Aerosol acidity as a driver of aerosol formation and nutrient deposition to ecosystems

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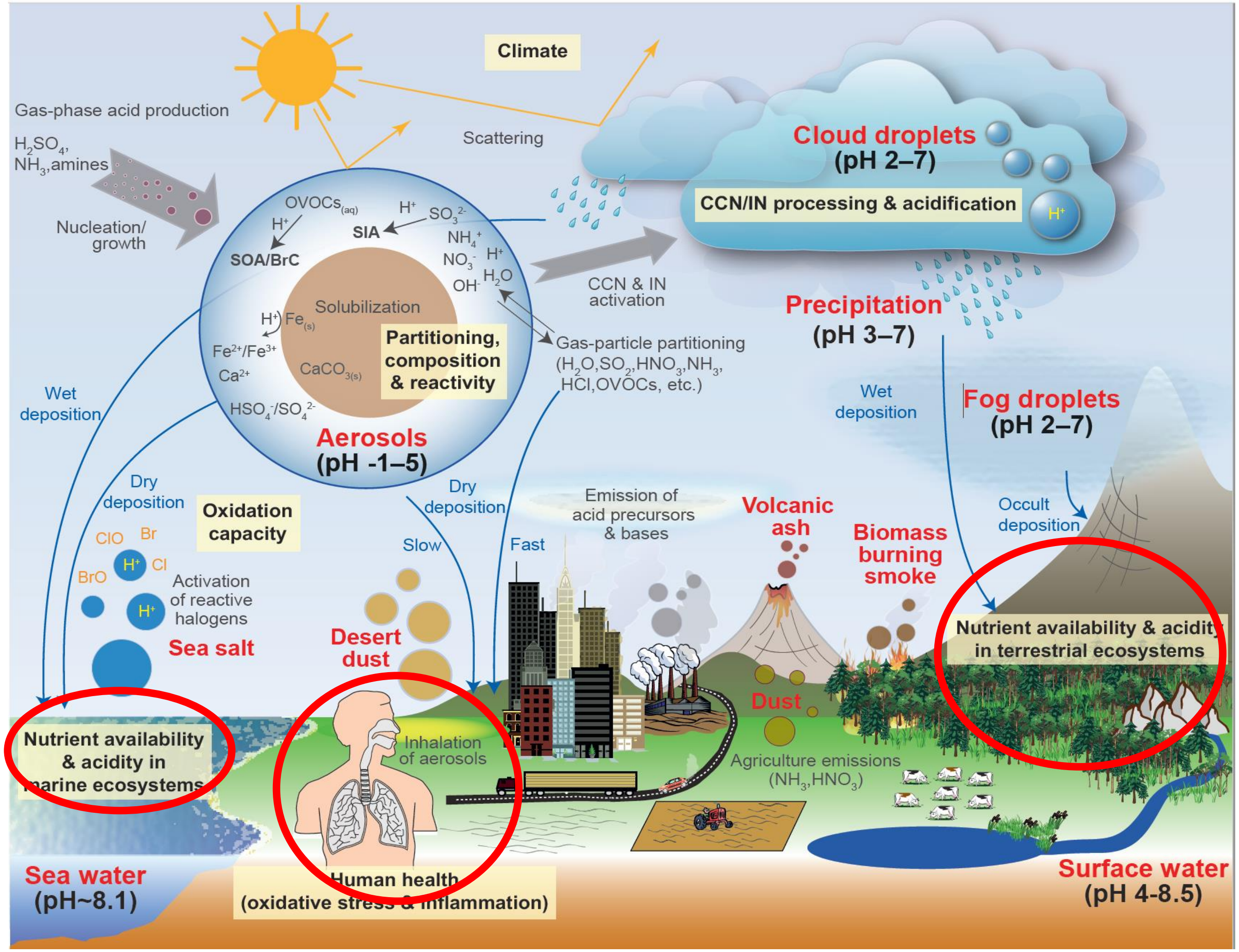
The Acidity of Atmospheric Particles



Pye et al., ACP, 2020

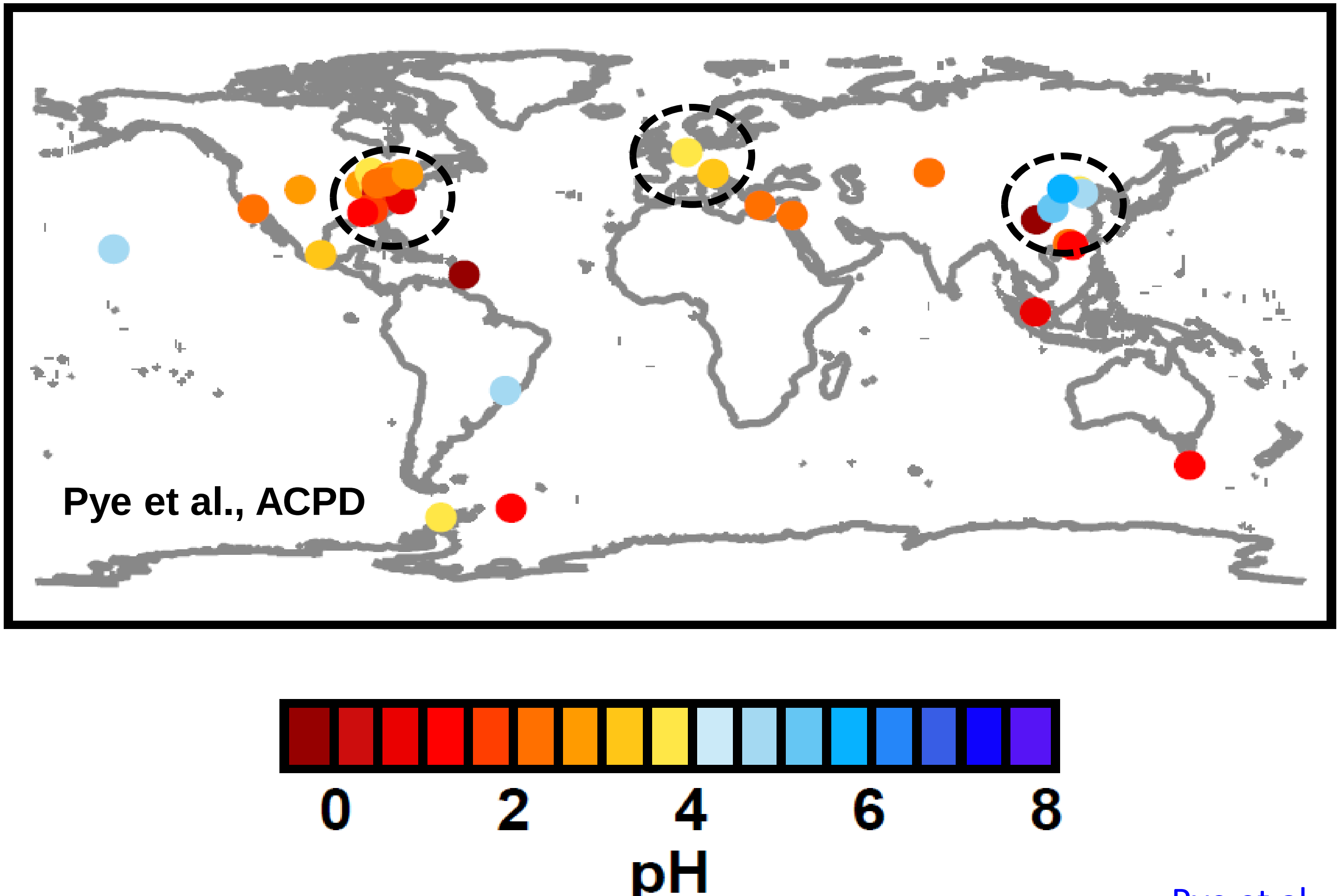
Particle acidity drives aerosol processes and environmental impacts:

- **Mass** - partitioning of semivolatile ions, formation of NH_4NO_3, $(NH_4)_2SO_4$, etc.
- **Dry Deposition** of reactive nitrogen and other nutrients (metals, P) that affect ecosystem productivity

Links between acidity, sensitivity of PM to emissions and dry deposition is *not* clear.

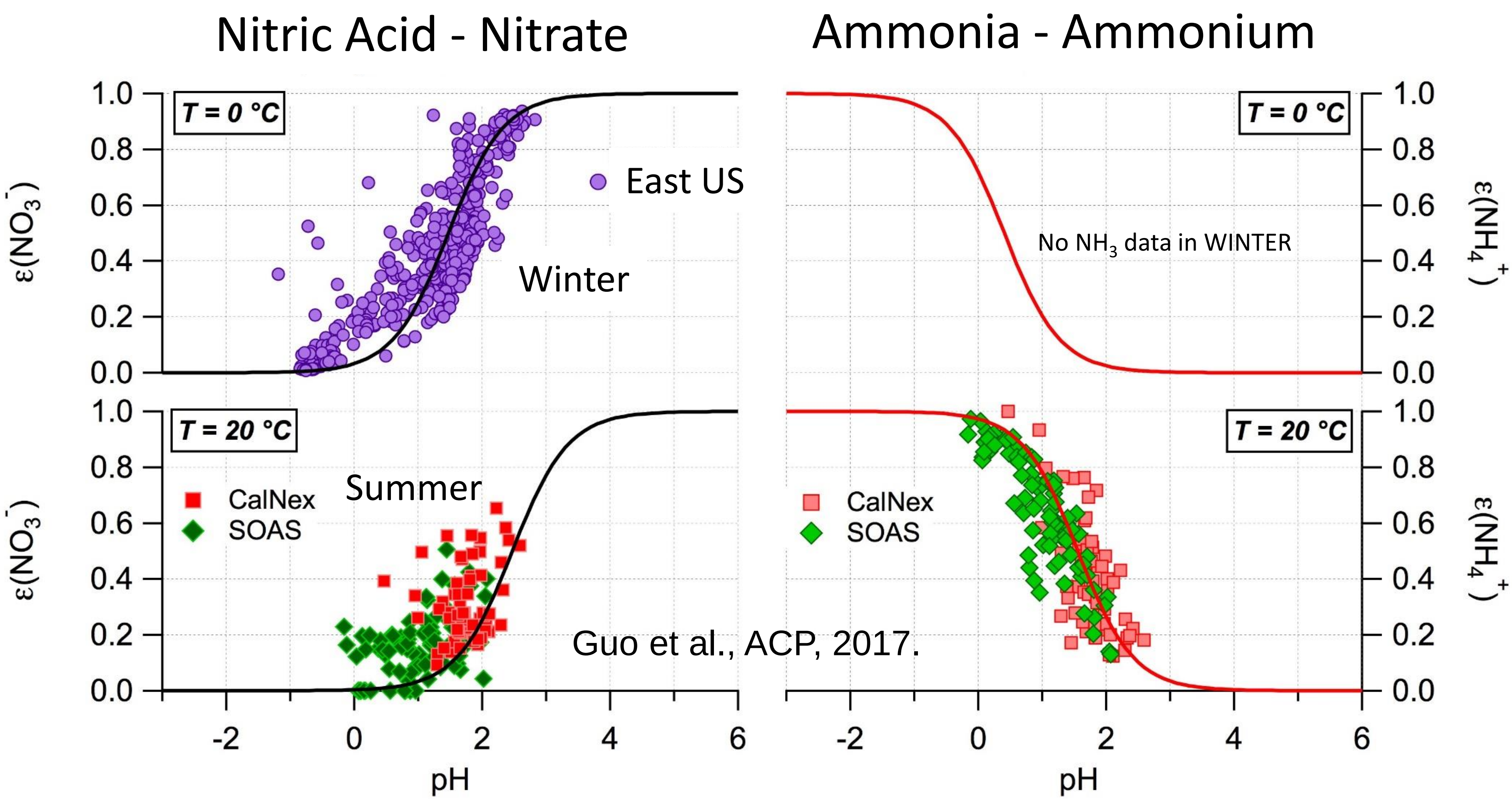
Acidic aerosol is everywhere

pH varies **alot**



[Pye et al., ACP, 2020]

pH and observed partitioning of nitrate and ammonium follow “S - curves”



Consistency between predicted and observed partitioning of both species affirms that predicted *acidity levels with models are reasonable*.

