Response to Reviewer #3

We thank reviewer for his thoughtful comments and suggestions that have helped to significantly improve this manuscript.

The reviewer's comments are shown in *blue italics* with the author responses in black.

This study develops and presents top-down estimates of high temporal (up to hourly) PM2.5 emissions using an ENKS. The goal of this study is adequate for a publication in this journal, and I expect this research would inspire other researchers and would lead to further advances in top-down estimates of pollutant emissions. However, there are some parts that can be misleading or need to be clarified. Also, I agree with two other reviewers who raised important issues, which are as follows.

1. It is not clear how secondary PM2.5 is ignored. Did you just assume that the increments or differences resulting from PM2.5 assimilation are all attributed to PM2.5 emissions? Or, the formation of secondary PM2.5 is ignored in the WRF-Chem modeling? I agree with the first reviewer who emphasized the importance of secondary PM2.5 formation. The authors should demonstrate how the ignorance of secondary PM2.5 can be justified and what potential errors are.

Thank the reviewer for the valuable comment. We agree with both Reviewer #1 and Reviewer #3 that secondary aerosol is important to observed $PM_{2.5}$ and $PM_{2.5}$ precursors (SO_2, NH_3, NO_x, VOC) play crucial roles in the formation of secondary aerosol. We did not clearly describe the assimilation process related with the secondary formation. As Reviewer #1 commented, the aerosol secondary formation is captured by the WRF-Chem model, while the $PM_{2.5}$, O_3, NH_3, and $PM_{2.5}$ precursors that have observations (SO_2 and NO), are updated by the observed quantities, respectively, but the VOC that are also $PM_{2.5}$ precursors are not updated due to the lack of direct and limited observations.

The detailed updated chemical variables and emission species follow Peng et al. (2018). Six conventional air pollutant observations (i.e., PM_{10}, $PM_{2.5}$, SO_2, NO_2, O_3, and CO) are obtained from the Ministry of Ecology and Environment of China. The concentrations and emissions related to the six observations are constrained by the observed quantities. $PM_{2.5}$ observations are used to constrain the mass concentrations of $P_{2.5}$ (the fine unspeciated aerosol contributions), S (sulfate), OC_1 (hydrophobic

organic carbon), OC_2 (hydrophilic organic carbon), BC_1 (hydrophobic black carbon), BC_2 (hydrophilic black carbon), D_1 (dusts with effective radii of 0.5 μm), D_2 (dusts with effective radii of 1.4 μm), S_1 (sea salts with effective radii of 0.3 μm) and S_2(sea salts with effective radii of 1.0 μm). Besides, the emissions of the unspeciated primary sources of $PM_{2.5}$, sulfate, nitrate and NH_3 are also updated. $PM_{10\text{-}2.5}$ observations (the differences between the PM_{10} observations and the $PM_{2.5}$ observations) are used to constrain the mass concentrations of P_{10} (the coarse-mode unspeciated aerosol contributions), D_3 (dusts with effective radii of 2.4 μm), D_4 (dusts with effective radii of 4.5 μm), D_5, S_3(sea salts with effective radii of 3.25 μm), S_4 and the emission of PM_{10}. SO_2 observations are used to constrain the SO_2 concentrations and emissions. NO_2 observations are used to update the NO and NO_2 concentrations and NO emissions. CO observations are used to constrain the CO concentrations and emissions, while O_3 observations are used to constrain the O_3 concentrations.

To clarify the details of the assimilation process and the treatment for the secondary formation, the text in Lines 171-177, Page 7, is added. The details of the updated chemical and emission species follow Peng et al. (2018), which is not include in the text.

"Since the secondary formation process can be captured by the WRF-Chem model, the impact of the secondary $PM_{2.5}$ is indirectly considered. The detailed updated state variables with the according observations follow Peng et al. (2018). The concentrations and emissions of $PM_{2.5}$, NH_3, and $PM_{2.5}$ precursors that have observations (SO_2 and NO), are updated by the observed quantities, respectively, but the VOC that are also $PM_{2.5}$ precursors are not updated due to the lack of direct and limited observations."

2. Related to the first comment and also commented by the second reviewer. Is PM2.5 concentration also updated? Or just PM2.5 emission?

