Earth and Space Science

Supporting Information for

An Examination of the Recent Stability of Ozonesonde Global Network Data

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S.1 Potential Indicators of the Source of the Dropoff

A potential contributor to the TCO drop at EnSci stations is the ozonesonde sensing solution type (SST) used at each station. Three SSTs are currently in use in the global network: 1% KI, full buffer (SST1.0); 0.5% KI, half buffer (SST0.5); 1.0% KI, one-tenth buffer (SST0.1; "low-buffer"). Tropical/subtropical stations are where the largest and most persistent TCO drops are found. Five of the seven tropical S20 EnSci stations use SST0.1 (Hilo, Costa Rica, San Cristóbal, Fiji, and Samoa) and show a larger post-S/N 25250 dropoff compared to the two SST0.5 stations (Nairobi and Ascension Island; 3.8% for SST0.1 vs. 2.7% for SST0.5; Ascension Island is listed at "N/A" in **Table 2** because it did not launch EnSci ECCs prior to S/N 25250). Given this fact and the results of **Figure 9b**, which indicates that non-S20 stations may also show small TCO drops, it is prudent to examine SST0.1 stations outside of tropical/subtropical latitudes.

Figure S6a presents an analysis of the EnSci S/Ns at three stations in the Contiguous U.S. (CONUS): Trinidad Head, Boulder, and Huntsville, that have used SST0.1 since 2005 (**Sterling et al., 2018**). The three stations show a TCO drop of 1.7% (significant with > 95% confidence) relative to OMI after EnSci S/N 25250, and now average -1.43% TCO relative to OMI. **Figure S6b** shows the Boulder EnSci S/N comparisons with the co-located Dobson TCO, which confirms the OMI results. The Boulder ozonesondes show a sharp 1.8% TCO drop (again, significant with > 95% confidence) relative to the Dobson after S/N 25250. From the results presented above, it appears that all EnSci stations may be subject to some change in ECC performance related to the TCO drop, with the magnitude of effects seemingly dependent on station-specific characteristics such as the SST formula. Although our analysis suggests that the SST0.1 plays a role in the dropoff, these results warrant further investigation and laboratory tests. In general, SST0.5, which is the ASOPOS-recommended SST for the EnSci ECC, is apparently less affected at global network stations.

Although we point out the possible contribution of the low-buffer SST0.1 solution to the TCO drop, the S20 study effectively ruled out other potential sources of the sudden EnSci low bias including the type of radiosonde paired with the ozonesondes and radiosonde pressure offsets (**Steinbrecht et al., 2008; Stauffer et al., 2014; Inai et al., 2015**). No single change to EnSci production was identified. In addition to scrutinizing global network data and metadata, laboratory tests of new and older EnSci ozonesondes are also being performed to verify the consistency of the speed of the ozonesonde pump motors, pump efficiencies at stratospheric pressures, and the effect of varying amounts of pH buffering chemicals used in the ozonesonde SSTs (i.e., there is a 5x difference in the pH buffer amounts in SST0.1 and SST0.5).

S.2 Input from the EnSci Manufacturer

The original EnSci company was purchased in 2011 by Droplet Measurement Technologies (DMT; Longmont, CO, USA), with production beginning at S/N 20052 in February 2011. Prior to this, each model of EnSci ozonesonde (Z, 1Z, 2Z; only the radiosonde interface board varies) had its own independent sequential serial numbering system. The repeated EnSci numbering for the three different models is the reason for the increased number of ECC/OMI TCO comparisons prior to S/N 20052 in **Figure 7**. Beginning with 20052, all Z, 1Z, and 2Z models began counting up from that point with no repeated numbers (see also the gap in S/N in **Figure S6**).

