

## Abating HCl and HNO<sub>3</sub> is more effective than NH<sub>3</sub> for mitigating high aerosol loading over the Indo-Gangetic Plain

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### Abstract:

This study investigates aerosol "sensitivity regimes" to explore the effectiveness of abating gaseous precursors to mitigate aerosols over the Indo-Gangetic Plain (IGP). A new mechanistic insight is proposed by integrating ISORROPIA-II thermodynamical model with high-resolution simultaneous measurements of precursor gases (HCl, HNO<sub>3</sub>, and NH<sub>3</sub>) and inorganic constituents of PM<sub>1</sub> and PM<sub>2.5</sub>, monitored for the first time in India using MARGA-2S instrument. The estimated aerosol acidity (pH) of PM<sub>1</sub> and PM<sub>2.5</sub> was 4.49±0.53 and 4.58±0.48, respectively. The sensitivity of phase-partitioning ( ) of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> to pH, ALWC, HCl, HNO<sub>3</sub>, and NH<sub>3</sub> showed that fine aerosols fall in the "HCl and HNO<sub>3</sub> sensitive regime", emphasizing that HCl and HNO<sub>3</sub> reductions would be the most effective pathway to reduce aerosols in NH<sub>3</sub>-rich IGP. Since existing mitigation strategies over IGP are random and ineffective, this novel insight is the first step in providing a thermodynamically consistent "roadmap" to mitigate aerosols effectively.

**Keywords:** Gas-to-particle partitioning; Aerosol mitigation; Thermodynamics; ISORROPIA II; Aerosol acidity (pH) and aerosol liquid water content (ALWC); Indo-Gangetic Plain (IGP)

**Plain Language Summary:**

Researchers have a long-standing conundrum for the apparent disconnection between immense aerosol loading and adopted mitigation policies. We show that pollution mitigation cannot be achieved by "randomly" reducing the primary pollutants; instead, a thermodynamically consistent "roadmap" is needed. Indo-Gangetic Plain (IGP) experiences severe air pollution every winter, with ammonium chloride, ammonium nitrate as the major inorganic fractions of fine aerosols. Thermodynamic controls for the high aerosol loading show that fine aerosols fall in the "HCl and HNO<sub>3</sub> sensitive regime", and HCl and HNO<sub>3</sub> reductions would be the most effective pathway to reduce high aerosol loading. Though NH<sub>3</sub> mass concentration is much higher than HCl and HNO<sub>3</sub> but NH<sub>3</sub> reduction would not effectively mitigate aerosols. This new mechanistic insight suggests considering aerosol acidity (pH) and aerosol liquid water content (ALWC) more robustly and accurately as these parameters profoundly control the aerosol loading. Since existing aerosol mitigation strategies over IGP are random and ineffective, this novel analysis is the first step in providing "actionable intelligence" to the policymakers to abate precursors in a thermodynamically consistent way, like those for Europe, the USA, and other climatic regions.

**1. Introduction**

Air pollution is a major cause of millions of premature deaths around the world (Cohen et al., 2015). Mitigating high aerosol loading is a major concern for researchers over the globe. But to regulate or mitigate something, it needs to be measured, monitored, and investigated thoroughly, but despite unprecedented efforts, the understanding of the intricate physical, chemical, and thermodynamical properties of atmospheric constituents has remained something of a mystery (Seinfeld and Pandis, 1997; Guo et al., 2018; Gultepe et al., 2007; Nenes et al., 2020).

Indo Gangetic Plain (IGP) is documented to be one of the most polluted regions in the world (WHO, 2016; Ravishankara et al., 2020). There is a growing need to abate high aerosol loading in IGP, as it severely affects the ecosystem and human health (Ghude et al., 2017; Sinha et al., 2019). During wintertime, the mass loading of PM<sub>1</sub>, PM<sub>2.5</sub> generally exceeds 400-600  $\mu\text{g m}^{-3}$ , which causes severe negative impacts on human health and the ecosystem. These fine aerosols are primarily composed of chloride, sulfate, nitrate, and ammonium (CSNA) in the IGP (Acharja et al., 2020). The observed hourly chloride concentrations sometimes exceeded 100  $\mu\text{g m}^{-3}$ , considered to be among the highest reported anywhere in the world. The gas-phase ammonia (NH<sub>3</sub>) was also found to be very high, which significantly affects the secondary aerosol formation in winter (Acharja et al., 2021). Extensive effort is needed to improve our scientific understanding, to regulate aerosol loading effectively. Several recent studies have

investigated the sensitivity of aerosols to the reduction in precursor gases over China, USA, and Europe (Nenes et al., 2020; Guo et al., 2018), but studies conducted over India remain elusive to date.

