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Article

Does Marine Surface Tension Have Global Biogeography? Addition for the OCEANFILMS Package

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Abstract: We apply principles of Gibbs phase plane chemistry to and across the entire ocean-atmospheric interface. Surface tension increments support a two dimensional, tangential pressure well known to determine rates of bulk gas, bubble, salt, spray and momentum transfer plus both sensible and latent heat fluxes. Hence it is worth asking whether tension mapping follows from current understanding of two dimensional composition. A history is provided dating back centuries and demonstrating that detrital organic macromolecules are central; subtle surfactant functional variation creates a microforcing field which dissipates turbulent energy at the sub-meter scale. Since we have just distributed major biopolymeric classes emitted as primary organic aerosol, further climate links can be established by considering full planar thermochemistry. Organic microlayer behaviors are reviewed with attention to confined, analog phase transitions among two dimensional "solid, liquid, (and) gaseous" states serving as elasticity indicators. We also discuss surfactant properties of general marine dissolved organic carbon, demonstrating that only proteins and lipids are capable of occupying significant local micro-area. The literature often suggests albumin and stearic acid as best proxies, and so we distribute their concentrations through multilevel global ecodynamic simulations. Consensus distributions are obtained in order to control adsorptive equilibria. Working from conservation of planar free energy, a parametric equation of state is devised relating excess coverage to the surface pressure-modulus. Constant settings for the proxy pair are drawn from laboratory study, and they successfully reproduce frequencies for surfactant solid-to-gas occurrence in ambient compression experiments. Functionally resolved organic measurements are rare and so we group them into super-ecological province tables showing that our bulk concentration estimates are reasonable. Outputs are then fed into a coverage-tension-elasticity code. Resulting contours traverse the critical range for piston velocity, bubble-spray and damping effects on either a regional or seasonal basis. There is also a possibility for widespread microlayer crystallization in polar seas. The concepts are a direct extension of our organic aerosol work, and the two approaches could be inserted into Earth System Models in tandem. Uncertainties in the logic are enumerated and include kinetic and thermochemical factors at multiple scales. But the problems are reducible through molecular modeling coupled to renewed laboratory and field study. Connections to marine colloids-gels, microlayer iron chelation, and linings of the ice channel network are discussed additionally.

Keywords: Gibbs phase plane; surface tension and pressure; gas, momentum and heat fluxes; biogeochemical mapping; organic macromolecules; surfactants; elasticity; proteins; lipids; compression; two dimensional equation of state

1. Introduction

Composition of the marine atmospheric interface determines surface tension across most of the exterior of the planet [1-9}, so that fluxes of multiple climate-critical quantities are effectively modulated through a single physicochemical-energetics filter. Transfer of trace greenhouse and aerosol-source gases, organic and salt aerosol mass, momentum, heat and water vapor are all defined by chemistry-driven gradients in tension at the sea-air boundary {10-15]. It has long been suspected that variable concentration patterns of detrital, surface-active biomacromolecules exert key control over upper ocean and microlayer dynamics, differing in their tension influence among diverse regional ecosystems. Structural identities must not only be known for the compounds involved but also distributed geographically in order to assess this possibility; organic functional groups closely constrain the two dimensional forces imparted [6,16-19]. Several attempts have been made to simulate the geophysical effects of high molecular weight surfactants at the level of Earth System Modeling, but this has been done mainly by assuming proportionality of the collective material to chlorophyll [20-24]. Mixed layer pigments are detectable from space, and indeed they necessarily track source biota for the surface organics, so that this has proven to be an eminently reasonable starting point. But detailed microchemical information remains lacking.

In our own aerosol-oriented group, we have recently become interested in constructing biogeographies for individual classes of macromolecule, since functionality plays strongly into the generation of sea spray [4,25-29]. Our initial angle has been that of adsorption -upper ocean films accumulate and are sculpted through surfactant equilibration and the intense physicochemical competition for microlayer sites. Such processes regulate both organic and salt mass entering primary marine aerosol modes through bubble breaking [30-33]. Isotherms representing surfactant families that reside along bubble interfaces were tested then inserted into global biogeochemistry calculations, accompanied by full modern mapping techniques [30,33]. Improvements to the simulation of primary aerosol mass have already been realized [31].

But adsorption of high molecular weight organics necessarily also implies alterations to the fundamental tension property of the global interfacial system. This takes place through classic two dimensional (Gibbsian) equivalency of the chemical potential [5,34-37]. In the present work, we extend the adsorptive surfactant calculations to assess any need which may exist for development of a further bioorganic geography –that of the film tension. We construct chemically driven global patterns and maps for this key quantity, or more precisely speaking for its absolute reduction known traditionally as the two dimensional pressure (tangential [2,36,38]). Crude, ideal equations of state are constructed which apply in a preliminary fashion to the full, planet encircling marine microlayer. We perform the implied mapping exercises first at the scale of marine biogeochemical provinces [39-40], selecting and grouping them to optimize our use of a fairly sparse measurement base. Offline semi-dynamic biogeochemistry calculations are then conducted as a further demonstration of principle [33,41-43]. These are postprocessed through a macromolecular distribution mechanism then a coupled surface pressure-area parameterization ([33]; appendix here). Emphasis is placed to begin with upon the two most basic issues involved -will geographic differences in surface tension be identifiable-computable? And will they be important to the many geochemical and climate-relevant fluxes with which they have been connected?

The arguments synthesized in this tension mapping effort rely heavily on surfactant physicochemical data and theory which are typically unfamiliar to students of global change. Since one goal of the exercise is to motivate tests at the level of Earth System Modeling, we are careful to proceed in a stepwise manner. A rough outline for the remainder of the text is as follows:

(Section 1 -Introductory material above then) Section 2 (Background) -A history of the problem is provided dating back centuries but moving forward into the post World War II era. This story line often involves wave calming by diverse organic substances, and it demonstrates clearly that global film composition could be pivotal. We also extend from the historical realm to related but much more recent research on trace gas and salt spray transfer, which have become understood only during the era of global change; Section 3 (Physical Chemistry) –Subtle variations in the functional structure of disperse, adsorbed detrital-biomacromolecules are described, causing them to exert Van der Waals, Coulombic and other microforces globally and tangentially at one and the same time. The result is dissipation of turbulent and wave energies at the centimeter to meter scale. Hence the suspected control over a broad spectrum of flux types through the surface tension property -or rather its difference-from-baseline the surface pressure (π). In this same area of the text we introduce the concepts of two dimensional “gas, liquid and solid” state analogs occurring within the phase plane, since they indicate film elasticity and so have utility in terms of validation; Section 4 (Observations) –A quick review of measurable influence on bulk gas piston velocities, bubble-foam-spray behavior and number generation, plus transfer of momentum and the various heat varieties. We end with the definition of a round-figure 2D pressure band characterizing the strongest effects in all cases. This is primarily to enable quick visual inspection of global maps for the relevant film chemistry contours.

Section 5 (The Compounds) – A brief tutorial regarding detailed composition and interactions of upper ocean dissolved organic carbon-containing material (the well known DOC). We demonstrate through surface chemical equilibrium arguments that among the broad variety of mixed layer macromolecules and degradation products, only proteins and lipids are likely to be capable of occupying any significant fraction of local micro-interfacial area. Hence these forms become our natural focus, since their influence on tension must be dominant; Section 6 (Surrogates) Both the general and chemical oceanographic surfactant literatures suggest as proxies the specific high molecular weight substances albumin and stearic acid. Together they therefore enable a proxy or substitute representation of the two main biomacromolecular families; Section 7 (Concentrations) -Distributions for the two surface active classes are mapped across the planetary mixed layer in standard units of µM carbon, calling upon multiple global biogeochemical models at multiple levels of complexity to do so. A rough consensus is obtained for regional scale protein and lipid levels, and this is presented in tabular form across super-eco-chemical provinces we christen “Surfactomes” for obvious reasons under present circumstances; Section 8 (Spreading) -Effective two dimensional equations of state are developed in an accompanying appendix then imported into the overall text for implementation, working from Gibbsian surfactant thermochemistry up to empirical isotherms. This leads to a simple parameterization for the critical variables film coverage, surface pressure and its modulus. All are thus unified for insertion into Earth System Models.

Arbitrary dissolved organics can be entered into the film spreading strategy, but for demonstration purposes we restrict ourselves to the selected proxy pair. Constants and switches for the calculation are drawn from decades of laboratory study spanning several disciplines, and it is shown that classic planar phase diagrams of the real ocean are readily reproducible. Our true global mapping exercise begins in Section 9 (and it includes Sensitivity Tests) -Global π plots (Δtension) are constructed from a down-selection of the readily available biogeochemistry models. A well-delineated, basin scale geography is immediately apparent, and regular crossing of the crucial 2D force band is tentatively identifiable. The sensitivity variations we conduct show that our film chemical geography is internally consistent, but may be subject to coastal and high latitude extremes which cannot yet be verified; Section 10 (Uncertainties) –In an attempt to be entirely forthright regarding complexities inherent to our manipulations, we table a fairly comprehensive list of potential error sources. Some are classified as parametric, others must be structural and many are large; Section 11 (Discussion) –Gaian consequences of the strategy are enumerated and then expanded upon. They include biological control on vertical ocean-atmosphere mixing, derived directly from detrital organic chemistry taking place at the boundary between the two media. We believe additionally that the community should consider the potential for –the steering of currents, winds and extreme weather events. Finally the case is built that our system of organization for organic tension is readily testable in coupled climate models. A highly parameterized Equation of (film surfactant chemical) State, as presented in the appendix and developed in the above sections, already has a strong parallel in our own coding: Very similar algorithms appear in the form of the OCEANFILMS package, which our group uses to adsorb carbon for emission into the primary marine aerosol.

2. Historical and Background

It has been known for millennia that certain organic liquids spread onto the natural water-air boundary can exert a calming effect on waves of many scales [9,17,44]. There have in fact been numerous documented attempts to actively, chemically de-engineer harbor mouth and shipping lane breakers. Some of these date back hundreds of years [45,46]. Well-known classical and eighteenth-nineteenth century figures mentioned in this connection include Plutarch, Pliny the Elder, Benjamin Franklin, Reynolds and Aitken. During and after the World Wars it became clear that the surfactant influence on upper ocean mixing must also be operative at regional to planetary scales [47-49], and furthermore that it extends to the turbulent eddy spectrum arising just below the atmospheric interface [38,50]. This latter connection implies influence upon large scale transfer of many other properties -solute mass, heat energy and also via temperature dependence of the vapor pressure, even water vapor must be included [2,46,51]. Extension of the concepts to surfactant-tension control on bubble and spray distributions lagged only slightly [25,52-54]. Effects on trace gas fluxes operating in the greenhouse and marine aerosol-cloud systems also began to draw attention during the era of global change biogeochemistry [2,6,55].

The physical mechanisms by which these linkages make themselves felt encompass intimate-intricate interactions among (to offer a set of partial examples) -Prandtl, Monin-Obhukov, Gibbs-Marangoni, laminar renewal, viscoelastic and microlayer rheological theories. As might be imagined, the fluid dynamics encountered as one moves through this list can become quite daunting in and of itself. Coupling of the requisite hydrodynamics with an equally complex environmental (organic) chemical assemblage is perhaps one reason such concepts have been slow to take hold within Earth System Models. We have collected and harvested some of the clearer explanations available for tight connections within the physical system [17,18,46,50,56-61], in order to provide the appropriate justification for our geochemical mapping efforts. The detailed approach presented later, however, remains purely empirical. We now provide the reader with an heuristic summary of surfactant influence on atmospheric and oceanographic mixing theories, incorporating and accounting the many tension and film rheological factors. But the text then zooms in on potential bio-geochemical-geographic differences and distinctions. It is argued that the latter are strong enough to be of interest in the context of boundary layer vertical transport as handled in Earth System Models.

Crudely speaking, a single thin and in fact monomolecular layer of appropriately mixed organics may exert unexpectedly dramatic control, on any and all fluid movement near the air-sea interface [8,45,46,48,59,61]. Working from the geometric top of the relevant environment downward as a conceptual device, it is often noted that surfactants can suppress the capillary (centimeter scale) waves that act upon boundary layer meteorology as roughness elements [8,9,18,59,62-65]. This occurs through modified hydrodynamic boundary conditions allowing for energy dispersion at certain key frequencies [17,56]. The normal cascade of momentum flow and turbulent exchange from the atmosphere into the sea is interrupted. In some cases it may be shut off almost completely, leading to a gross reduction in vertical stirring within only minutes [45,46,59]. A readily observable glassy slick will often follow, sometimes extending over large areas and lasting for many hours and detectable at altitude or from space [8,12,38,64]. The crucial chemical dependence of the effect is common knowledge to the shipping industry, because oily waste materials ejected at the water line are only sometimes calming. Clearly not all organic substances have the capability.

Simultaneously, ocean eddies approaching the water-air interface from below alternately dilate and compress the border that runs between the major geophysical phases [18,38].

Surface-constrained turbulent structures experience energy loss or extraction due to differential elasticities arrayed along the microlayer. These follow in turn from the presence of the macromolecules and biopolymers, for which distributions are patchy in both spatial and chemical senses. The effect may be tightly confined locally, but on the average it can also extend over hundreds of kilometers [6,8,18,59,64]. Multi-scale tension gradients are thus the rule across the top of global ocean, and they are most reasonably attributed to variability (heterogeneity) in the natural surfactant distribution [9,19,64]. The eddy-energy extraction processes may also be portrayed as an alteration to thickness of the hypothetical laminar layer barrier, which in many conceptions regulates both mass and energy transfer. Surface renewal may constitute a rate determining step so that the flow of either dissolved gases or heat is blocked [6,9,50,51]. Water vapor is in turn affected through skin temperature because this sets the vapor pressure [2,51,66,67]. Vivid demonstrations of the above phenomena have been documented over many generations –sometimes accidentally, sometimes intentionally, within laboratories, perhaps witnessed in the field or even detected from space up to the largest scales [6,18,28,45,46,50,59,64]. We now proceed to an analysis of the underlying marine chemical principles involved, their efficacy with regard to geophysical fluids, and their distribution over the ocean.