The manufacturer has indicated that there were changes made to the ECC cell ion bridge material/amount of material and ozonesonde pump motor prior to the purchase of EnSci by DMT in 2011. However, the exact timing of these changes is unknown. The ASOPOS 2.0 Task Team is gathering previously flown and recovered EnSci ozonesondes to perform laboratory tests and forensic analyses of the ECCs to narrow down the timing of these manufacturing changes, and to determine if and what effects they could have on the measurements. The company changed hands again in 2016 to its current ownership beginning with EnSci S/N 30265. No other changes, other than the plating of the ECC metal frame occurring at approximately S/N 28000, which altered the color of the frame from gold to silver, have been noted. Based on the abruptness of the TCO drop occurring near EnSci S/N 25250 (**Figure 9**), efforts will be focused on tests with S/Ns in this proximity.

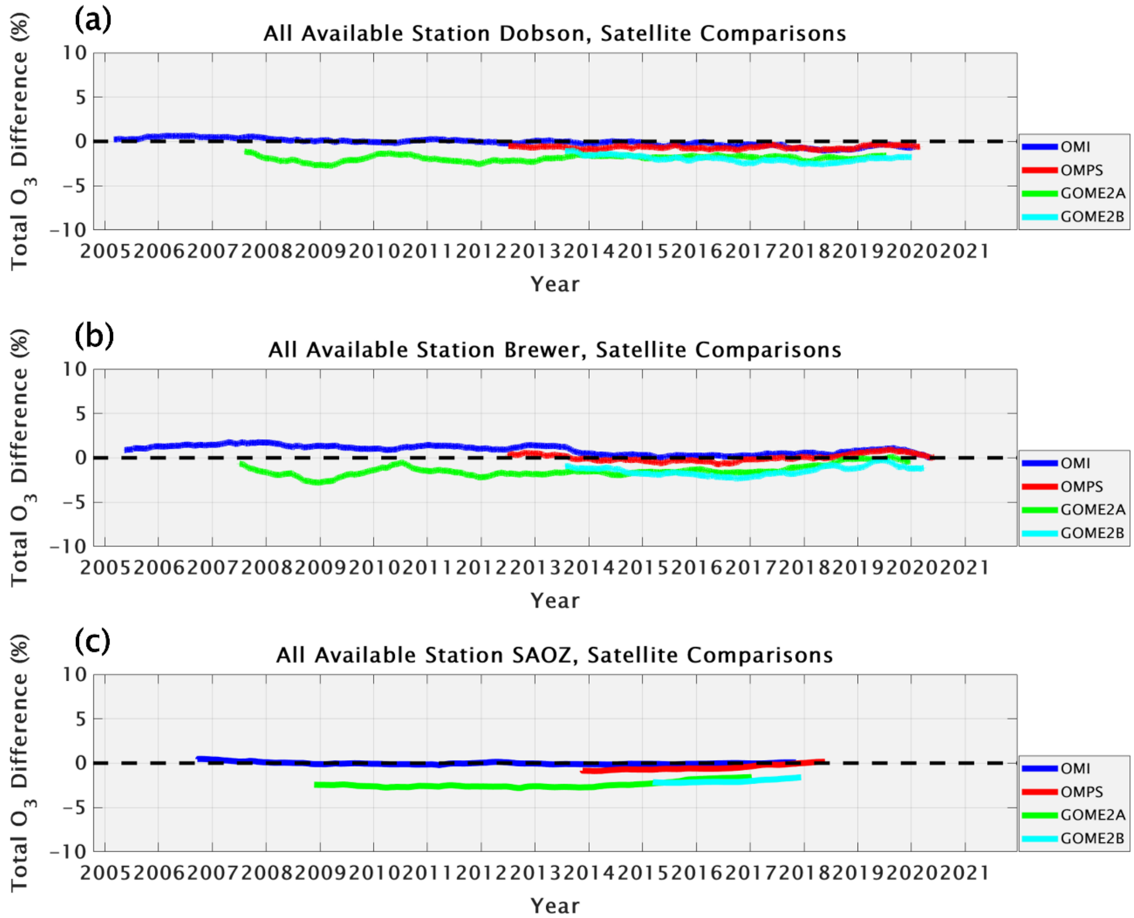

Figure S1. Comparisons in percent difference (ground-based minus satellite) among ground-based and satellite TCO at the 40 stations where ground-based TCO data are available (see Table 1). The solid lines represent 500-point, centered moving averages. The lines are not plotted for the first 250 and last 250 comparisons.