Thank the reviewer for the insightful suggestion. In our reply to the previous comment, both $PM_{2.5}$ emissions and their corresponding concentrations are updated in the DA experiments.

3. I seriously doubt the diurnal variations in PM2.5 emission (Fig. 6). Many studies assume that high emission rates during daytime (working hours) and low emission rates during nighttime as in Fig. 8. I think the highest emission rate in the morning in Fig. 6

is attributable to 1) high emission during rush hours and 2) shallow boundary layer. In other words, the diurnal variations in PM2.5 emissions estimated in this study do include the effects of time-varying boundary layer (and height). So, the effects of boundary layer are not separated from the emission estimates. We would expect high emission rates in the afternoon (working hours) and also during the late afternoon (evening rush hours). Because boundary layer height is generally highest in the late afternoon, the estimated emission rates in the late afternoon are too low (Fig. 6). I think monthly emission estimates or yearly estimates would be fine because the diurnally varying boundary layer is all averaged out at monthly and yearly time scales. To verify this, you can take a closer look at emission rates near industrial complex where diurnal variations in emissions are expected to be small (e.g., power plants, steel and cement companies …). I understand the horizontal grid of 45 km is too coarse to examine this, but I expect that there are some regions where many factories are concentrated.

Thank the reviewer for the insightful comment and suggestion. We performed an observing system simulation experiment (OSSE) to investigate the effects of time-varying boundary layer. A nature run is first conducted from 0000 UTC 25 December 2015 to 0000 UTC 2 February 2016, forced by the time-invariant source emissions PR2010 (the true emission). Synthetic observations of the six conventional air pollutant concentrations (i.e., PM_{10}, $PM_{2.5}$, SO_2, NO_2, O_3, and CO) are generated from the natural run. Hourly synthetic observations are created from 0000 UTC 29 December 2015 to 0006 UTC 1 February 2016, by interpolating the gridded true surface concentrations to the chemical observation locations with additive random errors of $N(0,R)$. R is the observation error variance, which is calculated by the formula in Elbern et al. (2007). Outputs from the first four days of the natural run are excluded to avoid the transient effect. Then the prior emissions are generated by $\mathrm{F}^{pr} = \left(1.8 + \delta(x,y,z,t)\right)\mathrm{F}^{tr}$, where F^{tr} is the true emission, δ is a random number sampled from the normal distribution $N(0,1)$ (Peng et al. 2015). Ensemble data assimilation experiments are conducted from 0000 UTC 29 December to 0006 UTC 1 February 2016. Outputs from the first two days of the OSSE are excluded due to the spin-up.

Figure S1 presents the monthly mean diurnal variations of $PM_{2.5}$ emission fraction from the OSSE. Please note that the magnitude of posterior $PM_{2.5}$ emission is closer to the

true emission than the prior. Figure S1 shows that a little larger estimated $PM_{2.5}$ emission fractions occurred in the morning and smaller estimated $PM_{2.5}$ emission fractions occurred in the afternoon, comparing to the time-invariant true emission. This result is consistent with the reviewer's expectation. But the diurnal variations of $PM_{2.5}$ emission fractions caused by the boundary layer are not as strong as that caused by the emission itself (original Figure 6).

Since we have hourly assimilated observations to simultaneously update the chemical concentrations and source emissions, the impacts of time-varying boundary layer on the posterior $PM_{2.5}$ emissions are limited. Nevertheless, the influences of time-varying boundary layer are still important to $PM_{2.5}$ emission estimates. Thus, the diurnal variations of $PM_{2.5}$ emission fractions are updated to exclude the impacts of time-varying boundary layer, following the reviewer's suggestion. We modified Figures 7 and 8, and Table 2, to reflect the revision.

Compared to the diurnal variations of $PM_{2.5}$ emission fractions estimated based on diurnal variation profiles from US and EU (Wang et al., 2010), the estimated $PM_{2.5}$ emission fractions are 1.25% larger during the evening, which greatly changes the diurnal variations of DEPE. In fact, the smaller evening peaks of Wang et al. (2010) occurred in November, December, January, February and March, while they are almost indistinct from April to October, similar to that from DEPE.

The text in Lines 271-281, Page 10, and Appendix is added. The manuscript is updated by considering the effects of the boundary layer.

