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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An exploration of ozone changes and their radiative forcing prior to the chlorofluorocarbon era" *by* D. T. Shindell and G. Faluvegi

J. Staehelin (Referee)

staehelin@atmos.umnw.ethz.ch

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Review of the paper: An exploration of ozone changes and their radiative forcing prior to the chlorofluorocarbon era, submitted by D.T. Shindell and G. Faluvegi (MS-NR: 2002-49) Reviewer: Johannes Staehelin

The paper makes a stimulating contribution with respect to our knowledge of the (probable) evolution of atmospheric ozone prior to the chlorofluorocarbon era. The study is based on numerical simulations and data analysis. The paper is separated into two parts, namely dealing with the period of 1957 to 1975 and the period from the 19th century to the middle of the 20th century. I find the first part (1957-1975) very interesting. To my opinion it needs improvements before publication (see below). However, I

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strongly object the analysis of the period of the 19th century ("preindustrial") to the middle of 20th century, because the analysis is (almost exclusively) based on the results of ozone measurements by Schönbein papers, which should be ignored for quantitative analysis because of well known problems in data quality (the measurements of Montsouris near Paris by another method can hardly be used to support the low ozone values of the Schönbein measurements) (see below). I am convinced that the uncertainty in the measurements of the Schönbein paper is much too large to be used for comparison with numerical simulations. In my opinion these suspicious data are worse than no data.

First part of the paper (1957-1975) In the first part of the paper, the study makes use of recent results which provided evidence for an increase in stratospheric water vapour concentrations, which started before the increase in stratospheric concentrations of ozone depleting substances (ODS) (around the beginning of the 1970s). The authors conclude from model simulations that this water vapour increase caused a decrease in stratospheric ozone already in the time between 1957 and 1975. During the same time the emissions of the anthropogenic precursors of tropospheric ozone formation strongly increased because of the dramatic economic growth in the industrialized world after World War II in the Northern hemisphere. The presented numerical simulations for tropospheric ozone seem to be capable to match the (few) summer surface ozone measurements available from the time period around the 1950s and the information of the few available ozone sonde series which stared around the late 1960s. The next question concerns: Why was this decrease in the ozone shield not detected by measurements ? Some measurements are available. However, these measurements concern column (total) ozone measurements by Dobson spectrophotometers which dont contain separate information of stratospheric ozone. The authors present the hypothesis, that the stratospheric ozone decrease was masked by the simultaneous increase in tropospheric ozone in the Northern hemisphere. However, a net loss in total ozone is expected for the Southern hemisphere because the large economic growth leading to tropospheric ozone increase took place in the Northern hemisphere but the ozone

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depletion by water vapour affected both hemispheres. The authors try to underline this hypothesis by the analysis of old Dobson measurements. They present evidence that the very few Dobson data of the Southern hemisphere show as expected from the stratospheric ozone depletion by water vapour a decrease while no such decrease in the Northern hemisphere is obvious because of the assumed compensation of stratospheric ozone depletion by the increase in tropospheric ozone. (We also thought about a compensating effect of total ozone decrease by the increase in tropospheric ozone in Europe (J. Staehelin, R. Kegel, N. R.P. Harris, "Trend analysis of the homogenized total ozone series of Arosa (Switzerland), 1926-1996", J. geophys. Res., 103, 8389-8399 (1998). We used the very few ozone ascents made by Brewer at Arosa in summer 1958 and compared the ozone concentrations at 500 hPa with measurements of the ozone sondes of Payerne (located in the Swiss plateau) of the late 1990s. From this analysis we concluded that tropospheric column ozone might have been increased by roughly ten Dobson units since around World War II. Subsequently we scaled the increase at 500 hPa with the temporal evolution of the European NOx emissions and found by sensitivity runs of multiple regression models that stratospheric ozone might have decreased considerably more since the beginning of the 1970s than when ignoring the increase in troposheric ozone). Comments to the part of the paper considering the period 1957-1975 1. Abstract, line 6 and 7: The results suggest, that stratospheric ozone depletion may have been roughly 50% more than generally supposed: Already the Abstract should contain the information of the considered period: Is this comparison with ozone depletion caused by ODS extending to 2000 ? 2. How compare the results of the study with the results of the study of V.L. Dvortsov and S. Solomon, "Response of the stratospheric temperatures and ozone to past and future increases in stratospheric humidity", J. geophys. Res., 106, 7505-7514, 2001 (cited in the reference list) ? 3. The documentation of the model runs is too short and should be extended. 4. p. 4, 3. paragraph: The aerosol loading was significantly higher for a few years in the 1960s: Please document the source of this information. 5. p. 5, 3. paragraph, tropospheric ozone simulations: The authors should declare, which emissions were used for the tro-

