Supplementary Material for

# Title: Chemical characterization of cloud water at Monte Cimone (Italy): impact of air mass origin and assessment of atmospheric processes.

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## Materials and Methods

Supplementary S1: Physicochemical analysis

*Ion chromatography:* Ion content was measured by ion chromatography (IC) analysis, using a Thermo ICS5000+ equipped with an IonPac AG18 (guard-column 4 × 50 mm) and an IonPac AS18 (analytical column 5 × 250 mm) for anions (formate, acetate, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $PO_4^{3-}$, oxalate) and an IonPac CG16 (guard-column 4 × 50 mm) and an IonPac CS16 (analytical column 5 × 250 mm) for cations ($Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$).

*Hydrogen Peroxide:* The spectrofluorimetric method based on the reactivity of p-hydroxyphenilacetic acid (purity > 98%) with horseradish peroxidase (solid containing 150-200 units per mg) and developed by Wirgot et al. was used to measure the concentration of hydrogen peroxide in cloud water.

*Dissolved Organic Carbon:* TC and IC are measured with a Shimadzu TOC-L analyser. TOC quantification is then obtained by the difference between the measured TC and IC.

*Carboxylic acids:* Short-chain carboxylic acids were analyzed using Ion Chromatography coupled with Mass Spectrometry (IC-MS, Thermo Scientific), utilizing a Dionex ICS-6000 platform, a single quadrupole mass detector, and a Dionex IonPac AS11-HC-4 μm analytical column (2 × 250 mm). The gradient elution was performed with KOH solution of varying concentrations at a constant flow rate of 0.36 mL $min^{-1}$. The column temperature was maintained at 40 ℃, and the injection volume of sample was 40 μL.

*Aldehydes and ketones:* Carbonyl compounds in cloud water samples were derivatized with DNPH solution *in situ* right after sampling and stored at 4 ℃. The DNPH solution was freshly prepared by mixing 20 mg of DNPH with 1.25 mL of 35 % HCl, 0.625 mL of acetonitrile (ACN), and 3.12 mL of MilliQ water well in order. 20 μL of DNPH solution was added to 1.2 mL of sample, which was analyzed by high-performance liquid chromatography coupled with diode-array detection (HPLC-DAD, 1260 Infinity II, Agilent), equipped with an eclipse XDB-C18 column (4.6 × 150 mm, 5 μm, Agilent). The elution was as follows: a linear gradient with 50% ACN and 50% MilliQ water to 60% ACN within 10 min, maintained for 4.5 min, and a linear gradient to 75% ACN within 10.5 min, then with a linear gradient back to 50% ACN within 0.5 min, maintained for 5 min. The flow rate was 1 mL $min^{-1}$. The injection volume was 5 μL. The column temperature was at 30 ℃. The detection wavelength was 365 nm.

*ICP-MS:* Aliquots of 3 mL of cloud water samples are directly transferred in 6 mL ICP-MS polystyrene vials previously conditioned by immersion for 24 h in diluted nitric acid followed by repeatedly washes with ultrapure (MilliQ) water. Samples are diluted with 3 mL of distilled $HNO_3$ 1 M in MilliQ water. Trace elements abundances are determined by ICP-MS (Agilent 7500). Sample solutions are aspired at a rate of 400 μL $min^{-1}$ using a peristaltic pump and introduced into the plasma using a quartz introduction system (Micromist Nebulizerand a Scott-type spray chamber). The signal is calibrated externally with multi-element standards (1 and 10 ng $g^{-1}$), which are prepared by gravimetric dilution of 10 μg $mL^{-1}$ certified solutions traceable to NIST (National Institute of Standards and Technology) (Inorganic Ventures).

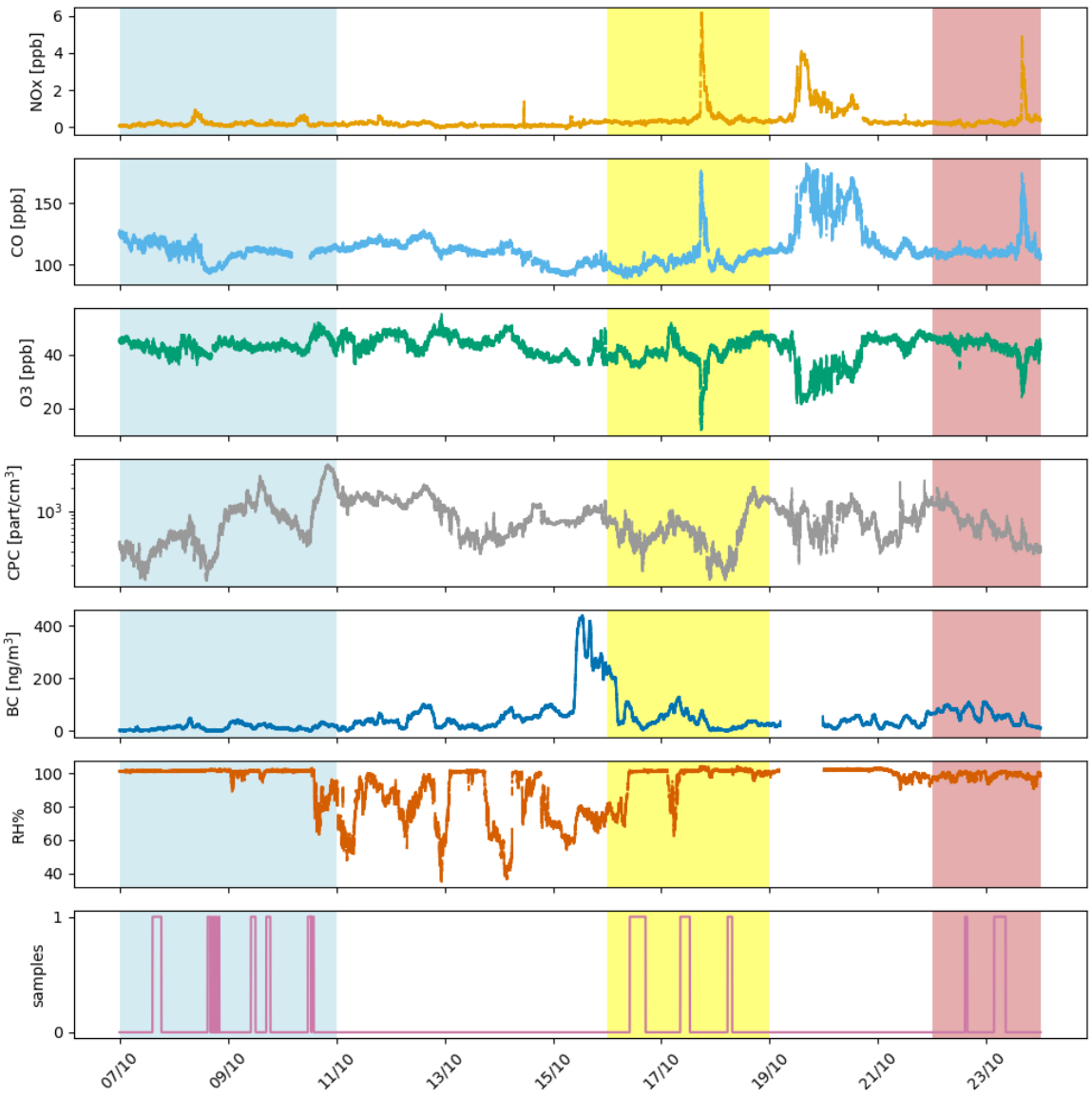
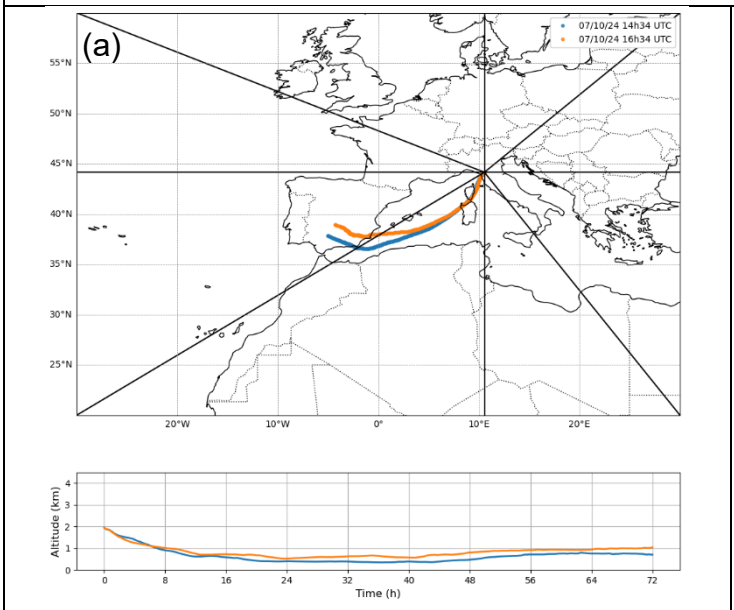
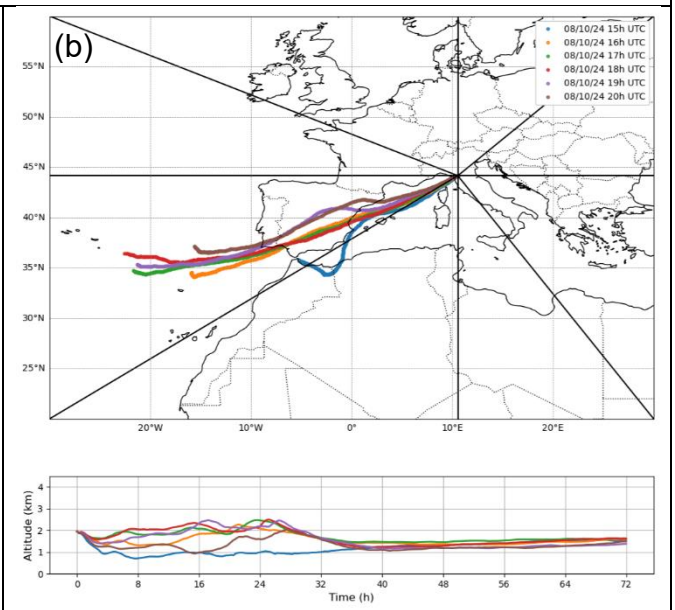
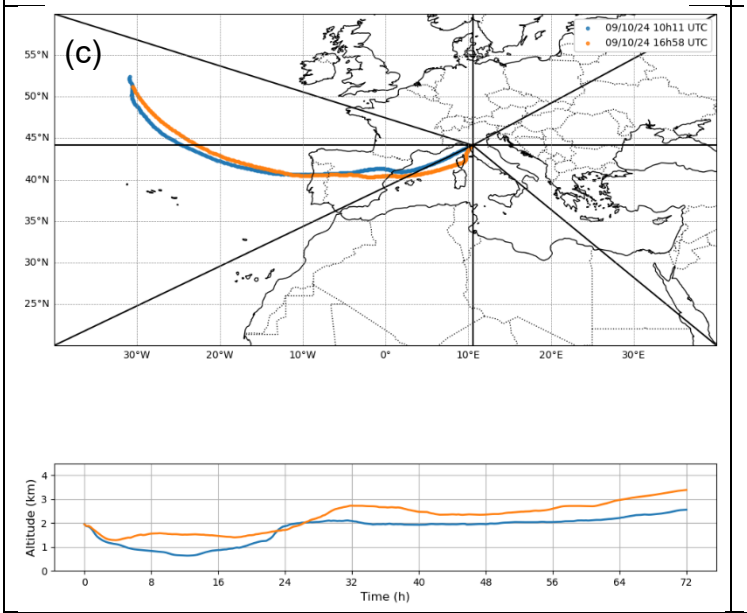