S-curves are explained by theory

$$\left.\begin{array}{ll} \mathrm{HNO_{3(g)}} \leftrightarrow \mathrm{HNO_3}, & K_H \\ \mathrm{HNO_3} \leftrightarrow \mathrm{NO_3}^- + \mathrm{H}^+, & K_a \end{array}\right\} \quad \varepsilon(\mathrm{NO_3^-}) = \frac{\mathrm{NO_3^-}}{\mathrm{HNO_3} + \mathrm{NO_3^-}} = f(\mathrm{pH})$$

From theory:

$$\varepsilon(NO_3^-) = \frac{K_{n1} H_{HNO_3} W_i RT}{\gamma_{H^+}\gamma_{NO_3^-}[H^+] + K_{n1} H_{HNO_3} W_i RT} \xrightarrow{\Psi = \frac{RT K_{n1} H_{HNO_3}}{\gamma_{H^+}\gamma_{NO_3^-}}} \varepsilon(NO_3^-) = \frac{\Psi \boldsymbol{W_i}}{[\boldsymbol{H^+}] + \Psi \boldsymbol{W_i}}$$

nitrate

$$\varepsilon(NH_4^+) = \frac{\frac{\gamma_{H^+}}{\gamma_{NH_4^+}} \frac{H_{NH_3}}{K_a} [H^+] W_i RT}{1 + \frac{\gamma_{H^+}}{\gamma_{NH_4^+}} \frac{H_{NH_3}}{K_a} [H^+] W_i RT} \xrightarrow{\Phi = \frac{\gamma_{H^+}}{\gamma_{NH_4^+}} \frac{H_{NH_3}}{K_a} RT} \varepsilon(NH_4^+) = \frac{\Phi [\boldsymbol{H^+}] \boldsymbol{W_i}}{1 + \Phi [\boldsymbol{H^+}] \boldsymbol{W_i}}$$

ammonium

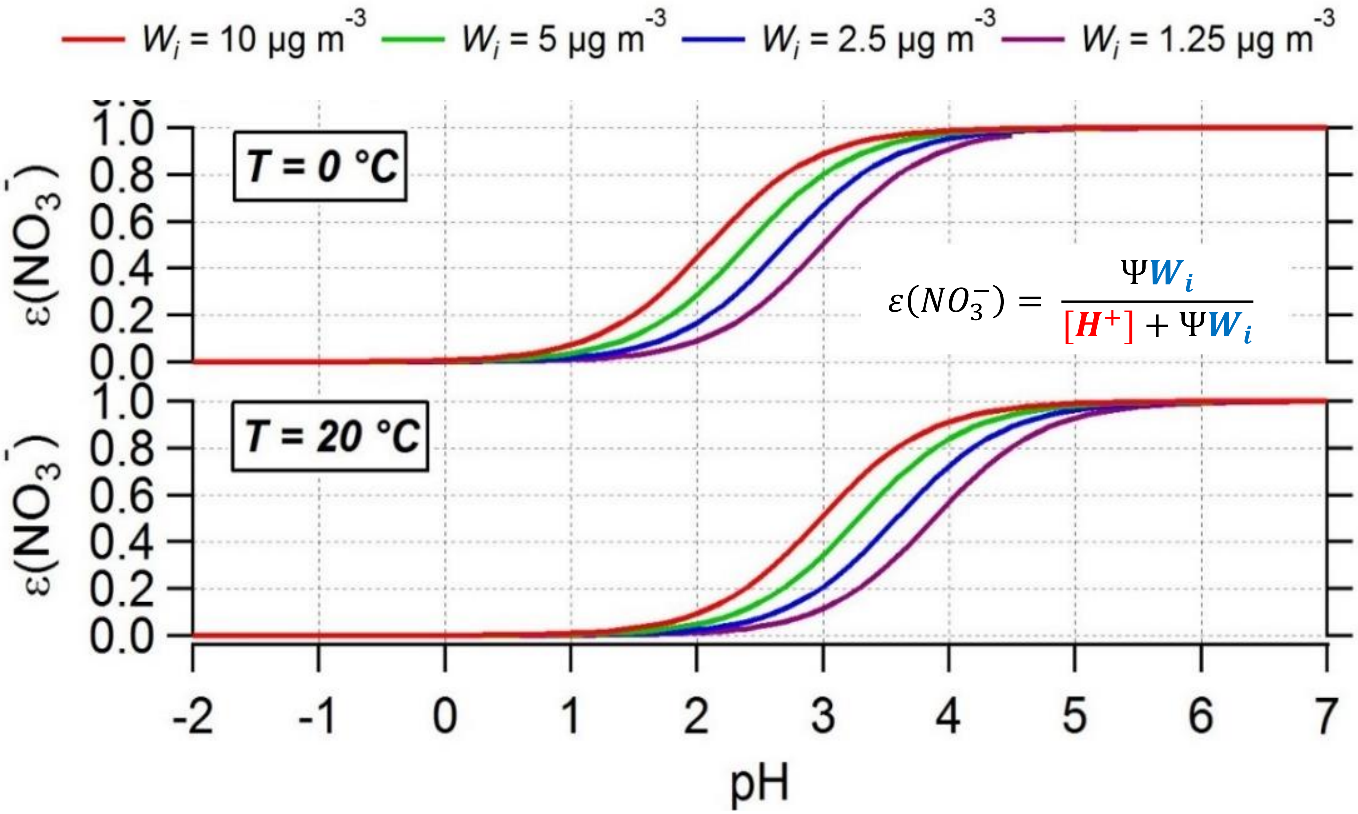
Gas-particle partitioning of nitrate, ammonium depends on

$[H^+]$ and W_i

$$\varepsilon(NO_3^-) = \frac{K_{n1} H_{HNO_3} W_i RT}{\gamma_{H^+}\gamma_{NO_3^-}[H^+] + K_{n1} H_{HNO_3} W_i RT}$$

Meskhidze et al., GRL (2003); Guo et al., ACP (2017); Nenes et al., ACP (2019)

S-curves are explained by theory



Gas-particle partitioning of nitrate, ammonium depends on

$[H^+]$ **and** W_i

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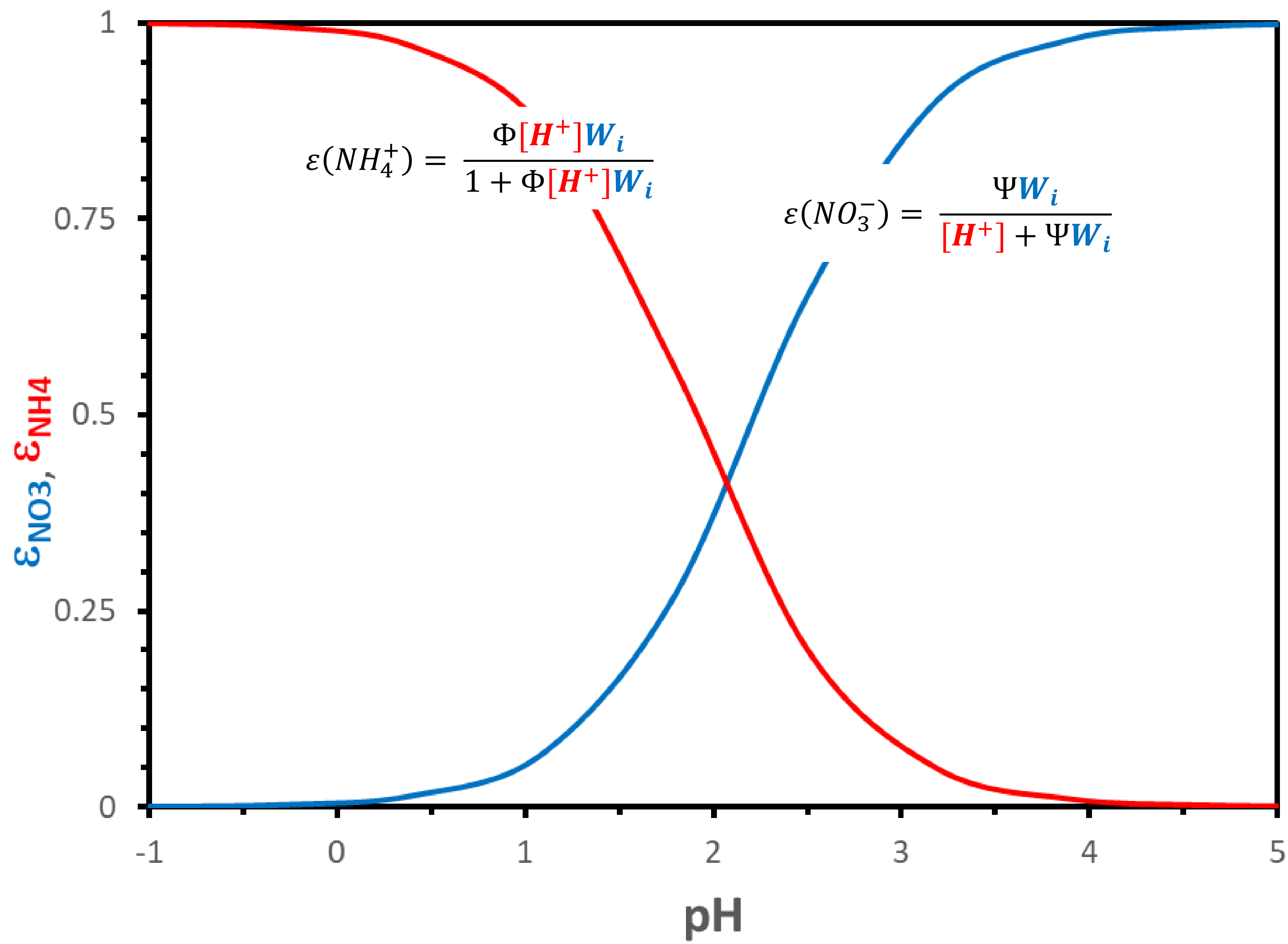
When is PM sensitive to NH_3 and HNO_3 levels?



Nenes et al., ACP (2019)

