

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

Reviewer 2:

This manuscript titled "Chemical characterization of cloud water at Monte Cimone (Italy): impact of air mass origin and assessment of atmospheric processes" examines the physico-chemical composition of cloud water at Monte Cimone, focusing on the role of air mass origin. The study presents valuable dataset covering a wide range of chemical components (e.g. major organic and inorganic ions, black carbon and dissolved organic carbon (DOC), trace gases, trace elements, and biological components) from 26 samples. The field work and the effort put into collecting and analyzing these samples are highly appreciated.

Overall, the manuscript provides useful and interesting results. However, some improvements in the abstract and the organization and clarity of explanations in the main paper would help make the paper easier to follow. My specific comments are listed below.

Specific comments:

1. The abstract mainly focuses on the three mass origins and major ions, but it did not mention other important components studied, such as oxidants, DOC, metals, and microbiological components. Since these are also key parts of the paper, it would be helpful to briefly include their main findings in the abstract to better reflect the full scope of the study.

We thank the reviewer for this suggestion. As reviewer 1 raised a similar comment, we have revised the abstract accordingly by adding further information on DOC and H₂O₂.

Lines 39-41: "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. In the abstract and conclusion, you mentioned that 26 cloud water samples were analyzed. But when I counted the cloud water samples in some figures (for example, in Fig. S3 upper panel, Fig. S5), I counted 27 samples. Could you clarify which one is accurate?

We agree with the reviewer's remark regarding the figure legend. We have corrected the label "23/10 A" to "23/10 Rain," as this sample corresponds to a rain event and not to a cloud water sample. Consequently, the study includes a total of 26 cloud water samples.

3. Line 256: "The composition is well balanced between inorganic ions (Cl⁻, NH₄⁺, NO₃⁻, and SO₄²⁻)". Could you clarify what is meant by well balanced? Does this refer to having similar concentrations? And also, is this for aerosol phase or aqueous phase? I am assuming aerosol phase, but please clarify and use the appropriate notation (PM or CW).

We agree with the reviewer that some formulations were not clear, and we rephrased the sentences accordingly. We used the term well balanced to indicate that the concentrations of inorganics species in the aqueous phase and aerosol phase are proportional. Notations have been corrected as suggested.

Line 257-260: "The marine influence is also confirmed by the sea-salt sulphate [ss SO₄²⁻] fraction, which averaged around 40% and reached up to 70% in individual

samples during Period 1. This is remarkably higher than in the other periods, where the average contribution remained below 10%, as shown in Figure S3”

4. Line 257: Did you calculate Cl depletion? It would be nice to quantify Cl depletion for each sample. You may refer to Edwards et al. (2024) for guidance on the calculations.

We thank the reviewer for this interesting comment. Based on the article by Edward et al 2024, we were able to calculate Cl⁻ depletion and find a value of 34.3 ± 20.3%. We used the following equations:

$$\%Cl_{Depletion}^{-} = 100 \frac{ssNa^{+} \left(\frac{Cl^{-}}{Na^{+}}\right)_{ss} - Cl_{bulk}^{-}}{ssNa^{+} \left(\frac{Cl^{-}}{Na^{+}}\right)_{ss}}$$

with ssNa⁺ calculated with the following equation :

$$ssNa^{+} = \frac{Ca_{bulk}^{2+} - Na_{bulk}^{+} \left(\frac{Ca^{2+}}{Na^{+}}\right)_{dust}}{\left(\frac{Ca^{2+}}{Na^{+}}\right)_{ss} - \left(\frac{Ca^{2+}}{Na^{+}}\right)_{dust}}$$

With :

- Cl_{bulk}^{-} , Ca_{bulk}^{2+} , and Na_{bulk}^{+} are the concentration of Cl⁻, Ca²⁺ and Na⁺ measured in the cloud water samples respectively.
- $\left(\frac{Cl^{-}}{Na^{+}}\right)_{ss} = 1.81$
- $\left(\frac{Ca^{2+}}{Na^{+}}\right)_{dust} = 1.78$
- $\left(\frac{Ca^{2+}}{Na^{+}}\right)_{ss} = 0.038$

The value found for Cl⁻ depletion are reported in Table 2:

