Acidity of atmospheric aerosol and its importance

Athanasios Nenes

Laboratory for Atmospheric Processes and Their Impacts (LAPI)
Ecole Polytechnique Federale de Lausanne, Switzerland

Foundation for Research and Technology Hellas, Patras, Greece

Honorary Professor, Department of Environmental Sciences, Aarhus University
Aarhus, Denmark.

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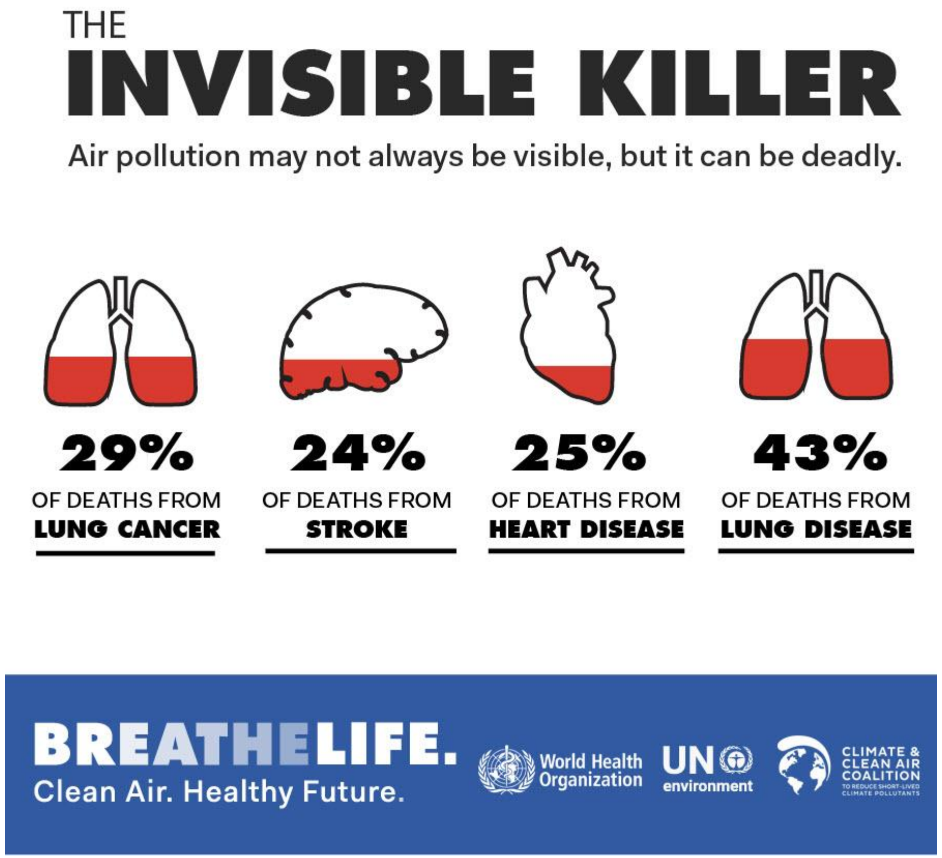
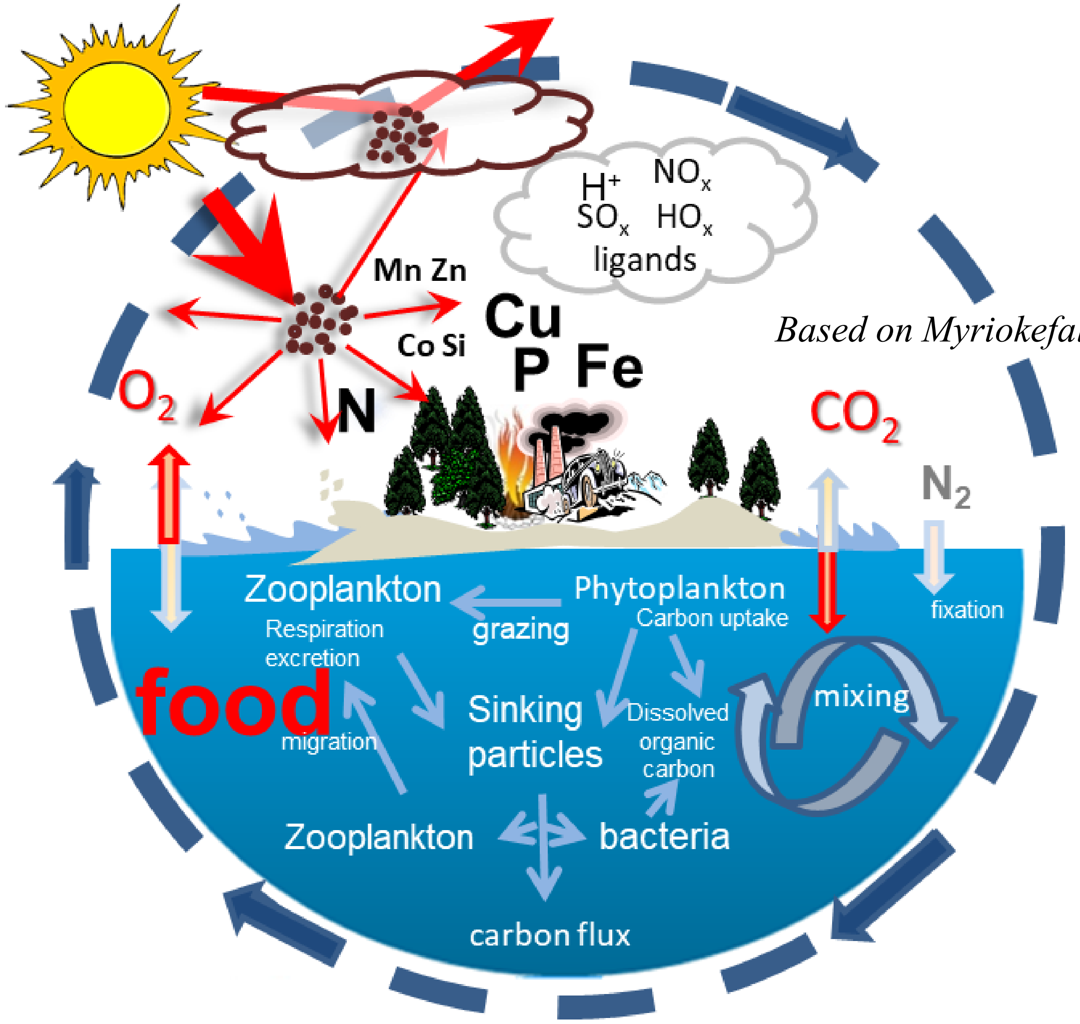
ETH Zurich, 01 June 2026

Why do we care about aerosols?



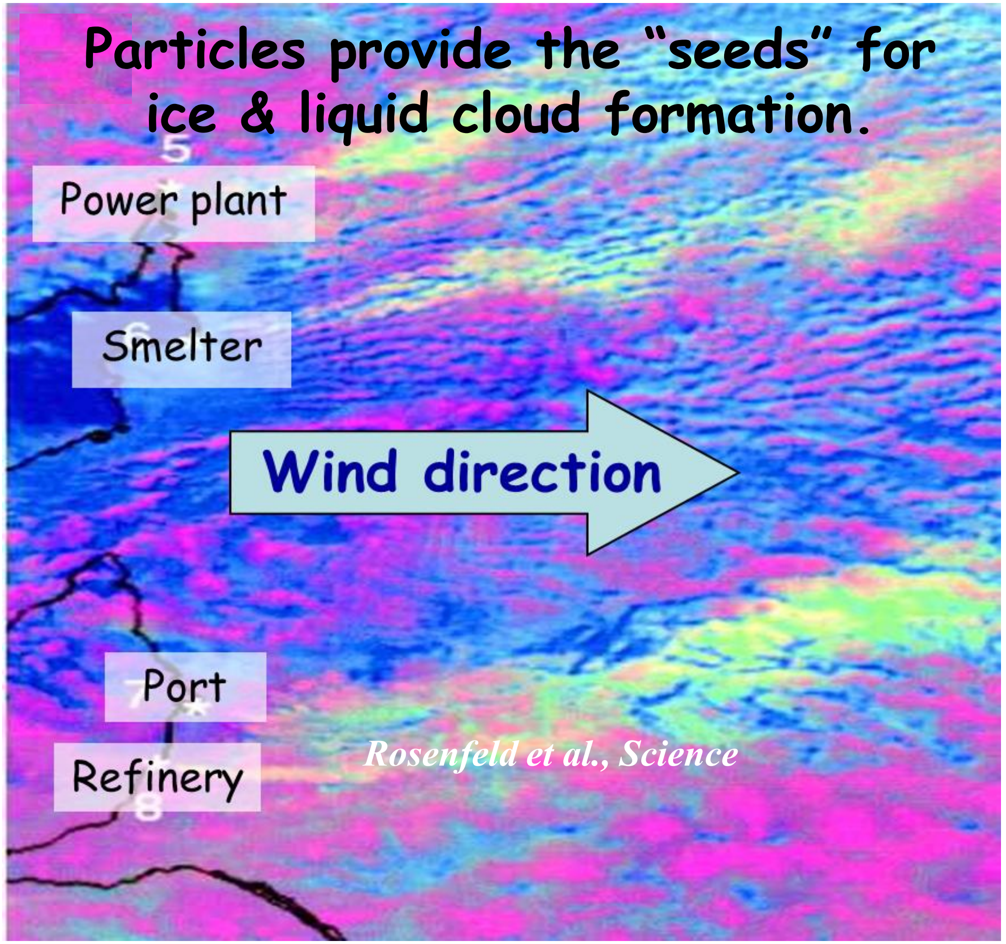
4.2 million people die prematurely (500k in Europe) WHO estimates



Based on Myriokefalitakis et al.

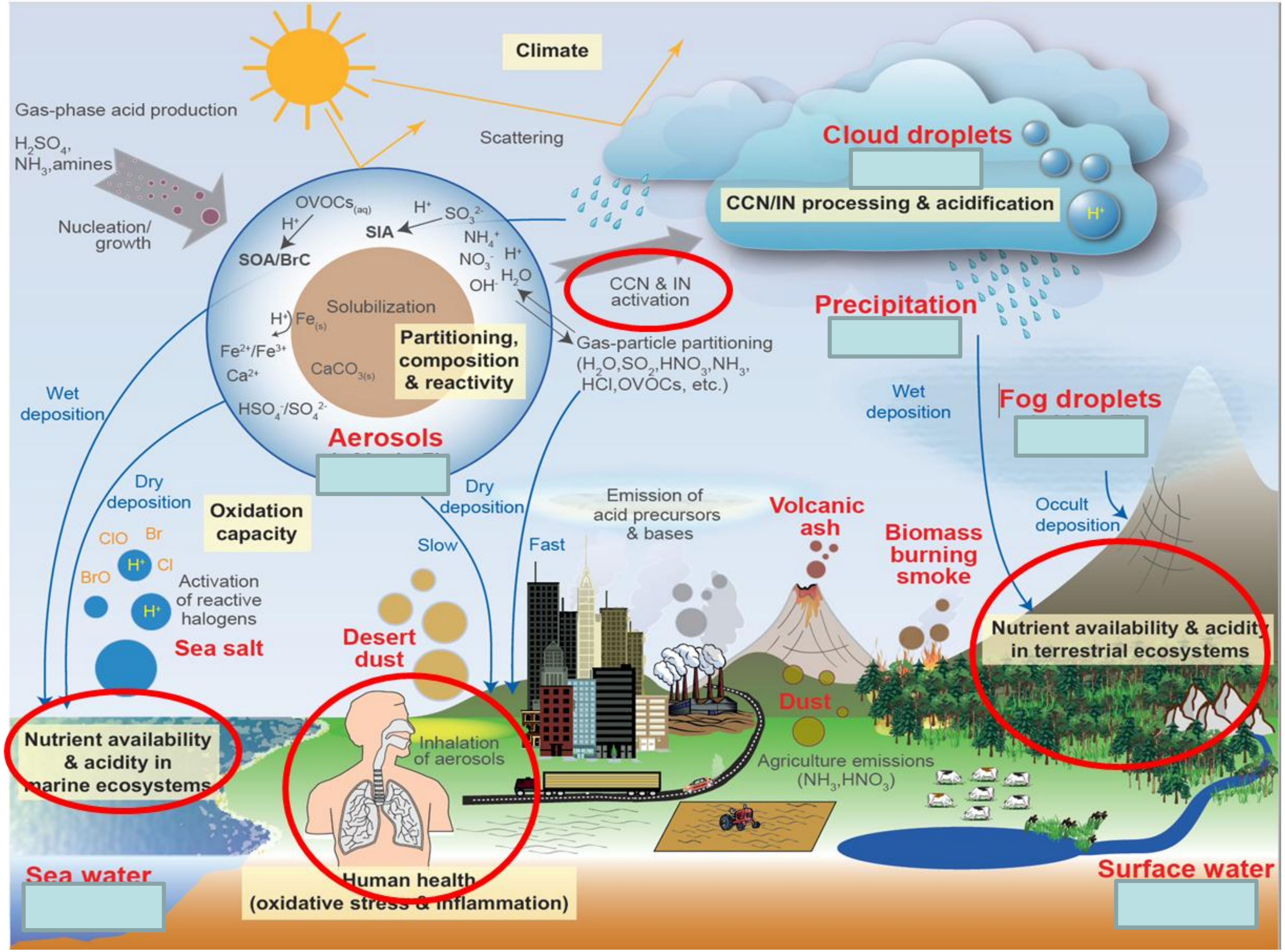
They affect biogeochemical cyles and ecosystems

Why do we care about aerosols?