This study aims to provide new mechanistic insights into aerosol mitigation by integrating the dataset of precursor gases (HCl, HNO<sub>3</sub>, and NH<sub>3</sub>) and inorganic constituents (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) of PM<sub>1</sub> and PM<sub>2.5</sub> acquired using the first deployment of the MARGA-2S instrument in IGP with the ISORROPIA-II thermodynamic equilibrium model simulations. The dataset filled the much-needed data gap for quantitative analysis and provided the best opportunity to investigate aerosol sensitivity to precursors over IGP. We explored a "thermodynamical framework" to show that aerosol mitigation cannot be achieved by "randomly" reducing the primary pollutants, rather a fundamental understanding of complex thermodynamical control of aerosol loading is needed. For this, we determined pH and ALWC using the ISORROPIA-II thermodynamic equilibrium model. The accuracy of the model simulation is checked by comparing the model predicted species concentrations with MARGA-2S observations. After verifying the reliability of the model prediction, the sensitivity of gas-to-particle partitioning of major aerosol species like chloride, nitrate, and ammonium to pH and ALWC is checked using the sigmoidal (S) curves. Finally, we investigated the sensitivity of gaseous precursors like HCl, HNO<sub>3</sub>, and NH<sub>3</sub> to the formation of fine particulate matter to explore the aerosol "sensitivity regimes" and establish a thermodynamically consistent framework for effective aerosol mitigation.

## 2. Materials and Methods

### 2.1 Sensitivity of aerosol mass loading to pH, ALWC using sigmoidal (S) curves

Factors that profoundly influence almost every aspect of aerosols are aerosol acidity (pH) and aerosol liquid water content (ALWC) (Weber et al., 2016; Nenes et al., 1999). The direct monitoring of aerosol pH is highly challenging since an established analytical method of directly determining aerosol pH does not exist. Previous studies used several proxy methods like H<sup>+</sup> ion concentration, ion balance, ammonium-to-sulfate ratio, and cation-to-anion ratio to indirectly infer the fine particle pH (Toon et al., 1986; Rindelaub et al., 2016). Pye et al. (2020) showed that these methods could not estimate aerosol acidity accurately, and a small bias in estimated pH may cause substantial errors in the chemical and thermodynamical properties of aerosols (Hennigan et al., 2015). To accurately estimate pH and ALWC, numerous studies have used thermodynamic models like E-AIM, MARS, EQUISOLV, and ISORROPIA-II, among which ISORROPIA-II is the most used that can predict pH and ALWC with great accuracy (Fountoukis and Nenes 2007; Nenes et al., 1999; Pye et al., 2020).

The sensitivity of the phase partitioning of nitrate [(NO<sub>3</sub><sup>-</sup>)], chloride [(Cl<sup>-</sup>)] and ammonium [(NH<sub>4</sub><sup>+</sup>)] to pH, ALWC, and T is estimated using the Henry's law constant (Pitzer et al., 1973; Clegg et al., 1998; Meissner et al., 1972) and

following the methodology given in Guo et al., (2016) as

$$\varepsilon(\text{NO}_3^-) = \frac{H_{\text{HNO}_3}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}}{\gamma_{\text{H}^+} \gamma_{\text{NO}_3^-} 10^{-\text{pH}} + H_{\text{NO}_3}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}} \quad (1)$$

$$\varepsilon(\text{Cl}^-) = \frac{H_{\text{HCl}}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}}{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-} 10^{-\text{pH}} + H_{\text{HCl}}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}} \quad (2)$$

and

$$\varepsilon(\text{NH}_4^+) = \frac{\frac{\gamma_{\text{H}^+} 10^{-\text{pH}}}{\gamma_{\text{NH}_4^+}} H_{\text{NH}_3}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}}{1 + \frac{\gamma_{\text{H}^+} 10^{-\text{pH}}}{\gamma_{\text{NH}_4^+}} H_{\text{NH}_3}^* R T \text{ALWC}_i \times 0.987 \times 10^{-14}}, \quad (3)$$

where  $\gamma$  is the activity coefficient of protonated species in the aqueous medium.  $H^*$  is the equilibrium constants of  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{NH}_3$  adopted from Clegg and Brimblecombe (1989), and Clegg (1998). Then, the units were converted from mole fraction-based unit  $\text{atm}^{-1}$  to molality-based unit  $\text{mole}^2 \text{kg}^{-2} \text{atm}^{-1}$  (Nenes et al., 1999; Patwardhan et al., 1986).  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and the value 0.987 is for the transformation of 1 atm to 1 bar. The equations describe the  $\text{HNO}_3\text{-NO}_3^-$ ,  $\text{NH}_3\text{-NH}_4^+$ , and  $\text{HCl-Cl}^-$  partitioning and the estimated values of  $\text{ALWC}_i$  and  $T$  were used to evaluate the sigmoidal (S) curves of  $(\text{NO}_3^-)$ ,  $(\text{Cl}^-)$ , and  $(\text{NH}_4^+)$  at different pH regimes.

