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Reply on RC2

Philippe Thunis et al.

Author comment on "Non-linear response of PM_{2.5} to changes in NO_x and NH₃ emissions in the Po basin (Italy): consequences for air quality plans" by Philippe Thunis et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-65-AC2>, 2021

In this work, Thunis et al. simulate and analyze sensitivities of PM_{2.5} to NO_x and NH₃ emissions over the Po valley in order to provide guidance for the designing of future air quality plans in the area. This study is of definite interest to the ACP audience since the Po basin is one of the most polluted regions in Europe and, therefore, it is of high importance to elucidate the complex chemical processes that lead to frequent exceedances of the EU PM_{2.5} concentration limits. The manuscript is well written, the methodology is scientifically sound, and the discussion is clear. However, the authors need to provide more details regarding the underlying aerosol (both organic and inorganic) formation processes considered by their model which is a prerequisite for the thorough interpretation of the results presented in this study. Furthermore, the illustration of the results needs to be improved. Overall, I recommend this study for publication. Below are a few comments to be considered prior to publication.

We would like to thank the reviewer for the positive appreciation of the paper and his/her useful and constructive comments that helped improving our manuscript.

General comments:

- The authors should include a description of the modelling framework used for the present study. The reader should be aware of the mechanistic details of the model in order to validate and interpret the simulated responses presented here. The model description should include the gas phase chemistry scheme used (including, if applicable, the heterogeneous chemistry), the thermodynamic aerosol model used for the formation of SIA, and the organic aerosol framework used for the formation of SOA (including the main NMVOCs used as SOA precursors and their photochemistry).

We agree with the Reviewer and added paragraphs (L107 – 131, new version) to address these aspects in the methodological section.

The gas-phase chemistry is based on the evolution of the so-called "EMEP scheme" as described in Simpson et al. (2012) and references therein. The chemical scheme couples the sulfur and nitrogen chemistry to the photochemistry using about 140 reactions between 70 species (Andersson-Sköld and Simpson, 1999; Simpson et al. 2012). In the EMEP Status Report 1/2004 (Fagerli et al., 2004) the reactions are described that cover acidification, eutrophication and ammonium chemistry. The aqueous phase chemistry

describes the formation of sulfate in clouds via SO_2 oxidation by ozone and H_2O_2 and catalysed by metal ions. An important pathway of particulate nitrate formation is through the hydrolysis of N_2O_5 on wet aerosol surfaces that converts NO_x into HNO_3 . More information on the chemical equations is given in Simpson et al. (2012), section 7.

The EMEP model has two size fractions for aerosols, fine aerosol ($\text{PM}_{2.5}$) and coarse aerosol ($\text{PM}_{10-2.5}$). The aerosol components presently accounted for are sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), anthropogenic primary PM and sea salt.

For inorganic aerosols, EMEP uses the MARS equilibrium module to calculate the partitioning between gas and fine-mode aerosol phase in the system of HNO_3 , NH_3 and (Binkowski and Shankar, 1995). Aerosol water is calculated to account for particle water within the $\text{PM}_{2.5}$ mass, which depends on the mass of soluble PM fraction and on the type of salt mixture in particles. Sea salt (sodium chloride) and dust components are not accounted for by MARS, which might lead to PM underestimations close to coastal sites and where the dust contribution is important. More information on the gas and aerosol partitioning is given in Simpson et al. (2012), section 7.6.

Regarding secondary organic aerosols (SOA), the EmChem09soa scheme is used, which is a simplified version of the so-called volatility basis set (VBS) approach (Robinson et al., 2007; Donahue et al., 2009). The VBS mechanism is discussed in detail in Bergström et al. (2012). The main differences between the VBS schemes and EmChem09soa is that all primary organic aerosol (POA) emissions are treated as non-volatile in EmChem09soa. This is done to keep the emission totals of both PM and VOC components the same as in the official emission inventories. The semi-volatile biogenic and anthropogenic SOA species are assumed to further oxidise (also known as ageing process) in the atmosphere by OH-reactions. This will lead to a reduction in volatility for the SOA, and thereby increased partitioning to the particle phase. More information on SOA is given in Simpson et al. (2012), section 7.7.

- It has been recently suggested that aerosol pH and liquid water content can be used to determine when PM is sensitive to NH_3 and/or HNO_3 availability (Nenes et al., 2020). It could be useful to directly compare (or at least discuss) the results of this method against the indicators presented here

We think that a direct comparison with this approach is difficult (because we did not directly analyse modelled water content and pH in this work) and beyond the scope of this paper, which is to determine the sensitivity of $\text{PM}_{2.5}$ concentrations to reductions in NH_3 and NO_x emissions. We chose to compare our results based on emission reduction scenarios to the information provided by the G-ratio because the variables used in both approaches were the same.

We also believe that considering the aerosol pH and water content as indicators for PM sensitivity to NH_3 and/or HNO_3 availability would be more of a static approach, therefore quite close to the G-ratio concept. Indeed, it looks at the status of the aerosol, which (as seen from the G-ratio) cannot tell about changes occurring when relatively large emission reductions are applied

Specific comments:

- Page 1, line 21 (and hereafter): Place 2.5 as subscript in $\text{PM}_{2.5}$ (i.e., PM_5).

Done as suggested.

- Page 2, line 55: Please rephrase. By definition, NMVOCs are not low-volatility.

We rephrased as: "a vast range of NMVOCs"

- Page 2, lines 58-76: Important studies regarding the effectiveness of NH₃ reductions to control PM concentrations are Pozzer et al. (2017);Guo et al. (2018);Nenes et al. (2020).

