We would like to thank the reviewer for the constructive comments and feedback on our manuscript. We considered all comments and have revised our manuscript accordingly. We provide below a point by point response to the comments. Reviewer comments are shown in *italic* and our responses follow.

Reviewer 2

Main comments

Comment 1:

The abstract and conclusions (line 481) emphasize K^+ levels drove the higher pH/less acidic nature of aerosols at IOA. How was that effect identified? Is that based on previous knowledge or a specific calculation/test? The K^+ as a driver of seasonality seems to be a separate conclusion supported by Figure 6 (line 490).

Response:

Indeed K^+ importance as a driver of aerosol pH in IOA is supported by the seasonality sensitivity (Fig 6) but it is not the only factor affecting the aerosol pH. We based our conclusion on the comparison of the aerosol pH and K^+ concentrations among the studied sites. In addition, Kaskaoutis et al. (2022) presented and analyzed the observations from IOA and found that residential wood burning was the dominant source of the aerosol in winter and that the accumulation process of the pollutants was further promoted by the meteorological conditions in the area.

The relevant text in the revised manuscript is now:

"The effect of K^+ ($\Delta pH=0.53$), sulfates ($\Delta pH=0.45$) and Ca^{2+} ($\Delta pH=0.43$), followed by organics (0.22), RH (0.21) and Na^+ (0.06) were also notable. High concentrations of K^+ affecting the aerosol pH are associated with biomass burning as discussed in Kaskaoutis et al., (2022)."

Comment 2:

How do organics affect inorganic species in ISORROPIA-lite? Section 3.2.3: What interaction cause the unexpected decrease in pH when organics were removed? Are any of the organics dissociating acids? Does the organic water combine with the inorganic water for calculation of NHx and TNO_3 partitioning?

Response:

The detailed description of ISORROPIA-lite is provided in Kakavas et al. (2022).

Briefly, the organic aerosol contributes additional aerosol water to the system beyond what is derived from inorganic species alone. The effect of the organic aerosol in ISORROPIA-lite is to increase the aerosol liquid water content, which in turn is allowed to affect the partitioning of semivolatile inorganics. Dissociation of organic acids is not considered in the thermodynamic equations. The particle water associated with the organic aerosol (W_{org}) is parameterized through the hygroscopicity parameter (k_{org}; Petters and Kreidenweis, 2007):

$$W_{org} = \frac{m_{org}\rho_w}{\rho_{org}} \frac{k_{org}}{\left(\left(\frac{1}{RH}\right)-1\right)}$$

where m_{org} is the organic mass (in μg/m^3), ρ_{org} is the organic density (1.35 g/cm^3), ρ_w is the density of water, k_{org} (0.12) is the organic hygroscopicity parameter and RH the relative humidity.

In IOA, during the last period of the campaign, when RH was higher than 80%, the increase in aerosol liquid water content due to organics was very large leading to lower H^+ concentration in the aerosol water and therefore a higher aerosol pH. During the other days of the campaign, relative humidity was

lower and the increase in aerosol liquid water content due to organics was not strong enough to substantially affect the aerosol pH.
This part of the discussion now reads as follows:
" The decrease in aerosol pH when OA was present, was observed on all the other days in January when the lower relative humidity and the addition of OA did not raise the aerosol water to levels that would result in increased pH. As a result of the addition of OA in the model, the concentration of H^+ increased, as well as the associated aerosol water. However, the increase in aerosol water does not counterbalance the increase in H^+ concentration resulting in a more acidic aerosol (lower aerosol pH)."

Comment 3:
Line 448, line 508, and elsewhere regarding NOx emissions and nitrate: Womack et al. (2019) show that nitrate formation can be NOx or VOC limited. Consider that VOC emissions may govern total nitrate abundance. Do you know if nitrate in the airshed(s) is more sensitive to NOx vs VOC controls?

Response:
Existing studies conducted in Greece/include Greece suggest that the nitrate formation is strongly correlated with local NOx emissions (over the greater Athens area, Myriokefalitakis et al., 2024). Reducing NOx and other anthropogenic emissions in the area of Athens decreases $PM_{2.5}$ mainly by reducing secondary inorganic aerosols (including particulate nitrate) (Im and Kanakidou, 2012). Moreover, Tsimpidi et al. (2025) attributed observed declines in particulate nitrate in Europe over the past two decades largely to NOx emission reductions. Finally, Megaritis et al. (2013) found that the particulate nitrate over Greece is most likely sensitive to NOx emission controls and VOC controls have a much smaller impact.

These sentences have been modified as follows:
"Consequently, for the studied period the inorganic $PM_{2.5}$ levels at THI in winter would be reduced by limitation of HNO_3 formation, which depends on VOC and NO_x conditions, and NH_3 controls in summer."
"Our results show that HNO_3 levels (could contribute to) regulate $PM_{2.5}$ mass concentration which however was mainly composed by OA and sulfate, hence policies targeted to reduce $PM_{2.5}$ levels in Greece would be more effective by reducing HNO_3 levels (i.e. transportation sector) in addition to OA and sulfate."

