1 Sampling Inlet

A high-resolution aerosol mass spectrometer, nephelometers, absorption and soot photometers, and CO/CO_2 analyzer were all situated behind a Solid Diffuser Inlet (SDI), with the nephelometers located closest to the inlet and the Aerosol Mass Spectrometer (AMS) and Single Particle Soot Photometer (SP2) located approximately 8m behind the inlet. The SDI brings ambient aerosol into the aircraft and can efficiently transmit aerosol particles smaller than 4μm in dry diameter (McNaughton et al., 2007). The SDI and ground-sampled submicron scattering data agreed to within 16% during the DC-8 Inlet Characterization Experiment (McNaughton et al., 2007). This establishes the particle loss to the inlet structure, instrument and tubing layout during the ORACLES campaign. Additionally, the sample flow through the inlet was measured and adjusted to ensure the air velocity equaled the flight speed to within 5%. This isokinetic sampling minimizes size-dependent sampling biases (Huebert et al., 1990). Although the inlet was maintained at isokinetic flow, the instruments required a constant flow. An online particle loss calculator (Aerocalc, created by Paul Baron, http://www.tsi.com/uploadedFiles/Product_Information/Literature/Software/ Aerocalc2001.xls) selected tubing material, length, and diameter to minimize particle loss between the SDI and aircraft instruments. The inlet was anodized aluminum, with the flow split into tubes of stainless steel. All lines to the mass spectrometer relied on ½" stainless steel (outer diameter) and ¼" (outer diameter) copper tubing, to reduce the possible presence of extraneous organic compounds. The conductive tubing also minimizes electrophoretic losses. Tubing to the scattering, sizing and counting instruments consisted of graphite-impregnated silicone tubing, with condensation of any released organic compounds upon particles within the air stream unlikely to affect the particle size over the short distance. Due to differences in flow rates and paths, additional losses may affect some instruments more than others. Figures S1-S2 show the plumbing diagram of the aerosol instruments for each year. Calculated losses were negligible, if inherently optimistic and unable to account for all features of the hardware and instruments.

2 Wall losses

The $\sim$8 m distance from the SDI increases the potential for particle wall losses for the AMS. The mass scattering efficiency from wall losses is accounted for through the ratio of the submicron scattering at 500 nm wavelength from two TSI nephelometers (model 3563) to the total of the AMS and SP2-derived aerosol and black carbon mass concentrations. The submicron aerosol is assumed to scatter 5 M m^{-1} at a wavelength of 500 nm per μg m^{-3} of aerosol (Reid et al., 1998; Haywood et al., 2003). The nephelometers were close to the aerosol inlet, where particle loss can be neglected. The nephelometer closest to the aerosol inlet measured total scattering, while a second nephelometer in series with the first measured both total and submicron scattering. The second nephelometer measured a ratio of total to submicron scattering of 1.02 in the free troposphere, indicating little contribution from coarse aerosol. The submicron mass scattering efficiency by the nephelometer closest to the aerosol inlet was estimated using this ratio at three different locations/altitudes per flight. The average mass scattering efficiency of 5.92 is close to the expected value of 5, and constrains wall losses to within 20% for the entire campaign.

3 Aerosol Mass Spectrometer

The AMS sampled the chemical composition of non-refractory aerosols with vacuum aerodynamic diameters between approximately 70 nm to 700 nm at a rate of 1.38 cm^3 s^{-1}. An aerodynamic lens selects and focuses particles at a constant 600 hPa pressure onto a 650°C heated surface. The non-refractory particles are then evaporated off the heated surface and ionized through electron impaction at 70 eV; the ions are carried forward and analyzed further, with some particles, such as soot, some organics, dust, and some salts remaining unvaporized (and unanalyzed). A 'V-mode' operation provided a higher time resolution for the same signal-to-noise, with only a modest loss in the mass resolution (see DeCarlo et al., 2006, for more description). The AMS chopper alternately open and closed every two seconds, to allow aerosol into the AMS and to then analyze it, with an additional second separating each duty cycle.