Net *cooling* effect on climate, but with large uncertainty that *inhibits climate change projections.*

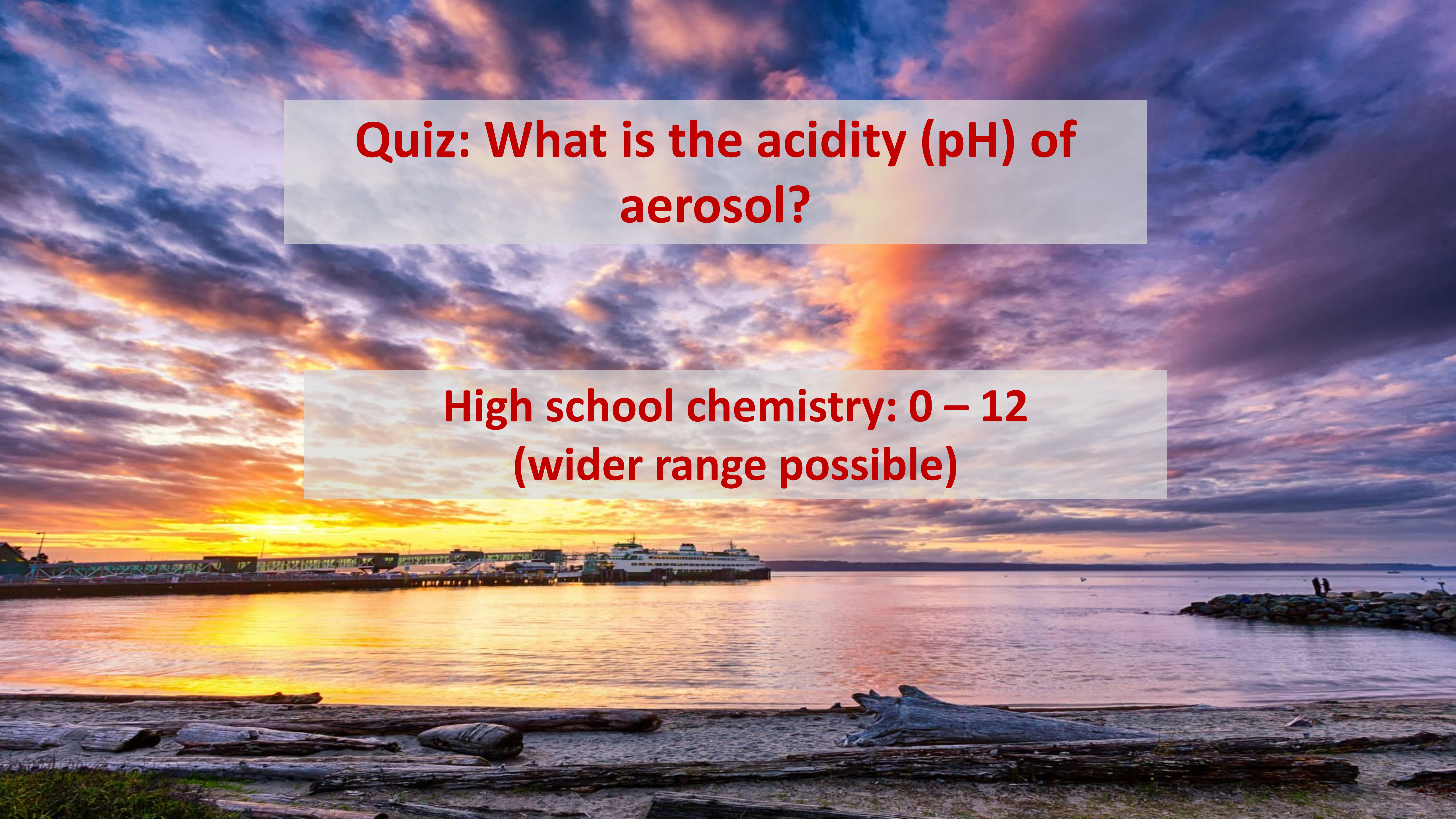
Acidity of particles at the heart of all these effects



Pye et al., ACP, 2020

Quiz: What is the acidity (pH) of aerosol?

High school chemistry: 0 – 12
(wider range possible)



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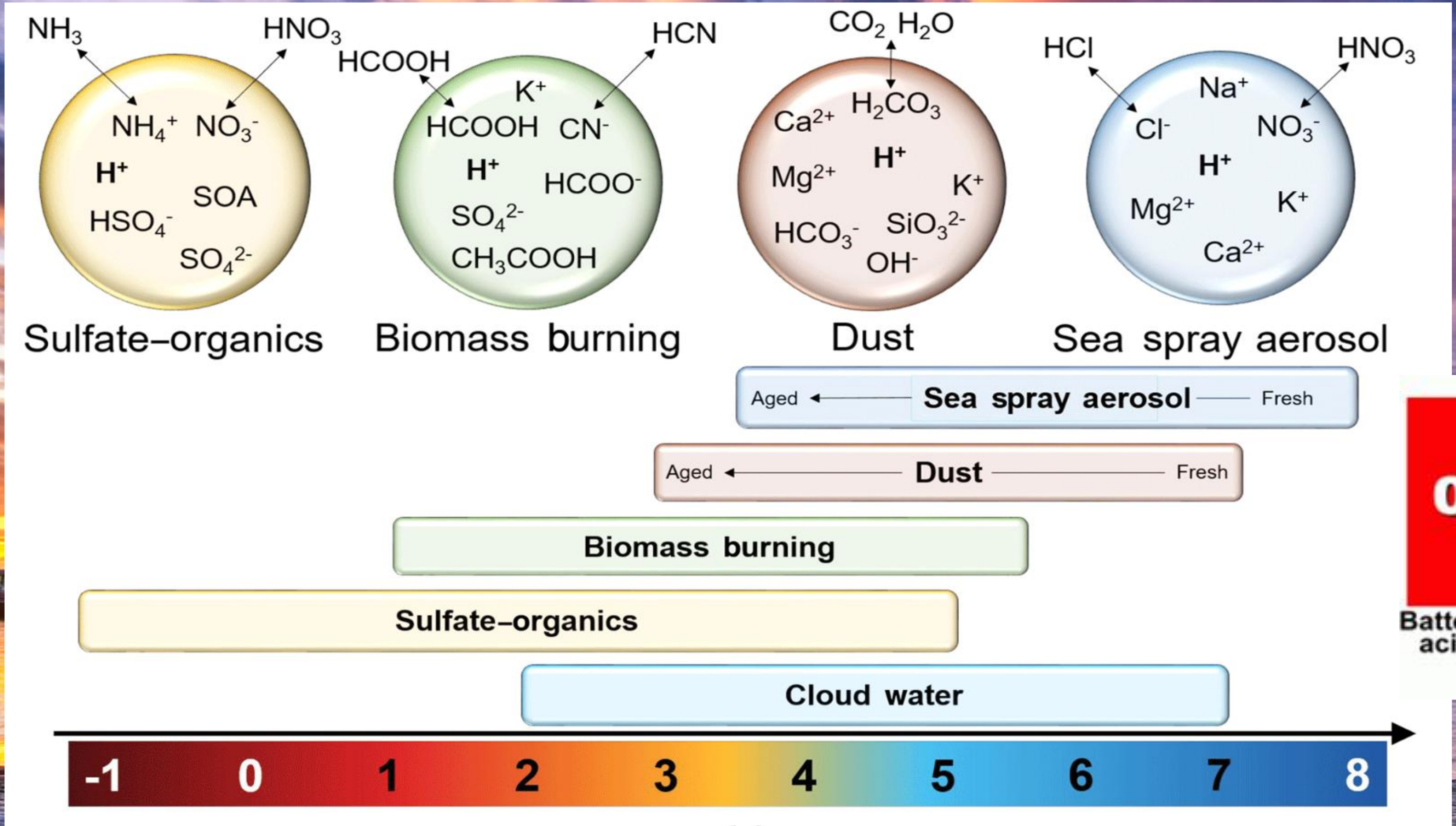

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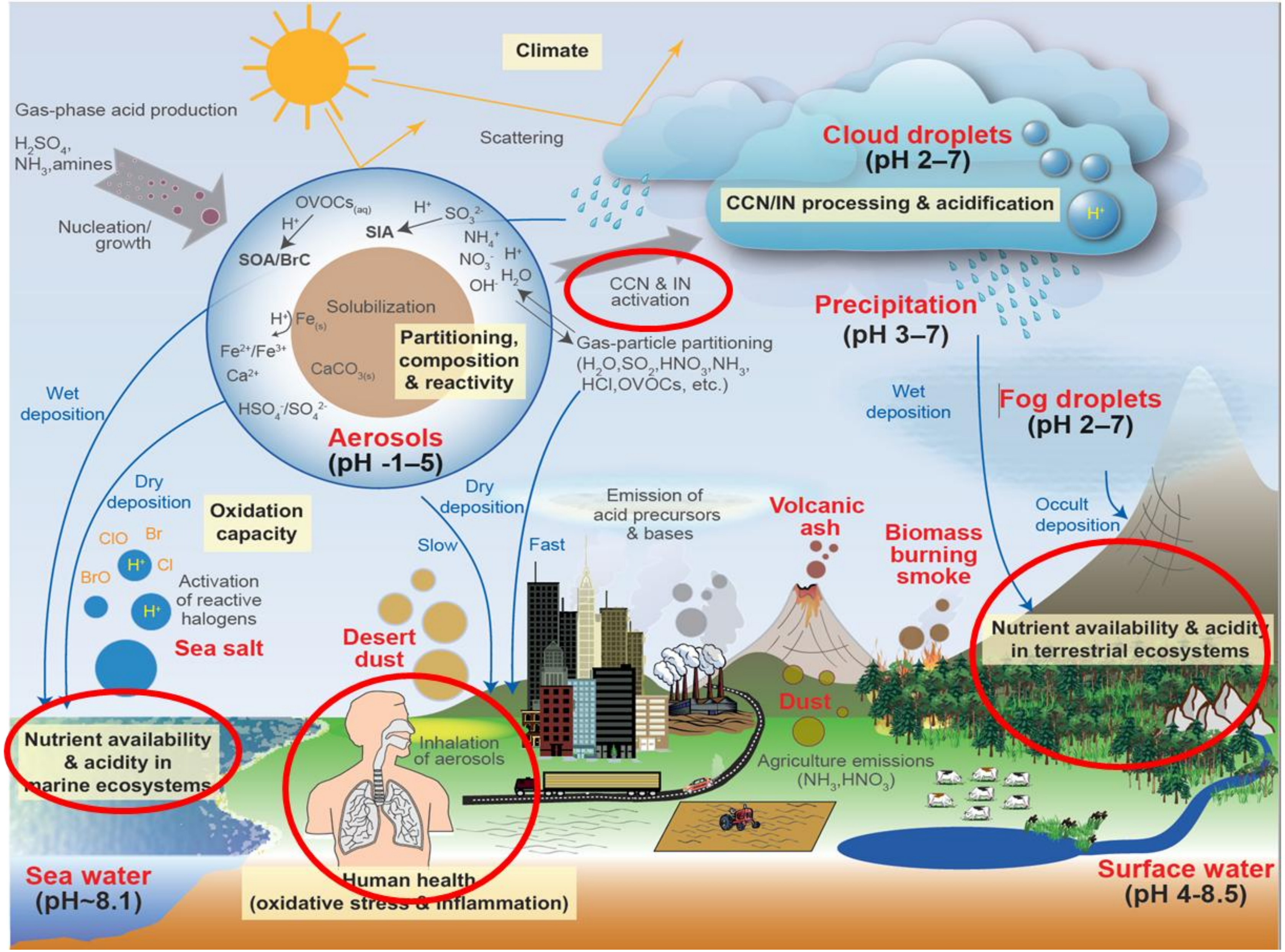


