), dissolved organic carbon (DOC), and particulate organic carbon (POC) are summarized in Table 4. In general, the magnitude of POC partitioning is found to be greater than that for DOC at the surface microlayer. The interrelationship between DOC and POC at the air-sea interface is discussed later in this section.

Duce et al (1972) reported fatty acids, hydrocarbons, and chlorinated hydrocarbons (PCBs) to be enriched from 1.5 to 28 times in the surface layer (100 to 150 μm) relative to the bulk liquid 20 cm deep. Bidleman & Olney (1974) indicated PCB and DDT enrichment in the surface microlayer. Enrichment of pesticides in the surface microlayer has also been reported by Seba & Corcoran (1969) who measured total microlayer residue (DDT, DDE, dieldrin, and aldrin) concentrations ranging from 0.093 to 12.75 ppb vs 1 ppt in bulk waters. W. MacIntyre et al (1974) found higher DDT in microlayer samples from Chesapeake Bay than in bulkwater samples but reported uniform distribution of PCBs. It is interesting to note that the atmospheric origin of PCBs and DDT in the marine environment corresponds to their relatively high levels in surface films. Thus, surface films may play a role in the marine accumulation

Table 3 Characterization of organic molecules at the air-sea interface

Nature of organics determined	Reference(s)
Glycoproteins and proteoglycans	Baier et al 1974, Baier 1970, 1972, 1975, 1976
Triglicerides, free fatty acids, wax esters, cholesterol, DDT, DDD, DDE, PCBs, and phthalic acid esters	Larsson et al 1974
Fatty esters, free fatty acids, fatty alcohols, and hydrocarbons	Garrett 1967a, 1970, Jarvis et al 1967
Free and esterified fatty acids, pollutant and natural product hydrocarbons	Morris 1974, Morris & Culkin 1974
Free and esterified fatty acids	Marty & Saliot 1974
Fatty acids, hydrocarbons, and chlorinated hydrocarbons (PCBs)	Duce et al 1972
Normal, branched, and cyclo-alkanes	Ledet & Laseter 1974a,b
Normal alkanes	Marty & Saliot 1976
Normal alkanes	Hardy et al 1977a,b
Hydrocarbons (alkanes and aromatics)	Wade & Quinn 1975
PCBs, chlorinated hydrocarbon pesticides, free fatty acids and esters, and normal paraffinic hydrocarbons	W. MacIntyre et al 1974
PCBs and DDT	Bidleman & Olney 1974, Bidleman et al 1976
Dieldrin, aldrin, DDT, DDE, acetone, butyraldehyde, and 2-butanone	Seba &Corcoran 1969
Carbohydrates (mono- and polysaccharides)	Sieburth & Conover 1965 Sieburth et al 1976

and transport of these organic pollutants in addition to their apparently important role with respect to trace metals. Concentrations of pesticides in surface layers might have greater effects on insects, fishes, and birds that inhabit or associate with this zone than on organisms in subsurface waters (Parker & Barsom 1970).

The identity of specific dominant microlayer organic constituents is the subject of some controversy. Garrett (1967a, 1970) holds that an apparent competition exists for surface adsorption sites, with the high molecular weight and less soluble fatty acids and alcohols being the most surface-active and therefore predominant. These organics are typical of those previously described in category (*a*). Garrett (1971) has qualitatively identified proteins and carbohydrates in surface water but concludes that their contribution to surface effects is small because of their greater water solubility.

Table 4 Enrichment of total, dissolved, and particulate organic carbon at the air-sea interface.

Location	Type of sampling device	Form of carbon	Average microlayer concentration (range)	Mean Partitioning	Reference
Delaware Bay (convergence zone)	V-shaped tube	TOC	6.2%	n.r.[a]	Szekielda et al 1972
Open ocean	Glass plate	TOC	18.4 ± 16.5 mg/l	10.2	Barker & Zeitlin 1972
North Atlantic Ocean	Screen	DOC	1.73 mg/l (1.55–2.13)	1.6	Sieburth et al 1976
Bay of Bruse	Rotating drum	POC	0.94 mg/l	2.7	Daumas et al 1976
	Screen	POC	0.56 mg/l	1.6	
Pacific Ocean	Screen	DOC	2.7 mg/l (1.9–4.4)	2.63	Williams 1967
	Screen	POC	0.98 mg/l (0.17–2.5)	7.0	
Open ocean	Screen	POC	0.42	10.5	Nishizawa 1971
	Screen	DOC	1.42	1.71	
Strait of Georgia	Glass plate	DOC	6.24 (3.11–11.89)	4.4	Dietz et al 1976
		POC	2.79 (0.76–5.83)	10.24	

[a] nr = not reported.

Baier's (1970, 1972) experiments indicate a different nature for aquatic surface films. By dipping germanium prisms in water bodies, surface materials were non-destructively analyzed by multiple attenuated internal reflection spectroscopy (MAIR). After MAIR analysis of thousands of samples Baier concluded that the air-water interface in fresh water and the marine environment is dominated by glycoproteins and proteoglycans; both are typical of compounds previously described in category (*b*). These results differ strikingly from the conclusions of Garrett; dominance of liquid-like material was not confirmed by Baier's results. Baier has also characterized sea foams as being dominated by glycoproteins and proteoglycans and as stabilized by silica-dominated particulate debris, including diatom fragments (Baier et al 1974).

Liss (1975) and Hunter & Liss (1977) have argued that the extraction and analysis technique employed by Garrett (1965) selects for only a small portion of the total DOC present. The qualitative organic analysis performed by Baier may more accurately determine the dominant organic compounds at the air-sea interface. However, Hunter & Liss (1977) note that the IR spectra obtained by Baier are consistent with those for carbohydrates and that Sieburth et al (1976) found mono- and polysaccharides to constitute an average of 28 percent of the DOC at the surface microlayer.