3. Physical Chemistry Concepts

The situation is apparently enormously complex even at a purely physical level. Since our initial research must be confined to biogeochemical and biogeographic issues, we adopt an almost entirely empirical view of the hydrodynamics. Henceforward it becomes a black box into which the physical chemistry is injected but with copious supporting data on hand. Emphasis is now placed on the development of realistic, large scale chemical parameterizations for the natural (surfactant) biomacromolecular properties and distributions. A few definitions are required and provided immediately, with details appearing along with more complete derivations/equations in the attached appendix.

In the common parlance, we refer to the any reduction to seawater tension as a two dimensional pressure, and for purposes of clarity the related quantities will often be prefaced as “2D” [2,38]. Certain inorganic solutes and coatings actually increase the energetic cost of area generation, giving values which are effectively negative. These substances act on the physics by default since they are segregated on a mass basis from the ambient microlayer, but we will not need to deal with them further [68-70]. The more familiar decreases in surface energy associated with amphiphilic organics can be understood as follows -hydrogen bond breaking among solvent water molecules may be partially compensated by reformation at the point of surfactant penetration if a film is present –head moieties are hydrophilic. But liquid-facing point groups tend also to be uniformly charged, meaning there are repulsions which must be accounted. Meanwhile phobic arms relegated to the gas phase contribute to the overall push-pull attributable to the surficial or planar interactions. Van der Waals attractions above the interface draw net area inward, while double bonds may repel one another thus working in the opposite direction. The overall physicochemical forces are merely Newtonian and can be tallied theoretically or studied in the laboratory -but in either case, they are best viewed collectively in units of per length. In fact all is analogous with traditional bulk pressure but aligned in a new dimension -along the water-air interface. It is the overall chemical assistance with, or boost to, formation of extra interfacial area that is termed a 2D or surface pressure. The usual symbol is π and see our quick but more formal treatment in the appendix.

Any real exposition of the surfactant-organochemical force-energy requires many pages to reach even a microscopic level of completeness. But high quality textbook approaches appear on about a decadal scale and they have been closely consulted [36,38,71,72]. We will not be so bold as to attempt a balance or comparison of the numerous competing surfactant processes which must operate among detrital carbon forms at the planetary scale. In fact the 2D forces of interest are embedded in, and must be exert themselves despite coexistence with -unexpected alternate rheologies including slimes, a size distribution of gelatinous particles buoyed from the mixed layer, dust and its coatings settling from the atmosphere, entire film-confined ecosystems dominated by bacteria but not lacking protozoa, plus injections of oxidizing power from the light rich medium above [58,73-76]. We focus for simplicity and of necessity on the (interfacial) spaces in between. It seems clear from our logic that molecular dynamic simulations of the micro-situation might someday be profitably undertaken, as support for a tension-globalization effort among Earth System modelers. For example, such (computational-theoretical) research could be geographically distributed point by point, by analogy with our province strategy. For the moment, however, the above notions of tangential physicochemical force are merely carried along conceptually, since we rely for quantitation on a rich but underexploited array of historical and experimental outcomes. These are drawn in balance from laboratory and ship-based research.

Our appendix argues that the set of macromolecules or biopolymers distributed along a liquid interface may be considered independently as a physical phase unto itself, with components in the plane undergoing transitions of state [5,18,38,71]. A thermochemical summary is given with the equations, but the reader is encouraged simply to picture surfactant phase transformations, defined in the Gibbsian sense and taking place directly beside the neighboring, massive concentration supply of the bulk. The processes are confined to a microlayer plane which is usually monomolecular. Analogies with simple gas, liquid and solid behaviors become a convenient organizational tool [5,17,63,77]. In the laboratory real organic films can be synthesized or collected, then spread on seawater samples and compressed by paddle devices, so that they impart increasing and measureable influence on the tension. The summed forces referred to as π increase together as area A is reduced. Mixing effects may be nonlinear but we set this issue aside for the present. Gently sloping π-A diagrams are classified with reference to the much more familiar textbook (bulk) P-V variety as the marker for a 2D "gas". In some cases a certain ideality is approached and the reader can likely guess the rather elegant form of the resulting equation of state [36,37].

By the same token a surface "solid" exhibits little change in π until a condensation threshold is reached -but then the forces rise rapidly (incompressibility is achieved). 2D liquids lie in between the extremes. Further parallels with our inherent understanding of bulk behaviors abound, and some are developed in the appendix. The pseudo-phase picture is naturally murkier for complex natural (aqueous) organic systems since actual mixtures and mixing rules cause deviations, but our task here is to distill and organize. The strict, clear-cut phase analogies will prove crucial to our verification process. For the moment, the reader is encouraged to visualize the plots or curves involved as a 2D gas is 'compressed' along a water surface -by contrast and-or comparison with a 2D surfactant solid. The planar gas will necessarily cause or respond to pressure increases faster and at lower concentration as area is systematically removed. This means that finite, measurable gradients will be associated with its adsorption, and they are precisely the ones with dissipative effect.

Refer to the fundamental sample plots in Davies and Rideal [38], Jarvis et al. [63], Barger and Means [5] and Frew [18] for further orientation. Surface tension slopes are normally monitored via the elastic modulus -dπ/dlnA as defined rigorously in the appendix section, and this is the real link from a fluid dynamic standpoint [17,18,59]. Notice that the slope quantity is typically computed over a natural log increment, effectively normalizing to fractional area so that 2D units are unaltered. But in any event, the derivative can only exist where π rises significantly above zero. Pressure is the first measured, more readily conceived and most often reported quantity. It is given priority in the analysis that follows.

4. Observation of Tension Effects

Surface pressure data are summarized in Table 1 for their association with multiple, critical Earth System flux types. Rough ranges of π are quoted for which significant alterations have been recorded with respect to bulk gas, salt, and momentum transfer. Literature sources are, on a row-by-row basis –trace gas transfer [6,18,19,21,50,78,79], salt spray flux [14,25,28,29,49,52,53], capillary waves and ripples [9,17,59,61,63,80,81], wind in the planetary boundary layer [20,46,59,65,82-84]. The tabled information is presented primarily for motivational purposes, since we will not make any direct fluid theoretical connections. Strong changes to bulk piston velocities, sea spray number production rates, ripple or capillary damping coefficients and observations of the drag coefficient and/or wind speed have all been documented in close conjunction with surfactant data. The π deltas have consistently been explained in the literature by appealing to the existence of two dimensional phases among varietal and heterogeneously distributed biomacromolecules of the film [6,18,19,59]. The influence and behaviors are always aligned with the phase states 2D gas, liquid, solid.

Table 1. A sampling of global ocean (2D) surface pressure ranges Δπ along with documented influence on several components-parameters related to sea-air flux types. All processes are dominated by the biomacromolecular surfactant effects cited here. While mechanisms of reduction actually trace to the elastic modulus, surface tension is more often reported and the two quantities are intimately interconnected.

Phenomenon	**Measured π**	**Parameter**	**Effect**	**References/Authors**
Trace Gas Transfer	0.3-3 mN/m	Piston Velocity	Lower 3x	Davies 1966 and 1972; Goldman et al. 1988; Frew 1997; Tsai and Liu 2003, Frew et al. 2006; Bell et al. 2013
Salt Spray Flux	1-10	Number or Efficiency	+-3x	Blanchard 1963; Garrett 1968; Paterson and Spillane 1969; Detwiler and Blanchard 1978; Lewis and Schwartz 2004; Modini et al. 2013; Alpert et al. 2015
Ripples/Capillaries	0.3-3	Damping e-Fold Distance	Lower 3x	Garrett 1967; Jarvis et al. 1967; Ermakov et al. 1986; Wei and Wu 1992; Bock and Frew, 1993; Hunter 1997; Dysthe 2006
Boundary Wind	>1 (so above background)	Drag Coefficient	Lower 3x	Hicks et al. 1974; Deacon 1979; Ermakov et al. 1986; Asher 1997; Mitsuyasu and Bock 2001; Simpson et al. 2014; Cox et al. 2016

Bulk tracer fluxes as for example of the most common greenhouse species carbon dioxide or else the atmospheric sulfur carrier dimethyl sulfide [21,79] are significantly slowed by removal of energy and small eddies from the far upper ocean turbulence spectrum [20,50]. The efficiency with which (foam) bubble domes can deliver spray particles to an adjacent atmosphere depends on the rate and degree of fluid withdrawal by marginal regeneration, which in turn requires stabilization due to Marangoni surfactant forces in the double layer [28,85]. In fact organic adsorbates are crucial across the sum total of time dependent bubble evolution, from wave entrainment through disintegration into the subsurface size spectrum and finally in determining the rising rates that fuel formation of white caps [25,29,86-88].

The suppression of capillaries regards dissipation of centimeter wave energy into surfactant gradients at the upper boundary [17,56,61]. Deacon attributed tropical wind speed reductions determined from a flux tower near coral reefs in Indonesia to a specific mucus mixture (dominated by cetyl palmitate [83]), but heterogeneity of the surfactant system is now much better appreciated. A dramatic historical rescue described anecdotally by Cox and company [46] demonstrates near-miraculous breaker control by fish oil, which is really a set of fatty acids boasting double bonded tail groups –and thus also expanded 2D gas behavior. The authors carefully distinguished a lack of activity for pure petroleum products, which are highly aliphatic so that they merely bead up at the interface [36]. Simpson et al. [84] have recently demonstrated that a new source of ocean roughness may be needed by CMIP class models to achieve balance with atmospheric reanalyses, in gyre and low marine productivity zones where surfactants are probably lacking. In all of these cases, detailed chemistry and surface tension are the critical interacting variables.

This brief sample of the literature in fact previews a majority of the most important tension modulation issues to be examined here. For reference purposes we now define a band of surface pressures over which the geophysical fluid impacts should be expected. The contours recommended can be applied by our reader with equal convenience to upcoming tabled or mapped data. Roughly speaking, the relevant pressure analog (area generating) π are recorded in an assortment of bench and field experiments to be on the order of 0.3 to 3 wherever substantial effects are encountered, in the tangential units mN/m (mJ/m^2). Such values are expected to lower several biogeochemical and climate flux coefficients or parameters by a factor of three or so across the board. Exceptions occur in the salt spray data, where physicochemistry becomes so complex that even the sign of the perturbation cannot be specified –but still it is reported to be of order 3. The underlying organic film structures have not been incorporated into any relevant, extant biogeochemistry or climate parameterizations [66,89-92]. Hence we begin by attempting to map the potential for such improvements, moving forward from regional ecogeographic scales [39,40]. Our survey has so far been restricted to trace gas, salt spray and momentum transfer data, so that extensions to heat and water vapor await attention [51,60,67,93].

Based on Table 1, we propose that a useful assessment of tension biogeography can be constructed by exploring the position of a plotted 0.3-3 mN/m band, distributed in the standard manner over global modeling maps of the sea surface. Patterns tracking on either side of unit π, as they color the top of the ocean, should constitute a reasonable initial guide as we attempt to answer the second key question put forward in the introduction –that of importance. Values lower than a few tenths may well prove insufficient to support global climate effects. Simultaneously there may be maxima, plateaus or optima so that higher quantities cannot be ignored, even though they may well prove to be coastal and rare. Downturns in Table 1-type influence have been reported at high π [9,80], and they likely have the related-symmetrical physicochemical explanation that tightly condensed microlayers again display constant tension, though at greatly reduced values [38,94,95]. Effectively then for the duration of this paper, we seek to identify trace contours of about 0.3 to 3 mN/m distributed over the microlayer of the total planet. It is postulated for purposes of initial evaluation that geochemical plus climatological effects of marine biosurfactants will be at their greatest within this band of surface pressures.

5. Compound Identities

The upper ocean contains about 50 micromolar dissolved organic carbon at high latitudes (DOC), rising to more than 80 at the equator [96]. This detrital mass is most often portrayed and studied as a conveyor of carbon atoms to the deep sea, or else as a long-lived reservoir for nutrient elements which may ultimately be recycled from reduced forms [97]. In order to elucidate more detailed physicochemical behaviors -here emphasizing top-of-the-ocean interfacial activity- additional information is needed regarding the wide variety of attached functional groupings. A (highly) condensed assessment is provided in Table 2, for the macromolecular and biopolymeric content of the dissolved, global marine carbon pool. Information is adapted from our own earlier work [30,33,37] but supplemented with data from Gagosian et al. 1982; Van Vleet and Williams, 1983; Kumar, 2000; Dittmar and Kattner, 2003; Tuckermann and Cammenga, 2004; Aluwihare et al. 2005; Petters and Kreidenweis, 2007; Petters and Petters, 2016 and Rossignol et al. 2016 [26,76,77,98-103].

Biomacromolecular classes protein, polysaccharide and lipid comprise the most abundant components of autotrophic cell interiors, and they are present almost uniformly within generic phytoplankton in the ratio 60 to 20 to 20 percent [37,104,105]. Setting aside mineral hard parts since our focus is on the dissolved fraction and its ability to occupy surfaces, we note that various primary producers also synthesize mildly amphiphilic protective polymers such as chitin and peptidoglycan [98,101,106]. All these high molecular weight substances plus familiar but trace-level organics such as the genetic carriers are released freely into the water column, whenever producer cells are disrupted by grazing, viral lysis or senescence [41,42,107,108]. Even during the freshest stages of the ensuing degradation sequence, denaturing and other reconfigurations must be taken into account [37,109]. Photochemistry, random enzyme attack, and bacterial consumption shuffle and remove the initial ordering-structures, while a certain amount of recondensation then repackages carbon chains into the heterogeneous material known as humic acid {110,111]. The global upper ocean chemical transformations described here have been amply reviewed by Benner [109], while typical loss constants are roughly known and can be constructed from time series and vertical profiles as noted by Elliott-Ogunro et al. [33,37]. Estimating biopolymeric longevity is an underpinning to our strategy, since even a crude knowledge permits dynamic distribution of regional mixed layer concentrations [33] and so potentially an attack on the 0.3-3 π contour.