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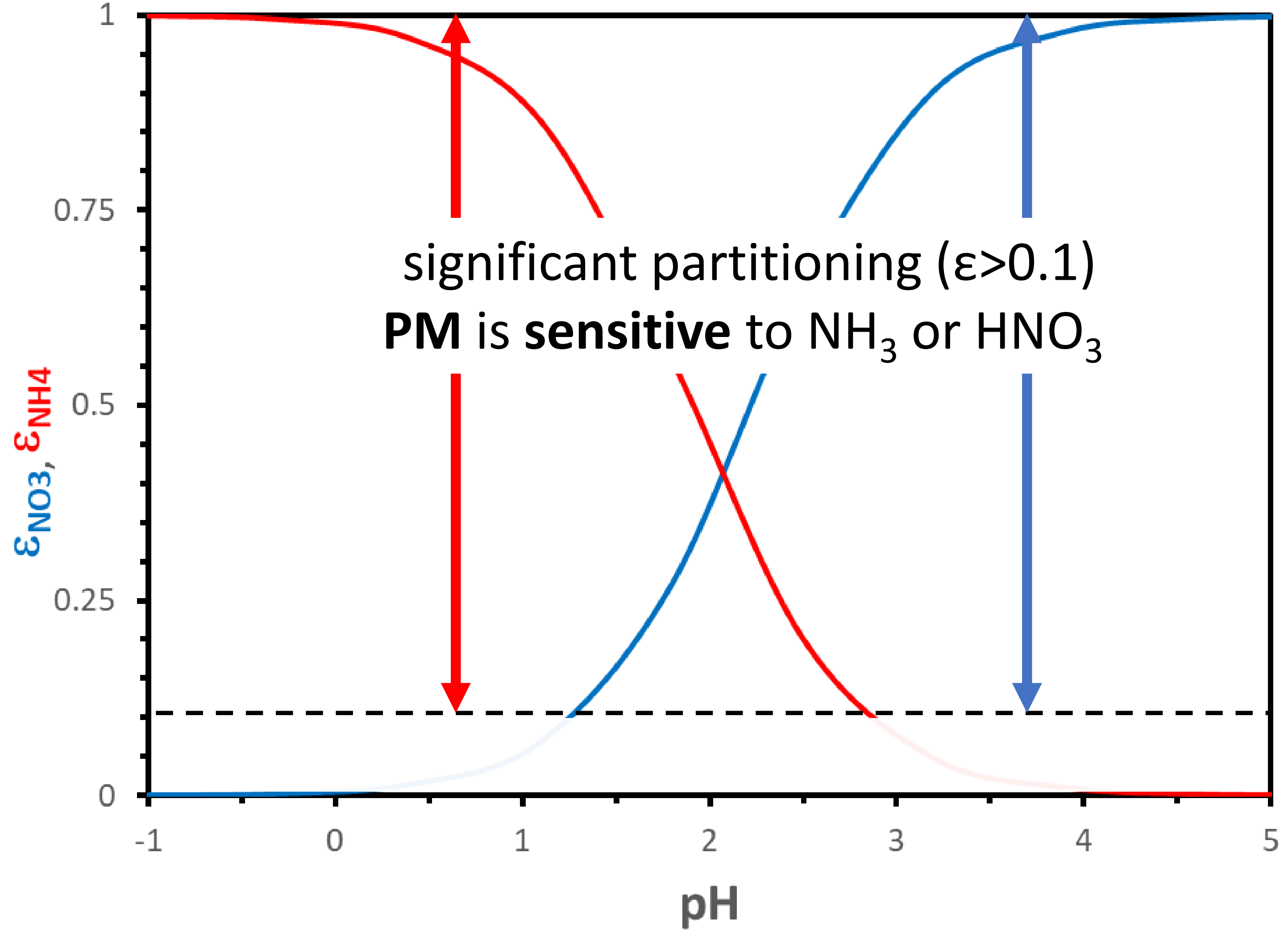

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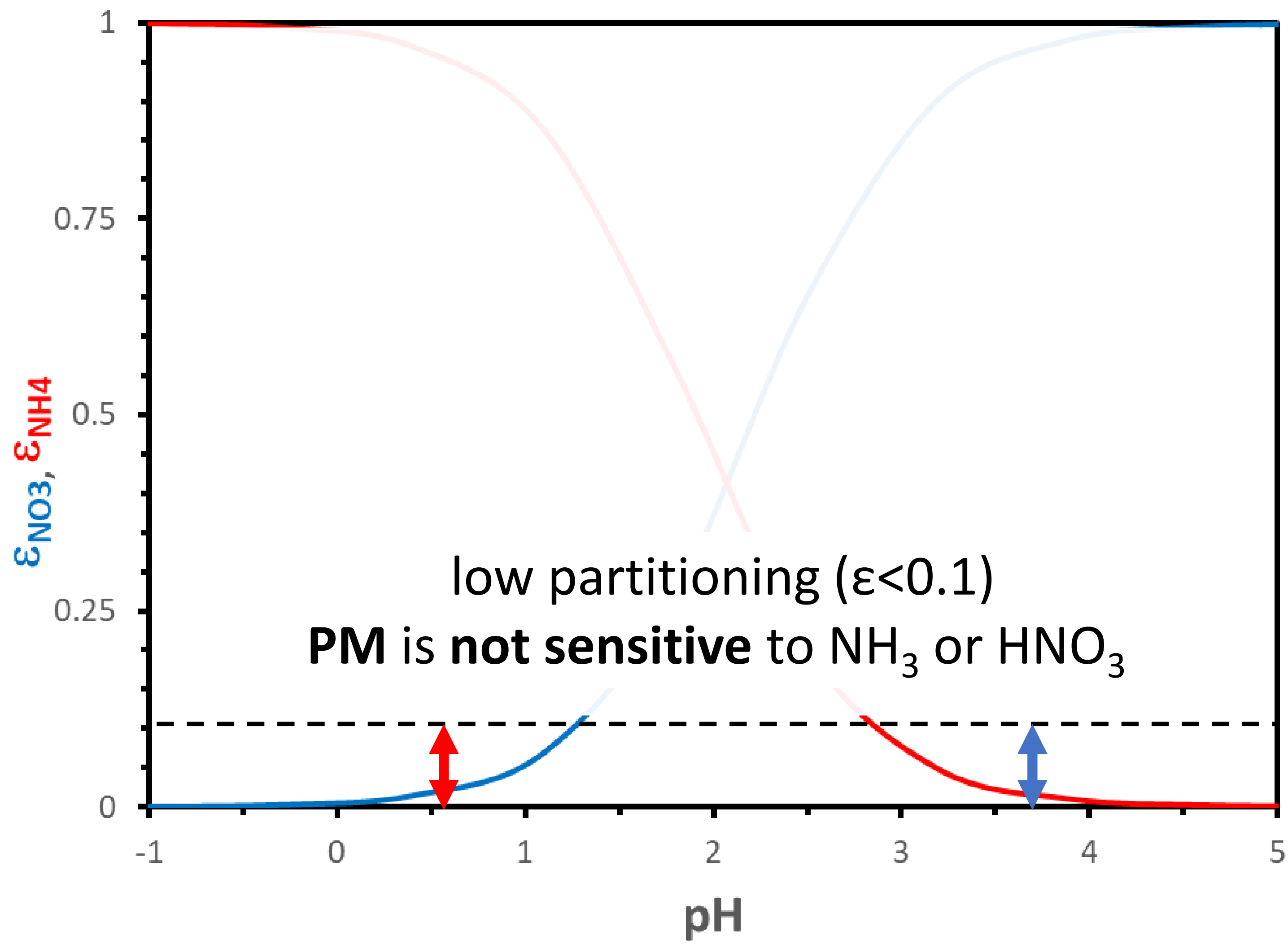

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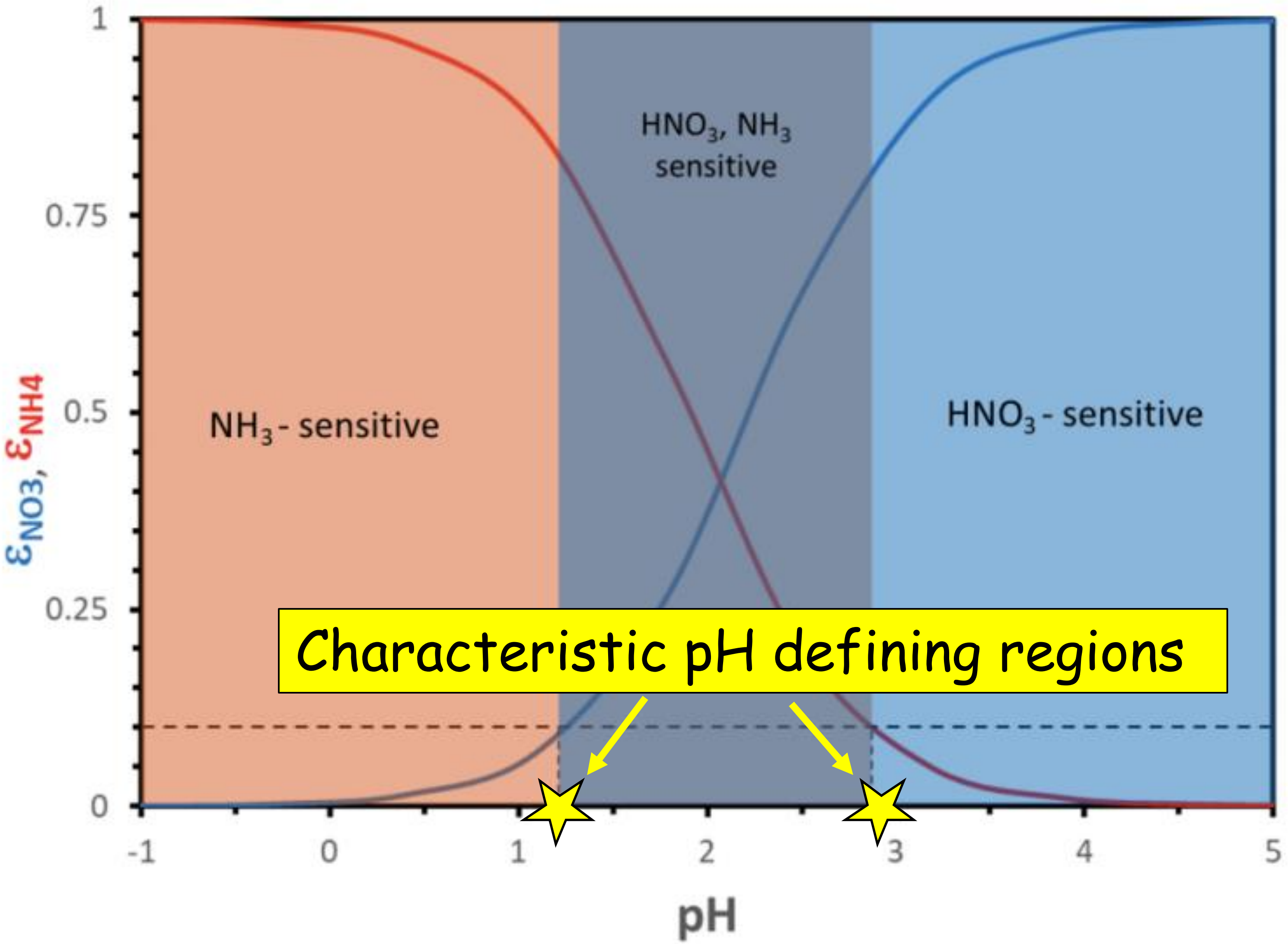

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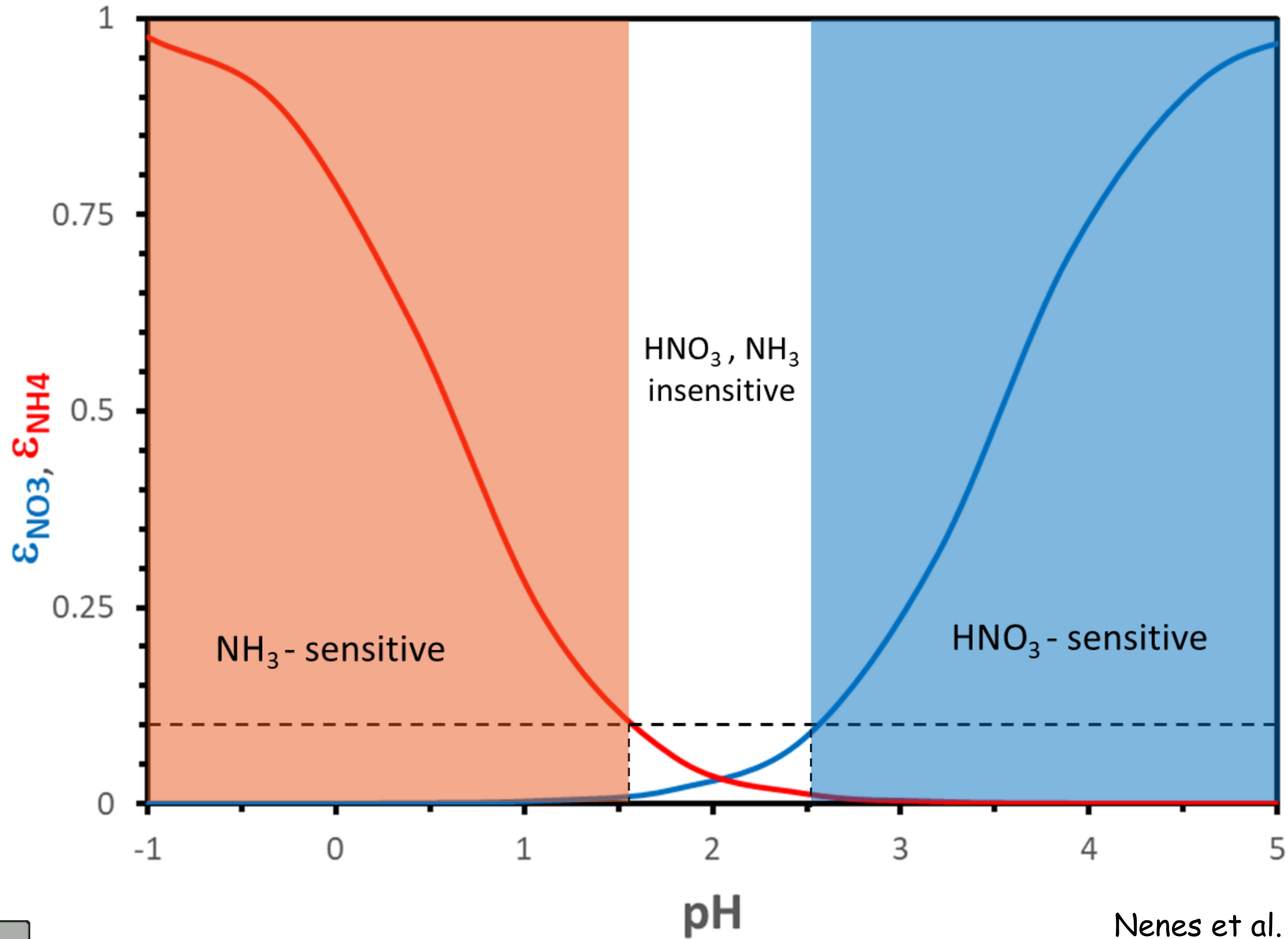