Morris (1974) has indicated that greater than 85 percent of extractable microlayer organics in the Mediterranean were pollutant hydrocarbons; however, he also measured free and esterified fatty acids [major constituents were C 16:0 and C 18:1 similar to those described by Garrett (1970)]. Wade & Quinn (1975) measured average hydrocarbon concentrations of 155 μg/l in the Sargasso Sea microlayer vs 73 μg/l in bulk water. Detailed characterization of microlayer alkanes in the Gulf of Mexico has been performed by Ledet & Laseter (1974b). They indicate approximately 70 percent by weight of sampled alkanes were branched, 50 percent 3-methyl branched, 13 percent cycloalkanes, and 3 percent n-alkanes. W. MacIntyre et al (1974) measured 300 to 500 μg/l (total) of C 10 to C 24 n-paraffinic hydrocarbons in Chesapeake Bay. Also measured were 700 to 7800 μg/l (total) free and combined fatty acids with C 14:0, 16:0, 16:1, 18:0, 18:1, and 22:0 fatty acids predominant.

Organic Complexation of Trace Metals

Regardless of the nature of the specific organic constituents of the surface microlayer, it seems safe to conclude that the interface represents a chemically unique and relatively concentrated solution. The interfacial enrichment of organic matter offers an increased potential for the formation of metal-organic complexes at the air-sea interface.

Trace metal-organic compounds have been classified by Siegel (1971) as:

1. Those species existing in equilibrium with their free components whose reactions can be described by a reversible reaction and an appropriate equilibrium constant, and
2. Those compounds whose relatively constant concentration in marine waters is the result of a steady-state condition as opposed to an equilibrium process, and are thermodynamically unstable relative to their concentrations in the ocean. Such compounds are termed "non-labile," "inert," or "robust," i.e. exchange of added metal ion with incorporated metal ion will occur slowly over a long period of time (Dwyer & Mellor 1964, Siegel 1971).

The availability of organics to react with trace metals in seawater has been the subject of some debate. Magnesium and calcium, in high concentration in the oceans, may associate with organic chelators making them unavailable to trace metals (Siegel 1971). However, Duursma (1970) suggests that trace metals that bind strongly with organics may compete for available organic ligands and calculates that at low chelate (EDTA) concentrations Fe^{+3} and Cr^{+3} will be preferentially complexed. Although organics are known to be concentrated in surface films with respect to underlying waters, it is not known whether organic chelators are present in excess amounts or are limiting.

The relative order of organic binding strength for some divalent cations with bidentate ligands has been compared by Baes (1973) using cadmium as a baseline. The relative bond strength that can be inferred for bidentate bonds with oxygen and/or nitrogen is approximately $Mn^{+2} < Fe^{+2} < Cd^{+2} < Co^{+2} < Zn^{+2} < Ni^{+2} < Cu^{+2} < Hg^{+2}$, which corresponds closely to the "Irving Williams" (Williams 1953) order of complex stability for metal-activated enzymes: $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$.

It is possible through the use of equilibrium models to calculate the effect of organic ligands on trace metal speciation in a simplified seawater matrix. Such calculations permit some clarification of metal competitive behavior given a reasonable internally consistent set of starting assumptions. These calculations have been performed by Lion (1980) for simulated surface microlayer solutions using the REDEQL computer program (Morel & Morgan 1972). The calculations indicate it is reasonable to expect that many trace metals (e.g. Cd, Ca, Cu, Ni, Pb, and Zn) may be complexed with surface-active organic ligands and/or adsorbed onto particulate surfaces at the surface microlayer. The calculated results also suggest that the aqueous chemistries of trace elements are sufficiently different so that the surface enrichment observed may vary from metal to metal.

Effects of Organic Surface Films

The presence of organics at the air-sea interface has ramifications other than those associated with binding of trace metals. Marine surface films have been observed to alter sea-surface temperatures, interrupting normal mass and thermal convection processes below the air-water interface (Jarvis et al 1962). Surface films may also damp capillary surface waves (Garrett & Bultman 1963, Garrett 1967c). Production of bubble film drops is reported to be suppressed by the presence of sea-surface films (Woodcock 1972), while insoluble monolayer films apparently can act to increase the production of condensation nuclei from bubbled seawater (Garrett 1968). Gas transport rates can be affected by the presence of compressed surface films which act as a molecular barrier and reduce flux of CO_2, H_2O, N_2, and O_2 in and out of the bulk liquid (Garrett 1971, Lou & Rasmussen 1973). Liss (1977) has argued that only a compressed surface film can substantially influence gas-exchange rates. In such situations, the transfer of gases whose exchange is controlled by gas-phase resistance (e.g. H_2O, SO_2, NO_2) would be affected to the greatest extent (Liss 1977, Hunter & Liss 1977). A thorough review of microlayer organic chemistry including a discussion of gas-exchange processes has been presented by Liss (1975).

The presence of surface-active materials in bulk solution and at the surface can extend the lifetime of bubbles at the air-sea interface. This phenomenon is illustrated by the presence of stable foams which may literally pile into windrows on the downwind side of lakes or in marine coastal areas and persist for long periods of time (Baier 1972). Bubble stability may be qualitatively predicted from the Gibbs adsorption isotherm [Equation (1)], which may be interpreted to indicate that a decrease in Γ (which would occur if a bubble were stretched) causes an increase in $d\gamma$ or in bubble strength. Such strengthening might be thought of as conferring "shock resistance" to bubbles with adsorbed monolayers. Resistance to decreases in bubble surface area may occur through repulsion of polar functional groups in the surface coating. Garrett (1967b) has shown that, in the sea, bubble stability is enhanced by soluble surface-active materials which "feed stabilizing molecules into a bubble-water interface and protect it against rupture." Compression of surface films was observed to decrease bubble lifetimes as less soluble rigid molecules replaced the soluble surface-active agents at the interface. Monolayers may also act to increase bubble lifetimes via viscosity effects, whereby drainage of liquid in bubble walls may be retarded. MacIntyre (1974b) has indicated that oceanic bubble film caps are more likely to be stabilized by wet surfactants (i.e. those that are relatively hydrophilic such as proteinaceous materials) than by dry surfactants (such as the more hydrophobic long-chain fatty acids and lipids).