Pye et al., ACP, 2020

Emissions & partitioning affect aerosol acidity

Acidic  → SO_2(g) NO_x(g) VOCs → *Oxidation* → H_2SO_4(p) HNO_3(p) Org acids (p)

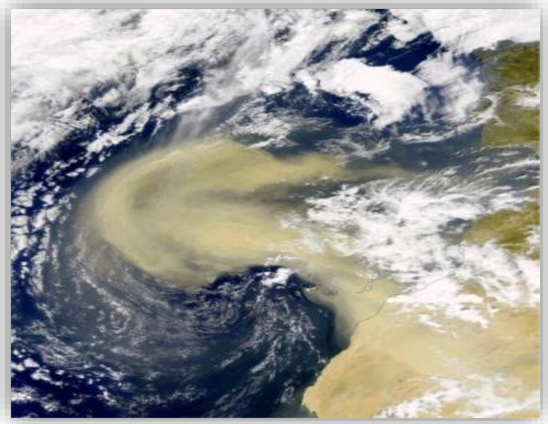
Basic  → NH_3(g) + Mineral dust, sea salt (Na, K, Ca, Mg, etc.)

Fine Mode
($D_p < 1$ µm)

Formation of aerosol species and amount **depends on particle pH**

pH varies a lot over space, time and particle size!

Chemical equilibrium with gas phase (acid/base gases AND H_2O vapor) **very important.**



Mainly in coarse mode ($D_p > 1$ µm)

adapted from: H.Guo

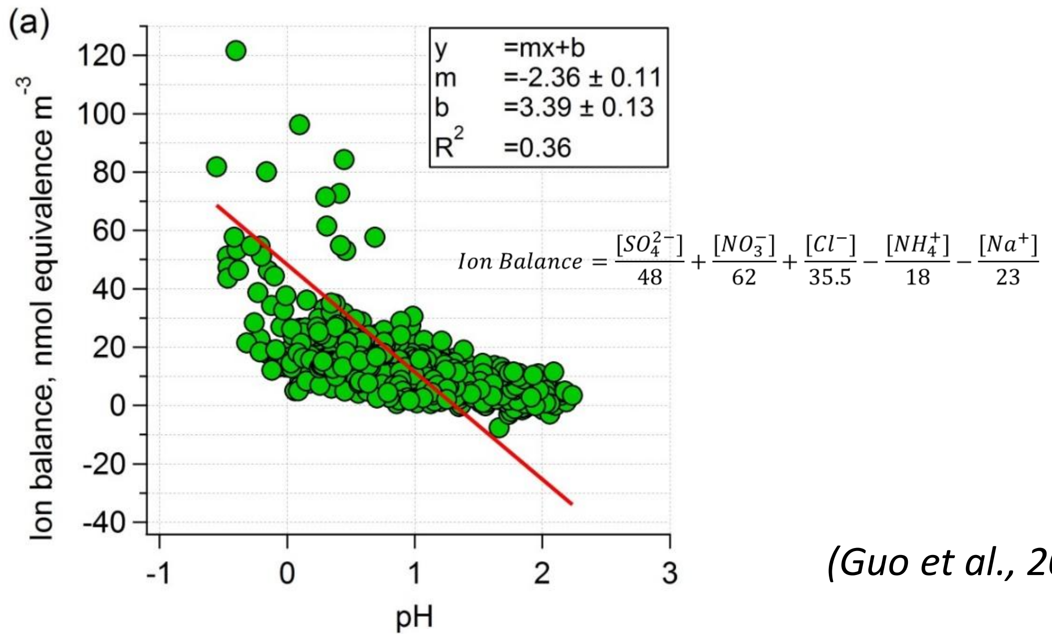
Measuring aerosol pH: The problem

- **Direct measurement of aerosol pH is challenging.**
- Emerging offline methods – but still under development.
- "pH proxies" (ion balance, molar ratios), do not strongly correlate with pH

$$pH = -\log_{10}[H^+] = -\log_{10}\frac{1000H^+_{air}}{LWC} \qquad H^+_{air}, LWC\ units:\ \mu g\ m^{-3}\ air$$

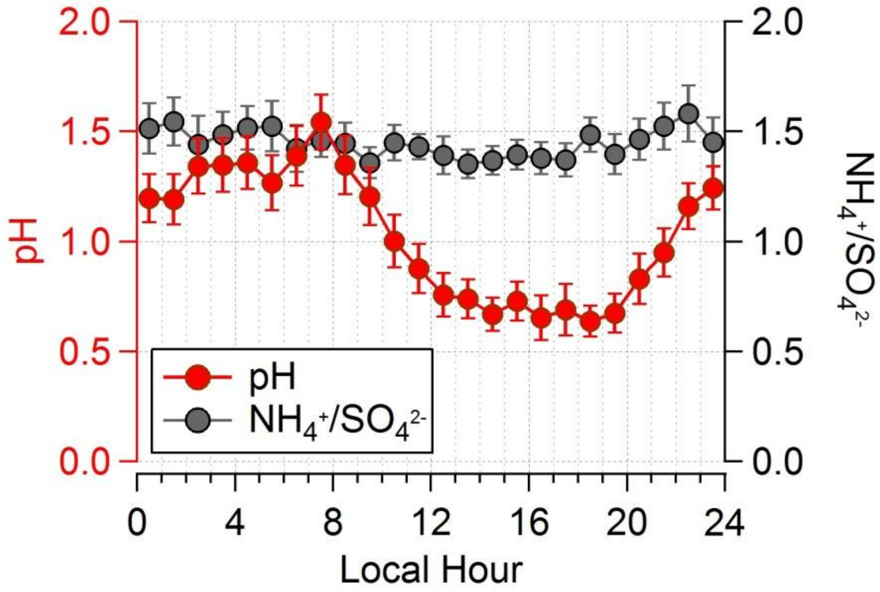
- Current gold standard: Measurements + Thermodynamic modeling

Ion balance:



(Guo et al., 2015)

NH_4^+/SO_4^{2-} Molar ratio:



Determining aerosol pH: Models provide solution

ISORROPIA-II / ISORROPIA-Lite calculates:

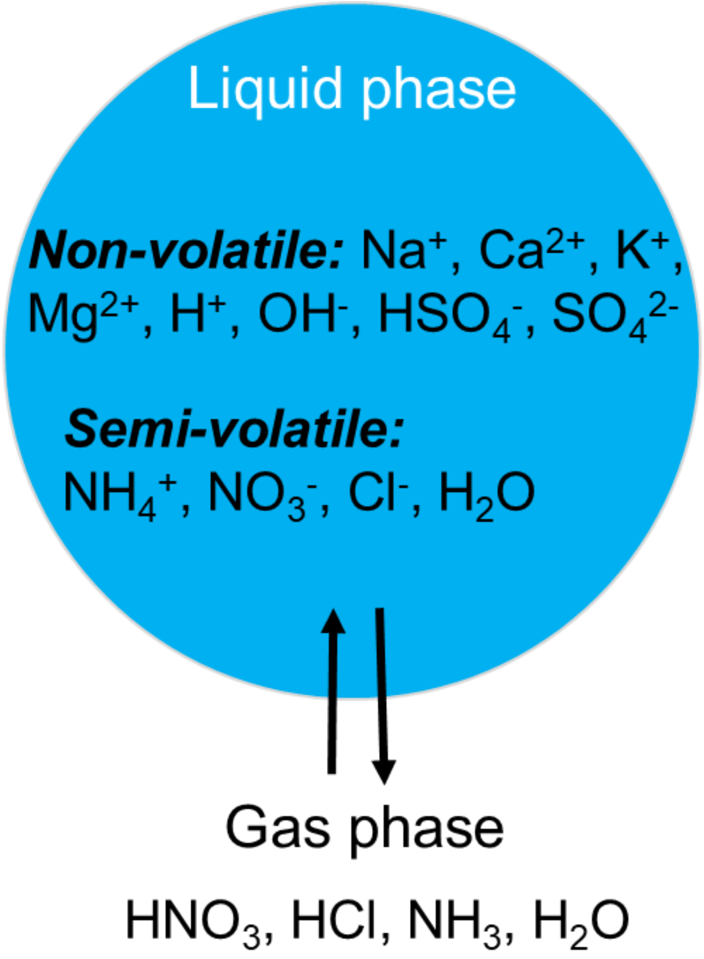
the composition and phase state of an NH_4^+-SO_4^{2-}-NO_3^--Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}-water inorganic aerosol in equilibrium with gases

Assumptions:

- $PM_{2.5}$ in equilibrium with gas phase
- Maybe some other assumptions about the presence of solids

Model output: H_2O, H^+ → pH

Other output: { HNO_3, NO_3^- ; NH_3, NH_4^+ } gas/particle partitioning of pH-sensitive species



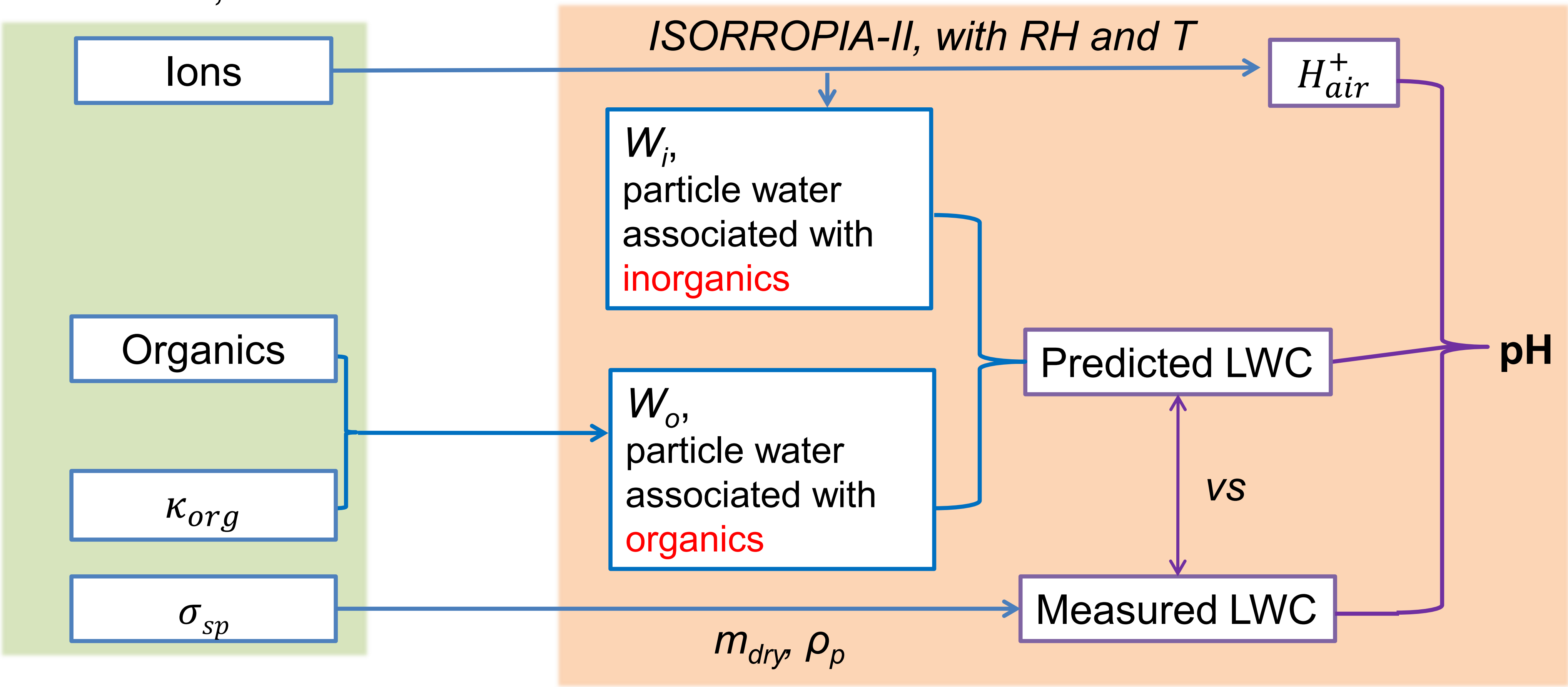
http://isorropia.epfl.ch

Determining aerosol pH with model+observations

Approach of Guo et al. (2015):