The bulk mass (not size-resolved) chemical species measurements are primarily processed using the SeQUential Igor data RetRiEval (SQUIRREL, v.1.57l Allan et al., 2003, 2004) data analysis package, with the Peak Integration by Key Analysis (PIKA) program (v.1.16; DeCarlo et al., 2006) resolving the O:C, H:C and OA:OC ratios. Further considerations for the

ORACLES AMS-derived aerosol mass concentration data accuracies include the instrument detection threshold, calibrations, and discrimination for organic versus inorganic nitrate. These are considered in that order. Many of the data quality assurance procedures follow those within Shank et al. (2012).

The aircraft-based background values are determined from the noise levels measured at 15,000 ft during a 10-minute time period on the 4 September, 2016 flight. This established detection limits of 0.15 μg m^{-3} for organics, 0.04 μg m^{-3} for nitrate, 0.03μg m^{-3} for sulfate, and 0.01μg m^{-3} for ammonium. Detection limits typically improve during a flight as the background material becomes effused. The AMS was heated pre-flight during the 2016 campaign to eliminate material built up in between flights. During the 2017 campaign, an initial high-altitude remote sensing leg provided time to drive off extraneous material before beginning the in-situ sampling.

The AMS was calibrated twice during the 2016 campaign (at the beginning and end), and after every 2-3 flights during the 2017 campaign for a total 8 calibrations, using ammonium nitrate particles. An ammonium nitrate solution is sent through an atomizer to produce desiccated submicron aerosol that is then sent to the AMS. A long differential mobility analyzer (LDMA) (TSI 3934) selects for 300 nm diameter particles, and a condensation nuclei counter (TSI3010) measures the aerosol number concentration. The ammonium nitrate aerosol is diluted by a factor of four in the atomizer to create a calibration curve. The ionization efficiency (IE) of nitrate is thereafter calculated from the aerosol mass and number concentrations. The ionization efficiency estimates the number of ions from a known amount of mass entering the AMS using the ion signals at *m/z* peak 30 (NO^+) and 46 (NO_2^+). The nitrate IE values centered on 1.31e-7, with a nominal 10% uncertainty assigned to it following Bahreini et al. (2009), slightly higher than the 1e-7 value within Alfarra et al. (2004). The ionization efficiencies for ammonium, sulfate and organics relative to those for nitrate are thereafter determined within SQUIRREL as: 4 for NH$_4$; 1.1 for measured nitrate relative to the calibration value; 1.2 for SO$_4$; and 1.4 for organics.

A time- and composition-dependent collection efficiency (CE) corrects for the incomplete vaporization of mixed phase particles (Middlebrook et al., 2012), as liquid aerosol is less likely to bounce off the heater and more likely to escape detection than is neutralized aerosol (Huffman et al., 2005; Drewnick et al., 2005). Liquid aerosol is primarily acidic, and the acidity of the free-tropospheric aerosol is assessed by comparing the molar ratio of NH$_4$ to NO$_3$+2SO$_4$ (Fig. S3). This is a simplification of the $NH_{4,measured}/NH_{4,predicted}$ relationship put forth in (Zhang et al., 2007), with the contribution of chloride neglected because it is small. $NH_{4,predicted}$ is the amount of ammonium required to neutralize the inorganic anions observed by the AMS. The applied collection efficiency, $CE = max(0.5, 1 - NH_4/(2SO_4))$, also neglects the small nitrate contribution, and establishes 0.5 as the lower limit, consistent with most field campaigns (Middlebrook et al., 2012). The ratio of the measured ammonium to the molar sum of nitrate and 2*sulphate is mostly below 1, but rarely below 0.75 (Fig. S3), typically establishing a CE of 0.5. The mildly acidic aerosol suggests mild suppression of inorganic acid formation. Wu et al. (2020) report nitrate aerosol that is fully neutralized based on independent AMS measurements from August-September 2017 further west of the ORACLES sampling, above Ascension Island (8°S, 14.5°W). This indicates further loss of the organic nitrate may be occurring between the ORACLES and Ascension locations. The CE values for the other species are set to 0.5; Middlebrook et al. (2012) do not find any dependence of the CE on the mass fraction of organics.