## 2.2 Sensitivity of aerosols to $\text{HCl}$ , $\text{HNO}_3$ , and $\text{NH}_3$ perturbations and aerosol "sensitivity regimes"

The estimated pH and ALWC of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were used as coordinates to represent aerosols in different "sensitivity regimes" where aerosol mass is sensitive to  $\text{HNO}_3$ ,  $\text{HCl}$ , and/or  $\text{NH}_3$  variability (Nenes et al., 2020). Three parameters  $\Psi$ ,  $\Omega$ , and  $\varphi$  are defined as:

$$\Psi = \frac{H_{\text{HNO}_3}^* R T \times 0.987 \times 10^{-14}}{\gamma_{\text{H}^+} \gamma_{\text{NO}_3^-}} \quad (4)$$

$$\Omega = \frac{H_{\text{HCl}}^* R T \times 0.987 \times 10^{-14}}{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}} \quad (5)$$

$$\varphi = \frac{\gamma_{\text{H}^+}}{\gamma_{\text{NH}_4^+}} H_{\text{NH}_3}^* R T \times 0.987 \times 10^{-14} \quad (6)$$

Substituting these three parameters in equations 1 - 3, the partitioning ratio of ( $\text{NO}_3^-$ ), ( $\text{Cl}^-$ ) and ( $\text{NH}_4^+$ ) can be expressed as a function of ALWC, like

$$\varepsilon(\text{NO}_3^-) = \frac{\Psi \times \text{ALWC}_i}{[\text{H}^+] + \Psi \times \text{ALWC}_i}, \quad (7)$$

$$\varepsilon(\text{Cl}^-) = \frac{\Omega \times \text{ALWC}_i}{[\text{H}^+] + \Omega \times \text{ALWC}_i}, \quad (8)$$

and

$$\varepsilon(\text{NH}_4^+) = \frac{\varphi \times [\text{H}^+] \times \text{ALWC}_i}{1 + \varphi \times [\text{H}^+] \times \text{ALWC}_i}. \quad (9)$$

To check the sensitivity of these partitioning fractions to aerosol pH and ALWC, we assume a characteristic partitioning ratio ( $\varepsilon$ ) value of 0.1, and define the threshold value of ( $\text{NO}_3^-$ ), ( $\text{Cl}^-$ ) and ( $\text{NH}_4^+$ ) as  $\alpha$ ,  $\beta$ , and  $\gamma$ , and they are respectively given as

$$\alpha = \frac{\Psi \times \text{ALWC}_i}{[\text{H}^+] + \Psi \times \text{ALWC}_i}, \quad (10)$$

$$\beta = \frac{\Omega \times [\text{H}^+] \times \text{ALWC}_i}{1 + \Omega \times [\text{H}^+] \times \text{ALWC}_i}, \quad (11)$$

and

$$\gamma = \frac{\varphi \times [\text{H}^+] \times \text{ALWC}_i}{1 + \varphi \times [\text{H}^+] \times \text{ALWC}_i}. \quad (12)$$

Above the threshold value ( $\varepsilon = 10\%$ ) the  $\text{PM}_{1,}$   $\text{PM}_{2.5}$  aerosols are sensitive to  $\text{HNO}_3$ ,  $\text{HCl}$ , or  $\text{NH}_3$  emissions. Based on these "characteristic" threshold values, we define "characteristic acidity" for nitrate, ( $\text{pH}'$ ), chloride ( $\text{pH}''$ ) and ammonium ( $\text{pH}'''$ ), respectively, as

$$\text{pH}' = -\log\left[\left(\frac{1-\alpha}{\Psi}\right) \times \text{ALWC}_i\right], \quad (13)$$

$$pH'' = \log \left[ \left( \frac{1-\beta}{\beta} \right) \varphi \times ALWC_i \right], \quad (14)$$

and

$$pH''' = \log \left[ \left( \frac{1-\gamma}{\gamma} \right) \Omega \times ALWC_i \right], \quad (15)$$

which vary logarithmically only function of  $ALWC_i$ . Using these characteristic values as coordinates, six "sensitivity regimes" are defined as

