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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011” *by* Q. Zhang et al.

Anonymous Referee #2

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This paper reports ground-based measurements of O3, NOx, VOCs and meteorological parameters from a central Beijing site over the period 2005 – 2011, which encompasses transient emissions reductions associated with the Olympic Games in 2008. In brief, significant positive trends for O3and Ox are reported, alongside negative trends for NOx and VOCs, in all cases with significant transient downward perturbations during the Olympics period. The trends in O3 and Ox are interpreted in terms of changing regional levels of O3 / Ox, changing local urban decrement from NOx emission reductions, and changing local chemical ozone production from VOC oxidation.

The key value in the paper is the clear and unambiguous trends in O3/Ox/NOx/VOCs

presented for this (highly populous) location, the striking impact of the transient policies brought in around 2008, and the predictions of the impact of trends in NOx and VOC emissions upon ozone production rates to date and looking ahead to the future; the paper makes a significant contribution to the public record of pollution trends and possible impact of air quality policies in this locale. I have some comments regarding the discussion and attribution for these trends (see below), and suggest that this aspect of the paper be significantly expanded to fully do the measurements justice. I have also made some more minor suggestions re presentation of the results and technical corrections.

-Cause of the increases in O3 / Ox. If changes in deposition (land use ?) and meteorology may be neglected, three factors could contribute to the observed increased in O3 : reduced urban decrement from lower NO emissions; reduced regional O3/Ox levels, and reduced local ozone production.

The first of these is dismissed on the basis that the NO trend (-0.2 ppb yr-1) is much smaller than the O3 trend (+2.6 ppb yr-1). However, this argument neglects that NOx is partitioned strongly into NO2 at these ozone levels (mean NO2:NO ratio of 5 – 6) – the NOx-O3 PSS needs to be taken into account to make this argument. Interestingly the data appear to show a shift in the PSS – the NO/NO2/O3 daily mean values imply a reduction in the inferred k(NO+O3)/j(NO2) values of around 10%. Possibly there is some contribution from trends in visibility to the NO2 photolysis frequency; alternatively this would suggest a similar order reduction in mean peroxy radical levels.

It would be nice if the authors could present more data to substantiate the changes (or lack thereof) in regional O3/Ox levels – if other datasets exist. Even with the data mentioned, the regional contribution could account for up to 40 % of the observed trend, which (with the urban decrement effect) would leave an important, but not dominant, role for local photochemistry.

The calculation of photochemical production is an approximation, but is useful here in highlighting (a) the changes in trend of NOx and VOC reductions over the 2001 – 2011 period, (b) the implications of these trends for future O3 and that (c) the observed trend in O3 is opposite in sign to that predicted by the P(Ox) analysis ! The authors need to address this contradiction in rather more detail – either in terms of shortcomings in the P(Ox) calculation (e.g. neglect of reactive intermediates such as OVOCs – although these wouldn't change the sign of the trend calculated) – or in terms of the conclusion regarding importance of local photochemistry vs regional abundance. Is a trend in monoterpene / BVOC abundance – not measured other than isoprene – possible ?

Other Comments

-The NO2 data are obtained using a Mo converter instrument. As the authors correctly comment, such systems suffer from positive interference from NOy. How might this affect the analysis ? The interference will not be 100% for all NOy species.

-VOC measurements – not clear if these were all online measurements (instruments present in Beijing) or offline measurements (samples taken to their respective laboratories). Please define all abbreviations where first used. Please be more precise re the comparisons between the instruments – "most" measurements in agreement – which / how many weren't, and by how much ?

-Fig 5 not referred to in the text

-The explanation of the P(Ox) equation is not clear, and needs expanding in this paper, in addition to the references given to the original derivation p.1030 first few lines – please give more specifics of the VOC trend comparison

Presentation / Minor Comments

-The English usage could be improved, although the meaning is clear throughout. The Abstract in particular would benefit from a little attention.

-In general: ppb is a measure of mixing ratio, not concentration. Conversely, on Fig 5, mg/m3 are not units of mixing ratio.

p.1024 line 25 be precise re "one" "the other one". Dual not duel.

p.1025 line 4 "previously commercial" ?

p.1027 line 6 RO2 or RO2 + HO2

p.1027 line 7 reaction not collision

p.1028 line 22 not clear precisely which years were then included in the trend

p.1030 line 23 this argument also depends upon how much C5H8 is present

Fig 7 VOCs: total ppb or ppbC ?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 1019, 2014.