The overall uncertainty to the reported aerosol mass concentrations is likely dominated by the uncertainty in CE, with additional uncertainty in the organic RIE.

Author contributions. The present work was conceived by P.Z., A.D., S.H. and P.S.. S.F. contributed to the HiGEAR data analysis, A.S. provided the BC datasets and P.S. the WRF-AAM model age estimates. Portions of this work first appeared in the M.S. thesis of A.D at U. of Hawaii. All authors contributed to the final writing.

Competing interests. The authors declare no competing interests.

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Table S1. Level legs used for Figures 14-16

Flight	Latitude °N	Longitude °E	Time (UTC)	Altitude (m)
08312016-RF02	-13.8 :-13.13	3.7:3.9	11:14-11:27	3830
09062016-RF05	-12.9:-12.2	9.2:9.5	11:40-11:50	2670
09062016-RF05	-15.9:-15.17	10.3:10.5	12:18-12:28	2250
09242016-RF12	-12.1:-11.0	11.0	12:08-12:21	4830
08312017-RF12	-8.6:-7.5	-1.27:-0.88	11:43-11:57	3100
08312017-RF12	-7.5:-6.7	-1.58:-1.3	11:31-11:42	3035
08312017-RF12	-6.4:-5.6	-1.99:-1.65	11:15-11:30	2935
08312017-RF12	-5.29:-4.12	-1.64:- 2.01	10:52-11:11	2870
08312017-RF12	-8:-5.12	-1.09:-2.15	12:12-12:50	2970
08312017-RF12	-2.5:-0.5	-0.44:0.8	14:10-14:34	2880
08312017-RF12	-1.9:-1.23	-0.105:-0.404	1:55-14:05	2720
08312017-RF12	-2.4:-1.35	-0.70:-0.15	13:32-13:48	2570
08312017-RF12	-3.8:-1.27	-0.12:-1.49	10:12-10:49	2790