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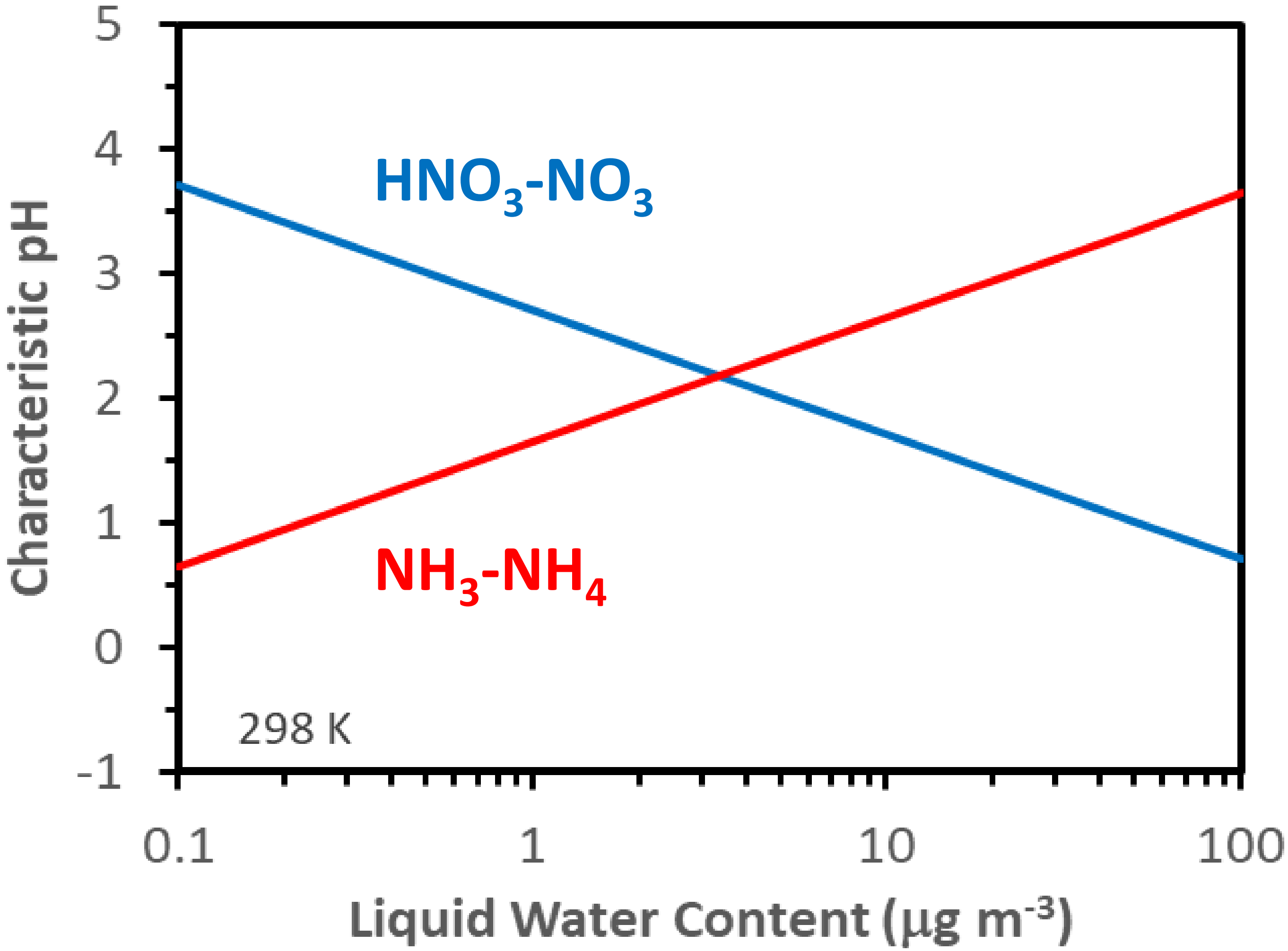

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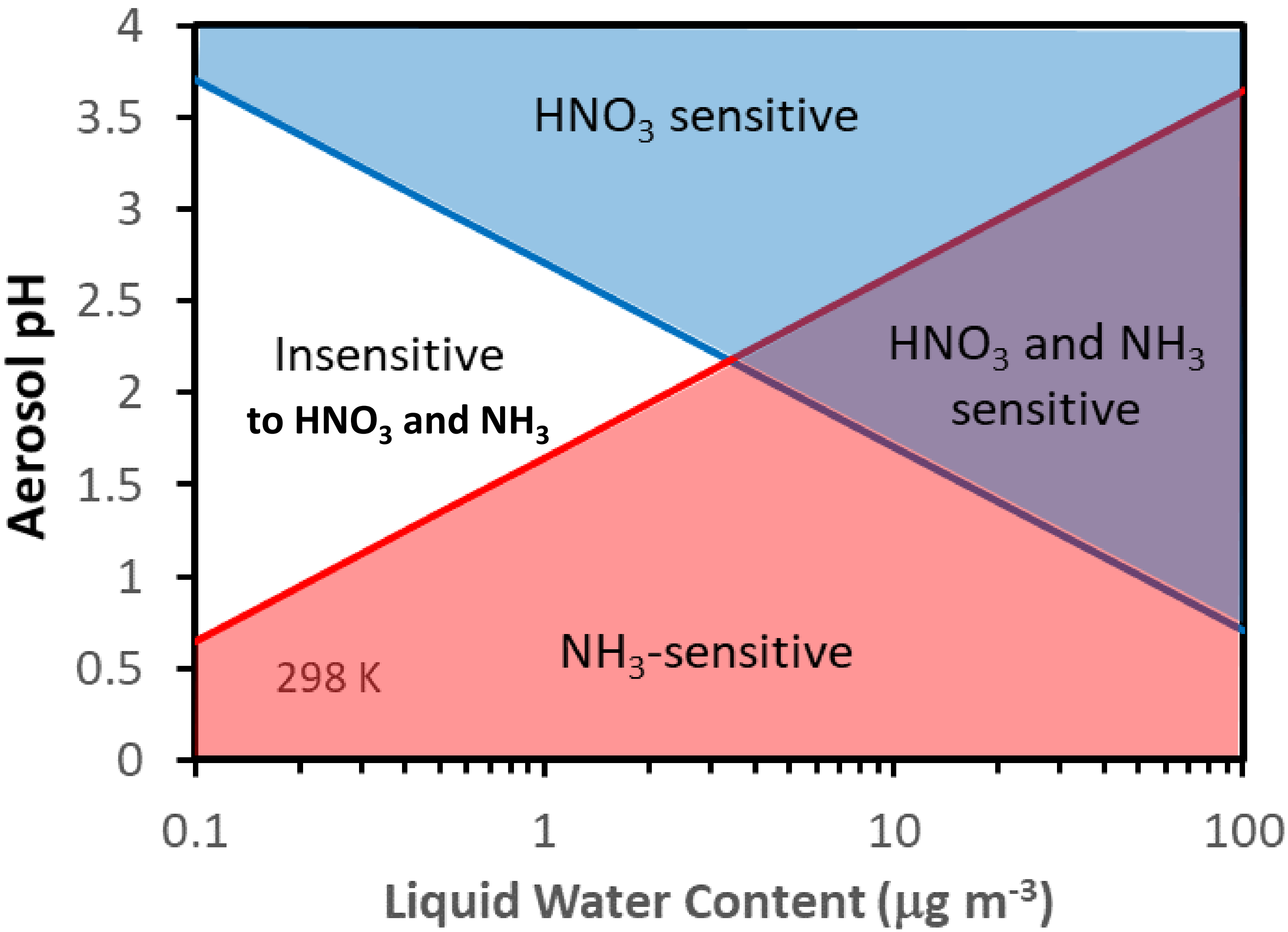
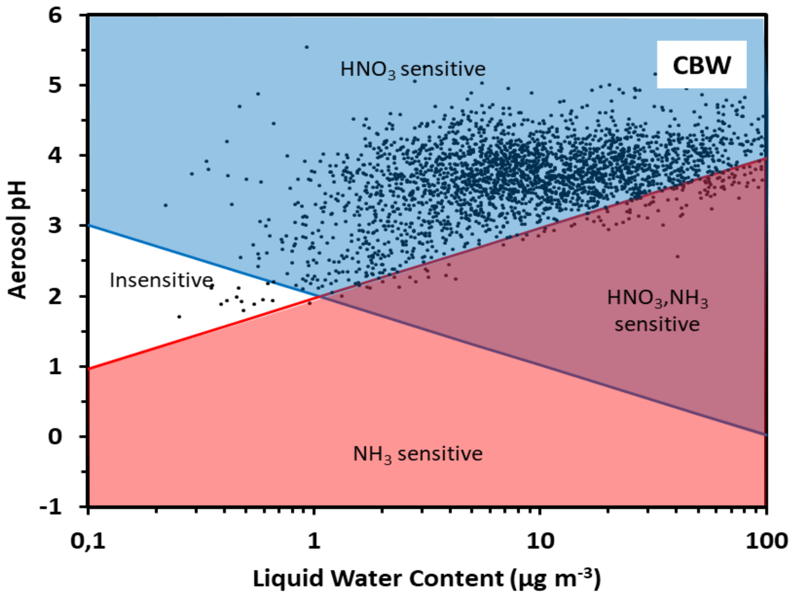


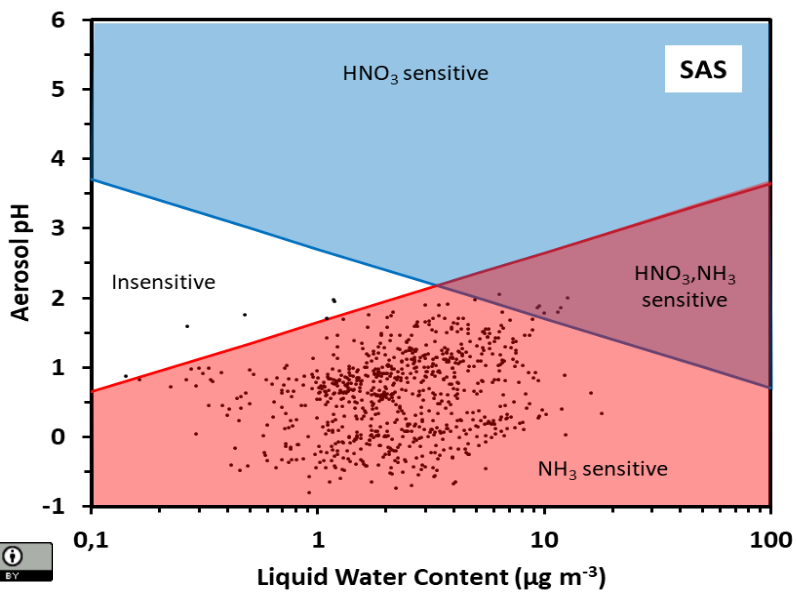
Nenes et al., ACP (2019)

Application of framework to locations



Cabauw Netherlands (05/12-06/13):

- Aerosol is exclusively in the HNO_3-sensitive regime.
- NH_3-reduction policies *less efficient* for PM reduction.
- NO_3 (and SO_4) reduction policies most efficient for PM reduction.

