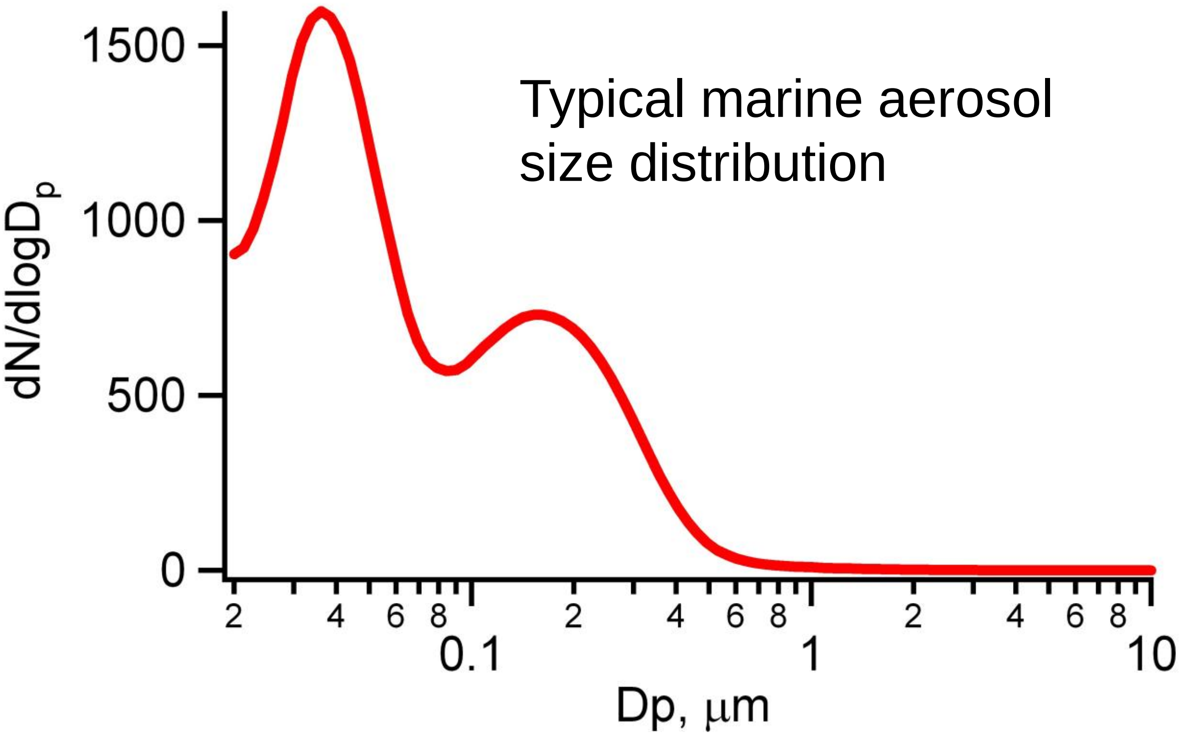
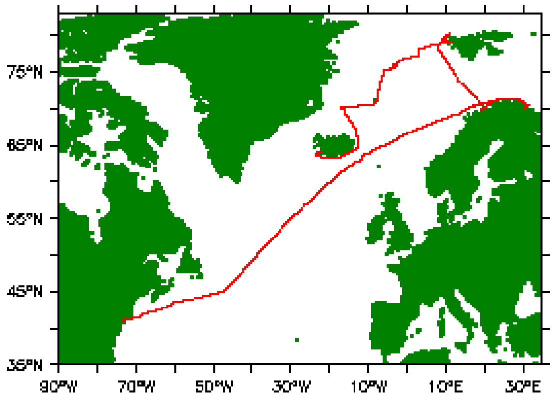
Measurements to Identify and Constrain Sources of Ocean-Derived CCN

Trish Quinn, Tim Bates, Derek Coffman, Jani Hakala,
Paola Massoli, and Bill Keene

11th AeroCom Workshop
Seattle, WA
Sept. 2012

Marine Aerosol Number Size Distributions and CCN Formation





• For the supersaturations of marine boundary layer clouds and the chemical species found in the marine atmosphere critical diameters for activation are > 40 nm.

• Particle number concentrations drop off sharply > ~300 nm.

• What are the sources of 40 to 300 nm particles in the remote marine boundary layer?

• Composition of CCN can reveal information about sources and production mechanisms.

Mechanisms of Oceanic Production of CCN: Primary emission

Primary emission or wind-driven production of sea spray

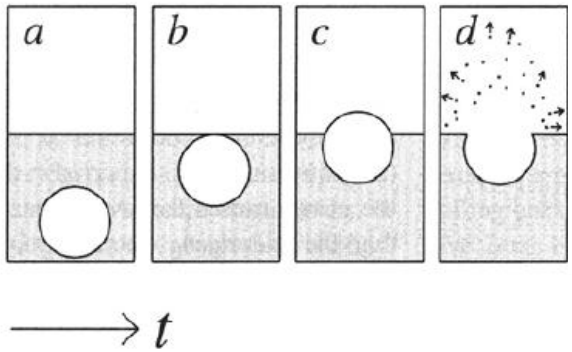
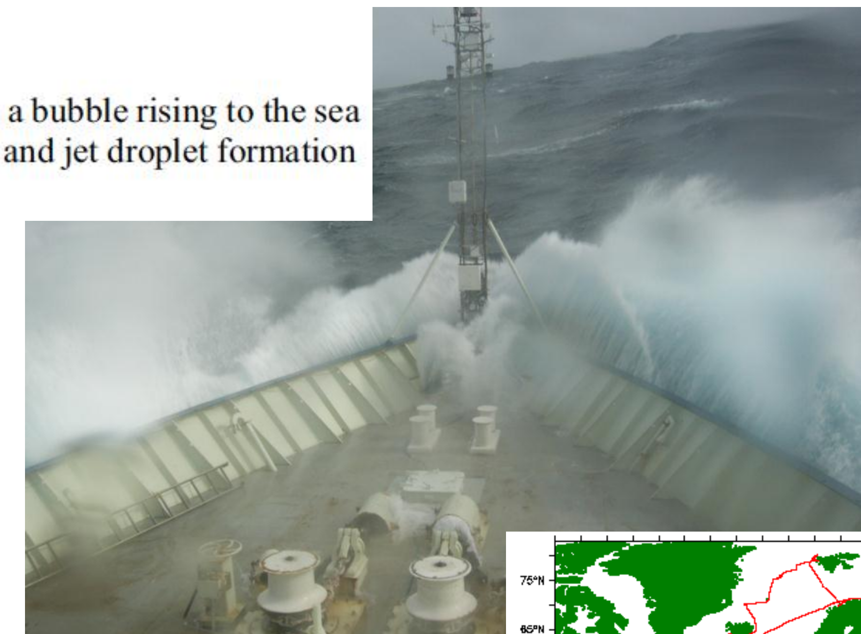
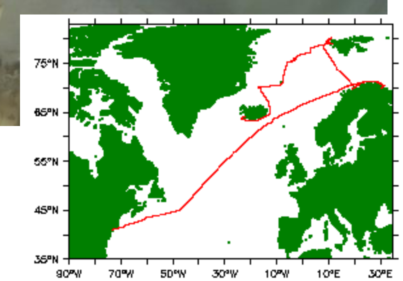


Figure 10. Conceptual model of seasalt aerosol formation from a bubble rising to the sea surface and bursting. Film droplet formation occurs in panel *d*, and jet droplet formation occurs in panel *f* [*Lewis and Schwartz*, 2004].



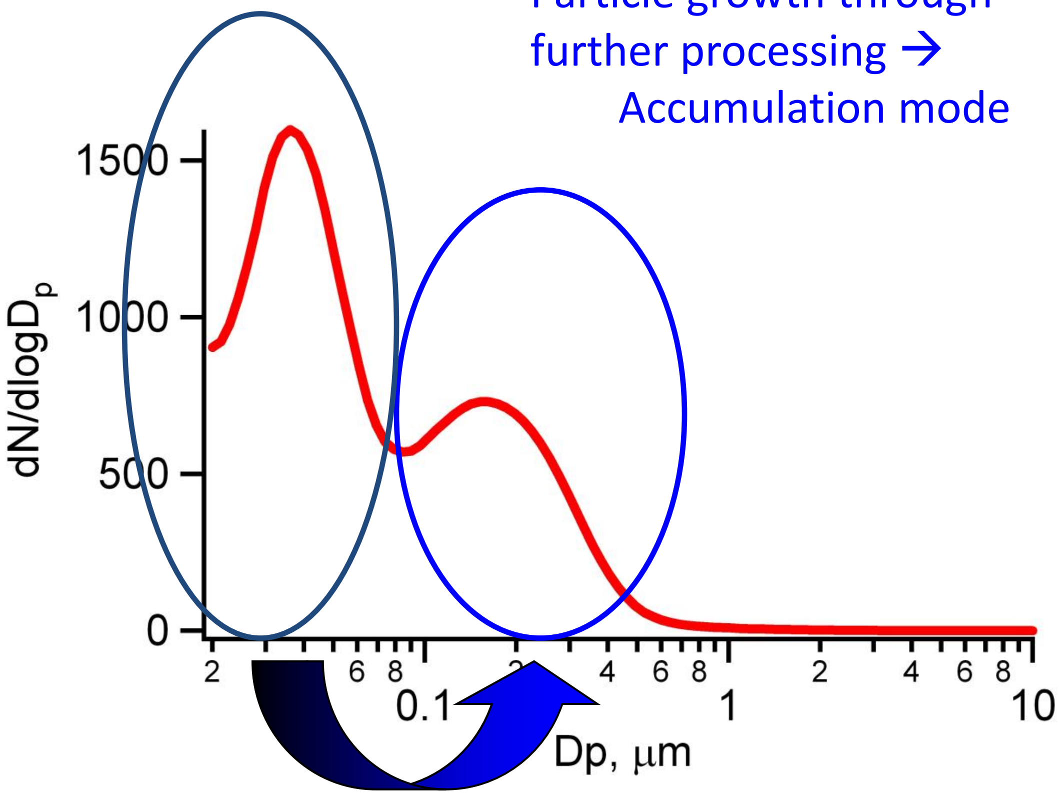


- Breaking waves entrain air bubbles into ocean surface waters
- Bubbles rise to the surface and burst
- Result is primary, sea spray particles composed of inorganic salts and organic matter

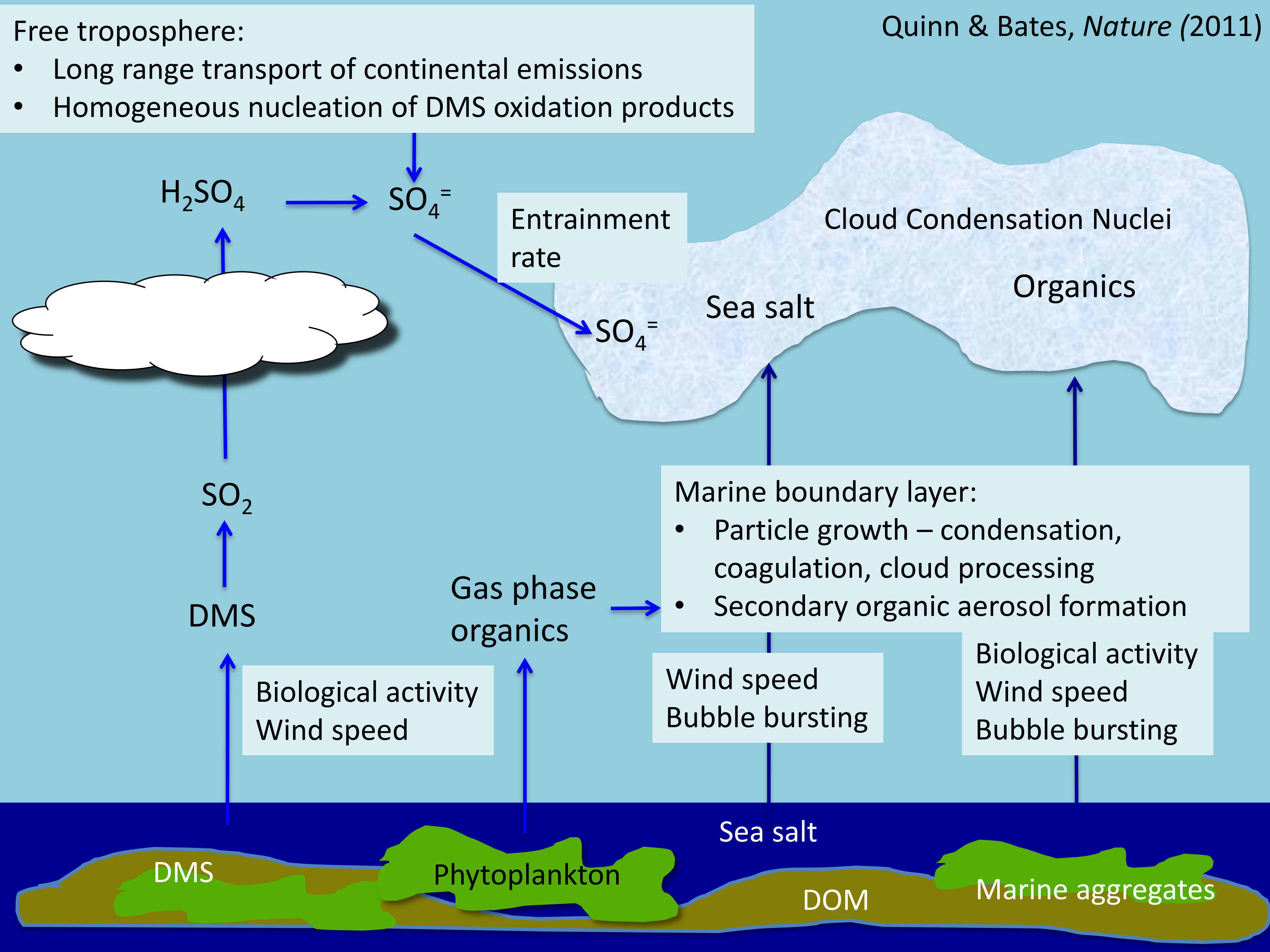
Mechanisms of Oceanic Production of CCN: Secondary processing of gas phase species emitted from the ocean