Table 2. Selected families of marine biomacromolecules with representative half saturation concentrations for adsorption, and corresponding two dimensional phase states within the mono-microlayer system.

Chemistry	**Monomeric Units**	**Examples**	**C(1/2 π max)** (μM)	**Surface Phase**
Protein	Amino Acids	Enzymes, Collagen and structural	10^1-10^2	2D Gas
Polysaccharide	Sugars	Alginates, Uronics	10^5	(soluble)
Lipid	(aliphatic with some double bonding)	Fatty Acids, Sterols, Triglycerides	10^0 (estimate)	2D Solid (often)
Aminosugars	Replace OH by N- in the saccharide	Chitin, Chitosan	(insoluble)	2D Solid (Chitos)
Hybrids of above	Combined	Peptidoglycan, Lipopolysaccharide	10^4 (Peptido)	Planar Mixing Interactions
Humic/Fulvic	Recondensates	Suwannee River, Deep Arctic	10^5	2D Liquid
Atmospheric	(C chains, rings)	Levoglucosan, dicarboxylics, lipids, then oxidation	>10^6 (Levo)	(soluble, Levo)

Actual complexity of the marine organic system is only hinted at in the Table –beyond the major macro-chemical classes lie numerous subcategories and it is often noted that only a few tens of percent of the total composition has ever actually been characterized by laboratory analysis (ship board or otherwise [105,109,112}). For the exclusively surface-chemical purposes at hand, however, a convenient simplification can immediately be invoked. Experimental data on adsorption equilibria are often available as evidenced by our ability to harvest and utilize them in the earlier, primary organic aerosol work. As a quick reflection of surface activity we tabulate the most readily obtained metric, which is in fact the solution half maximum concentration for surface pressure (this can be viewed as a thermochemical constant –penultimate column). Most of global DOC resides in the refractory humic reservoir when taken on an integrated basis. We can safely assume that other types are present at (order) tens micromolar or less, and thus it is immediately obvious that only proteins and lipids need to be propagated further through the current exercise. Only these particular organic structures can occupy any significant portion of a given local film area or monolayer mesh. The question of characterizing their two dimensional chemical behavior remains, but at this stage we can follow longstanding tradition while simultaneously promoting it to the level of global modeling –students of the marine surfactant system have long since converged on a small and closely related set of proxy compounds.

6. Surrogates or Proxies

Multiple surfactant research groups, operating across the decades, have agreed upon standard surrogates which can be exploited to understand the oceanographic tension losses imparted by natural biomacromolecules [5,18,38,63,77,94,95]. A long version of their collective list would contain albumin, lysozyme, casein and collagen to represent protein behaviors, and this is true even though the compounds are mainly terrestrial. To substitute for the lipid family, add the couple stearic acid-stearyl alcohol to provide 2D solid activity. And finally we note that many authors include the less extreme but also lipidic species oleic acid and oleyl alcohol. These act as 2D liquid-to-gaseous contributors rather than “crystals”. The approach can be further refined by down-selecting albumin and stearic acid alone, since they have been the most commonly referenced. Plus we carry oleic acid additionally (olive oil), as a convenient optional sensitivity member since the total variety of lipids is especially intricate [109,113].

This leaves us with just two primary compounds to adsorb and mix onto conceptual or simulated microlayer surfaces, prior to switching-in the oleic. The Table 1-2 situation has thus been rendered quite tractable for initial calculations. The reader will find that commercial surfactant analogs are often discussed in the literature, including polyethylene glycol derivatives, sodium dodecyl sulfate and the PEG-lipid hybrid Triton X-100 [5,28,59,85,114]. But the ease with which synthetic, artificial substances can be applied and studied in fact becomes problematic, since their 2D phase behaviors often go uncharacterized and are difficult to match with authentic global detritus [65,114,115]. Our tendency is to remain as natural (organic) as possible in our surrogate choices, even when they cannot be truly marine in nature –albumin, stearate and oleate are all typically obtained from terrestrial biomass. But the historical chemical oceanographic literature is completely consistent –the albumin-to-stearic pairing is a preferred starting point.

These two main model compounds are characterized respectively by 1.) gradualized tension effects at low but increasing coverage (the protein, 2D gaseous behavior), versus 2.) total inactivity during accumulation then a sudden structural collapse (the fatty acid, 2D solid). A parameterization for the dual-surfactant equation of state is developed in the appendix. Our reader is referred to the classic chemical oceanographic publication Jarvis et al. [63] for an early portrayal of the two-component relationship, and also to view π-A (PV analog) mixing and compression curves which can be mimicked and which are actually drawn from real, distributed marine microlayers. Related older works from Liss [2] and the Barger group [3-5] may also prove helpful. Much of this research was in fact sponsored by the U.S. Navy in the interest of understanding global patterns of wave suppression. Having down-selected an historically grounded proxy subset, we now have all the new information needed to begin scanning variable organic-tension situations around the planet.

7. Mixed Layer Concentrations

It has already been noted that disruption injects cell internal carbon at the 60-20-20 ratio and so we adopt the first and last values for protein versus lipidic substance. Grazing and mortality rates are readily computed from contemporary biogeochemical models [42,108]. In conjunction with macromolecular residence time estimates (above), bulk mixed layer concentration patterns can thus be estimated quite directly. This is done working first from about a generation and a half of ecological geographies which by now happen to be available [39,40,116], and then further in an offline mode relative to the global simulations [33,43]. Checks are performed against the hundred or so molecule-specific measurements (collected in Ogunro et al. [33] but see for example Lee and Bada {117] for a flavor of the analytical chemistry challenges). Finally, the combined upper ocean dissolved material is mixed adsorptively into/onto the microlayer per the appendix. This is done by ignoring the potential nonlinear interactions in the plane, but should be adequate as a scanning device [36,38].

Specific mixed layer concentration results are given in Table 3, with primary references Longhurst [39,40], Ogunro et al. [33] and Letscher et al. [43] placed as information sources in the first column. The sequence of development is as follows. A well-known general marine biogeography series [116 and derivatives] was mined for province level definitions most applicable to our surfactant questions. Due attention was paid to the combination of proximity to measurement tracks-stations plus relevance to the climate system. For example, the equatorial Pacific has been often sampled and figures prominently in the interaction of biogeochemistry with the Southern Oscillation [118,119]. The provinces were aggregated across basins (longitudes) to build super-divisions which we will refer to here as “surfactomes”. There are similarities with the biologist’s notion of an ecotone, but our nomenclature is tailored to the microfilm. Regional primary production values computed as in Platt and Sathyendranath [116] then promoted to the textbook level in Longhurst [39,40] were binned as background versus bloom level, assumed to be in balance with grazing (diatom events excluded), partitioned according to standard ecodynamic model routings [42], fractionated by 60 and 20, then placed in steady state with their respective macromolecular lifetimes [33,37]. Note that the more intense values associated with seasonal peaks are presented as parentheticals. Offline but more (semi-) dynamic simulation results for the collective global proteins and lipids were then duplicated directly from the original work Ogunro et al. [33]. Plus the Ogunro mechanism was further tested by superposition on output from a related ecodynamics code tailored specifically for dissolved organic work [43]. Summary values for use in surfactant calculations were selected and placed in end lines for each of the two macromolecular classes. Fully dynamic biopolymer transport is now being computed in the Department of Energy global marine systems model, on variable mesh numerical ocean grids. These latest results have been scanned informally for general agreement, but are not yet suitable for publication.

Table 3. A summary of community knowledge for global concentration distributions of the major surface active macromolecules (μM dissolved carbon). Steady background levels are non-parenthetical, and are followed where relevant by (bloom) values. Tropical concentrations tend to vary little over an annual cycle. Province definitions are taken from the Longhurst ecological geographies then bundled -in order to optimize the use of sparse individual compound data- into what we refer to as “Surfactomes” (e.g. Coastal middle latitudes etc.). Ecodynamic models here share the same heritage but have been applied in two divergent contexts –studies respectively of Arctic methane cycling leading to dynamic global macromolecular distributions, or else dissolved organic elemental ratios (Ogunro then Letscher). Observations are transferred directly from the validation list for the first code, summarizing about three dozen chemically resolved studies. Most involve multiple ship cruises. The abbreviation “na” should be read as not available.

Provinces	CALC CNRY	CAMR PNEC ARAB	BPLR BERS ARCT	KURO NPPF GFST	PEQD ETRA	WARM WTRA MONS	NPTG NAST NATR
Surfactomes	**Coastal (mid-lat)**	**Coastal (low-lat)**	**Polar**	**Westerly**	**Equator (East)**	**Equator (West)**	**Gyre**
Protein							
Longhurst	4 (22)	6 (20)	1.5 (27)	0.8 (8)	5	1	0.8
Ogunro 2015	3 (10)	3 (10)	1 (10)	3 (7)	3-10	1-3	1
Letscher 2015	5 (10)	5(7)	1 (10)	3 (7)	3-10	7	3
Measurements			1 (na)	0.3 (3)	0.5-1		0.5-1
Carry forward	**4 (15)**	**5 (15)**	**1 (15)**	**1 (5)**	**5**	**3**	**1**
Lipid							
Longhurst	0.1 (0.7)	0.2 (0.7)	0.03(0.9)	0.03 (0.3)	0.2	0.05	0.03
Ogunro 2015	0.03 (1)	0.01 (0.05)	0 (3)	0.01 (0.3)	0.03-3	0.01	0.01-0.03
Letscher 2015	0.01 (0.3)	0.01 (0.03)	0 (3)	0 (1)	0.03-0.3	<0.01	0.01
Measurements	0.3 (3)				0.1-3		0.003-0.3
Carry forward	**0.1 (1)**	**0.03 (0.1)**	**0 (3)**	**0.01 (0.3)**	**1**	**0.03**	**0.01**

The super-provinces are arranged in the table moving from left to right in roughly decreasing order of bloom-period biological activity (coast, pole, westerly, equator, gyre). This sequence is in turn controlled largely by convective nutrient supply since most of the ocean experiences light replete conditions at least some time during a typical year. Meanwhile our initial tabular arrangement highlights seasonality via the background (bloom) pairings. The potential for tension gradient patterns to arise is already hinted at, since concentrations for the global 2D gas (protein) approach then recede from saturation levels whether in the time or space dimension (C at half max in Table 2). But we must also consider the 2D solids (lipids) and this requires a more rigorous treatment of the equation of surface-active film state (appendix). It is also clear from Table 3 that systematic global measurements remain sorely needed. Even relative to the lumped "surfactomes" only a few cells could be filled for the current effort. The total number of data points referred to is of order dozens at most [33]. Lack of analytical chemical information is one of the reasons for applying a variety of modeling approaches, ranging from steady states based on satellite chlorophyll to semi-dynamics drawing on partially labile DOC [39 or 40 versus 33]. Agreement between the computations and sparse global measurements may be assessed by scanning downward along the columns, toward the lines labeled "carry forward". It is only within about a factor of 3 at best, and this point becomes crucial in later sections.

8. Spreading Exercises

Our original organoaerosol papers plus follow ons [30-33,37] have thus far dealt exclusively with the foundational Langmuir isotherm, and we quickly determined here that simple, initial functional forms work well to represent laboratory profiles of the protein π [95]. The lipid proxy by contrast constitutes an extreme, textbook instance of 2D solidification in π-A space. Hence in the appendix area, we introduce what will be referred to as a "power-Langmuir" form in which the classic sigmoid is adjustable. This is primarily to handle stearate, though there are also benefits in dealing with the protein multiplex (ring formation, bunching and balling at the interface). Dominant terms are raised to the nth degree and thus are capable of loosening or tightening the standard pressure plot as a function of concentration (area). Steepness of the 2D solid collapse can therefore be captured. The function we propose is really nothing more than a saturating Freundlich isotherm. Interfacial molecular dynamics modeling can and should be called upon to improve this situation. But empirical approaches are a typical and acceptable expedient in surface chemistry, and in the current context they should be more than sufficient to proceed [5,36,72]. Our rudimentary π have been carefully adjusted for near agreement with laboratory data [63,94,95]. The modulus is defined as usual to be the derivative against fractional surfactant area change (ε per reference [17]). Its value is computed here numerically. Finally, a nominal surface phase state is assigned given results from the simulations or data based on the most common 2D definitions [5,18]. We also supplemented with the more recent interpretations of Frew et al. [19]. This procedure allows us the opportunity to check against the magnitude, form and planar phase of real oceanographic π-A.

Results of these conceptual global exercises are summarized in Table 4. Ambient π and phase state identifications are drawn from a variety of the above references and more [2-7,9,17,18,85,120-124]. To complete the presentation, ratios of final surfactome-level protein to lipid concentration were fed systematically into our appendix π-A-modulus code. We imagined or hypothesized skimming (harvesting) the ocean microlayer over divergent ecozones, skillful laboratory-style extraction of the organics, then redistribution onto artificial seawater. Furthermore fast equilibration is assumed, in order to guarantee closely tracking reference concentrations just below the Gibbs plane. The interfacial composition and accompanying solute levels are then tightened together in a computational Langmuir-Blodgett (trough) experiment to give π Typical curve suites attributable to the open ocean are readily reproduced, given one critical proviso: In detailed laboratory work material is often lost to redissolution, stacking or the extraction medium (see especially [63] but also [2-5]). At local ambient concentrations for the biomacromolecules, we compare with several decades worth of film pressure measurements. Though as usual in the world of marine organics data remain scarce, the tabled patterns and trends are quite encouraging. Surface pressures tend to increase in reverse order and migrate across the crucial Table 1 range -moving from gyre or warm pool toward either neighboring equatorial ecosystems or (bloom period) boundary current extensions. Given the inherent uncertainties, polar and coastal values could actually traverse the 0.3-3 mN/m band on a seasonal basis. Modulus translated into 2D phase information per for example {18} gives the appropriate relationships along the g-l-s spectrum of possibilities. Exact alignment among the states is not perfect but is not anticipated. Overall, our fourth table allows us to begin addressing, for the first time, the two key questions proposed at the top of the paper. Based on a coarse regional view, biogeographic dependencies are likely for the tension difference and there is a potential for spanning of the crucial geophysical fluidic π range. For an integrated global perspective, we now move on to the mapping exercise.

