AMS Observations over Coastal California from the Biological and Oceanic Atmospheric Study (BOAS)

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The BOAS Field Campaign

Figure 1: The CIRPAS Twin Otter

The BOAS campaign comprised 15 flights aboard a Navy Twin Otter (Figure 1) between 2 July and 24 July 2015. Flights were based out of the Naval Postgraduate School's Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) in Monterey, CA, and flew primarily over the San Jose area and coastal waters (Figure 2).

Unique conditions:

- A persistent pool of **unseasonably warm water** (Figure 2) sat off the California coast for the duration of the campaign.
- During the campaign, the central California coast experienced a massive **phytoplankton bloom** (Figure 2), particularly notable for the diatom *Pseudo-nitzschia* (Figure 3) which produces domoic acid, the neurotoxin responsible for amnesic shellfish poisoning.

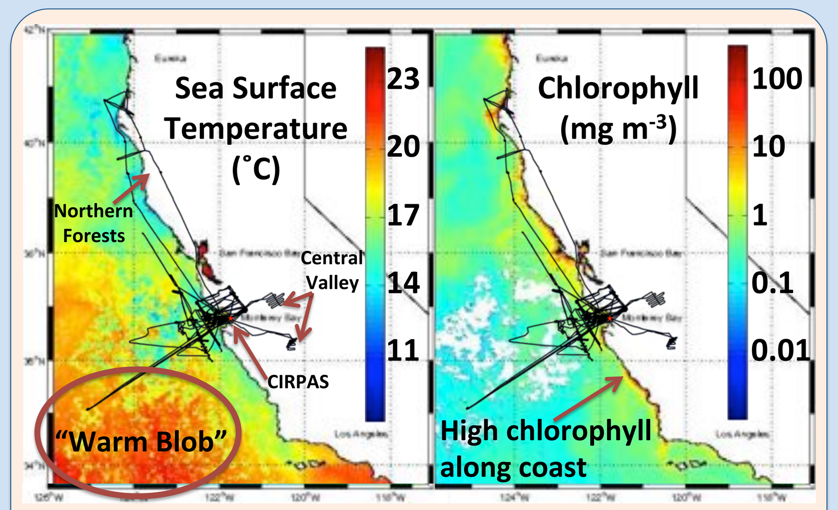

Figure 2: Sea surface temperature (L) and chlorophyll concentration (R) for July 10-17 2015 (CeNCOOS), overlaid with BOAS flight paths in black

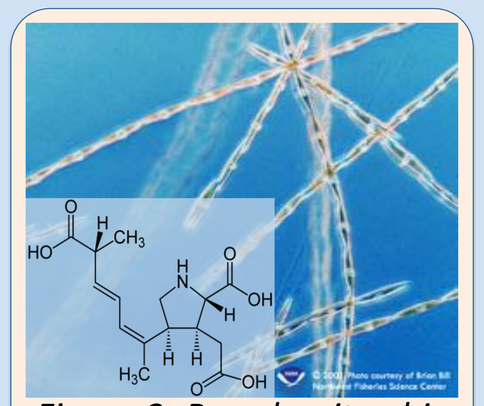

Figure 3: Pseudo-nitzschia and its product, the neurotoxin domoic acid

Goals of the campaign:

- Characterize the distribution and composition of **bioaerosols** over various environments
- Examine the effects of this summer's unique oceanic conditions – particularly the plankton bloom – on **marine aerosol**
- Continue ongoing analysis (since E-PEACE[1] 2011 and NiCE[2] 2013) of **aerosol-cloud interactions** and the cloudy-clear interface (see A. Sorooshian's talk tomorrow, 10:20am, A52E-01, West 3002)
- Characterize the aerosol properties of the San Jose **urban plume**[3] and its interactions with nearby airmasses

Instrumentation

A **unique combination of instruments** – in particular the Aerosol Mass Spectrometer (AMS) and Wideband Integrated Bioaerosol Sensor (WIBS) – allowed for characterization of physical, chemical, and biological properties of ambient aerosol.