Particulate Organics

One of the most interesting (and controversial) of interfacial phenomena is the reported conversion of DOC into POC. This phenomenon was first reported by Sutcliffe et al (1963) and stimulated considerable debate concerning its authenticity in nature. Experiments by Riley (1963), Baylor & Sutcliffe (1963), and Riley et al (1964, 1965) all indicated that bubbles could produce particulate aggregates from filtered seawater containing dissolved organic material. It was shown that the aggregates formed might serve as a source of particulate food for marine organisms (Baylor & Sutcliffe 1963) and that the particulate aggregates scavenged (adsorbed?) phosphate and organics from solution (Sutcliffe et al 1963, Riley et al 1965). Subsequent experiments by Menzel (1966) using a carefully filtered air supply implicated organic contamination as the source of particulates produced by the other investigators. Experiments by Barber (1966) indicated that bacteria must be present in order to obtain particles. Extensive investigations by Batoosingh et al (1969) support the conclusion that the formation of POC from DOC can occur under specific conditions (i.e. in the presence of small numbers of 0.22–1.2 μm seed particles). Wangersky (1972, 1976) speculated that POC aggregates that form at the sea surface may be polymerized by ultraviolet light and altered into forms that are increasingly insoluble. Results by Johnson (1976) show that dissolution of small-sized rising bubbles can produce POC in seawater. Wheeler (1975) presented data that suggest POC can be formed from the collapse of surface films such as might result from wind, or wave forces, or possibly Langmuirian circulation. Trent et al (1978) have made in-situ and laboratory measurements on macroscopic particulate aggregates (marine snow) taken from seawater and indicate adsorption onto rising bubbles as one possible mechanism for their formation. Bubble aggregation of DOC combined with the UV energy input from high-intensity sunlight have been suggested as a possibility for the primevil origin of life (Goldacre 1958, Wangersky 1965).

Association of metals with colloidal or particulate organic material may range from weak attractive interactions (physical adsorption) to strong associations comparable to chemical bonding (chemisorption). Since sinking solids of various sorts have been implicated in trace metal transport in the marine environment (Martin 1970, Turekian et al 1973, Boyle et al 1977, Brewer & Hao 1979), it is interesting to consider the transport potential of the POC generated at the microlayer. Nishizawa & Nakajima (1971) have measured vertical variations in POC and calculate a downward flux of 260 mgC/m^2/day which they estimate to be the rate of POC formation at the microlayer. Wangersky & Gordon (1965) analyzed POC and particulate Mn in the North Atlantic and concluded that DOC and Mn are incorporated into bubble-produced organic particulate aggregates which can settle to the sediments. Hirsbrunner & Wangersky (1975) produced organic aggregates containing Na, K, Mg, Ca, and Fe by shaking filtered seawater samples. However, Siegel & Burke (1965) found trace metal (Zn and Mn) adsorption onto bubble-produced organic aggregates to be minimal, indicating that sinking particulates may not remove significant quantities of these metals from the microlayer by adsorptive processes. Wallace & Duce (1975) have shown that rising bubbles can effectively transport POC and particulate trace metals (PTM) to the surface microlayer under laboratory conditions. Wallace et al (1977) measured PTM and POC in a series of marine-surface water samples. The relative variations in PTM, POC, and particulate Al indicated sinking of POC may regulate PTM abundance in open-ocean surface waters. PTM removal rate by sinking POC was estimated to be of the same order of magnitude as the rate of supply of trace metals to surface waters through atmospheric aerosol deposition.

An important aspect of the interrelationship between DOC and POC at the surface microlayer is the special case of pollutant hydrocarbons. The fate of oil introduced into the marine environment through oil spills, shipping traffic, and other anthropogenic sources has received considerable study. The sequence of hydrocarbon weathering at the microlayer encompasses (*a*) loss of volatile components, e.g. aromatic and aliphatic acids (Garrett 1974, Hansen 1975, 1977, Harrison et al 1975), (*b*) UV oxidation resulting in the production of water-soluble carboxylic acids and oil in water emulsions (Hansen 1975, 1977), and (*c*) formation of a tar-like particulate residue (Garrett 1974). Baier (1972) has shown that bubble bursting is an efficient way of removing surface oil films, while Fontana (1976) has shown millimeter-thick oil slicks reduce the amount of spray produced by bursting bubbles. Particulate hydrocarbons have been found to constitute a significant portion of surface microlayer particulate phase in the Atlantic and Pacific Ocean and the Mediterranean (Horn et al 1970, Morris 1971, Wong et al 1974, Morris et al 1975, Wade & Quinn 1975). An additional anthropogenic source of microlayer organic particulates is plastic particles (Carpenter & Smith 1972, Colton et al 1974). Both tar and plastic particles apparently are used for attachment by sesile marine organisms including bryozoans, diatoms, hydroids, barnacles, isopods, algae, and bacterial films (Horn et al 1970, Carpenter & Smith 1972, Wong et al 1974). The fate of hydrocarbons in the marine environment has been reviewed by Hardy et al (1977a).

The literature summarized here shows that organic ligands will be partitioned at the air-sea interface. To a certain extent the types of organics that will be surface enriched may be predicted *a priori*; such estimates agree with observations made in the marine environment. Surface-active organics at the air-sea interface may bind with trace metals and thereby enhance metal partitioning. The formation of particulate organic aggregates at the sea surface has a potentially important role with respect to metal transport. In addition, the presence of elevated organic concentrations at the surface microlayer has important implications for surface microbiota. Possible interactions include the utilization of organics as a microbial substrate and the amelioration of trace metal toxicity through complexation with organic ligands. These latter topics are discussed below.

