

We would like to acknowledge the reviewers for the time and effort in critically evaluating the manuscript. We have considered their suggestions and remarks, made answers to the reviewers' questions, and carefully modified the manuscript according to the revision comments.

Reviewer 1

The manuscript titled "Chemical characterization of cloud water at Monte Cimone (Italy): impact of air mass origin and assessment of atmospheric processes" presents a detailed description on the cloud water chemistry in Italy mountaintop by emphasizing the significant impact of air mass sources. In general, this study shows a very comprehensive analysis of inorganic and organic ions, dissolved organic carbon (DOC), H₂O₂, trace metals and microbial cells in the collected 26 cloud water samples. I very appreciate the field work and valuable data provided by the authors. Although the authors show nearly all matters about individual samples, I have some concerns regarding the logical structure, figures/tables organization, and reasonable explanations. Substantial revision is still necessary for a better readability. My comments, either major or minor, are listed below in the order of main text.

We thank the reviewer for the constructive comment and we worked on the text, especially section 3.1 to rearrange the discussion and the storyline.

1. The abstract summarized the three types of origins of cloud chemistry with major ions, but didn't mention the other important subsections studied, for example the oxidants, DOC, metals and microorganisms. That partial abstract will mislead my first view of this paper. Please revise the abstract with key findings of cloud components.

We have revised the abstract following the reviewer's suggestions by adding more information about DOC and H₂O₂ in the description of the three periods in line 39-40.

Lines 39-40: "Across the campaign, DOC ranged from 1.6 to 4.3 mgC L⁻¹ while H₂O₂ reached its maximum during period 3 (71.8 ± 35.4 μmol L⁻¹), highlighting enhanced oxidant levels under polluted conditions."

2. Page 6, line 132, and Table S4, Figure 6: as the BOOGIE cloud impactor is made by aluminum (Vaitilingom et al., 2025), it may contain other metals besides Al. For example, the blank sample had a concentration of Cu, Mn, and Sb higher than that of cloud samples as shown in Table S4. Therefore, when the authors discuss the metals in cloud water in section 3.5, please make it clear that if the sample concentrations have deduced the blanks, and if the high blanks of some metals affect the conclusion. That is to say, could we believe the determined concentrations of specific metals with high blanks for cloud water sampler.

Section 2.3 (line137) has been revised to provide additional clarification on the use of the blank. It was not subtracted from the cloud water samples because some samples exhibited concentrations lower than those measured in the blank. The relatively high concentrations of Cu, Mn, and Sb observed in the blank can be explained by the blank collection procedure. It was prepared in clear-sky conditions by spraying MilliQ water onto the clean cloud collector. During this process, atmospheric particles, with a concentration of 766.6 ± 24.0 #/cm⁻³, may have dissolved into MilliQ water, thereby increasing the concentrations of certain trace metals. For this reason, we considered it more appropriate to focus on relative proportions rather than on absolute differences between the blank and the cloud water samples.

Line 137-140: "The result in section 3.5 presents the comparison between blank and cloud water samples: as some samples had values below the blank, the blank was not

subtracted. As the blank is prepared in clear sky conditions, atmospheric particles, with concentration of $766.6 \pm 24.0 \text{ \#/cm}^3$, may dissolve into MilliQ water, thereby increasing the concentrations of certain trace metals.”

- Section 2.4.1: Here the authors provided the measurements of trace gases. I am also interested in SO₂, the important precursor of sulfate, for comprehensive understanding. Is that possible to add the information of SO₂?

SO₂ concentrations are measured continuously at the observatory and data are available at GAW website. However, as shown in Figure 1 below, SO₂ levels remained very low throughout the sampling period and most of the time below the nominal detection limit of 0.11 ppb. Given these low concentrations, SO₂ is unlikely to have a significant impact on the concentration measured of SO₄²⁻ in the cloud water samples.