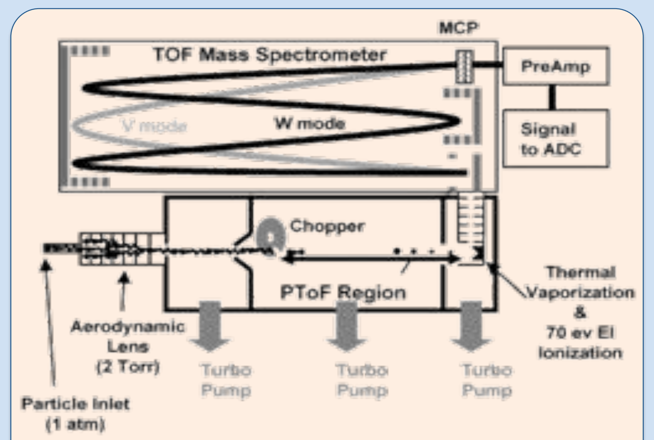

Figure 4: Schematic of the AMS

The high-resolution time-of-flight (ToF) **AMS** (Figure 4, Aerodyne Research Inc.) provides quantitative real-time information on chemical composition and mass loadings of non-refractory sub-micron aerosol. Particles are thermally vaporized at 600 °C and their components detected by ToF mass spectrometry following electron impact ionization. The AMS was operated in V mode with 10 s time resolution, and data were analyzed with IGOR Pro (WaveMetrics Inc.) using the SQUIRREL v 1.56 and PIKA v 1.15 modules.

The **WIBS** (Figure 5, Droplet Measurement Technologies Inc.) provides sensitive real-time bioaerosol measurements. Particles are detected by forward scattering of 635 nm light and excited sequentially by two Xe lasers (280 & 370 nm). Their fluorescence is then detected at two channels: 310-400 nm, sensitive to tryptophan, and 420-650 nm, sensitive to NADH. The WIBS was operated at 1 LPM sample flow (2.3 LPM total) with 1 s time resolution.

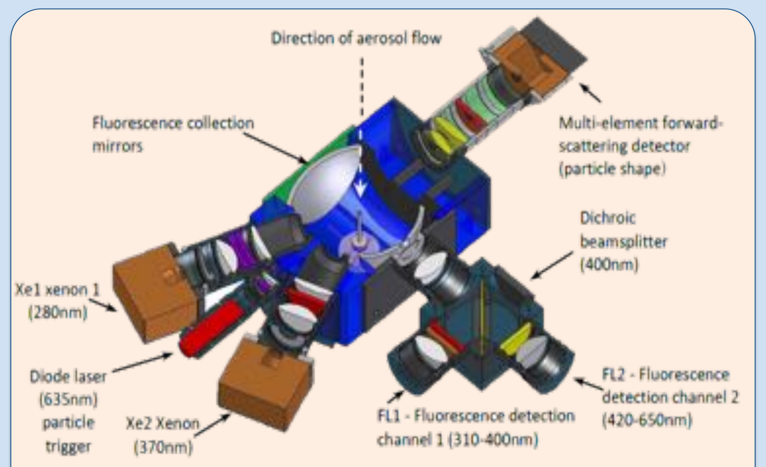

Figure 5: Schematic of the WIBS

Additional instruments included: • Forward scattering spectrometer probe (FSSP, 2-40 µm) • Counterflow virtual impactor inlet (CVI) • Cloud condensation nuclei counter (CCN) • Cloudwater collector • Passive cavity aerosol spectrometer probe (PCASP, 0.1-2 µm) • Differential mobility analyzer (DMA) • Condensation particle counter (CPC, >10 nm) • Ultrafine CPC (UFCPC, >3 nm) • SpinCon II Advanced Air Sampler (SpinCon, Innovaprep) • Liquid water content probe (LWC) • Gas analyzers (O_3, NO_x, CO, CO_2) • Meteorological probes

