Supplementary materials

Evaluating the performance of the Thermodynamic Equilibrium Model ISORROPIA 2.1 for different aerosol compositions

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Figure S1: Italian territory divided in macroregion 1 (MR1, in green), macroregion 2 (MR2, in orange) and macroregion 3 (MR3, in yellow).

Figure S2: TSP sampler ECHO PUF together with radiometric measurements on the atmospheric mast of ATLANTE.

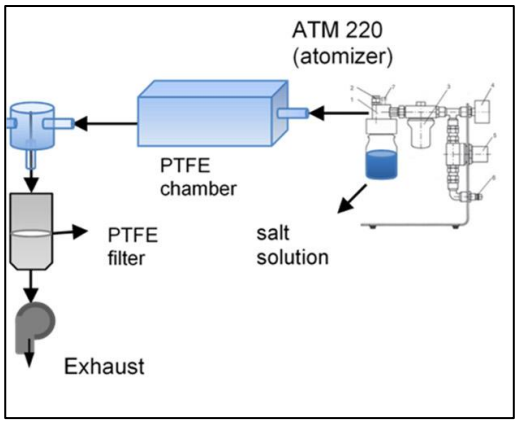

Figure S3: Outline scheme of the mixed saline generation and sampling system.

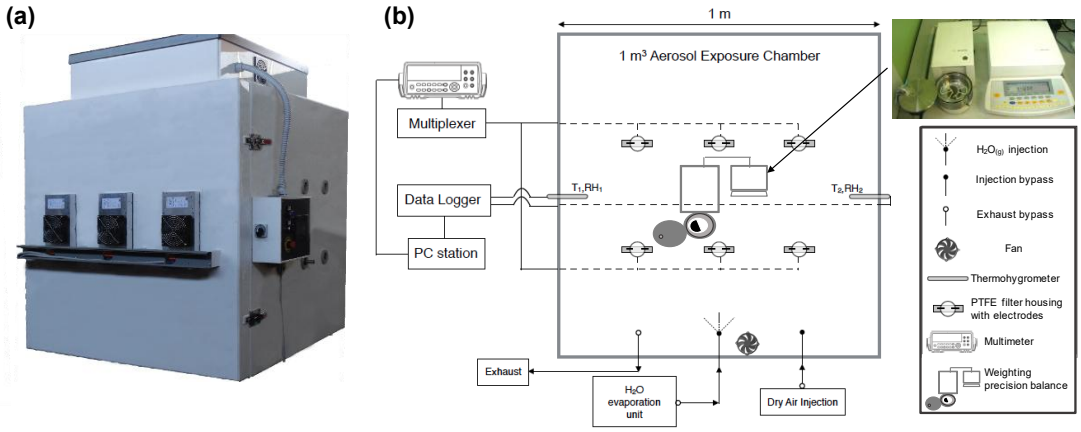

Figure S4: Aerosol Exposure Chamber (AEC): a picture (a), its scheme (b).

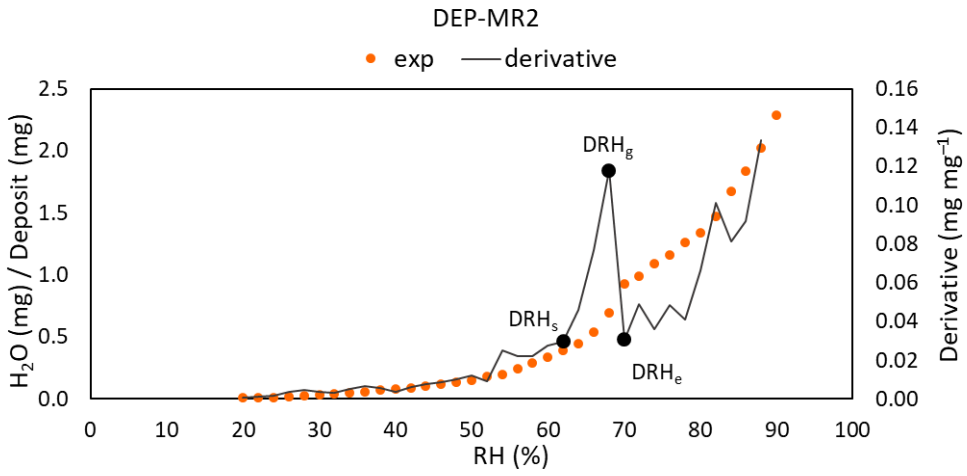

Figure S5: an example of the gradient method. The method consists of evaluating the variation of water mass derivatives as a function of RH. The derivative is read on the secondary axis. The peak identifies the three fundamental points of the process, expressed in terms of deliquescence relative humidity (DRH):DRH_s (start_: "s"), corresponding to the relative humidity at the onset of the deliquescence process, DRH_g (gradient: "g"), the maximum rate of the process, DRH_e (end: "e"), the relative humidity marking the completion of deliquescence, after which hygroscopic growth begins.