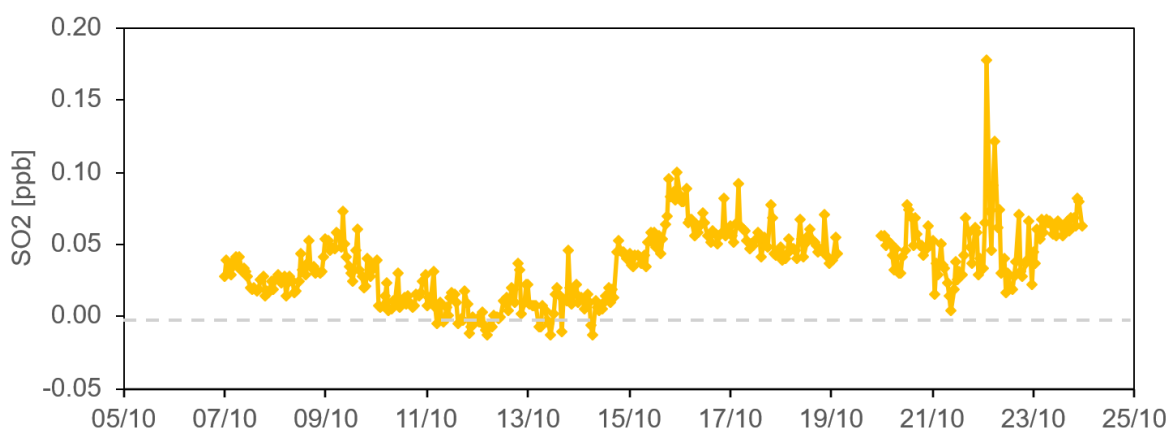


Figure 1: Temporal evolution of SO₂ during the campaign.

- Section 3.1 is an important part of the paper, but it is too detailed and sometimes verbose for me to follow. I am afraid that most of the discussed figures are in the supporting information, rather than Figure 1 in the main text, which is the most inconvenient thing to be improved. I suggest to add a time-series figure of the full set of major chemical compositions (like Fig. S5 and Table S2) to the main text. The pies in Figure 1 should have different size indicating their relative concentrations. Also, why does Figure 1 only show 6 out of 8 measured ions and exclude DOC?

We appreciate the reviewer’s comments regarding Section 3.1. The section was rearranged substantially to improve the readability and narrow its focus. Following the reviewer’s suggestion, we have moved Fig. S5 to the main text, as suggested, it is now Figure 2. We chose not to modify the size of the pie charts in Figure 1, as scaling them proportionally would have made it difficult to read. The reviewer pointed out that only six out of the eight measured ions are presented in Figure 1 and we excluded DOC. The contributions of Mg²⁺ and K⁺ were negligible during all three periods (consistently below 3%), as shown in Table 1 of this document. For this reason they were not included in the pie plots. Nevertheless, as suggested, we have included DOC relative concentration as a text in the three periods in Figure 1 of the manuscript, as reported below.

Period	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	K ⁺
1	34.0 %	9.0 %	4.3 %	30.7 %	11.9 %	4.7 %	2.1 %	3.3 %

2	7.2 %	14.9 %	11.2 %	7.9 %	22.6 %	32.1 %	1.7 %	2.4 %
3	25.0 %	16.4 %	11.6 %	22.1 %	13.5 %	8.4 %	1.5 %	1.6 %

Table 1: Percentage contribution of the analyzed ions in the cloud water samples for each period.

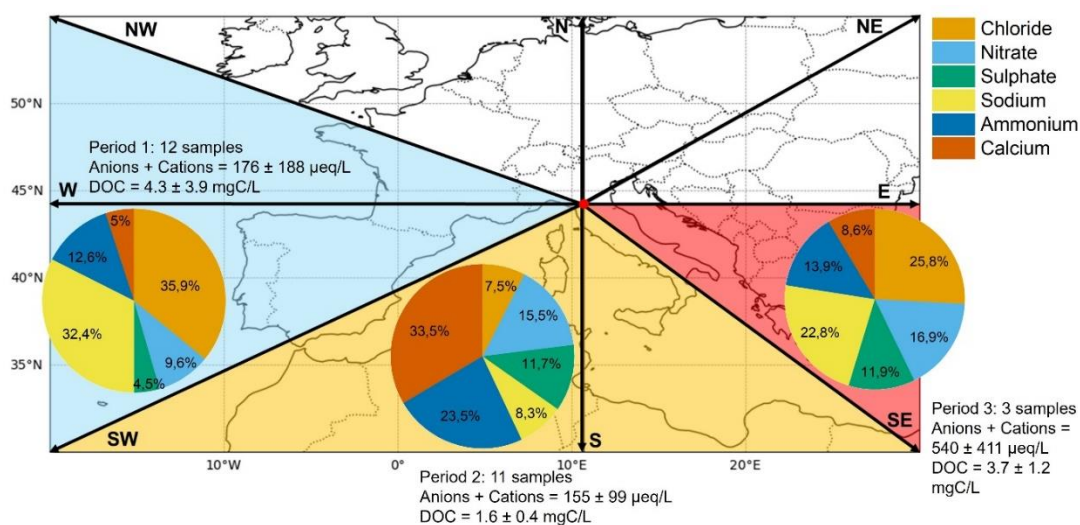


Figure 1 of the manuscript

- Why the main text did not explain Figure 2 or should Figure 2 be replaced by other type of figures?