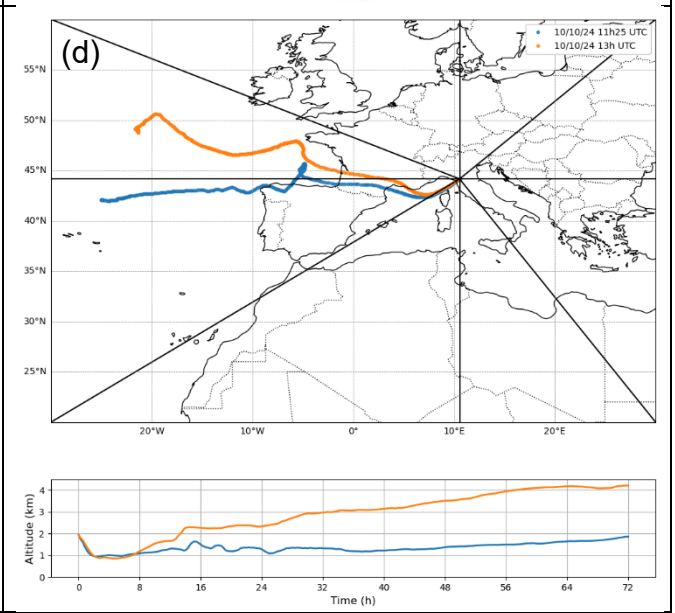

**Fig. S1.** Temporal evolution of meteorological parameters during the campaign. The three periods are shown in blue (period 1), yellow (period 2) and red (period 3). The variable "samples" equals 1 for each cloud water sampling and 0 when no sample was collected.