MICROBIAL ECOLOGY OF THE AIR-SEA INTERFACE

It is far from obvious that viable organisms should exist at the marine surface. The ecological conditions of the surface microlayer imply that it is an extremely high-stress environment. For example, Zaitsev (1971) indicated that the upper 10 cm of the sea captures about half the total entering sunlight and more than 75 percent of 254 mμ UV radiation. An increase in surface-water temperature would be expected in response to the surface absorption of light energy. Temperatures of 27.6°C and 26°C have been reported at depths of 10 and 30 cm, respectively, in the Caspian Sea (Zaitsev 1971). Other phenomena that may stress biological communities at the surface include evaporative cooling and salinity disturbances caused by atmospheric precipitation.

In the previous sections the presence of high concentrations of toxic trace metals and chlorinated hydrocarbon pollutants were documented at the air-sea interface. Depending upon the degree of their surface concentration and the extent of organic chelation, metal concentrations at the surface could prove quite toxic to organisms. The toxic effects of oil pollutants represent a further stress which occasionally can drastically alter conditions in the surface layer.

Trace metal toxicity to marine organisms is not well understood. Association of metals with living organisms can occur via adsorption to the general body surface or cell membrane in the case of bacteria, or in higher order organisms adsorption through special areas such as gills or across the walls of the gut (Bryan 1971). The following list of atoms, functional groups, and molecules which are probably bonded to various metals in living organisms (in decreasing order of occurrence) is excerpted from a review by Saxby (1969):

Fe: porphyrin, imidazole (a monocyclic nitrogen compound), $—NH_2$, $=NH$, R_2S, $—S^-$, $—COO^-$, $—O^-$, $=PO_4^-$
Mg: $—COO^-$, $=PO_4^-$, porphyrin, imidazole
Cu: $—NH_2$, $=NH$, R_2S, $—S^-$
Zn: $—NH_2$, $=NH$, R_2S, $—S^-$
Cd: R_2S, $—S^-$
Cr: $—COO^-$, $=PO_4^-$

Typically the growth rate of marine microbiota is accelerated by the presence of trace metals and a chelating agent (Johnston 1963). There are two interpretations for this phenomenon, the first being that organic chelators (i.e. EDTA) convert free essential trace metals (i.e. Fe) to organically bound trace metals, thereby improving their availability to microbiota and the second being that metal chelation reduces inhibition of toxic metals (e.g. Cu) to the organisms. Recent studies by Sunda & Guillard (1976) and Rueter et al (1979) have shown that complexation of cupric ion reduces its toxicity to aquatic organisms. Toxic effects were observed at free cupric ion concentrations as low as 10^{-10} M. Jackson & Morgan (1978) using an equilibrium chemical model to determine copper speciation, and kinetic calculations to estimate iron availability, have argued that the presence of chelators in solution *must* act to increase organism growth through reduction of copper toxicity. Whether the extent of organic binding of trace metals at the surface microlayer is increased relative to bulk seawater will depend on many factors including the relative magnitudes of ligand and metal enrichment and metal-ligand binding strengths.

In contrast to the array of stresses at the air-sea interface, there are some beneficial features that might be conducive to microbial life in this habitat. Drachev et al (1965) reported that the high content of surface-active organic compounds and suspensates at the marine surface may serve as a favorable substrate for the development of microorganisms. The iron, phosphorus, and nitrogen content of foams were determined to be 10 to 100 times concentrations in the bulk water; the biochemical oxygen demand of foams was said to be comparable to that of sewage. These results confirm the work of Wilson (1959) who found high nitrogen and phosphorus concentrations in sea foam. Further verification is provided by Szekielda et al (1972), who measured 6.2 percent organic carbon, 0.8 percent nitrogen, and 500 to 2500 ppm phosphorus in a condensed surface film taken from a convergence zone in Delaware Bay. Williams (1967) reported high surface-microlayer concentrations of particulate and dissolved nitrogen and phosphorus relative to concentrations in subsurface water. Concentration ratios for DOC, dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) in surface films (screen samples) relative to concentrations at 15 to 20 cm depth ranged from 1.7 to 4.9. Typical surface DOC, DON, and DOP concentrations were 3,000, 300, and 20 μg/l, respectively. Barker & Zeitlin (1972) reported a four-fold enrichment of total phosphorus and 10-fold enrichment of nitrate nitrogen in open ocean microlayer samples taken with a glass-plate sampler. Nitrate enrichment was not observed in surface samples (3-mm depth) taken by Goering & Menzel (1965) but higher levels of NH_3, NO_2, and PO_4 were found. Nishizawa (1971) reported order-of-magnitude enrichment of particulate organic nitrogen in the surface microlayer as did Dietz et al (1976). Higher phosphorus concentrations for <0.2-mm surface samples were reported by Balashov et al (1974).

Zaitsev (1971) indicated that sea foam can stimulate plant root systems, extend the survival rate of shrimp larvae, accelerate hatching and prolong the life of eggs of the goby *Pomatoschistus* sp., and apparently increase the hatching rate of *Artemia salina* (brine shrimp) eggs. Baylor & Sutcliffe (1963) have demonstrated that particulate matter formed by bubble aggregation will support the growth of *Artemia*.

The available literature demonstrates that the air-sea interface is, from a biological point of view, a high-stress ecological niche with some ameliorating rewards for those organisms able to adapt to life there. It is interesting to observe that many members of the microlayer planktonic community or neuston have specific physiological adaptions to maintain them at the microlayer. Maynard (1968a) has observed that many periphytic "benthic" organisms are able to use the marine surface film as a habitat, and found high concentrations of diatoms as well as small numbers of dinoflagellates, green, and blue-green algae in sea foams. Surface-layer utilization by attached organisms has been observed by Norris (1965) who classified many of the neustonic choanoflaggellates which attach themselves to the surface film by a protuberance of the protoplast or by appendages. Typical surface-film hangers described by Norris (1965) are extremely interesting; these organisms have apparently adapted to hanging upside down from the marine surface and feed upon the abundant marine bacteria using their flagellae to carry food-rich currents to the cell.