As Figure 2 was only used to support specific points discussed in Section 3.1, it has been moved to the Supplementary Material, where it is now presented as Figure S5.

- Line 286: all ions concentrations of Period 2 are low, for which part? Cloud water, or PM1? Please show the concentrations of Ca^{2+} in Figure S5 for clarifying the dust effect on cloud and PM.

The full section was reorganized to better clarify the impact of dust on the chemical composition of cloud water, especially Ca^{2+} . Below, the reviewer may find a figure combining dust events and calcium concentration in cloud water. As highlighted in the correlation plot (Figure S7), Ca^{2+} concentrations increase during dust events. Nonetheless, high Ca^{2+} concentrations are also observed in the last period, especially on 22/10. This sample was not identified as a dust event based on aerosol measurements, which showed similar coarse and fine mass concentrations. This may indicate mixed sources during the entire Period3. The present figure was not included in either the main manuscript or in supplementary to avoid overloading the manuscripts with figures.

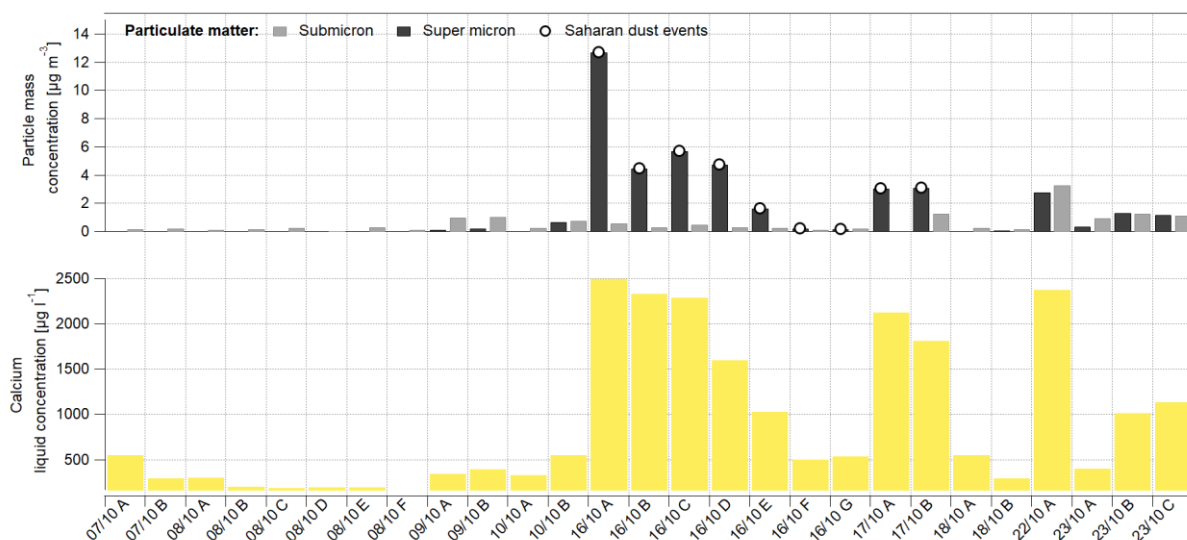


Figure 2 Temporal evolution of particle mass concentration and calcium liquid water concentration.

- Line 348: “Nevertheless, the absence of Cl^-_{PM} and the depletion of $\text{NO}_3^-_{\text{PM}}$ in particles, compared to cloud water, attest the marine input, similarly to samples of Period 1.” Why SO_4^{2-} in particles are due to pollution but NO_3^- is depleted? And is it possible that the Cl^- depletion in particles can be further discussed for atmospheric conversion?

A more detailed analysis on the $\text{NO}_3^-_{\text{PM}}$ indicates a slight increase in Period 3 (average period 3) compared to the rest of the campaign (average period 1 and 2), so $\text{NO}_3^-_{\text{PM}}$ is not depleted.