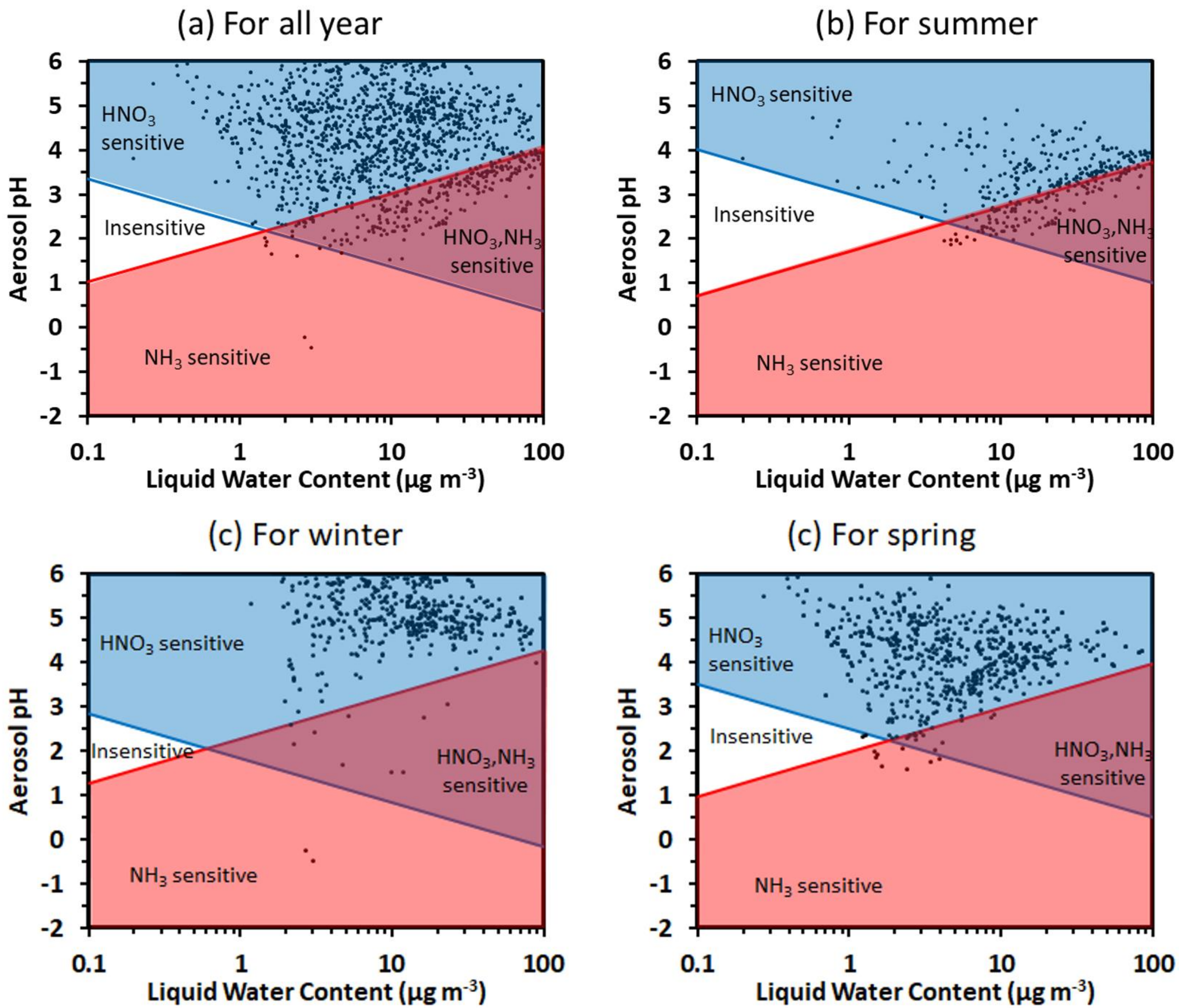


Southeas United States (06/13-07/13):

- Aerosol is exclusively in the NH_3-sensitive regime.
- NH_3 (and SO_4) reduction policies *efficient* for PM reduction.
- NO_3 reduction policies not efficient for PM reduction.

Nenes et al., ACP (2019)

Application of framework to locations



Tianjin China:

- Aerosol is **dominated** by the HNO_3-sensitive regime.
- NH_3-reduction policies *less efficient* for PM reduction (except in summer).
- HNO_3 (and SO4) reduction efficient for decreasing PM throughout the year

Zhao et al. (in review)

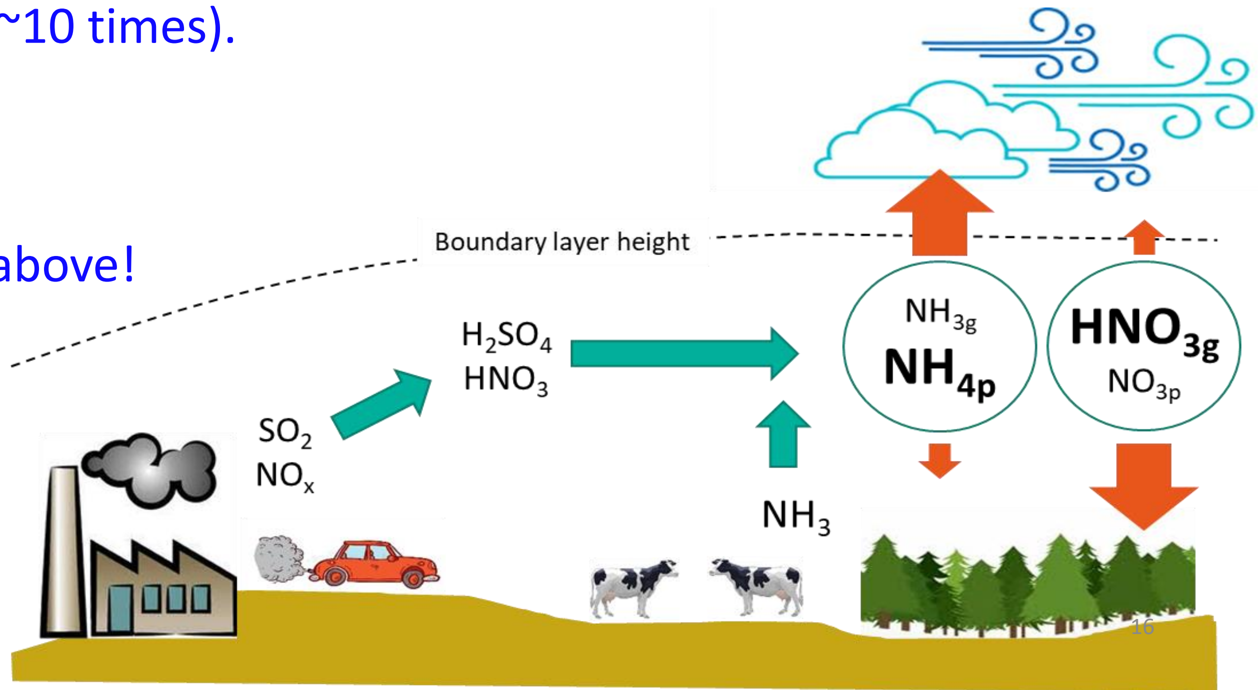
Effects of pH on dry deposition of N

Some facts about reactive nitrogen:

- Largely dominated by the inorganic reduced (NH_4/NH_3) and oxidized (NO_3/HNO_3) constituents.
- In the absence of wet deposition, dry deposition determines the ***lifetime*** and ***deposition pattern*** of reactive nitrogen!
- Lifetime determines concentration in boundary layer.
- The dry deposition velocity of both species varies *dramatically* if it is in the aerosol or gas phase (~10 times).

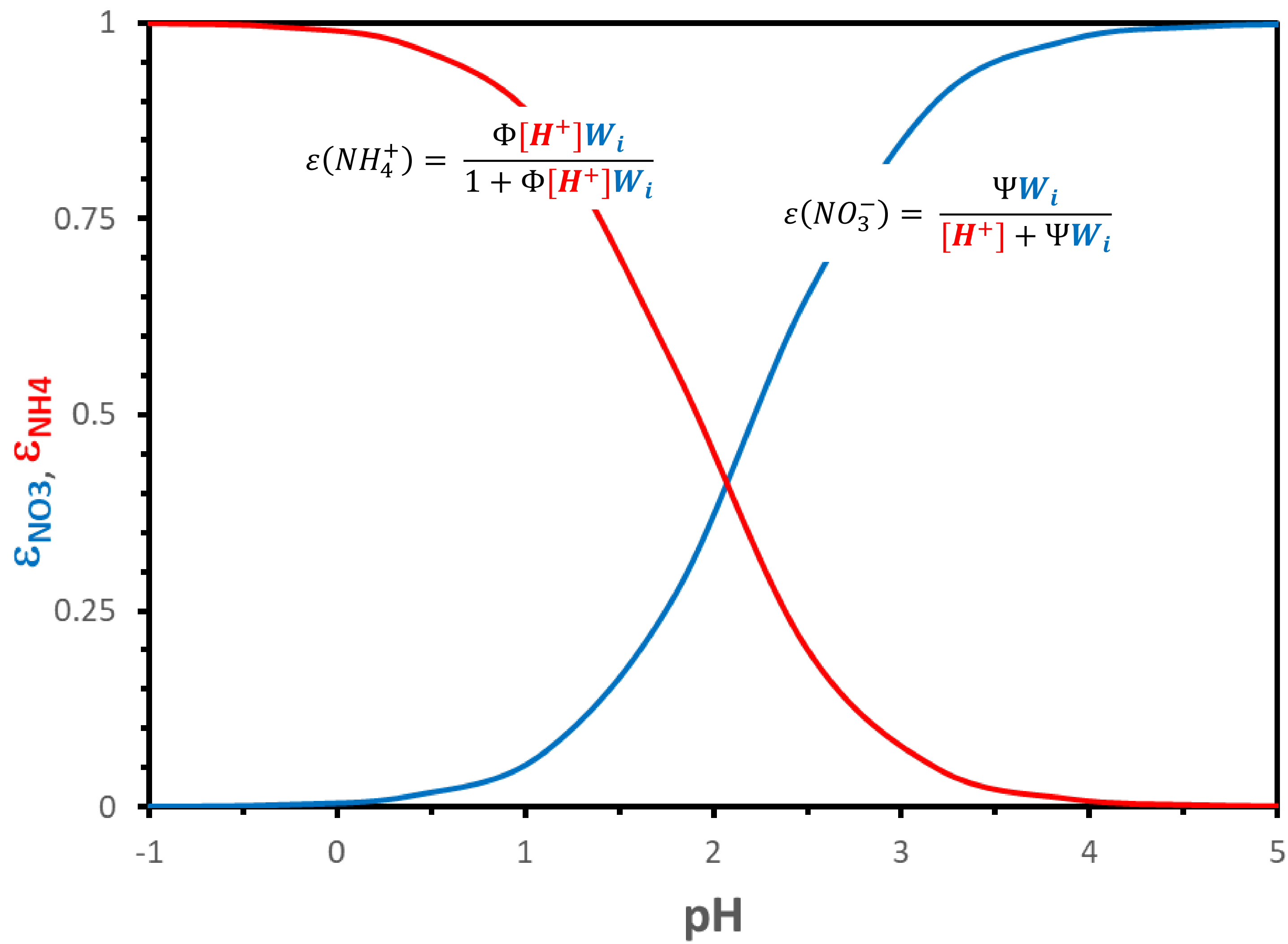
Realization:

- Acidity affects all the above!