Parker & Barsom (1970) have observed that many bloom-producing blue-green algae use their gas vacuoles to produce bouyancy in order to concentrate at the marine surface. This feature may allow them to more effectively capture light, absorb gas, and to escape water-soluble algicides. David (1965) described a variety of surface-adaptive techniques, ranging from physiological adaptions, such as chitonons floats, to behavioral adaptions, such as the use of bubble rafts or attachment to flotsam.

Also dwelling at the air-sea interface are insects of the genus *Halobates*, commonly referred to as water striders. These insects support themselves on top of surface films via non-wetable appendages and use surface ripples as a means of communication (Milne & Milne 1978, Wilcox 1979).

The neustonic community apparently encompasses a diverse array of organisms. Zaitsev (1971) has listed the following members of the neuston in order of their appearance in the food chain: (*a*) microorganisms; (*b*) protozoa, the primary consumers; (*c*) small metazoans (invertebrates), including several species of rotifers, larvae of many species of polychaetes, gastropod and lamellibranch mollusks, copepods, cirripeds, echinoderms, some species of cladocerans, etc; (*d*) large metazoans, including representatives of the Polychaeta, Isopoda, Amphipoda, Cumacea, Mysidacea, and Decapoda; and (*e*) fish eggs, larvae, and fry.

Selective adaption for the air-sea interface also occurs in the microbial community. Young (1978) has observed web-like extracellular exudates produced by marine bacterioneuston which might act to improve organism surface activity. Protective pigmentation may be a physiological mechanism used by microorganisms to permit life in the microlayer. Tsyban (1971) has noted the brightest and most diverse shades of bacterial strains (yellow, yellow-green, orange, brown, and red) to be associated with cultures of marine bacterioneuston. Carlucci & Williams (1965) found a selective enrichment of pigmented vs non-pigmented bacteria in aquatic foam. Pigmentation was not thought to be a significant factor in fractionation, but to indicate a different type population in the foam. Blanchard & Syzdek (1978) presented evidence suggesting that pigmented cells of the marine bacterium *S. marcescens* have a greater tendency (relative to non-pigmented cells) to remain at bubble surfaces and thus may be more easily transported from bulk solution to the surface microlayer.

Microorganisms may also select for the microlayer by attachment to partitioned particulate materials. Recent field studies indicate that bacterial fractionation at the air-sea interface is closely correlated with degree of particulate fractionation (Harvey & Young 1980). Microscopic observation using acridine orange epifluorescence showed a high percentage of interfacial microorganisms to be associated with particulate surfaces. Carlucci & Williams (1965) reported that the presence of particulates in solution enhances the bubble transport of bacteria to the surface.

Bacteria and POC represent overlapping categories in the analysis of marine samples, and few investigators have simultaneously categorized both these entities in the same samples. The association of bacteria with particulate matter (both inorganic and organic) represents a chicken-and-egg type dilemma. It is not known whether bacteria attach to surfaces that are first partitioned at the air-sea interface or whether the particulates are partitioned because associated bacterial activity has resulted in a change in their surface activity.

There is some controversy over the activity of microbiota at the air-sea interface. Marumo et al (1971) reported order-of-magnitude levels of bacterial partitioning, but plate counts on different growth media indicated most bacterial cells in the microlayer to be dead or senescent. [The reader should note that bacterial enumeration by plate counting selects for a relatively small portion of metabolically active bacteria. Use of a range of different growth media is designed to help overcome this difficulty; however, alternate procedures, such as measurement of ATP or ^{14}C uptake, are currently preferred as indicators of biological activity.] Dietz et al (1976) reported two order-of-magnitude enrichment of microbial populations (colony-forming units) in the surface microlayer but lower ATP levels and heterotrophic activity (measured by ^{14}C uptake rate). Wallace et al (1972) found that rising bubbles most efficiently fractionate organisms in the post-stationary growth phase. However, the data of Sieburth et al (1976) show surface microlayer enrichment of ATP in seven out of nine stations sampled in the North Atlantic. Di Salvo (1973) measured up to a three order-of-magnitude increase in the number of bacteria that attached to glass surfaces at the air-sea interface. Since bacterial attachment may take place through cellular production of bridging polymers, stimulated air-sea interfacial bacterial activity is implied. Daumas et al (1976) measured greater enrichment of ATP in surface samples taken with a rotating drum (50 to 80 μm), than with screen (440 μm) suggesting stratification of living biomass at the upper surface microlayer. The opposite effect was observed for photosynthetic pigments indicating planktonic algae did not accumulate in the uppermost surface layer. Gallagher (1975), using a glass-plate sampler, measured greater than two order-of-magnitude enrichment of plant pigments in the surface microlayer of a Georgia salt marsh. Enrichment varied over a tidal cycle with highest levels on flood tide. An average of 37 percent of total net plankton photosynthesis was contributed by surface-film organisms.

Although the activity of surface-dwelling organisms may be in question, there is no dispute over the occurrence of elevated population numbers. Observations of organism densities in the field have been reported by Sieburth (1965, 1971), who found mean surface microlayer (150 μm) concentrations of 2398 organisms/ml vs 8, 26, 23, and 4 at 1, 10, 51, and 105 meters depth, respectively. Dominant film isolates were *Pseudomonas*; 86

percent of 200 isolates were able to oxidize glucose, 93 percent could hydrolyze lipids; 91.5 percent proteins and only 23.5 percent were able to attack starch. The bacterial proteolytic and lipolytic capabilities coincide with the previously discussed predominance of glycoproteins and/or fatty acid esters in the microlayer. Elevated field levels of bacteria and algae at the surface have been found by Harvey (1966) who detected changes in concentration with time of day. Parker & Barsom (1970) reported 5000 colorless flagellates, 31,270 dinoflagellates, 330 ciliates, and 930 diatoms per liter at the surface in contrast to 0, 3900, 370, and 3770 individuals per liter at a depth of 10 m.