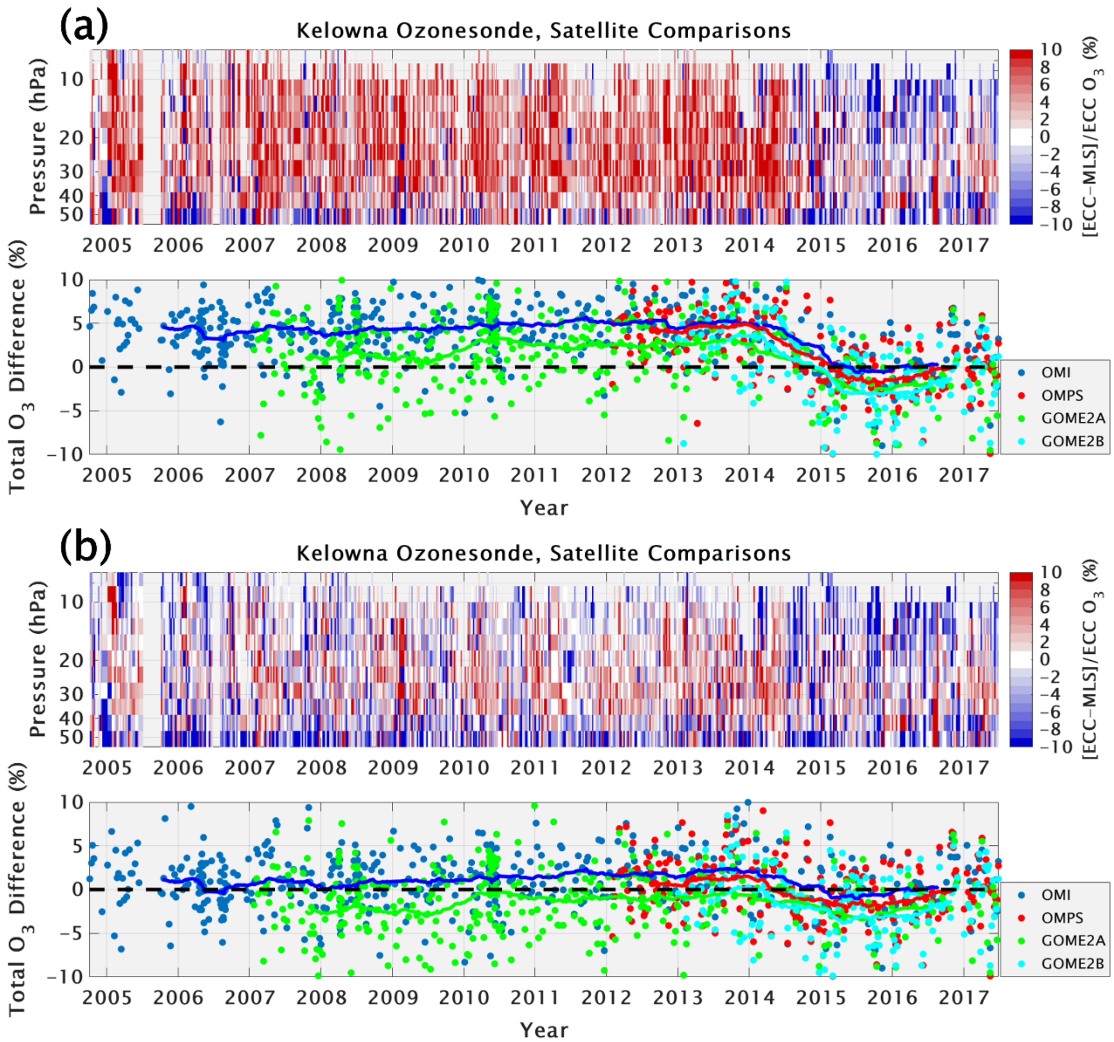

Figure S2. Time series of comparisons at Kelowna among ozonesondes and MLS ozone profiles (top panels), and OMI (blue dots), OMPS (red dots), GOME-2A (green dots), and GOME-2B (cyan dots) TCO (bottom panels). Solid lines corresponding to each TCO satellite instrument on the bottom panels indicate 50-ozonesonde centered, moving averages. No average lines are plotted for the first 25 and last 25 comparisons. Horizontal dashed lines on the bottom panels indicate the 0% line for TCO comparisons. Red or blue colors on the top panels indicate where the ozonesonde ozone is greater or less than