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Prospects for simulating macromolecular surfactant chemistry at the ocean–atmosphere boundary

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Abstract


Biogenic lipids and polymers are surveyed for their ability to adsorb at the water–air interfaces associated with bubbles, marine microlayers and particles in the overlying boundary layer. Representative ocean biogeochemical regimes are defined in order to estimate local concentrations for the major macromolecular classes. Surfactant equilibria and maximum excess are then derived based on a network of model compounds. Relative local coverage and upward mass transport follow directly, and specific chemical structures can be placed into regional rank order. Lipids and denatured protein-like polymers dominate at the selected locations. The assigned monolayer phase states are variable, whether assessed along bubbles or at the atmospheric spray droplet perimeter. Since oceanic film compositions prove to be irregular, effects on gas and organic transfer are expected to exhibit geographic dependence as well. Moreover, the core arguments extend across the sea–air interface into aerosol–cloud systems. Fundamental nascent chemical properties including mass to carbon ratio and density depend strongly on the geochemical state of source waters. High surface pressures may suppress the Kelvin effect, and marine organic hygroscopicities are almost entirely unconstrained. While bubble adsorption provides a well-known means for transporting lipidic or proteinaceous material into sea spray, the same cannot be said of polysaccharides. Carbohydrates tend to be strongly hydrophilic so that their excess carbon mass is low despite stacked polymeric geometries. Since sugars are abundant in the marine aerosol, gel-based mechanisms may be required to achieve uplift. Uncertainties distill to a global scale dearth of information regarding

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two dimensional kinetics and equilibria. Nonetheless simulations are recommended, to initiate the process of systems level quantification.

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1. Introduction

Marine biogeochemistry models are beginning to resolve the dissolved organic carbon (DOC) reservoir as a transported tracer class (Moore *et al* 2004, Hansell *et al* 2012) and may soon be able to decompose the material as far as specific polymer types (Benner 2002). By contrast, closely related atmospheric simulations treat primary organic aerosol emissions as structurally uniform. In sea spray-to-cloud coupling calculations, differential chemical influences are therefore lost with respect to size, hygroscopicity and other properties of the reduced carbon (Meskhidze *et al* 2011, Westervelt *et al* 2012). Here we use a combination of biogeographic and physical surfactant data to ask whether detailed molecular architectures should in fact be considered in the context of ocean–atmosphere interactions. A bottom-up (marine chemical) view is adopted and leads to several potentially novel conclusions. Molecular identities and distributions may exert regional oceanic control over gas/vapor transfer plus cloud droplet growth. This will occur through critical organic parameters such as interfacial coverage, the two dimensional phase state, chemically dependent hygroscopicities, mass to carbon ratio and even the basic property of density (Frew 1997, Petters and Kreidenweis 2007). Variability, temporal evolution and uncertainty of the physical processes involved will all be determined to some extent by source patterns as high molecular weight material is lofted into the atmosphere.

Our development begins with a short description of the production, types and surface film influence of global marine surfactants. The basic principles involved have all been well established for decades (Liss 1975, Hoffman and Duce 1976, Van Vleet and Williams 1983, Blanchard 1989). In the current work we stress recent advances in comprehension with respect to phase state, structurally and regionally resolved concentrations, and bubble/particle chemistry (Frew 1997, Benner 2002, Petters and Kreidenweis 2007, Hansell *et al* 2012). In a succeeding section, typical mixed layer ecodynamic scenarios are defined for which macromolecular distributions can be roughly estimated (e.g. Carlson *et al* 2000 in the context of provinces/biomes, Longhurst 1998). The surface physical chemistry literature is then surveyed to extract key adsorption constants. In this portion of the text we restrict ourselves to a discussion of traditional Langmuir monolayers, operating at the water–air interfaces so pervasive along the sea surface (Adamson and Gast 1997, Liss *et al* 1997, Cunliffe *et al* 2011). Local compound concentrations and adsorptive tendencies are combined to identify classes, ranks, and two dimensional crystalline states along critical interfaces (Barger and Means 1985, Frew 1997). Comments are offered regarding the variability of influence

on gas transfer, organic enrichment and aerosol chemical effects (Frew 1997, O’Dowd and de Leeuw 2007). The logic is supported in turn by an online supplementary appendix of equations, available at (stacks.iop.org/ERL/9/064012/mmedia) with free energy conservation providing for interdisciplinary unification.