- *Particle ions (**SO_4^{2-}, NH_4^+,** NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2})*
- *Gas (**NH_3**)*
- *Particle water or **total organics & κ_{org}***
- ***RH** and T;*

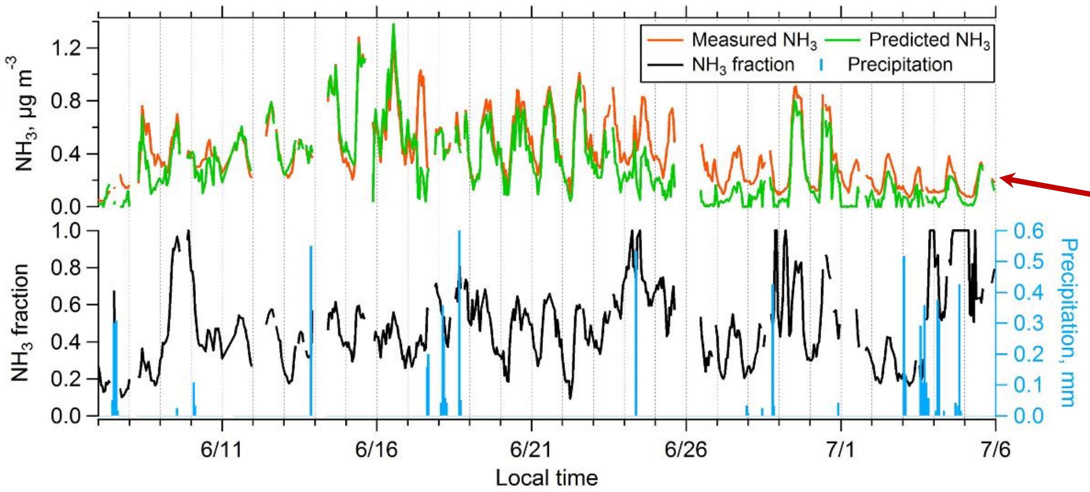
→ pH



Lu et al. (2015) PNAS; Guo et al., (2015) ACP; Bougiatioti et al., (2016) ACP

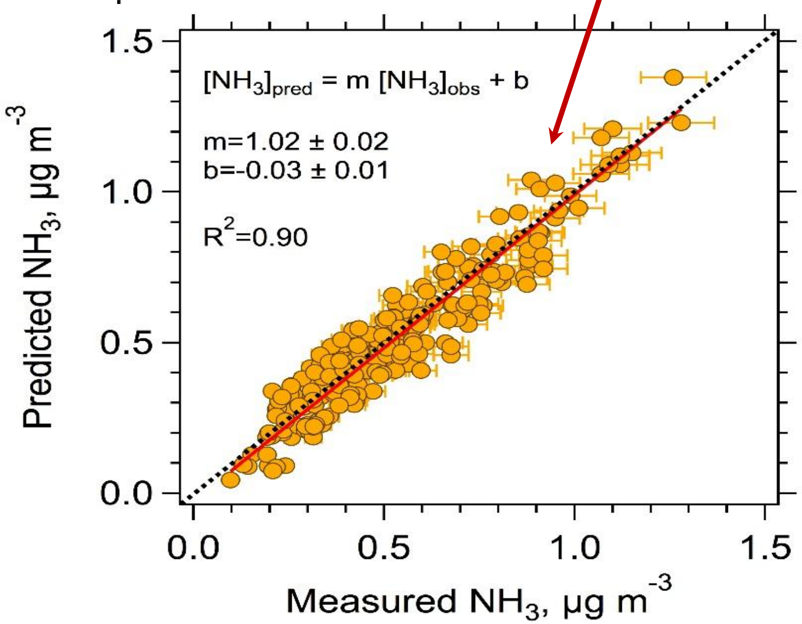
pH model predictions evaluated by NH_3-NH_4^+ partitioning

SOAS: *(Southern Oxidant Aerosol Study)* 6/7, 2013 Centreville, AL (CTR)



Guo et al., ACP, 2015.

Comparison of predicted vs. observed gas-phase NH_3.



Wonderful agreement of observations with model !!!!

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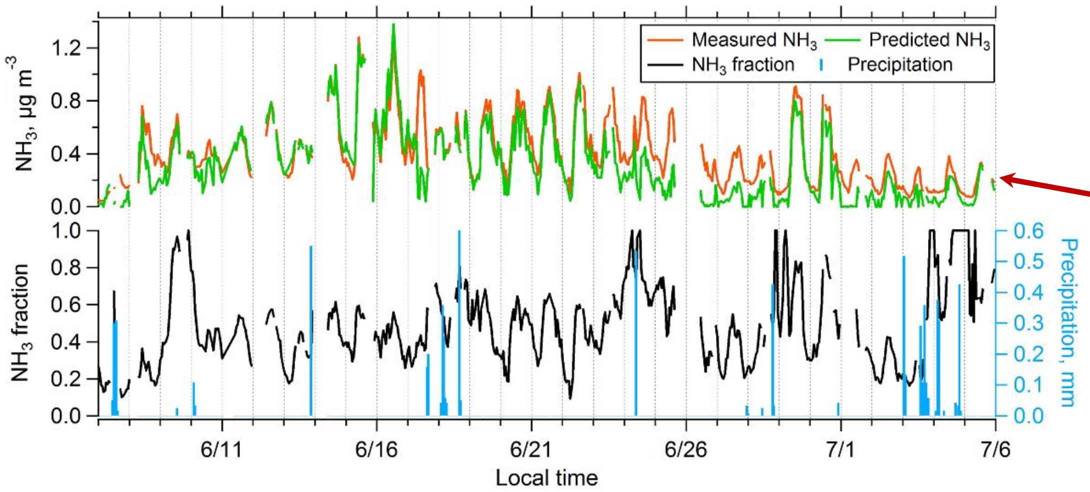

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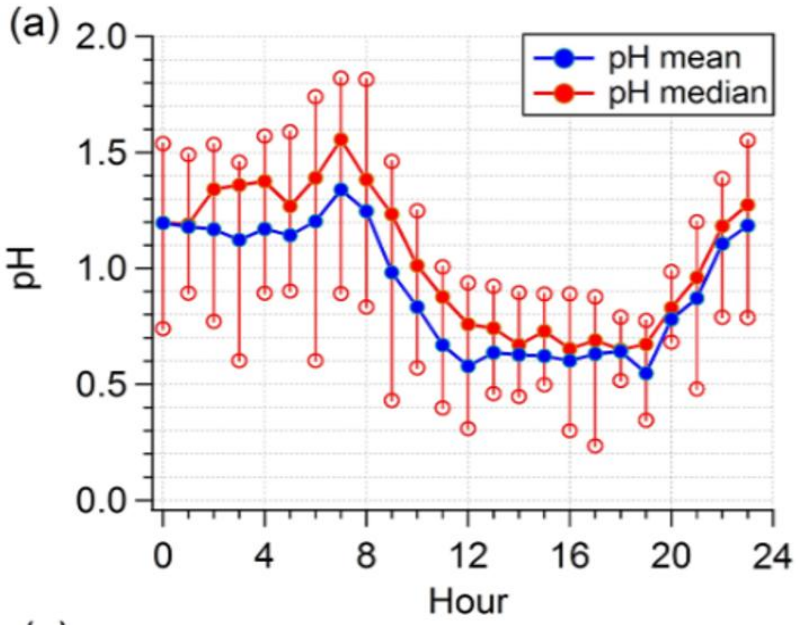
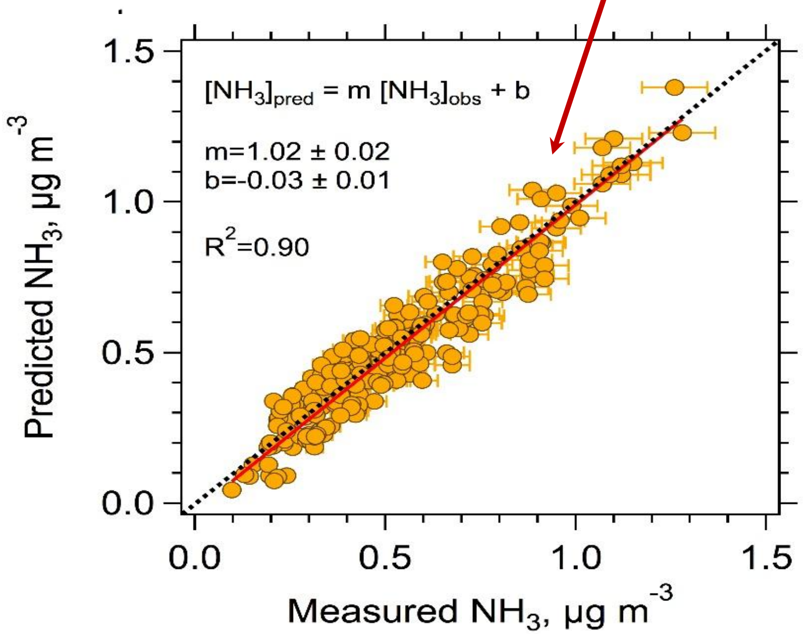
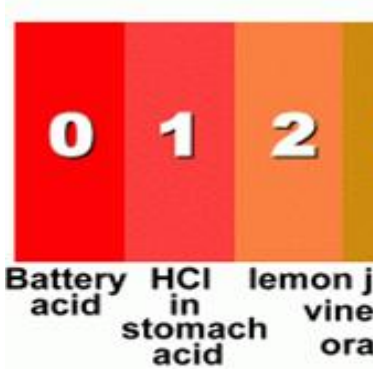