*Period 1*

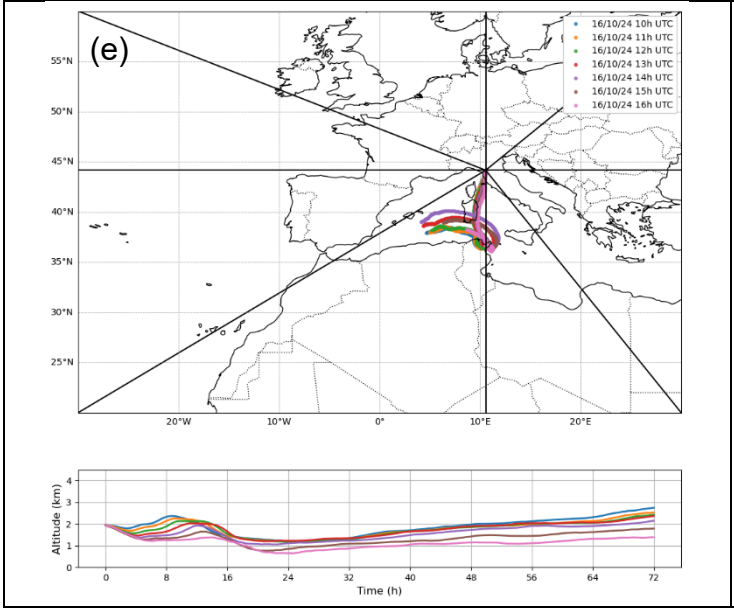


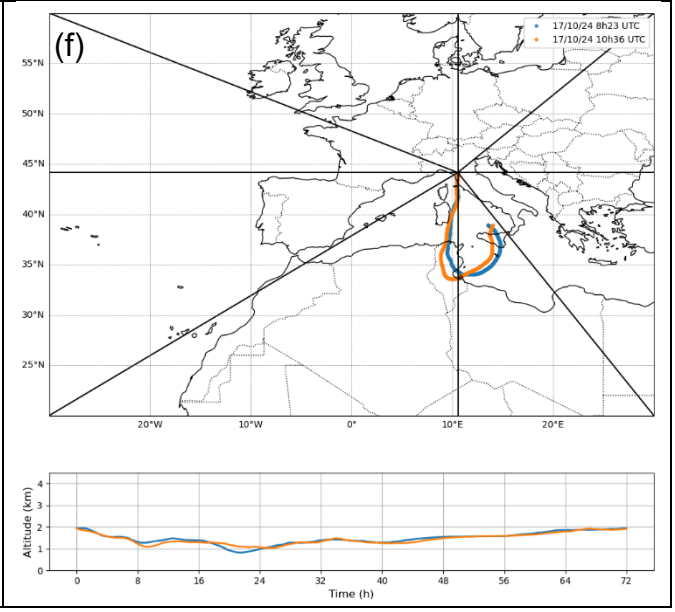




*Period 2*



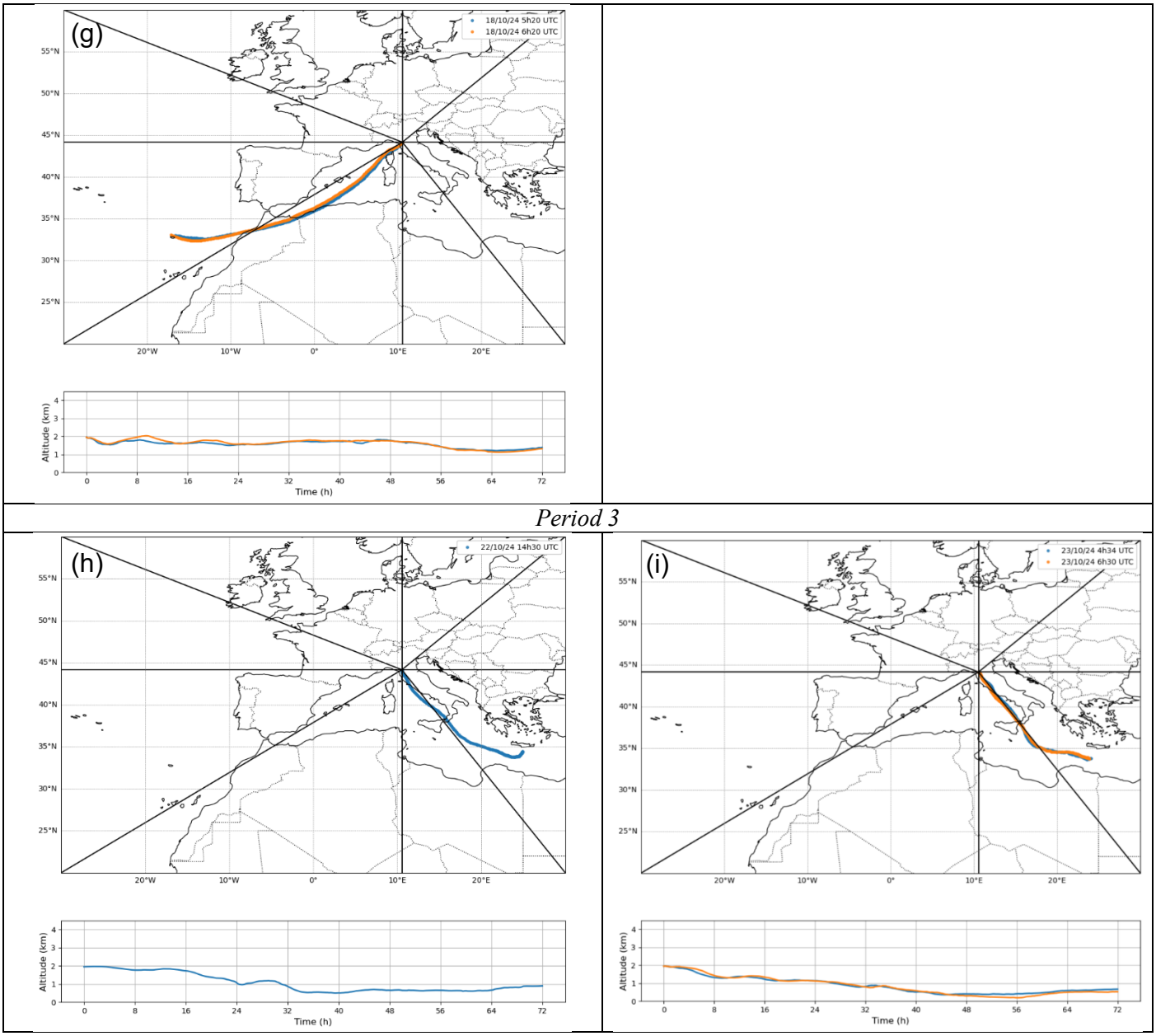



**Fig. S2 a, b, c, d, e, f, g, h, i**. Clusters of 72h-back-trajectory plots of air masses reaching CMN during cloud sampling from October 7th to October 23rd . The upper panels show the trajectories projected on a horizontal map, and the lower panels show the temporal evolution of altitude for each backtrajectory.

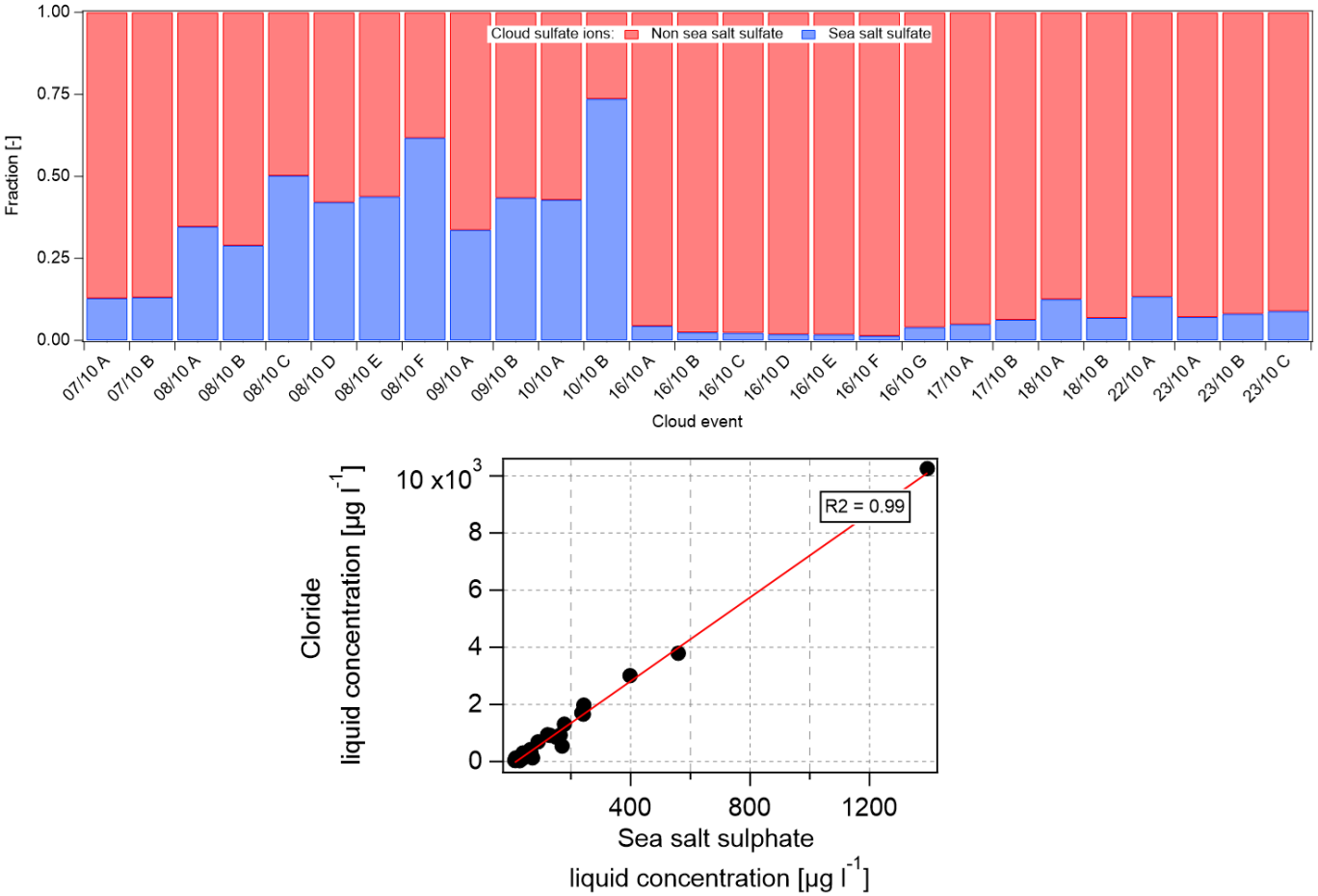



**Fig. S3.** Upper panel: fraction of non-sea salt sulphate, in red, and sea salt sulphate, in blue, in cloud water samples. Lower panel: correlation between chloride and sea sulphate in cloud samples.