Primary Production → Aitken mode

Particle growth through further processing → Accumulation mode

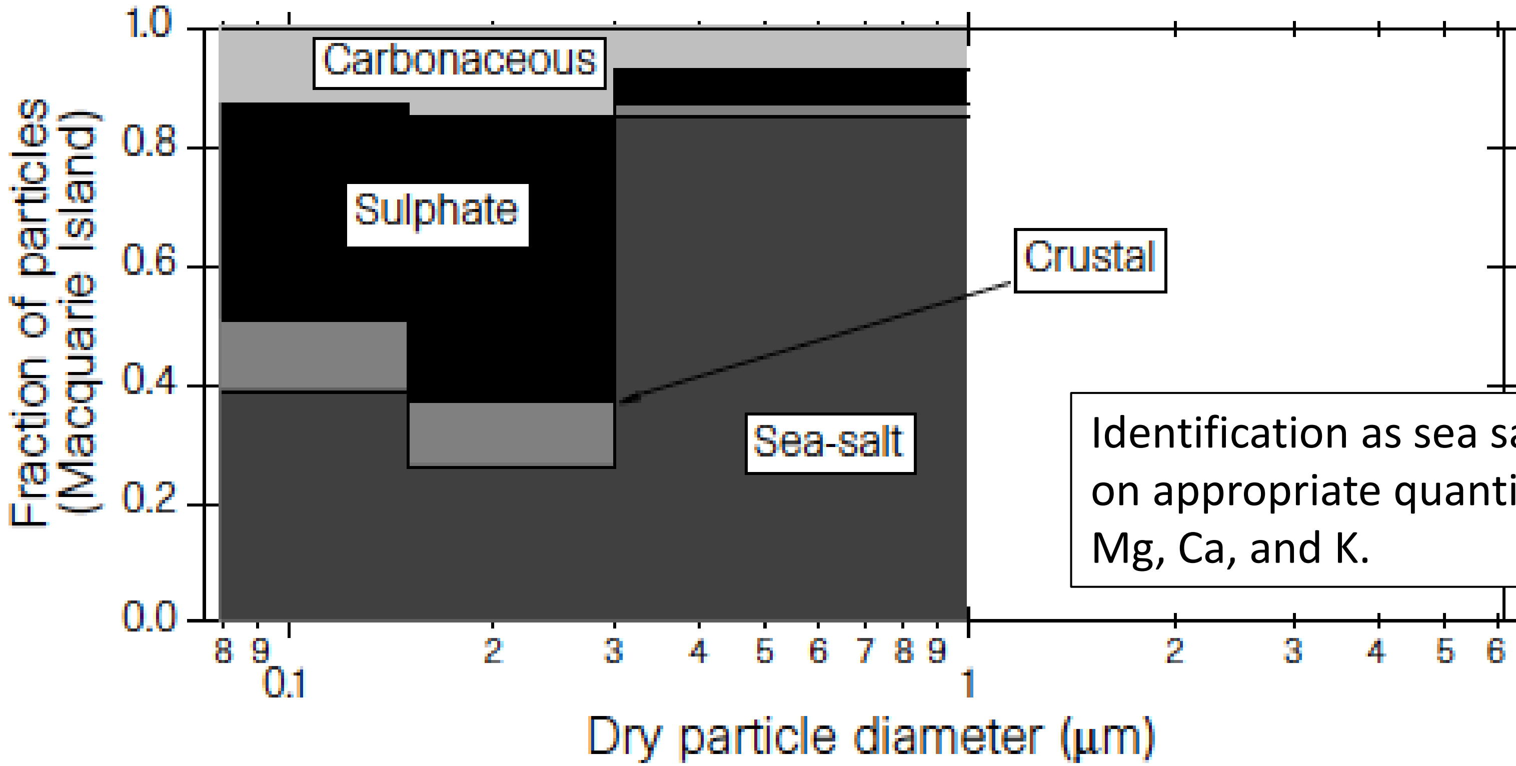


Accumulation of mass through ***condensation of gas phase species,*** coagulation of particles, and cloud processing leads to an accumulation mode.


Quinn & Bates, *Nature* (2011)
Free troposphere:
• Long range transport of continental emissions
• Homogeneous nucleation of DMS oxidation products
H_2SO_4
$SO_4^=$
Entrainment rate
Cloud Condensation Nuclei
Organics
Sea salt
$SO_4^=$
SO_2
DMS
Gas phase organics
Marine boundary layer:
• Particle growth – condensation, coagulation, cloud processing
• Secondary organic aerosol formation
Biological activity
Wind speed
Wind speed
Bubble bursting
Biological activity
Wind speed
Bubble bursting
Sea salt
DMS
Phytoplankton
DOM
Marine aggregates

Direct Chemical Evidence of Sea Salt in the CCN Size Range based on Manual TEM Analysis

ACE-1 , Macquarie Island, Southern Ocean (Murphy et al., Nature, 1998)

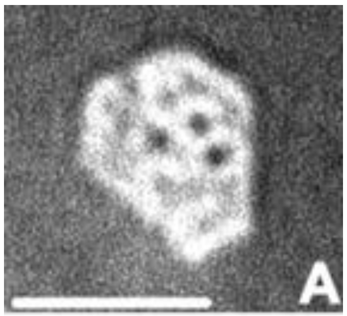


Identification as sea salt based on appropriate quantities of Na, Mg, Ca, and K.

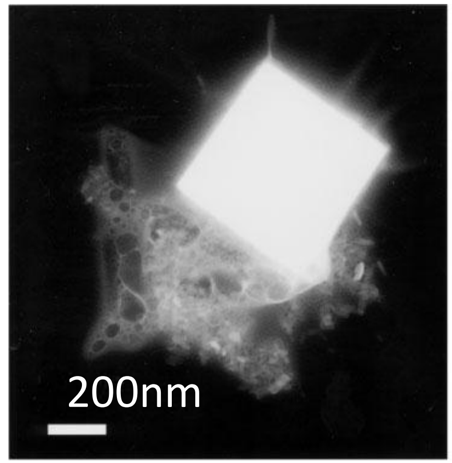
Sea-salt containing particles were observed in particles as small as 80 nm. Particles < 80 nm were not sampled.

Direct Chemical Evidence of Organics in the CCN Size Range based on Manual TEM Analysis

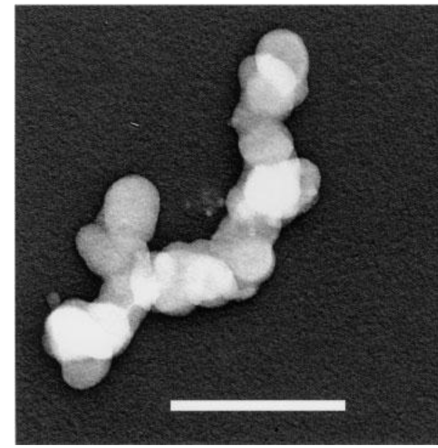
High Arctic, Great Barrier Reef, and Cape Grim
(Leck and Bigg, Tellus, 2008; Bigg, Env. Chem., 2007)



Virus-like particles



NaCl with exopolymer gel attached



Aggregate of marine material

A significant fraction of sampled particles with diameters < 200 nm contain organic matter in the form of exopolymer gels and airborne marine aggregates.

Bigg and Leck, Tellus, 2008.

TEM-derived size distributions of these airborne aggregates of marine organic material

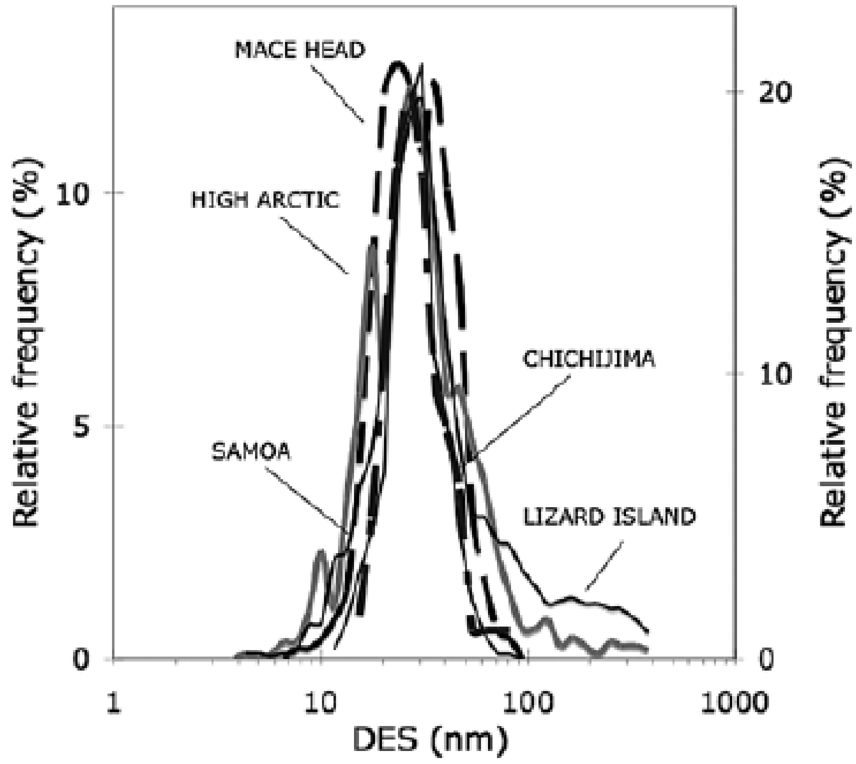


Figure 2. TEM size distribution of airborne aggregates of microcolloids and their components or building blocks at Mace Head (53°N, 10°W: 477 particles photographed, left scale), in the Arctic (89°N, 0°W) 1240 particles photographed, left scale), 600 Lizard Island (14.6°S, 145.5°E: 600 particles photographed, left scale), American Samoa (14°S, 172°W: 234 particles photographed, right scale) and Chichijima, (27°N, 142°E: 345 particles photographed, right scale). Each particle was assumed to be spherical.

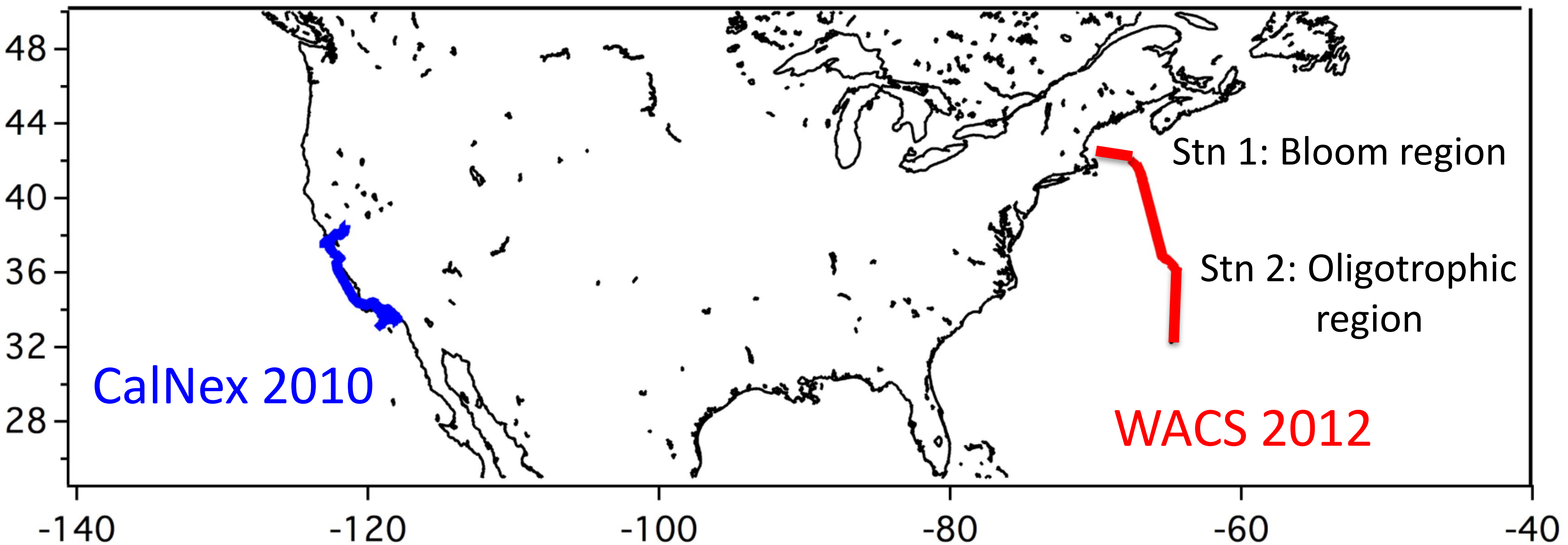
But these observations are based on measurements of ambient aerosol particles:

- Marine and non-marine origin
- Have undergone aging and modification through reactions with gas phase species, cloud processing, etc.

