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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Ozone decomposition on Saharan dust: an experimental investigation” *by* F. Hanisch and J. N. Crowley

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The following are replies to the specific comments of referee 1

Comment, Page 1813 and 1817: Densities of the dust sample.

The different densities discussed can lead to confusion; please elaborate. To what does the phrase "true density" refer? Is that the density of a single grain of dust (presumably averaged over many grains)? Is that what the pyknometer measures (which you call simply "density" on p. 1813, line 14?).

Please explain more carefully how the "bulk density" is determined. On p. 1813, line 15, you imply that each bulk sample had a known geometric surface area and uniform thickness (which was measured to determine its volume) and was weighed to determine the overall density of the prepared sample. But then on p. 1817, line 21, a single bulk density of 1.2 g/cm3 is reported. Does this mean that each sample prepared had the same ratio of mass to measured volume? to what precision? It seems circular to me to say in lines 2 and 3 of p. 1818 that the heights are calculated from the bulk density, when on p. 1813 you state that the bulk density was determined from the height!

Reply

The helium pyknometer determines the density of single dust particles, averaged over an ensemble. We refer to this as "true" density as opposed to the "bulk" density in which the interstitial volume is important in a bulk sample. The text on page 1813 will be modified to incorporate a definition of the "true" density.

The bulk density of the substrate was not determined for each sample used to measure O_3 uptake, but derived in separate experiments in which larger amounts of dust were used (ca. 1 g), for which the sample height could be precisely determined using a calibrated cylinder. Measurements of bulk density were frequently undertaken to investigate the reproducibility of the procedure, which was found to be better than $\pm$ 10 %. For dust samples used in the uptake experiments (typically 5 - 50 mg) the sample height could not be determined in this way with sufficient precision, and was derived from the bulk density, and the geometry of the sample holder, as stated on page 1813. The inherent assumption is that the light samples have the same bulk density as the heavy ones. The text on page 1813 will be modified to incorporate this.

Comment, Page 1816, Eq. (2)

What is the uncertainty in S(infinity)? Is there a physical basis for this expression?

Reply

The statistical errors associated with the fitted value of S(infinity) are less than 1%. There is no physical basis for the expression used to derive S(infinity). This expression merely allows us to derive precise, extrapolated values of S(infinity) from the "approach to steady uptake". Lower bounds to S(infinity) obtained by visual inspection rather than

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data fitting lay about 10 % lower. The text on page 1816 will be modified to incorporate this.

Comment, Page 1819, line 20

Can you suggest an explanation for your observed dependence of gamma on [O3]? What physical process leads to "the enhanced availability of reaction sites at lower O3 concentrations"? Do you have a hypothesis for the discrepancy between your observation and the [O3] independence reported by Michel et al. (p. 1821,line 8)?

Reply

A potential explanation for the apparent enhanced reactivity at low ozone concentrations could be related to the blocking of reactive sites by ozone molecules temporarily occupying neighbouring non-reactive sites. This is apparent in Figure 6, where the reactivity is first lowered at high ozone concentrations, but increases when [ozone] is lowered again for the same dust sample. Surface sensitive studies could clarify this. We note that a comparable ozone concentration dependence for uptake to carbonaceous surfaces has been observed (Stephens et al., Int. J. Chem. Kin. 18, 1133-1149, 1986). We have no explanation why such effects were not seen by Michel et al. The text on page 1819 will be extended to include this hypothesis, and the reference to Stephens et al.

Comment, Page 1825, line 26, or Page 1828, line 28

This manuscript does an excellent job of explaining how the results can (and cannot) be appropriately applied to models of the atmosphere. To put things in perspective, can you provide a rough idea of the time it would take for ambient dust particles to transition from the initial to the steady state regime, and then to the passivated regime? If one were to ignore the reactivation of surfaces, could you estimate if dust would become passivated towards ozone within an hour, a day, or a month?

Reply

Firstly we note that at O_3 concentrations typical of those found in the troposphere, we have no evidence for complete passivation, as re-activation processes can take place on the same time scale as surface passivation. We can therefore not speculate on the transition regime between steady-state uptake and complete deactivation. In the absence of reactivation processes, the capacity of mineral dust to destroy ozone is defined in section 3.3 as 2.1 x 10^{14} molecules per cm^2 of dust surface. The capacity of a single dust particle of 1 micron diameter is approximately 1 x 10^7 molecules of O_3. Combining the measured uptake coefficient of ca. 1 x 10^{-5} with an ozone concentration of 40 ppb (ca. 1 x 10^{12} O_3 / cm^3) and the calculated collision frequency we can derive an approximate time for passivation of 100 s. Text will be added to mention this in section 3.5. We emphasise however that re-activation processes almost certainly do occur in the atmosphere.

Technical Corrections:

Page 1824, line 26 should read "dependence on [O_3]" Capitalization in references is not consistent. Page 1832, line 1: "Japanese" should be capitalized. Fig. 9 axis should be labeled in seconds, not minutes

The technical corrections will be incorporated into the final version.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1809, 2002.