

Interactive comment on “Photochemical age of air pollutants and oxidation products in transboundary air observed on Fukue Island, Nagasaki, Japan” by S. Irei et al.

Anonymous Referee #4

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Review of “Photochemical age of pollutants and oxidation products in transboundary air observed on Fukue Island, Nagasaki, Japan” for Atmospheric Chemistry and Physics

The authors have collected an interesting data set of trace gas and aerosol observations from a site in Japan which is exposed to continental outflow from the Chinese mainland. The title leads with “Photochemical age”. Figure 10 based on NO_x/NO_y shows a reasonable trend in that there is more ozone in older air masses. There is a link between photochemical age and f₄₄, though very noisy. An apparent conflict with the authors earlier work is examined with a model that gives f₄₄ in terms of the properties of HOA and LVOOA, the amounts and properties of which differed between campaigns. A parameterization is arrived at with multiple constants for fitting, some

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of which may be derivable. That aspect deserves discussion. Unfortunately the differences between campaigns is not fully resolved.

In regard to the trajectory analysis I recognize that the accuracy of individual trajectories is generally not high enough to make definitive statements. When considered in groups one can gain insights as to source information. I believe that the source identification would be more persuasive if the experimental period were divided into sets with 1) episode levels of CO and 2) mid or low levels of CO and the ensemble of trajectories for these conditions compared.

In regard to photochemical age: There are many ways in which ratios can give biased age. In parts of this paper photochemical age is treated as having quantitative potential, as in the discussion of rate constant for OH+NO₂. But in the end the authors seem to get it right, a valuable tools to give information on the relative effects of atmospheric processing

Some of my comments are ways in which this manuscript could be improved. Some are critical. There are conclusions, which may or may not be correct, but are not substantiated. There are serious errors concerning nighttime chemistry of NO_y and the lifetime of NO_y which need to be corrected before this manuscript is considered for publication.

Comments

Abstract, line 9-11 correlation of NO_y with CO implies negligible loss of NO_y by reaction with OH radical. Loss from the NO_y family of compounds due to reaction with OH is very slow. Loss of NO_y is mainly from wet and dry deposition. Oxidation of NO₂ to form HNO₃ is rapid, but does not lead to loss of NO_y. HNO₃ so formed could partition to the aerosol phase but still would be detected as NO_y by a NO_x detector with a heated Mo catalyst.

Abstract, line 21. the f₄₄ increase rate was 1.05(-9) h⁻¹ molecule⁻¹ cm⁻³. The

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terminology is confusing. f_{44} is dimensionless and its rate of change should have units of 1/time. The f_{44} increase rate is actually given by $1.05(-9) \text{ h}^{-1} \text{ molecule}^{-1} \text{ cm}^{-3} [\text{OH}]$, where $[\text{OH}]$ has units of molecules/cm³. The presentation in Eq. 3 is correct.

Page 5 Discussion of inlets and NO_y measurement. Given the inlet dimensions and flow rate, there is approximately a 30 second transit time from the top of the inlet to the NO_y instrument. Unlikely that HNO₃ would make it through. A description of the measurement used in the present study should include the converter location

Page 11, line 15-17 CO was highly correlated with NO_y ($r^2 = 0.674$), ethyne ($r^2 = 0.724$) and organic aerosols ($r^2 = 0.562$) These correlations are not that high in comparison to observations in other studies. I do not know if the modifier “highly” is warranted. The present data set is accumulated over a few seasons and at a location that has long range transport from multiple directions. The diversity of emission sources and degrees of atmospheric processing will suppress the overall correlation.

Page 11, lines 20-21 at an average OH of 5×10^5 the lifetime of NO_y is 1.7 days. This is incorrect. 1.7 days is the right order of magnitude for oxidation of NO₂ by OH under the assumed low OH concentration. Oxidation of NO₂ transforms one member of the NO_y family to another. It does not change the NO_y concentration. The lifetime of NO_y is set by wet and dry deposition and is affected by OH only in so far as reaction changes wet and dry deposition rates.

Page 11, line 23-25 NO_y and CO were transported over a short distance This conclusion relies on a 1.7 day lifetime for NO_y and is therefore suspect.

Page 11 – 12. Discussion of NO_y to CO ratio. The observed ratio from a linear regression is 0.03. A study published in 2002 gave a ratio of 0.1 and a model calculation published in 2012, for air masses which had been transported long distances, gave a ratio of 0.03. The change in the ratio from the 2002 study to that from the present paper and the 2012 study is ascribed to recently improved emission of NO_y.

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The text implies that these few scattered numbers are due to emission changes. If that claim is made it should be documented. In the U.S., emission controls have caused urban ratios of NO_x to CO to increase, at least up to around 2010 (see work by Parrish et al). Low NO_y/CO ratios of order 0.03 are usually indicative of long range transport in which NO_y has been partially removed by deposition. A minor point: One usually does not refer to NO_y emission but rather NO_x emissions.

Page 11, line 4-5 and following. high correlation of particulate organics and ammonium suggest that in major the organics composed of carboxylic acids In my opinion this conclusion, true or not, is not demonstrated by the data provided. An air mass that comes from a polluted region is likely to have high concentrations of multiple pollutants. Thus a correlation between organics and NH₄ could be due to 1) a correlation between sulfate and organics and 2) a correlation between sulfate and ammonium. It is difficult to disentangle multiple interactions. One could start with multi-variable regressions or PMF calculations that include inorganic ions.