Table 4. Upper lines -surface pressure estimates based on collected results from Table 3 and computed per the appendix, with a selection of data spanning several decades for comparison. In the center of the table some local (appendix-style numerical) elastic modulus results are offered. Finally in the lower lines, model and data π-A experiments are reported in the form of phases. The background (bloom) nonparenthetical (parenthetical) convention is retained. Letters g, l and s stand for 2D gas, liquid and solid.

Surfactomes	**Coastal (mid-lat)**	**Coastal (low-lat)**	**Polar**	**Westerly**	**Equator (East)**	**Equator (West)**	**Gyre**
Surface Pressure and **Modulus**, units mN/m both cases							
π (appendix)	2.4 (9.4)	2.9 (6.7)	0.65 (50)	0.65 (2.9)	6.5	1.8	0.65
π (data)	0.3 (23)	0.1 (10)		0.1 (5)			0.1-1 (na)
ε (local)	6.6 (25)	8.0 (18.1)	1.6 (175)	1.5 (8.2)	10	4.9	1.6
2D Phase							
Model	g (l-s)	g (g)	g (s)	g (l)	s	g	g
Data	g-l (l)	g-l (l)			l-s		

9. Maps and Sensitivity

Protein and lipid distributions from the Ogunro et al. computation [33] were called upon to support initial attempts to map surface tension at a detailed global scale. The O15 values are central among Table 3 model outputs. Background biogeochemistry in this work traces to early marine methane cycle simulations [125] and so ultimately to the foundational BEC ecodynamics code [41,42]. Ogunro and company proposed source-removal functions closely matching our Longhurst biogeographic steady state, but phytoplankton and zooplankton levels were extracted directly from model history files. They may thus be viewed as dynamic and the whole procedure as semi-dynamic. Our appendix surface pressure algorithm was migrated into a common offline data analysis package (NOAA Ferret), so that it could operate on upper mixed layer concentrations to produce π patterns suitable for analysis. We now discuss the fully mapped results referring to central months of the seasons –primarily February and August corresponding to winter and summer in the two hemispheres. All results represent a generic year near the turn of the last century [41,125]. Major sensitivity tests are also described in this section. Any monthly output not shown can be made available on request from the first author.

The original Ogunro mechanism is adopted verbatim as our global baseline, and in Figure 1 we scan Northern Hemispheric winter then summer results (opposite for the Southern Ocean). A logarithmic color bar is arranged so that the suggested indicator band 0.3-3 mN/m is central and can easily be located (-0.5 to 0.5 in log space). An upper limit of 100 was chosen as a round decadal value bracketing the large lipid π maximum recorded for stearic acid [94]. It is immediately clear in the very first panel that marine surface tension probably does indeed possess a computable and measurable biogeography. Hence question 1 as posed above has already been answered in the affirmative. A limit of detection for the classic fluid drop technique is of order tenths mN/m [2,81]. If our proxy assemblage is at all realistic, it should be possible for the shipboard analytical chemist to identify 2D pressure lows in many areas –e.g. in the absence of biological activity during polar night- and moreover, planar solid-driven peaks may be observable in high latitude summer (Antarctic coast then Sea of Okhotsk and Bering in our 6-monthly plots). In the North Pacific and Atlantic, a swath of low π flows from the subpolar regime across middle latitudes and into the subtropics moving generally east to west. In autumn it is bracketed by lingering activity in the respective western boundary current extensions and along equatorial upwellings.

The overall patterns displayed in Figure 1 seem accessible and familiar, perhaps because the colors are bright and follow typical biogeochemical markers such as the remotely sensed chlorophyll distribution [39,40]. But such relationships are long suspected [20,21]. In the present work we add a new dimension to the problem –the set of dynamic physicochemical (interfacial) explanations for the phenomena. A marine geography of tension is readily apparent in broad outline, indeed driven by biology in the general sense but more fundamentally by surfactant behavior of specific detrital macromolecules and polymers. At middle latitudes, the estimated surface pressure values only fall to a minimum of about unity in the remote central ocean (log=0). Blue to purple tones are largely absent from this initial color distribution. The geophysical fluid dynamic effects defined in Table 1 would be more strongly indicated if there were obvious regional or seasonal transitions across the 0.3-3 ribbon recommended earlier as a reference. And so we dig a bit deeper into the matter.

Mixed layer biogeochemistry models underlying Tables 3 and 4 (whether conceptual, productivity and biogeography based, or ultimately semi-dynamic) were all consulted first and foremost because measurements of the individual macromolecular classes are so disperse [33,37,109]. There could be no opportunity for space filling or interpolation from a mere handful of province scale averages, typically all that may be at hand for a specific macromolecular carbon concentration. But in fact the reader should note that both our protein levels and the π driven by them could well be biased high (contrast with lines led by the terms “measurements” in 3 or “data” in 4), while computed lipid values may by contrast fall on the low side of ambient. There are good reasons to suspect that these discrepancies may be real. Enzymes released from a disrupted phytoplanktonic cell do not remain in their pristine, operative state. Denaturing, segregation into peptides and amino acids, recombination and oxidation in the submarine light field will all modulate concentrations and amphiphilicities. Regarding the lipids, we merely remark that no global model can resolve rich generation occurring coastally then transported outward to the pelagic realm [113,126]. In a second simulation we therefore lowered (raised) the protein (lipid) distributions (respectively) by factors of three. This was accomplished by adjusting the removal time constants in both cases. February and August results are shown as our Figure 2. Well-characterized features emerge in the pre-defined 0.3-3 mN/m regime. And solidification (2D crystallization) is pervasive at high latitudes. Thus several crucial properties of the tension distribution system are amplified, and they deserve specific comment.

We focus first on middle latitude Northern Hemispheric surfactants in the August plot –or rather their absence therefrom. The double-triangular 2D pressure minimum running from California over Hawaii to the Philippines may be attributed to restricted gyre and warm pool biology, bordered on either side by nutrient upwelling regions –the boundary current extension plus equatorial divergence. A westerly bloom remains imprinted upon the interface since succession and chemical persistence carry the macromolecules through into summer. The central Pacific path of the minima falls precisely in an area where reanalyses indicate that CMIP class climate models may be overestimating wind speeds [84, Figure A1]. A straightforward resolution suggests itself -the ocean surface is perhaps rougher than expected here, because Table 1 damping relaxation is not model-accounted. Brunke and company have demonstrated several times in several ways [67,93] that turbulent flux parameterizations attempting to functionalize oceanic ripples tend to overestimate momentum transfer. This may occur because they are typically formulated from a purely meteorological perspective. Lack of the smoothing influence of marine organic chemistry is therefore a contending explanation. It is worth recalling that aerodynamic drag studies are most often conducted (for obvious reasons) either in the coastal context, at middle latitudes or else in seasonable weather [92,126,127]. These are conditions under which our arguments and figures suggest that regional slicking should be operative. At least some versions of the tension biogeography thus imply that flux measurement designs should factor in film geochemistry.

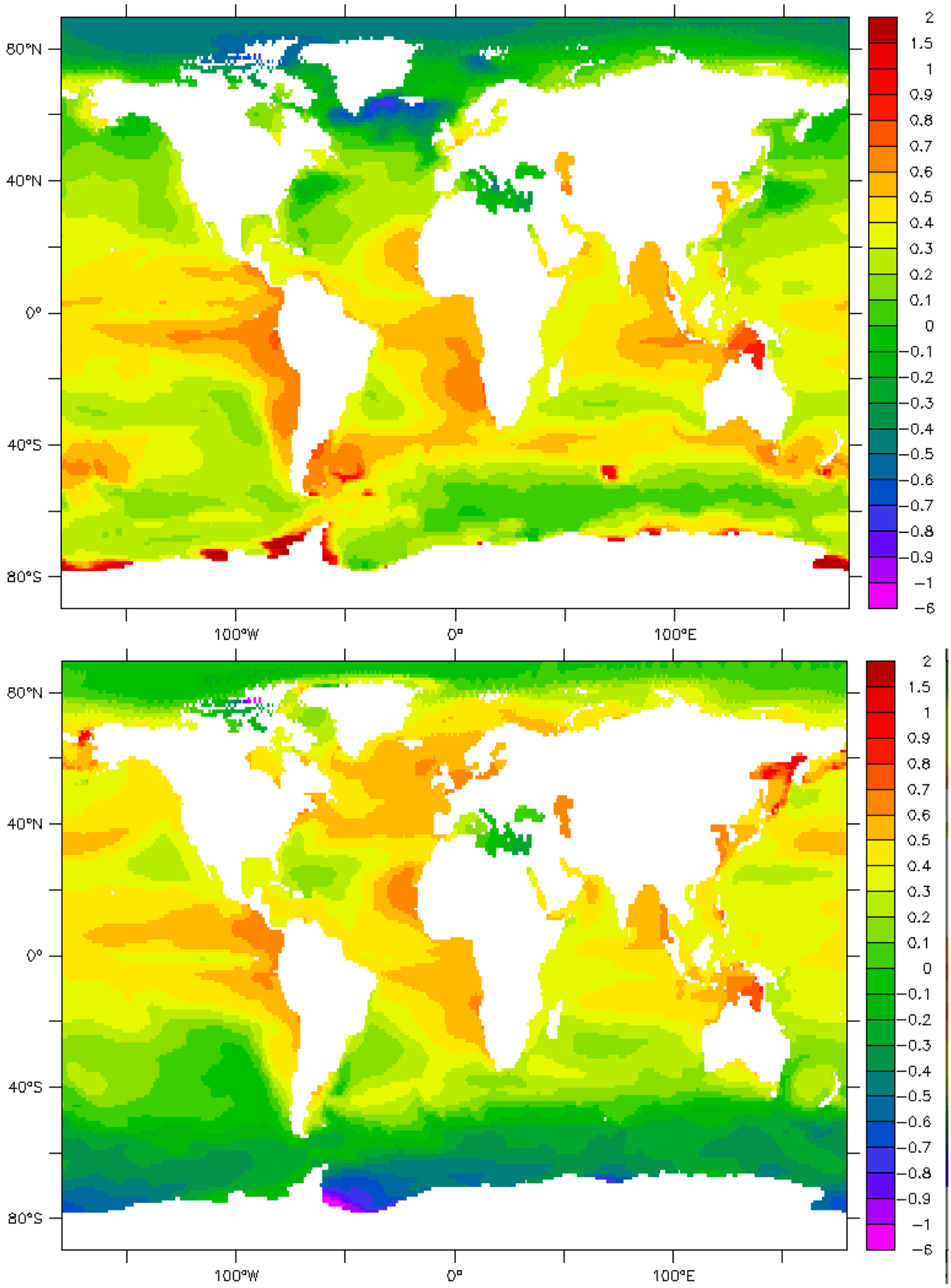

Figure 1. Log surface pressure maps (Δtension) assembled using baseline Ogunro et al. model output [33] plus marine 2D equations of state described in the appendix. Color bar has been set so that a reference range of 0.3-3 mN/m is central (-0.5 to 0.5 in log units). February and August monthly averages are shown for a typical year near the turn of the millennium.

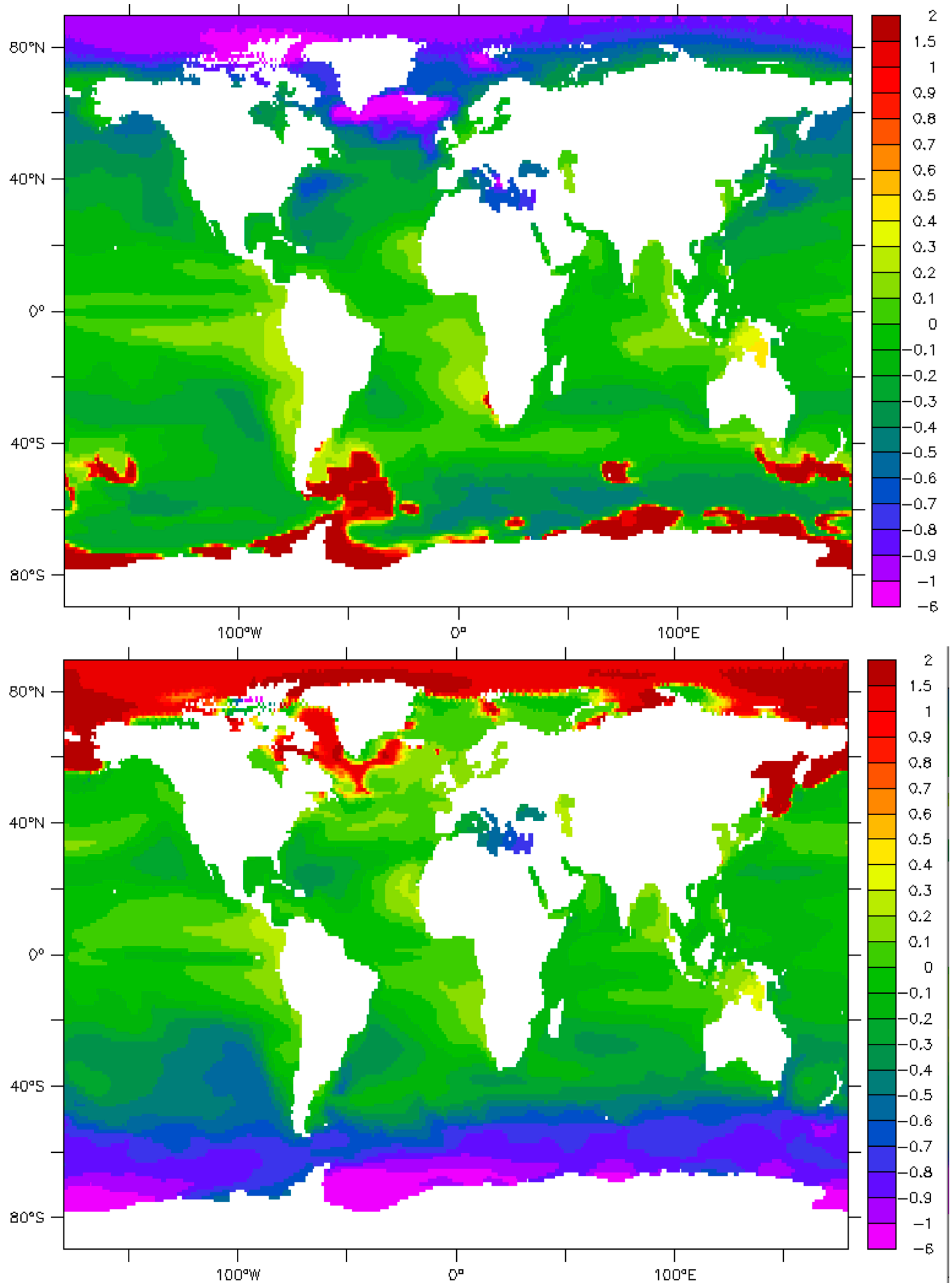

Figure 2. Log surface pressure maps (Δtension) constructed as in Figure 1 but with protein (or lipid) levels lowered (or raised) by a factor of three. Color bar has been set so that a reference range of 0.3-3 mN/m is central (-0.5 to 0.5 in log units). February and August monthly averages are shown for a typical year near the turn of the millennium.

