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Estimation of surface O_3 from lower-troposphere partial-column information: Vertical correlations and covariances in ozonesonde profiles

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HIGHLIGHTS

► We parametrize vertical autocorrelations and covariances structure of N American O_3.
► Covariances define a mapping from the remotely retrievable to the pollution-relevant.
► Sources and mixing processes explain lower-troposphere O_3 variability.
► Near-surface ozone mapscan be inferred from 0 to 3 km averages.
► New satellite remote-retrieval instruments can map near-surface ozone.

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ABSTRACT

Analysis of the spatial correlation of ozone mixing ratio in the vertical provides information useful for several purposes: (a) it aids description of the degree of regionality of the ozone transport-transformation processes, (b) the information provided in the form of a priori covariance matrices for remote retrieval algorithms can simplify and sharpen accuracy of the resulting estimates, and most importantly, (c) it allows a first evaluation of the improvement that remote retrievals can give over boundary-layer climatology. Vertical profiles of mean, variance, and vertical autocovariance, and vertical autocorrelation of ozone mixing ratios were estimated and given parameterizations. The WOUDC ozonesonde network database was used. During the years 2004–2006, these were considerably augmented by sondes taken by NASA, NOAA, and Canadian agencies during recent summertime intensive periods in North America. There are large differences across the North American continent in the patterns and magnitudes of correlation, especially in the lowest 2–3 km of the troposphere. This is especially significant for the near-surface layers (100's of meters deep) which determine actual surface O_3 smog exposure and phytotoxicity, since satellite retrievals typically characterize at best a thick layer extending 3 km or more from the surface. The relative variation of O_3 decreases in the vertical, particularly for the somewhat polluted launch stations, and this affects inference of surface O_3 significantly. We outline a simple synthesis of mixed-layer and ozone-chemistry behavior to aid discussion of this and similar phenomena. Regional differences suggest broad if qualitative explanations in terms of larger-scale (interstate-transport) and local-scale phenomena (lake and sea breezes, degree/frequency of subsidence), inviting future study. The character of near-surface-to-full-layer covariance suggests that remote retrieval can describe surface ozone surprisingly well using 0–3 km partial-column ozone… for many situations. This indicates that there is substantial utility for new remote-retrieval methods that exploit ozone absorption in multiple wavelength regions, e.g., UV + Vis, UV + IR, or UV + Vis + IR. In summary, we find considerable value in interpreting retrievable O_3 columns to estimate O_3 quantities that are closely relevant to air pollution mitigation.

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1. Introduction

The measurement of atmospheric ozone from space has a long history and retrievals of the total column have become so precise (Liu et al., 2010) that it is natural to use retrievals to map pollutant

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ozone near the surface. The characterization of near-surface ozone is important for human health and plant growth (Szykman, et al., 2011, US EPA Ozone (O_3) Standards: http://www.epa.gov/ttn/naaqs/standards/ozone/s_o3_cr.html). Promising newly refined methods for remote retrieval of tropospheric ozone (Worden et al., 2007; Landgraf and Hasekamp, 2007; Natraj et al., 2011) allow samples for more appropriate regions, i.e., partial column estimates with 2–3 pieces of information for the whole troposphere. The lowest layer can be about 3 km deep. Description of the vertical profile in higher layers of the troposphere is also relevant. Middle and upper tropospheric ozone need to be mapped for the interest of several agencies (e.g., in the USA, EPA, NOAA, and NASA) in understanding hemispheric and global pollution, particularly as it progressively has increasing effects on the radiation budget and global climate changes. For these reasons, it is important to quantify ozone by altitude and by concentration as accurately as possible, and to understand how relevant partial-column estimates are to the determination of vertical profiles.

One goal of this report is to aid retrieval of the whole profile of tropospheric ozone by describing the sounding-to-sounding means and variances of ozone at a level as they vary—significantly—by geographical location and in the vertical. These aid ozone retrievals. It is easy for the convergence search of estimation procedures to stray to clearly unreasonable solutions since the retrieval problem is poorly posed and susceptible to solutions far from the norm (solutions that are mathematically allowable but not likely in terms of our prior experience) (Backus and Gilbert, 1970). The range of reasonable estimates e.g., mean, standard deviations, and the likelihood that these change rapidly in the vertical, also aids the algorithm by suggesting soft limits for parameter estimates as well as first-guess values. The expected covarying structure of estimated parameters like χ_{O_3} between differing levels is also useful in estimation algorithms (Rodgers, 2000; Maddy and Barnet, 2008). Understanding the vertical covariance structure of ozone mixing ratio, χ_{O_3}, level to level, helps to prescribe the smoothness of solutions.