Page 15, line 7 to Page 16, line 6 Paragraph on NO₃ chemistry. The gas phase reaction of N₂O₅ with H₂O is very slow. Removal of N₂O₅ by reaction with water occurs in aerosol. It is rapid for acidic aerosol but slow for near-neutral aerosol (Brown et al, Science, 311, 67-70, 6 Jan 2006; Zaveri et al, JGR 115, D12304, 2010). If the N₂O₅ is not removed, NO_x will be regenerated. NO₃ can also react with VOCs, primarily olefins. Depending on conditions, nighttime chemistry can remove most or almost no NO_x. The reaction rate cited for NO₂ + O₃ is just the one way flux through one of a series of reactions.

Page 16, line 7-20 Relative effects of nighttime and daytime NO_x chemistry on O₃. The effects of daytime chemistry have to be considered. Photochemical O₃ production in the day is a chain reaction creating several O₃ for each NO_x removed. By taking differences between the 75th and 25th percentile data in Table 1 (best I could do with data on hand) one obtains a qualitative estimate of 7.5 molecules of O_x produced per molecule of NO_x oxidized. The actual value is lower by an unknown amount because

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of NO_y deposition. Nighttime chemistry is less efficient in using NO_x to remove ozone. If the same amount of NO_x is removed in the day and night, there will still be a positive correlation between O₃ increase and NO_x decrease.

Page 19, Section 3.6 Dependence of f₄₄ on t[OH] There is some increase in f₄₄ with age. Perhaps this would show up better if the data was binned or lowess fitted. It is puzzling that different studies gave different results. Eq. 4 makes sense. I don't understand why a and b are arbitrary parameters. What must be measured to get their values?

Minor points

Page 5, Line 23-24. Could you please supply DL for NO and NO₂. I am surprised to see a single figure for both as the measurement of NO₂ is done by subtraction and involves the LED efficiency.

Page 6, line 16-17 Are the AMS detection limits for a 10 minute period?

Page 6, line 23 and 25 What averaging times are used in specifying detection limits for NO_x, NO_y, O₃, and CO?

Page 14-15 Photochemical age, in particular choice of reaction rate constant for OH+NO₂. The range of values due to temperature and pressure is small compared with other systematic errors such as the ratio of NO₂ to NO_x and the occurrence of reaction channels (e.g. PAN formation) that remove NO₂.

Page 15, line 1-5 I am confused by the sensitivity calculation. As I understand, kNO₂ is between 9.3e-12 and 1.1e-11. A nominal value of 1.0e-11 was used in the calculations. The product of kNO₂ *t[OH] must remain constant as it is determined by a measured ratio of NO_x to NO_y. From Eq. (1) if 1.1e-11 is used in place of 1.0e-11, t[OH] decreases by 9%. Going the other way, t[OH] increases by 8%. The stated range in bias is different; -10% and 5%. A change in temperature of plus or minus 5K is brought up but evidently is not what is used in arriving at the kNO₂ values in line 330. But more

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important why bother with the extended discussion of the temperature dependence of NO₂+OH, when there are much more significant factors. Factors left out are the ratio of NO₂ to NO_x and the occurrence of other reaction such as PAN formation.

Page 20, line 19 extent of reaction Needs a definition.

Figure 9. Why is the f₄₄ of HOA exactly zero? OA/OC for this PMF component has an O to C ratio approximately equal to one.

Supplement The text implies that Figures S1 to S-7 show trajectories for end of each episode terminating in Pacific Ocean or Mongolia. This is a hard feature to pick out. In some cases (S-7) the last trajectory passes over the same regions as trajectories that are part of the episode, but with a greater wind speed. In Fig S2 the last trajectory terminates over the East China Sea. However, this trajectory is shorter than the others and appears to point toward the mainland.

Table S1 The main text, line 223, promises qualitative information on the concentrations of other (non-CO) chemical species. I was expecting average or peak values, not check marks. The foot note to Table S1 specifies that the check marks are for observation of remarkably high concentrations without specifying what "remarkably high" means, either on an absolute basis or relative to the average or frequency distribution of the ensemble of measurements. Additional information needs to be added to Table S1.

TYPOs, wording Page 4, line 2 "east to west" Should be west to east

Page 9, line 1. emission sources of nitrate Should be emission sources of NO_x.

Page 11, line 5 in major the organics composed of carboxylic acids Suggest: organics are primarily composed of carboxylic acids

Page 21, line 7 photoxidation toluene Suggest: toluene photoxidation

Page 21, line 8 ".. parameter, the 4 of which are determined by PMF analysis" Eliminate "the"

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Page 21, line 8 starting with "More progress.." Not a sentence.

Page 21, line 10 "containing a significantly low continues to increase. Words are missing

Page 39, Symbols on Figure 6. Colors for top two categories difficult to distinguish. I have normal color vision.

Page 41, x-axis of Figure 8. Dates should be the same as used in other figures, i.e. Dec 1, Jan 1, Feb 1, etc.

Figure 11 appears to be missing from last version that I downloaded. In a previous version it had a time axis that did not match others figures.

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