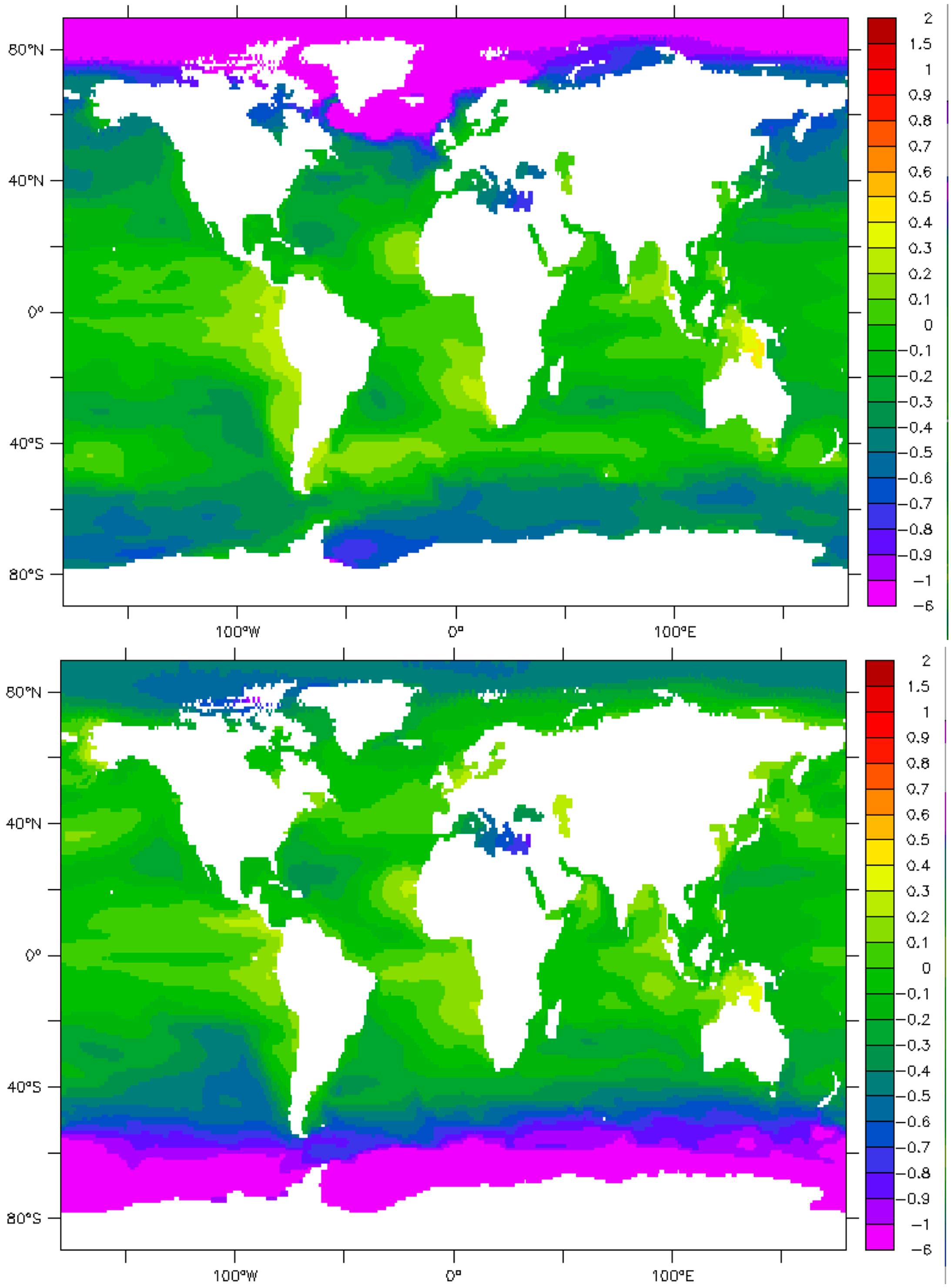

Figure 3. Log surface pressure maps (Δtension) constructed as in Figure 2 but with lipid levels returned to baseline. Color bar has been set so that a reference range of 0.3-3 mN/m is central (-0.5 to 0.5 in log units). May and November monthly averages are shown for a typical year near the turn of the millennium.

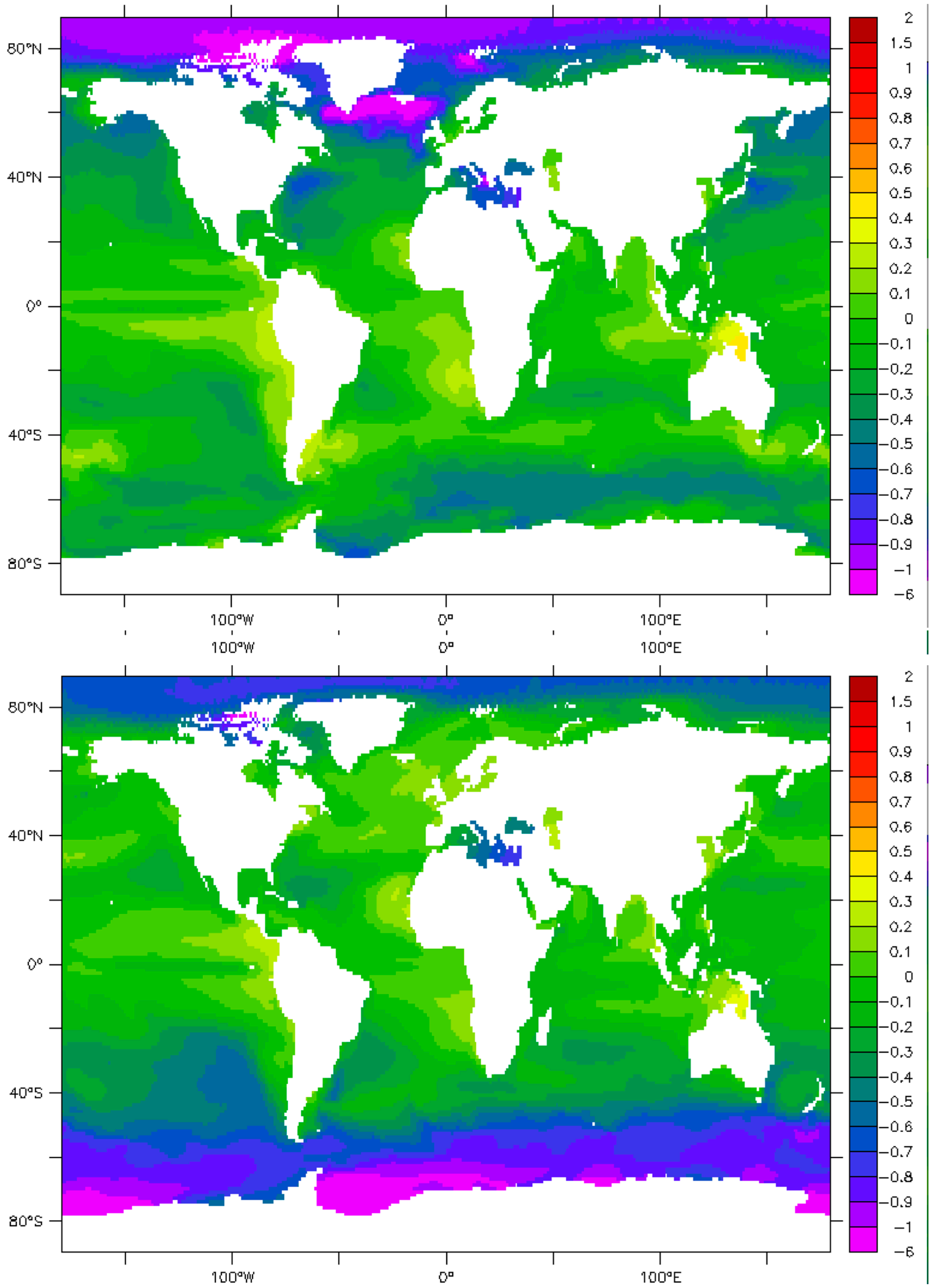

Figure 4. Log surface pressure maps (Δtension) constructed as in Figure 2 so that albumin is cut by three relative to the baseline -but with lipid levels zeroed. Color bar has been set so that a reference range of 0.3-3 mN/m is central (-0.5 to 0.5 in log units). February and August monthly averages are shown for a typical year near the turn of the millennium.

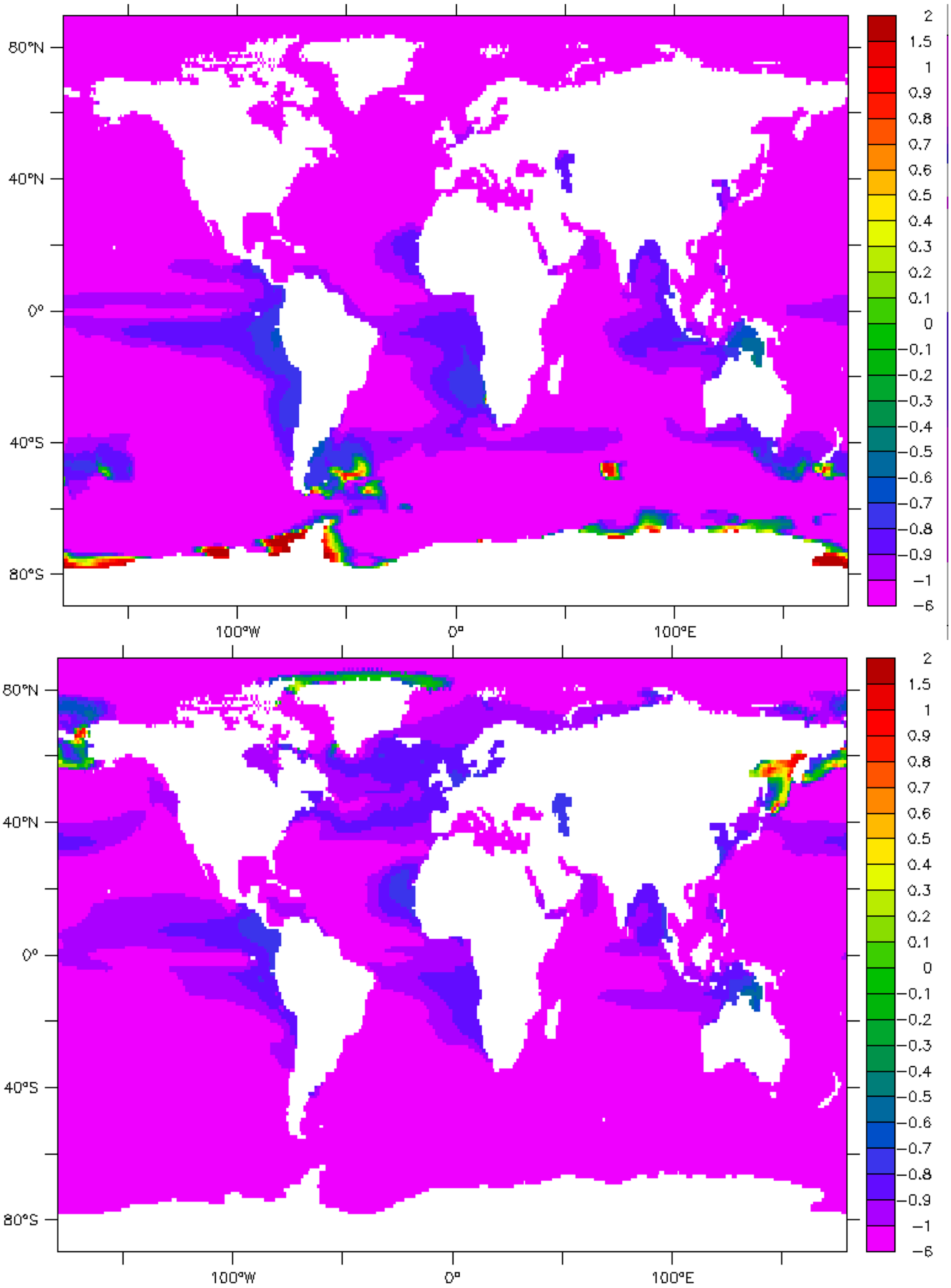

Figure 5. Log surface pressure maps (Δtension) with protein levels decremented 10x while lipids are returned to baseline. Color bar has been set so that a reference range of 0.3-3 mN/m is central (-0.5 to 0.5 in log units). February and August monthly averages are shown for a typical year near the turn of the millennium.