General Results

- Marine aerosol was **heavily oxygenated** compared to other oceanic field studies,[2,4-6] and showed additional signatures that have previously been observed from plankton blooms (Figure 13), including high fractions of CHO_1, $CHO_{>1}$, organosulfates (CS), and unsaturated organics (C_nH_{2n-1}, C_nH_{2n-3}).[6,7]

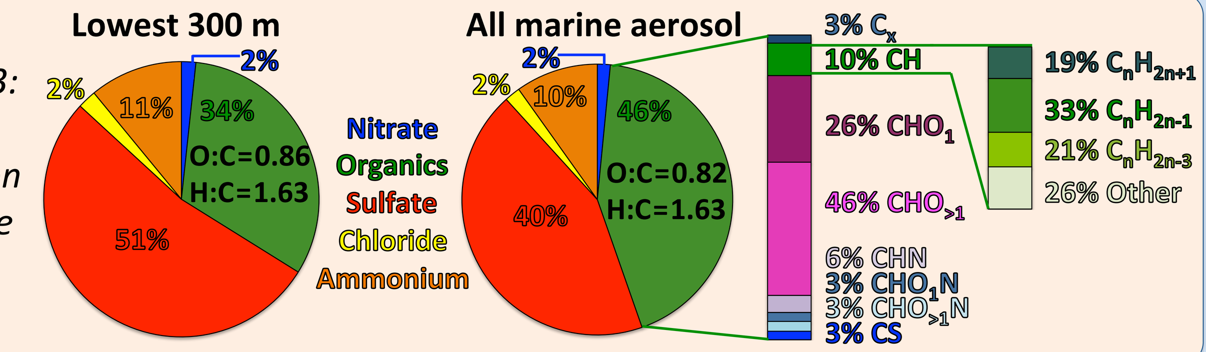

Figure 13: AMS speciation of marine aerosol

- Marine aerosol showed a strong and **persistent $CH_3SO_2^+$ signal** on the AMS, corresponding to methanesulfonic acid (MSA),[8] an oxidation product of dimethyl sulfide (DMS), which is produced and emitted by phytoplankton.[9]
- **$CH_3SO_2^+$ was the most highly correlated organic AMS species with CCN and PCASP concentrations** in the marine environment (Figure 14); accumulation mode particles also correlated strongly with SO_x and NH_x, which, along with MSA, contribute to maritime particle formation and growth (Figure 15).[10-15] In contrast, UFCPC counts correlated most strongly with large hydrocarbons from ship emissions, and CPC counts with small oxidized organics.