To assess the processes controlling the production and chemical composition of freshly emitted ocean-derived CCN, a simpler system needs to be examined.

One empirical approach is to separate out the nascent, freshly emitted ocean-derived aerosol and determine their chemical, physical, and cloud-nucleating properties before they undergo modification in the atmosphere.

Two cruises: CalNex 2010 - Coastal WACS 2012 - Open Ocean

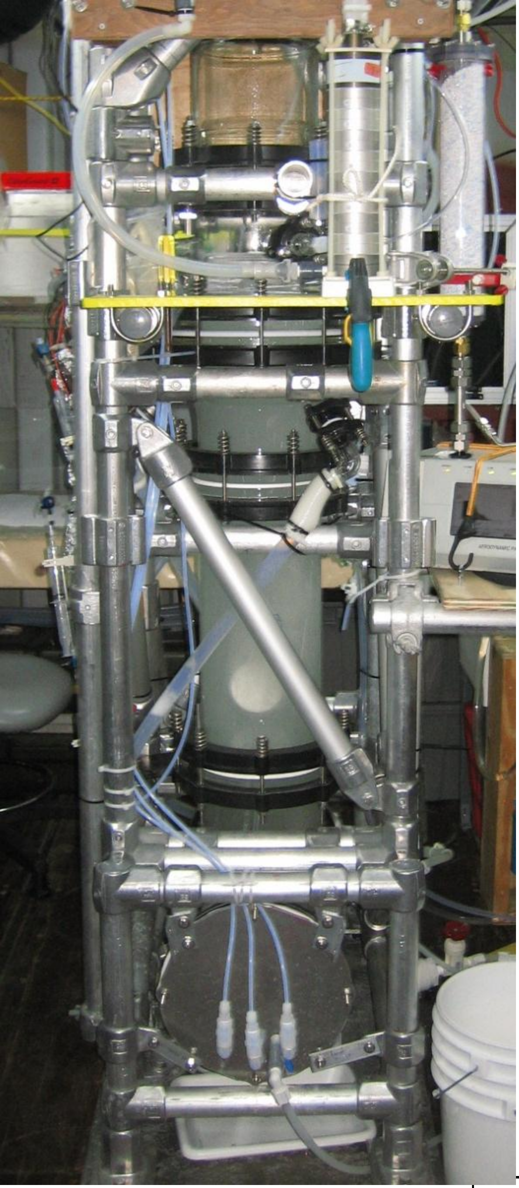


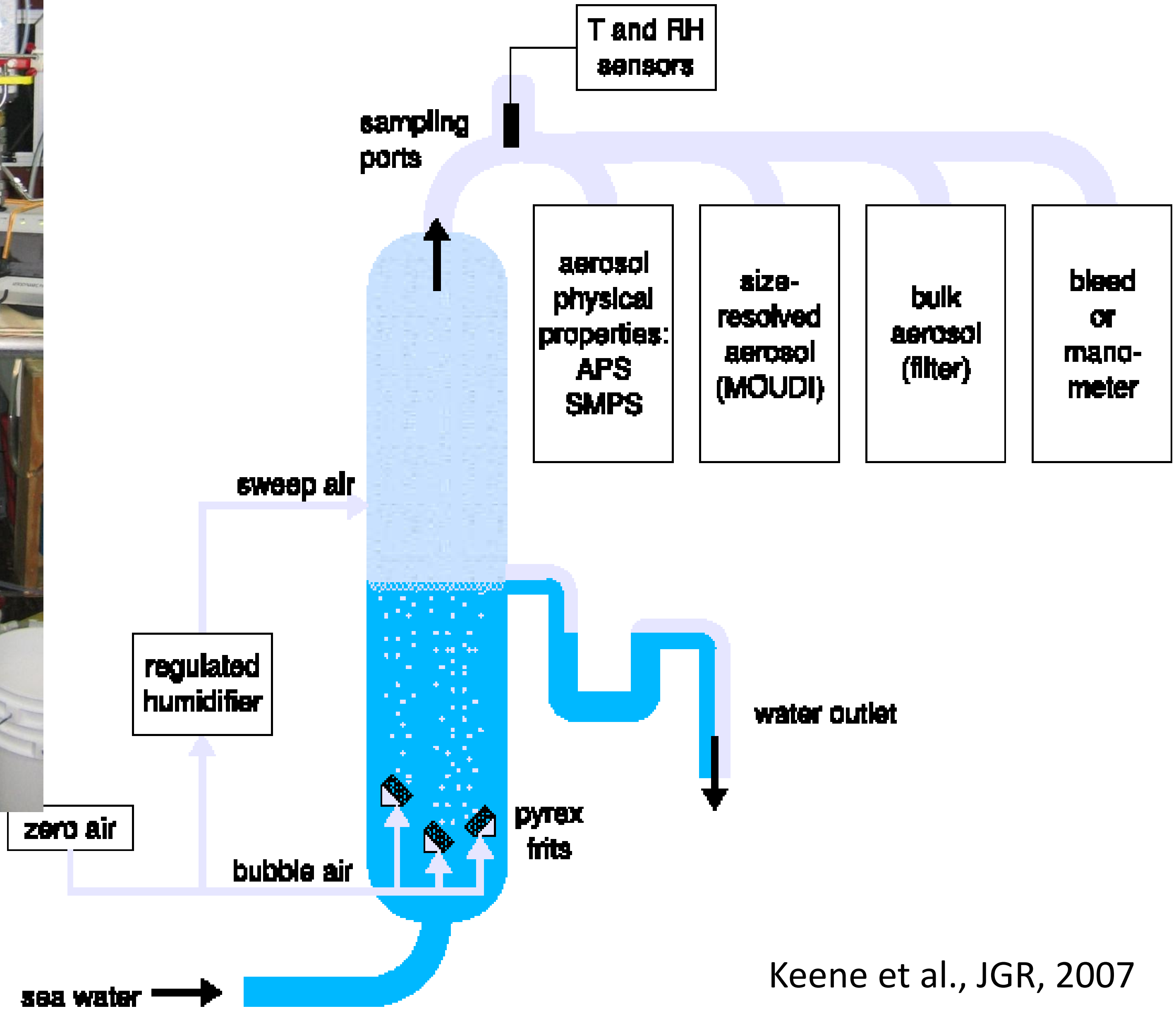
Two complementary methods for generating nascent, sea spray aerosol:

- Bubble generator – able to quantify size resolved number production flux (U Va)
- Sea Sweep – able to produce large number and mass concentrations for analysis of chemical and physical aerosol properties and CCN (PMEL)

University of Virginia Bubble Generator – Bill Keene

Yields size resolved number production fluxes

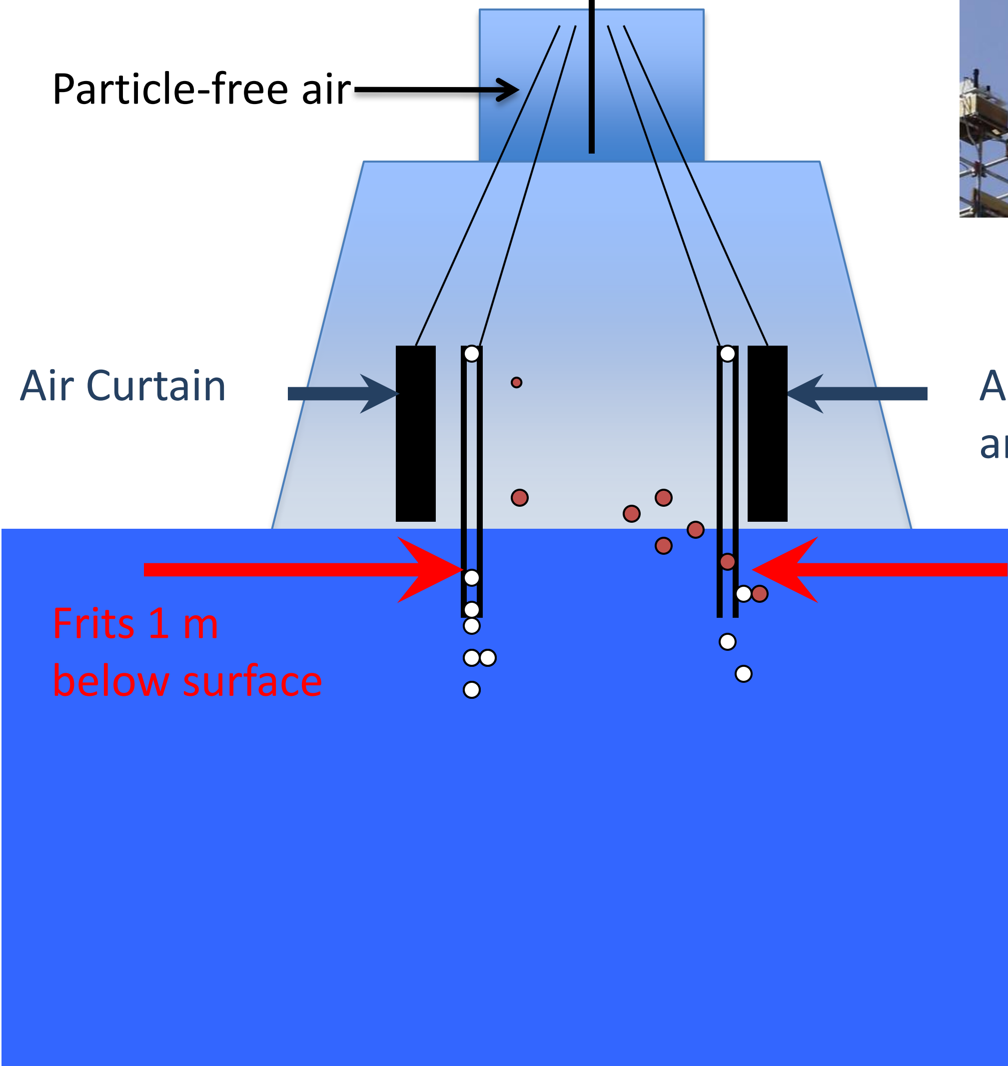


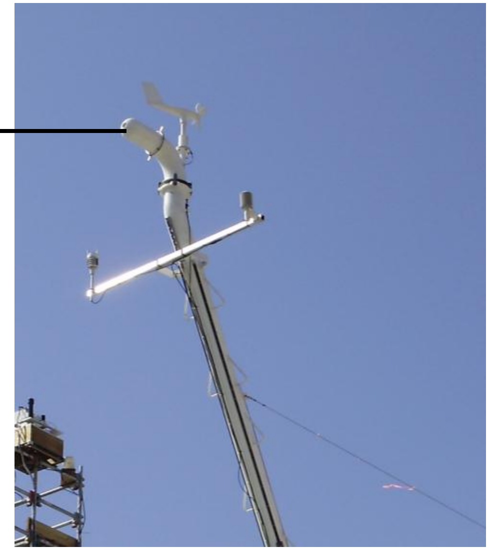


Keene et al., JGR, 2007

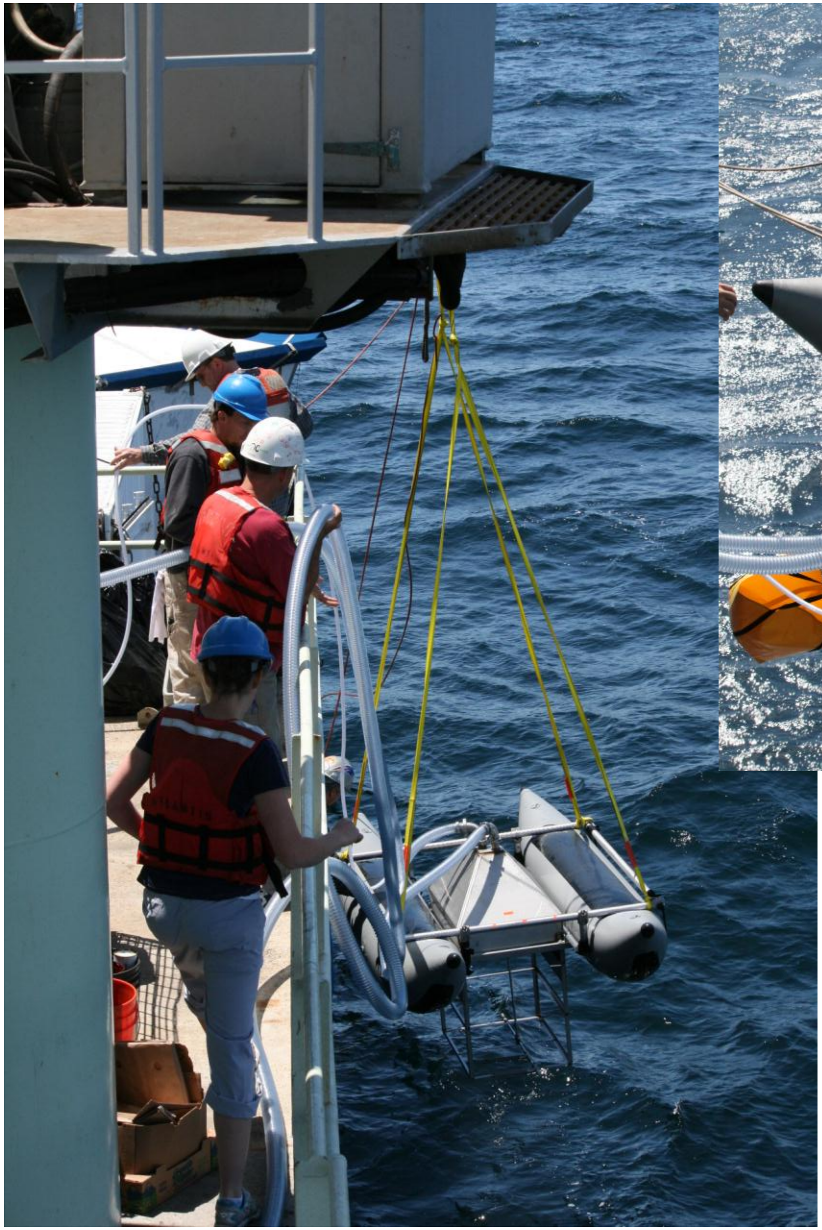
PMEL Sea Sweep:
Yields large number and mass concentrations