Yellow-to-red tones in the bottom panel of Figure 2 suggest a “crystallization” of the regional scale microfilm over the entire Arctic Ocean, due to just a small augmentation in average lipid concentrations (stearate). This result would be fascinating if real, but it cannot currently be verified. Potential implications include unexpected microlayer effects on wind fields of the ice domain, and on gas-bubble-aerosol mass transfer both at the pack edge and along leads. In fact the 2D condensation result penetrates far beneath the contour of summer ice coverage, tracking BEC primary production. It should be clear that even a minor underestimate of generalized surfactant levels could have very major implications for high latitude climate. Closely related (detrital) biomacromolecules are also generated independently inside of sea ice, by the resident sympagic algae. At extreme temperatures and salinities characterizing the interior of the pack, organics tend to coalesce, gel and also coat pore spaces and their interconnecting channels [128]. They could thus alter brine drainage rates, nutrient resupply chains, and possibly the average regional scale freezing point [129]. Surface physicochemistry yet again offers the relevant theoretical framework. Equations will strongly resemble room temperature film thermodynamics as outlined in our appendix [130].

Figure 2 very directly addresses the second issue raised at the top of the text -but without offering a definitive answer. It seems likely that the specific surrogate pairing of albumin with stearic acid, put forward by so many environmental surface chemistry groups over the years, is actually giving us a fair representation of the relative regional tension variation. The π maps presented here would then be consistent with 1.) unexpected roughness across broad sectors of the middle latitude open ocean, 2.) overestimation of momentum transfer in turbulent flux parameterizations lacking film chemistry, and even 3.) 2D microfilm collapse over large areas at high latitudes. But data remain lacking to assess these options. For the moment all that can be done is to respectfully provide guidance for molecular dynamics models or any renewed experimental work.

We believe due to (slightly) improved agreement with (highly) impoverished data sets for protein-like material and for π Tables 3 and 4) that the albumin/3 calculation may be our most realistic product. For the sake of completeness we append as Figure 3 the associated May and November plots. They are somewhat less eye-catching because lipid blooms have been subdued by a return to baseline, but on the other hand the two-triangle depression is emphasized in autumn as it runs across the northern basin Pacific. Alb/3 is finally taken as a sub-baseline for two further maps of interest –lipid and protein influence switched off in turn. With the stearate contribution removed, no zones of high surface pressure remain (all below 10 mN/m in Figure 4, contrast for example 1 and 2). But such waters and their microlayers have always been clearly identifiable given sufficiently sensitive analytical tools, for example in many of the classic (surfactant) chemical oceanographic studies. In particular, condensed behavior seems to be common along the equatorial Pacific [4,63]. Coastal π-A experiments provide numerous examples as well, with dozens of curves attributable to the California Current alone [3,77}. The suggestion is this - at least some form of 2D solid will be a necessary component in successful parameterizations (appendix Figure A1). Under reduction of a protein proxy (Figure 5), central basin surface pressures fall below tenths mN/m whereas historical droplet determinations demonstrate that such values should often be detectable [2,81]. Conceptual interplay between Figures 4 and 5 therefore indicates that the appendix surrogate combination is quite an effective one, as predicted by many surfactant chemical groups over the decades.

Global tests for which results will not be shown include (2D) liquefaction of the lipid proxy by substituting oleic acid profiles [5,63], swapping-in of casein or lysozyme in place of the albumin gas-liquid [95], alterations to the half saturation reference points, and finally sensitivities to other equation of state parameters as outlined in the appendix (Table A1). Results of the previous figures are not contradicted, and largely in fact they are continually confirmed by these further exercises. Overall it seems safe to say that the marine biosurfactant family of macromolecules and polymers should indeed describe a distinct biogeography of surface tension, along with its absolute difference the 2D pressure, while intra-basin and seasonal variations may well push global film dynamics regularly across the 0.3-3 mN/m reference contour band. The latter transition, per Table

1, implies a fluid geography of effects on both ocean and atmosphere boundary layer physics. Patterns may be decipherable through the phase plane equation of state approach.

10. Uncertainties

Some of the errors inherent in the above development are unambiguously parametric, and were explored in part as the figure set 1 through 5. Examples include macromolecular release rates and surrogate choices. Many of the potential uncertainties are more pervasive, however. Several derive unavoidably from our general oversimplification of the tightly coupled, nested phase, kinetic-thermochemical system residing at the global microlayer. These might be termed "structural" issues. To influence the energetics of tension, polymers must undergo a full life cycle of transformations playing out over hours to weeks and including at least the following steps – biological release (becoming detritus); chemical reactions in a warm, oxidizing and light permeated medium (the mixed layer); transport toward the atmospheric interface across the very spectrum of turbulent eddies about to be controlled; equilibration at some locality along the undulating wave system and finally, surfactant function within the Gibbs plane. By now we hope to have convinced the reader that the latter constitutes an intimate, rich and layered biogeochemical medium in its own right. The two dimensional phase experiences continual compression and dilation by the wave field, interactions with constituents of the bulk atmospheric gas phase sometimes in bubble or aerosol form, and more besides. Approximations already stated or implied but well worth reiterating –we have assumed a rapidly stirred upper ocean; uniform heteropolycondensate evolution among the DOC except for a few adjustable exponential time constants, instant stabilization into the surfactant medium, fixed moderate thermochemical temperatures which are actually confined to the laboratory and middle latitudes, undisturbed occupation of an idealized pristine monolayer, experiment-like responses constrained to be nonstacking and nonhysteretic, a complete lack of 2D-internal removal or reactive processes. And again more besides.

Potential sources of error in calculations of this nature are so numerous that we feel compelled to construct yet another Table for the convenience of the reader (number 5). Row by row (topic-wise) literature sources including new additions are –organic release [128,131,132], water column processing [133-137], transport [138-141], interfacial attachment [1,29,46,62,77,80,142], monolayer (mixing state) [36,38,142-144], monolayer (crowding) [2,74,75,145-147], monolayer (temperature) [38,95,148], monolayer (salt effects) [94,95,149], monolayer (pH) [77,94,149,150], the multilayer—plex [31,36,95,135,142], caps and foam [28,151-154], atmospheric interactions [76,103,155,156]. We will not attempt to quantify net effects of these biases. Any one of them could arguably inject a factor of three flexibility into the logic train, and some would operate in two directions. In fact we have already used a round half-decadal value several times just in carrying out our plotting procedures. Since uncertainties must propagate, both cancellation and large misjudgments are statistical possibilities. It may be that either the sum of uncertainty disappears, or else that it is much greater than suspected. Measurement constraints are few but real (earlier tables) and we exploit them as fully as possible. Effectively we posit that traditional fluid drop methods, skim sampling and experimental π-A curves are all consistent with our results. Thus they support our hypotheses, or at least do not offer contra-indications. But it is of course difficult not to view sparse comparisons with skepticism.

Our position, as might be imagined, is that parameter flexibility explored in the figures already points to major opportunities, for the international community of environmental and surfactant chemists. It is obvious that improved geographic coverage is sorely needed for all of the quantities concerned –the families of lipids, polymers, hybrids and degradation products among high molecular weight compounds, their concentration gradients (provincial and vertical), planar densities and specific behaviors during surface activity. We include in our thinking the potential for molecular dynamics and statistical mechanics modeling, plus contributions from analytical environmental chemistry groups oceanographic and otherwise. There is also much to be learned from marine aerosol research, which has long focused on aqueous/salt/organic phase relationships critical to ccn number and cloud brightness [102,103,143,144,157].

Table 5. Itemization of uncertainty areas in the present work. Staging refers to the life cycle of events which must be tracked for detrital then surface active biomacromolecules if they are to influence energetics at the sea-air interface. An "issue" here may be biological or physical-chemical and reflects (over?) simplifications in the logic. The comment column adds detail. Referencing is limited to just a brief selection in all cases. Blanks carry information downward.

Stage	**Issue**	**Comment**	**Sample references**
Organic Release Mechanism	Exudation could add to mass and functionality	Siderophores common pelagic examples, but also in brine channels	Hassler and Schoemann 2009; Hassler et al. 2011; Krembs et al. 2011
Water Column Processing	Polymer kinetics and colloid formation, rapid bacterial consumption	Gel adsorption could divert… or contribute to upward carbon fluxes	Alldredge et al. 1993; Passow et al. 1994; Chin et al. 1998; Wells 2002; Verdugo et al. 2004
Transport upward to the Interface	Time scale…Do our horizontal averages omit gradients?	Diffusion likely sufficient, bubble impact speeds, 1D needed	Kraus and Turner 1967; Bowden 1975; Johnson et al. 1981; Woolf 1997
Surface Attachment and Detachment	Equilibration to surface not instantaneous, nor is the reverse process	Anecdotal evidence that time scale ~seconds but could be minutes	Garrett, 1967; Jarvis 1967; Van Vleet and Williams 1983; Babak et al. 2000; Alpert et al. 2015; Cox et al. 2016
Within the Monolayer	Mixing interactions among competing surfactants	2D solids may enhance condensability of 2D liquids etc.	Adamson 1960; Davies and Rideal 1963; Babak et al. 2000; Dutcher et al. 2010 and 2012
	Crowding within the compressed planar system	Sites with gels, organisms… white cap-style area partition?	Liss, 1975; Erickson 1993; Hardy 1997; Callaghan et al. 2008; Cunliffe et al. 2011; Wurl et al. 2011
	Temperature effects on surface thermochemistry	Observed to be small, but Van't Hoff isochore should be implemented	Ward and Tordai, 1952; Davies and Rideal 1963; Graham and Phillips 1979
	Salt effects at 35 psu (or higher inside pack ice)	Most studies from food-pharma labs so low ionic strength	Christodoulou and Rosano 1968; Graham and Phillips 1979; Parra-Barraza et al. 2005
	pH (acid base reactions)	Bulk surface seawater 8.1… but the (aqueous) electrical near field?	Christodoulou and Rosano 1968; Van Vleet and Williams 1983; Kanicky and Shah 2002; Parra-Barraza et al. 2005
Multilayering-Multiplexing	Substrata, collapse, rings, stacks, balls, wrapping, hysteresis	Likely common with divalent cations below, gels at interface	Adamson 1960; Graham and Phillips 1979; Chin et al. 1998; Babak et al. 2000; Burrows et al. 2016
White caps and Foam	Organic accumulation, storage, ejection, losses to atmospheric aerosol	This reservoir and its throughput are difficult to quantify	Blanchard 1964; Lewis and Schwartz 2004; Selligri et al. 2006; Callaghan et al. 2012; Modini et al. 2013
Interactions with the Free Atmosphere	Oxidation states, redox	Bulk gas oxidants, dicarboxylic acids, reduced iron	Zhuang et al. 1992; Meskhidze et al. 2005; Petters and Petters 2016; Rossignol et al. 2016
	Macromolecular to organic cycling back to the sea	SOA and POA return to the microlayer in only days, carbon with them	Appears never to have been considered

The required research could be organized geographically via "surfactome" principles drawn from Tables 3 and 4. Refinements would lead down to the ecological province level and to coastlines. Automated sensors and their respective platforms should definitely play into the mix of techniques. Many groups have demonstrated that centimeter scale waves or conversely, the slicks left behind by damping, are detectable en masse by robotic instruments whether shipboard or airborne, and also from space [8,9,19,64]. In this regard, a particularly intriguing suggestion has recently been conveyed to us by one of our coauthors (DS). Remotely sensed white cap distributions and residence times have been used to estimate the variable air entrapment caused by open ocean wave breaking events. Data on the entrained volumes feed into bubble plume energetics calculations. Tank experiments suggest, however, that surfactant identities in ambient foam impose a large mode of uncertainty [28,151,158]. From our perspective this sequence can easily be inverted –it may be that a spread in white cap results conceals information on the chemical and biological geography of marine films.

Some of the uncertainties characterized in Table 5 loop back on the individual analyst or his/her community, defining/creating new projects -this is another positive spin that we can give to complexities of the situation. For example, proteins and lipids comprise a poorly understood portion of the total DOC at any given location (Table 3). Marine colloids ultimately become optically active carbon carriers [75,134-136], and they happen to form dominantly from the remaining (fresh) macromolecular mass –the 20% or so of cell spillage which dissolves as polysaccharide. Colloidal chemistry fuels the gel phase. Gel particles are buoyant and therefore advect vertically into a dead end at the microlayer. There they occupy an undetermined fraction of the local area as a pseudo-polymeric phase (Table 5). If our proteins and lipids adsorb to the chained sugars, we have identified a surfactant velocity (pathway) additional to the expected bubble sweep [37,141].

Further instances can readily be cited -dust iron input in Table 5 as a type of redox chemistry which has not been closely accounted here, or perhaps inputs by very short lived bulk gas radicals [76,155]. Photoreduction in mineral aerosol coatings can solubilize trace metals during long range atmospheric transport [155,156], but organic ligands determine the eventual point of equilibrium as well as persistence. One of us (NM) is now conducting laboratory dust iron research into the strength of far upper ocean chelation. That which sets in quickly as mineral particles enter the sea turns out to be crucial to reoxidation rates and bioavailability. But shouldn't solid aerosol particles acquire a thick wrapper of (surfactant) organics as they punch through the ubiquitous global microlayer? Strong multidentate ligands must be numbered among the macromolecules considered here [110] and the process of monolayer penetration-aquisition appears not to have been considered by iron cycle specialists. We've remarked elsewhere that our pelagic biomacromolecules have close cousins, generated and processed in a very similar manner inside of sea ice. A significant fraction of this organic mass will be surface active at the bulk solid boundary of brine channels, with the potential to alter the average freezing point [128-130].