- Regime I:  $pH < pH'$ ,  $pH''$  and  $pH > pH'''$ , where aerosol is not sensitive to  $HNO_3$ ,  $HCl$  or  $NH_3$  change and defined as "insensitive",
- Regime II:  $pH > pH'$ ,  $pH < pH''$  and  $pH > pH'''$ , where aerosol is sensitive to  $HNO_3$  and not sensitive to  $HCl$  and  $NH_3$  perturbations and defined as " $HNO_3$  sensitive",
- Regime III:  $pH > pH'$ ,  $pH''$  and  $pH > pH'''$ , where aerosol is sensitive to  $HCl$ ,  $HNO_3$  and not sensitive to  $NH_3$  perturbations and defined as " $HCl$  and  $HNO_3$  sensitive",
- Regime IV:  $pH > pH'$ ,  $pH''$  and  $pH < pH'''$ , where aerosol is sensitive to  $HCl$ ,  $HNO_3$ , and  $NH_3$  perturbations and defined as " $HCl$ ,  $NH_3$  and  $HNO_3$  sensitive",
- Regime V:  $pH > pH'$  and  $pH < pH''$ ,  $pH'''$ , where aerosol is sensitive to  $HNO_3$  and  $NH_3$  and not sensitive to  $HCl$  and defined as " $HNO_3$  and  $NH_3$  sensitive", and
- Regime VI:  $pH < pH'$ ,  $pH''$  and  $pH < pH'''$ , where aerosol is sensitive to  $NH_3$  and not sensitive to  $HCl$  and  $HNO_3$  and defined as " $NH_3$  sensitive".

### 3. Results

#### 3.1 Evaluation of ISORROPIA-II thermodynamical model simulations

Running a thermodynamical equilibrium model like ISORROPIA-II to predict  $pH$  and  $ALWC$  is not necessarily straightforward and is comparatively new to the atmospheric science community in India. The ISORROPIA-II model was run in the "forward" mode using the hourly measured total (gas + particle) species concentrations instead of only particle-phase concentrations as input (Hennigan et al., 2015). This mode is considered to be more accurate, and the predicted data is thoroughly checked and compared to MARGA-2S measurements to validate the model simulations.

Figure 1 shows the comparison between the predicted and measured concentrations of  $NH_4^+$ ,  $NO_3^-$ ,  $Cl^-$  of  $PM_{10}$  and  $PM_{2.5}$ . The predicted  $PM_{10}$   $NH_4^+$  ( $r = 0.97$ ),  $NO_3^-$  ( $r = 0.93$ ),  $Cl^-$  ( $r = 0.98$ ) and  $PM_{2.5}$   $NH_4^+$  ( $r = 0.87$ ),  $NO_3^-$  ( $r = 0.98$ ),  $Cl^-$  ( $r = 0.99$ ) showed very good correlation with the measured concentrations. Along with these particle-phase species, the predicted and measured gas-phase  $NH_3$  ( $r = 0.93$ ) and gas-to-particle partitioning ratio ( $\Gamma$ ) of ammonium

( $\text{NH}_4^+$ ) ( $r = 0.90$ ) also correlated well. The normalized mean bias (NMB) between the measured and predicted  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NH}_3$  concentrations was very low (10%). These high correlations were attributed to the reliability of the ISORROPIA-II model simulations.

### 3.2 Temporal variation of pH and ALWC of $\text{PM}_{10}$ and $\text{PM}_{2.5}$

The pH and ALWC of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were estimated during 19 December 2017 to 10 February 2018. The predicted pH of  $\text{PM}_{10}$  varied between 2.19 to 5.63, and the mean  $\text{PM}_{10}$  pH (average $\pm$ SD) was  $4.49\pm 0.53$ . The  $\text{PM}_{2.5}$  pH ranged between 2.55 to 6.54 with a mean value of  $4.58\pm 0.48$ . The predicted pH of  $\text{PM}_{2.5}$  was similar to the measured  $\text{PM}_{2.5}$  pH of  $4.6\pm 0.5$  over Delhi, estimated during the WiFEX campaign period of 2015-16, showing the reliability and accuracy of the ISORROPIA-II model simulation (Ali et al., 2019). The accuracy of ISORROPIA-II thermodynamic model simulations is crucial, as most chemical transport models often underestimate aerosol acidity (Nault et al., 2021).

As liquid water makes up a significant part of the aerosol volume, the temporal variation of ALWC was investigated. The mean ALWC of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  was  $169\pm 205$  and  $324\pm 393$   $\mu\text{g m}^{-3}$ , respectively, showing that higher ALWC corresponds to higher PM concentrations. This is evident from Henry's law, which shows that particles with high ALWC would take up more gaseous pollutants, and the equilibrium would lead to an increase in their water content and the formation of more secondary aerosol.