Nenes et al., ACPD (2020)

pH effects on dry deposition of NH_3^T, HNO_3^T



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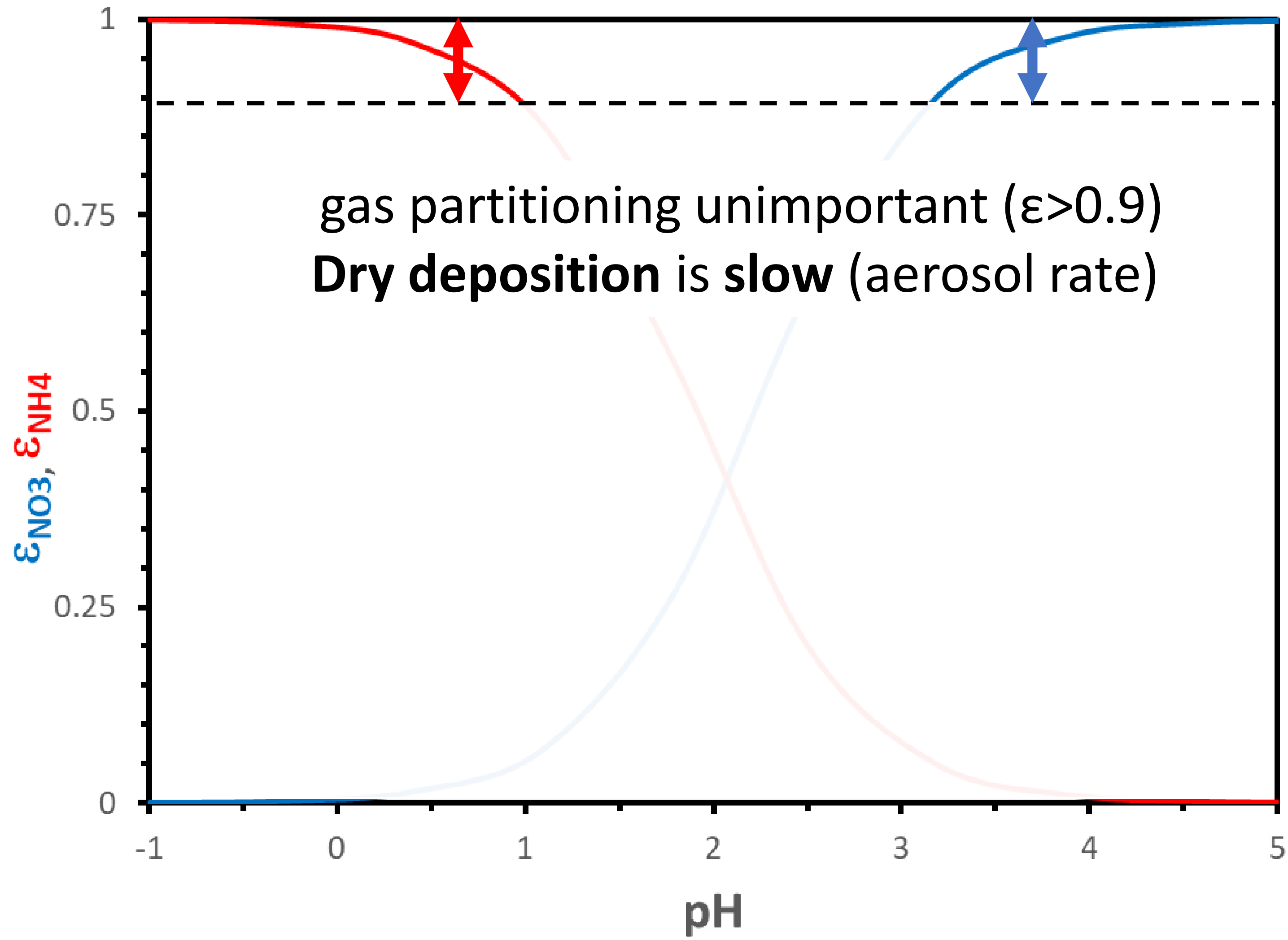

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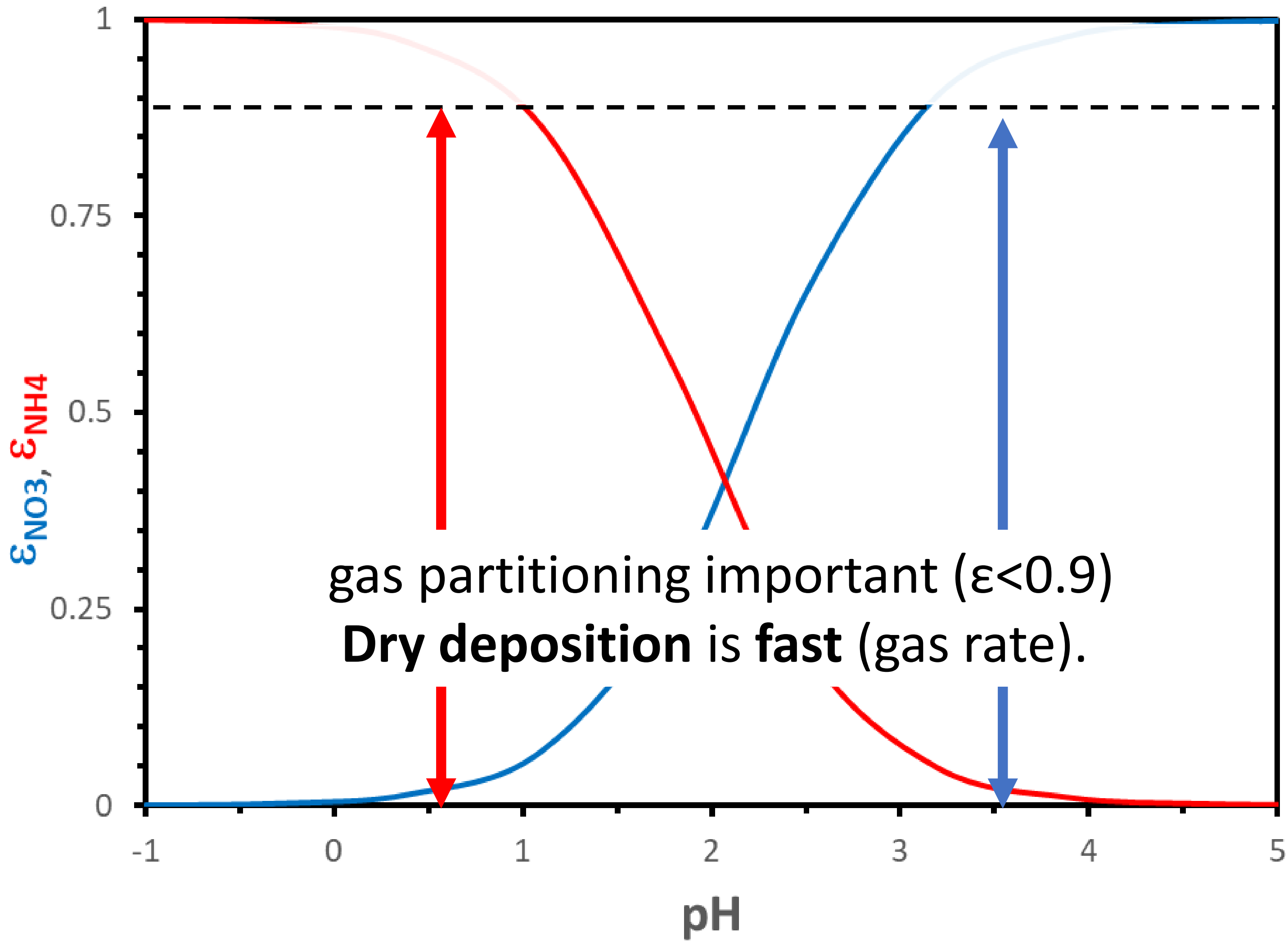

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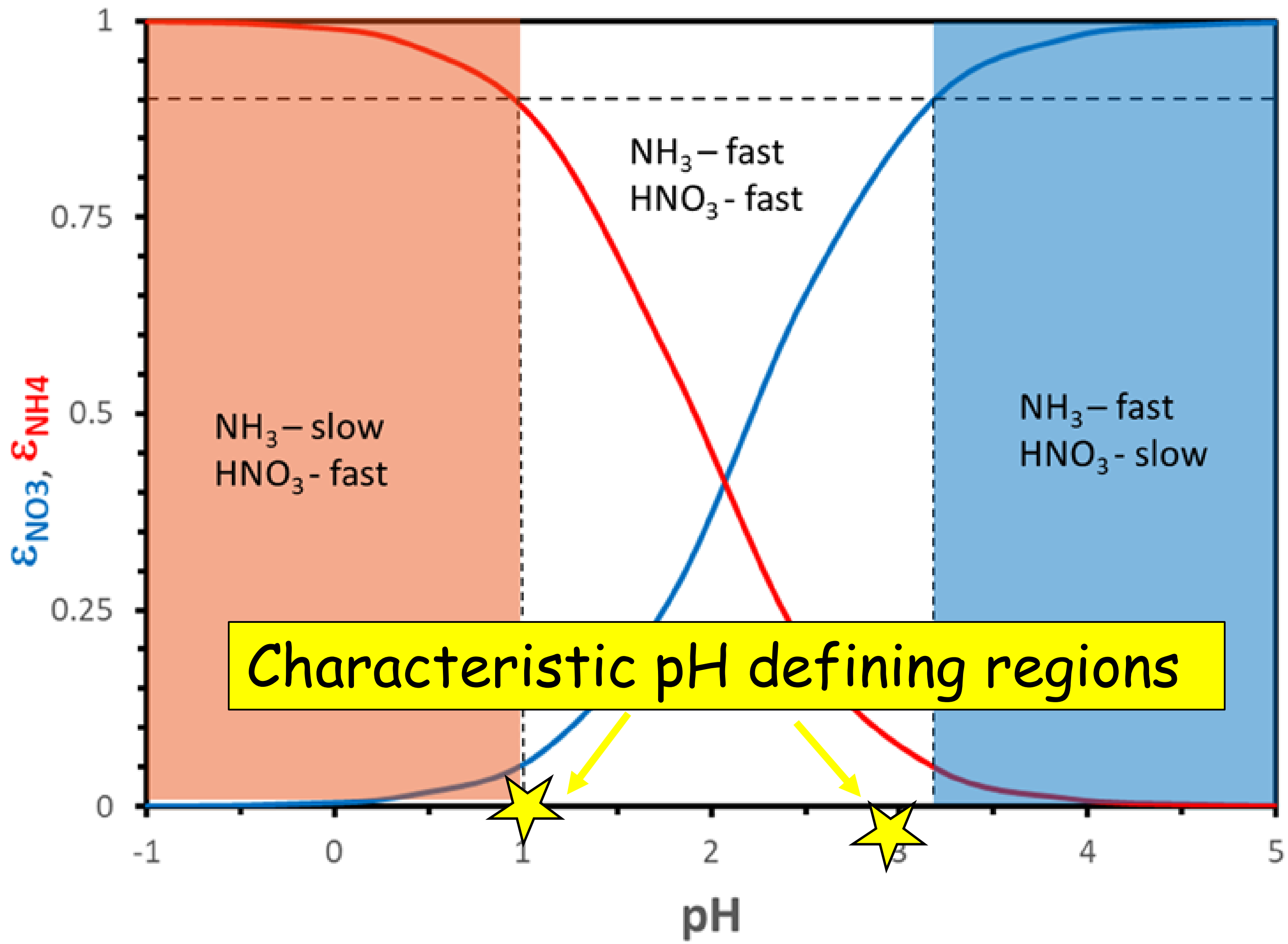