11. Summary and Discussion

Principles of surfactant chemistry operating in the Gibbs plane have been applied to the global ocean-atmosphere interface, through a combination of ecodynamic, nutrient-carbon cycle and organic (surfactant) chemistry modeling. Surface tension increments comprising a tangential pressure field within the marine film modulate -bulk trace gas transfer, salt spray and momentum fluxes plus both sensible and latent heat flow (Sections 1 through 4, Table 1). All this takes place at the planetary scale, with attendant influences on coupled ocean-atmosphere climate. We seek to organize the physical chemistry involved and search for regional patterns which may underlie the influences. Hence it has been asked whether tension and its difference quantity termed the "surface pressure" (π can be adequately and usefully mapped. We work from both historical and modern understanding of the fundamental marine organic, interfacial and physico-chemical issues involved (Sections 3 through 6), supplementing with state of the art biogeochemical systems modeling. The potential has been assessed for assigning specific biogeographies to macromolecular surfactants and their tension properties. Both tabled and plotted results show that the answer to our several fundamental π questions lies in the affirmative –given the contemporary community knowledge base this can definitely be accomplished (Sections 5 through 8, Tables 3 and 4 then figures). Efficacy of the computed tensions was evaluated by comparison with a leading indicator, the range of two dimensional pressures spanning reported effects on (Sections 4 and 9) -regional piston velocities, bubble film breakage, sea spray number, centimeter scale (capillary) wave damping and finally the drag coefficient. Results are tentative but tantalizing. The potential for regional to basin scale effects on the several geophysical transport modes cannot be excluded (Section 9).

Along the way we have called upon standard (surface chemistry) text materials as well as long standing literature to define (Gibbsian) planar phase states within the film (Section 3), community knowledge of the detailed macromolecular composition for marine dissolved organics with special emphasis on functionalities and amphiphilicities (Section 5), classic chemical oceanographic surfactant research providing a recommended and tractable proxy or surrogate set (Section 6), global ecodynamic systems modeling performed at several levels yielding similar, self-reinforcing distributions (Section 7), numerous marine (2D or surface) pressure-area diagrams reproduced in order to establish credibility (Section 8), and finally global maps demonstrating that tension gradients driven by the macromolecular organics should be real and detectable (Section 9). We conclude with an enumeration for the large number of uncertainties involved, alongside an attempt to turn at least some of these to our advantage –the unknowns can and should motivate further research (Section 10).

In a fascinating historical analysis, Cox and company [46] have recently and vividly recreated nineteenth century wave calming experiments, conducted fortuitously (accidentally) using petroleum liquids and fish oil. The former substances (hydrocarbons) simply gather and bead at the ocean interface having little effect, while the latter are 2D gases (elastic [36]). The authors perform an heuristic but theoretically grounded analysis of breaker suppression at the kilometer scale. Their claim is that this occurs through the cascade of effects outlined in Section 2, propagating from the atmospheric turbulent field into and through upper ocean eddy spectra. Cox and company conclude by citing geoengineering and Gaian ramifications of their investigation. For example, there would seem to be the potential for control of extreme storm events. Global wind systems are also mentioned prominently. Our novel addition to such arguments would run as follows; it may be possible to decompose and re-synthesize organic and physical chemistry issues underlying the surfactant wave effects. We track phytoplanktonic and generalized detritus from regional food webs through individual biomacromolecular (organofunctional) identities into the Gibbs phase plane, where critical and quantitative comments can be made regarding interfacial energetics. It seems plausible to submit, as do Cox and colleagues, that enhanced knowledge of surfactant and biopolymer chemistry could lead to enhanced control over either local or global wind-wave-current–aerosol systems. Our work thus reinforces a prospect recurring over many decades: There may well exist closely inter-related, basin scale biological feedbacks onto a long list of planetary transfer types -gas, salt, heat, momentum, carbon, radiation and water vapor fluxes [2,18,20,22,46,83,159]. All this is previewed here offline but in fact it has become possible only given contemporary, state of the art modeling and mapping techniques. We believe this is all the more reason to attempt a full integration, for understanding of the shifting, flux-filtering 2D equilbria at play. The time for Earth System Modeling of the phase plane may well be at hand.

Our research actually distills to an almost ludicrously simple parameterization for the planar Equation of State (EOS), but we have nevertheless been so bold as to wrap it around the entire planetary microlayer. This of course implies there will be many inadequacies (Section 10 and Table 5), but it also means the fundamental strategy is easy to test. Textbook expositions of the EOS concept naturally begin from bulk aqueous media, making connections from forces to 2D density and then on to chemistry. There is a tendency to emphasize ideal, Van der Waals and then virial approaches [5,38,130]. Surfactant specialists have experimented with such systems regularly over the decades, whether from the standpoint of pure physics, chemical engineering or extrapolation to the environment [5,36,77,94,95,103]. On occasion and especially within the aerosol community, dynamic and statistical computational methods are applied to this type of problem [143,144,160]. Our appendix approach is almost purely empirical, but we fully expect it to lead back in these rigorous directions. A guess is that our "power Langmuir" equation, or something close to it, must be derivable from first principles; similar forms have been found to represent low kinetic reaction molecularities on catalytic surfaces. We propose computational experiments at the level of our Tables 3 and 4 surfactomes, as a potential starting point. Interested researchers could test the

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various molecular modeling tools for application at microscopic to provincial scales. Meanwhile, first order concepts from the current development could be incorporated into our own OCEANFILMS package, which is already running in global systems mode [30-32]. It is now the mainstay of our effort to simulate primary marine organic emissions, since it can represent detrital macromolecules adsorbed to breaking bubbles. The fit should be a convenient one. O-FILMS is based on a traditional Langmuir isotherm for the chemically resolved mass excess. All that is suggested here is an extension to a surface pressure with exponents.

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Author Contributions: SE functions as the primary and corresponding author -SB, PCS, NJ, MM, SW, and WW are currently working together in various capacities as the DOE marine biogeochemistry modeling team to implement primary organic aerosol sources from the OCEANFILMS parameterization -EH, NJ, CD and MJ provided polar marine systems simulation knowledge and expertise -YL, RL, OO and OW acted as consultants on details of the marine organic chemistry -MB, LVR and IS offered insights into large scale momentum transfer issues -DS and LR assisted in particular with sections involving coastal and wave driven bubble surfactant chemistry –FH and OO focus on validation of the marine organic chemistry simulations.

Conflicts of Interest: The authors declare no conflict of interest.

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Appendix: Theory and Equations

Properties of a physicochemical bulk-to-bulk interface are often sufficiently unique that it is useful to imagine a separate phase residing there in microscopic form [36,69,71,161]. To the extent that we succeed in a global mapping exercise for this abstraction, a hypothetical but distinctive new material is added to the usual geochemical suite, for consideration by Earth System Models/modelers. As expected, thermodynamic and/or geochemical properties are characterized by various low dimensionality equations of state [38,143,162]. But forces leading to contraction or expansion comprise, in the abstract planar medium, a complex interplay of Van der Waals interactions plus hydrogen bonding and electrostatics. Since we emphasize the monolayer, there are necessarily intimate and immediate interactions with three dimensional material sources on either side of the partition. The situation is ripe and well delineated for molecular modeling, whether through dynamic or statistical methods [144,162-164]. Marine examples have been provided recently during the Deepwater Horizon episode. Dispersants were tested both at the well-head petroleum injection site and further along the Gulf Coast. The international energy industry had strong motivation to assist in assessing the possible chemical engineering fixes [165-167]

Surface tension is just the energy required to create more of the ultra-thin interface locally. Equivalently, it is the force per unit length exerted to do so. The value for pure seawater is about 72 mJ/m^2 or mN/m without allowing for slight variations due to temperature and salinity [9,47,71,168,169]. Oceanographic state variables can be set aside for our purposes, because their effects are small and we will be able to focus on deltas (differences). While physically fundamental, the tension value itself is subsumed as a baseline. Forces which must be opposed to generate new area include the chemical bond making-breaking and Coulombics mentioned above. Repulsions, whether from head groups penetrating the bulk liquid or hydrophic tails extending into the atmosphere above, will provide a boost to surface formation so that they lower the tension. By contrast, Van der Waals attractions tend to rein in the process. By and large we can side step the detailed terms and balances here, since whether in the laboratory or at sea empirical data serve our mapping purposes quite well. But this situation is only temporary. Deeper understanding will at some point be required. For the moment, we recommend as a reference for the above issues a classic textbook. Davies and Rideal [38] is especially clear on the subject because it appeared just as the chemical engineering importance to interfacial eddies was recognized. Several follow-on works are shorter but equally instructive [50,78]. Analogous bubble surfactant issues are handled nicely in Clift and Grace [86]. The aerosol community faces similar challenges, and there are close relationships with Szyskowski curves [34,69,70].

Microlayer thermochemical logic has already been reviewed in the global context by Elliott, Ogunro and colleagues [33,37], so that their basic results can now be strongly condensed. Free energy change must be accounted per the First and Second Laws, but an additional term is inserted due to contributions from area formation. Simplifications are readily identified even in the earliest equations. The conceptual Gibbs plane has no volume, and we are free to think of temperature as a local constant. Gibbs-Duhem style integration followed by application of the product rule defines a molar area quantity, and further establishes the connection with chemical potential. The μ must match across our column of phases bulk and otherwise, plus they are always proportional to log concentration at equilibrium, so that:

$$dG = -Sdt + Vdp + \sigma dA + \sum_i \mu_i dn_i \ (general) \tag{1}$$

$$dG^{Surface} = \sigma dA + \sum_i \mu_i\, dn_i^{Surface};\ G^{Surface} = \sigma A + \sum_i \mu_i\, n_i^{Surface} \tag{2}$$

$$dG^{Surface} = \sigma dA + Ad\sigma + \sum_i n_i^{Surface} d\mu_i + \sum_i \mu_i\, dn_i^{Surface} \tag{3}$$

$$Ad\sigma = -\sum_i n_i^{Surface}\, d\mu_i;\ n_i^{Surface}/A = \Gamma_i;\ A_i = \Gamma_i^{-1} \tag{4}$$

$$\mu_i^{Surface} = \mu_i^l = \mu_i^g\ (phase\ inclusive, and\ now\ to\ a\ system\ of\ one\ i\ \ldots) \tag{5}$$

$$d\sigma = -\Gamma d\mu; d\mu = RTdlnC;\ \partial\sigma/\partial C = -\Gamma RT/C \tag{6}$$

$$\sigma = \sigma^* + -const.C;\ \pi = \sigma^* - \sigma;\ \pi = const.C;\ \partial\sigma/\partial C = -const.;\ \pi = \Gamma RT \tag{7}$$

Here all symbols have their usual thermochemical meaning plus the tension is σ, A represents total area of the system under study, i carried through most of the development is one member from among a set of environmental chemical components (some populating the interface), and molar coverage is Γ. This latter quantity is sometimes also referred to as the surface "excess", since from a laboratory perspective it merely exists over and above storage in the bulk. Note that for practical purposes in actual computations, we deal with specific coverage or area carried not in moles but rather mass expressed as total milligrams.

Chemical potential equivalency enters at an intermediate step in our condensed treatment. In the interest of clarity, we quickly focus on a single surface active organic inhabiting the plane. Super-subscript combinations can thus be obviated. As the reader will recall from the main text, summations only return to a total of two (surrogates). The earliest and simplest of all surfactant behavior isotherms is that of Gibbs, included in several forms [36,38,71]. The asterisk indicates pure water tension. Plus in this location we formally define 2D pressure and take the (admittedly but conventionally) strong step of linearizing its variation. A precise parallel to the ideal gas law is revealed. Many groups have explored Van der Waals and virial type improvements to this situation, whether in the general physicochemical or marine realms (see e.g. [5,94]. There will later be ample opportunity for statistical mechanical and molecular dynamic approaches to be applied. For purposes of preliminary assessment, however, we avail ourselves of a strictly empirical approach.

Since in the current work we deal, of necessity, with phases nested inside of phases (a thermochemical Russian Doll could be held in mind), it is important to issue a reminder at this stage. To the current level in our appendix arguments, the terms liquid-gas or symbols l-g have retained familiar textbook meanings. They have referred to the usual bulk materials –here seawater and the atmosphere in some regional geophysical scenario. But now we rapidly transition to, and zoom in upon, chemical activity confined to the Gibbs wrapper. The term "solid" takes on a new significance and does not point, for example, to bulk sea or cloud ice. Rather we discuss those analog surfactant phase changes which allow comparison with the surface-chemical oceanographic literature. Further remarks on s-l-g are prefaced directly as two dimensional or 2D whenever possible. But a careful reader must remain sensitive to the recursive nature of our language. This awkwardness is a small price to pay for introduction of a new planetary scale phase.

The two dimensional ideal (gas) law is most useful as a device for demonstrating that the planar thermochemistry artifice is robust. Perfect behavior among surfactants is rarely observed, and normally only at excess values so low that they are not relevant here [36,170]. But it becomes clear that the interfacial, microscopic forces listed operate in some proportion to coverage and concentration. This is of course a classic equation of state situation, with Newtonian interactions responding to densities. They will exert their geophysical influence, whether at the local scale or across regions, where gradients develop –by contrast, a uniform 2D pressure field would not be of interest. A commonly encountered and convenient differential form is that of the elastic modulus ε [7,17,19,38]. This is just an increment in π ratioed to fractional area change, so that overall units are unaffected. As a point of reference, it can be shown for the ideal (2D) gas that pressure and elasticity are equal [18].

$$\varepsilon = -\,\partial\pi/\partial lnA\ (= -\partial\pi/(\partial A/A)) = \partial\pi/\partial ln\Gamma\,;\ recall\ that\ ideally\ \ \pi = \Gamma RT \qquad (8)$$

$$ln\Gamma = ln(\pi/RT);\ isothermal\ so\ dln\Gamma\ = dln(\pi/RT) = d\pi/\pi;\ hence\ \varepsilon = \pi \qquad (9)$$

Note the sign flips involved –they reinforce the fact that π α (1/A) under extreme dilute circumstances. But perfection requires linearity on the tension, and assumptions rapidly break down with increasing chemical intensity and complexity. Still, understanding the ideal analog is part of our strategy since actual 2D gases plus (Gibbs plane) liquids/solids forming from or around them can all exhibit much higher elasticities [18]. Ultimately this is our means for distinguishing the surface phases, and for comparing with ambient results [2-7,63]. We follow the definitions provided in Frew primarily [18].