Alternate types of polymer layering, adhesion and phase transition certainly take place at cavity/particle boundaries within the water column (Wells 2002, Azetsu-Scott and Passow 2004, Verdugo *et al* 2004). They are treated for the moment solely by deduction, relative to the more fundamental monolayer properties. For purposes of a short communication, extended surfactant chemistry is considered primarily at the level of discussion. Model compounds and equilibria are acknowledged throughout our development as highly uncertain (contrast Van Vleet and Williams 1983 with Benner 2002). But a set of tentative key conclusions may nonetheless be reached. Major parameters such as Langmuir coverage/excess, intra- and intermolecular structure of the two dimensional state, surface affinity in sea spray and the chemical influence on aerosol vapor uptake should all vary geographically. We end the text with a review of the potential errors inherent in such arguments, while simultaneously recommending that they should be implemented and tested in global systems coding.

2. Background

Proteins, polysaccharides and lipids are all released into ocean mixed layer waters due to the disruption of phytoplanktonic cells (Parsons *et al* 1984, Kujawinski *et al* 2002). Organic injections may occur in pulses following bloom events, or as a steady background in stratified waters. Long chain aliphatic and polymeric forms are all surface and particle active to some degree (Van Vleet and Williams 1983, Barger and Means 1985). They will thus adsorb to various available water–air interfaces, and the extent of this partitioning can be quantified via the archetypal Langmuir kinetic/equilibrium theory (Adamson and Gast 1997, Tuckermann 2007, supplement). At high enough concentrations for some of the substances involved, alternate phases are also expected to form including multilayers, micelles, gels and colloids (Vorum *et al* 1992, Babak *et al* 2000, Wells 2002). These provide surfaces for adherence which are less well understood (Verdugo *et al* 2004). Our strategy is to begin by estimating relative retention along simple monolayers at aerobic interfaces. Such situations are ubiquitous and receive substantial attention in the laboratory. We attempt to reconstruct additional surface chemical processes only by inference.

Positioned along bubble perimeters, adsorbed macromolecules influence (1) gas transfer into and out of a disperse, massive and buoyant oceanographic phase (Woolf 1997, Leifer and Patro 2002), (2) the average rate of rise of individual cavities (Clift *et al* 1978, Woolf and Thorpe 1991), and also (3) integrated upward sourcing of separate organic classes toward the atmosphere (Wurl *et al* 2011a). Although chemistry of the global sea-level microlayer is characterized by extreme heterogeneity and the presence of condensates (Cunliffe *et al* 2011, Gantt *et al* 2011), a true aqueous phase is also present and it is additionally subject to mono- and multilayer coverage. At both bubble and air interfaces, two dimensional phase states thus determine mass transfer rates, in the sense of analogy with gas dynamics (Barger and Means 1985, Frew 1997, Donaldson and Vaida 2006). A solid lipidic monolayer, for example, may act as a simple physical barrier to mass transport (Clift *et al* 1978). Meanwhile, extended liquid-like structures permit nominal passage of small volatiles but modulate viscoelasticity in the upper few microns (laminar layer thickness—Frew *et al* 1990, 2004, Frew 1997). Alterations to bulk and trace gas transfer imply large scale biogeochemical consequences, whether effects may be strongest on cavities or across the sea–air interface proper (Leifer and Patro 2002, Tsai and Liu 2003).

Bubbles carrying adsorbates eventually penetrate the global microlayer, to which further organics are attached. Breakage then injects both advecting and topmost films into the spray aerosol (Blanchard 1989, Oppo *et al* 1999). The ensuing enrichment of atmospheric particles may determine cloud droplet numbers through Kelvin, Raoult's Law and film kinetic effects (Feingold and Chuang 2002, Petters and Kreidenweis 2013). In what follows we construct qualitative indices for the geographic variation of all the above. Macromolecular concentrations are estimated based on local measurements and a generalized composition of the phytoplankton. Water–air adsorption, maximum surface excess and the two dimensional monolayer state follow from marine and purely physical chemical studies of Langmuir–Szyszkowski relations (LS as in Tuckermann 2007 or supplement). Aerosol chemical influences are characterized through measurements of atmospheric organic mass, partitioning within droplets, and physical chemical properties such as the surface tension, hygroscopicity, structure and density of the compounds involved (Turpin and Lim 2001, Dinar *et al* 2006, Petters and Kreidenweis 2007, Lapina *et al* 2011, supplement).