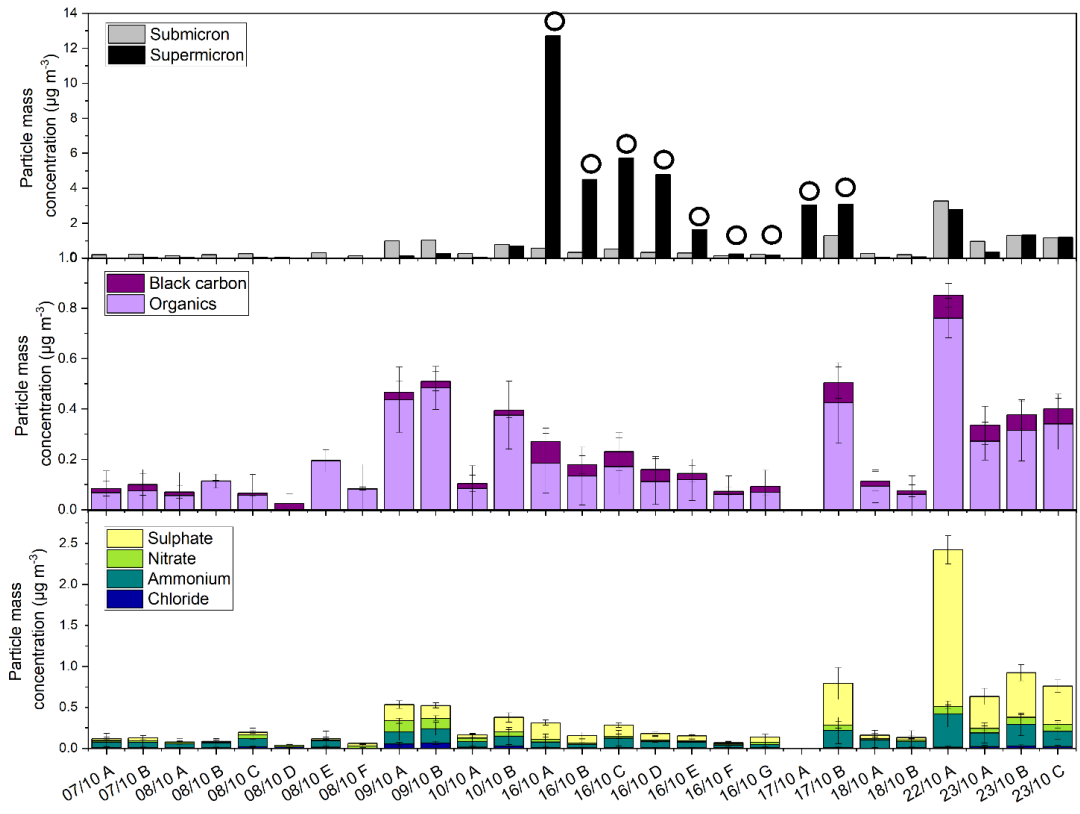



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**Fig. S4.** Upper panel: particle mass concentration of submicron and supermicron aerosol. Saharan dust events are highlighted with a circle. Middle panel: particle mass concentration of organics and black carbon in aerosol. Lower panel: particle mass concentration of main inorganic ions in aerosol.

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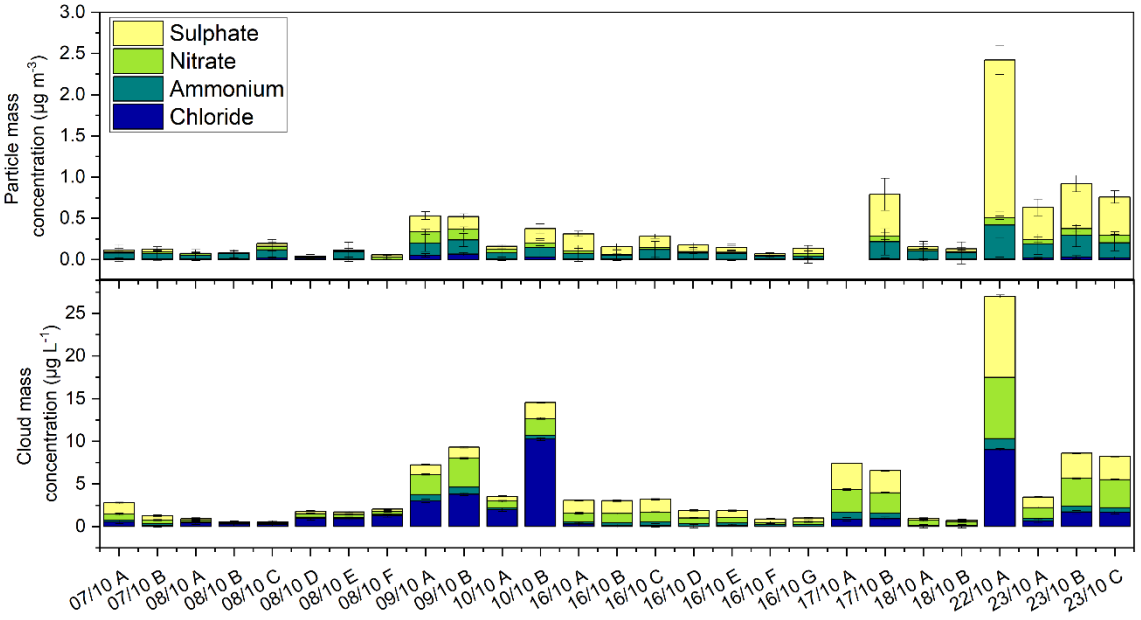


**Fig. S5** Mass concentration of main inorganic ions (chloride, nitrate, sulphate and ammonium) in aerosol (upper panel) and in clouds (lower panel).