MLS. Panel (a) shows the ozonesonde data used in S20, and Panel (b) shows the corrected data used for this study.

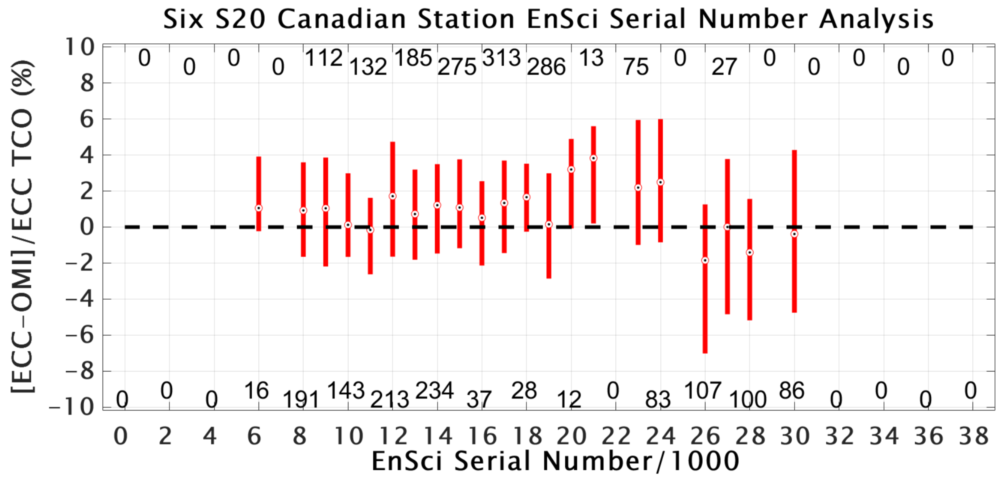

Figure S3. Comparisons of EnSci ozonesonde TCO with OMI from the six Canadian S20 stations in percent difference (using corrected Kelowna and Yarmouth data). EnSci S/Ns are grouped into bins of 1000 (26 = 26000 to 26999) for analysis. The bars show the 25th to 75th percentiles for each bin, with the dots representing the median value. The total number of valid ozonesonde/OMI comparisons for each bin are shown by the numbers along the top and bottom, aligned with the bars.