Bates et al., *JGR,* 2012



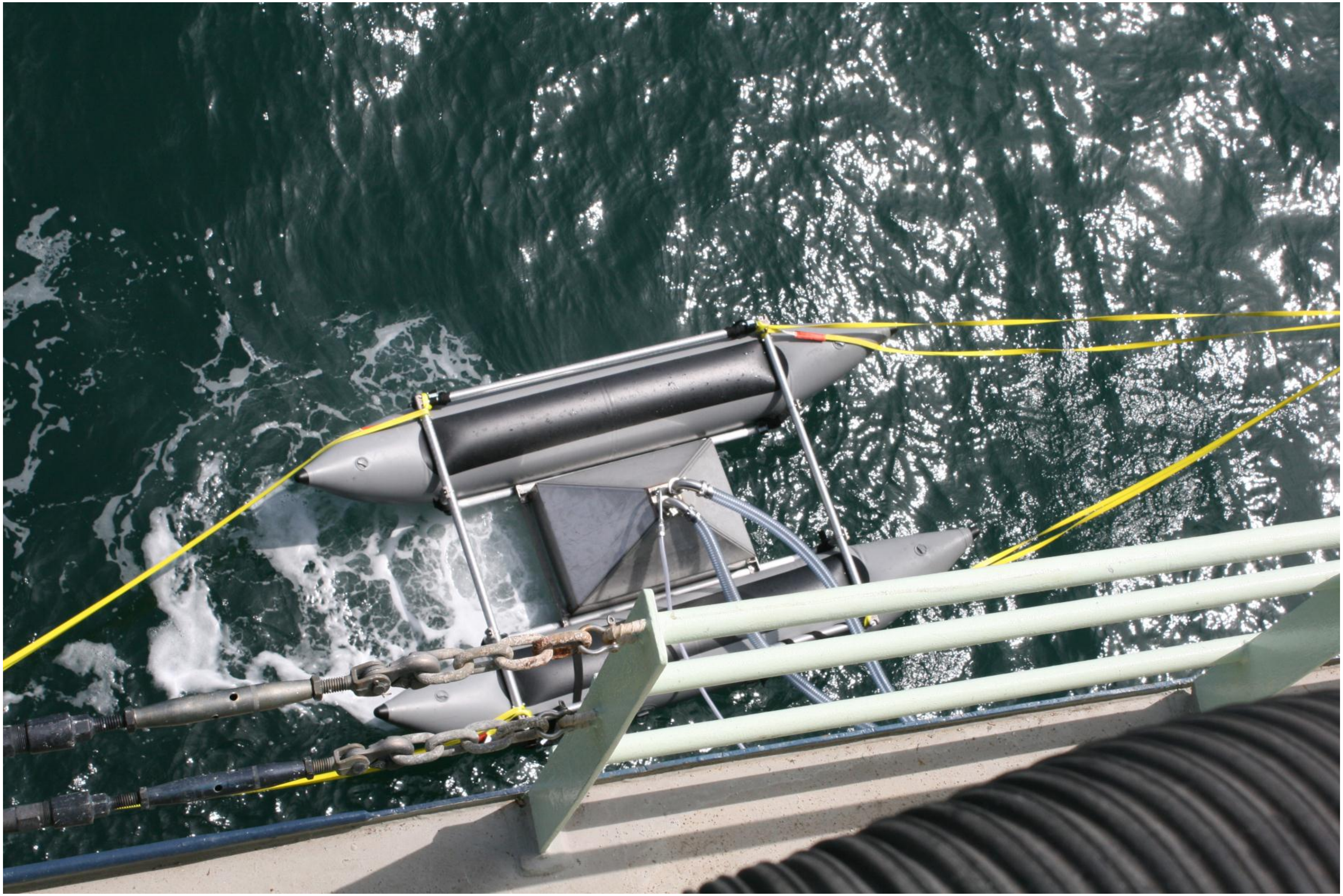


Deployment of Sea Sweep



Attaching inlet from sea sweep to sampling mast

Sea Sweep during Sampling



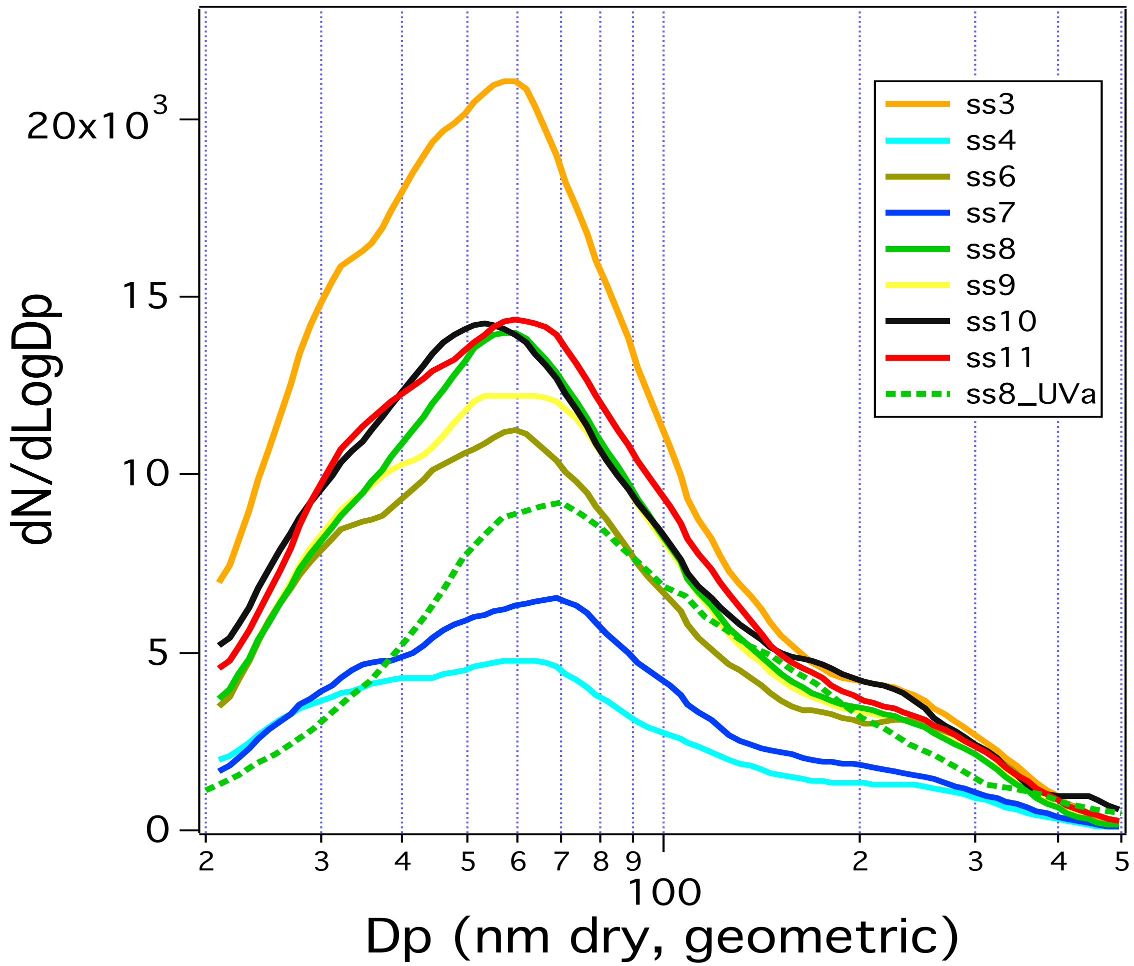
Characterization of Sea Sweep Nascent Sea Spray Particles (Added for WACS)

- Number size distribution (20 nm to 10 um) (PMEL)
- Number size distribution heated to 230°C (particle volatility) (PMEL)
- Hygroscopic growth at selected sizes (Univ Helsinki)
- CCN activation ratio for bulk and monodisperse aerosol (PMEL)
- Particle composition and morphology (TEM) (Univ Stockholm)
- Organic carbon concentration (Sunset Labs) (PMEL)
- Organic functional groups (FTIR) (Scripps)
- Non-refractory sea salt, POM, SO_4 (Q-AMS, HR-ToF-AMS) (PMEL & Scripps)
- Inorganic ion concentrations (Impactors + Ion chromatography) (PMEL)

Characterization of Surface Sea Water

- Chlorophyll (Fluorescence), Temperature, Salinity (PMEL)
- DMS concentrations (PMEL)
- Particulate Organic Carbon (POC) concentrations (Sunset Labs) (PMEL)
- Total Organic Carbon (TOC) and Nitrogen (PMEL)
- Dissolved Organic Matter (DOM) spectral absorption (SUNY)
- Particle composition and morphology (Univ Washington)
- Community Structure (OSU)
- Phytoplankton VOC turnover rates (OSU)

CalNex: Measured Particle Number Size Distributions



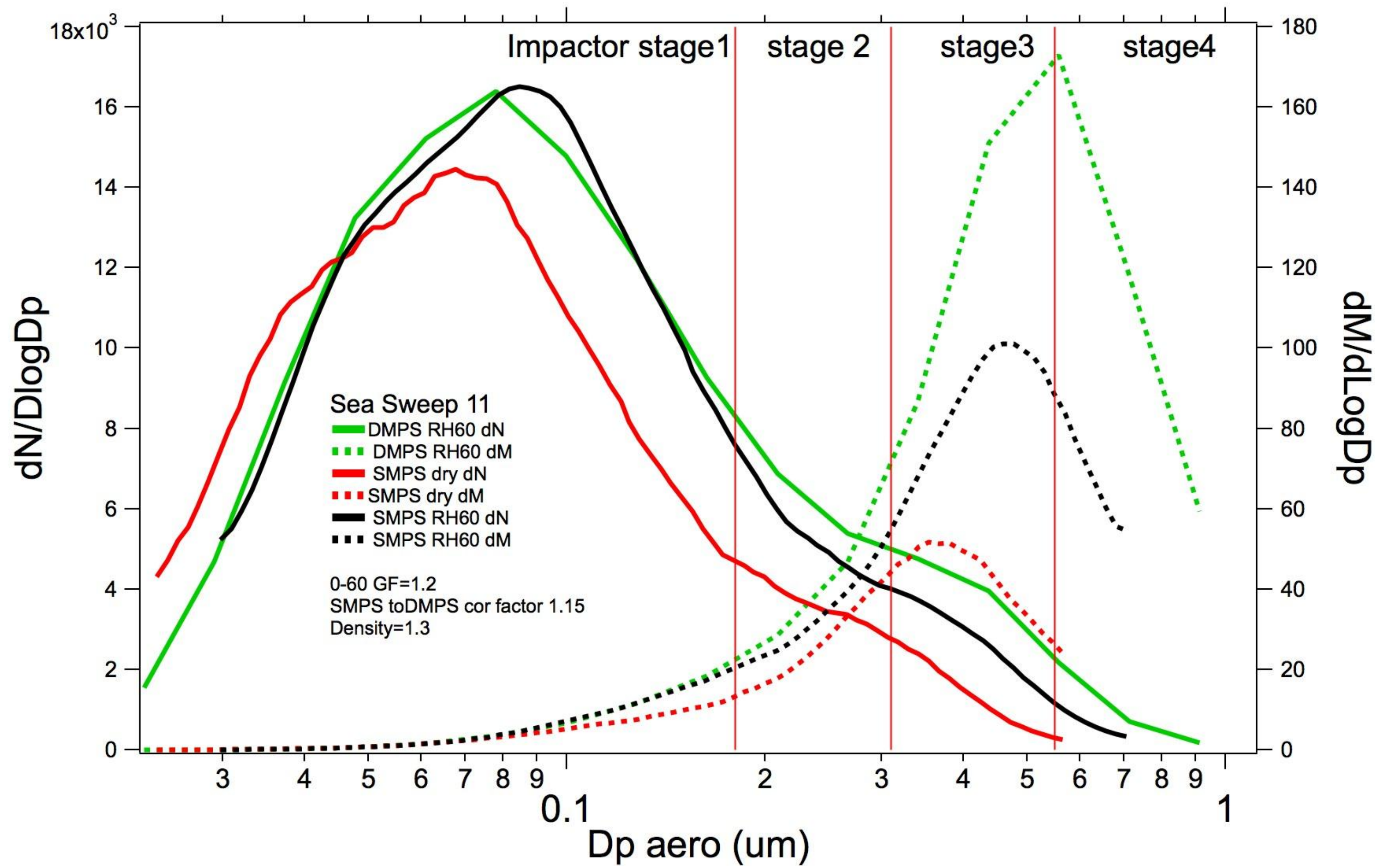
- Magnitude of the number of particles varies with flow rate of air through frits for Sea Sweep.
- Consistent Aitken mode with a peak diameter between 50 and 80 nm
- Shoulder peak around 30 nm. Additional peak around 200 to 300 nm.
- Good agreement between Sea Sweep and Univ VA bubbler.