The ALWC variability generally controlled the pH variability. The lesser ALWC of  $\text{PM}_{10}$  caused it to be slightly more acidic than  $\text{PM}_{2.5}$ , as  $\text{H}^+$  gets more diluted in higher liquid water in  $\text{PM}_{2.5}$ . The aerosol liquid water serves as a reaction medium and enhances the chemical reaction rates of heterogeneous, multiphase reactions, and the multiphase reactions inside aerosol water are much faster than heterogeneous reactions on the solid surface (Ravishankara et al., 1997; Hanson et al., 1994; Rood et al., 1989). This implies the crucial role of pH and ALWC in high aerosol loading.

### 3.3 Gas-to-particle phase partitioning of aerosols during winter over IGP

The average chloride partitioning ratio ( $\text{Cl}^-$ ) of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  was  $0.93\pm 0.09$  and  $0.96\pm 0.07$  respectively, implying the dominant presence of chloride in the particle-phase during winter. The ( $\text{Cl}^-$ ) was 0.4 at RH = 50%, and at RH = 80%, the ( $\text{Cl}^-$ ) sharply increased to 0.95, showing the enhanced chloride formation in the particle-phase. The increased phase-partitioning of total chloride ( $\text{HCl} + \text{Cl}^-$ ) at high humid conditions can further promote chloride formation caused by increased ALWC. The enhanced ALWC increases pH by dilution, further increasing total chloride partitioning and significantly increasing  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  chloride in a positive feedback loop (Guo et al., 2018; Song et al., 2018).

The average ( $\text{NO}_3^-$ ) of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  was  $0.83\pm 0.11$  and  $0.89\pm 0.08$  respectively. This shows the dominance of particle-phase nitrate over gas-phase  $\text{HNO}_3$

during winter. The high particle-phase nitrate concentrations significantly impact the total aerosol loading as the presence of more ammonium nitrate reduces the mutual deliquescence relative humidity (MDRH) of aerosols resulting in the formation of more secondary aerosols in polluted conditions (Davis et al., 2015; Shi et al., 2017; Nah et al., 2018). When the ammonium nitrate concentration is high, especially in humid and ammonia-rich conditions, it could promote secondary aerosol formation through uptake kinetic regime and changing the particle state (Liu et al., 2021). So, it is crucial to investigate the sensitivity of  $(\text{NO}_3^-)$  to factors like pH, ALWC, and  $\text{HNO}_3$  following the Eq 1.

Interestingly, ammonium ( $\text{NH}_4^+$ ) phase partitioning showed the opposite behavior to chloride and nitrate. Not the particle-phase ammonium ( $\text{NH}_4^+$ ), but the gas-phase ammonia ( $\text{NH}_3$ ) dominated, and the average ( $\text{NH}_4^+$ ) was  $0.42 \pm 0.17$ ,  $0.55 \pm 0.15$  for  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  respectively. This abundant gas-phase ammonia plays a crucial role in developing high ammonium salts loading (Acharja et al., 2021). Thermodynamically, ammonia neutralizes the atmospheric acids like HCl,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$  based on the order of solubility, and as HCl is the strongest acid,  $\text{NH}_3$  first reacts with HCl to form  $\text{NH}_4\text{Cl}$ . Then the excess  $\text{NH}_3$  reacts with  $\text{H}_2\text{SO}_4$  over highly volatile  $\text{HNO}_3$ , forming  $(\text{NH}_4)_2\text{SO}_4$  first and then  $\text{NH}_4\text{NO}_3$  (Dentener and Crutzen 1994; Collett et al., 1994; Toon et al., 1986; Nemitz et al., 2004). However, it is crucial to note that the  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were moderately acidic despite the ammonia-rich atmosphere, depicting the weak sensitivity of pH to ammonia and the significance of complex thermodynamic control on aerosol loading.