Comment 4:
If a figure/analysis can be added to address the uncertainty introduced by the lack of complete gas-phase NH_3 and HNO_3 measurements, that would be useful. That could inform future work by letting the community know how precise they likely need to with estimated NH_3 and HNO_3 concentrations if they need to fill in that data due to lack of measurements. Did the authors consider an iterative technique in which an initial guess of gas-phase NH_3 and HNO_3 was used to construct total NHx and TNO_3 input to predict a new NH_3 and HNO_3 gas estimate and run until predicted aerosol NH4 and NO3 converged to measurements? Zheng et al. (2020) showed that the lack of NH_3 gas values can lead to an incorrect direction in the pH trend over time. It is unclear what size error in NH_3 is acceptable.

Response:
Regarding the initial conditions of the semi volatile species used in the model, gas phase NH_3 and HNO_3 were used. This input data originates from in situ, and satellite measurements of the gas phase, as well as in situ measurements of the particle phase (NH_4^+, NO_3^-). (see the revised supplementary Table S2).

The use of gas phase NH_3 and HNO_3 concentrations in the thermodynamic model is now clearly stated in Section 2.3.
"Daily values were used as input to the model. These were gas phase (NH_3, HNO_3) and particulate phase (ions and OA) concentrations, OA hygroscopicity and density, and meteorological data (temperature and relative humidity)."

In section 3.4 we address the impact of gas phase NH_3 and HNO_3 uncertainty on aerosol pH calculation. We found a 0.25 pH units change when NH_3 was doubled and -0.19 when NH_3 was halved. This sensitivity is consistent with previous studies showing that a 10-fold change in NH_3 results in one unit change of aerosol pH (Guo et al., 2017; Weber et al., 2016). For HNO_3 a range between 0.01 to 0.15 pH units difference was found when half and double the amount of HNO_3 was used.

In the revised manuscript we added the following discussion at the end of Section 3.4, also addressing a relevant comment of the other reviewer:
"According to this sensitivity analysis, the uncertainty in the gas phase NH_3 could explain about half of the seasonal difference in aerosol pH that was presented and discussed in section 3.2.4 about the factors affecting the seasonality of pH. The uncertainty in gas phase NH_3 could explain a larger fraction of the seasonal difference in aerosol pH in IOA than in FKL and THI, which is expected since at these two sites aerosol pH seasonality was predominately driven by sulfates. Our results show a factor of 2 uncertainty in NH_3 lead to an average pH difference of 0.25 units that has minor impact on our findings discussed below."

Regarding the iterative technique, we did not apply such method in our study. However, we are aware that Ibikunle et al. (2024) examined if aerosol pH and gas-phase NH_3 can be constrained from measurements of NH_4^+, total nitrate and nitrate partitioning, with promising results for aerosol pH. The same study examined other iterative approaches proposed in the literature and showed that they could lead to numerical instability.

Minor comments

Comment 1:
Line 86: Define "neutral levels".

Response:
We added in parenthesis the neutral pH level.
"Negative values appear when sulfates are the dominant constituent of particulate matter, while the aerosol pH rarely rises above neutral levels (pH = 7)."

Comment 2:
Section 2.3: What time averaging was used for the input conditions to ISORROPIA-lite?

Response:
We thank the reviewer for this comment. Daily values were used as input in the model.
For clarity, we added the following sentence to the revised manuscript in section 2.3 (pH estimation):
"Daily values were used as input to the model. These were gas phase (NH_3, HNO_3) and particulate phase (ions and OA) concentrations, OA hygroscopicity and density, and meteorological data (temperature and relative humidity)."

Comment 3:
Line 360-361: Order the variable impacts from largest to smallest impact.

Response:
We changed the order and now the variables are mentioned from largest to smallest impact as suggested.

The text now reads:
"The availability of total HNO_3 ($\Delta pH=0.98$), temperature ($\Delta pH=0.76$) and the total NH_3 ($\Delta pH=0.59$) had the greatest influence on the seasonal aerosol pH difference."

Comment 4:
Line 431: Change "most insensitive" to "relatively insensitive" or "least sensitive".

Response:
We changed "most insensitive" to "relatively insensitive".

Comment 5:
Line 464: check wording.

Response:
The following revision to this sentence was made: "On the other hand, nitrate's deposition rate varies between fast (as gaseous HNO_3) and slow (as particulate NO_3^-), leading to local removal or long-range transport, respectively."

Comment 6:
In several figures (Fig 3, 6, 8), subplot labels on the figure would be useful.

Response:
We added the labels on the subplots as suggested.

Comment 7:
Does the inclusion of organics and their associated water substantially affect Figures 9-10?

Response:
We thank the reviewer for this comment. We included two figures (Fig. S6 and S7) in the supplement with the frameworks of Fig. 9 and 10 using the aerosol liquid water content calculated including the organics. In the main text we included the following comments:
At the end of 3.5.1:
"The inclusion of the OA in the aerosol pH and water calculations resulted in a small difference in terms of these sensitivity maps. As the aerosol water increased slightly, in a few cases in XAN the PM sensitivity was shifted from insensitive to HNO_3 sensitive, while in a few cases in IOA and FKL, PM also became sensitive to NH_3 (Fig. S6)."
At the end of 3.5.2:
"Including the OA in the calculations did not change as much the deposition rates (Fig. S7). In a few cases during January in THI and PTR the deposition rate of HNO_3 shifted from fast to slow due to the addition of OA water."

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