Published particle number size distributions of nascent, ocean-derived aerosol

Reference	Diameter of Dominant Subum Mode (nm)	RH	Method
Tyree et al. 2007	100	Dry	Diffuser frit Scripps Pier
Keene et al. 2007	70 – 80	Dry	Diffuser frits Oligotrophic Sargasso Sea
Hultin et al. 2010	100	Dry	Impinging jet NE Atlantic
Fuentes et al. 2010	45 (productive waters) 52 (non-productive waters)	Dry	Impinging jet West African coast
CalNex - Sea Sweep	60	Dry	Diffuser frit submerged in ocean surface, E. Pacific
CalNex – Univ. VA	70	Dry	Diffuser frit in generator E. Pacific

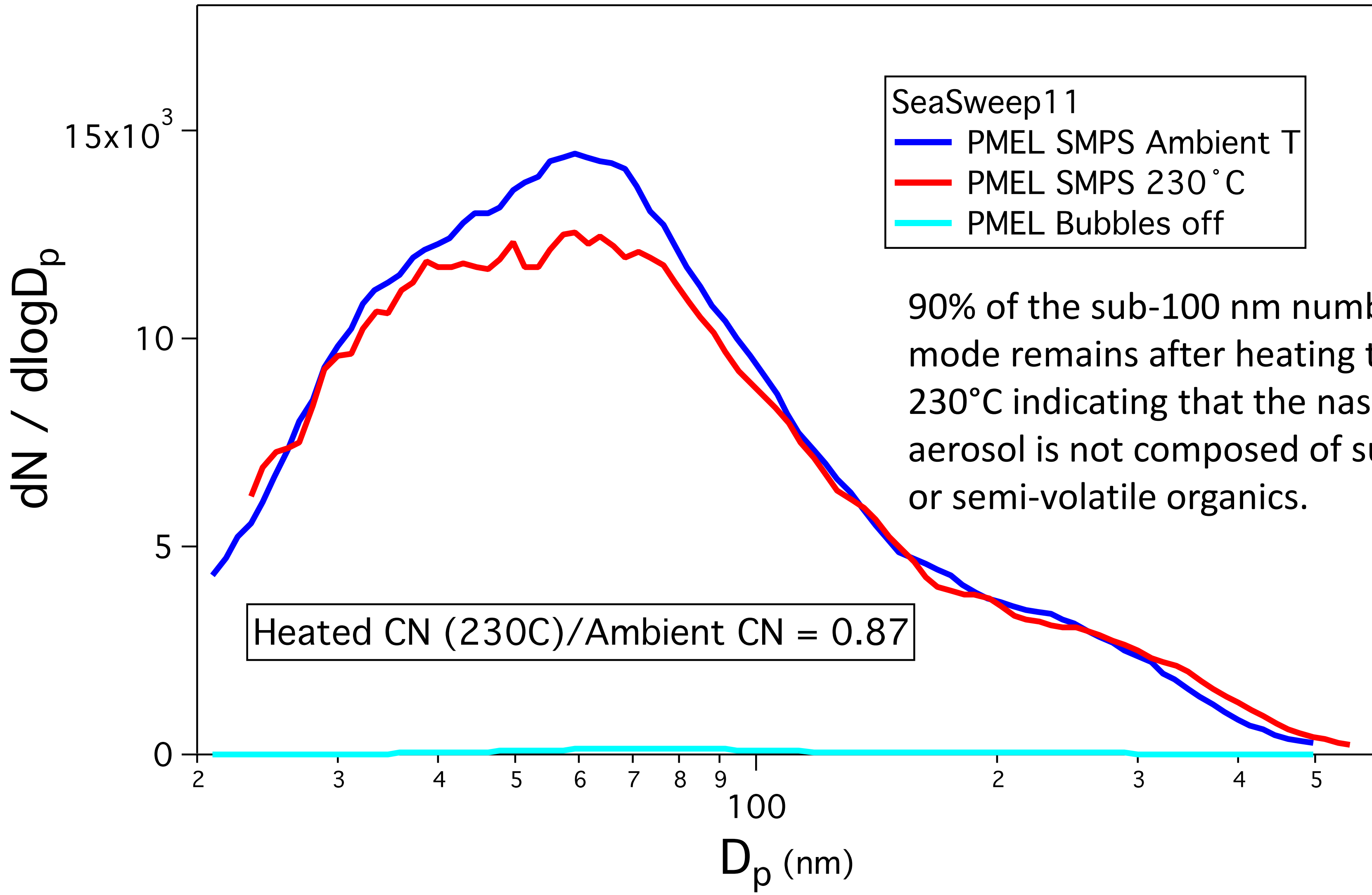
There is a sub-100 nm mode that recurs in all nascent aerosol generation experiments providing evidence for a primary, ocean-derived source of CCN.

CalNex: Comparison of Sea Sweep number and mass size distributions



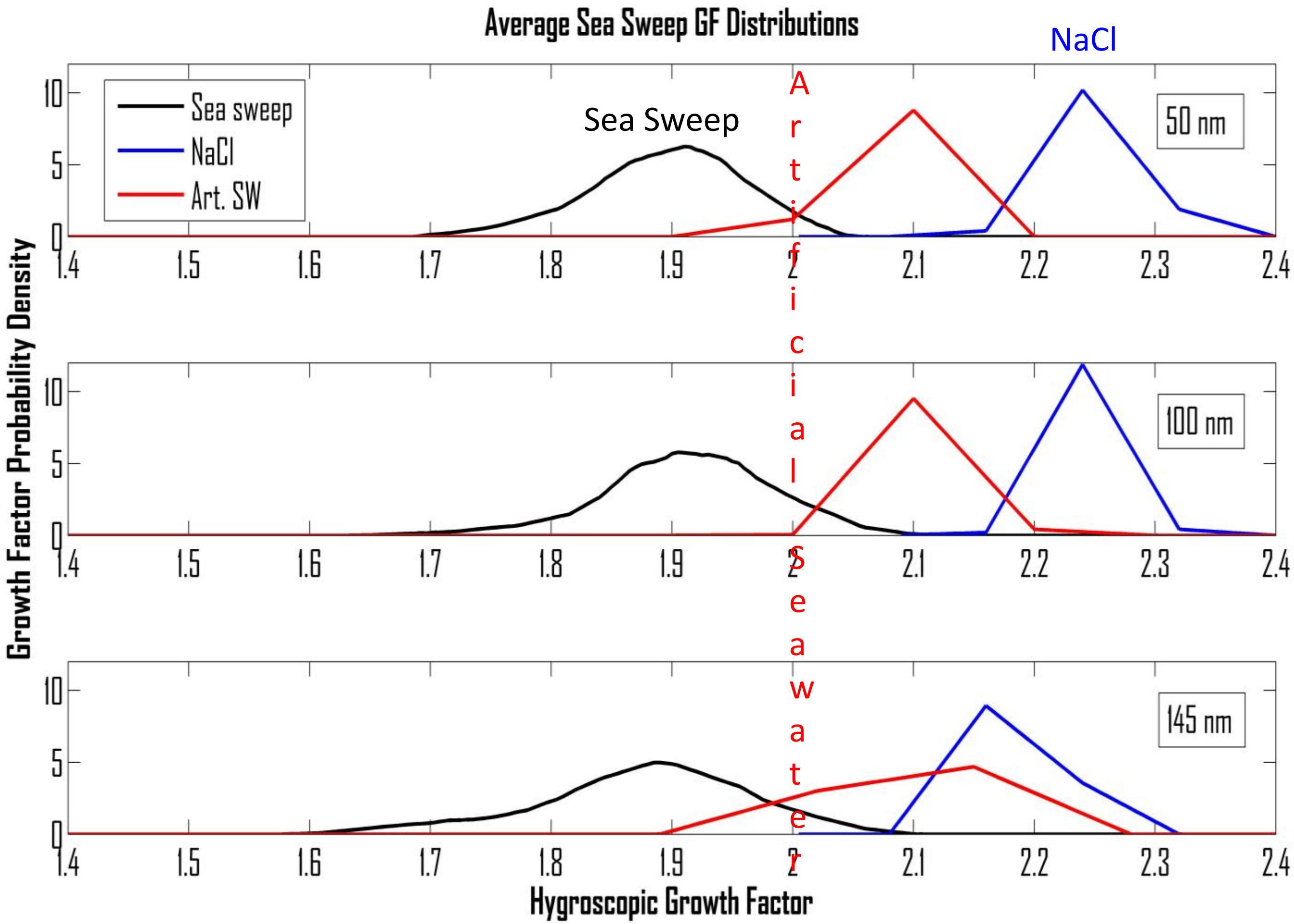
Particles with Dp < 200 nm dominate the number size distribution while particles with Dp > 200 nm dominate the mass size distribution.

CalNex: Comparison of unheated and heated Sea Sweep size distributions



90% of the sub-100 nm number mode remains after heating to 230°C indicating that the nascent aerosol is not composed of sulfate or semi-volatile organics.

CalNex: Average hygroscopic growth (dry to 90%RH) of selected particle sizes for Sea Sweep Aerosol



- Single homogeneous mode at all diameters
- ~ 10% smaller than artificial seawater generated in the laboratory
- These diameter particles are not composed only of sea salt.

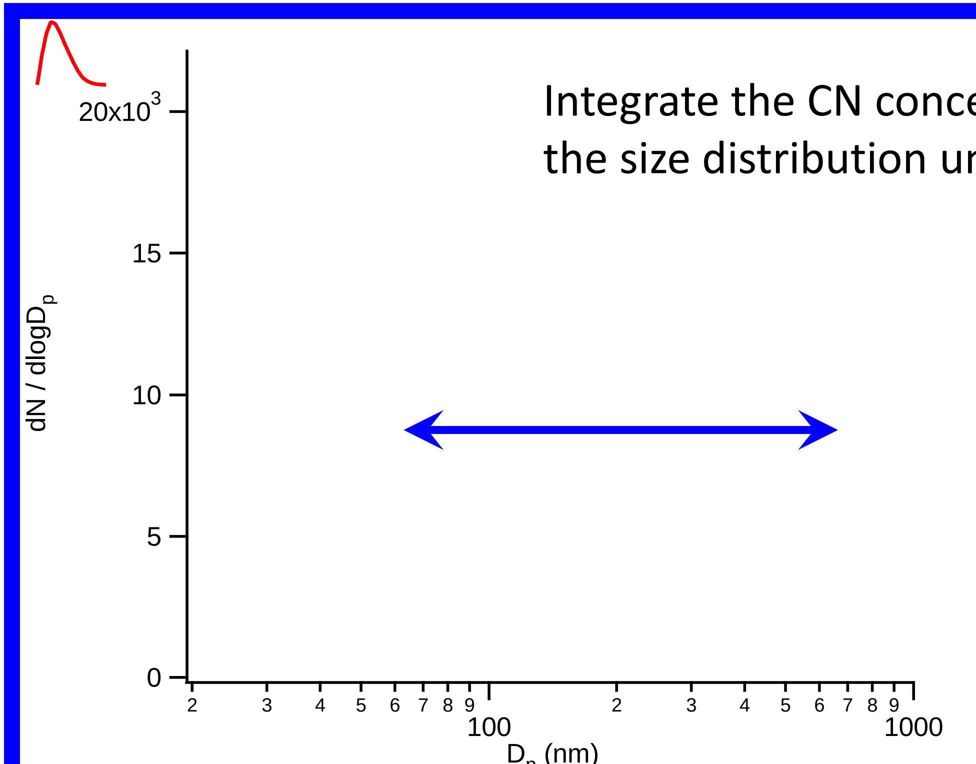
Relationship between particle size, composition, and supersaturation required for a particle to act as a CCN

$$s_c \approx \sqrt{\frac{4}{\kappa D_p^3}\left(\frac{4\sigma M_w}{3RT\rho_w}\right)^3}$$