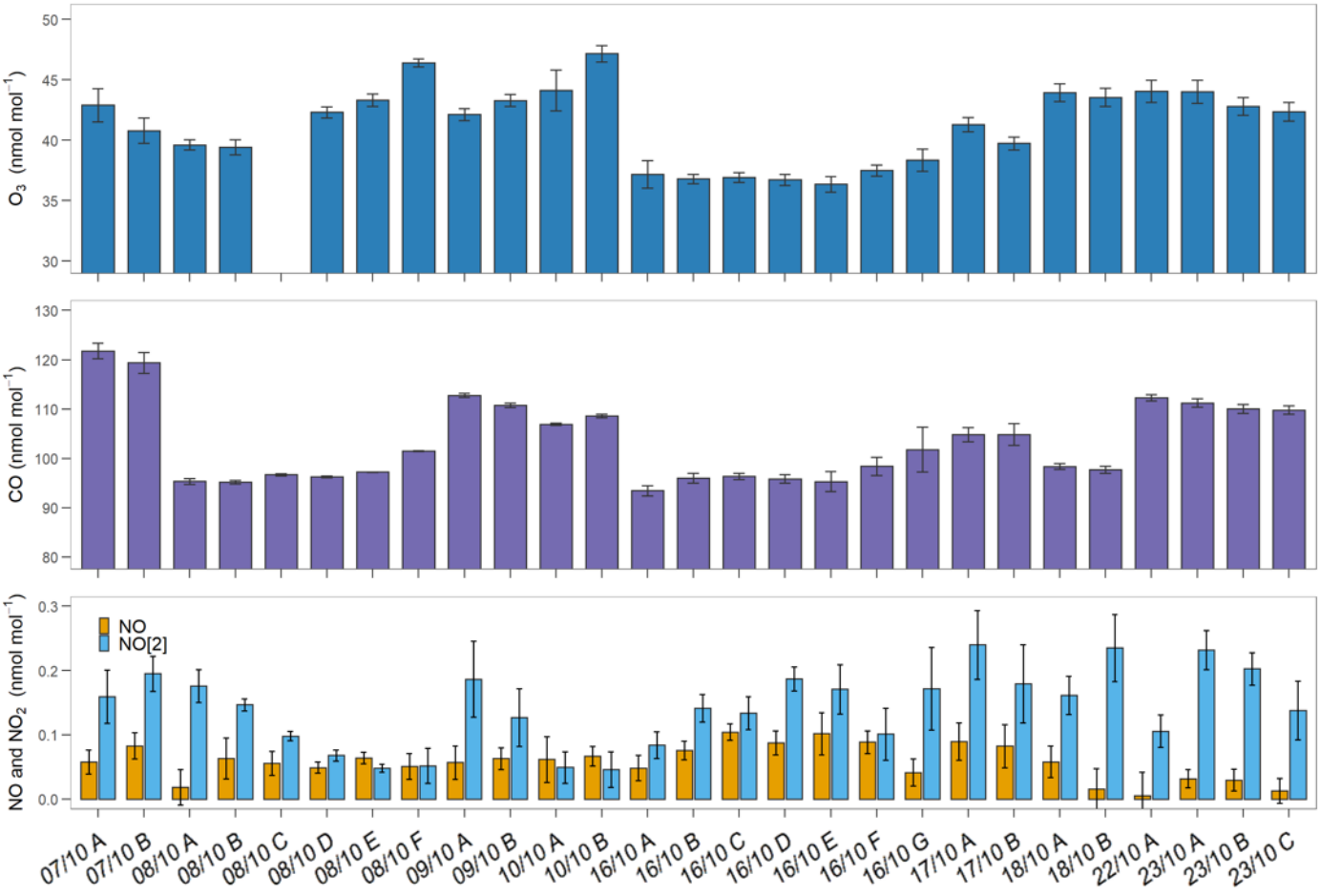


**Fig. S6.** Upper panel: atmospheric ozone mole fraction. Middle panel: atmospheric carbon monoxide mole fraction. Lower panel: atmospheric nitrogen oxide and nitrogen dioxide mole fraction.

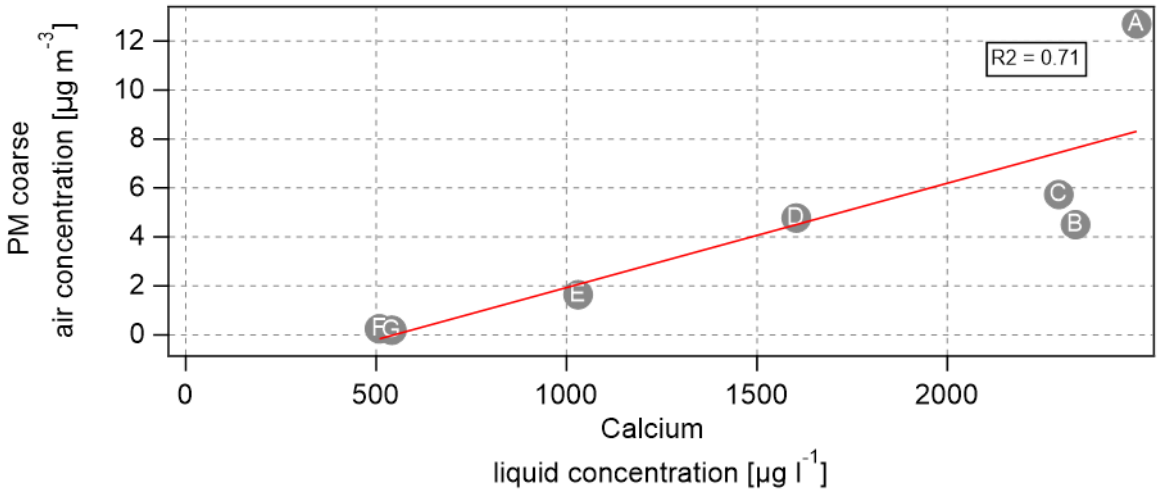


**Fig. S7.** Evolution of the coarse particle mass concentration vs calcium concentration for samples 16/10 A to 16/10 G.