09252016-RF13	-9.8:-8.9	-0.344:-1.0	12:16-12:32	4500
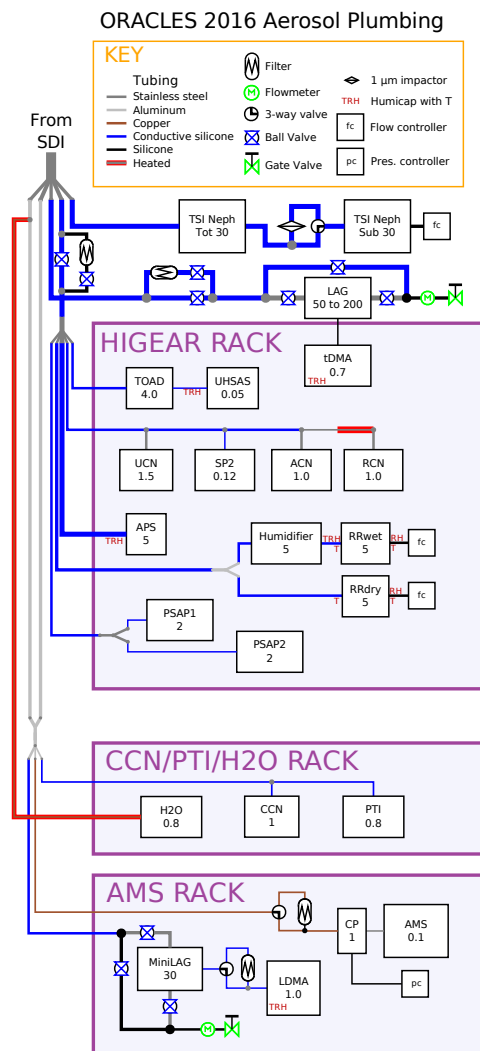
Figure S1. Layout of aerosol instrumentation relative to the inlet for the 2016 campaign. The numbers below the instrument acronyms represent flow rates in lpm. Note the lag and mini-lag include a small leak included to equalize the pressure between the two. The line widths are proportional to the nominal diameter of the tubing (outer for metal, inner for silicone). Exceptions are the AMS, SP2, and UHSAS, which have very low flow rates and such tiny inlet tubes that they wouldn't be visible.
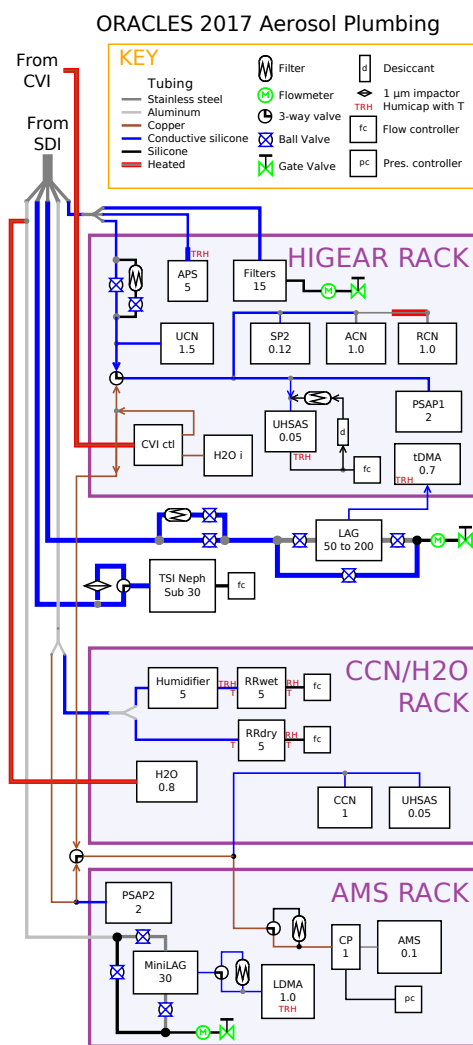
Figure S2. Layout of aerosol instrumentation relative to the inlet for the August 31, 2017 flight. Most flow is down and to the right, the addition of a counter-flow virtual impactor inlet (CVI) modified some flow direction to be up and to the left; flow direction arrows are included in critical spots to aid understanding. Other comments on the diagram Fig. S1 for 2016 also apply here.
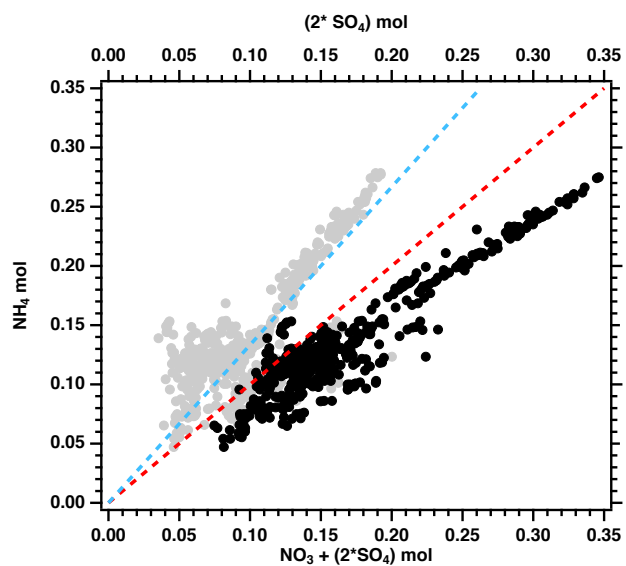
Figure S3. Measured ammonium in moles as a function of the molar sum of nitrate and 2*sulphate for one-minute measurements from all 6 flights (one-minute averages), constrained to the free troposphere. Dashed-red and dashed-blue lines indicate the 1:1 and 1:0.75 ratios respectively.