S_c = critical water vapor supersaturation

κ = hygroscopicity parameter

D_p = dry particle diameter



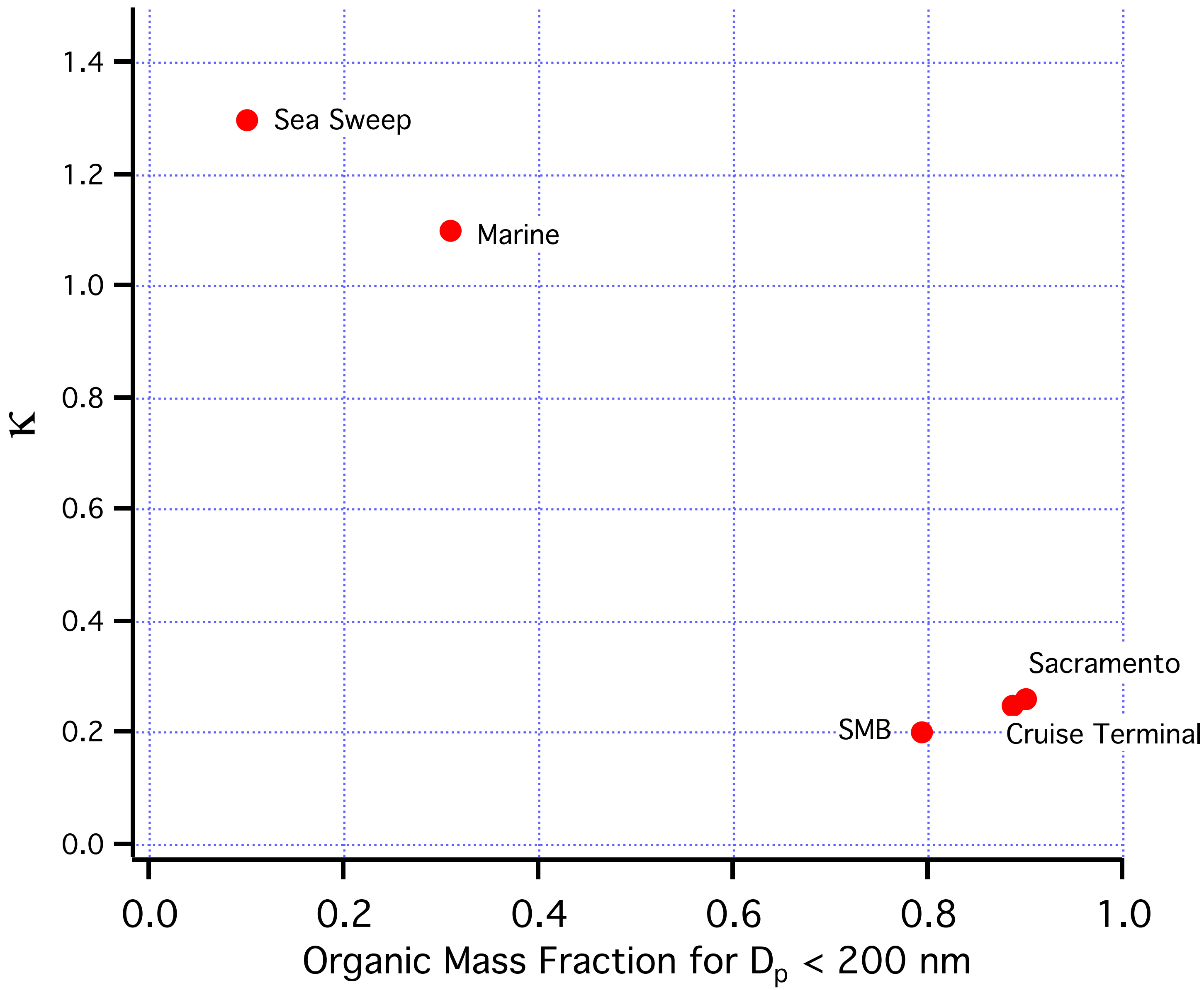
Integrate the CN concentration over the size distribution until CCN = CN

Critical diameter is defined as the diameter at which:

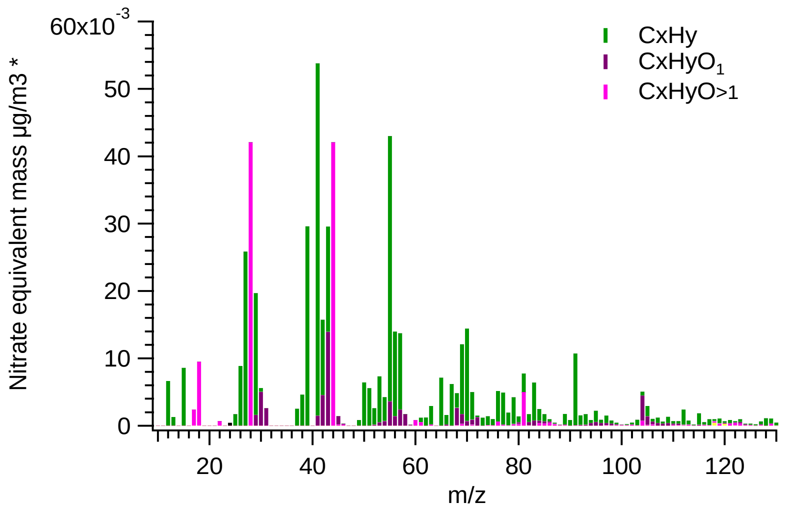
$CCN_{measured}$ = CN Concentration

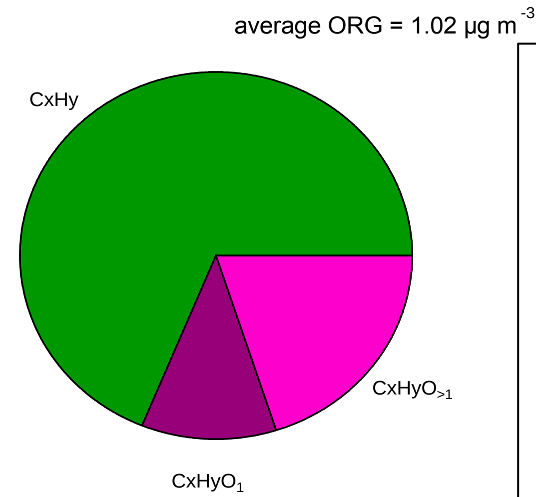
$D_p = D_c$

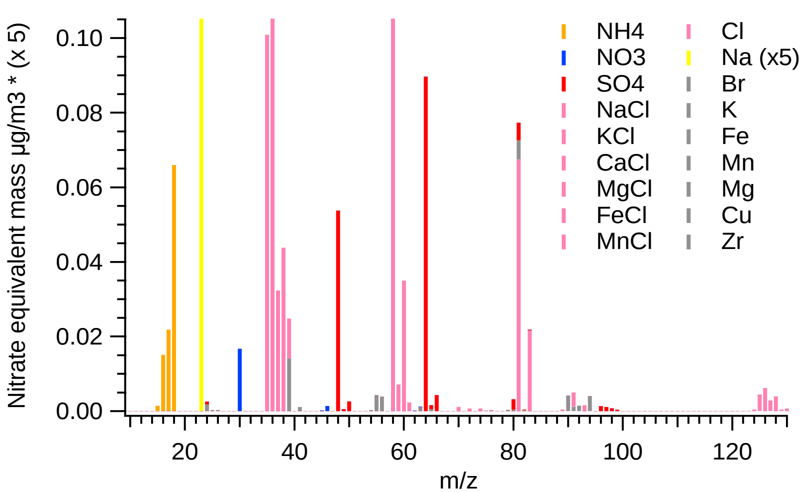
Kappa as a function of sub-200 nm POM mass fraction

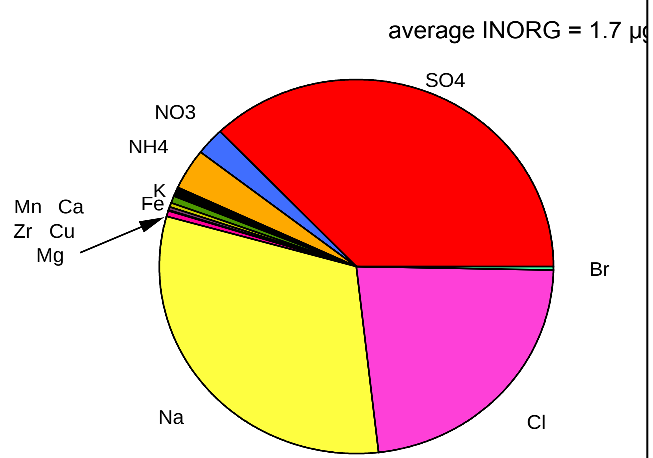


HR-ToF-AMS Mass Spectra and Mass-Weighted Pie Charts of the NR Organic and Inorganic Components of Sea Sweep Aerosol





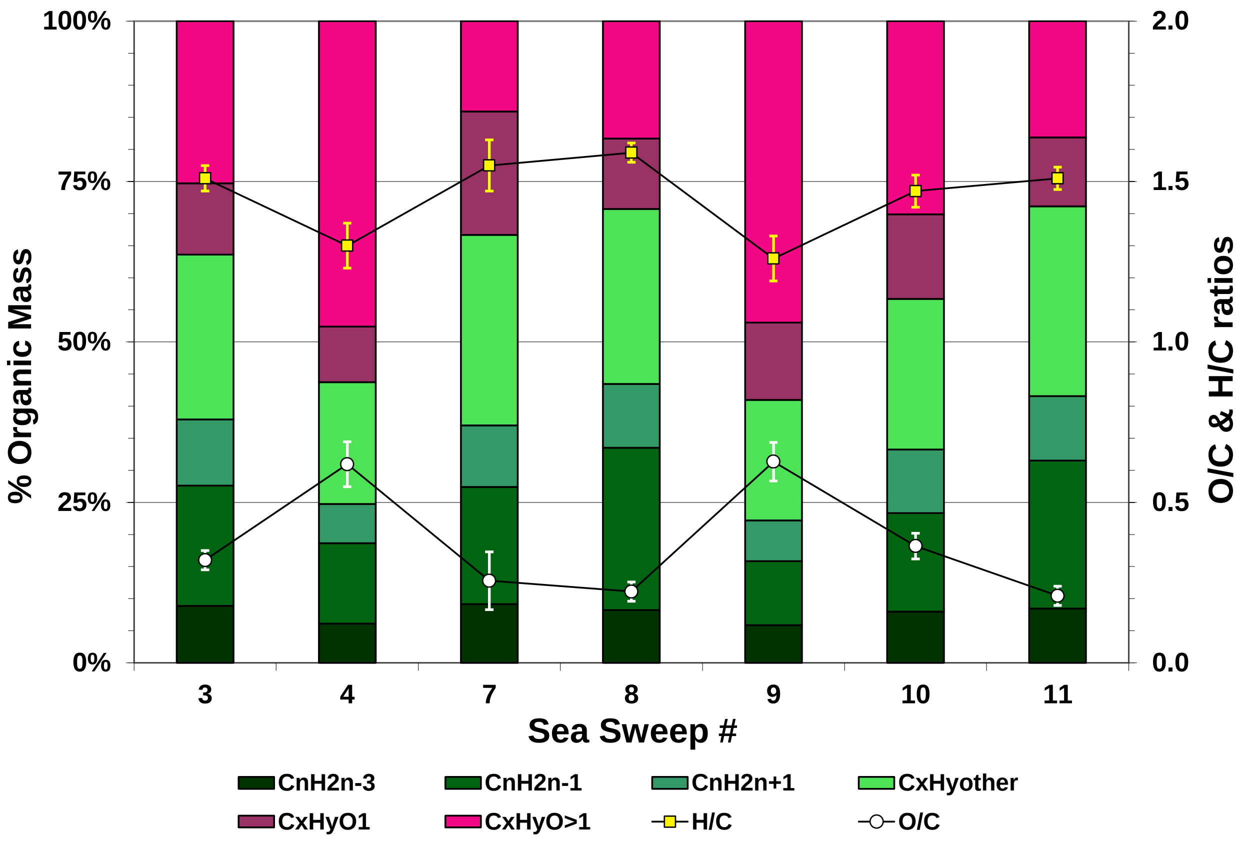




- Most of the nascent aerosol is unsaturated hydrocarbons
- Only 1/3 is oxygenated
- Nascent aerosol also composed of metal halides
- Ionization efficiency is low for NaCl at 600C so the total abundance of inorganic ions is uncertain

Organic Mass Fractions of Unsaturated Hydrocarbons and Oxygenated Organics

Unsaturated hydrocarbons (CnHn)
Oxygenated organics (CxHyO)