The statement at line 343-347 was modified as: “The low NO/NO_2 ratio (Figure S6) and $\text{NO}_3^-_{\text{PM}}$ average concentrations ($0.08 \pm 0.01 \mu\text{g}/\text{m}^3$, the highest of the campaign) would suggest the occurrence of relatively aged anthropogenic emissions.”

Regarding Cl^- , it does not vary significantly across the whole campaign, including period 3. Hence, we could not provide more insight on Cl^- conversions or other cloud-aerosol related processes. Hence, the statement at line 348 was removed.

Regarding $\text{SO}_4^{2-}_{\text{PM}}$, when the degree of neutralization, defined as the equivalent ratio of ammonium to the sum of sulphate, nitrate and chloride in PM is very low (0.55) and the amount of SO_4 is the highest, it explains that the pH reaches its lowest value and therefore the anthropogenic influence of the trajectory of 22/10.

The sentence at line 352-353 was modified as: “However, it decreases to 4.1 on 22/10, coinciding with peak $\text{SO}_4^{2-}_{\text{PM}}$ and a low neutralization degree, which confirms that this sample is under continental influence with anthropogenic input.”

- Line 395: “The concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is below...”, please reword this statement to avoid misleading of the measurement of total dissolved Fe rather than speciated Fe ions in this study.

As suggested by the reviewer, this statement has been reworded.

Line 393: “The concentration of total iron is below $0.3 \mu\text{mol L}^{-1}$ ”

- Lines 408-414: I did not find SO_2 concentration in Figure S1. The high concentrations of H_2O_2 were attributed to direct industrial emission. Can you estimate how long time

will the released H₂O₂ exist in the atmosphere and transport to the observation site at which concentration level?

SO₂ concentrations are not reported in Figure S1, because they are always below 4.7 ppb and thus not significant for H₂O₂ depletion.

The concentration of 104 μM in sample 22/10 is potentially due to the release of hydrogen peroxide from the industrial plant of Rosignano Solvay, the biggest producer of peroxides and hydrogen peroxide in Europe. The plant is also a major producer of sodium carbonate and bicarbonate, but no sulfur-containing products are produced at this site.

It is extremely difficult to estimate the concentration at the source point without using a 3D atmospheric model, which is beyond the scope of this work. We tentatively estimate the losses due to H₂O₂ photolysis using the distance between the two locations as the crow flies (96.75 km) and the differential equation

$$\frac{d[H_2O_2]}{dt} = -J[H_2O_2]$$

Where J is the photolysis rate in s⁻¹. This one was estimated from the simulations presented in Pailler et al. (2023) for a location with similar actinic flux (same latitude) between 10 AM and 4 PM. If we considered an average wind speed of 6 m/s, the time needed to cover this distance is ≈ 4.5 h. Since the sampling started at 4.30 PM (local time) we can assume that the corresponding emission was around noon. The numerical resolution of the differential equation gives a concentration of H₂O₂ at the source point of 113 μM. Nevertheless, this calculation is based only on H₂O₂ photolysis, without considering dilution through air mass mixing. Moreover, we considered only “in cloud” photolysis, but cloud could have appeared hours after the emission.

Given these limitations, this estimate should be interpreted with caution, and no modification have been made to the article.

10. Line 426: “Figure 4a reports in yellow the concentration in daytime samples and in blue in night-time. The concentrations in night-time samples are generally higher than in daytime samples, except for sample 16/10 G, collected at sunset.” The sentences are redundant to the caption of Figure 4.

As suggested by the reviewer, to avoid repetitions between line 417 and Figure 4, the caption was revised.

Lines 994-999:” Figure 4: a) Boxplot of hydrogen peroxide concentration in cloud water. b) Correlation between nitrate concentration (left y-axis, black dots) or sulphate concentration (right y-axis, red circles) and hydrogen peroxide in cloud water. The linear correlation is reported in grey for nitrate and in red for sulphate, with 95% confidence intervals. Equations and coefficient of determinations are reported in the inset tables”

11. Please revise the caption of Figure 3 to be more concise.

The caption of Figure 3 has been revised to be more concise.

Lines 987-991:” Figure 3: Biplot of the principal component analysis (PCA) performed on cloud samples collected at CMN. Loadings represent the ions, scores represent the samples. Colored areas depict the different classes of samples: plain, Saharan,

polluted/continental, highly marine, and, highly marine or polluted. The blank sample is reported in red. The red arrow highlights the depletion of Ca^{2+} during the cloud event 16/10.”