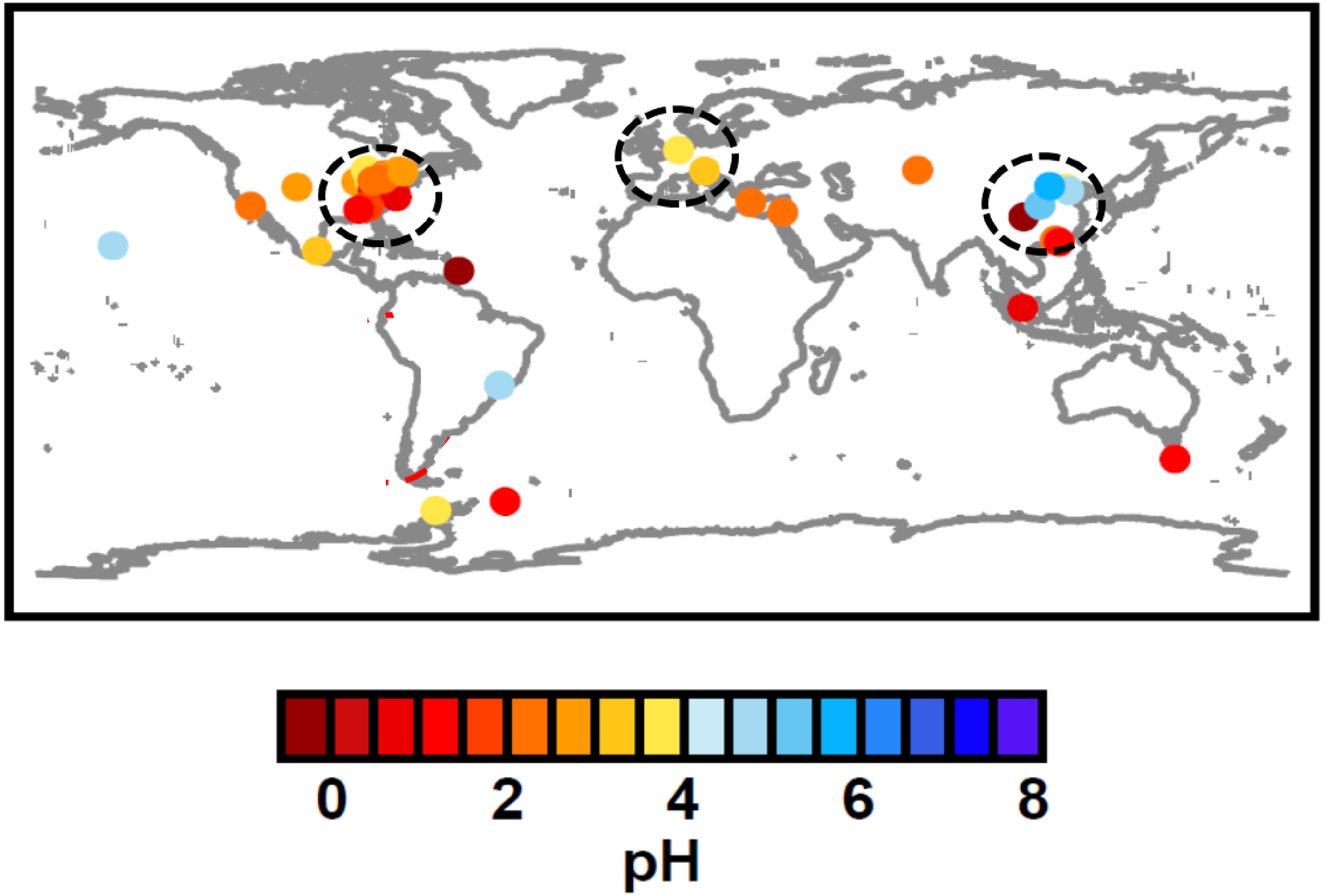


Wonderful agreement of observations with model !!!!

Reproducing observed partitioning of semi-volaties confirms that pH determined is *reasonable*.

Method applied to global datasets show acidic aerosol is **everywhere**. pH varies **a lot.**

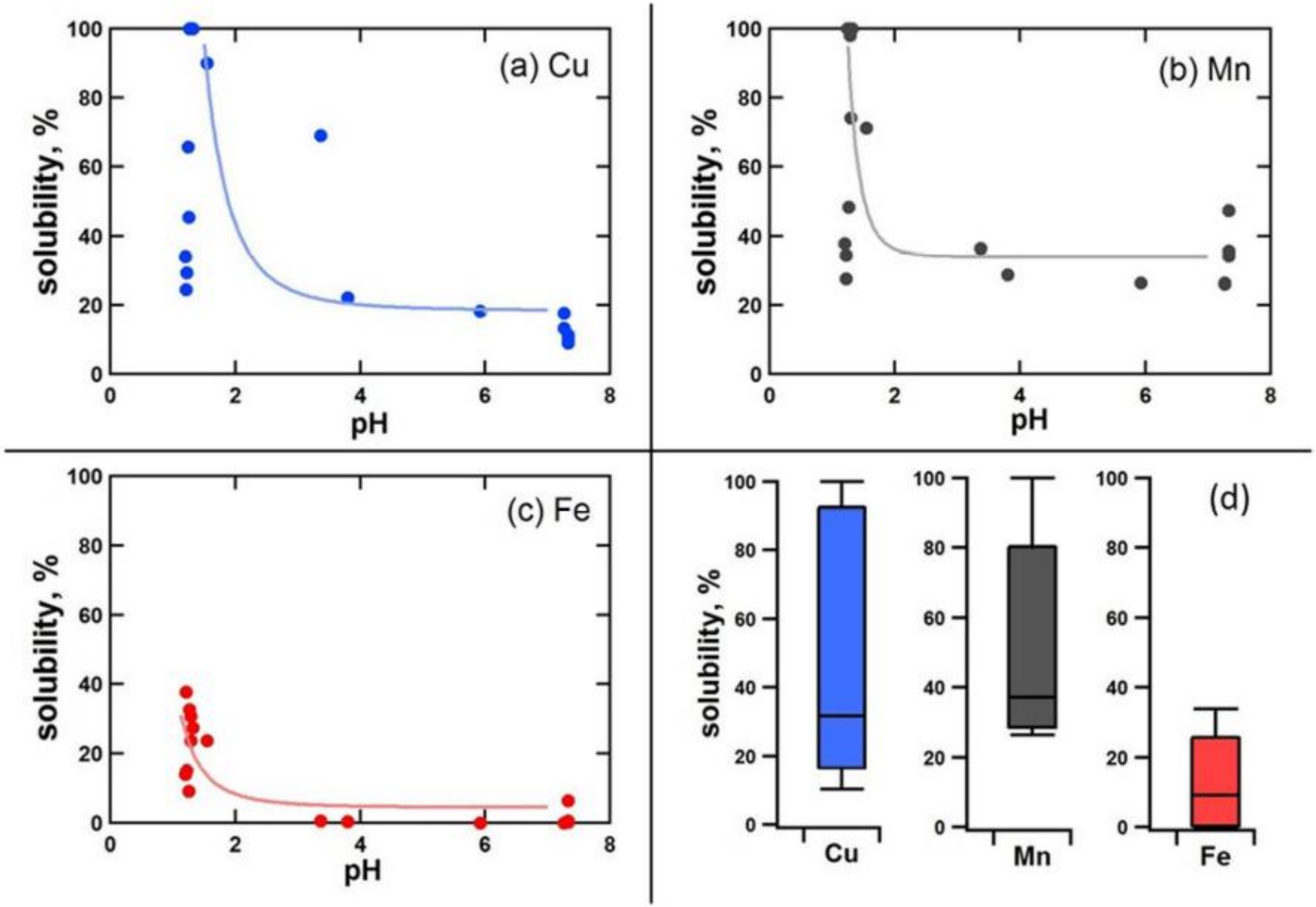




et al., ACP, 2020

Acidity dissolves metals & affects health

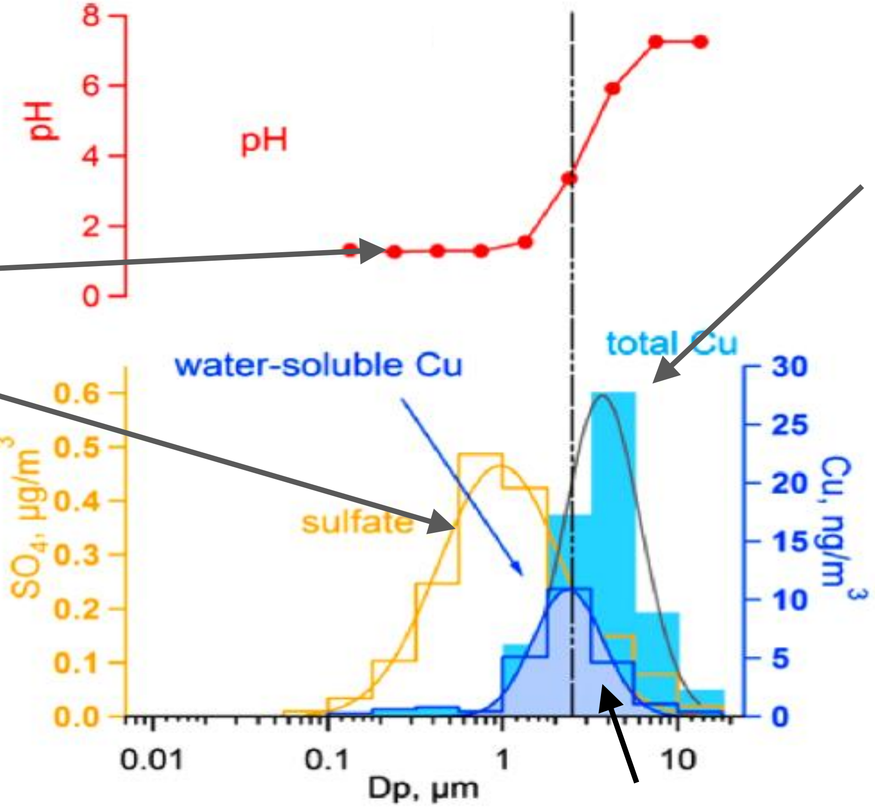
- Strongly acidity levels can dissolve metals (metallic or oxides) in particles.
- Acidification of dust (desert or road-dust) can increase its toxicity.



Fang et al. *ES&T* 2017

Acidified road dust has high OP (toxicity)

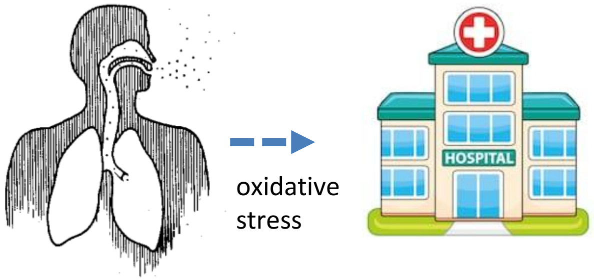
Acidic PM_1 due to presence of sulfate and few NVCs.



Emitted insoluble metals in coarse mode.

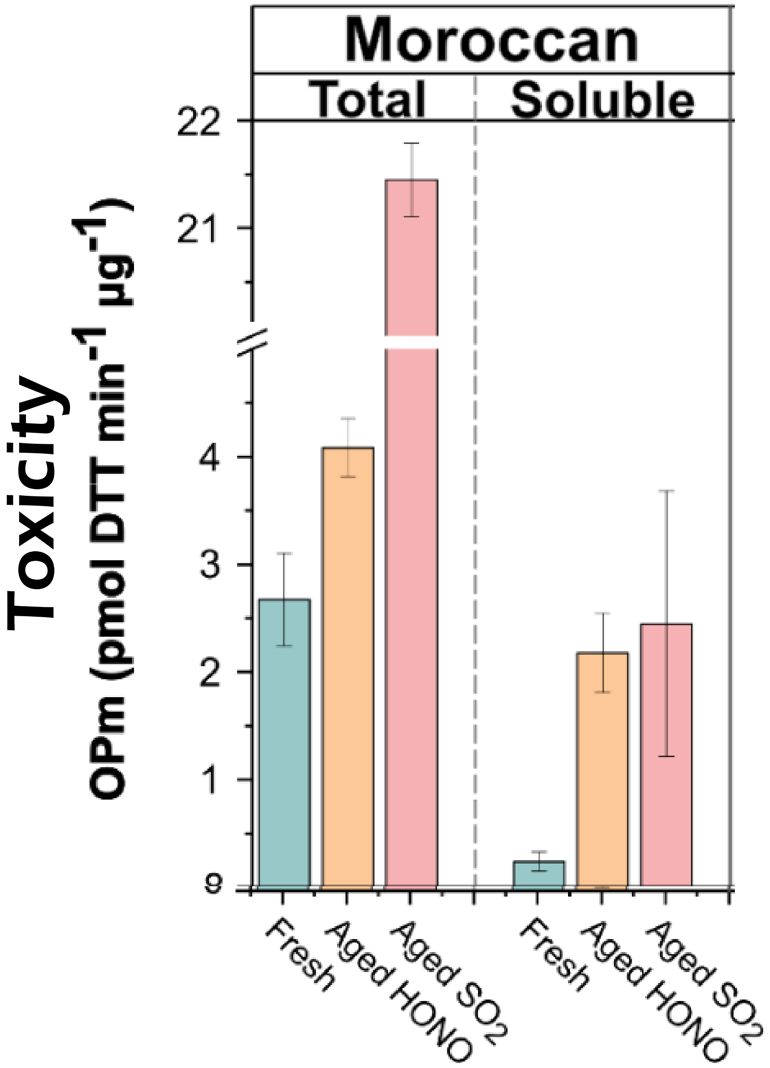
Cu becomes soluble by acid dissociation, drives toxicity
Larger particles have too little acidity and soluble Cu