3. Surfactant chemistry

We investigate four generic scenarios for primary production in the open ocean, estimating macromolecular concentrations in each case. Blooms are represented by a set of closely scrutinized polar events (Carlson *et al* 2000), and their decay phase by the kinetics of conversion of labile forms—or else a lack thereof for refractory substances (Carlson 2002, Hansell *et al* 2012). Subtropical and gyre situations are investigated based on oceanographic station studies entailing extensive vertical profiles and time series (Kaiser and Benner 2009,

Goldberg *et al* 2009). Convective overturn at high latitudes assumes column compositions determined specifically for the Atlantic Arctic sector (Hubberton *et al* 1994, Dittmar and Kattner 2003). Direct measurements of the individual macromolecular types and their mixed products are utilized wherever possible (Zsolnay 1977, Gagosian *et al* 1982, Kuznetsova *et al* 2004, Moore *et al* 2008). Otherwise an injection ratio for protein, polysaccharide and lipid is assumed to be 60, 20 and 20% based on total average phytoplanktonic composition (Parsons *et al* 1984, Benner 2002). From this point in the development, we will often adopt for simplicity the abbreviations 'Prot, Poly, and Lip' when referring to the pure substances. They are converted by photochemistry and random enzymatic action into heterogeneous oligomers as accumulation takes place in the central gyres (Tranvik and Kokalj 1998, Benner 2002). These mixed polymers we denote by 'Proc' signifying processed carbon. Humic acid-like substances 'Hum' are similarly generated in the deep sea but remote from photochemistry and experiencing large terrestrial inputs, so that compositions are likely distinct (Hedges *et al* 2001, Dittmar and Kattner 2003).

For each type of macromolecule a set of marine and laboratory model compounds is selected to represent the potential for remote surfactant chemistry (Van Vleet and Williams 1983, Barger and Means 1985, Frew 1997). The proteins are mapped to lysozyme or albumin when they are near the cell, and as such they retain higher order structure (Graham and Phillips 1979). Polysaccharides are conceived of as soluble starches (Van Vleet and Williams 1983, Plavsic and Cosovic 2000, Nilsson and Bergenstahl 2006, Shogren and Biresaw 2007), with attention also to pectin since it exhibits intermediate surface affinity (Perez *et al* 2011). Members of the diverse lipid class are aliphatic, with the exception of a few oxygenated functional groups (Gagosian *et al* 1982, Parrish 1988). They will be represented simultaneously here by stearic acid and cholesterol (McGregor and Barnes 1978, Brzozowska *et al* 2012). The former is a traditional straight chain fatty acid and the latter a plate-like ringed molecule. Langmuir equilibrium constants are derived from the literature as half saturation concentrations $C_{1/2}$ in units of moles carbon per liter, then translated to micromoles per liter for ease in comparison with ambient levels (table 1). Surface excess Γ_{\max} is expressed for convenience in carbon atoms per square angstrom, but conversion to moles is straightforward for later manipulations (supplement). The tabled values are perhaps more intuitive because they offer a quantitative feeling for the degree of stacking around the water–air interface—the unit reference area is about one C–C single bond across (Adamson and Gast 1997, Babak *et al* 2000, Damodaran and Razumovsky 2003).

In plumes flowing away from a remote oceanic bloom zone we presume that at least some lipid forms are removed quickly (Parrish 1987), the proteins are converted to processed oligomers (Benner 2002) and polysaccharides survive longer than the other major classes (Goldberg *et al* 2009, Kaiser and Benner 2009). Before-and-after conditions are estimated in this manner for the Ross campaigns, as summarized in the first two column sets of table 2. A first version

Table 1. Ocean macromolecular classes investigated in the present work, along with literature values for the major Langmuir parameters (1) half saturation concentration, and (2) maximum surface excess. Basis for the interpretation of laboratory results is described in the supplemental appendix. Units are carbon moles or atoms. References in final column provide the most direct access to data, with supporting information included in the text. Lipids are difficult to observe in solution (Sebba and Briscoe 1940, Vorum *et al* 1992) so that $C_{1/2}$ is an upper limit defined for the one dimensional dissolution steady state of a spread film, as analyzed in Brzozowska *et al* (2012).