### 3.4 Sensitivity of gas-to-particle partitioning ( $\alpha$ ) to pH and ALWC using sigmoidal (S) curves

Figures 2a, 2b shows the variability of  $\alpha(\text{Cl}^-)$ ,  $\alpha(\text{NO}_3^-)$  with pH, ALWC, and T. Three prominent regimes are shown, in which  $\alpha$  varies between complete gas-phase ( $\sim 0\%$ ) to complete particle-phase ( $\sim 100\%$ ). In regime 1,  $\alpha(\text{Cl}^-)$ ,  $\alpha(\text{NO}_3^-)$  asymptotically approaches 0, and the total species primarily remain in the gas-phase. In regime 3,  $\alpha$  asymptotically approaches 1, and the whole species is in the particle phase. In regime 2,  $\alpha$  varies between 0 and 1, and the species remain as a mixture of gas and particle-phase. Modulating this "pH window" the particle-phase can be shifted to gas-phase resulting in less particle-phase loading in the atmosphere.  $\text{pH}_{50}$  is defined, where  $\alpha(\text{Cl}^-)$  and  $\alpha(\text{NO}_3^-)$  is 0.5 and total chloride, nitrate remained 50% in the gas-phase and 50% in the particle-phase. Modulating the phase partitioning ratio ( $\alpha$ ) to  $\alpha_{(\text{pH}50)}$  value, the particle-phase loading of chloride and nitrate can be reduced to 50%. Figures 2a, 2b shows that a pH change from 4.45 to 2.4 and 4.45 to 1.9 is required to reduce  $\alpha(\text{Cl}^-)$  and  $\alpha(\text{NO}_3^-)$  to 50%. The variability in  $\alpha$  at a constant pH is caused by the variation in ALWC, implying the significance of ALWC in modulating the particle-phase fraction.

In Figures 2c and 2d, we have included the variability of ammonium ( $\text{NH}_4^+$ ) phase partitioning along with chloride ( $\text{Cl}^-$ ) and nitrate ( $\text{NO}_3^-$ ). The sigmoidal (S) curves show that the particle-phase chloride and nitrate increase with pH,

whereas ammonium decreases. This inverse relation of ammonium compared to chloride and nitrate is due to opposite acid and base partitioning responses to pH and needs to be considered to develop effective abatement measures. We estimated the sensitivity and effectiveness of phase-partitioning to precursors like HCl, HNO<sub>3</sub>, and NH<sub>3</sub> and defined "sensitivity regimes" in different colors.

In the blue regime, a marginal change in HCl and HNO<sub>3</sub> would significantly shift the particle-phase fraction of (Cl<sup>-</sup>), (NO<sub>3</sub><sup>-</sup>). We defined this regime as "HCl and HNO<sub>3</sub> sensitive regime", where ammonia remains almost exclusively in the gas-phase, and perturbation in NH<sub>3</sub> concentrations would not change the ammonium particle-phase fraction regardless of the level of total ammonia present. So the "HCl and HNO<sub>3</sub> sensitive regime" is also an "NH<sub>3</sub> insensitive regime". A fractional change in NH<sub>3</sub> concentrations would significantly change (NH<sub>4</sub><sup>+</sup>) in the pink regime, and we termed it the "NH<sub>3</sub> sensitive regime". In the mid-range of the sigmoidal curves, a small perturbation in the HCl, HNO<sub>3</sub>, and NH<sub>3</sub> concentrations would directly impact the particle-phase loading of chloride, nitrate, and ammonium and defined as the "HCl, HNO<sub>3</sub>, and NH<sub>3</sub> sensitive regime".

The estimated pH of PM<sub>1</sub> and PM<sub>2.5</sub> falls in regime 3, on the flat side of the S curves. Here, two possibilities emerge as the pathway to modulate high aerosol concentrations. First, a substantial reduction in pH is needed, which would evaporate NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> and shift them to the gas-phase, which may not be feasible due to the health and environmental implications of high aerosol acidity. Second, reducing HCl and HNO<sub>3</sub> concentrations would most effectively reduce particle-phase loading as aerosols are in the "HCl, HNO<sub>3</sub> sensitive regime". This pathway is feasible compared to the other, and we conclude that HCl and HNO<sub>3</sub> controlling policy should be adopted to reduce aerosol loading in the IGP.

### 3.5 Aerosol mass loading sensitivity to HCl, HNO<sub>3</sub>, and NH<sub>3</sub> perturbations

We explored a mathematical framework to reduce ammonium chloride and ammonium nitrate concentrations by following the methodology of Nenes et al., (2020). Using pH and ALWC as coordinates, we defined six "sensitivity regimes", where aerosols are sensitive to HCl, HNO<sub>3</sub>, and NH<sub>3</sub> perturbations. As chloride dominates the inorganic mass fraction of fine aerosol in the IGP, we rigorously investigated the aerosol mass sensitivity to HCl emissions and defined the "HCl sensitive regime" for the first time. This is significantly different from studies conducted over China, Europe, and USA, where researchers have investigated aerosol sensitivity to only HNO<sub>3</sub> and NH<sub>3</sub> and did not investigate the "HCl sensitive regime".

