

Interactive comment on “Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003” by C. Ordóñez et al.

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Answer to comments of Referee # 1

Referee 1 mentions that the manuscript could be shortened and the discussion made in a slightly more condensed way.

The second last paragraph of Sect. 4.1.1 (p. 7061) has been omitted. We think that the information given in that paragraph did not contribute much to the discussion. Because of the omission of that paragraph, the beginning of the paragraph “As already explained in Sect 4.1.1, there was high consistency” (p. 7067) had to be slightly changed. Additional minor changes: We have omitted or shortened some sentences in the manuscript

to remove some unnecessary or superfluous details.

Referee 1 thinks that the conclusion that large emission reductions have not led to significant changes in the daily maximum ozone concentrations is striking. He wonders how good indicator the seasonal median of daily ozone maxima is and suggests using another indicator that reflect the changes in the high percentiles.

In the initial manuscript we calculated the trends for the seasonal medians of daily O₃/O_x maxima. In the revised manuscript we have also calculated the trends of the seasonal 90th percentiles of daily O₃/O_x maxima. This provides some additional information: significant downward trends in the summer 90th percentiles of daily O_x maxima (daily O₃ maxima in the case of Weerswilen) are found for 6 (instead of 4) stations around the region of Zurich. This suggests that the precursor emission decrease had at least an effect on the highest summer ozone peaks in the most industrialised region around Zürich. We changed the section 4.2, the conclusions and the abstract accordingly.

Referee 1 is concerned about the location of the monitoring sites. Their annual median NO_x concentrations suggest a rather short distance to the sources. If the stations were be located in the transition regime where the NO_x/ozone relationship changes from a destruction regime to a production regime, that location would be the reason why no changes in ozone are seen.

As mentioned by referee 1, the NO_x (=NO+NO₂) levels in Table 1 correspond to annual median concentrations. The real NO_x concentrations are lower than those shown in the table, because NO₂ is measured with molybdenum converter at the 12 sites. By using simultaneous measurements of NO₂ performed with molybdenum converter (upper limit of the real NO₂ concentrations) and photolytic converter (real NO₂) at Tänikon during the period 1995-2001, we have observed that under cloud-free conditions the ratio (NO₂ measured with photolytic converter) / (NO₂ measured with molybdenum converter) is around 0.5 during the summer months and higher than 0.8 in winter. This

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means that the measured NO₂ concentrations are overestimated by a factor of 2 in summer. Apart from the effect of the higher overestimation of the measured NO₂ concentrations in summer, we observed that these concentrations are much lower in summer than in winter. Therefore the effect of the ozone destruction by titration with NO is much less important in summer than in winter, as already explained in the manuscript. Moreover, from the analysis of the main explanatory variables in the different seasons, we have concluded that ozone production prevails in summer (positive effect on the ozone concentrations of parameters like temperature and number of days after a frontal passage) while destruction is more important in winter (more ozone is usually predicted by the model with instability and ozone is destroyed day after day with the stability of the following days after a frontal passage). In addition, we already thought that the ozone titration might be important at the most polluted stations and in the cold seasons. That is the reason why we have calculated the Ox (=O₃+NO₂) trends. The parameter Ox is much more conservative than O₃ and is not affected by the ozone titration with NO. As the NO₂ measurements are overestimated and the NO₂ concentrations have decreased in Switzerland during the analysed period (this second effect is not so important, as explained in the manuscript), the calculated Ox trends are lower limits of the real Ox trends. As seen in the answer to the previous referee's comment, significant downward trends of the summer 90th percentiles of daily Ox maxima (O₃ for Weerswilen) are found for most of the stations around the region of Zurich. This suggests that the precursor emissions decrease had at least an effect on the highest ozone levels in that area. One important conclusion is that not only the O₃ trends but the Ox trends have to be calculated to interpret the effect of the precursor emission changes on the O₃ levels at very polluted (e.g. Lausanne) or average-polluted sites. We think that the referee's concerns about the monitoring sites have already been addressed in the initial manuscript and no new changes (apart from the mentioned 90th percentiles) have been included in the revised version.

Technical corrections suggested by referee 1:

- p. 7051, line 21: Could replace the word “works” by another phrase.

The word “works” has been replaced by “studies” in the revised version.

p. 7051, line 22: Typo. “ad” should be “and”

Replaced

p. 7052, lines 1-4: Use either the abbreviation “Sect.” or “section” not both.

Only the abbreviation “Sect.” is used in the revised version.

p. 7061, lines1-5: Clarify if it’s warm fronts or cold fronts that are discussed.

The parameter frontal passage indicates the presence/absence of a frontal passage - warm front, cold front or occlusion - in Zurich on the investigated day. This is now mentioned in the last paragraph of section 2 .2, which describes the meteorological data used.

p. 7065, lines1-5: The mentioning of a possible future paper is not relevant unless this is an accompanying paper submitted together with the present one.

The whole sentence where we mention the possibility of a future paper has been removed.

p. 7066, line 28: “This made it possible to..”?

Changed according to the referee’s suggestion.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 7047, 2004.

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