Compound	Abbreviation	$C_{1/2}$	Γ_{\max}	Primary references
Units		M (μM)	atom/angstrom ²	
Proteins	Prot	10^{-4} (10^2)	1	Graham and Phillips (1979), Damodaran and Razumovsky (2003)
Polysaccharides	Poly	10^{-1} (10^5)	10–100	Damodaran and Razumovsky (2003), Perez <i>et al</i> (2011)
Lipids	Lip	10^{-6} (10^0)	1	Christodoulou and Rosano (1968), Brzozowska <i>et al</i> (2012)
Processed type 1	Proc I	10^{-5} (10^1)	0.5	Graham and Phillips (1979), Benner (2002)
Processed type 2	Proc II	10^{-1} (10^5)	10–100	Babak <i>et al</i> (2000), Moore <i>et al</i> (2008)
Humic material	Hum	10^{-1} (10^5)	0.5	Svenningsson <i>et al</i> (2006), Tuckermann (2007)
Deep amphiphiles	Amph	10^{-5} (10^1)	0.5	Graham and Phillips (1979), Dittmar and Kattner (2003)

Table 2. Biogeographic situations highlighting surfactant behaviors of the open sea. For each case we provide concentrations, normalization to half saturation and relative two dimensional excess as a function of macromolecular type (supplement). Bloom and decay values are estimated based on comprehensive studies in the Ross Sea (Carlson *et al* 2000) and known emission ratios plus decay rates (Parsons *et al* 1984, Parrish 1987). The subtropics are characterized mainly by oceanographic station studies (Kaiser and Benner 2009). Arctic data are added to represent turnover conditions in high latitude winter (Hubberton *et al* 1994, Dittmar and Kattner 2003). At the asterisk we apply central ocean molecular weight restrictions for the dissolved state as described in Benner (2002).

Units	Bloom			Decay			Gyre			Convection		
	C	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	C	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	C	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	C	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$
	μM	Nondim	mole m ⁻²	μM	Nondim	mole m ⁻²	μM	Nondim	mole m ⁻²	μM	Nondim	mole m ⁻²
Prot	24	2×10^{-1}	3×10^{-5}	0	0	0	1	1×10^{-2}	2×10^{-6}	0	0	0
Poly	8	8×10^{-5}	4×10^{-7}	8	8×10^{-5}	4×10^{-7}	4	4×10^{-5}	2×10^{-7}	0	0	0
Lip	8	8×10^0	1×10^{-3}	0	0	0	0	0	0	0	0	0
Proc I	20	2×10^0	2×10^{-4}	44	4×10^0	4×10^{-4}	0	0	0	0	0	0
Proc II	20	2×10^{-4}	1×10^{-6}	20	2×10^{-4}	1×10^{-6}	75	8×10^{-4}	$*7 \times 10^{-8}$	0	0	0
Hum	0	0	0	0	0	0	0	0	0	25	3×10^{-4}	2×10^{-8}
Amph	0	0	0	0	0	0	0	0	0	25	3×10^0	2×10^{-4}

of Proc labeled Roman numeral I is given adsorptive physical chemical properties of the nonstructured but oft studied casein molecule (Graham and Phillips 1979, Damodaran and Razumovsky 2003). Converted protein accumulates in this bin. A second processed form II is presumed akin to the polysaccharides but must be less regular in structure. Here the LS parameters are derived from Gulf Stream samples analyzed in connection with the primary marine aerosol (Moore *et al* 2008) and no buildup is permitted. For the oceanographic station entry headed ‘Gyre’ (Kaiser and Benner 2009), monomers hydrolyzed and accounted separately during the analysis are summed. The aim is to reconstruct original local steady states for the Prot/Poly. Processed forms are computed by difference relative to a recent global simulation of total DOC (Hansell *et al* 2012). In this instance the surface excess must be lowered relative to stacked laboratory polysaccharide values. Central ocean dissolved carbon is primarily short in chain length. The alignment of hydrophiles is therefore subject to strict mass limits (Benner 2002).