The "sensitivity regimes" are shown in different colors in Figure 3. 1100 hourly observational data points are plotted to check the instantaneous response of aerosol loading to HCl, HNO<sub>3</sub>, and NH<sub>3</sub> variability. Figures 3a and 3c show PM<sub>1</sub> and PM<sub>2.5</sub> aerosols to remain in the pink shaded region, where aerosols respond proportionally to changes in the HCl and HNO<sub>3</sub> emissions but tend

to be insensitive to  $\text{NH}_3$  emissions. We defined the pink regime as "HCl and  $\text{HNO}_3$  sensitive regime", indicating that HCl and  $\text{HNO}_3$  reduction would be the most effective pathway in controlling aerosol pollution over IGP. Ammonia is much higher than HCl and  $\text{HNO}_3$  in IGP, but fine aerosols are not sensitive to variations of it. Instead, HCl and  $\text{HNO}_3$  are by far the limiting factors in aerosol loading, which should be controlled by controlling the major HCl and  $\text{NO}_x$  emissions over IGP.

In Figures 3b and 3d, all the data points are color-coded with  $\text{PM}_1$  and  $\text{PM}_{2.5}$  concentrations respectively. The figures demonstrate that higher aerosol loading is often associated with higher ALWC in the "HCl and  $\text{HNO}_3$  sensitive regime". Interestingly, the ALWC usually ranges between tens to hundreds of micrograms per cubic meter in climatic regions like China and USA, but over IGP the ALWC is an order of magnitude higher, sometimes reaching  $\sim 2000\text{-}2500 \mu\text{g m}^{-3}$  for  $\text{PM}_1$  and  $\text{PM}_{2.5}$ . This acidic aerosol liquid water significantly influences the phase-partitioning and demonstrates the impact of pH and ALWC on aerosol loading. Fewer cases with low  $\text{PM}_1$ ,  $\text{PM}_{2.5}$  levels were found in the  $\text{NH}_3$  sensitive regime, showing the less importance of  $\text{NH}_3$  abatement to modulate high aerosol loading. It is also interesting to note that a significant reduction in  $\text{NH}_3$  emissions may affect agricultural productivity and potentially increase aerosol acidity. So the HCl and  $\text{HNO}_3$  reductions should be adopted to mitigate aerosols most effectively.

#### 4. Discussion

The complex interaction of intricate physical, chemical, and thermodynamical processes influencing the aerosol loading is schematically shown in Figure 4. Two different atmospheric scenarios are characterized: clean atmosphere and polluted atmosphere, where photochemistry plays a distinct role during the clean period, and multiphase, heterogeneous chemistry dominates the pollution episodes, as the homogeneous gas-phase reactions were suppressed due to reduced solar radiation. As schematically shown, the acidic gases are first absorbed on the surface layer of aerosols, and heterogeneous reactions rapidly occur at the surface resulting in the rapid increase in secondary aerosols concentrations. The newly formed particles then get dispersed through the liquid phase in high ALWC, where multiphase reactions govern. The higher surface-area-to-volume ratio of  $\text{PM}_1$  than  $\text{PM}_{2.5}$  suggests the heterogeneous chemistry in  $\text{PM}_1$  to be more crucial than  $\text{PM}_{2.5}$ .

From a thermodynamic perspective, the equilibrium of phase-partitioning is governed by the complex interplay between chemical composition and parameters like pH, ALWC, and T. We show that there are two fundamental ways to modulate semi-volatile species like ammonium chloride and ammonium nitrate, (i) either by controlling the emissions of precursors HCl,  $\text{HNO}_3$ , and  $\text{NH}_3$  or (ii) by moving the chloride, nitrate, and ammonium out of the particle-phase and shifting to the gas-phase. The explored "sensitivity regimes" of  $\text{PM}_1$  and  $\text{PM}_{2.5}$  show that abating HCl and  $\text{HNO}_3$  is more effective than  $\text{NH}_3$  for mitigating high aerosol loading over the IGP.

A recent study conducted in Europe and USA suggested that ammonia reduction would be the most effective pathway to reduce aerosol loading as it is more cost-effective than  $\text{NO}_x$  reduction (Gu et al., 2021). But, this study shows that the sensitivity and effectiveness of the adopted reduction mechanisms are more crucial than the cost-effectiveness. If aerosols are not sensitive to the reductions of a specific precursor, then the cost-effectiveness would not assist in developing an effective mitigation policy. Rather, the thermodynamically consistent sensitivity analysis would effectively address the outstanding air pollution mitigation problem, as evidenced by this study.