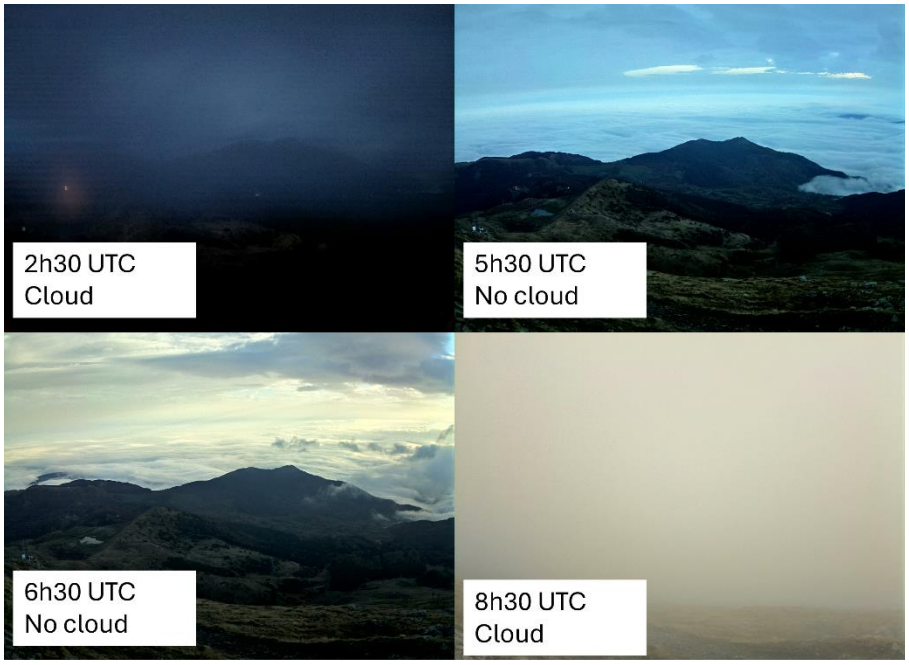


**Fig. S8** Webcam images from the top of CMN on 17 October between 2.30 a.m. and 8.30 a.m.

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| Sample Id | Date | Start (local) | Stop (local) | Start (UTC) | Stop (UTC) | | Collector | Sterile/Not sterile | Volume collected |
|---|---|---|---|---|---|---|---|---|---|
| | dd/mm/aaaa | hh:mm | hh:mm | hh:mm | hh:mm | | # | | mL |
| 07/10 A | 07/10/2024 | 16:34 | 18:39 | 14:34:00 | 16:39:00 | day | 3 | Sterile | 725 |
| | | 16:34 | 18:39 | 14:34:00 | 16:39:00 | | 4 | Sterile | 736 |
| 07/10 B | 07/10/2024 | 18:39 | 20:30 | 16:39:00 | 18:30:00 | night | 3 | Sterile | 710 |
| | | 18:39 | 20:30 | 16:39:00 | 18:30:00 | | 4 | Sterile | 750 |
| 08/10 A | 08/10/2024 | 17:00 | 18:00 | 15:00:00 | 16:00:00 | day | 3 | Not sterile | 571 |
| | | 17:00 | 21:20 | 15:00:00 | 19:20:00 | | 4 | Sterile | 367 |
| 08/10 B | 08/10/2024 | 18:00 | 18:10 | 16:00:00 | 16:10:00 | day | 3 | Not sterile | 20 |
| 08/10 C | 08/10/2024 | 19:00 | 19:10 | 17:00:00 | 17:10:00 | night | 3 | Not sterile | 20 |
| 08/10 D | 08/10/2024 | 20:00 | 20:10 | 18:00:00 | 18:10:00 | night | 3 | Not sterile | 20 |
| 08/10 E | 08/10/2024 | 21:00 | 21:10 | 19:00:00 | 19:10:00 | night | 3 | Not sterile | 20 |
| 08/10 F | 08/10/2024 | 22:00 | 22:10 | 20:00:00 | 20:10:00 | night | 3 | Not sterile | 20 |
| 09/10 A | 09/10/2024 | 12:11 | 14:11 | 10:11:00 | 12:11:00 | day | 3 | Not sterile | 368 |
| 09/10 B | 09/10/2024 | 18:58 | 20:45 | 16:58:00 | 18:45:00 | night | 3 | Not sterile | 158 |
| | | 18:58 | 20:45 | 16:58:00 | 18:45:00 | | 4 | Sterile | 144 |
| 10/10 A | 10/10/2024 | 13:25 | 14:55 | 11:25:00 | 12:55:00 | day | 3 | Not sterile | 535 |
| | | 13:25 | 16:00 | 11:25:00 | 14:00:00 | | 4 | Sterile | 348 |
| 10/10 B | 10/10/2024 | 15:00 | 16:00 | 13:00:00 | 14:00:00 | day | 3 | Not sterile | 36 |
| 15/10 Blank | 15/10/2024 | Blank | | | | | 3 | Not sterile | |
| 16/10 A | 16/10/2024 | 12:00 | 13:00 | 10:00:00 | 11:00:00 | day | 3 | Not sterile | 454 |
| | | 12:00 | 14:00 | 10:00:00 | 12:00:00 | | 4 | Sterile | 338 |
| 16/10 B | 16/10/2024 | 13:00 | 14:00 | 11:00:00 | 12:00:00 | day | 3 | Not sterile | 443 |
| 16/10 C | 16/10/2024 | 14:00 | 15:00 | 12:00:00 | 13:00:00 | day | 3 | Not sterile | 408 |
| | | 14:00 | 16:00 | 12:00:00 | 14:00:00 | | 4 | Sterile | 400 |
| 16/10 D | 16/10/2024 | 15:00 | 16:00 | 13:00:00 | 14:00:00 | day | 3 | Not sterile | 502 |
| 16/10 E | 16/10/2024 | 16:00 | 17:00 | 14:00:00 | 15:00:00 | day | 3 | Not sterile | 453 |
| 16/10 F | 16/10/2024 | 17:00 | 18:00 | 15:00:00 | 16:00:00 | day | 3 | Not sterile | 731 |
| 16/10 G | 16/10/2024 | 18:00 | 19:00 | 16:00:00 | 17:00:00 | day-night | 3 | Not sterile | 529 |
| 17/10 A | 17/10/2024 | 10:23 | 12:36 | 08:23:00 | 10:36:00 | day | 3 | Not sterile | 255 |
| | | 10:23 | 13:07 | 08:23:00 | 11:07:00 | | 4 | Sterile | 283 |
| 17/10 B | 17/10/2024 | 12:36 | 14:36 | 10:36:00 | 12:36:00 | day | 3 | Not sterile | 559 |
| | | 13:07 | 14:45 | 11:07:00 | 12:45:00 | | 4 | Sterile | 307 |
| 18/10 A | 18/10/2024 | 07:20 | 08:20 | 05:20:00 | 06:20:00 | day | 3 | Not sterile | 261 |
| 18/10 B | 18/10/2024 | 08:20 | 09:20 | 06:20:00 | 07:20:00 | day | 3 | Not sterile | 203 |
| 22/10 A | 22/10/2024 | 16:30 | 17:30 | 14:30:00 | 15:30:00 | day | 3 | Not sterile | 48 |
| | | 16:30 | 17:30 | 14:30:00 | 15:30:00 | | 4 | Sterile | 38 |
| 23/10 Rain | 23/10/2024 | 05:25 | 06:34 | 03:25:00 | 04:34:00 | night | 3 | Not sterile | 281 |
| 23/10 B | 23/10/2024 | 06:34 | 08:30 | 04:34:00 | 06:30:00 | night-day | 3 | Not sterile | 221 |
| | | 06:34 | 08:30 | 04:34:00 | 06:30:00 | | 4 | Sterile | 172 |
| 23/10 C | 23/10/2024 | 08:30 | 10:30 | 06:30:00 | 08:30:00 | day | 3 | Not sterile | 310 |
| | | 08:30 | 10:30 | 06:30:00 | 08:30:00 | | 4 | Sterile | 242 |

**Table. S1.** Sampling conditions (day/night; sterile/not sterile) and parameters (date, start/stop time, and collected volume) for each sample.

