Supplementary Information

Latitudinal distribution of reactive iodine in the Eastern Pacific and its link to open ocean sources

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IO mixing ratios for selected clear days were retrieved from the Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) Differential Slant Column Densities (DSCDs) in two steps. First, O_4 DSCDs were forward modeled using the NIMO fully spherical Monte Carlo radiative transfer model (Hay et al., 2012) by prescribing aerosol profiles with varying aerosol optical depths and shapes. The surface albedo was set to 0.07 and the Henyey-Greenstein parameterization for aerosol scattering was used with an asymmetry parameter of 0.75, appropriate for sea salt aerosols, and a single scattering albedo of 0.97. Since the vertical distribution of O_4 in the atmosphere is known and decreases in proportion to the square of pressure, O_4 DSCDs are a good proxy for the average effective path lengths of observed photons in the boundary layer for the different viewing geometries (Wagner, 2004). Second, the aerosol profile that resulted in the best fit of the modeled O_4 DSCDs to the measurements was prescribed in the forward model calculation of weighting functions that characterize the sensitivity of the DSCDs to changes in the trace gas concentration in a given altitude layer. A linear maximum *a posteriori* (MAP) inversion (Rodgers, 2000) of the IO DSCDs was performed using the weighting functions to obtain vertical profile information. The MAP inversion is essentially a least squares fit of the model to the measurements using the weighting functions weighted by the measurement and *a priori* errors. An *a priori* profile is required as a constraint as the measurements alone do not contain sufficient information to arrive at a single solution. A linearly decreasing *a priori* profile was used, based on previous measurements and chemical modeling, with a layer grid height of 50 meters from the surface to four kilometers. The *a priori* error for each layer was set to 80% of the peak *a priori* value in order to minimize the RMS of the model fit to the measurements while still providing some constraint on the profile shape. In most cases, an aerosol profile could be found which resulted in an approximate fit of the modeled O_4 DSCDs to the measurements. However, if multiple scattering in clouds is not accounted for, in some cases an aerosol profile may be found which leads to a good fit, yet gives a poor representation of the true light paths. This results in systematic errors in the weighting function profile, thus biasing the retrieved IO mixing ratios.

Therefore, for comparison, MBL mixing ratios were also obtained by using the O_4 DSCDs for the 1° elevation angle to derive the effective path lengths. A similar technique has been used by other groups (Sinreich et al., 2010). The O_4 DSCDs were divided by the mean extinction coefficient of O_4 from the surface to 200 m a.s.l. to obtain the path length. This layer height was based on the average last scatter altitude calculated with the RT model using the aerosol profiles selected by forward modeling. A wavelength correction, calculated with RT model, was applied to the path length since the O_4 spectral analysis was performed on an absorption band at 360 nm whereas the IO analysis was centered on 427 nm. IO mixing ratios were then obtained by dividing the IO DSCDs by these corrected path lengths. This method is less sensitive than the inversion to the effect of clouds since the last scattering altitude for the 1° elevation angle is below the cloud base altitude (the spectra were filtered to remove much of the cloudy data) and most of the O_4 absorption can be assumed to occur on the extended path through this low layer. However, this technique relies on the assumption that the IO profile in the boundary layer is similar to the O_4 profile.

The IO mixing ratios calculated with this method were in agreement within the errors of the values calculated by the MAP optimal estimation technique. The errors were derived from the DOAS fitting errors in the O_4 and IO DSCDs, combined with small errors in the mean O_4 concentration and the air density due to the uncertainty of the layer height. Further errors are likely to be introduced by the assumption that the IO layer has a constant mixing ratio up to the last scatter altitude and that the entire differential O_4 absorption, relative to the zenith sky viewing direction, occurs in the line of sight direction.

References:

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Figures:

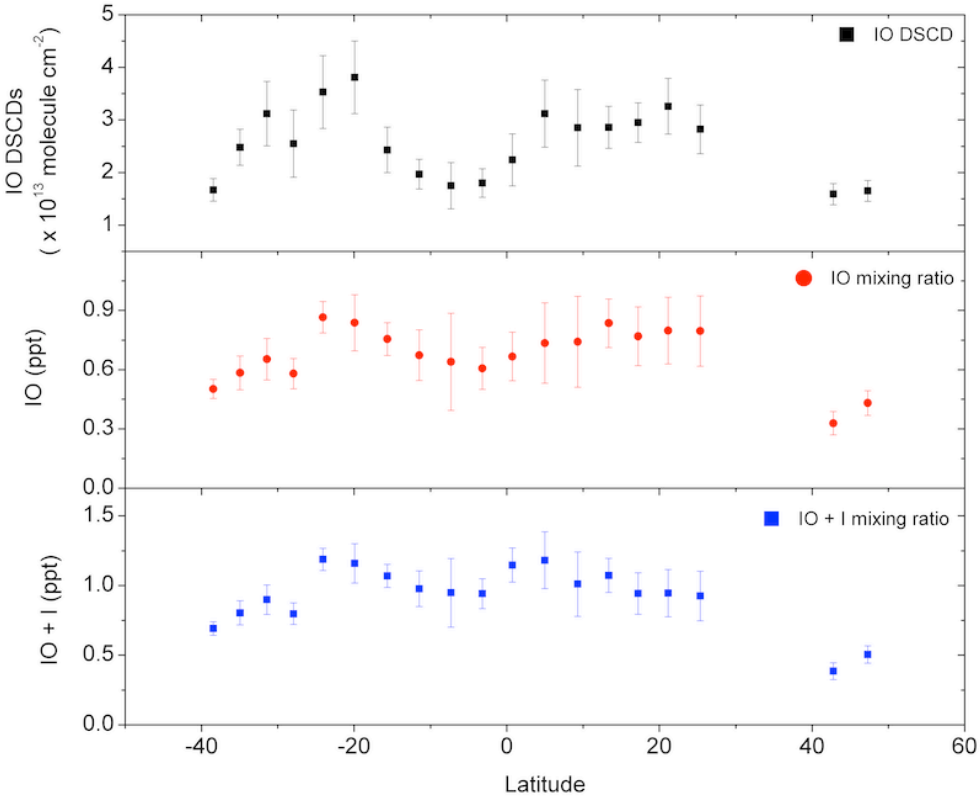

Figure S1: The latitudinal distribution of IO DSCDs (top panel), the calculated IO mixing ratios using the method described above (middle panel) and the total IO_x (= I + IO) mixing ratio estimated using the THAMO model (bottom panel).