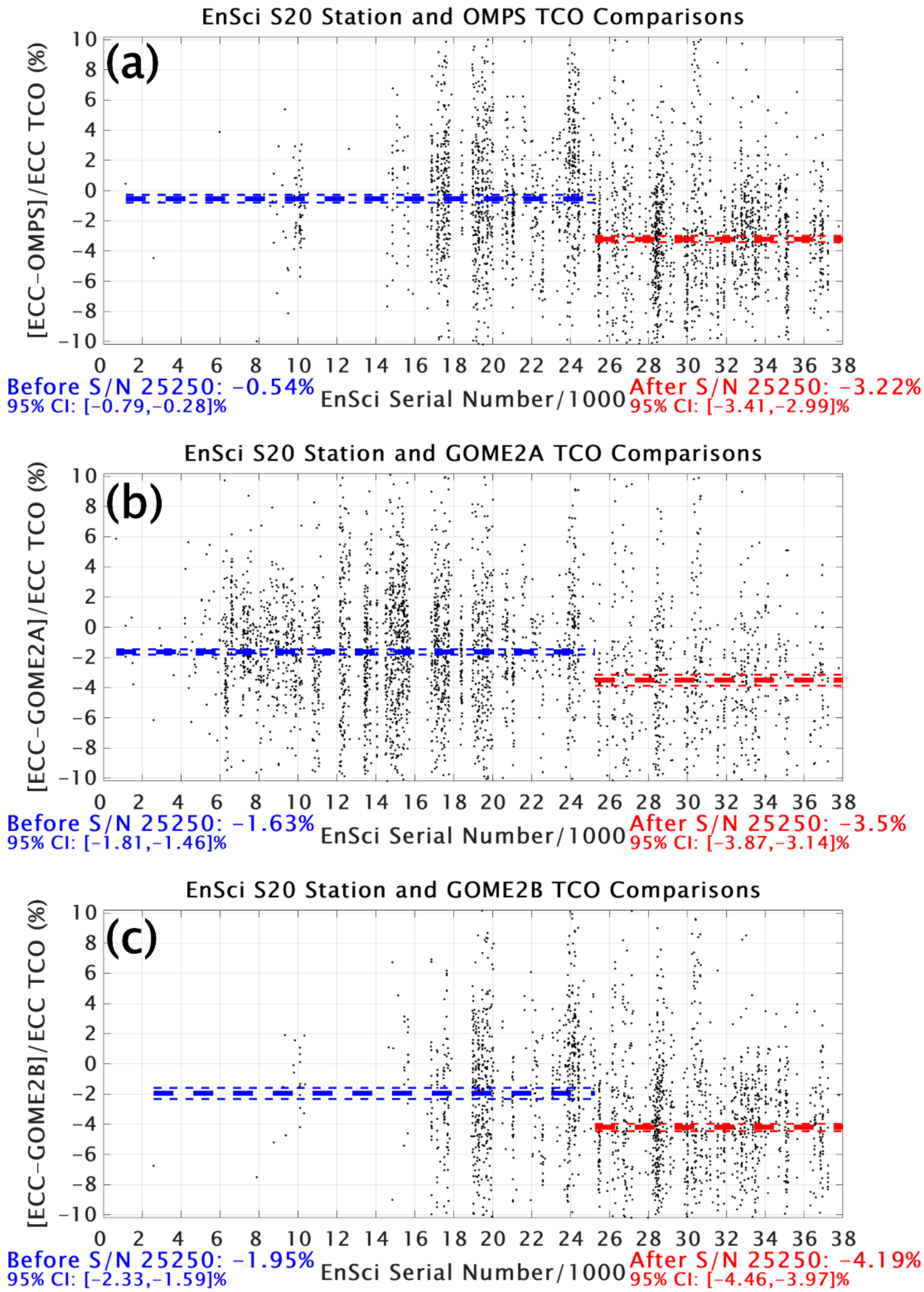

Figure S4. Comparisons in percent difference between ozonesonde and satellite TCO for all 14 S20 station EnSci S/Ns (a: OMPS; b: GOME-2A; c: GOME-2B). The blue dashed lines indicate the mean value for S/Ns prior to 25250, and the red dashed lines indicate the mean value after S/N 25250. The mean values and their 95% confidence intervals are shown in text below both figures and are indicated by the thin dashed lines.