Crow et al (1975) have measured bacterial concentrations of the order of 10^5 cell/ml in coastal surface interface waters using a membrane-adsorption sampling procedure. Microlayer bacterial concentrations were two orders of magnitude greater than those of the bulk (10 cm) water. Tsyban (1971), Marumo et al (1971), and Dietz et al (1976) all reported one to two orders-of-magnitude enrichment factors for marine bacterioneuston.

If the microlayer is indeed a stressful habitat it would follow from ecological principles that the diversity of organisms there should be reduced. Certain genera of bacteria would be expected to display relatively greater concentrations at the microlayer, and, as already seen, their concentrations may outstrip those in bulk solution. These predictions are confirmed by the results of Tsyban (1971) who observed the genera *Bacterium* and *Pseudomonas* to dominate the Black Sea microlayer vs *Bacterium* and *Bacillus* at 0.5–3 m depth and *Bacterium*, *Mycobacterium*, and *Pseudomonas* at 4–10 m depth. W. MacIntyre et al (1974) compared diversity index values for microlayer and one-meter plankton communities and showed increased diversity in the subsurface population. These results contradict those of Taguchi & Nakajima (1971) who reported increased diversity of plankton in surface microlayer samples. Most of the identified cells in microlayer samples were diatoms; fifteen species were found to occur only at the surface microlayer. The predominance of diatoms in the air-sea interfacial plankton has also been observed by R. Harvey (personal communication) in samples taken from south San Francisco Bay.

In summary, a variety of conflicting ecological pressures may be seen to operate at the air-sea interface. High intensity UV radiation and elevated concentrations of pollutant chemicals stress surface communities, while increased levels of organic substrate and nutrients reward organisms adapted for surface living. Although the activity and diversity of neustonic organisms are in dispute, there is general agreement over the presence of concentrated surface microlayer populations.

The occurrence of so many marine organisms in the surface microlayer invites speculation with respect to their interaction with the elevated trace metal and chlorinated hydrocarbon concentrations which are also present in the surface environment. The opportunity is presented for the direct incorporation of high pollutant concentrations into the marine food chain at many trophic levels. The importance of pollutant uptake and concentration occurring at the microlayer with respect to subsurface uptake by organisms has yet to be evaluated.

Microbiota at the air-sea interface might influence the fate of trace metals both directly through active or passive uptake or indirectly through production of extracellular metal-complexing organics and/or through modification of particulate surface activity (via their attachment). The alternatives for transport of microbiota, particulates, surface-active organics, and associated trace metals are discussed below.

TRANSPORT OF METALS, ORGANICS, AND ORGANISMS AT THE AIR-SEA INTERFACE

Interest in transport processes at the air-sea interface dates to early investigations which sought an explanation for the ionic content of rainwater and atmospheric aerosol (Blanchard 1963). The primary sea-to-air transport process indicated was jet drop ejection by bursting bubbles. When bubbles break at the air-water interface, current evidence indicates that they act as extremely effective microtomes, skimming material from the surface and ejecting it as jet drops into the atmosphere (MacIntyre 1968, 1970, 1974a). The bursting of bubbles has powerful implications for the transport and distribution of surface-concentrated materials. Zobell & Mathews (1936) have observed marine bacteria in atmospheric aerosols 30 miles inland and terrestrial bacterial species 130 miles at sea. Bubble bursting is also indicated as a source for the atmospheric occurrence of marine diatoms, microflagellates (Stevenson & Collier 1962), and algae (Maynard 1968b). Bacterial concentrations in jet drops from bursting bubbles may be 1000-fold greater than concentrations in the bulk liquid from which they emerge (Blanchard & Syzdek 1970, 1972, Bezdek & Carlucci 1972). The water-to-air transfer of virus through bubble jets and film drops has also been shown to occur (Baylor et al 1977a,b).

Baier (1970) has observed that oil films that built up on lakes due to recreational use can be eliminated within three days and that the principal mechanism of material removal is bubble bursting. Similar results have been reported by Bezdek & Carlucci (1974) who were able to remove stearic acid monolayers from seawater in the laboratory. MacIntyre (1970, 1974a) and Blanchard (1964) have indicated that jet drops from bursting bubbles at a solution surface coated with organic molecules may in turn be coated with compacted or multiple organic layers. Thus bubble breaking can serve as a source for the introduction of marine organic materials into the atmosphere. Barger & Garrett (1970, 1976) and Blanchard (1964) have found surface-active organics on marine aerosols. Baier (1975, 1976) has found surface-active organic materials with characteristics similar to those found on surface microlayers in sea fog samples. Wilson (1959) suggested that the ocean surface can also serve as a source for airborne nitrogenous materials and phosphorus. Bubble transport and aerosol enrichment of organic materials have been studied in laboratory systems by Blanchard & Syzdek (1974a), Hoffman & Duce (1976), and Pueschel & Van Valin (1974). Bubble path length and the presence of surface-active organics were shown to be important variables that control the transfer of organics from solution to aerosols.

The importance of bubble bursting with respect to removal of trace metals from the marine surface and subsequent redistribution is not well understood. Ion fractionation by bubble bursting and distribution of elements with aerosol particle size is currently the subject of intense investigation (Bloch et al 1966, Barker & Zeitlin 1972, Bloch & Leucke 1972, Chesselet et al 1972, Hoffman & Duce 1972, Seto & Duce 1972, Tsunogai et al 1972, Wilkniss & Bressan 1972, Glass & Matteson 1973, MacIntyre 1974b,c, Van Grieken et al 1974, Hsu & Whelan 1976). An excellent review of interface-atmosphere exchange of microorganisms, nutrients, trace metals, and major marine cations and anions has been prepared by Duce & Hoffman (1976).