Fang et al. *ES&T* 2017
Dallenbach et al., Nature, 2020



- Soluble metals appear where acidity is strong (pH low)
- Toxicity related to inhalation of soluble metals
- ***Mechanism explaining why PM 2.5 sulfate in the environment is associated with toxicity***

Acidifying dust in the lab has high toxicity



Molina et al., in review

When you acidify dust:

1. Soluble metal fraction increases
2. Oxidative potential (toxicity) increases A LOT
3. Important impacts on health and ecosystems

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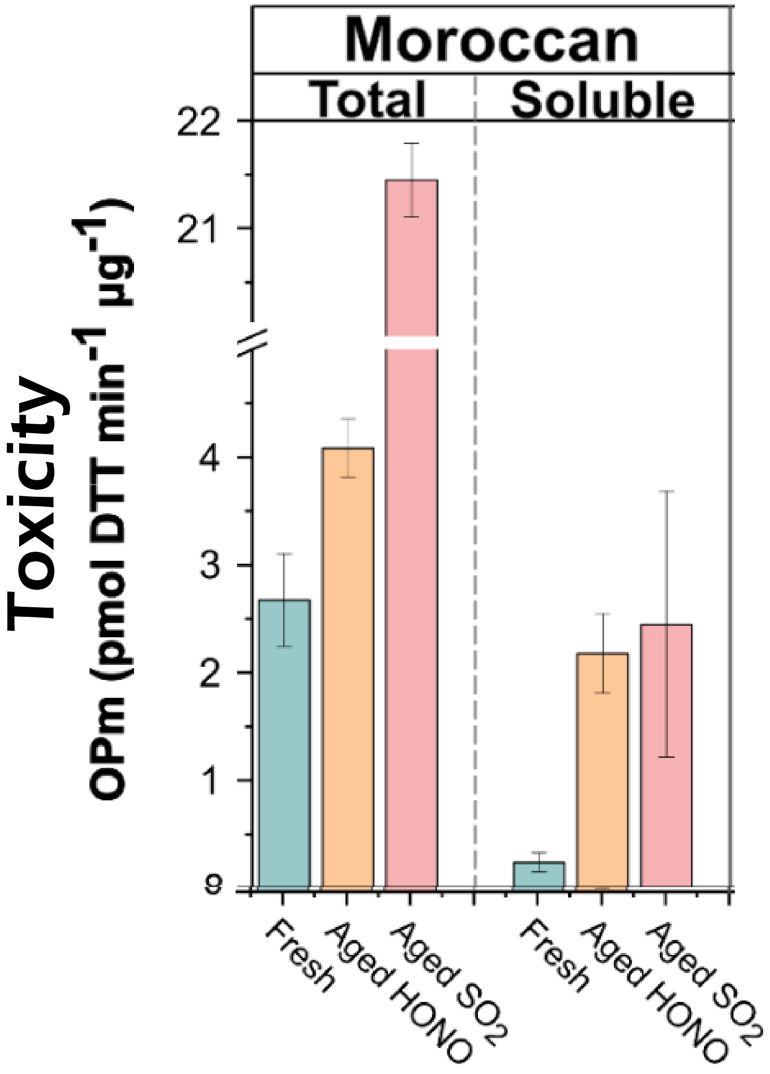

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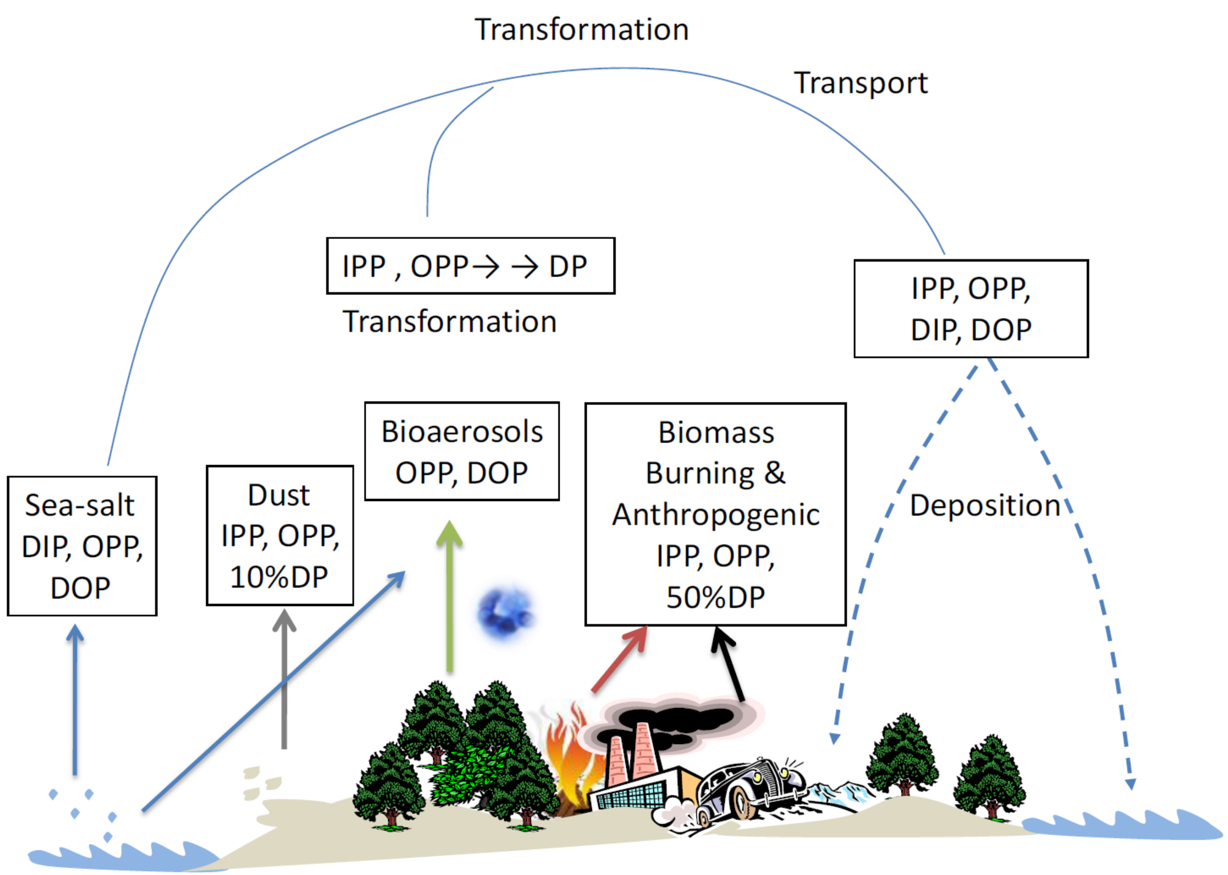
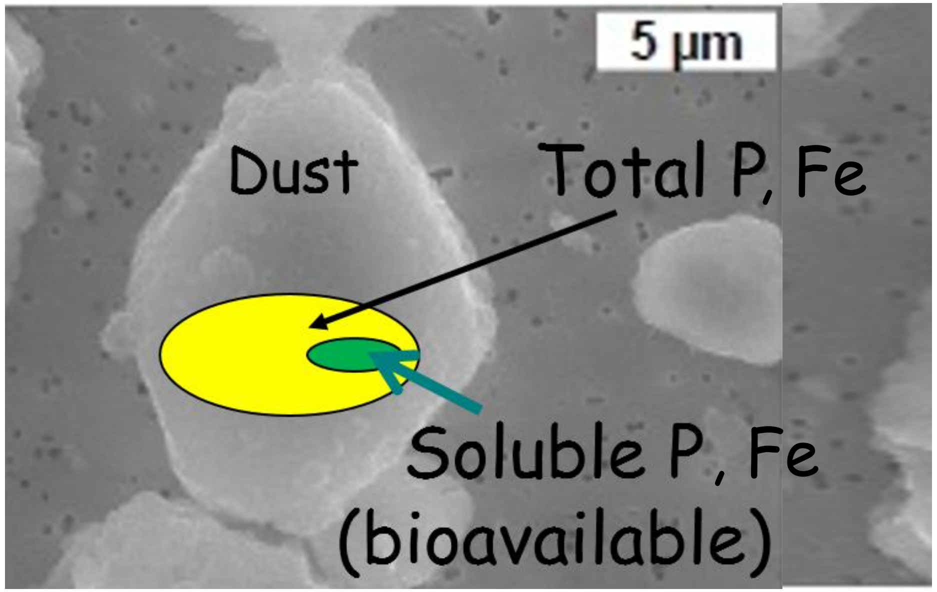
Acidification impacts the ability of dust to make ice too (CleanCloud PIANO experiments) – not shown but love to talk offline!

Same mechanism affects nutrient cycles & ecosystems



Myriokefalitakis et al., Biogoeosci., 2016

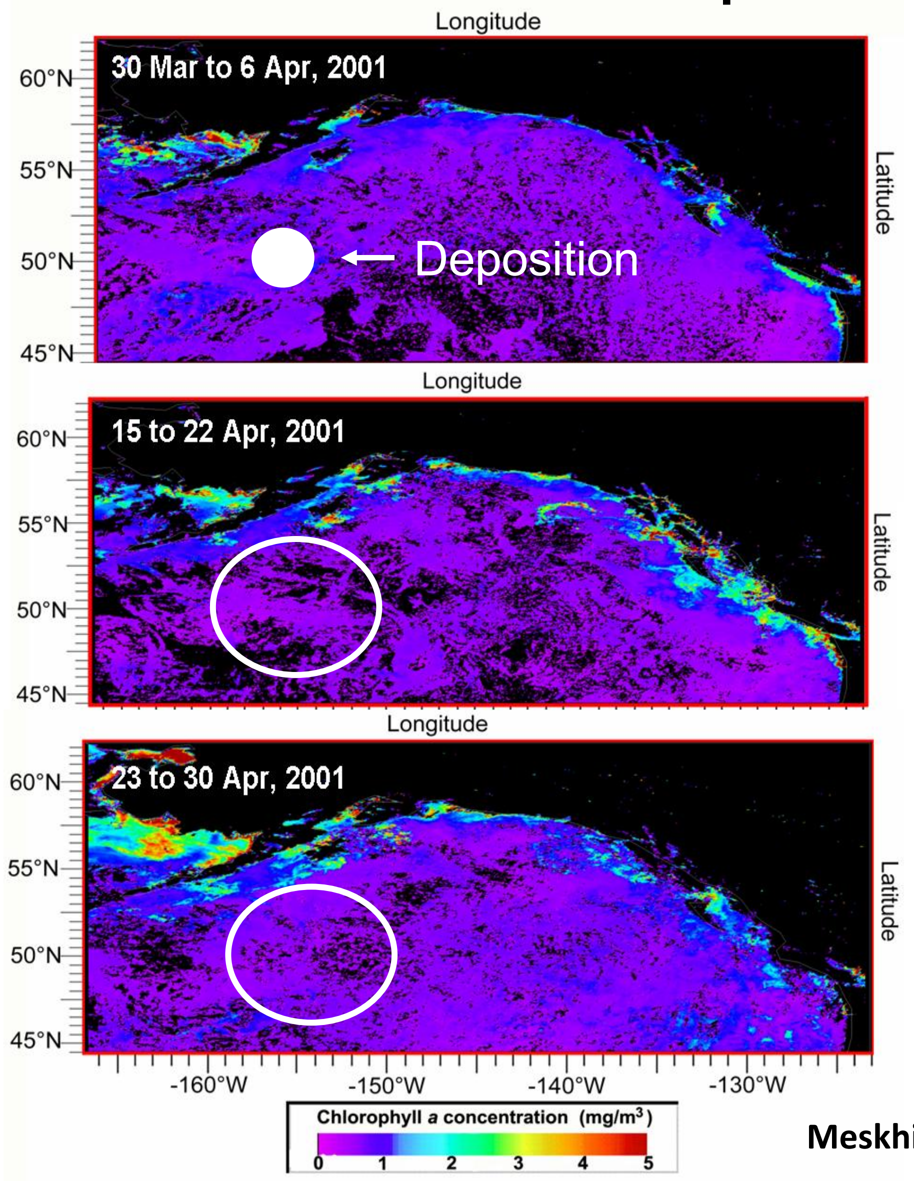


(same applies to Fe, Cu)