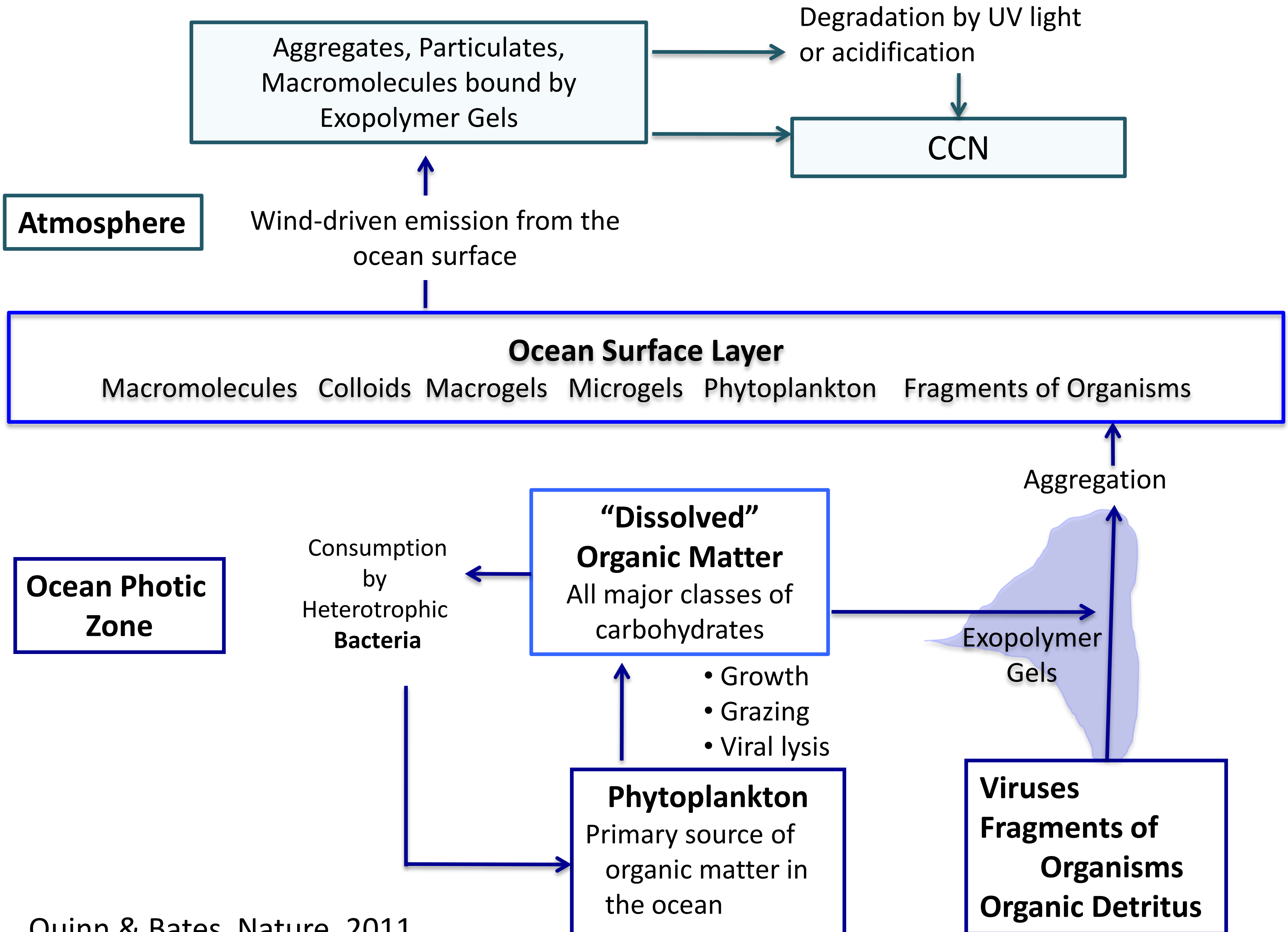
- Organic mass dominated by unsaturated hydrocarbons
- O/C ratio is low (typically 0.9 to 1.0 in aged aerosol).

Modeling the climate impacts of ocean-derived CCN requires a sea spray aerosol source function that can be used in global climate models to calculate global distributions.

The complexity of the sources of ocean-derived aerosol makes this challenging.

Source functions for the inorganic fraction of sea spray (Sea Salt) are based on wind speed and white cap fraction.

How can the organic fraction of sea spray be parameterized?



Quinn & Bates, Nature, 2011

Sea spray source function based on Chlorophyll and Wind Speed

O'Dowd et al (2008).

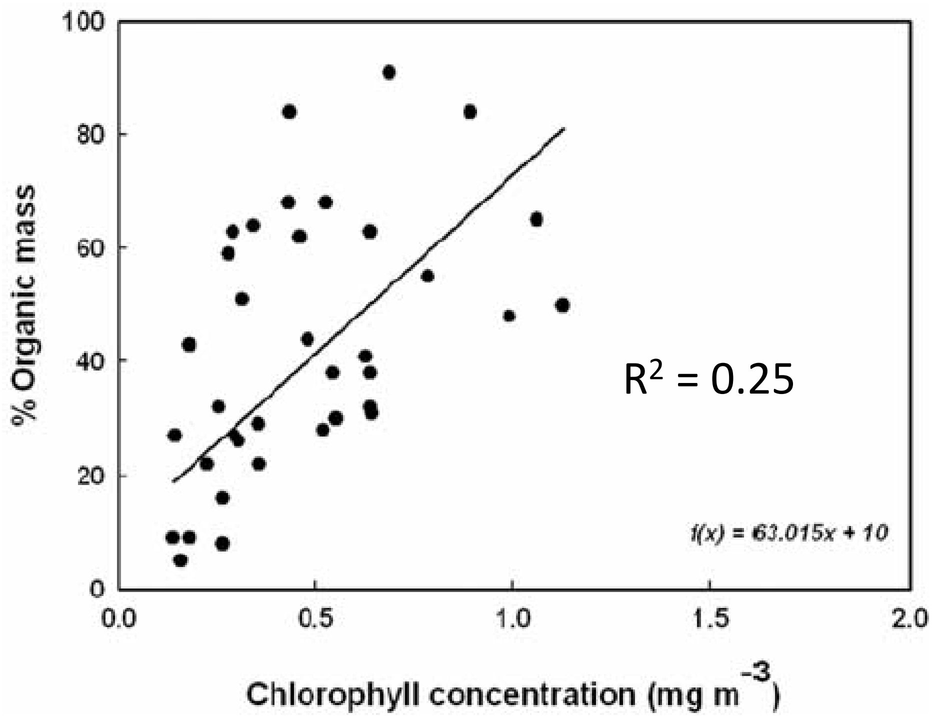
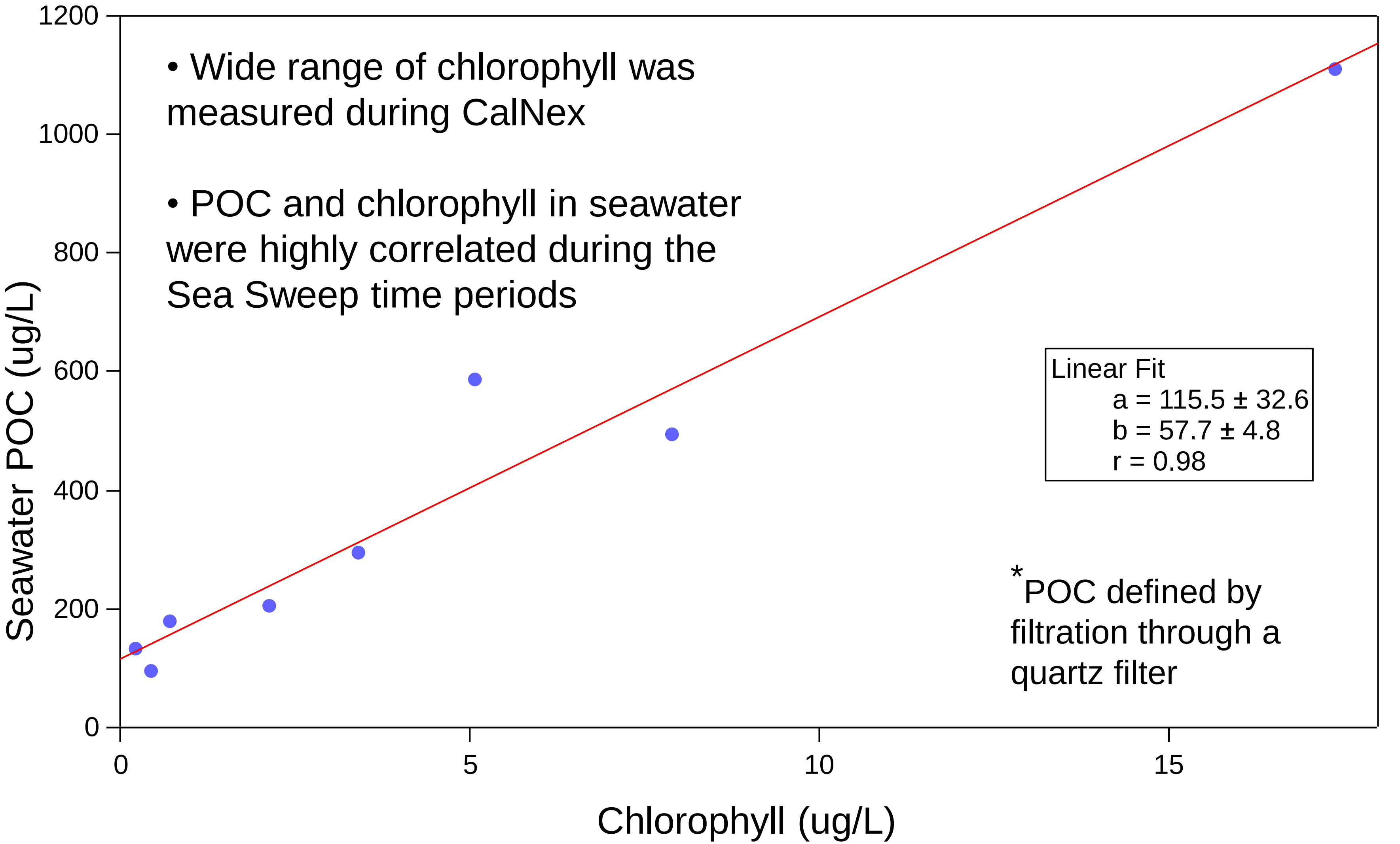
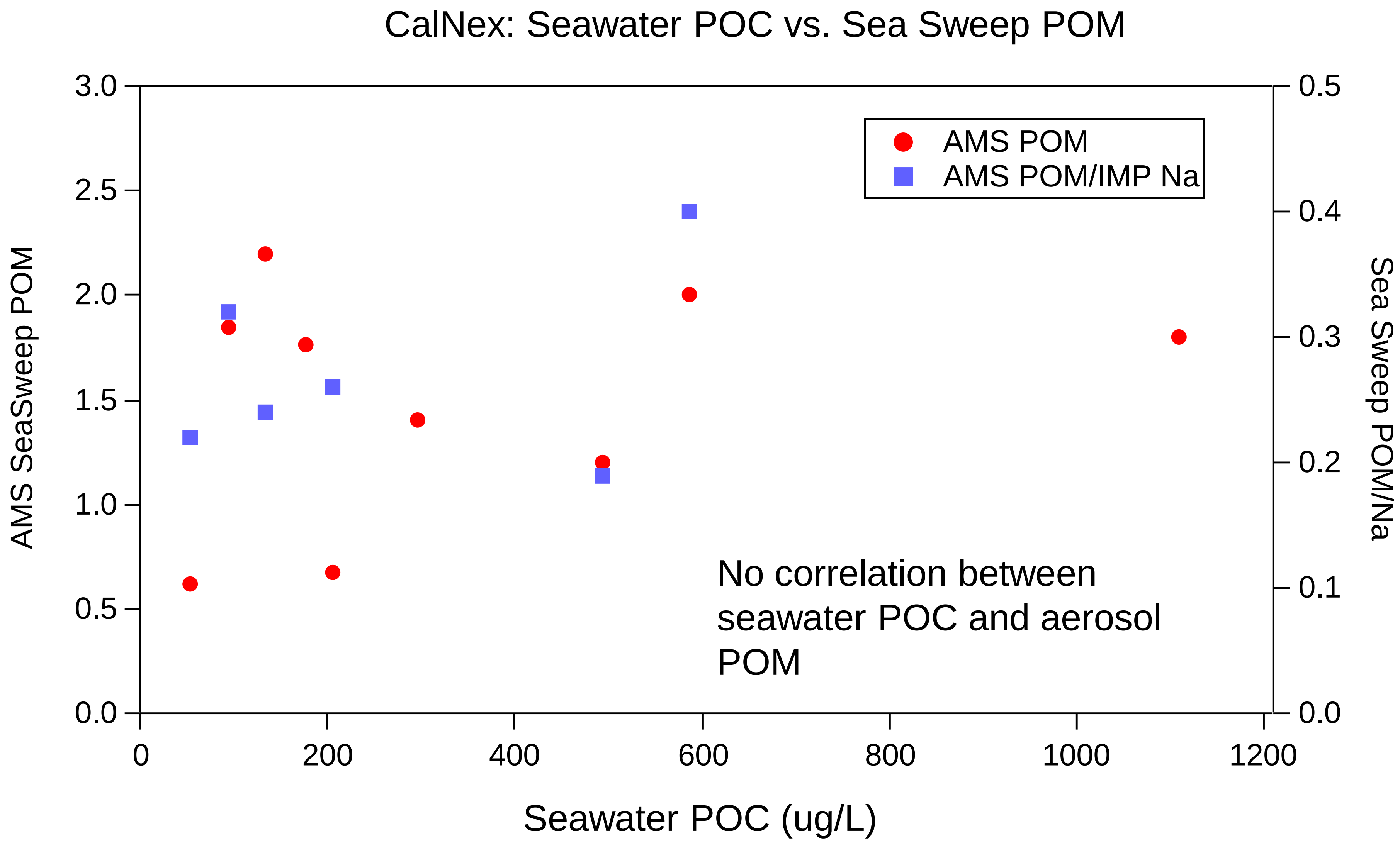


Figure 2. Correlation between fractional WIOC component of sea-spray as a function of grid-average chlorophyll-a concentration.