A more immediate use of a better description of vertical covariances is to assess the correspondence of the *retrievable* (a layer average of tropospheric ozone) to the *relevant* (maps of ozone as it determines daily human exposure). Satellite mapping can serve several purposes to the extent that a retrieval of a partial column can relate strongly to what we will describe as "near-surface ozone," nsO_3. We wish nsO_3 to have dimensions of a mixing ratio, ppb, and to be a useful description for the ozone budget over many hours of the day, not necessarily a mixing ratio measured at a single site, e.g., a particular existing measurement station. More discussion of the averaging implied by this desire appears below. We used a pressure coordinate system for the vertical, which simplifies averaging; however, the near-surface layer had to respect surface pressure variation. We chose the bottom of the layer to be the 80th percentile surface pressure level $p_{Sfc,80}$, and the top of the layer to be $p_{Sfc,80} - 50$, i.e., 50 hPa lower pressure, ca. 500 m higher altitude. The $p_{Sfc,80}$ varies from 0 to ca. 125 m off the surface. This allows a pressure coordinate but also describes a region ca. 500 m deep, sometimes slightly less deep. The reasons for this choice will become more evident in a later section on origins of vertical variation of ozone.

2. Background

From early in the era of ozone-remote-sensing instruments, the advent of TOMS (Total Ozone Mapping Spectrometer, launched 1978), there have been repeated observations of features identifiable as regional smog in total ozone imagery (Fishman et al., 1987). Early methods concentrated on removing the large partial column of stratospheric ozone from the TOMS signal, leaving a much smaller partial column of ozone, a Tropospheric Ozone Residual or "TOR," (Fishman et al., 1990). The noisy difference, the TOR, represents at best ozone in the whole the troposphere; correlations between total tropospheric ozone and surface ozone may therefore be sporadic, depending on the variance in ozone above the polluted boundary layer. Nevertheless, statistical relationships of TOR and geographical patterns of surface ozone and surface effects have been noted repeatedly, although surface concentrations are not typically estimated (Hudson et al., 1995; Fishman et al., 2010; Wang et al., 2011). Accuracy of algorithms has improved, and the successor to TOMS, the OMI (Ozone Monitoring Instrument), provides retrievals of total ozone column to a very few percent. A more recent TES (Tropospheric Emission Spectrometer) technique using thermal IR appears to give good resolution of two layers (partial column estimates) of ozone 2–5 km, and 5–12 km (Nassar et al., 2008). As mentioned, a common feature of retrieval sets to contain some widely unrealistic appearing profiles. As a conspicuous example, as Nassar's Section 6 indicates, in the first release of TES estimates, a large number of retrievals which minimized error also differed greatly in shape and 0–1 km magnitude from results that conform to prior experience and also the initial guess. This is probably due to a minimization finding a physically unrealistic minimum (Rodgers, 2000), can be ameliorated when there is better knowledge of a mean expectable profile and the typical (We will address this feature of retrievals again in the latter portion of our report.). IASI or future instrumentation may do slightly better than TES (Natraj et al., 2011).

Thermal techniques have nearly zero information at the surface (see Fig. 1), where air and surface temperatures are nearly equal, denying any distinction of a vertical scale. Techniques based on UV alone also have markedly decreased sensitivity near sea level due to rapidly increasing competition of Rayleigh scattering with O_3 absorption (Natraj et al., 2011). However, several retrieval situations, e.g., with low clouds or scattering aerosol can improve the discrimination of near-surface ozone. Ziemke et al. (2001, 2009) have shown how cloud-slicing can enhance retrievals of boundary

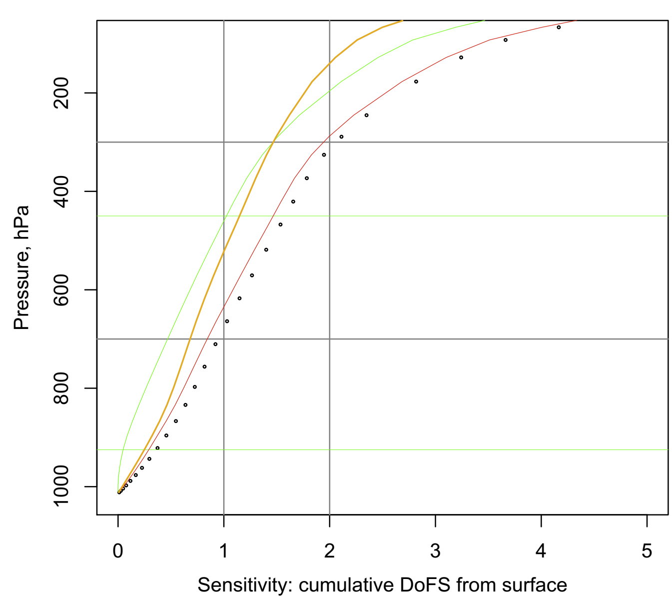

Fig. 1. Ability of several instrumental combinations to resolve lower tropospheric ozone, using data from Natraj et al. (2011). In this presentation, the degrees of freedom for signal are integrated from the surface upwards. Green: IR only, Orange: UV + Vis, Red: UV + IR, black dots: UV + Vis + IR. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)