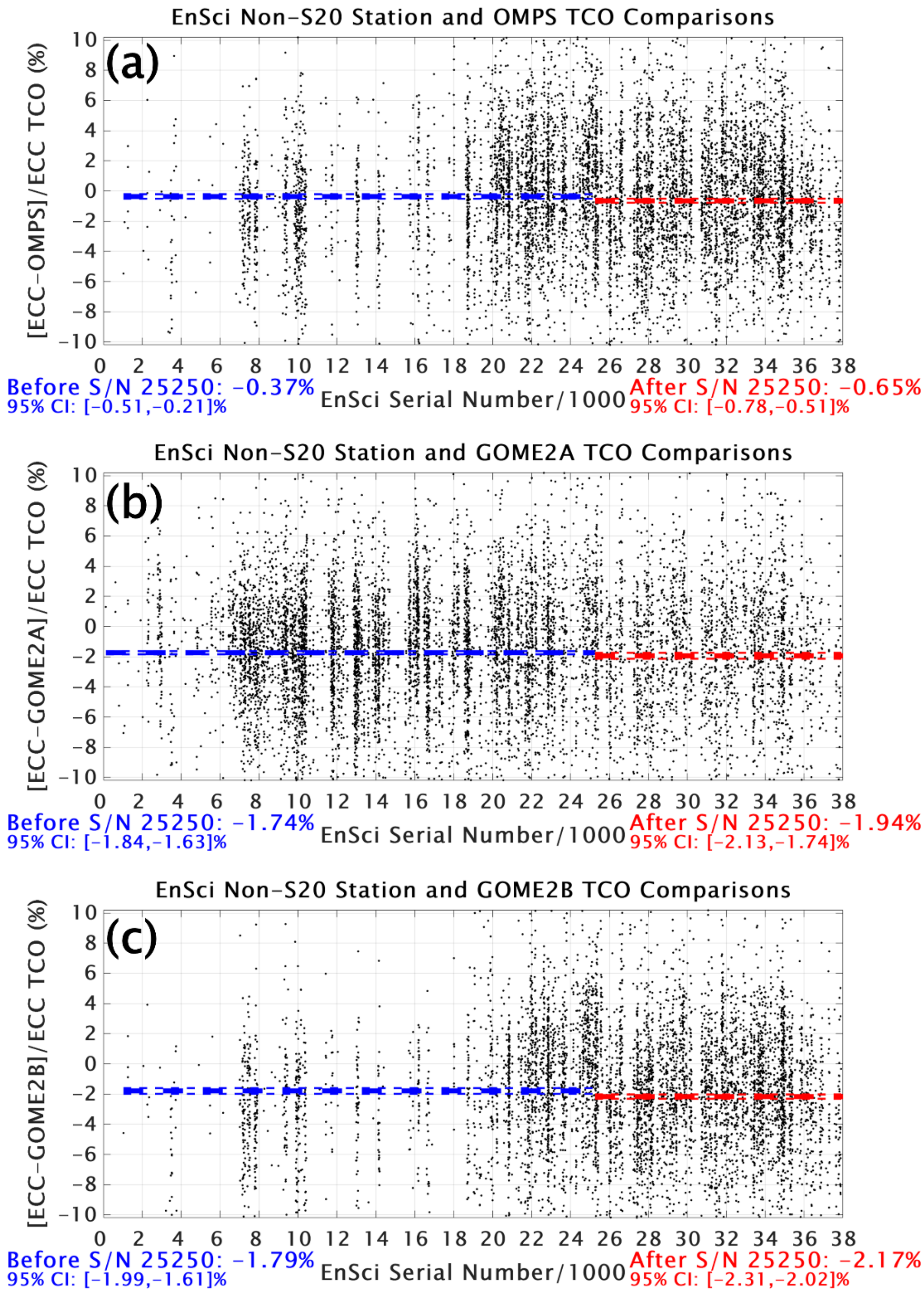

Figure S5. As in Figure S4, but for the 46 non-S20 stations.