To progress further, we must now think in traditional terms working from surface adsorption isotherms. Usually these are couched by the chemist as expressions of excess for a given bulk concentration. We attempt to extend the basic concepts to more general surface properties. Although planar equations of state are available, we will be unable to escape making an intimate but parameterized connection with the massive, neighboring bulk ocean. We have already mentioned the fundamental Gibbs isothermal results, but they are inherently incremental. Langmuir derived the most expedient early form [30,35-37] working from dynamic surface encounters -but homogenous configurations and siting had to be assumed. The BET form superimposes multilayers but we will not move so far in the current work. Although our group has relied in the past on the classic Langmuir for organic aerosol emission computations, surface homogeneity will not suffice here. Unsurprisingly, imperfection becomes the crux when we consider an entire global film. Our hope is to capture regionally distinctive interactions among the variety of marine biomacromolecules, if only empirically and through the lens of surrogates. Subtleties which enter as a function of mixed layer organic concentration will include -changes in hydrogen bonding density along the interface, nonlinear Van der Waals contact in the monolayer, tail or polymer reconfiguration as area tightens, ring formation, bundling, stacking etc.

Empirical isotherm versions are not only acceptable to the surface chemistry community – they serve as essential tools [36,72]. Utility is the watchword. An oft-cited example is the basic yet eminently flexible relationship of Freundlich [171], which he himself applied in a diversity of situations. The form θ=a(C)^{b} was a mainstay in twentieth century catalysis studies. Normally a Freundlich is used to represent fractional mass coverage, but we generalize here to an “operative” set up which remains entirely notional. Our goal is to represent the influence of mixed bulk organic concentrations upon either of the quantities surfactant excess or 2D pressure. The two must be juggled and balanced in order to reproduce literature π-A analyses. The very natural Langmuir saturation feature can be rolled in ad hoc, and so we propose the functions

$$\theta_i^t = (K_i^t C_i)^{n_i^t} \Big/ \left(1 + \textstyle\sum_j \left(K_j^t C_j\right)^{n_j^t}\right);\ K_j^t = 1/C_j^t\ (reference) \qquad (10)$$

$$\Gamma_i = \theta_i^{\Gamma}(\boldsymbol{C})\Gamma_{i,max};\ \pi_i = \theta_i^{\pi}(\boldsymbol{C})\pi_{i,max};\ \Gamma = \sum_i \Gamma_i\ likewise\ \pi \qquad (11)$$

where θ is merely a weighting for the various Γ or π since it is purely operational, t signifies a process "type" here limited to the excess or tension, reference concentrations converted into equilibrium constants are specific to half maxima, and a bold quantity signifies an algebraic vector of surrogates (the proxy-tuple). The sole restriction on exponents n is that they should be positive values –integers are not required, or rather n=1/m is acceptable [171]. The reader will see that n<1 flattens a profile while n>1 sharpens, and we exploit this tradeoff to deal simultaneously with the extremes of 2D phase behaviors (elasticity in Graham and Phillips [95] versus rapid collapse in Christodoulou and Rosano [94])

The combination of equations finally presented here is what we refer to for obvious reasons as a "power Langmuir". The attempt is unify and begin to comprehend bulk solute control over multiple surface properties of the global ocean. It must be strongly stated that the relationships have not been derived in any fundamental physicochemical way -although close analogs can be for certain circumstances such as the pure, uniform adsorption competition [172]. The intent is to offer a reasonable hybrid, providing Earth System Models with both adjustable and appropriate asymptotic surfactant behaviors (low and high individual or collective concentrations). The reader may wish to perform the thought experiments of conceptually zeroing and raising the ***C***. Laboratory source data are returned with the exception of proteinaceous bunching and hysteresis. As additional approximations, all effects are decoupled from one another then treated linearly and additively.

For the moment, the exclusive justification we offer for this result is that it works –surface chemical behaviors are adequately represented for either laboratory proxy or real oceanographic situations. To test and demonstrate this proposition, a small offline package was constructed in the R statistical code suite. We quickly explored combinations of, and relationships between, mass normalized areas for pure compounds and mixtures, their surface pressures and the elastic moduli implied. Values for property maxima and for reference (half-saturation) concentrations were taken from Graham and Phillips [95] for the protein surrogate albumin, and from Christodoulou and Rosano [94] in the case of lipidic stearic acid. Exponents were adjusted to fit laboratory plots in the literature. In some cases in order to match the extreme 2D solid wall encountered by nonbranching fatty acids, the choices had to be relatively large single digit integers. But bear in mind that all is empirical and the chemistry well documented.

Table A1. Parameter settings drawn from the general physical chemical surfactant literature to describe interfacial behaviors of our proxy compounds. While the full range of biomacromolecular references for Table 2 or [33,37] has been consulted, we settle upon the following as best startup information sources: Albumin data are taken exclusively from Graham and Philips [95], plus stearic acid from Christodoulou and Rosano [94]. Both appear to be very high quality early experimental studies and parameters are discussed in a clear manner. CR do not actually quote bulk liquid concentrations, but they have been estimated from Ter Minassian-Saraga [173] and Brzozowska et al. [174]. Values are inserted into the appendix equations to generate for example – the π-A plots shown in Figure A1, π-ε as in the main text tables and any global maps presented.

Surrogate	**Reference concentrations** 1/2 max, all µM carbon		**Maxima** (Γ mg/m2, π as mN/m)		**Exponents** Values for n	
	Excess	2D Pressure	Excess	2D Pressure	Excess	2D Pressure
Protein (Albumin)	10	30	2	20	0.5	1
Lipid (Stearate)	0.5	2	2.5	50	1	8

The matrix of values adopted is listed in Table A1. Sample results are then provided for inspection in the appendix figure, for which two new references are needed to establish equilibria via kinetic arguments [173,174]. We performed synthetic, computational film compression experiments by assuming that in hypothetical neighboring seawater, a reference bulk concentration set is established immediately relative to the surfactant chemistry. It is then carried along beneath our abstract paddle-in-a-trough. The reader should compare this image with the very similar but classical (chemical-oceanographic) laboratory version in Jarvis et al. [63] in order to be build confidence in our method. It will also be instructive to draw parallels with an assortment of π-A diagrams from the heyday of marine surfactant studies several decades ago [2-5]. Tests could readily be performed upon alternate proxy selections. Oleic acid is shown as a sample 2D gaseous (elastic) lipid. Its (mainly) aliphatic molecular tail contains electron rich double bonds which reduce cohesion and so augment surface expansion [38].

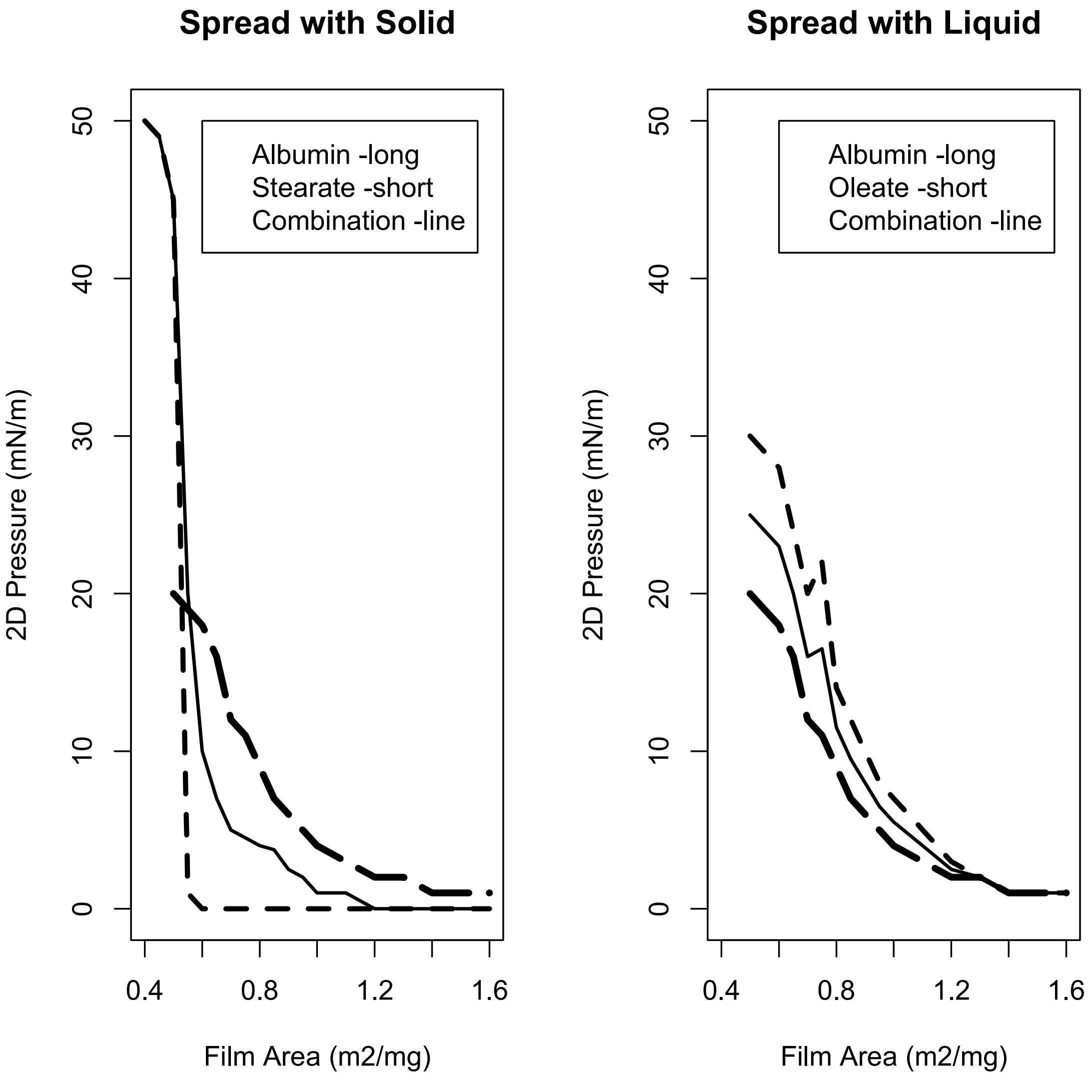

Figure A1. Comparison of film pressure versus area isotherms as calculated using the appendix (power Langmuir) equations of state for A.) the main proxy compounds adopted here along with a sample mixture containing 3% fatty acid as judged by carbon atom solute concentration, B.) oleic acid substituted for stearic acid. The potential for loss of 2D condensed behaviors is clear. “Long” and “short” refer to the dashed curves.

We have previously simulated the full spectrum of marine biomacromolecules in a semi-dynamic (global) manner, in research providing organic aerosol source distributions based on a standard Langmuir ([30-33] and Table 2). More recently, the three crucial cell-fresh families protein, polysaccharide and lipid have been introduced with complete chemistry-transport into the ocean of an upcoming, variable mesh Earth System Model (Department of Energy ACME). The final equations developed here can be viewed as a light-weight parameterization for surface tension which is easily tested in any coupled simulation of ocean-atmosphere interaction. Systems-modeling for chemical effects on the many biogeochemical and physical fluxes involved is therefore only a small step away.

We eventually envision incorporation of our appendix material into the OCEANFILMS package, which is already improving simulations of sea spray organic aerosol distributions at the global scale [31]. Its current and highly idealized approach to adsorption must clearly be enhanced to acknowledge 2D s-l-g phase distinctions. The "power" Langmuir approach could serve as a natural starting point. In fact our collected main text tables and figures show that initial tests could be limited to a single species. At most latitudes over the ocean surface, the steep solid films deriving from 2D lipid condensation will be of interest in just a few regions (e.g. peripheral seas). The fatty acid proxy may actually deliver its greatest value as a means of validation. Proteins appear to be responsible for defining tension patterns over must of the sea-air interface [18]. In the several simulations of surfactant behavior presented thus far ([33,37] and this piece), open water lipid levels have been at their highest during polar blooms. It may be that the influence of 2D solids is limited to the high latitude regime.

All values for π and ε were constructed for insertion into the main text tables by direct application of the tailored R code, configured as in Table A1. The two dimensional phase states we venture to identify are based mainly on the interpretations in Frew [18], with some additional reliance on Barger and Means [5]. Once confirmed, the final surface pressure equation set was lifted whole from R and imposed on Ogunro et al. [33] model netcdf output in an offline mode, in order to generate the global plots. Any further manipulations were conducted in the NOAA Ferret graphics system. Modulus ε was computed numerically in R over total area increments of 1% (per unit mass). All programs developed during our tension mapping effort are available from the first author on request, though it should be clear that the ideas we ultimately put forward are quite streamlined -results should be readily reproducible from one brief class of expressions having a familiar, surface chemical saturation form.

In the interest of maintaining clarity and in order to build momentum, we have historically treated all physicochemical media whether in the laboratory or at sea as though they are somehow fixed at STP for an unspecified water type. Most of the data available to us for making preliminary marine surfactant estimates were collected at around room temperature -from mild conditions in or above the real ocean [3,6-9,16-18,48,49,83,85], or else in some comfortable laboratory setting [18,28,50,54,88,94]. Many of the experiments we tap for data were originally driven by research needs in the pharmaceutical and food chemical industries [37,142,149,175]. They were thus almost universally conducted at relatively low ionic strength.

In some cases distilled or deionized water may constitute an adequate approximation to the real world systems involved. This is particularly true for global model investigations still in their infancy. But there may soon be a need for more detailed study. Only in a few instances have oceanographic temperatures [95] and aquatic chemical pH ranges [77] been explored systematically. Indications are that the approximations we propose are adequate as a first cut, but further laboratory research is definitely called for. Salt strengths vary randomly throughout the source literature from ionic strength zero to one. Temperature, acidity and ion chemical effects seem to be weak and manageable, but surprises should be expected. We definitely anticipate the need for both experimental and molecular modeling studies arrayed along the axes of these most basic aqueous chemical state variables [110].

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