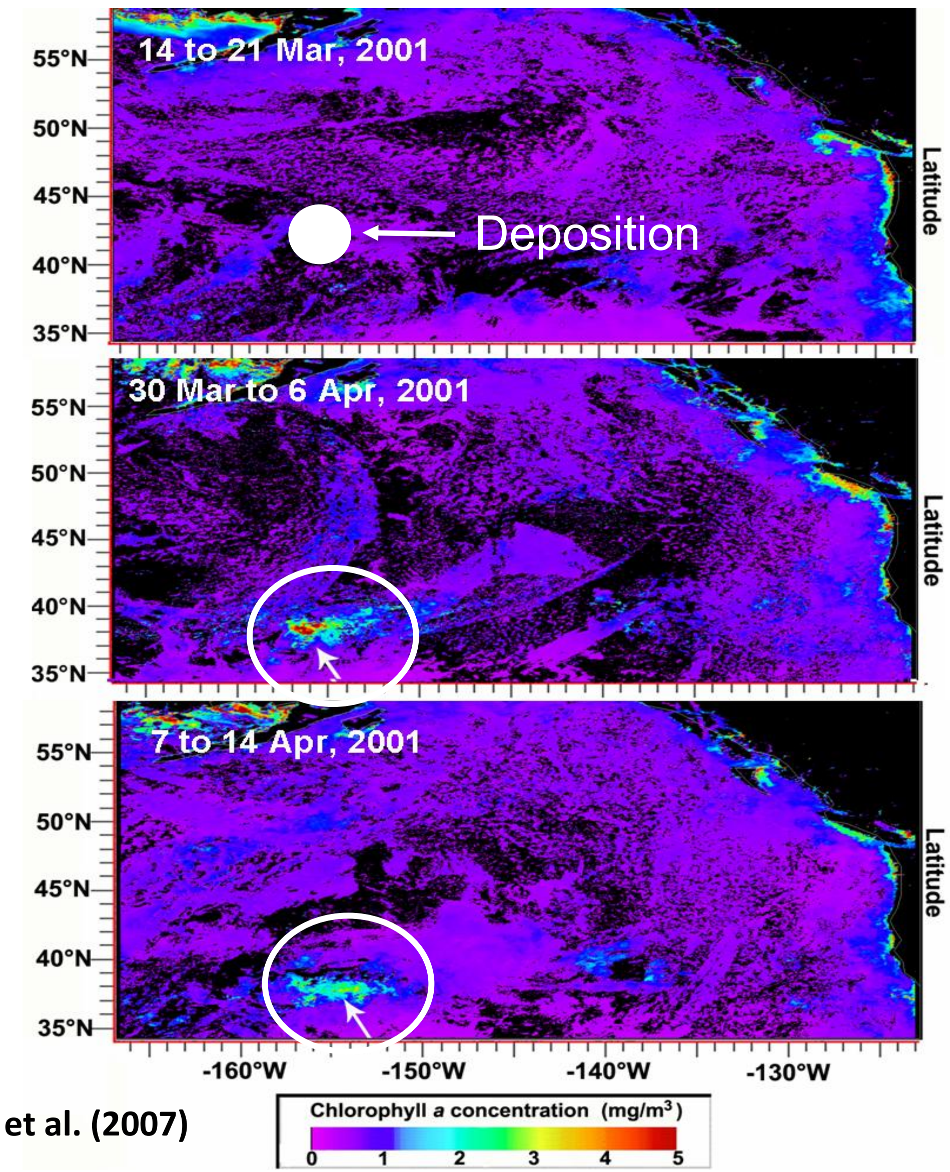
- Mineral dust is a prime source of P, Fe, Cu to the (offshore) ocean.
- Acidification of Dust by mixing with pollution, volcanic aerosols and natural acids affects their soluble (bioavailable) fraction.

Ecosystem response to nutrient deposition from acidified dust

Dust + no acids -> no response

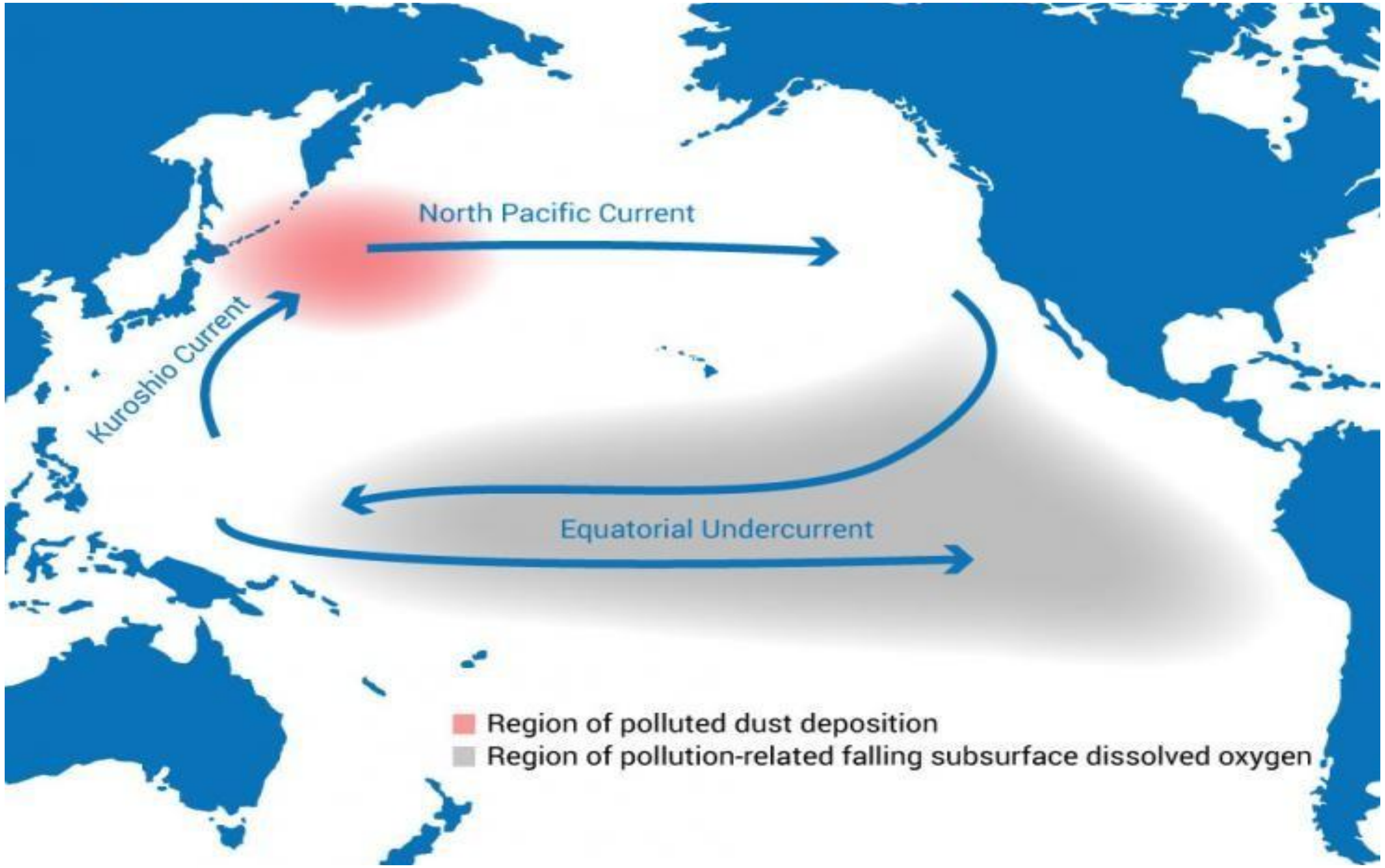


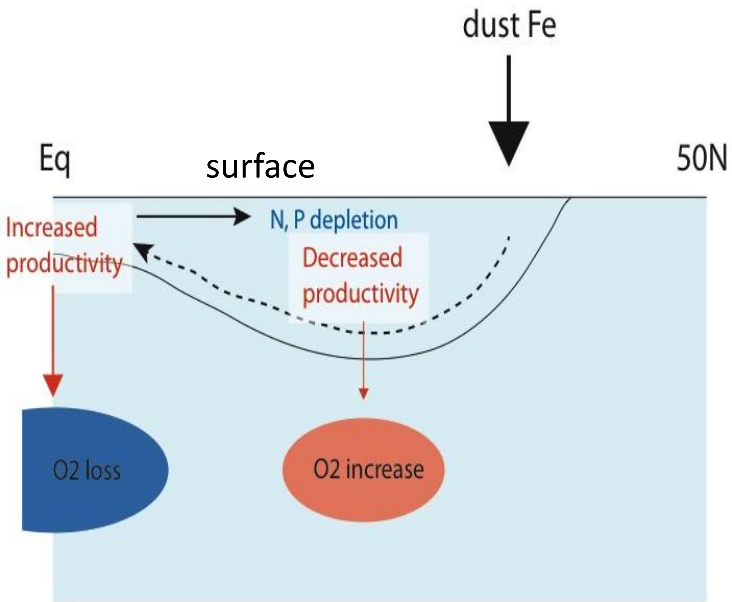
Dust + acids(pollution) -> strong response



Meskhidze, Nenes et al. (2007)

Excess nutrients from acidified dust can transport and cause eutrophication - far from deposition regions !!!



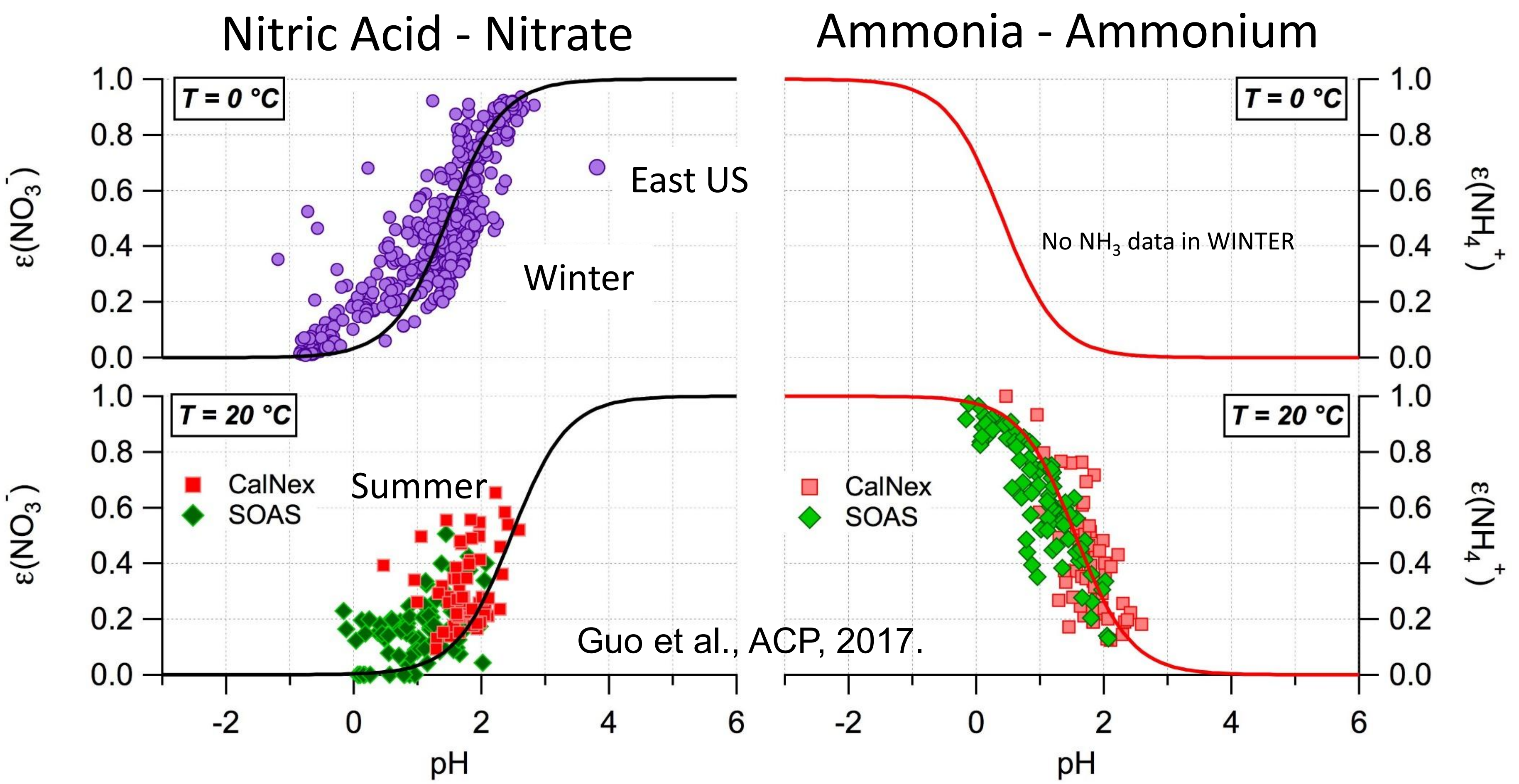


Acceleration of oxygen decline in the tropical Pacific over the past decades by aerosol pollutants