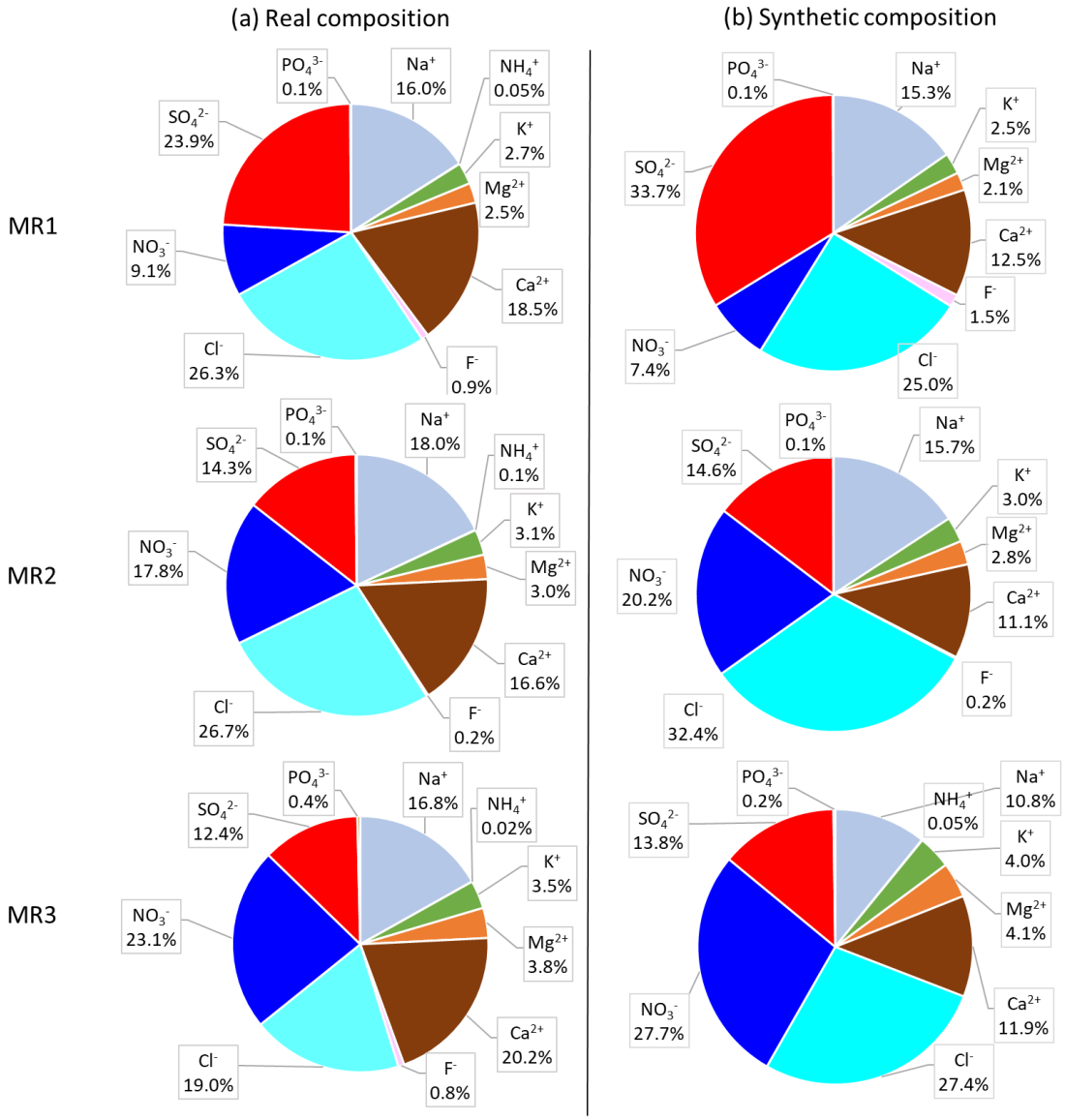

Figure S3: panel (a): the real chemical composition of the deposit for MR1, MR2, and MR3; panel (b): the synthetic aerosol composition generated in laboratory and exposed to humidification and dehumidification cycles in AEC.