## 5. Conclusions

After a long-standing quest for an effective aerosol mitigation framework, here we present the first thermodynamically consistent "roadmap" over the Indo-Gangetic Plain (IGP) to effectively mitigate aerosols. The proposed framework categorically considers aerosol acidity (pH) and aerosol liquid water content (ALWC) as the crucial parameters and investigates the effectiveness of gaseous precursor reductions in aerosol mitigation. Six "sensitivity regimes" are defined as (a) " $\text{HNO}_3$  sensitive", (b) " $\text{HCl}$  and  $\text{HNO}_3$  sensitive", (c) " $\text{HCl}$ ,  $\text{NH}_3$  and  $\text{HNO}_3$  sensitive", (d) " $\text{HNO}_3$  and  $\text{NH}_3$  sensitive", (e) " $\text{NH}_3$  sensitive", and (f) "insensitive" to explore the sensitivity of gaseous precursors in the formation of fine aerosols. The application of the framework to the observational dataset shows  $\text{PM}_1$  and  $\text{PM}_{2.5}$  aerosols to fall in the " $\text{HCl}$  and  $\text{HNO}_3$  sensitive regime", emphasizing that  $\text{HCl}$  and  $\text{HNO}_3$  reductions would be the most effective pathway to reduce aerosol loading over IGP. The thermodynamic control suggests that although  $\text{NH}_3$  is much higher than  $\text{HCl}$  and  $\text{HNO}_3$ , but  $\text{NH}_3$  reduction should not be explicitly prioritized to mitigate aerosols. This is in disparity with the existing aerosol mitigation strategies over IGP, which are mostly ineffective and not thermodynamically favorable. This novel insight provides "actionable intelligence" to the policymakers to abate precursors not at "random" but in a thermodynamically consistent way.

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## Open Research

The data used to prepare this manuscript can be found in the link: <https://osf.io/6HGS7/>.

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### Figure captions:

**Figure 1:** Comparison of ISORROPIA-II predicted and MARGA-2S measured  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  of  $\text{PM}_{10}$  (a, b, c) and  $\text{PM}_{2.5}$  (d, e, f), gas-phase  $\text{NH}_3$  (g) and (h) gas-to-particle partitioning ratio [ $(\text{NH}_4^+)$ ]. The correlation (r) between the predicted and measured species concentrations are shown to check the validity of the model prediction. Data are color-coded by ambient air temperature (T).

**Figure 2:** The variability of gas-to-particle partitioning ratio of (a) ( $\text{NO}_3^-$ ), (b) ( $\text{Cl}^-$ ) with pH shown by the sigmoidal (S) curves. Three regimes are defined, where ( $\text{NO}_3^-$ ) and ( $\text{Cl}^-$ ) range between complete gas-phase ( $\alpha = 0$ ; regime I) and complete particle-phase ( $\alpha = 100\%$ ; regime III). A definite pH value called  $\text{pH}_{50}$  has been defined where total nitrate and chloride remained 50% in gas-phase and 50% in particle-phase (regime II). In figures c and d, we included ammonia ( $\text{NH}_4^+$ ) phase-partitioning for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  and defined the "sensitivity regimes" expressed in different colors. The particle phase fractions are sensitive to precursor concentrations HCl,  $\text{HNO}_3$  and  $\text{NH}_3$  and ( $\text{NO}_3^-$ ) (blue curve), ( $\text{Cl}^-$ ) (green curve), and ( $\text{NH}_4^+$ ) (red curve) vary as a function of pH.

**Figure 3:** Chemical regimes of aerosols with "coordinates" being pH and aerosol liquid water content (ALWC) of  $\text{PM}_{10}$  (a,b) and  $\text{PM}_{2.5}$  (c,d). Aerosols are sensitive to HCl,  $\text{HNO}_3$ , and  $\text{NH}_3$  concentrations and the black, blue, and red lines

define the "characteristic pH" where chemical regimes are separated by a pre-defined threshold value of  $\alpha = 10\%$ . Above  $\text{pH}'$ ,  $\text{pH}''$ , and  $\text{pH}'''$  the aerosols are sensitive to the variation in precursors like HCl,  $\text{HNO}_3$ , and  $\text{NH}_3$ , and below which aerosols are deemed insensitive to variations in precursors. The data points in b, d are colored by mass concentrations of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  monitored during the WiFEX 2017-18 campaign period.

**Figure 4:** Schematic description of intrinsic physical, chemical, and thermodynamical mechanisms of fine aerosols during winter. The influences of aerosol acidity (pH) and aerosol liquid water content (ALWC) on the phase partitioning of total chloride ( $\text{HCl} + \text{Cl}^-$ ), total nitrate ( $\text{HNO}_3 + \text{NO}_3^-$ ), and total ammonium ( $\text{NH}_3 + \text{NH}_4^+$ ) are shown during two conditions, clear sky and polluted atmosphere. Photochemistry dominates during the clean atmosphere, whereas heterogeneous, multiphase chemistry dominates during the polluted atmosphere. The particle-phase of chloride, nitrate, and gas-phase of ammonia dominates during winter over the Indo-Gangetic Plain (IGP).