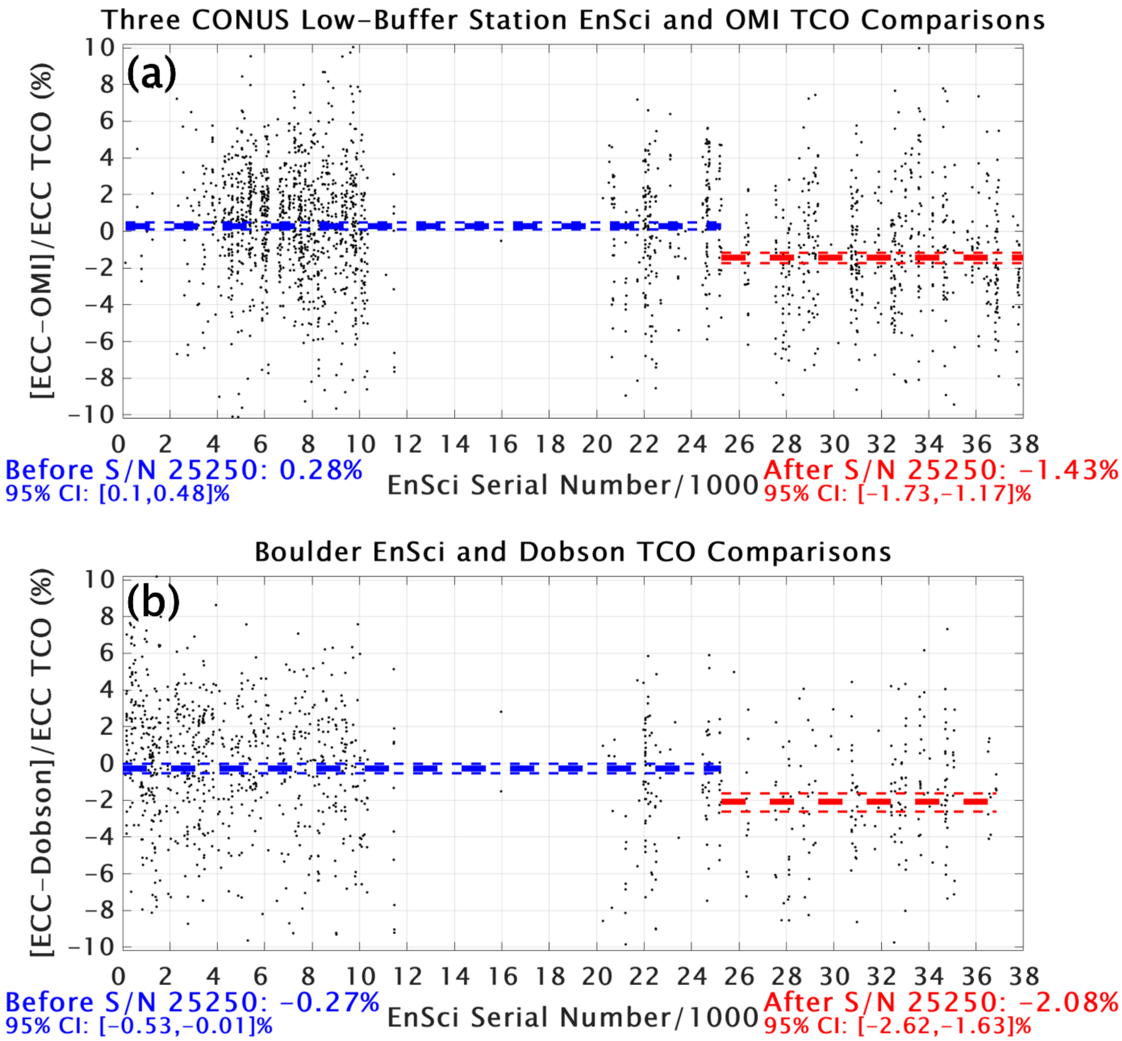

Figure S6. As in Figure 9, but for (a) three Contiguous United States (CONUS) stations (Trinidad Head, Boulder, and Huntsville) that use the low-buffered SST0.1 ozonesonde sensing solution, compared to OMI TCO, and (b) Boulder EnSci S/N comparisons with the co-located Dobson spectrophotometer TCO.