Final columns of table 2 are designed to represent an organic chemical milieu resulting from unstable water mass turnover, common at high latitudes in the winter. The deep Arctic may contain both classic humic substances and poorly known amphiphiles ‘Amph’ in roughly equal quantities (Benner 2002, Dittmar and Kattner 2003). Both classes must currently be defined chromatographically (operationally). Humic acids are relatively well studied for their surface properties, most often through commercial riverine fulvic surrogates (Svenningsson *et al* 2006). For abyssal compounds displaying strong amphiphilicity, we again call upon a casein model. Convective events will significantly dilute mixed layer polymers relict from the previous summer (Longhurst 1998) and so we allow the constituents of central water layers to dominate entirely. The reader will note that conceptually extreme kinetic or mixing processes leading to the zero entries in table 2 must be quite artificial. Low remainders or weak steady states will be the reality for remote ocean areas (Zsolnay 1977). This is in fact among the main reasons we ultimately hope

to perform dynamic macromolecular simulations in the marine system.

Local polymer and lipid concentrations in the table are normalized immediately in a set of intermediate columns, to half saturation levels obtained during the literature search. The ratio ($C/C_{1/2}$) serves as a simple indicator for relative adsorptive capability to cover surfaces (Adamson and Gast 1997, supplement). Values are high for lipids due to their insolubility (McGregor and Barnes 1978, Vorum *et al* 1992) and for the proteins since aliphatic groups render them intrinsic amphiphiles (Graham and Phillips 1979, Damodaran and Razumovsky 2003). The polysaccharides exhibit low normalized concentrations since they are strongly hydrophilic (Nilsson and Bergenstahl 2006). For present purposes, we elect not to display fractional Langmuir site occupation directly. But competitive coverages are readily derivable and could be coupled to the global bubble field to provide absolute rise rates (compare Woolf 1997 with Tuckermann 2007). We are currently constructing such calculations, as a first step in the quantification of global emission fluxes for primary organic sea spray (Burrows *et al* 2014).

The surface excess measurements of table 1 are remarkably constant near unity (one carbon atom per angstrom), except for the polysaccharides and processed type two patterned after them. Sugar polymers appear to be capable of supporting rods, chains or loops in solution, suspended below a few critical hydrophobic moieties (Rosilio and Baszkin 2000, Babak *et al* 2000, Damodaran and Razumovsky 2003). In every third column of table 2, macromolecular excess is multiplied onto relative coverage to yield the quantity $\Gamma_{\max}(C/C_{1/2})$. This can be viewed as a further index reflecting relative total storage and transport (supplement). We performed the surface mass calculation mainly to estimate compensation by complex geometries of the adsorbed polysaccharides. An intermediate factor of 30 atoms per area is chosen for simplicity. While the relative standing of marine sugars is raised significantly by such an adjustment, dominance is not achieved in any given situation. Since the polysaccharides are sometimes observed as primary constituents of the high latitude aerosol (Cavalli *et al* 2004, Russell *et al* 2010), a corollary of the present work is that other mechanisms might be found for moving them into the atmosphere.

4. Results

In a final phase of the analysis, we focus on the strongest surfactant for each biogeographic scenario (table 3). The rankings derived are independent of our choice of indicator (nondimensional relative concentration versus hypothetical areal density). Thus for the moment at least, there is no ambiguity and issues of coverage versus mass flux can be set aside. By the logic developed here, collective lipids are the dominant surfactants in an immediate bloom situation. But the small ratio to rank two compounds indicates that denatured proteins may be competitive additionally. Langmuir

equilibrium constants are uncertain by orders of magnitude at this stage, depending on detailed substituent effects (Graham and Phillips 1979, Shogren and Biresaw 2007). Downstream relative to the fresh polar injections, newly processed protein-like structures are the strongest surfactants. But they are somewhat arbitrarily defined for present purposes and their chemistry has been linked of necessity to a terrestrial cousin (casein as in Graham and Phillips 1979). In the oligotrophic gyres, pure proteins come to the top of our list and this occurs in part because the massive Proc II bin is afforded humic behavior (Gulf Stream samples by Moore *et al* 2008). Benner (2002) argues persuasively that the aged material in stagnant mixed layer waters must in general have a molecular weight less than 1000 Daltons. We therefore hypothesize that rod or chain amplifications to the excess cannot occur. In the convectively active Arctic, chromatographic amphiphiles are the most surface active polymers since they adopt the behavior of destructured proteins. But their existence has only been confirmed in a few studies and they must be defined operationally (Dittmar and Kattner 2003).