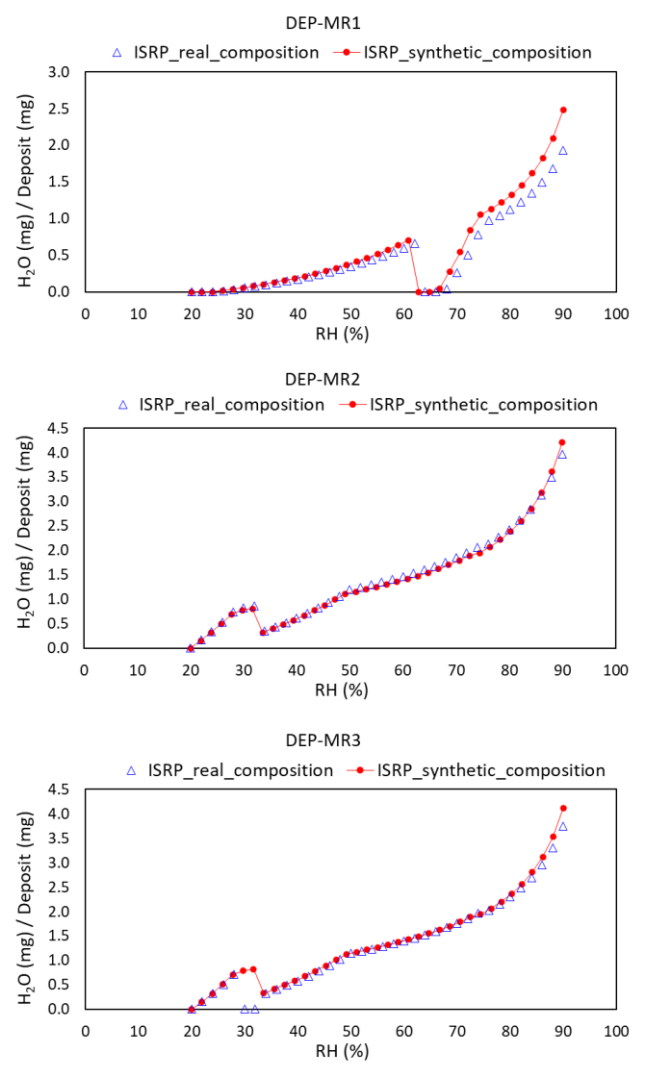

Figure S4: Simulations of ISORROPIA with the real chemical composition of deposits collected on insulators (blue) and with the synthetic chemical composition, reproduce in laboratory to perform the analyses in AEC (red).

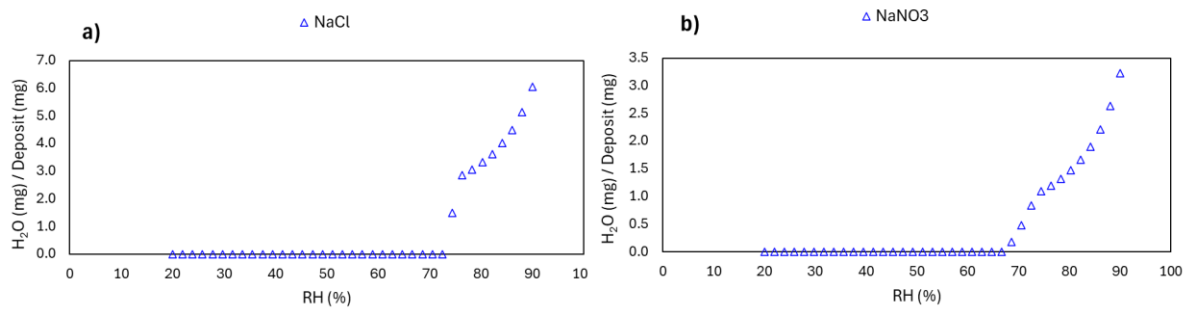

Figure S5: simulations of ISORROPIA of sodium chloride, NaCl, (a) and sodium nitrate, $NaNO_3$, (b).