	Chloride μmol L ⁻¹	Sodium μmol L ⁻¹	Calcium μmol L ⁻¹	ssNa ⁺ μmol L ⁻¹	% depletion Cl ⁻
071024 A CMN	15.2	30.2	13.9	22.9	63.2
071024 B CMN	3.8	12.5	7.4	8.5	75.6
081024 A CMN	11.9	11.2	7.6	7.1	7.0
081024 B CMN	8.6	6.9	5.1	4.1	0.0
081024 C CMN	6.7	11.1	4.8	8.5	56.6
081024 D CMN	26.5	21.5	4.9	19.2	23.5
081024 E CMN	25.9	23.1	5.0	20.8	31.1
081024 F CMN	37.0	31.5	4.1	29.9	31.5
091024 A CMN	84.8	70.4	8.7	66.9	30.0
091024 B CMN	107.0	99.1	10.0	95.5	38.1
101024 A CMN	55.8	43.0	8.3	39.1	21.2
101024 B CMN	289.2	246.9	13.9	244.3	34.6
161024 A CMN	8.3	11.6	62.3	0.0	0.0
161024 B CMN	2.9	6.5	58.3	0.0	0.0
161024 C CMN	3.4	6.1	57.2	0.0	0.0
161024 D CMN	1.0	2.9	40.0	0.0	0.0
161024 E CMN	3.6	2.6	25.7	0.0	0.0

161024 F CMN	<DL	1.0	12.7	0.0	0.0
161024 G CMN	<DL	3.0	13.5	0.0	0.0
171024 A CMN	24.2	26.4	53.0	0.0	0.0
171024 B CMN	26.1	28.9	45.2	3.6	0.0
181024 A CMN	0.9	4.9	13.9	0.0	0.0
181024 B CMN	1.2	2.1	7.4	0.0	0.0
221024 CMN	254.7	224.7	59.2	195.7	28.1
231024 Rain CMN	19.4	15.8	10.1	10.4	0.0
231024 B CMN	48.1	41.8	25.4	28.2	5.7
231024 C CMN	46.8	42.8	28.4	27.4	0.0

Table 2: Chemical Characterization of Cloud Samples (Major Ions, ssNa^+ and Cl^- Depletion).

5. Line 261: " Cl^- and NO_3^- ". Please clarify whether this refers to the aerosol or aqueous phase.

As requested by the reviewer, we have clarified the sentence.

6. Line 302: I am curious how the chemical species correlate to each other. Did you perform a simple correlation analysis between all the measured components (other than correlation shown in Fig. 4b, Fig. S3, and Fig. S7)?

We thank the reviewer for this very relevant question. We performed the same PCA as presented in Figure 3, this time including the ion concentrations from the aerosol phase. Magnesium, sodium, and calcium were excluded from the analysis because their concentrations were only available for the aqueous phase. The results, shown in Figure 2 of this document, show a strong correlation between the aerosol and aqueous phases for sulphate and ammonium. In contrast, nitrate and chloride do not exhibit a similar correlation. This discrepancy can be explained by the fact that Cl^- and NO_3^- measured in the cloud water are present as inorganic ions (NaCl and NaNO_3), which are not detected by ACSM (as shown line 268 from section (3.1)).