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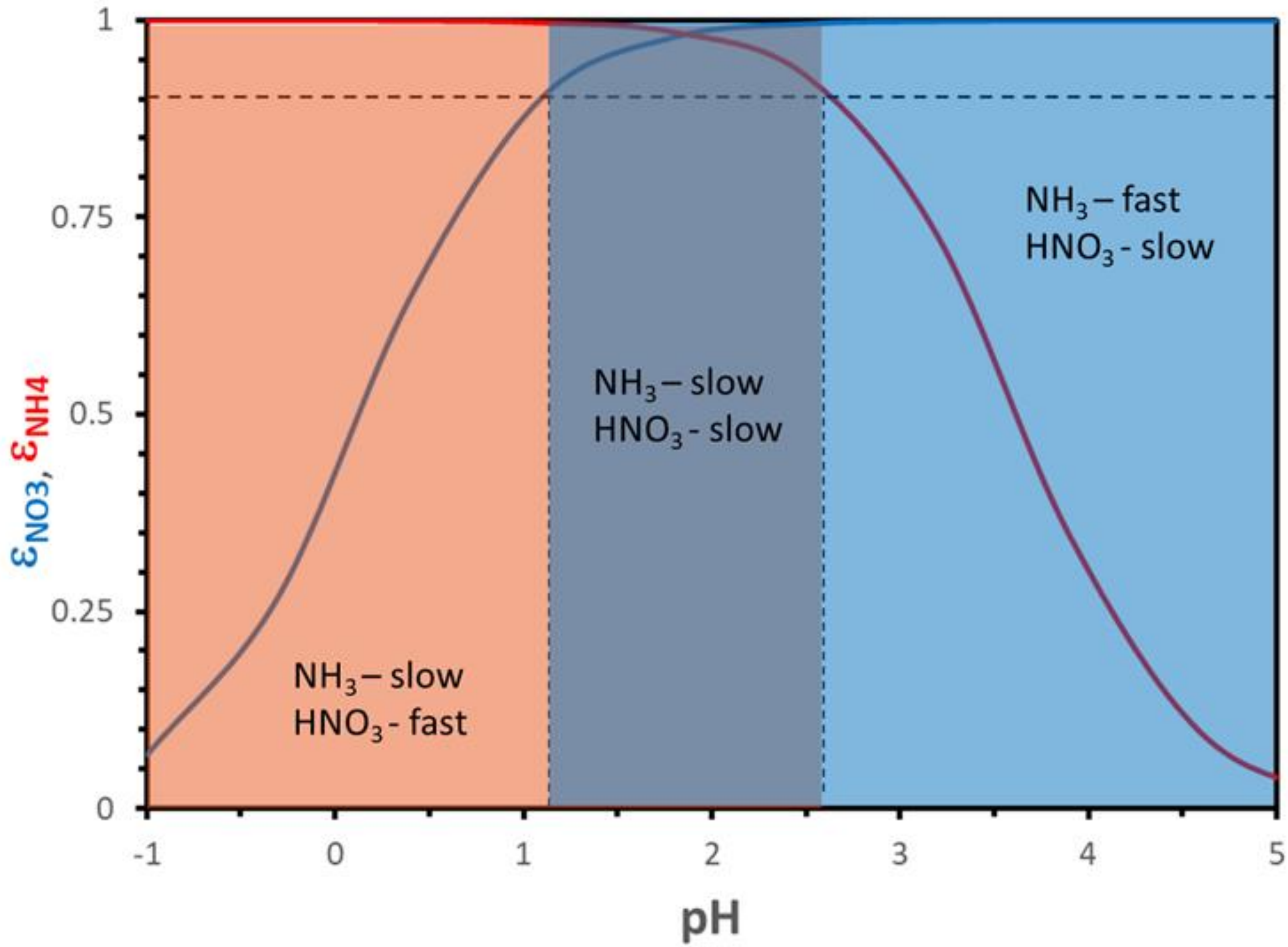
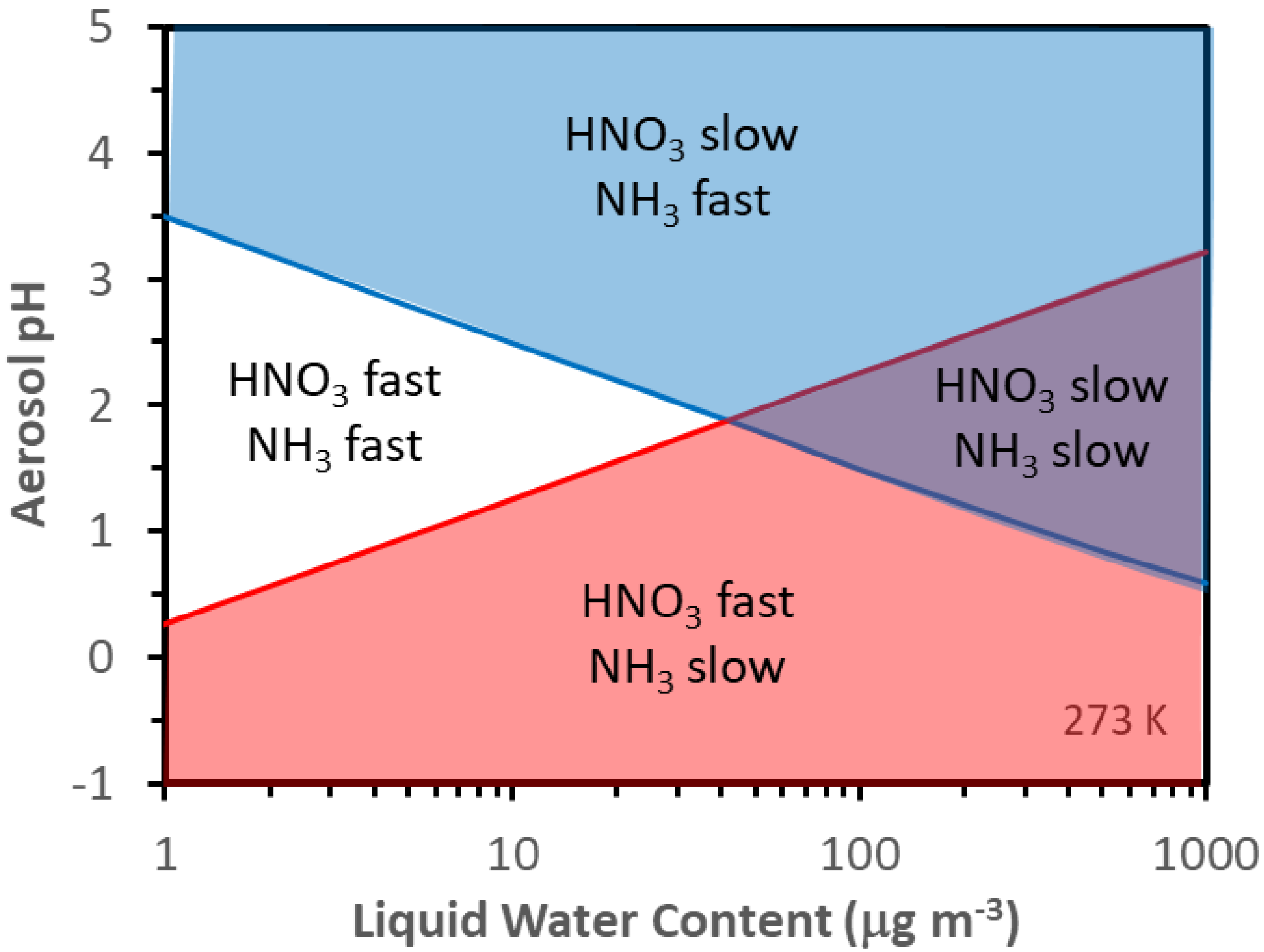


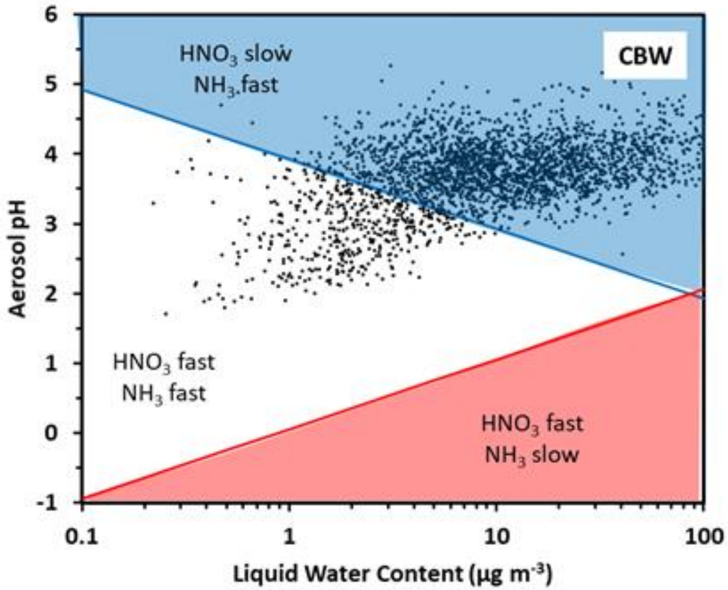
[Nenes et al., ACPD (2020)]

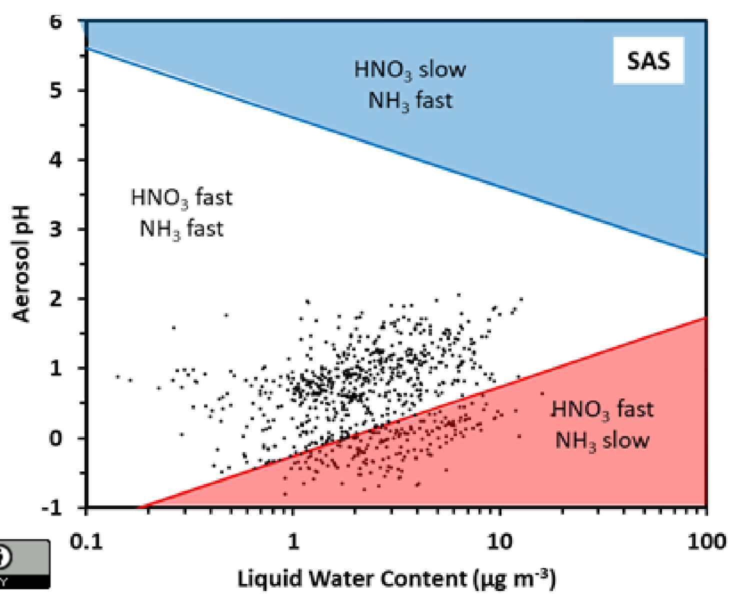
Dry deposition acidity regimes



Nenes et al., ACPD (2020)

Impacts of acidity on deposition velocity





Cabauw Netherlands (05/12-06/13):