12. What does the error bar mean in Figure 4a for individual sample? Set the same y-axis scale for nitrate and sulfate concentrations in Figure 4b using only left y-axis.

The error bar in Figure 4a for individual sample represents the analytical error between 3 measurements on each sample. As suggested, the same y-axis scale for nitrates and sulphate concentrations was modified according to the reviewer’s comment.

13. Line 430 suggests the positive correlations between H_2O_2 and nitrate or sulfate. It is contrast to line 414 stating low SO_2 concentration to explain high H_2O_2 . Can we imagine that H_2O_2 had similar anthropogenic sources with other pollutants?

We agree with the reviewer that SO_2 and H_2O_2 could have similar sources and we checked the potential emissions of SO_2 in the region of interest. As explained in point 9, the industrial plant in Rosignano Solvay is also leader in the production of sodium carbonate and bicarbonate, but no sulfur-containing products are produced at this location.

The emission and formation pathways of H_2O_2 is highly uncertain, especially due to multiphase chemistry, as recently summarized by Duan et al., (2025). Considering the conditions at the Cimone stations, characterized by frequent cloud formation, variable atmospheric circulation and strong diurnal variability of the atmospheric boundary layer thickness, it is impossible to address univocally H_2O_2 emissions/formation with gas (NO_x and SO_2) and aerosol particles (black carbon, sulfate and nitrate) typically emitted by anthropogenic sources. Said that, a potential direct source could be leakage from the hydrogen peroxide production plant in Rosignano Solvay as discussed in the answer to Comment 9.

14. Figure 5: As it shows much less information and is discussed in 3 sentences in the main text, I suggest move it to SI.

We understand the reviewer’s concerns regarding Figure 5. While it is true that the figure is briefly discussed in the main text, we consider it important to retain it because our ongoing research focuses on the characterization of dissolved organic matter in cloud water (Pailler et al. 2024, Bianco et al. 2018). This figure serves to introduce our future work.

15. Section 3.6: there are too much short paragraphs, which can be shortened into about four paragraphs.

We agree with the reviewer that the reading is difficult with this separation and Section 3.6 has been modified into 3 paragraphs.

Lines 509-555:” Living microorganisms are ubiquitous in the atmosphere. Most of them originate from vegetation, soil and sea and can travel long distances (Griffin et al., 2001). It is thus particularly important to better understand their impact on cloud water, as they may modify cloud composition and reactivity (Delort et al., 2017). As reported in the Section 2.7, cloud samples dedicated to microbiological analysis are collected in sterile conditions. The two collectors deployed are operated almost at the same time. Nevertheless, some time differences are unavoidable, mainly due to the mounting and dismounting of the collectors. The precise sampling times are reported in Table S1. Tables S5 and S6 details the concentrations of culturable bacteria-like CFUs and

mycelial fungi, and total cells for each cloud sample in which a microbiological analyses are carried out.

Cell concentrations are highest during October 16th and 17th sampling events (samples A and B), ranging from $2.4 \pm 0.5 \times 10^5$ to $1.0 \pm 0.3 \times 10^6$ cells·mL⁻¹. This peak is likely explained by a Saharan dust event occurring on those dates, which transports large quantities of particles and likely increase the number of particle-attached microorganisms. Interestingly, culturable cell concentration do not follow this trend, with only 470 culturable cells·mL⁻¹ (including both mycelium and colony-forming units), a value very close to the median culturable concentration for the entire campaign (median = 470 cells·mL⁻¹; range = 400–563 cells·mL⁻¹). This sample is also one of only two in which bacteria-like CFUs outnumber mycelium-forming units, the other being collected on 07/10. However, this pattern does not appear to be related to air mass origin, as the two samples are under Saharan and marine influence, respectively. Samples influenced by marine air masses contained 8.0×10^3 to 4.1×10^4 cells·mL⁻¹, approximately one order of magnitude lower than in Saharan-influenced clouds. These concentration differences are associated with the altitude of air mass transport over the Mediterranean Sea. In comparison, polluted clouds contain between 3.1×10^4 and 1.4×10^5 cells·mL⁻¹. These values are within the range of concentrations typically observed in cloud water at puy de Dôme 1465 m, Central France, a site exposed to air masses from oceanic and continental influences), between $\sim 3 \times 10^3$ to $\sim 3 \times 10^5$ cells/mL. Typically, it is reported that the abundance of airborne microbes increases with increasing influence of terrestrial sources (Mayol et al., 2017), and is higher in urban than continental and coastal contexts (Shaffer & Lighthart, 1997). Values as low as $< 10^3$ bacteria cells/m³ of air are reported near the surface over oceans (Mayol et al., 2017; Rossi et al., 2025). Consecutive sampling on 17/10 (2-hour interval, same cloud event) reveals marked differences in culturable microbial concentrations (20 vs 63 bacteria-like CFUs·mL⁻¹, and 427 vs 163 mycelium-forming units for samples A and B, respectively), despite no significant variation in total cell concentrations (2.4×10^5 vs 2.9×10^6 cells·mL⁻¹). This illustrates the dynamic nature of clouds, even on short timescales: while total microbial abundance may remain relatively stable, community viability and culturability can fluctuate rapidly, likely due to environmental change or microphysical processes within the cloud. Consistently with our observations, it is typically observed that much fewer than 1% of the total bacteria in clouds can be recovered by culture under classical conditions, while fungi often maintain higher cultivability rate (e.g., Vaitilingom et al., 2012). The ability of microbial cells to form colonies (i.e. grow on a culture medium) can be affected by many parameters, including viability, culture conditions, and others less understood mechanisms leading to a viable-but-non-culturable (VBNC) state (Pinto et al., 2015), which is often recognized in bacteria as a strategy to tolerate stressful conditions (Dong et al., 2020).

