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Title: Dust-driven changes in particle pH differentially regulate secondary inorganic aerosol formation in central China

The synchronous, hourly measurements of ions, elements, OC/EC and precursor gases at seven sites in Henan during the April 2023 dust event constitute a valuable dataset, and the question the authors pose — why cities under the same dust plume respond differently — is a sensible one.

The problem is that the paper's central conclusions are not observations but outputs of a thermodynamic model and of rate calculations whose assumptions are fragile enough to overturn those conclusions. More seriously, the manuscript does not confront the places where its own calculations and its own observations disagree. That dust raises particle pH, weakens the TMI pathway and shifts nitrate toward the particle phase is already established (Karydis et al., 2021; Ding et al., 2019; Lang et al., 2025). What this study could add to ACP is a quantitative explanation of the intercity contrast, and that part remains largely qualitative.

1. Major comments

(1) The claimed increase in ε(NO_3^-) contradicts the observed decrease in NOR. The authors conclude that higher pH promoted nitrate partitioning, most notably in SQ (ε from 0.81 to 0.95; L402–412 and Abstract). Yet Sect. 3.2 reports that NOR decreased in every city on dust days (Fig. 4), and no clean-day NO_3^- concentration for SQ is given against which the dust-day value can be judged. If partitioning had strengthened, the measured nitrate should show it. Unless the calculated Δε (0.05–0.14) is confronted with the observed nitrate response, the argument merely restates the shape of a sigmoid. The statement that low-pH cities show larger Δε (L409–412) is true by construction of the curve.

(2) The omission of gaseous HNO_3 is not shown to be harmless. With TNO_3 set equal to particulate NO_3^- (L166–172), forward-mode ISORROPIA-II re-partitions part of the input nitrate to the gas phase, biasing both modelled NO_3^- and pH. The authors argue the effect is minor because ε is insensitive above pH 2.5–3, but their own clean-day ε for SQ is 0.81 — roughly a fifth of total nitrate missing from the input — and SQ is precisely the city on which the headline result rests. Either correct the TNO_3 input iteratively using the modelled ε, or

provide an explicit sensitivity analysis. Computing ε separately with Eq. (4) duplicates the ISORROPIA output, and setting the activity-coefficient product to unity is hard to defend at dust-period ionic strengths.

(3) The TMI "suppression" is a pure function of pH and ignores the measured Fe and Mn. Fe(III) and Mn(II) are derived solely from the solubility products of $Fe(OH)_3$ and $Mn(OH)_2$ (Text S2, Eq. 1), so their concentrations depend on nothing but pH. The reported 75–97% decline in the TMI rate is therefore an arithmetic consequence of the pH rise, not an assessment of the Fe and Mn that dust delivered — quantities the authors actually measured by XRF. Wang et al. (2021, Nat. Commun.), cited here, report the opposite tendency for surface Mn on dust. A parallel calculation using measured Fe/Mn with literature solubility fractions is needed. The justification for neglecting ionic strength (Text S2: because ISORROPIA predicted high values) inverts the logic; high ionic strength is exactly why it must be included (Cheng et al., 2016).

(4) The magnitude of the calculated sulfate production is incompatible with the observations. Clean-day TMI rates of 0.25–2.0 μg m^{-3} h^{-1} (L379) imply up to ~48 μg m^{-3} of sulfate per day, against observed SO_4^{2-} of 4–6 μg m^{-3}. This points to overestimation from the Fe(III) treatment and the neglect of ionic strength, and undermines the conclusion, based on absolute rates, that TMI oxidation "consistently dominated". Excluding H_2O_2 is not a minor omission in April, when O_3 is high.

(5) Low-RH exclusion and pH uncertainty. Fig. S3 shows RH falling to 10–30% at the dust peak (11–12 April), and hours with RH ≤ 30% were discarded. How many dust-period hours survive, and do they represent the peak? The dust-day whiskers in Fig. 5 (2.7–6.9) are the familiar signature of unstable pH retrieval at very low ALWC. Furthermore, dust Ca^{2+} resides largely in externally mixed coarse $CaCO_3$/$CaSO_4$; MARGA measures ions dissolved after steam-jet condensation and may overstate the Ca^{2+} actually available in aerosol water. The limits of the internally mixed, metastable assumption under dust conditions must be stated explicitly.

(6) Baseline pH values in the supplementary sensitivity analyses are mutually inconsistent. Each panel varies one parameter with the others fixed at their means, so the pH at the mean value must be identical across panels for a given city. For SQ it is 3.87 (S5), 4.05 (S6), 3.86 (S8) and 3.95 (S9), while the text gives 3.58 (L332); PY shows 3.90, 4.05, 4.11 and 3.97. Different inputs or settings were evidently used, and Sect. 3.3, which relies on Figs. S5–S11,

cannot be trusted until this is resolved and recalculated.

(7) Double counting in the mass reconstruction. Fig. 2 lists CM and Ca^{2+} as separate components, but Eq. (1) already includes XRF Ca with a coefficient of 1.4. Adding water-soluble Ca^{2+} again inflates dust-day totals. Mass closure against TEOM $PM_{2.5}$ should be shown and the discrepancy explained (e.g., ZZ dust day: 134.5 μg m^{-3} in Table 1 versus ~95 μg m^{-3} in Fig. 2a).

(8) Absence of statistical support. The clean/dust classification (exact dates; whether the 14–16 April secondary peak is included) is not defined, and no significance tests are provided for any of the contrasts. Given the IQRs in Fig. 5 and the strong autocorrelation of hourly data, it must be demonstrated that pH differences of 0.45–0.75 are meaningful. The single-factor substitution (L342–346) is order-dependent in a nonlinear system and the individual ΔpH terms do not sum to the total; this is not acknowledged.

(9) The policy conclusion overreaches. Recommending coordinated NO_x and fugitive-dust management on the strength of an unverified Δε of 0.05–0.14 goes beyond what the results can bear, particularly for an event of Mongolian long-range origin in which the leverage of local dust control is nowhere quantified.

2. Specific and technical comments

- L111–112: "in an urban agglomeration in central China agglomeration" — duplicated word.
- L189–191: 24-h back-trajectories are too short to support a Mongolian origin; 48–72 h recommended.
- L376–377: "marked in the figure" — figure number (Fig. 7) missing.
- L415–423: the comparison values (Beijing 45.6%, Horqin 69%, Henan 4.5–5.2) lack citations.
- L279: "0.5-fold increase" is ambiguous.
- Sect. 3.2: dust-day SO_4^{2-} and NO_3^- are given without the corresponding clean-day values.
- Synopsis, Highlights and Graphical abstract are not ACP elements.
- Data availability: ACP requires deposition in a public repository; "available on request" does not meet the journal's policy.

- Supplement: residual Chinese characters in Text S2 ("$Fe(OH)_3$和$Mn(OH)_2$"); "Table S3 and S4" should read S2 and S3; "Aanyang" and "Xinxaing" in Fig. S4; unbalanced brackets in the TMI rate expression of Table S1.