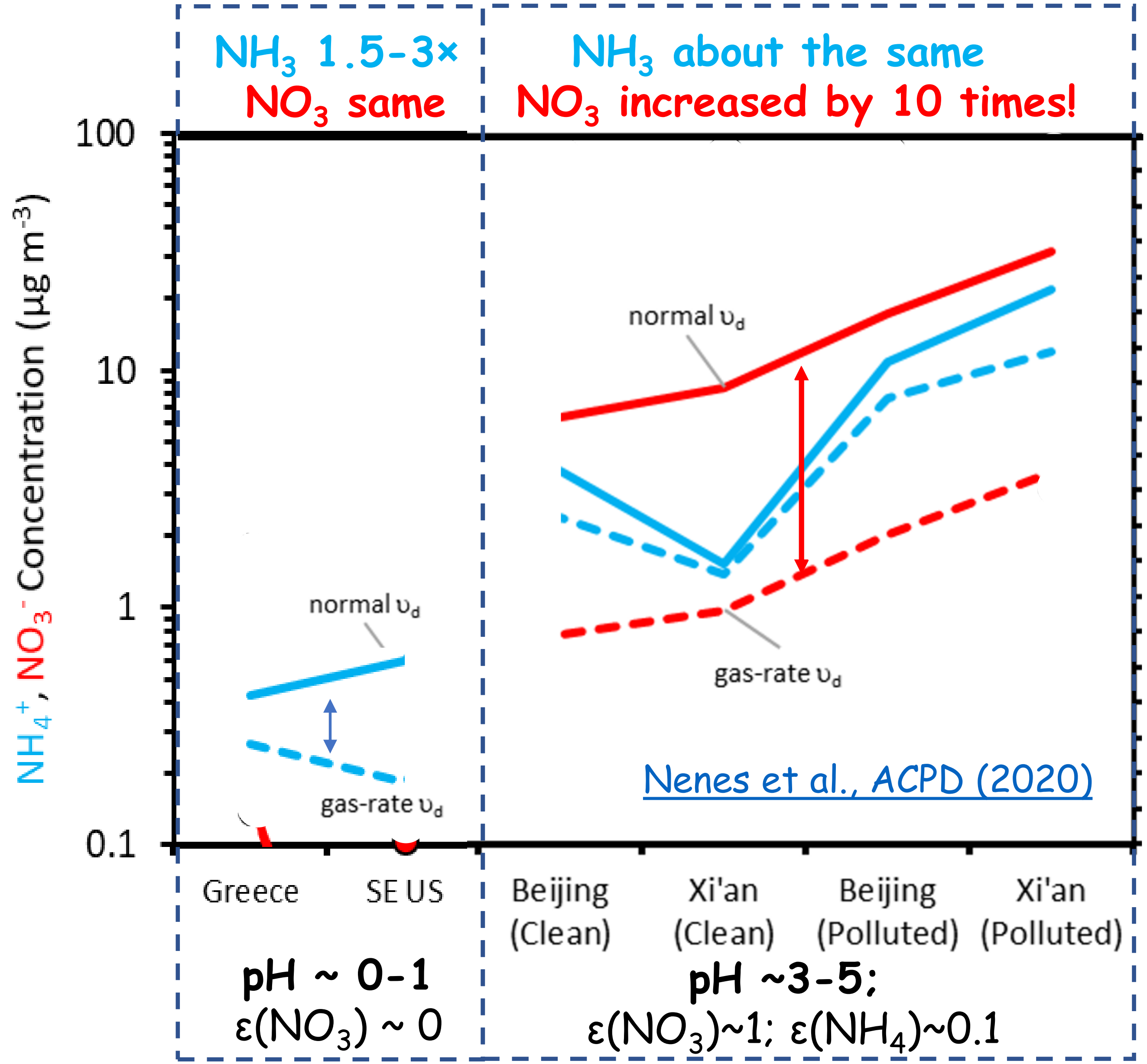
- Aerosol is almost exclusively in the HNO_3-slow regime.
- NH_3 deposits rapidly.
- **NO_3 accumulates in the boundary layer and causes nitrate-rich haze!**
- NH_3 is the lowest concentration in the BL.

Southeast US (06/13-07/13):

- Nitrate rapidly deposits, low conc.
- NH_3 deposits sometimes slowly.
- **NH_3 would tend to accumulate more in the boundary layer, and affect pH.**

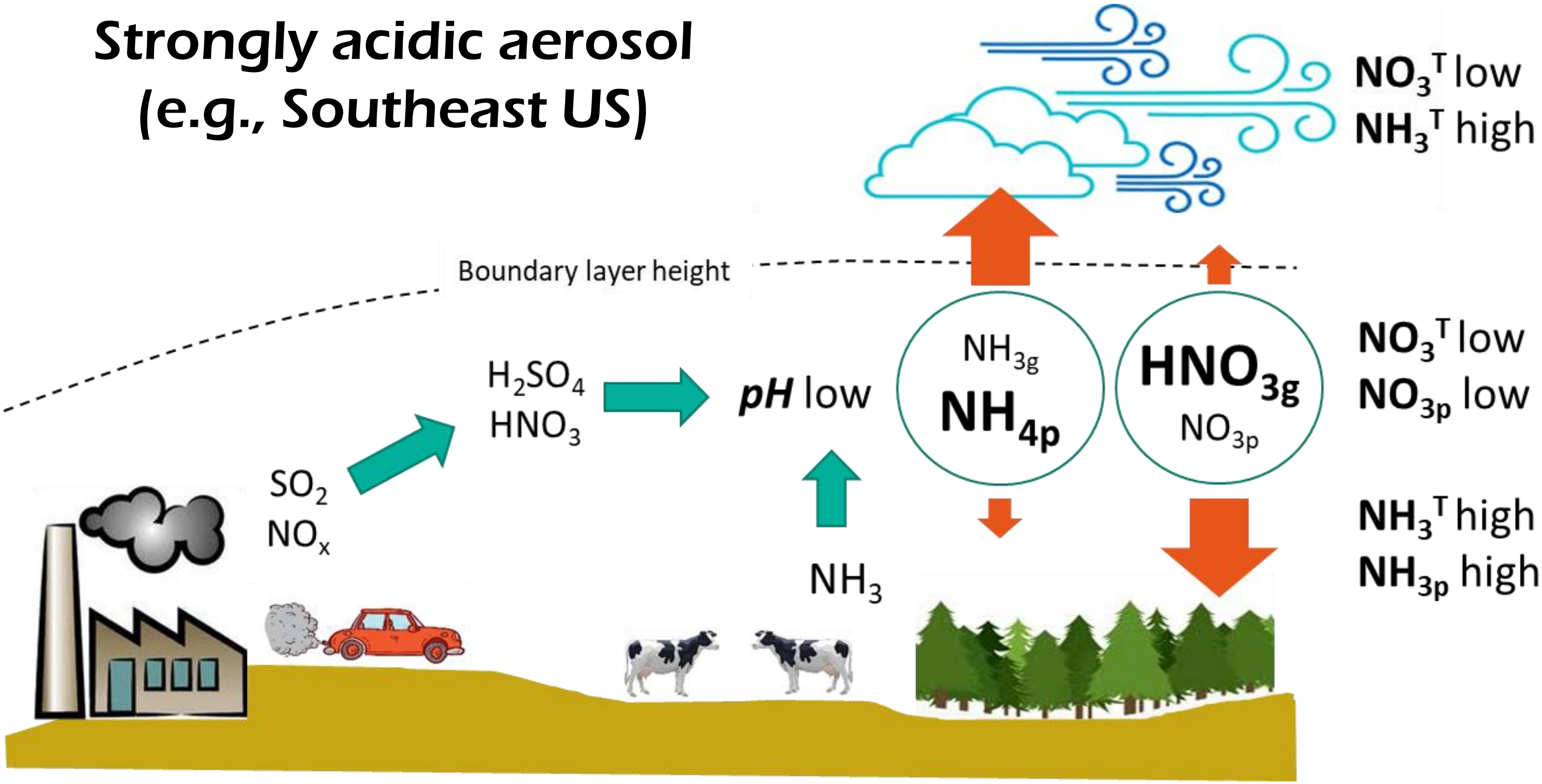
Nenes et al., ACPD (2020)

Reduced deposition velocity increases aerosol nitrate



Acidity effects on deposition

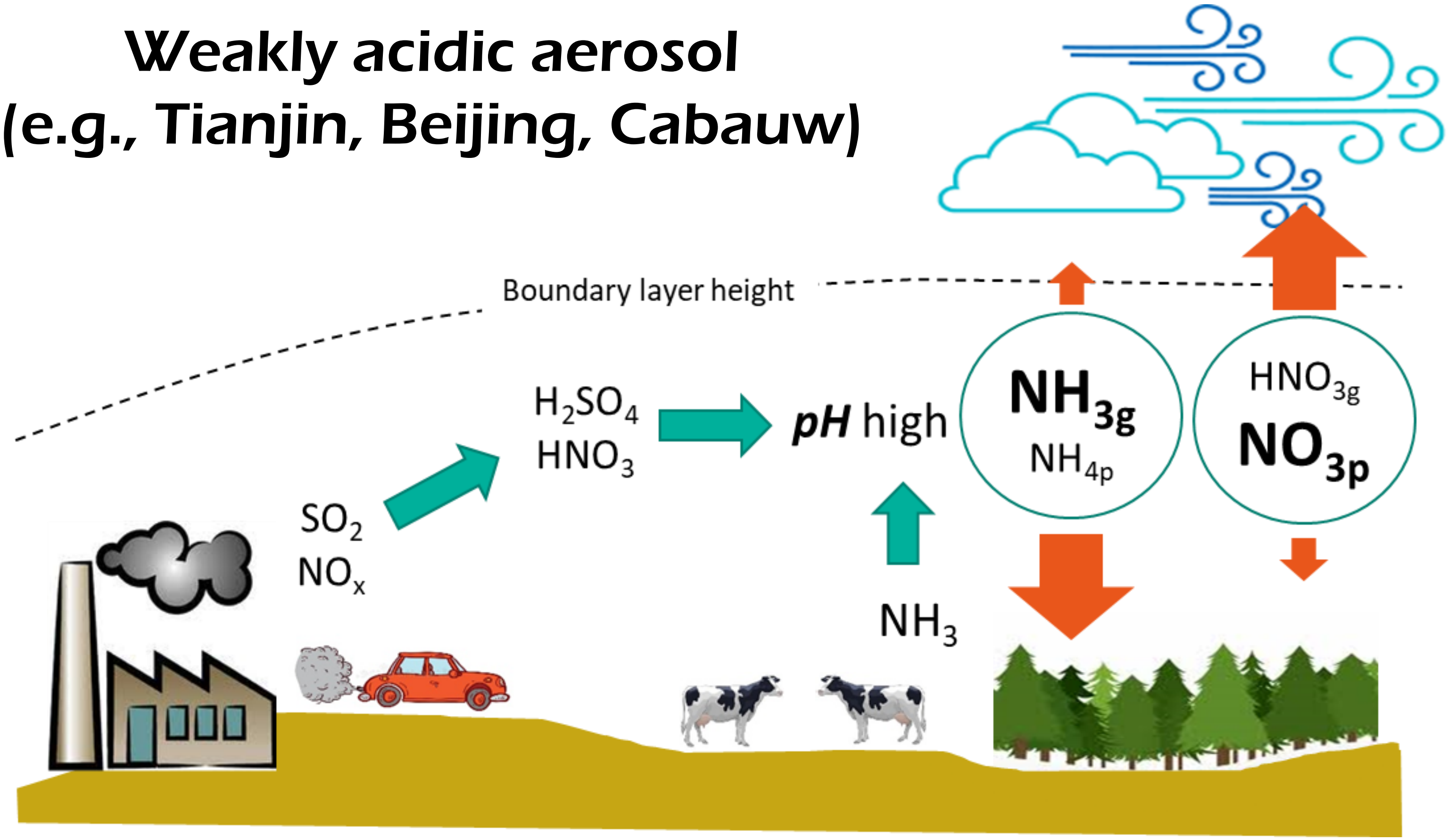
Strongly acidic aerosol (e.g., Southeast US)



Nenes et al., ACPD (2020)

Acidity effects on deposition

Weakly acidic aerosol
(e.g., Tianjin, Beijing, Cabauw)



NO_3^T high
NH_3^T moderate

NO_3^T high
NO_{3p} high

NH_3^T moderate
NH_{3p} moderate

[Nenes et al., ACPD (2020)](#)

Some final take-home messages

- Aerosol acidity control its composition, PM sensitivity to precursors, bioavailability and deposition rates.
- Thermodynamic analysis brings out natural dependence of PM sensitivity and deposition velocity to pH and LWC.
- First identified regimes of slow deposition of NH_3 and HNO_3, and insensitivity of PM to NH_3, HNO_3 changes.
- For mildly acidic aerosol (e.g.,Tianjin), PM most effectively responds to nitrate (and sulfate) reductions.
- In mildly acidic conditions, slow depositon of nitrate increases its concentration in aerosol by up to 10x. **This may cause the rapid increase and high concentration of nitrate during why haze episodes in Tianjin, etc.**
- Ammonia tends to respond less to acidity changes, unless the aerosol is extremely acidic (pH < 1).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