Two dimensional phase state is assessed here based on the combination of surface tendency as embodied in ($C/C_{1/2}$) with known monolayer configurations (supplement). At high coverage in the pure form, fatty acids are capable of arranging themselves head to head (aliphatic tail to tail) so that their behavior may be almost crystalline (Adamson and Gast 1997, Brzozowska *et al* 2012). Lipid layers of the global environment will be a mix of 14 : 20 unit carbon chains, some with double bonding and augmented by unique phytoplanktonic sterols (Gagosian *et al* 1980, Parrish 1988). It is not entirely clear that such films are solid, but the possibility should at least be considered (Barger and Means 1985, Frew 1997). Proteins we classify as expanded surfactants since the term 'liquid' is problematic when applied to polymers (Frew 1997). Low surface concentrations can be conceived of as existing in a gaseous or chaotic state. We prefer, however, to categorize such situations more conservatively as dilute in the sense of the Gibbs plane. At this point in the development, the reader should note based on tables 2 and 3 that both identity and phase of the primary covering species are strongly dependent on biogeography. We believe that this circumstance will extend to both the regional and global scales, and that it can be demonstrated following the introduction of resolved macromolecular chemistry into systems models.

Within the marine aerosol, organics often constitute tens of percent of the core dry mass (Lapina *et al* 2011). This translates to internal concentrations of much greater than unit molarity at ambient relative humidities (O'Dowd and de Leeuw 2007), and the composition is primarily macromolecular (Cavalli *et al* 2004). Reciprocal of the half saturation constant ($1 \text{ molar}/C_{1/2}$) thus serves as a convenient measure of the tendency to remain at (or remix to) the surface of sea spray (supplement). In all of our first ranking cases, the atmospheric thermodynamic driving force amounts to orders of magnitude. Given an assumption of unit molarity, the dimensionless product ($\Gamma_{\max}/1 \text{ molar}$) (A/V) is just the ratio of moles carbon on versus in the spray aerosol at saturation $-A$

Table 3. Surface chemical indicators for the highest ranking compound type in each of the table 2 scenarios, listed first for conditions below and then above the sea–air interface (supplement). Normalized local concentrations and excess are reiterated from table 2 in the interest of clarity. Phase state designators follow Frew (1997). (A/V) is the area to volume ratio of an 0.3 micron aerosol particle, near the spray and remote marine mode radii (Seinfeld and Pandis 2006, O’Dowd and de Leeuw 2007). Surface pressures are from Christodoulou and Rosano (1968) for stearic acid with all others from Graham and Phillips (1979). Hygroscopicity values are given in Petters and Kreidenweis (2007) except as explained in the text. Organic to carbon ratios are likewise from Turpin and Lim (2001) plus text references. Deep amphiphiles are given humic structure (Dinar *et al* 2006, Svenningsson *et al* 2006).

	Bloom		Decay		Gyre		Convect	
	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$	$C/C_{1/2}$	$\Gamma_{\max}C/C_{1/2}$
Rank 1 macromolecule	Lip	Lip	Proc I	Proc I	Prot	Prot	Amph	Amph
	8×10^0	1×10^{-3}	4×10^0	4×10^{-4}	1×10^{-2}	2×10^{-6}	3×10^0	2×10^{-4}
Ratio (Rank 1/Rank 2)	4	5	20 000	400	12	10	10 000	10 000
2D phase state	Solid		Expanded		Dilute		Expanded	
1 Molar/ $C_{1/2}$	10^6		10^5		10^4		10^5	
($\Gamma_{\max}/1$ Molar) (A/V)	5/3		5/6		5/3		5/6	
Π_{\max} (mJ m^{-2})	>30		25		20		25	
κ	0.001–0.1		0.001–0.3		0.001–0.3		0.001–0.3	
O : C	1.3		2.5		2.5		1.8	
Density (g/cc)	0.9		1.3		1.3		1.5–1.7	