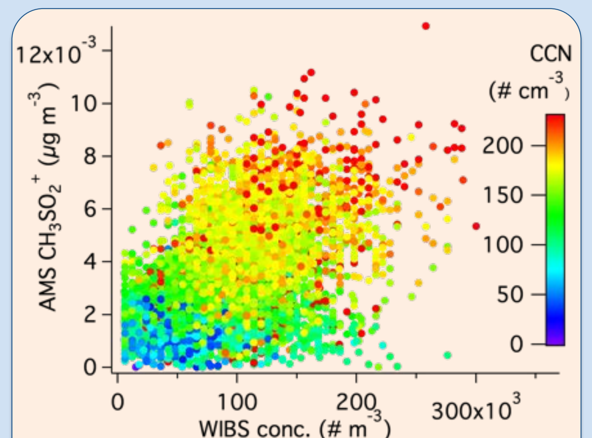

Figure 14: $CH_3SO_2^+$, WIBS, and CCN concentrations in marine aerosol

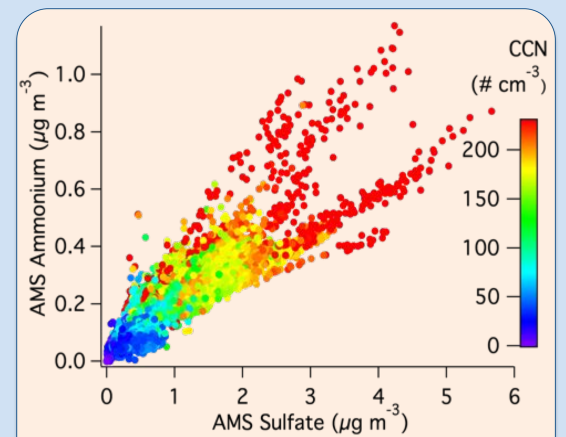

Figure 15: SO_x, NH_x, and CCN concentrations in marine aerosol

- **$CH_3SO_2^+$ was the single AMS species most highly correlated with WIBS counts** over the ocean (Figure 14); bioaerosol loading also correlated positively with AMS families presumed to derive from biogenic sources, including CS, CHO, SO_x, NH_x, and C_nH_{2n-3}.
- The **highest bioaerosol loadings** (WIBS) in the campaign were measured over forests and farmlands; these regions also experienced high AMS organics, especially large masses from the CH, CHO, and CHN families.

Case Studies: Marine Aerosol Characterization

Flight 5: Spatial Characteristics of the Bioplume

Flight plan: "racetrack" patterns to sample altitude gradients at three near-coast sites (see Figures 6 & 7)

Conditions: calm, with morning clouds before the flight

Observations:

- **Distinct layers** (Figure 8): moderate loadings at surface, where WIBS correlated strongly with AMS sulfates, oxidized organics, and unsaturated hydrocarbons; clean air in upper boundary layer; high loadings above inversion, with signs of cloud processing (increased O/C ratio) and weaker correlation between WIBS and AMS traces.
- **Strong latitudinal gradients:** modeled oceanic *pseudo-nitzschia* concentrations were highest in the north, moderate in the south, and lowest in the middle racetrack (Figure 6); this was reflected within the surface layer, where WIBS counts, PCASP and CCN concentrations, and many AMS families (CS, CHO, SO_x, NH_x, C_nH_{2n-3}) showed **latitudinal patterns identical to those of *pseudo-nitzschia*** (despite little variation in wind speed; Figure 8). In contrast, the higher altitudes showed no latitudinal gradient.

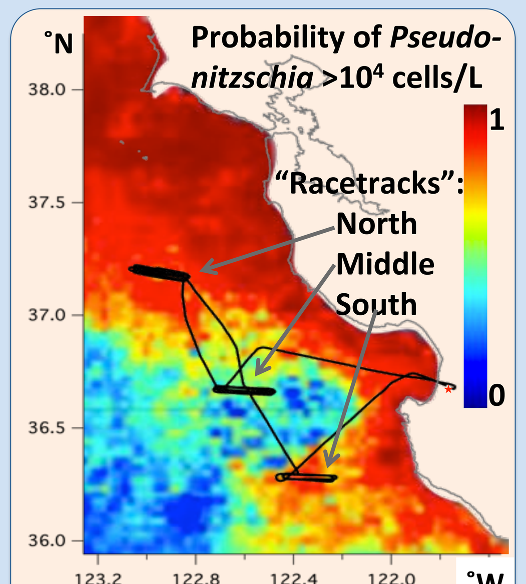

Figure 6: July 7 flight path and pseudo-nitzschia conditions

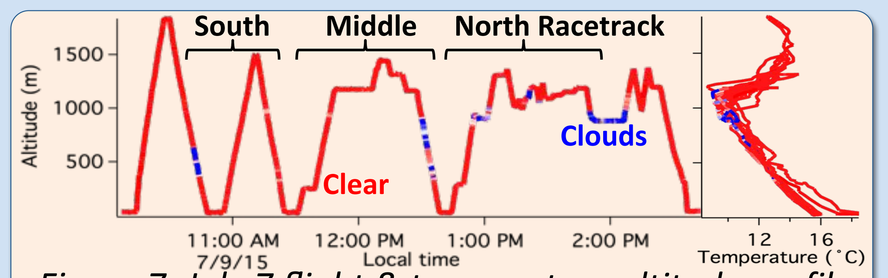

Figure 7: July 7 flight & temperature altitude profiles

Flight 13: Longitudinal Gradients & Diurnal Variability

Flight plan: two long legs to SW –in the morning and afternoon – to examine coastal gradients and diurnal variations (Figures 9 & 10)