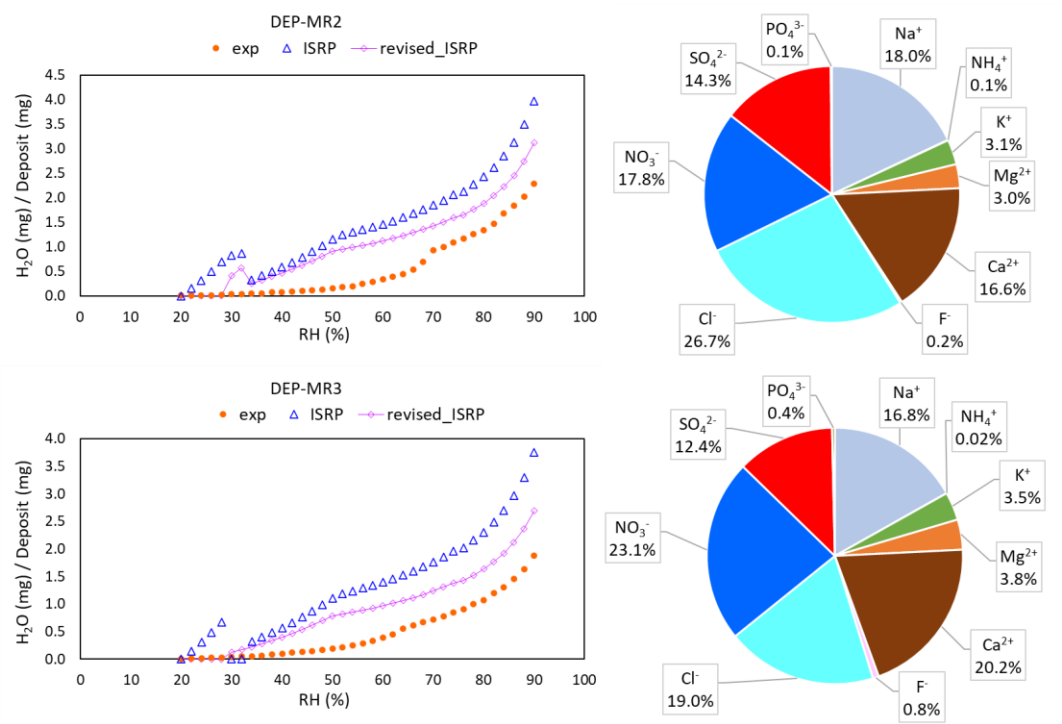

Figure S6: Comparison between experimental (orange) and modeled humidification curves with standard version of ISORROPIA (green) and refined version (pink) for DEP-MR2 and DEP-MR3.

ISORROPIA refinements

The refinements implemented in ISORROPIA mainly concern the U and W subroutines, which are engaged in DEP-MR1, DEP-MR2, DEP-MR3 and EURECA cases.

DEP-MR1: DEP-MR1 case was identified as a sulfate–poor, dust–and–sodium–rich and dust–poor regime, involving subroutine U. While ISORROPIA decided whether to consider only solid or both solid and liquid phase based on the presence of *any* salt among NH_4NO_3, NH_4Cl, $NaNO_3$ or NaCl, revised ISORROPIA based this selection on the presence of *all* the aforementioned salts. More specifically, at 24 % RH, ISORROPIA entered subroutine U1, SUBCASE 2, which computes both the solid and liquid aerosol phases by calling CALCMDRPII. Consequently, aerosol water uptake begins at very low RH, leading to a deviation from the experimental reference. In the revised ISORROPIA ensure a more physically consistent treatment of deliquescence and aerosol water uptake.

DEP-MR1 also showed irregular behavior between 60 and 65 % RH, when ISORROPIA switched from U1, SUBCASE 2 to U2, SUBCASE 2; this transition can produce noticeable discontinuities in the predicted phase state and aerosol water content. This discrepancy was resolved by modifying the above-described subroutine selection criteria.

Within the subroutine CALCACT1, called within CALCU2A and CALCU3A, adjustments to the calculation of ionic activity were made, to avoid unintended modification of molality variables while correctly evaluating ionic strength.

DEP-MR2, DEP-MR3 and EURECA: DEP-MR2, DEP-MR3 and EURECA cases were classified as a sulfate–poor, dust–and–sodium–rich and dust–rich regime, involving subroutine W. In the original configuration, the selection between CALCW1A (solid phase only) and CALCMDRPII (solid + liquid phases) at low RH depended exclusively on the RH threshold:

- RH < 20%: only solid phase is considered (CALCW1A)
- RH ≥ 20%: both solid and liquid phases are considered (CALCMDPII)

This criterion, based solely on RH, was found to be overly simplistic and not fully representative of the chemical system. Therefore, in the revised ISORROPIA, the selection mechanism was updated to explicitly account for the presence or absence of specific hygroscopic salts, namely $CaCl_2$ and $MgCl_2$.

In the update formulation:

- If $CaCl_2$ is present, ISORROPIA allows the coexistence of solid and liquid phase for RH ≥ 20 %
- If $CaCl_2$ is absent but $MgCl_2$ is present, the coexistence of solid and liquid phase is allowed for RH ≥ 24 %.

This modification provides a more realistic representation of aerosol deliquescence behavior, as it links the onset of the liquid phase not only to RH but also to the chemical composition of the aerosol, improving the agreement with observed thermodynamic behavior.
Within the subroutine CALCACT1, called within CALCW2A and CALCW3A, adjustments to the calculation of ionic activity were made, to avoid unintended modification of molality variables while correctly evaluating ionic strength.