- Only captures about 25% of the variance in the organic mass fraction of sea spray aerosol
- Source functions that rely solely on chlorophyll to represent sea spray organics are not sufficient

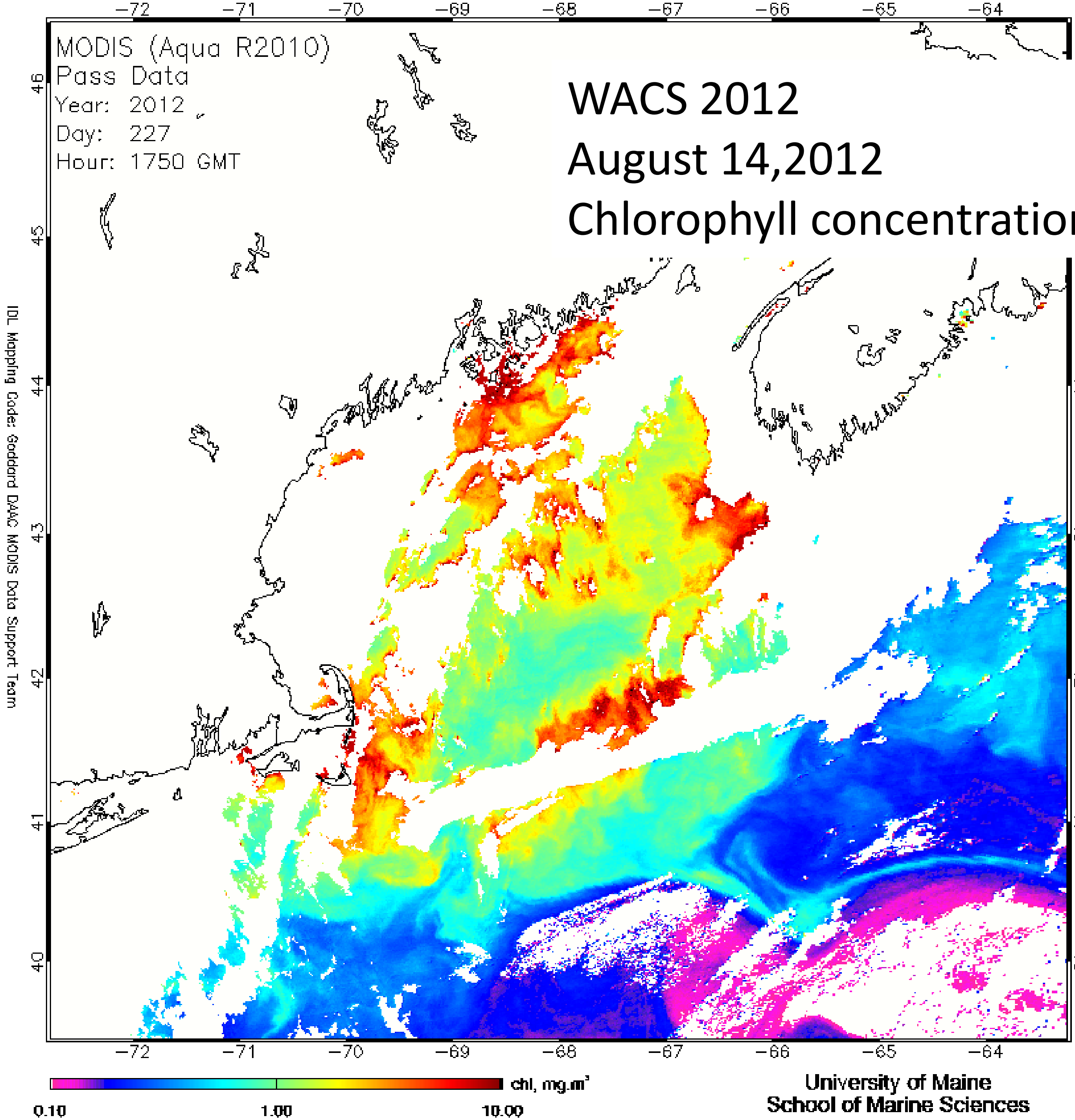
CalNex: Seawater chlorophyll vs. Seawater Particulate Organic Carbon*



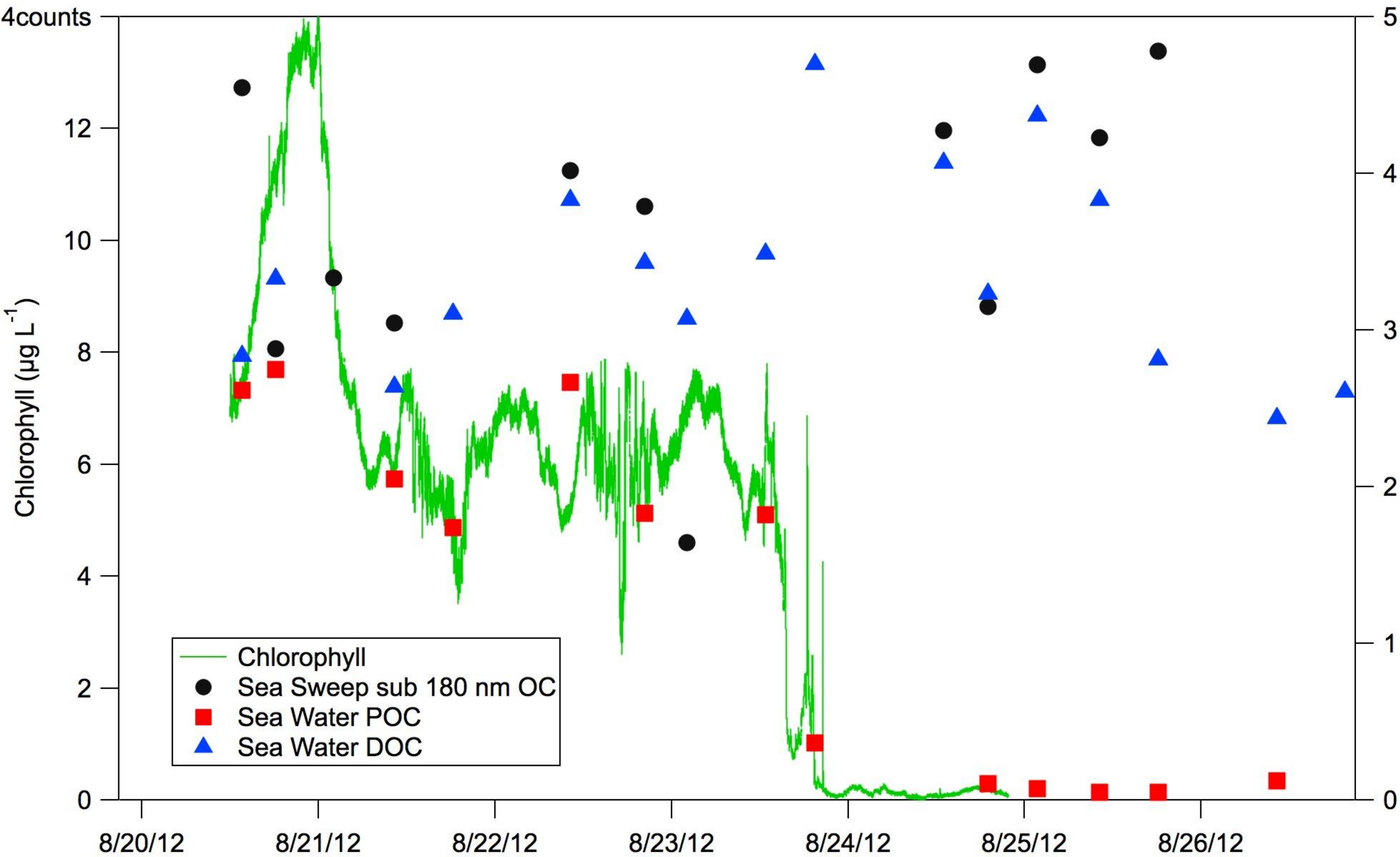


CalNex: No relationship between chlorophyll and nascent aerosol organic concentrations.

WACS 2012
August 14,2012
Chlorophyll concentrations



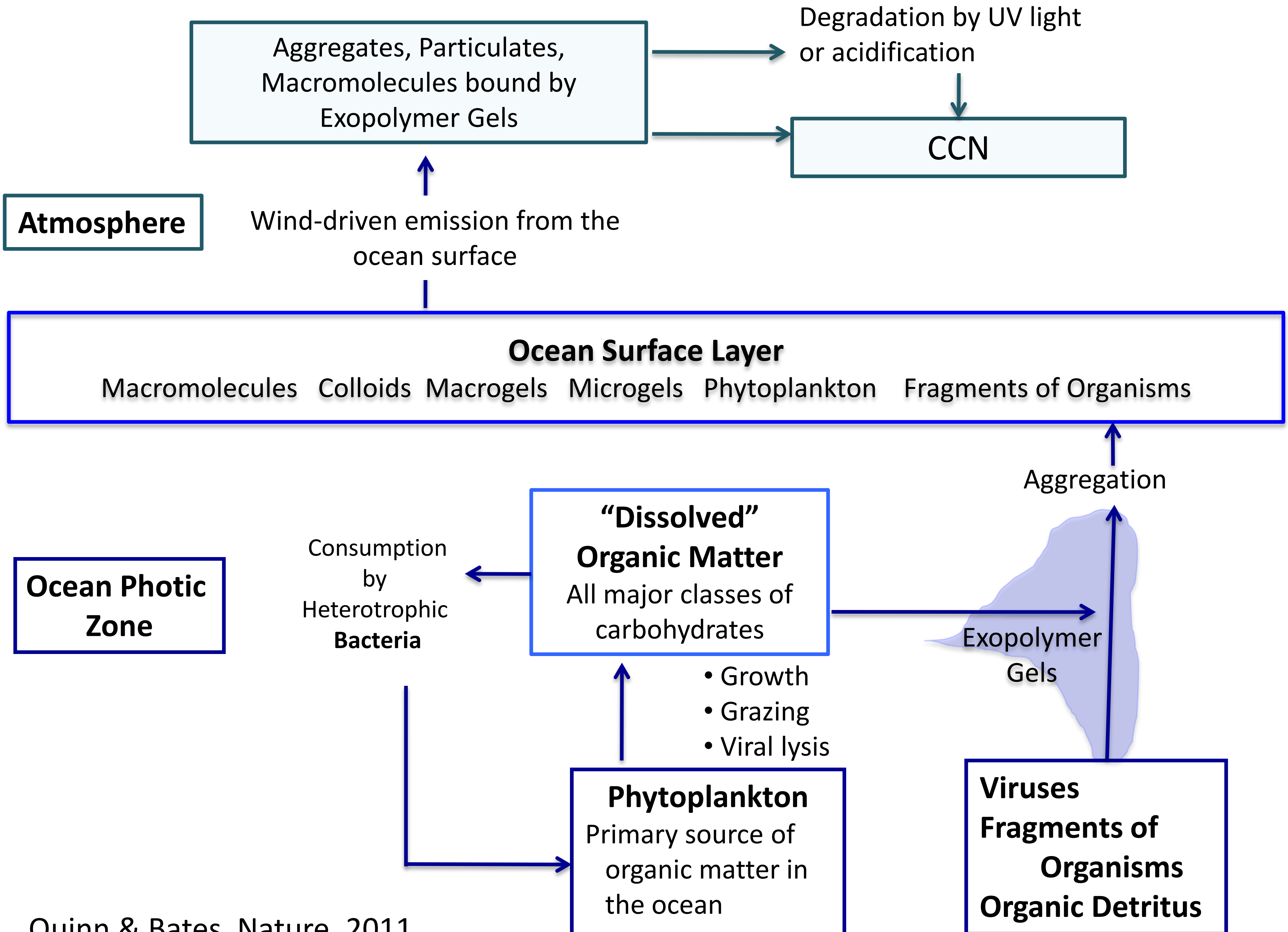
WACS: No correlation between chlorophyll and Sea sweep nascent aerosol OC concentrations



Organics are enriched in the sub-180 nm size fraction

Summary

- Organics are enriched in the sub-180 nm size fraction
- No correlation between chlorophyll and nascent sea spray organic concentration
- Sea spray organics are a result of the large pool of dissolved organic carbon in ocean surface waters
- Local biology has little influence on this large reservoir of DOC and, therefore, on organics that are incorporated into sea spray aerosol



Quinn & Bates, Nature, 2011