Conditions: windy, with persistent clouds at 600 m (Figure 10)

Observations:

- **Little diurnal variation** was seen on the WIBS, AMS, or particle counters (Figure 11).
- **Longitudinal gradients** (Figure 12): surface layer showed slightly decreasing biogenic signature (AMS $CH_3SO_2^+$ and families of CS, CHO, C_nH_{2n-3}, SO_x, and NH_x, along with WIBS, PCASP, and CCN) with increasing distance from coast in both flights, as previously observed off the Chilean coast;[16] the gradients **mirrored modeled oceanic *pseudo-nitzschia* concentrations** (Figure 9).
- **Altitude gradients** (Figure 11): surface layer showed high biogenic signature, which dropped off sharply within and above clouds.
- Increased $CHO_{>1}$ species as a proportion of AMS organics in and above clouds showed evidence of **cloud processing** (Figure 11).[17]

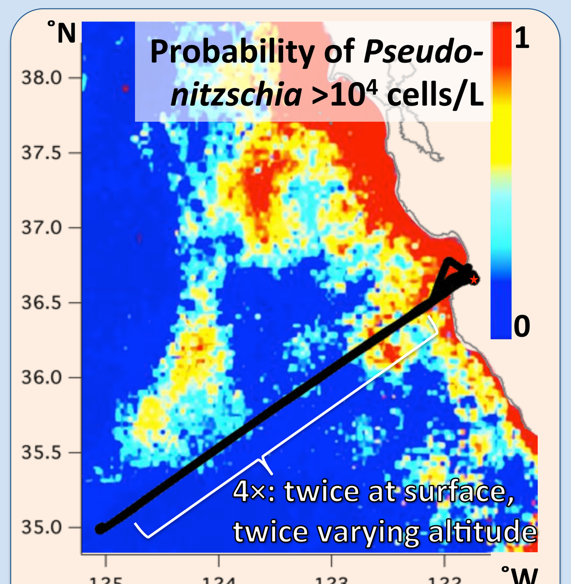

Figure 9: July 23 flight path and pseudo-nitzschia conditions

