VOC Observations over the Southern Ocean during ORCAS

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Overview
The NCAR/NSF G-V O2/N2 Ratio and CO2 Airborne Southern Ocean Study (ORCAS) took place in Jan-Feb 2016 and was based in Punta Arenas, Chile. The primary goal of the study was to investigate the air-sea exchange of O2 and CO2 over the Southern Ocean where the uptake of anthropogenic carbon is a key process that is poorly represented by models.

In addition to many long-lived gases, measurements of reactive volatile organic compounds (VOCs) were measured using the Trace Organic Gas Analyzer (TOGA) and advanced whole air canisters (AWAS), and are used to better understand and constrain air-sea exchange in the southern ocean region.

TOGA
The NCAR Trace Organic Gas Analyzer is a fast online gas chromatography/ mass spectrometer (GC/MS) that makes simultaneous measurements of 50+ VOCs every 2 minutes.

ORCAS Flights
Figure 1. ORCAS flights during January and February 2016, overlaid on the monthly average chlorophyll concentrations from AQUA/MODIS. (AQUA/MODIS imagery produced by the Earth Observatory Group in coordination with Gene Feldman and Norman Kuring, NASA Goddard Ocean Color Group.)

O2, CO2, CO
Figure 2. Observed O2, CO2 and CO from the ORCAS project, binned by altitude. Shown on each plot as box and whiskers are the median, 10th, 25th, 75th and 90th percentiles of these data from a TOGA time base merge, with the number of data points in each bin shown on the plots.

Transport of VOCs from NH to SH
Figure 3. From several Jan-Feb studies over the Pacific/Southern Ocean (TORERO 2012; CONTRAST 2014, ORCAS 2016), composites of VOCs from -75°S to 40°N show significant interhemispheric differences, and indicate transport pathways from the NH and tropics to the SH. Longer-lived CHCl3 is transported from the NH to the SH via the UTLS, while CH3COCH3 and CH3OH are transported to high southern latitudes via the mid-troposphere from the tropics.

VOC correlations with O2
Figure 4. VOCs observed over oceans binned by altitude and O2 (high O2>540 per meg>mid O2=560 per meg>low O2<540 per meg) Several ocean-emitted halogenated VOCs were correlated with O2 in the marine boundary layer (MBL) and mid-troposphere, consistent with air more recently in the MBL. Several OVOCs and nitriles were anti-correlated with O2 in the MBL, but was slightly correlated with O2 in the mid-troposphere, consistent with more polluted air having less ocean influence, while less-soluble anthropogenic species (e.g., benzene, CH3CO2) were not correlated with O2 in the lower troposphere.

VOC correlations with CO2 and CO
Figure 5. Observed VOCs binned by altitude and CO2 and CO (high CO2>399 ppm>low CO2 high CO>43 ppb>low CO). CHBr and CHBr were anti-correlated with CO in the MBL and mid-troposphere, while CH3I was correlated with CO in the MBL. This is due to elevated CH3I west of Chile, where CO2 is elevated (see Fig. 6). Several OVOCs and nitriles were correlated with CO and CO in the MBL and mid-troposphere (e.g., acetone, CH3CN), suggesting losses to the ocean surface. Less soluble anthropogenic species (e.g., CH2Cl, benzene) and DMS have no clear correlation with CO2 in the lower troposphere, although benzene is correlated with CO even at very low benzene mixing ratios, consistent with elevated SH CO.

Summary
The air over the Southern Ocean is extremely clean, with very low mixing ratios of anthropogenic VOCs, and indications of losses of soluble OVOCs and nitriles to the ocean surface. CHBr and CHBr are correlated with O2 emissions from the Southern Ocean, suggesting a common source with similar enhanced atmospheric lifetimes. DMS is not correlated with O2, however, and emissions of DMS decreased significantly between January and February.