Tropospheric Ozone Assessment Report: Tropospheric Ozone Observations – How Well Do We Know Tropospheric Ozone Changes?

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From the earliest observations of ozone in the 19th century, both measurement methods and the portion of the globe observed by them have evolved and changed significantly. These methods have different uncertainties and biases, and the data records differ with respect to coverage (space and time), information content, and representativeness. These records are reviewed and compared, based on validation and intercomparison experiments, and related to the modern ultraviolet (UV) standard. There are significant uncertainties with the 19th and early 20th century measurements by potassium iodide methods in urban areas that are related to interference of other gases. Sulfur dioxide (SO_2) levels in particular appear to have been quite high in urban areas, and may have negatively biased ozone measurements. There is no firm evidence of very low ozone values in the 19th century, although there is evidence of a modest increase in the 20th century, primarily in the Northern Hemisphere. Spectroscopic methods are not subject to SO_2 interference, but differing values of ozone absorption coefficients used before 1960 may have caused ozone to be underestimated by 11% at the surface and by about 24% in the free troposphere.

The great majority of validation and intercomparison studies of free tropospheric ozone measurement methods are undertaken with electrochemical-concentration (ECC) ozonesondes. ECC sondes have been compared to UV-absorption measurements in a number of intercomparison studies. They show a modest (~1-5%) high bias in the troposphere, with an uncertainty of 5%, but no evidence of a change with time. Other methods – Umkehr, lidar, FTIR, and commercial aircraft – all show modest low biases relative to the ECCs, and so, using ECC sondes as a transfer standard, all appear to agree to within 1σ with the modern UV-absorption standard. Relative to the UV standard, Brewer-Mast sondes show a 20% increase in sensitivity to tropospheric ozone from 1970-1995. In combination with the gradual shift of the global network to ECC sondes, this will, if uncorrected, induce a false positive trend in the free troposphere, in analyses based on sonde data.

Satellite biases are often larger than those of other free tropospheric measurement systems, ranging between -10% and +20%, and standard deviations are large: about 10-30%, versus 5-10% for sondes, aircraft, lidar, and ground-based Fourier-transform infrared spectroscopy. There is currently little information on temporal changes of bias for satellite measurements of tropospheric ozone. This is an evident area of concern if satellite retrievals are used for trend studies. The importance of ECC sondes as a transfer standard for satellite validation means that effort should be put into reducing their uncertainties.

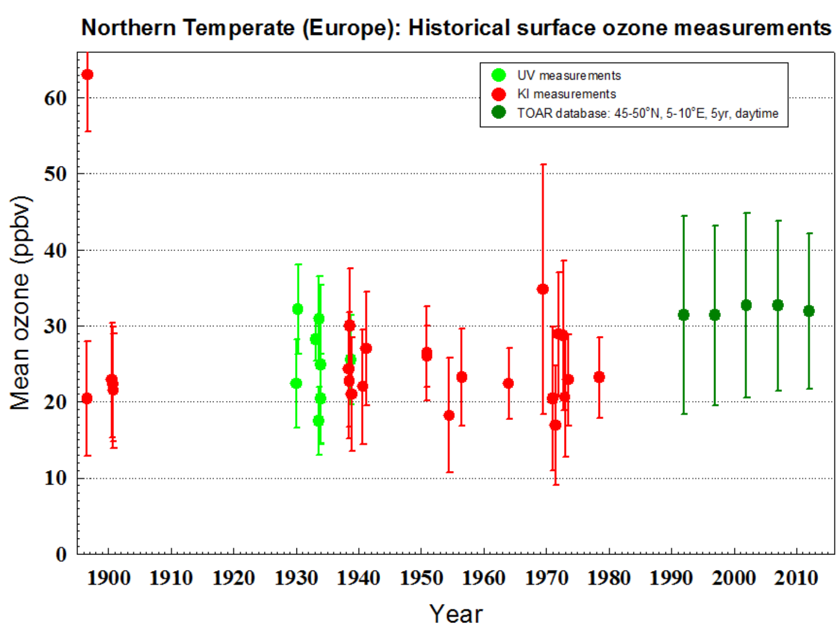

Figure 1. Historical measurements of surface ozone in northern temperature regions (almost exclusively Europe). Error bars represent standard deviations of the measurement averages (atmospheric variability), not uncertainty of the measurement. Five-year averages of modern UV measurements at sites classified as "rural" in the Tropospheric Ozone Assessment Report (TOAR) database are also shown (Schultz et al. 2017).