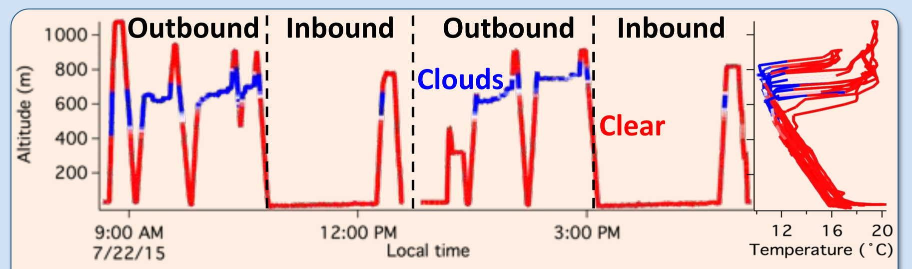

Figure 10: July 23 flight & temperature altitude profiles

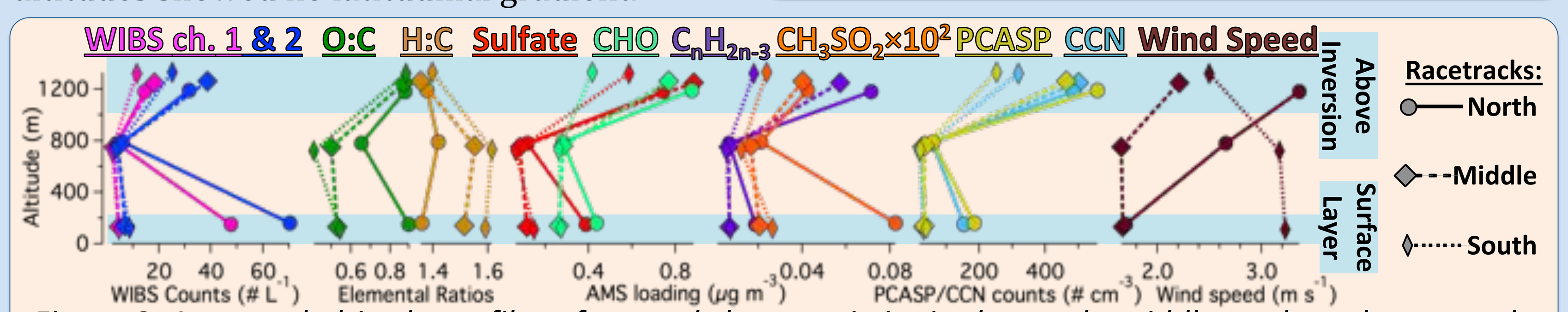

Figure 8: Averaged altitude profiles of aerosol characteristics in the north, middle, and south racetracks

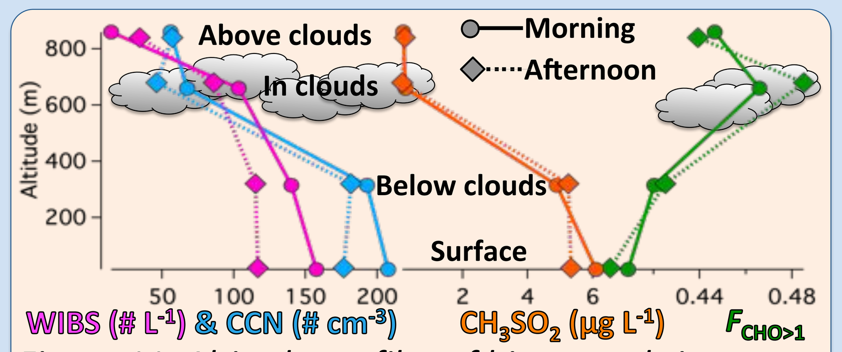

Figure 11: Altitude profiles of bioaerosol signatures

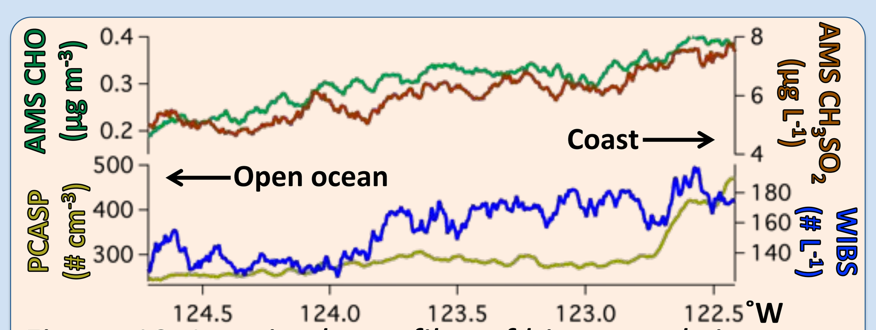

Figure 12: Longitude profiles of bioaerosol signatures

Ongoing Analysis

- Additional characterization of AMS organosulfate species and correlations between presumed biogenic tracers
- Comparison to previous field campaigns at the same location (E-PEACE in 2011, NiCE in 2013) with more typical oceanic conditions
- Flow cytometry and other bioaerosol analysis from samples collected with SpinCon, along with analysis of size-resolved WIBS data

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