It is interesting to note that aerosols of marine origin may act as a primary source for atmospheric Na, Cl, K, Mg, and SO_4 (Rancitelli & Perkins 1970, Buat-Menard et al 1974, Duce et al 1976) and that a significant fraction of atmospheric Cu may also originate from the seas (G. Hoffman et al 1972, Cattell & Scott 1978). In-situ sea-to-atmosphere transport of Fe, Zn, and Cu by bursting bubbles has been demonstrated by Piotrowicz et al (1979). The study was conducted using a bubble interfacial microlayer sampler developed by Fasching et al (1974) and showed that bubble scavenging from bulk solution was a factor influencing the degree of aerosol enrichment of Cu and Zn, while aerosol enrichment of Cu (in part) and Fe apparently resulted from their accumulation at the surface microlayer.

A wide array of studies has been published in which atmospheric elemental ratios are compared to those of crustal materials and seawater as a means of identifying their source (Rancitelli & Perkins 1970, G. Hoffman et al 1972, Buat-Menard et al 1974, Chester et al 1974, E. Hoffman et al

1974, Korzh 1974, Peirson et al 1974, Yano et al 1974, Zoller et al 1974, Duce et al 1976). Although the investigators do not totally agree, typically the elements Al, Ce, Co, Cr, Fe, Sc, Th, and possibly V are thought to have a continental origin, while Ag, As, Cu, Hg, Pb, Sb, Sd, Se, Sn, and Zn are enriched relative to reference elements suggesting an anthropogenic source. Elevated metal concentrations may not necessarily indicate man-made inputs, since plants have recently been shown to release Zn and Pb containing particles to the atmosphere (Beauford et al 1977).

If the sea surface can serve as a source of atmospheric trace metals, the reverse process is certainly also a possibility. Martin et al (1976) measured higher surface microlayer enrichments of cadmium in nearshore Pacific Ocean samples than in samples taken further out to sea. Eaton (1976) has measured higher Cd concentrations in Atlantic surface waters and suggests an anthropogenic origin. The atmosphere serves as a primary source of automobile-generated lead to marine surface waters (Chow et al 1969, Patterson & Settle 1974, Benninger et al 1975, Patterson et al 1976). Fitzgerald (1976) has estimated rainfall input of Hg to the oceans to be 30×10^8 g/year. In the Southern California Bight, Young & Jan (1977) estimated that the airborne inputs of Fe, Mn, and Pb from forest fires were 10 to 100 times the inputs from municipal wastewater discharge. Atmospheric input of Cd and Pb to the New York Bight has been estimated by Duce et al (1976) as respectively 4.1 metric tons/year and 220 metric tons/year from dry fallout and 8.2 metric tons/year and 400 metric tons/year from rainfall. Atmospheric deposition was estimated to account for up to 13, 8, 5, and 1 to 2 percent of the total Bight inputs of Pb, Zn, Fe, and Cd, respectively. Wallace et al (1977) estimated the atmospheric flux of Al, Mn, Fe, Ni, Cr, Cu, Zn, Pb, and Cd to the ocean; the calculated atmospheric input closely compared to the calculated removal rate of these metals via sinking of organic carbon particulates, which was estimated independently. Sedimentary records in both marine and fresh water environments indicate a recent anthropogenic input of Cd, Cu, Hg, Pb, and Zn which is thought to be deposited from the atmosphere (Winchester & Nifong 1971, Bruland et al 1974, Schell & Barnes 1976, Elzerman et al 1979, Galloway & Likens 1979, Hamilton-Taylor 1979).

Dusts of continental origin can transport geochemically significant quantities of materials to the marine environment (Goldberg 1971). One major dust source is the African Sahara Desert which Prospero & Carlson (1972) estimated may supply enough material to account for the present rate of pelagic sedimentation in the north equatorial Atlantic Ocean. The marine dust veil is reported to have high concentrations of Co, Cr, Mn, Ni, and V associated with it and may act as an important input source for Cd, Hg, Pb, and Zn (Chester 1971). G. L. Hoffman et al (1974) report microlayer concentrations of Fe near the African coast to be associated with dust loadings from the Sahara.

In addition to its role in inorganic transport, airborne deposition may act as a source of organics in the marine enviroment (Goldberg 1970). The importance of airborne inputs relative to those from continental runoff is not known with any precision, but primary production is clearly the principal source of marine organics (Duce & Duursma 1977, Handa 1977). Atmospheric deposition may, however, be a major source for input of pollutant chlorinated organics including DDT and PCBs (Bidleman et al 1976) and CCl_4 (Hunter & Liss 1977).

Aside from their important role in the transfer of materials from the oceans to the atmosphere, bubbles are also strongly implicated in the transport of materials from the bulk ocean waters to the air-sea interface. Use of bubbles to concentrate bacteria at surfaces has been applied in the laboratory to separate algae and bacteria from dilute suspensions (Boyles & Lincoln 1958, Gaudin et al 1960, Levin et al 1962, Rubin et al 1966, Grieves & Wang 1967, Wallace et al 1972). Laboratory researchers have discovered that flotation can be influenced by a wide range of parameters including bubble size, the presence of surfactants, gas flow rate, foam height, salt concentration, pH, age of bacterial components to be harvested, cell type, and cell surface functional groups.

Carlucci & Williams (1965) observed that dissolved organic material in seawater solutions may adsorb to rising bubbles and that bacteria may become attached to rising bubbles depending upon their size, shape, and individual affinity for the organic matrix. Rods were concentrated more effectively than cocci. Blanchard & Syzdek (1974a,b) have shown that the bactierum *Serratia marcescenes* attaches to bubbles at a rate of 3.1 cells per cm of bubble rise, giving a calculated collection efficiency of 0.12 percent. Transfer efficiency for bacteria to bubble jet drops was considerably higher and varied with the distance of bubble rise; efficiencies of 14 and 25 percent were given for 1.05-mm diameter bubbles rising 2.2 and 20.3 cm. Low bacterial transfer efficiencies from bulk solution to bubbles have been reported by Carlucci & Bezdek (1972).

Aside from the special case represented by bacterial particulates, rising bubbles have proven to be effective in transporting particulate materials in general. Separation of naturally occurring marine particulate organic carbon and nitrogen from bulk solution to the surface has been performed by Wallace et al (1972) and Wallace & Duce (1979). Quinn et al (1975) have used rising bubbles to transport latex particulate spheres.