Overall, cell concentrations measured at Monte Cimone are consistent with those reported at other cloud sampling sites ($\sim 10^3$ to 10^5 cells·mL⁻¹) (Amato et al., 2005; Bauer et al., 2002; Sattler et al., 2001). On average, cultivable cells represent only 0.5–6% of the total community, a proportion commonly observed in atmospheric samples (Amato et al., 2007). Although they represent a small fraction of the total microorganisms present in samples, cultivable organisms remain essential for downstream applications such as laboratory experiments (e.g. Vaitilingom et al., 2013) or cloud simulation chamber studies (e.g. Amato et al., 2015).”

16. Line 540: it seems that air masses originating from continental areas contain one order of magnitude more microbial cells. Besides the altitude, can you find data or literatures comparing the abundant of atmospheric microbials in land and marine areas to support your findings?

We thank the reviewer for this relevant comment. We indeed indicate that marine air masses carried « 8.0×10^3 to 4.1×10^4 cells·mL⁻¹, approximately one order of magnitude lower than in Saharan-influenced clouds”, and « In comparison, polluted clouds contain between 3.1×10^4 and 1.4×10^5 cells·mL⁻¹ ».

These values are within the range of concentrations typically observed in cloud water at puy de Dôme 1465 m, Central France, a site exposed to air masses from oceanic and continental influences), between $\sim 3 \times 10^3$ to $\sim 3 \times 10^5$ cells/mL. In general, the abundance of airborne microbes increases with the influence of terrestrial sources (Mayol et al., 2017), and is higher in urban compared to continental and coastal environments (Shaffer and Lighthart, 1997). Values as low as $< 10^3$ bacteria cells/m³ of air are reported near the surface over oceans (Mayol et al., 2017; Rossi et al., 2025).

This information has been added to the text (as, lines 530-536: “These values are within the range of concentrations typically observed in cloud water at puy de Dôme 1465 m, Central France, a site exposed to air masses from oceanic and continental influences), between $\sim 3 \times 10^3$ to $\sim 3 \times 10^5$ cells/mL. Typically, it is reported that the abundance of airborne microbes increases with increasing influence of terrestrial sources (Mayol et al., 2017), and is higher in urban than continental and coastal contexts (Shaffer and Lighthart, 1997). Values as low as $< 10^3$ bacteria cells/m³ of air are reported near the surface over oceans (Mayol et al., 2017; Rossi et al., 2025).” and the corresponding references were included.

17. Lines 546-549: can you further explain the primary factors influencing culturable microbials?

Thank you for raising this point. We propose to insert in the lines 542-548 the paragraph:

« Consistently with our observations, it is typically observed that much fewer than 1% of the total bacteria in clouds can be recovered by culture under classical conditions, while fungi often maintain higher cultivability rate (e.g., Vařtilingom et al., 2012). The ability of microbial cells to form colonies (i.e. grow on a culture medium) can be affected by many parameters, including viability, culture conditions, and others less understood mechanisms leading to a viable-but-non-culturable (VBNC) state (Pinto et al., 2015), which is often recognized in bacteria as a strategy to tolerate stressful conditions (Dong et al., 2020). »