| | pH | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | Acetic | Formic | Oxalic | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | Formaldehyde | Acetaldehyde | Acetone | Acrolein | $H_2O_2$ | CCT TC (mgC/L) | CCT TOC (mgC/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **07/10 A** | 6.1 | 15.2 | 11.1 | 13.8 | 22.3 | 10.4 | 6.9 | 30.2 | 15.7 | 12.3 | 4.1 | 13.9 | 2.7 | 1.7 | 1.9 | 0.2 | 25.5 | 4.5 | 4.0 |
| **07/10 B** | 5.9 | 3.8 | 6.6 | 5.6 | 6.7 | 7.0 | 6.8 | 12.5 | 13.4 | 4.1 | 1.8 | 7.4 | 2.7 | 1.9 | 2.3 | 0.2 | 24.8 | 1.7 | 1.3 |
| **08/10 A** | 6.4 | 11.9 | 3.7 | 1.9 | 17.4 | 2.2 | 6.5 | 11.2 | 7.3 | 7.4 | 1.5 | 7.6 | 2.7 | 1.6 | 1.8 | 0.2 | 8.8 | 2.3 | 1.8 |
| **08/10 B** | 6.5 | 8.6 | 1.1 | 1.4 | 20.6 | 0.1 | 5.0 | 6.9 | 4.4 | 7.3 | 1.3 | 5.1 | 2.2 | 1.6 | 2 | 0.2 | 4.0 | <DL | <DL |
| **08/10 C** | 6.7 | 6.7 | 1.8 | 1.3 | <DL | 1.6 | 4.1 | 11.1 | 7.5 | 2.5 | 1.5 | 4.8 | 2.7 | 1.6 | 1.8 | 0.2 | 14.5 | <DL | <DL |
| **08/10 D** | 6.3 | 26.5 | 6.8 | 3.0 | <DL | 5.1 | 4.2 | 21.5 | 11.2 | 2.0 | 1.9 | 4.9 | 3.3 | 1.8 | 2.2 | 0.3 | 23.8 | <DL | <DL |
| **08/10 E** | 6.8 | 25.9 | 6.1 | 3.1 | 0.3 | 4.9 | 3.5 | 23.1 | 9.8 | 2.5 | 2.0 | 5.0 | 3.1 | 1.7 | 2 | 0.2 | 21.9 | <DL | <DL |
| **08/10 F** | 7.0 | 37.0 | 5.7 | 3.0 | <DL | 2.5 | 2.7 | 31.5 | 6.9 | 1.3 | 2.3 | 4.1 | 3 | 1.7 | 2.2 | 0.2 | 21.5 | <DL | <DL |
| **09/10 A** | 6.1 | 84.8 | 37.0 | 12.3 | 14.2 | 13.3 | 2.8 | 70.4 | 54.5 | 8.4 | 3.9 | 8.7 | 5.4 | 1.9 | 1.6 | 0.2 | 43.9 | 4.6 | 4.1 |
| **09/10 B** | 4.5 | 107.0 | 54.8 | 13.4 | 11.5 | 18.0 | 2.9 | 99.1 | 58.8 | 6.1 | 5.4 | 10.0 | 4.2 | 2.2 | 1.3 | 0.2 | 73.7 | 12.7 | 12.2 |
| **10/10 A** | 5.5 | 55.8 | 13.0 | 5.9 | 3.4 | 9.9 | 2.0 | 43.0 | 14.1 | 2.9 | 2.7 | 8.3 | 2.9 | 1.2 | 1.1 | 0.1 | 21.3 | 1.5 | 1.0 |
| **10/10 B** | 5.6 | 289.2 | 31.6 | 19.7 | 3.9 | 12.8 | 2.1 | 246.9 | 31.9 | 7.8 | 12.2 | 13.9 | 4.5 | 1.8 | 1.2 | 0.2 | 50.3 | 6.4 | 5.9 |
| **16/10 A** | 6.5 | 8.3 | 16.6 | 15.6 | 3.4 | 2.4 | 1.9 | 11.6 | 18.0 | 4.4 | 2.4 | 62.3 | 1.9 | 0.7 | 0.8 | 0.2 | 15.7 | 3.4 | 1.9 |
| **16/10 B** | 6.6 | 2.9 | 17.0 | 15.7 | 5.3 | 2.3 | 1.9 | 6.5 | 26.4 | 3.5 | 2.2 | 58.3 | 2.5 | 1.4 | 1.6 | 0.2 | <DL | <DL | <DL |
| **16/10 C** | 7.0 | 3.4 | 18.6 | 15.6 | 11.1 | 2.0 | 2.0 | 6.1 | 30.1 | 3.1 | 2.1 | 57.2 | 2.5 | 1.5 | 1.8 | 0.2 | 53.2 | 3.3 | 1.7 |
| **16/10 D** | 6.4 | 1.0 | 10.8 | 9.2 | 4.3 | 1.1 | 1.0 | 2.9 | 21.8 | 2.0 | 1.7 | 40.0 | 2.2 | 1.4 | 1.6 | 0.2 | <DL | <DL | <DL |
| **16/10 E** | <DL | 3.6 | 9.7 | 8.4 | 3.0 | 0.7 | 1.4 | 2.6 | 23.4 | 1.8 | 1.5 | 25.7 | 2.4 | 1.3 | 2.1 | 0.2 | 24.4 | 2.3 | 1.2 |
| **16/10 F** | 7.1 | <DL | 4.5 | 4.2 | <DL | <DL | 0.2 | 1.0 | 14.2 | 0.9 | 1.3 | 12.7 | 2.7 | 1.6 | 1.9 | 0.3 | <DL | 2.3 | 1.3 |
| **16/10 G** | 6.6 | <DL | 4.8 | 4.4 | 2.4 | 1.6 | 0.2 | 3.0 | 19.9 | 2.0 | 1.3 | 13.5 | 3.1 | 1.3 | 1.8 | 0.2 | 22.8 | 2.0 | 1.1 |
| **17/10 A** | 6.5 | 24.2 | 43.0 | 32.0 | 14.5 | 8.9 | 1.4 | 26.4 | 57.3 | 4.3 | 3.0 | 53.0 | 4 | 0.8 | 0.8 | 0.1 | 74.6 | 3.5 | 2.3 |
| **17/10 B** | 6.8 | 26.1 | 38.5 | 27.1 | 12.0 | 3.8 | 1.4 | 28.9 | 46.3 | 3.5 | 2.8 | 45.2 | 3.7 | 1.8 | 2.1 | 0.3 | 77.5 | 2.0 | 1.2 |
| **18/10 A** | 6.1 | 0.9 | 9.4 | 2.3 | 6.3 | 9.7 | <DL | 4.9 | 8.5 | 2.6 | 1.6 | 13.9 | 2.3 | 1.5 | 2.1 | 0.3 | 7.0 | 2.8 | 2.2 |
| **18/10 B** | 5.8 | 1.2 | 7.1 | 1.8 | <DL | <DL | <DL | 2.1 | 7.9 | 1.5 | 1.3 | 7.4 | 2.6 | 1.8 | 2.5 | 0.3 | 11.0 | 2.4 | 1.7 |
| **22/10 A** | 4.1 | 254.7 | 115.7 | 99.1 | 9.9 | 16.5 | 2.9 | 224.7 | 91.6 | 11.3 | 12.8 | 59.2 | 4 | 1.9 | 2.2 | 0.3 | 104.1 | 4.9 | 4.2 |
| **23/10 Rain** | 5.1 | 19.4 | 20.4 | 13.0 | 4.8 | 4.6 | 0.5 | 15.8 | 19.9 | 4.3 | 1.9 | 10.1 | 2.5 | 1.1 | 1.7 | 0.2 | 21.8 | 4.2 | 3.6 |
| **23/10 B** | 5.0 | 48.1 | 53.3 | 30.5 | 5.5 | 12.3 | 0.5 | 41.8 | 46.5 | 3.6 | 3.5 | 25.4 | 4.2 | 1.1 | 1.5 | 0.2 | 86.1 | 5.1 | 4.5 |
| **23/10 C** | 6.0 | 46.8 | 52.8 | 28.2 | 3.7 | 13.7 | 0.9 | 42.8 | 41.1 | 4.2 | 3.6 | 28.4 | 4 | 1.3 | 1.8 | 0.2 | 74.1 | 2.9 | 2.3 |
| **15/10 Blank** | 6.4 | 0.8 | 1.4 | 2.0 | <DL | <DL | 0.7 | 2.4 | 0.7 | 0.4 | 2.4 | 6.6 | 0.5 | 0.7 | 1 | 0.1 | <DL | <DL | <DL |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Median** | 6.4 | 17.3 | 10.9 | 8.8 | 5.9 | 4.9 | 2.0 | 14.2 | 18.9 | 3.5 | 2.1 | 13.1 | 2.7 | 1.6 | 1.8 | 0.2 | 24.1 | 3.1 | 2.0 |
| **Average** | 6.1 | 42.8 | 21.5 | 14.0 | 8.5 | 6.7 | 2.6 | 36.8 | 25.3 | 4.2 | 3.1 | 21.9 | 3.1 | 1.5 | 1.8 | 0.2 | 37.8 | 3.7 | 3.0 |

**Table S2.** Concentration in μmol $L^{-1}$ of main organic, inorganic anions and cations, carboxylic acid, $H_2O_2$, TC, TOC and pH of the cloud water samples studied in this work. "<DL" is reported for values below the detection limit

| Samples | Chloride | Nitrate | Sulphate | Sodium | Ammonium | Magnesium | Calcium |
|---|---|---|---|---|---|---|---|
| **07/10 A** | 15.2 | 11.1 | 13.8 | 30.2 | 15.7 | 4.1 | 13.9 |
| **07/10 B** | 3.8 | 6.6 | 5.6 | 12.5 | 13.4 | 1.8 | 7.4 |
| **08/10 A** | 11.9 | 3.7 | 1.9 | 11.2 | 7.3 | 1.5 | 7.6 |
| **08/10 B** | 8.6 | 1.1 | 1.4 | 6.9 | 4.4 | 1.3 | 5.1 |
| **08/10 C** | 6.7 | 1.8 | 1.3 | 11.1 | 7.5 | 1.5 | 4.8 |
| **08/10 D** | 26.5 | 6.8 | 3.0 | 21.5 | 11.2 | 1.9 | 4.9 |
| **08/10 E** | 25.9 | 6.1 | 3.1 | 23.1 | 9.8 | 2.0 | 5.0 |
| **08/10 F** | 37.0 | 5.7 | 3.0 | 31.5 | 6.9 | 2.3 | 4.1 |
| **09/10 A** | 84.8 | 37.0 | 12.3 | 70.4 | 54.5 | 3.9 | 8.7 |
| **09/10 B** | 107.0 | 54.8 | 13.4 | 99.1 | 58.8 | 5.4 | 10.0 |
| **10/10 A** | 55.8 | 13.0 | 5.9 | 43.0 | 14.1 | 2.7 | 8.3 |
| **10/10 B** | 289.2 | 31.6 | 19.7 | 246.9 | 31.9 | 12.2 | 13.9 |
| **15/10 Blank** | 0.8 | 1.4 | 2.0 | 2.4 | 0.7 | 2.4 | 6.6 |
| **16/10 A** | 8.3 | 16.6 | 15.6 | 11.6 | 18.0 | 2.4 | 62.3 |
| **16/10 B** | 2.9 | 17.0 | 15.7 | 6.5 | 26.4 | 2.2 | 58.3 |
| **16/10 C** | 3.4 | 18.6 | 15.6 | 6.1 | 30.1 | 2.1 | 57.2 |
| **16/10 D** | 1.0 | 10.8 | 9.2 | 2.9 | 21.8 | 1.7 | 40.0 |
| **16/10 E** | 3.6 | 9.7 | 8.4 | 2.6 | 23.4 | 1.5 | 25.7 |
| **16/10 F** | 0.0 | 4.5 | 4.2 | 1.0 | 14.2 | 1.3 | 12.7 |
| **16/10 G** | 0.0 | 4.8 | 4.4 | 3.0 | 19.9 | 1.3 | 13.5 |
| **17/10 A** | 24.2 | 43.0 | 32.0 | 26.4 | 57.3 | 3.0 | 53.0 |
| **17/10 B** | 26.1 | 38.5 | 27.1 | 28.9 | 46.3 | 2.8 | 45.2 |
| **18/10 A** | 0.9 | 9.4 | 2.3 | 4.9 | 8.5 | 1.6 | 13.9 |
| **18/10 B** | 1.2 | 7.1 | 1.8 | 2.1 | 7.9 | 1.3 | 7.4 |
| **22/10 A** | 254.7 | 115.7 | 99.1 | 224.7 | 91.6 | 12.8 | 59.2 |
| **23/10 Rain** | 19.4 | 20.4 | 13.0 | 15.8 | 19.9 | 1.9 | 10.1 |
| **23/10 B** | 48.1 | 53.3 | 30.5 | 41.8 | 46.5 | 3.5 | 25.4 |
| **23/10 C** | 46.8 | 52.8 | 28.2 | 42.8 | 41.1 | 3.6 | 28.4 |