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pospheric model runs of the 1950s and the 1970s. I suggest to add a table including the anthropogenic and biogenic emission source strengths of NOx, CO and hydrocarbons for the beginning and the end of the period, possibly for different continents. 6. Annex: The data presented in the Annex support only in a very qualitative sense the hypothesis of the authors. The very large scatter of trends of Northern hemispheric data hardly convinces me and I suggest significant improvements before publication. The listed changes range from 10% increase to -5% decrease, and the differences are sometimes very large for very close stations (see e.g. Oxford and Bracknell). The cause of these discrepancies are most likely serious problems in data quality and not the lack of the coverage of the measurements. (The Dobson observations in this time were used to document large day to day variabilities to study the interaction between total ozone at midlatitudes and meteorology and the precision necessary for trend analysis was never intended.) The inherent hypothesis, namely that these problems are cancelling out by using a large number of stations is not convincing and difficult to prove. I think, SO2 is a serious problem which can not be solved by ignoring only the data of capitals which have a population of more than 3 millions (comp. also p. 6, first sentence). For instance it is well known from D. De Muer and H. De Backer, "Revision of the 20 years of Dobson total ozone data at Uccle, (Belgium): fictitious Dobson total ozone trends induced by sulfur dioxide trends", J. geophys. Res., 97, 5921-5937, 1992 that the Dobson series of Uccle suffers from decreasing SO2 pollution of the capital of Brussels since the 1980s (at one monitoring site close to Brussels the annual mean values of SO2 concentrations decreased from 180 mg/m3 in 1968 to 90 mg/m3 in 1975). I therefore suggest to exclude the data of Uccle because this effect is expected to be large and therefore it most probably obscures the column ozone trend of 14.8 DU during this period. In order to avoid any impression of arbitrariness in the data selection I strongly recommend to use an objective treatment of the data quality problems. I propose to revise this part by using clearly defined criteria as documented by WMO 1992, Handbook of Dobson ozone data re-evaluation, WMO Global ozone research and monitoring project, Rept. No 29, Geneva. I recommend to use local 100 hPa temperatures and

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300 hPa geopotential heights for a screening of the data using NCEP/NCAR reanalysis data. By this procedure breaks in the series can be identified. After such a screening of obvious breaks the statistical analysis should be repeated. I think, the paper could strongly benefit by improved data analysis and its proper documentation. I think less but more reliable data are more appropriate. I also suggest that the authors should contact Stefan Brönnimann (stefanb@lpl.arizona.edu), who has large experience with the analysis of old Dobson data. 7. p.6, second paragraph dealing with the estimate of the "multiscore stratospheric ozone trends" using mean and 2-sigma uncertainties based on all five data sets: How were 2-s uncertainties including different data sets calculated in the study ? How was the weighting of the different types of uncertainties originating from different types of measurements and model runs performed ? In dont understand the sentence: "By weighting the mean according to the uncertainty of each data set, the ... ". Did you give the total ozone measurements, the few tropospheric summer ozone measurements, and the ozone sondes and the numerical results different weights of uncertainties ? How ? Please describe exactly the used procedure, possibly in a separate Appendix. Technical improvement: 10. Please spell Staehelin correctly (p.2, line 5 and 19; p. 5, line 10) I think this part of the paper is very stimulating and worth to be published when improved by including these suggestions.