and V are area and volume with the fixed ratio $3/r$. The results provided as fractions are close to unity for all situations, confirming that surface re-equilibrium will not greatly deplete the bulk (Sorjamaa *et al* 2004, supplement). Collectively then, our bottom-up chemical oceanographic logic suggests that newly formed droplets of the ocean boundary layer are often surrounded by complete monolayers. Two dimensional solids are additionally considered effective barriers to vapor above the ocean interface (Feingold and Chuang 2002). Simultaneously, lipid and protein surface pressures maximize at tens of mJ m^{-2} (Sebba and Briscoe 1940, Christodoulou and Rosano 1968, McGregor and Barnes 1978, Graham and Phillips 1979). The potential for total coverage by marine organics thus raises dual issues of (1) kinetic slow down of water accumulation (Feingold and Chuang 2002) and (2) reduction to the Kelvin vapor pressure effect (Petters and Kreidenweis 2007 and 2013, supplement). Neither accommodation coefficients nor interfacial tensions have been determined *in situ* for the remote nascent spray.

We end the series of tabulations with a quick list of internal physical properties that may be relevant to aerosol modelers (supplement). The κ parameter is indicative of Raoult’s law influence for a given compound, acting upon the water vapor pressure (Petters and Kreidenweis 2007). It may be weighted by the volume mixing ratio and inserted into Kohler curve analyses to predict the threshold diameter for cloud particle growth (Seinfeld and Pandis 2006). For values greater than one tenth (dimensionless), the atmospheric behavior of a given macromolecule approaches that of inorganic marine salts. Weighted change to the threshold for droplet growth size may be small in such cases. By contrast, low κ coupled to a large organic content could discourage vapor uptake since the Kelvin effect is not as fully counteracted. The possibility of chemical segregation in the sense of internal versus external mixing cannot currently be excluded for sea spray carbon, and it would amplify these arguments (Wex *et al* 2010, Westervelt *et al* 2012). We characterize

literature ranges for the hygroscopicity as follows. With respect to proteins, the closest laboratory analogs have usually been amino acids. But in one prominent study of an albumin, surface reactions, filamentation and hysteresis may have all been in evidence (Mikhailov *et al* 2004, Kanakidou *et al* 2005). In the polysaccharide case the only relevant model has been levoglucosan, which is in fact a pyrolysis product. For lipids the long chain dicarboxylic acids are most similar, but they are actually of terrestrial origin (Petters and Kreidenweis 2007). Humic materials are often represented by riverine substances, and they are the most directly studied among aqueous environmental organics. Nevertheless the spread in reported κ is significant (Svenningsson *et al* 2006, Moore *et al* 2008).

In all top ranking cases presented in table 3, the range of hygroscopicity data is broad. Typically, representative values are rare and extend from nearly zero up to the vicinity of salt solutes. We determine that for the moment, our several marine biogeographies could either alter Raoult’s law as applied to remote dry aerosol particles or else leave vapor pressures unaffected. From our particular oceanographic perspective, the κ are thus largely unconstrained. Organic to carbon mass ratios and densities are provided just below the table 3 hygroscopicity line, for each primary macromolecule (Adair and Adair 1936, Tanford 1961, Parrish 1988, Phleger *et al* 1997, Turpin and Lim 2001, Azetsu-Scott and Passow 2004, Mikhailov *et al* 2004, Dinar *et al* 2006, Svenningsson *et al* 2006). These simple physical chemical quantities play intimately into aerosol growth calculations and exert primary influence on particle size spectra (Seinfeld and Pandis 2006, Petters and Kreidenweis 2007, supplement). But in contemporary global models, they are most commonly given average values for all marine organics everywhere over the ocean (Meskhidze *et al* 2011, Westervelt *et al* 2012). In fact from our standpoint it appears that they must vary regionally by about a factor of two, due at least in part to the polymeric and surfactant dynamics under investigation.