Elbern, H., Strunk, A., Schmidt, H., and Talagrand, O.: Emission rate and chemical state estimation by 4-dimensional variational inversion, Atmos. Chem. Phys., 7, 3749–3769, https://doi.org/10.5194/acp-7-3749-2007, 2007.

4. Related to the effects of meteorology (or boundary layer), I would suggest some extra experiments (also related to the first reviewer's 4th minor comment asking "weather effects"). Let's fix anthropogenic emissions all the time, and only consider time-varying meteorology. Assume the observations that will be assimilated here are the model outputs with the same emissions but time-varying meteorology (not real observations). Then, assimilate these fake observations (actually model outputs) and estimate emissions. Would your estimated emissions be almost identical to the prior emissions that are fixed with time? I'm curious if your estimated emissions depend on / are

influenced by meteorology. A month-long simulation would be enough for this type of simulation.

Thank the reviewer for the insightful suggestion. In our reply to the previous comment, an OSSE was performed to investigate the impacts of time-varying boundary layer on the diurnal variations of $PM_{2.5}$ emission fractions. The results indicate that the diurnal variations of the estimated $PM_{2.5}$ emission fractions from the OSSE do deviate from the true time-invariant emissions, although the magnitudes are not as large as those caused by emission itself. The diurnal variations of $PM_{2.5}$ emission fractions are updated by excluding the effects of time-varying boundary layer, following the reviewer's suggestion.

5. line 306-307. Did you mean that emissions in 2019 were higher than those in 2020? I think in 2020 there were few firework activities due to the lockdown. If this is true, the color for BTH and SCR in Fig 11e should be blue (lower emissions in 2020 than in 2019). If not, please clarify. In addition, some studies highlighted that the PM2.5 concentration during Feb. 2020 is due to unfavorable meteorological condition in the BTH region (Sulaymon et al. 2021). Le et al. (2020) also showed that for the severe haze in northern China during the lockdown is due to 1) anomalously high humidity that promoted aerosol heterogeneous chemistry, 2) stagnant airflow 3) uninterrupted emissions from power plants and petrochemical facilities, and 4) secondary aerosol formation associated with increased ozone.

Thank the reviewer for pointing out this mistake. The massive emissions from firework burning on the Chinese New Year Eve of year 2019 occurred on February 4, 2019. But in the following 7-day spring holidays, the smaller $PM_{2.5}$ emission rates are obtained (Figure 10). The possible reason of the increased PM2.5 emissions for BTH and SCR in 2020 is the long national vocation of spring holiday of year 2019. We changed the sentence in Line 356, Page 13.

We agree with the review that although there were significant reductions of $PM_{2.5}$ emissions over the central and northern China in February 2020, a severe air pollution event occurred over the north China in early February 2020. Previous studies have shown that the factors influencing the severe air pollution event include the still intensive emissions from industrial, power and residential, unfavorable meteorological condition, anomalously high humidity that promoted aerosol heterogeneous chemistry,

and secondary aerosol formation associated with increased atmosphere oxidants (Le et al. 2020; Sulaymon et al. 2021; Li et al., 2021). This discussion is added in the text at 363-369, Page 13.

6. Constant emissions can be misleading (line 149, line 183, line 233…). Did you mean time invariant emissions? That is, emission rates do not vary with time at all at a grid cell. If so, I would recommend saying time-invariant emissions or constant emissions with time because the constant emissions can be interpreted as spatially homogeneous emissions.

Thank the reviewer for the insightful comment. We mean time invariant emissions and we have changed *constant* emissions to *time-invariant* emissions in the revised manuscript.

7. Figure 9. The x-axis label should be date, not time, right? And recommend representing mm/dd, format.

The x-axis label is Date. We have changed this figure.

References

Sulaymon et al. 2021. Persistent high PM2.5 pollution driven by unfavorable meteorological conditions during the COVID-19 lockdown period in the Beijing-Tianjin-Hebei region, China. Environmental Research. https://doi.org/10.1016/j.envres.2021.111186

Le et al. 2020. Unexpected air pollution with marked emission reductions during the COVID-19 outbreak in China, Science. DOI: 10.1126/science.abb7431