Part of the paper dealing with changes between the 19th century and the middle of the 20th century I recommend to exclude this part from the paper. Comments to the part of the paper considering the earlier period (middle of the 19th to the middle of the 20th century) 11. The influence of changes in increasing N2O emissions and methane could be assessed. However, the scaling of stratospheric water vapour increase with anthropogenic CO2 emissions is not convincing to me. 12. In this part the documentation of the paper is also not satisfactory as the authors did not show, how they obtained such low surface ozone values (which emissions were used ?). 13. Surface measurements with the method of Schönbein papers: Schönbein developed a method which allowed him to show that ozone is present in ambient air. However, the method is not suitable to obtain reliable quantitative results. In my opinion a large number of

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publications basically supports this point of view. Three problems have been reported and discussed extensively in the literature: (i) The method is obviously sensitive to water vapour. The proposed procedures to account for this effect are not convincing me. (ii) It was demonstrated, that the discoloration of the Schönbein papers give an non-linear response with ozone and the results therefore depend on exposure time (see D. Kley, A. Volz and F. Mülheims, "Ozone measurements in historic perspective", in Tropospheric Ozone, I.S.A. Isaksen (Ed.), D. Reidel Publishing Company, 1988, p. 63-78. The study indicated that too long exposure times lead to erroneous results which are too low. (iii) The used materials (papers) are difficult to reproduce today and in many cases the exact description of the preparation of the Schönbein papers is lost. The discussion started (after controversial discussions in the 19th century) by the paper of D.E. Linvill, W.J. Hooker, and B. Olson, "Ozone in Michigan's Environment 1876-1880", Month. Weather Rev., 108, 1883-1891, 1880. The authors performed laboratory tests with Schönbein papers and published surface ozone data based on historical Schönbein measurements. The mean value of 35 ppb for the years 1876-1880 for a station at Michigan (USA) is large for this time. The authors compared these data with measurements made by a modern UV instrument at the same site. Unfortunately, they did not show a comparison of simultaneous measurements of the Schönbein method and the modern method for present ambient air. Unfortunately, the Schönbein method was only investigated in the laboratory. All these problems are well known. They are often listed in a number of subsequent papers but they are not properly solved (e.g. R. D. Bojkov, "Surface ozone during the second half of the nineteenth century", J. Clim. Appl. Meteorol., 25, 343-352, 1986; A. Marenco et al., "Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series: Consequences: Positive radiative forcing", J. geophys. Res., 99, 16,617-16,632, 1994 and many others). The authors of these publications often refer to simultaneous measurements between the measurements with the Schönbein method and another method used at the Montsouris laboratory near Paris ("arsenite method", see A. Volz and D. Kley, "Evaluation of the Montsouris series of ozone measurements made in the nine-

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teenth century", Nature, 332, 240-242, 1988). However, the "quasi-calibration" of the measurements of the Schönbein method at the Montsouris observatory can not be transferred to other stations, because e.g. of the humidity and the non-linearity influence (see Kley et al., 1988). Furthermore, the Montsouris measurements are hardly suitable to document the low tropospheric ozone in the "preindustrial troposphere" as suggested by the Schönbein data (the Montsouris data show a mean ozone value around 10 ppb, see Volz and Kley, 1988). The Montsouris ozone measurements contain a large number of very low values as shown by the frequency distribution which was compared with measurements of Arosa (see Fig. 8 on p. 84 in J. Staehelin, J. Thudium, R. Buehler, A. Volz-Thomas and W. Graber, ""Trends in surface ozone at Arosa (Switzerland)", Atmos. Env., 28, 75-87, 1994). We believe, that these low concentrations can not be viewed as representative for the free troposphere. The method of the Montsouris measurements is known to be sensitive to SO2. Volz and Kley, 1988 used simultaneous wind direction measurements of the observatory of Montsouris in order to exclude the data contaminated by SO2, i.e. they eliminated the data when the wind blew from Paris. The Montsouris data used in the comparison with the Arosa data (still including many very low ozone values) only include the Montsouris ozone readings after elimination of the measurements in which the air was transported from Paris. However, the local wind direction data are possibly not completely adequate to exclude all measurements polluted by SO2 or the ozone values were possibly very low as consequence of a strong effect of dry deposition in the Paris basin. Therefore, the low ozone values of the Montsouris measurements should not be used to support the results of the low ozone values of the measurements of the Schönbein papers. In the recent attempt of E.G. Pavelin, C.E. Johnson, S. Rughooputh and R. Tuomi, "Evaluation of pre-industrial surface ozone measurements made using Schönbein's method", Atm. Env., 33, 919-929, 1999 many Schönbein measurements were carefully evaluated. The authors tried to obtain a suitable correction for the water vapour bias. Finally the measurements of the Southern hemisphere at a remote site were compared with numerical simulations. The authors made the reasonable assumption, that no evi-