**Table S3.**

Matrix used for the PCA based on ion concentrations dissimilarities (concentrations in μmol $L^{-1}$). The matrix was not normalised prior to analysis as the predefined function on R was used.

| Elements | As | Cd | Co | Cr | Cu | Fe | Mg | Mn | Mo | Ni | Pb | Pd | Rb | Sb | Sn | Sr | Tl | V | W | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **15/10 Blank** | <LQ | 0.2 | 0.5 | <LQ | 160.9 | <LQ | 4432.5 | 123.4 | 0.1 | 9.0 | 0.3 | <LQ | 0.4 | 0.2 | 0.2 | 13.0 | <LQ | 0.5 | 0.4 | 246.2 |
| **07/10 A** | 0.3 | 0.7 | 4.9 | 4.1 | 122.4 | 36.4 | 8342.8 | 407.2 | 3.4 | 176.7 | 1.5 | 0.0 | 5.8 | 0.9 | 1.1 | 27.7 | 0.0 | 3.4 | 1.2 | 2489.8 |
| **07/10 B** | <LQ | 0.4 | 2.6 | <LQ | 65.3 | 29.6 | 2562.1 | 112.9 | 1.0 | 48.0 | 1.3 | <LQ | 2.4 | 0.6 | 0.5 | 15.7 | 0.0 | 3.6 | 1.3 | 1781.0 |
| **08/10 A** | <LQ | 0.7 | 1.3 | <LQ | 87.7 | 27.7 | 1655.1 | 46.0 | 0.5 | 39.1 | 1.1 | 0.0 | 3.3 | 0.6 | 0.6 | 13.5 | 0.0 | 1.2 | 1.9 | 1599.9 |
| **09/10 A** | 0.7 | 0.2 | 0.9 | 2.2 | 66.6 | 29.5 | 8579.4 | 39.5 | 1.6 | 25.2 | 1.9 | 0.0 | 4.1 | 0.4 | 0.4 | 20.7 | 0.0 | 6.0 | 2.3 | 809.0 |
| **09/10 B** | 0.7 | 0.3 | 0.8 | 2.1 | 112.9 | 54.4 | 11581.8 | 49.9 | 0.5 | 26.7 | 2.5 | 0.0 | 2.3 | 0.4 | 0.4 | 25.4 | 0.0 | 7.4 | 1.2 | 541.6 |
| **10/10 A** | <LQ | 0.4 | 1.2 | <LQ | 60.6 | 17.3 | 5887.2 | 44.0 | 1.7 | 34.5 | 2.7 | 0.0 | 2.4 | 0.5 | 0.4 | 17.8 | 0.0 | 2.6 | 1.2 | 1548.0 |
| **10/10 B** | 0.7 | 0.4 | 1.0 | 2.1 | 88.4 | 30.5 | 27403.5 | 58.2 | 2.0 | 26.3 | 2.4 | 0.0 | 2.7 | 0.4 | 0.2 | 50.9 | 0.0 | 4.8 | 1.7 | 1220.4 |
| **16/10 A** | 0.4 | 0.1 | 2.0 | 1.8 | 25.3 | 89.3 | 3836.3 | 231.0 | 2.3 | 25.6 | 0.1 | 0.1 | 2.6 | 0.6 | 0.3 | 92.2 | <LQ | 3.7 | 3.4 | 351.7 |
| **17/10 A** | 1.3 | 0.3 | 2.2 | 2.2 | 35.2 | 44.9 | 5555.8 | 199.5 | 0.7 | 17.2 | 0.2 | 0.1 | 3.0 | 1.1 | 0.3 | 93.9 | 0.1 | 19.0 | 5.0 | 231.6 |
| **18/10 A** | <LQ | 0.3 | 1.3 | 2.5 | 32.2 | 24.2 | 1757.9 | 45.1 | 6.0 | 35.8 | 0.4 | <LQ | 1.5 | 0.6 | 0.5 | 23.9 | <LQ | 1.5 | 1.3 | 3386.6 |
| **22/10 A** | 7.7 | 1.3 | 2.7 | 4.4 | 596.0 | 283.0 | 28024.7 | 176.4 | 0.8 | 26.7 | 42.1 | 0.1 | 6.0 | 1.6 | 1.0 | 137.8 | 0.5 | 17.8 | 1.5 | 1189.6 |
| **23/10 Rain** | 0.6 | 0.8 | 1.0 | <LQ | 80.8 | 20.1 | 2461.5 | 57.7 | 0.2 | 24.9 | 1.9 | <LQ | 2.2 | 0.7 | 0.3 | 19.5 | 0.0 | 2.9 | 1.0 | 1844.4 |
| **23/10 B** | 2.1 | 0.5 | 1.4 | 2.9 | 150.4 | 64.5 | 6665.8 | 105.0 | 0.6 | 21.7 | 4.0 | 0.1 | 2.2 | 0.9 | 0.6 | 61.8 | 0.1 | 7.2 | 1.5 | 893.3 |
| **23/10 C** | 1.9 | 0.6 | 4.9 | 5.5 | 109.9 | 75.0 | 8166.8 | 113.2 | 1.1 | 38.9 | 2.2 | 0.1 | 2.7 | 1.1 | 0.7 | 69.0 | 0.1 | 6.5 | 0.9 | 1561.9 |

**Table. S4.** Concentration of the main metals in nmol $L^{-1}$ detected in the samples. "LQ" is reported for values below the quantification limit.

| | Mycelium forming unit | Bacteria-like CFU | # replicates |
|---|---|---|---|
| | $mL^{-1}$ | $mL^{-1}$ | |
| 10/07/2024 A | 70 | 420 | 1 |
| 10/08/2024 A | 225 ± 78 | 175 ± 7 | 2 |
| 10/09/2024 B | 380 ± 35 | 183 ± 23 | 3 |
| 10/10/2024 A | 245 ± 49 | 235 ± 106 | 2 |
| 10/16/2024 A | 137 ± 61 | 333 ± 65 | 3 |
| 10/17/2024 A | 426 ± 45 | 20 ± 10 | 3 |
| 10/17/2024 B | 163 ± 47 | 63 ± 21 | 3 |

**Table. S5**. Concentration of culturable fungi and bacteria-like CFUs for the different samples after 3 or 4 days of incubation at 17°C (mean ± SD). Replicates varied because of fungi invasion in Petri dishes.

| Samples | Concentration (cell $mL^{-1}$) |
|---|---|
| **07/10/24 A** | $(4.0 \pm 0.5)\ 10^4$ |
| **08/10/24 A** | $(2.8 \pm 0.4)\ 10^4$ |
| **09/10/24 B** | $(1.5 \pm 0.1)\ 10^4$ |
| **10/10/24 A** | $(8.0 \pm 0.3)\ 10^3$ |
| **16/10/24 A** | $(1.0 \pm 0.3)\ 10^6$ |
| **17/10/24 A** | $(2.4 \pm 0.5)\ 10^5$ |
| **17/10/24 B** | $(2.9 \pm 1.0)\ 10^5$ |
| **22/10/24 A** | $(3.1 \pm 0.2)\ 10^4$ |
| **23/10/24 B** | $(1.4 \pm 0.1)\ 10^5$ |

**Table. S6.** Total cell concentration from flow cytometry (mean ± SD).