Thanks for the suggested references, they have been added.

- Page 2, line 81: You can also add Tsimpidi et al. (2016) for a detailed comparison of OA composition against AMS-measurements which elucidates important OA formation pathways that are still missing by the models

Thanks for the suggested reference, it has been added.

- Section 2: The methodology should include a model description. It is of prime importance to briefly present the details of the model such as the thermodynamic model used. A brief description of the organic aerosol framework is also important since the NO_x reduction can impact the oxidant levels and thus the SOA formation.

We added several paragraphs in the methodological section to address this point (see general comment - point 1)

- Pages 4, lines 170-176: Furthermore, low temperatures during winter favor the aerosol phase during the equilibrium partitioning of semi-volatile components (e.g. ammonium nitrate).

We added the sentence proposed by the Reviewer in the text.

The increased emissions from the residential sector (heating, especially wood burning) foster this process (Ricciardelli et al., 2017; Hakimzadeh et al., 2020). Wintertime low temperatures also favour the partitioning of semi-volatile components (e.g. ammonium nitrate) towards the particulate phase. Overall, the relative contribution of secondary inorganic particles (SIA) ranges between 40 and 50%, regardless of the season and is quite homogeneously distributed spatially over the entire area.

- Page 5, equations 5, 6: These belong to model description. Does the model include any heterogeneous chemistry?

Yes, it does. This aspect is now discussed in the methodological section (see general comment - point 1)

- Page 5 line 208: Correct "of" with "or"

Done as suggested.

- Page 8, equations 10-15: Are these included in the model?

Yes, these equations are included in the model. This aspect is now discussed in the methodological section (see general comment - point 1).

- Page 8, lines 327-335: Maybe it is worth drawing a map of the VOC/NO_x concentration

ratio to illustrate the NO_x-limited (i.e., with ratio values higher than 5.5) and NO_x-saturated areas of the model domain (Tsimpidi et al., 2008).

Saying that the chemical regime is VOC limited is in fact not enough. For a given NO_x reduction, we also need that the O₃ increase be stronger than the related NO₂ decrease (because of equation $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$). This is certainly the case for Bergamo with a 100 % increase of O₃ for -25% NO_x emissions. These changes are more related to titration, so simply the NO_x concentration is a good tracer, or NO₂ which we have already and which shows a maximum in both Milano, Bergamo region. We therefore believe that a VOC/NO_x map would not help in this context

- Page 8, line 330: correct "that" with "than"

Done.

- Page 8, line 333: Does the model include heterogeneous or aqueous phase production of SOA as implied here?

There are NO aqueous phase reactions of SOA. We mentioned this in the description of the methodology by adding the following paragraph:

Regarding secondary organic aerosols (SOA), the EmChem09soa scheme is used, which is a simplified version of the so-called volatility basis set (VBS) approach (Robinson et al., 2007; Donahue et al., 2009). The VBS mechanism is discussed in detail in Bergström et al. (2012). The main differences between the VBS schemes and EmChem09soa is that all primary organic aerosol (POA) emissions are treated as non-volatile in EmChem09soa. This is done to keep the emission totals of both PM and VOC components the same as in the official emission inventories. The semi-volatile biogenic and anthropogenic SOA species are assumed to further oxidise (also known as ageing process) in the atmosphere by OH-reactions. This will lead to a reduction in volatility for the SOA, and thereby increased partitioning to the particle phase. More information on SOA is given in Simpson et al. (2012), section 7.7.

- Page 17, Figure 1 (and hereafter): In order to improve the illustration of the plotted maps I suggest to increase the number of colors used, draw the border lines bolder, and move the color bars to the right of the figure (using only one instead of three).

Done as suggested.

- Pages 18-19, Figures 3, 5 (and thereafter): I suggest using diverging colors for the figures (e.g., shades of blue colors for negatives and shades of red colors for positives)

Done as suggested.

- Page 18, Figure 4: I suggest using diverging colors below and over the value of 1 for the G-ratio.

We agree that 1 would be the logic value to use as separator. However, we show that the G-ratio map is comparable to the regime map only when this separator is around 6. This is why we use this value to separate the low and high G-ratio areas. By the way, we changes the colour scale so that values within the "0-1" range appear explicitly.

- Page 20, Figure 6: Values are missing on the y-axis for Summer. The color-bar title is

also missing. Please add more value points in the color-bar as well.

Figure has been updated as suggested.

- Page 21, Figure 7: The color-bar is missing

Color bars have been added.

- Page 22, Figure 8: Please consider revising the map on the left. The way it is represented is not clear.

The map is indeed challenging because all values are small. As the scatter plots deliver this information already, the map has been removed.

- Page 26, Figure 13: Color-bar is missing

The color bar has not been added as precise values do not matter in this example but an explanation of the colors used has been added in the caption.

References:

Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., and Weber, R. J.: Effectiveness of ammonia reduction on control of fine particle nitrate, *Atmos. Chem. Phys.*, 18, 12241-12256, 10.5194/acp-18-12241-2018, 2018.

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Pozzer, A., Tsimpidi, A. P., Karydis, V. A., de Meij, A., and Lelieveld, J.: Impact of agricultural emission reductions on fine-particulate matter and public health, *Atmospheric Chemistry and Physics*, 17, 12813-12826, 10.5194/acp-17-12813-2017, 2017.

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Tsimpidi, A. P., Karydis, V. A., Pandis, S. N., and Lelieveld, J.: Global combustion sources of organic aerosols: model comparison with 84 AMS factor-analysis data sets, *Atmos. Chem. Phys.*, 16, 8939-8962, 10.5194/acp-16-8939-2016, 2016.