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dence exists for a large increase in surface ozone at remote stations in the Southern hemisphere. At the end the authors noted: Given these interferences it is our opinion that Schönbein readings normalized to the Montsouris series using the present method can only give a rather uncertain estimate to the monthly variation in ozone. The estimated pre-industrial seasonal cycle of ozone in Tasmania is out of phase with both recent measurements and with pre-industrial seasonal cycle of Tasmania and this is attributed to uncertainties in the magnitude of the humidity correction". In addition one should note the substantial difference in absolute concentrations (see Fig. 8 on page 928 for the numerical simulations to be compared with the corrected measurements of Fig. 3 on page 923). In an other recent paper of L. J. Mickley, D.J. Jacob and D. Rind, "Uncertainty in preindustrial abundance of tropospheric ozone: Implications for radiative forcing calculations", J. geophys. Res., 106, 3389-3399, 2001 the authors made several attempts to reproduce ozone measurements obtained by the Schönbein method. The authors showed, that the measurements of the Schönbein paper can only be reproduced, if the NOx emissions from lightning and soils are drastically reduced (and industrial emissions are turned off). There are arguments that the lightning emission estimates on its own are subject to large uncertainties. However, I have the feeling, that if these values would be drastically decreased, it would be much more difficult to reproduce the present day atmosphere by numerical simulations. The authors of the cited paper pointed out several times the problems with the data quality of the Schönbein method. Therefore, I dont believe that it is adequate to cite the paper in the sense as presented in the reviewed manuscript: "Those models are driven by preindustrial emissions, which are so poorly constraint (underlining by the reviewer) that forcings from simulations should actually be uncertain by at least a factor of two" (see p. 8 of the manuscript, line 29-31). For me this looks as a vicious circle. If the data are suspicious it makes no sense to conclude that the emissions are not adequately known. I can not see any argument why the Schönbein measurements should be more reliable than the generally used emission estimates. Many modelers have tried to reproduce many times the Schönbein data, but they were basically unsuccessful. Also

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in a semi-quantitative sense the doubling of tropospheric ozone from the beginning to the middle of the 20th century is questionable to me: I think, we all agree that tropospheric ozone concentration depends on transport of ozone from the stratosphere and its formation from biogenic and anthropogenic emissions. The large increase in ozone precursors started after World War II with the large industrialisation and the large economic growth. Therefore, it is not astonishing that tropospheric ozone formation started to increase strongly around the 1950s. However, an increase by a factor of two in the earlier part of the last century seems unlikely to me: Before this time one also has to consider that ozone concentrations in the troposphere depend on the stratospheric input and photochemical formation from biogenic precursors. In a zero order assumption, I can not see any convincing argument why stratospheric input and biogenic precursor emissions changed that dramatically before World War II. Thus, my basic conclusion: One should ignore these data for comparisons with numerical simulations. Therefore, they should no longer be used to constrain numerical simulations, or in other words I suggest to eliminate Section 4. 14. Section 5 needs to be rewritten considering the part dealing with the part 1850-1950.

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