The use of bubbles to scavenge both particulate and solute metals from solution in the presence of a surface-active "collector" is a well-established practice and various bubble separation processes have been used by the mineral processing industries since 1912 (Fuerstenau & Healy 1972). Bubble or foam separation of Cd, Cr, and Na (Kubota 1975, Kubota & Hayaski 1977), Cd (Chou & Okamoto 1976), Cd, Cu, and Pb (Huang 1974), and Cu and Zn (Jacobelli-Turi et al 1972) has been studied in laboratory systems.

Separation processes that may play an important role in trace metal removal from the bulk liquid and concentration at the surface have been categorized by Lemlich (1972b) and include:

1. Foam separation in which bubble-generated foams or froths are used to separate both particulate phases and solutes from solution. Separation of an individual species may be accomplished through a variety of processes, such as direct adsorption to bubble surfaces, induction of surface activity through addition of dissolved surface-active "collectors," and adsorption or coprecipitation of solutes onto surface-active solids.
2. Non-foam separations in which a foam or froth is not formed and materials are transported to the surface by rising bubbles.

It is not difficult to conceive that many of the separation processes listed by Lemlich (1972b) may occur in the marine environment. The possibility that trace metal separation occurs is strongly suggested by the presence of a wide array of potential chelating and surface-active agents in the sea. Nakashima (1979) and Kim & Zeitlin (1971a,b,c, 1972) have successfully separated dissolved Cu, Mo, Se(IV), U, and Zn from a seawater matrix through adsorption to or coprecipitation with $Fe(OH)_3(s)$ and bubble flotation in the presence of artificial surface-active organic collectors.

Wallace & Duce (1975) have demonstrated that rising bubbles can fractionate particulate trace metals (PTM) from seawater; for most metal species (except Cd) PTM transport to the surface correlated well with particulate organic transport. Based on their laboratory data, Wallace & Duce estimated the rate of bubble transport of trace metals to the sea surface from bulk solution via rising bubbles and compared this to the estimated atmospheric deposition rate of metals to the microlayer. Bubble transport was estimated to be a significant source for the elements Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn.

Recent field results and model calculations by Hunter (1980) suggest that atmospheric deposition of trace metals in North Sea coastal waters competes effectively with bubble transport as a source for microlayer enrichment under calm weather conditions. The relative rates of metal transport from Brownian diffusion, gravitational settling, rising bubbles, and atmospheric deposition were estimated by Hunter (1980). These calculations suggested that rising bubbles may, in general, be a more effective mechanism for surface enrichment of Cu, Zn, and Cd in the coastal waters of the North Sea. Gravitational settling was indicated as a removal process to account for observed microlayer depletions of Fe and Mn.

The literature available makes it abundantly clear that rising bubbles can act as a powerful transport vehicle for the delivery of dissolved surface-active organics and/or particulate materials to the sea surface microlayer. It should also be clear that rising bubbles certainly do not constitute the only transport process that might bring about partitioning from bulk solution to the air-sea interface. Thermal convection cells, turbulent mixing, and diffusion processes also would contribute to molecular movement and aggregation. MacIntyre (1974a) provides an excellent review of surface transport and ion fractionation processes.

The data summarized here leave little doubt that trace metals associated with transported species, i.e. metals that are complexed with surface-active ligands or adsorbed onto particulate surfaces, are transported in concert with these materials to the sea surface. In the complex marine matrix trace metals will compete with one another and the major marine cations for the available organic ligands and adsorption sites. It follows that in situations in which the available concentrations of complexing organics and solid surfaces are limiting, those trace metals that have relatively stronger binding strengths may be preferentially enriched at the air-sea interface.

SUMMARY

The available data describing the chemical and biological nature of the air-sea interface are still very limited. Useful comparisons are hindered by diverse sampling techniques. There are, nevertheless, recognizable trends in reported results. The occurrence of elevated trace metal concentrations in the surface microlayer is widely reported to occur and appears to correlate well with the presence of observable condensed organic slicks. Particulate and organic forms of metals show the highest degrees of enrichment at the air-sea interface.

Both dissolved and particulate organic carbon are partitioned into the surface microlayer. There is some controversy over the specific nature of DOC, but evidence favors the predominance of proteinaceous or carbohyrate materials. Pollutant hydrocarbons and chlorinated hydrocarbons are also enriched at the microlayer and might be transferred there to surface microbiota.

In spite of stresses at the air-sea interface, surface biological populations are elevated above those in bulk solution. Adaptive behavior for dwelling at the air-sea interface is exhibited by some surface species. Activity of surface bacterial populations is uncertain; there is some indication that diversity of populations at the surface microlayer may be reduced.

Rising bubbles and atmospheric aerosol deposition are indicated as processes that supply trace metals and organics to the air-sea interface. Bubble droplet formation and sinking of particles are indicated to be important material-removal processes. DOC at the microlayer may be converted to POC (which then sinks) through the action of breaking bubbles. Bubble transport appears particularly effective at transferring surface-active organics and particulates to the surface microlayer. This corresponds to the observed accumulation of organically associated and particulate trace metals at the surface microlayer. The high interfacial concentrations of organic ligands and solids also favor complexation and adsorption reactions in situ.

Trace metal levels at the surface microlayer may be toxic to the microbial population there. However, the possibility of metal binding by a wide array of organic chelating agents or adsorbing surfaces obscures the picture. It is not known whether the metals at the interface are substantially available to the microbial population.

All in all, very little is known about the interrelationships of the trace metal, microbial, particulate, and organic constituents of the air-sea interface. Better definition of metal-organic, metal-microbial, and microbial-organic interdependence at the microlayer would not only offer the potential for delineating the important processes involved in the transport of the component species, but would indicate the importance of microlayer interactions in the fate and distribution of pollutants which mankind inflicts upon the seas.

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