5. Discussion

Surfactant chemistry and regional concentration distributions have been surveyed for the marine macromolecules, focusing on several key biogeographic locations of the open sea. Model compounds and Langmuir parameters are suggested for the major high Dalton release products of phytoplanktonic cell disruption (Parsons *et al* 1984, Benner 2002, Kujawinski *et al* 2002). Relative adsorptive coverage and two dimensional excess are computed for several polar, subtropical and convective scenarios. We conclude that lipids/polymers of divergent structure and Gibbsian phase state may populate the regional water–air interfaces which are critical to bubble, interfacial and spray processes. Due to vertical organic enrichment (Kuznetsova *et al* 2004, O’Dowd and de Leeuw 2007, Lapina *et al* 2011), surface affinities are strengthened once the material reaches the aerosol. Strong nascent surface pressures are indicated, with implications for the Kelvin effect (Seinfeld and Pandis 2006, Petters and Kreidenweis 2013). Hygroscopicities, mass to carbon ratios and densities are also geographically variable (Turpin and Lim 2001, Petters and Kreidenweis 2007). Taken collectively, the above parameters influence sea–air gas transfer plus aerosol–cloud dynamics (Frew 1997, Meskhidze *et al* 2011). The subtleties to which we draw attention here may therefore have regional scale biogeochemical significance (Tsai and Liu 2003, Westervelt 2012). Our analysis suggests that macromolecular distributions and surface activity should be considered for inclusion in upcoming marine systems simulations.

Earth System Models are on the verge of resolving certain marine organic precursor quantities which may be required in order to drive an integrated surfactant chemistry. For example, the Biogeochemistry Ecosystem Circulation code of the Community Earth System Model (BEC inside of CESM, Moore *et al* 2004, www.cesm.ucar.gov) explicitly tracks aggregate semi-labile DOC, giving it a residence time of several months. Likely this form of carbon constitutes some combination of the freshly released protein and polysaccharide. In a series of simulations distinguishing dissolved organic classes by time constant, Hansell *et al* (2012) treat the semi-labile and refractory forms individually. We have examined global output concentration patterns closely with respect to both these modeling presentations. It should be possible in the near term to apportion grouped, dissolved organics such that their surface and aerosol chemical properties are readily distinguishable. True Langmuir isotherm calculations can eventually be imposed so that natural adsorbates are permitted to equilibrate onto modeled interfaces and also the rising bubble field. Upward and atmospheric fluxes follow directly in this framework.

In the interest of maintaining brevity during a preliminary survey, parameter uncertainties have intentionally been deemphasized here. But since we rely initially on the most convenient available laboratory data, error bars will necessarily be large. Data quoted in the tables are usually specific to standard ambient temperature, low ionic strength and a flat,

resting surface (e.g. Graham and Phillips 1979). The current choice of model compounds will prove to be only partially complete (contrast Van Vleet and Williams 1983 with Barger and Means 1985). For example, analog proteins and polysaccharides recommended here are exclusively of terrestrial origin (Graham and Phillips 1979, Perez *et al* 2011). And mixed functional group oligomers remain under-characterized, whether they are found in stagnant upper ocean waters or the deep sea (Dittmar and Kattner 2003, Kaiser and Benner 2009). Their processing extends over a period of decades at the surface and up to thousands of years in the abyss. Furthermore it is embellished by long periods of intense photochemical activity and random enzyme attack (Tranvik and Kokalj 1998, Benner 2002). The situation is daunting as a computational problem, but not hopeless. In fact we believe that a heterogeneous polymeric content lends itself to environmental chemical engineering approaches, with the evolution of equilibrium constants based on a statistical treatment of reaction and substituent effects.

From the point of view of marine aerosol systems, a particularly compelling issue emerges from the polysaccharide lines of tables 1 and 2. The classic chemical oceanographic literature recommends soluble starches as a front line surrogate for ambient carbohydrate (Van Vleet and Williams 1983). But this class of compounds turns out to be exceptionally hydrophilic (review in Nilsson and Bergensstahl 2006 or data in Shogren and Biresaw 2007). In the current work, sugar polymers are thus categorized by definition as weak adsorbers. Yet they are often detected and analyzed *in situ* as contributors to the aerosol fine mode (Cavalli *et al* 2004, Russell *et al* 2010). A tentative but simple conclusion is that this particular polymer class may exhibit alternate means of moving upward through the water column, followed by the standard bubble-breaking introduction into sea spray. Several groups have documented the colloid forming, buoyant, and micro-layer coating propensity of polysaccharide material accumulating within the mixed layer (Wells 2002, Azetsu-Scott and Passow 2004, Wurl *et al* 2011b). In our own effort to resolve ocean surfactant chemistry, an early priority will be to simulate some combination of the following relevant microphysical processes: slow background gel rise, bubble impaction/adherence of sugar particles, and energetic bubble breaking into the boundary layer. The goal will be to explain the empirical atmospheric presence of a less surface-active compound from among those investigated here.

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