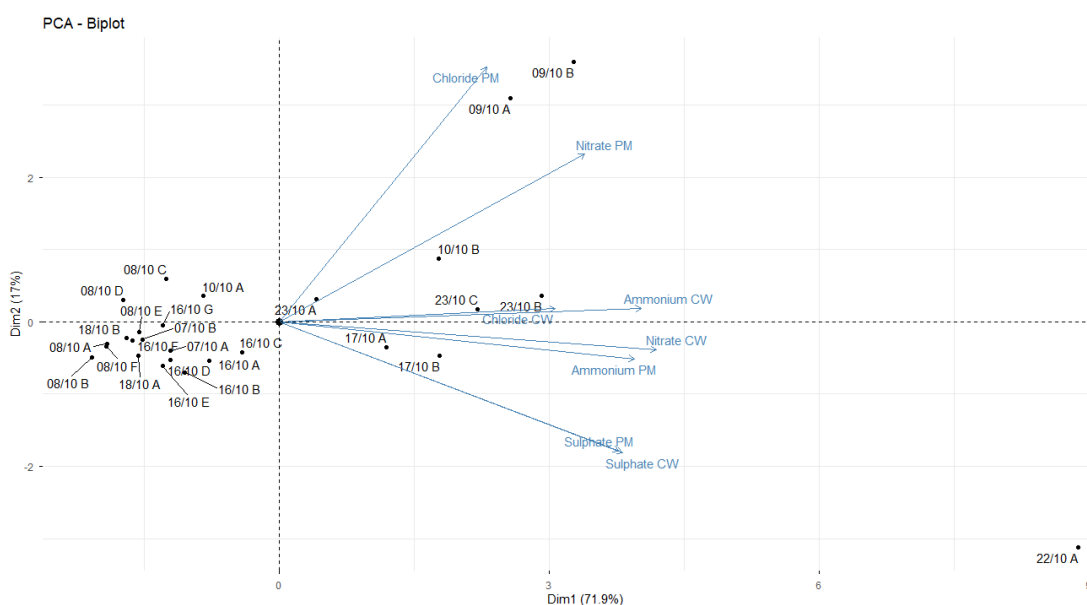


Figure 2: Biplot of the principal component analysis (PCA). Loadings represent ions from the aqueous phase and aerosols phase. Scores represent the samples.

7. Lines 439-441. You mentioned that “LWC is not measured during the campaign”, but then you proceeded with “the LWC for the last samples”. Please clarify this point.

The reviewer is right. We encountered an issue with the LWC measurements, as the instrument (PVM), kindly lent by TROPOS colleagues D. Van Pinxteren, S. Mertes and U. Käfer, did not arrive to Monte Cimone until 23/10. Consequently, no LWC measurements were not available prior to the last day of the campaign.

8. Line 980: For Figure 6a, did you correct the sample concentration for the blank concentration? The concentrations of Mn and Cu are a bit high, and some samples were even lower than the blank concentration.

As requested by Reviewer 1, we have provided additional information on the use of the blank. 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. It was prepared in clear-sky conditions by spraying MilliQ water on the clean cloud collector. During this process, 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. 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.

Technical comments:

Line 126: should be ‘TOC-VCPH/CPN analyzer’ instead of “TOCVCPH/CPN TOC analyzer”

The sentence has been modified.

Lines 248-252: The sentence is a bit confusing, consider revising.

The sentence has been modified.

Line 253: should be ‘PM_{TOT}’ instead of “total PM_{TOT}”

The spelling has been modified.

Lines 273-279: These lines can be shortened into two sentences to improve flow.

We thank the reviewer for this suggestion. The lines have been revised and shortened into two sentences to improve the flow of the text.

Line 422: “..reported by (Laj et al., 2001) and (Vione et al., 2003)” should be ‘reported by Laj et al. (2001) and Vione et al. (2003)’. Please check similar issues throughout the paper since I’ve seen a few like this.

We have taken the reviewer’s comment into account and corrected these issues.

Lines 426-428. Be consistent with the use of “daytime and nighttime” versus “day-time and night-time”.

The manuscript has been corrected to use “day-time” and “night-time” consistently.

Line 504: should be ‘hypothesis’ instead of “hypothesis”.

It has been corrected.

Line 969. It's hard to read the coefficient of determination in Figure 4b. Consider minimizing the significant figures to 2-3 and improve the quality of the figure. Nitrate and sulfate can also share the same y-axis since the range of values is similar.

The plot has been modified according to the reviewer's suggestions.

Line 974. For Figure 5 x-axis label, please be consistent with the samples naming convention. Use dd/mm instead of ddmmyy.

Figure 5 has been revised in accordance with the reviewer's comment.

Line 981. I don't think Figure 6c is mentioned in the main manuscript.

The reviewer is right, Figure 6c is now mentioned in the main manuscript (line 491), as well as Figure 6a (line 483) and Figure 6b (line 476).

Figure S3 (lower panel). Y-axis label should be 'Chloride' instead of "Cloride"

The plot has been modified according to the reviewer's suggestions.

In Tables S1-S3, you used the sample ID 23/10 Rain. Does this sample refer to 23/10A in Fig.S3 upper panel and Fig.S5? Please clarify.

We thank the reviewer for pointing this out. Sample 23/10 A has been renamed 23/10 Rain to maintain consistency across all figures.