T. Ito[1]*, A. Nenes[1,2,3,4], M. S. Johnson[5], N. Meskhidze[6] and C. Deutsch[7]

16 MAY 2016 | DOI: 10.1038/NGEO2717

pH- driven aerosol-gas partitioning
Profound implications for air quality & environmental policy



The amount of "total" ammonia and nitrate that is in aerosol depends on pH

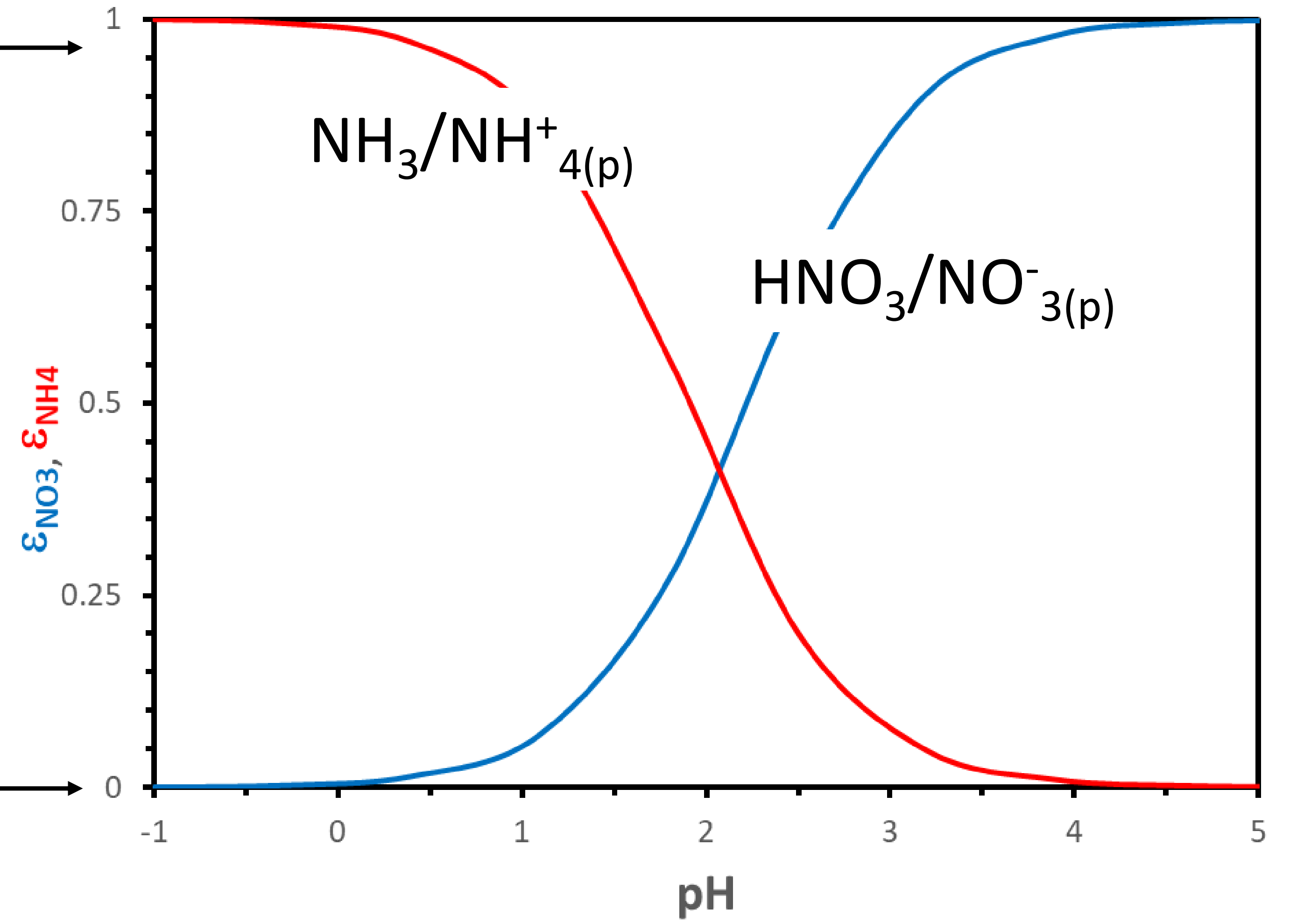
Meskhidze et al., GRL (2003); Guo et al., ACP (2017); Nenes et al., ACP (2020)

Can pH tell us when PM is sensitive to NH_3 & HNO_3 levels?

Yes! Take the "partition" curve for total NH_3 and HNO_3, for a given liquid water content

100% of species in aerosol →

100% of species in gas phase →



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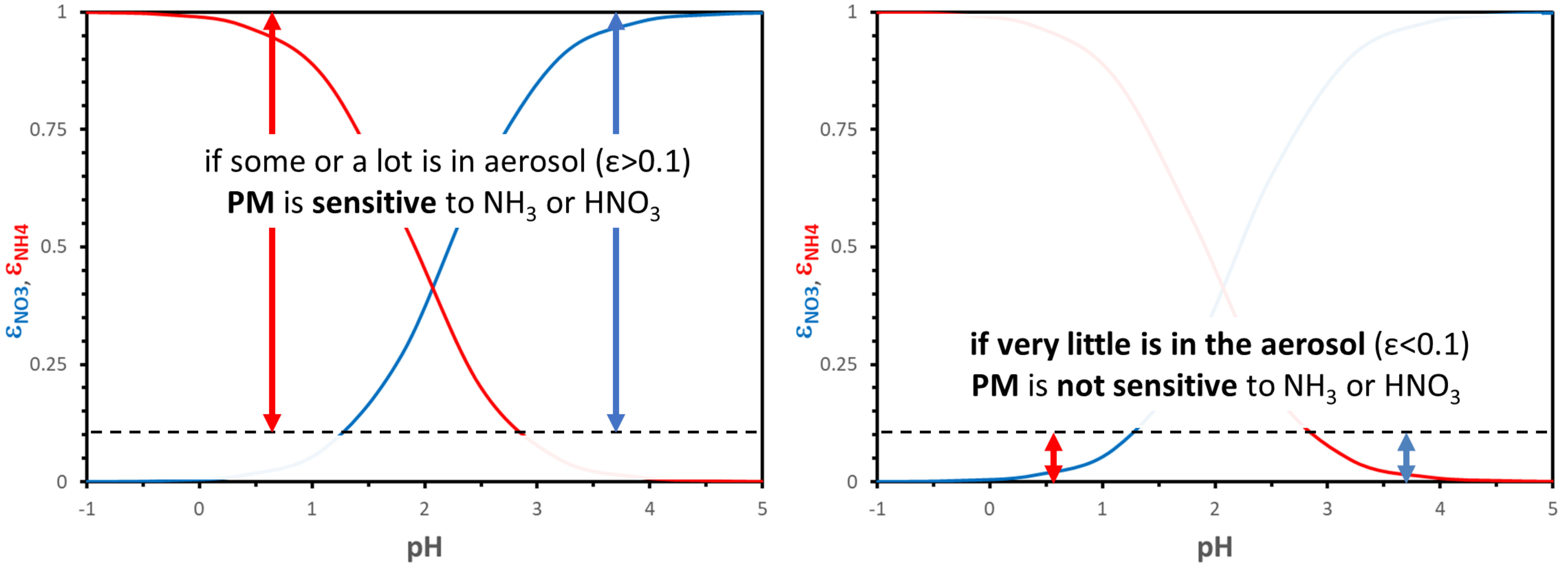

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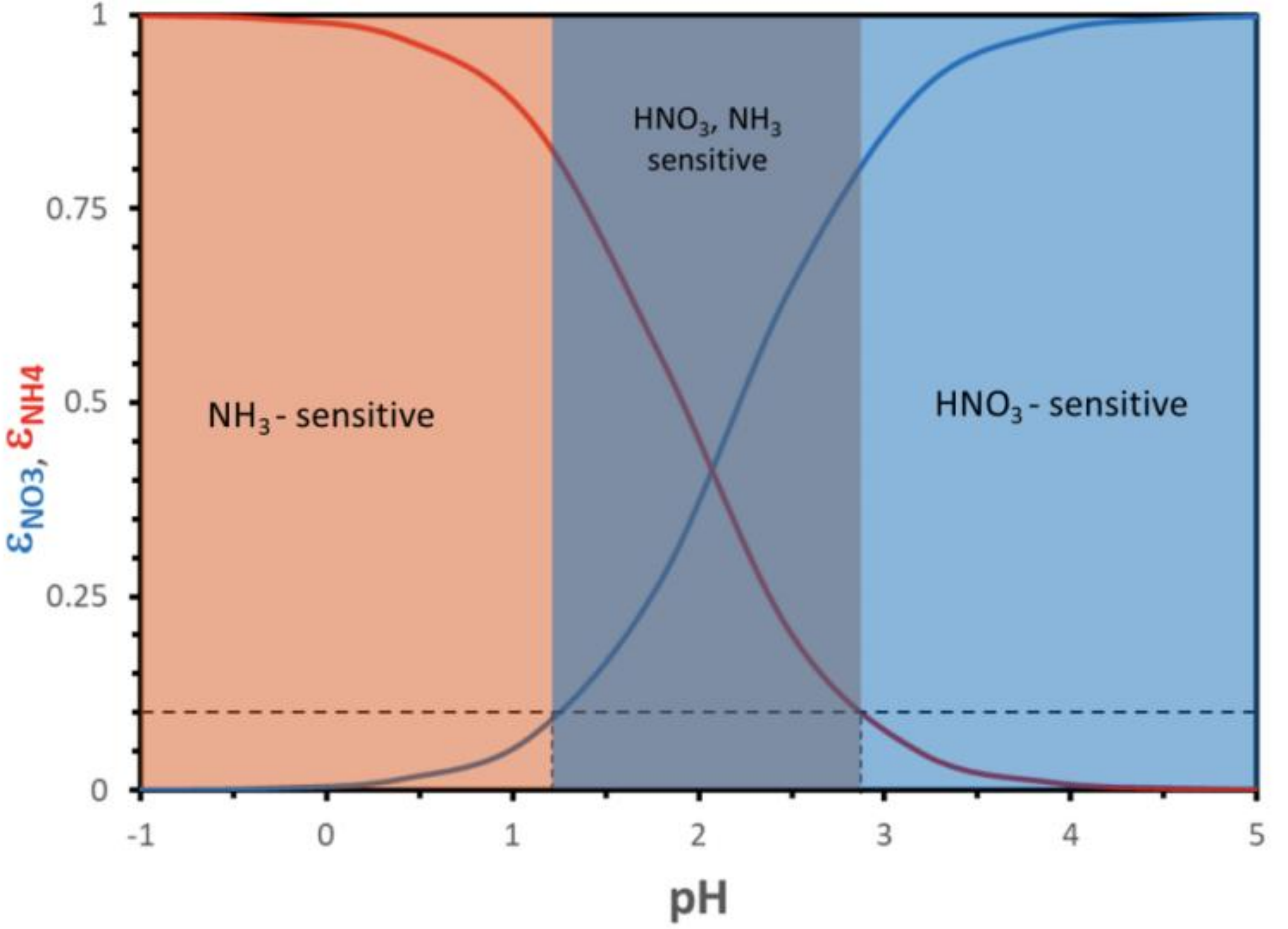
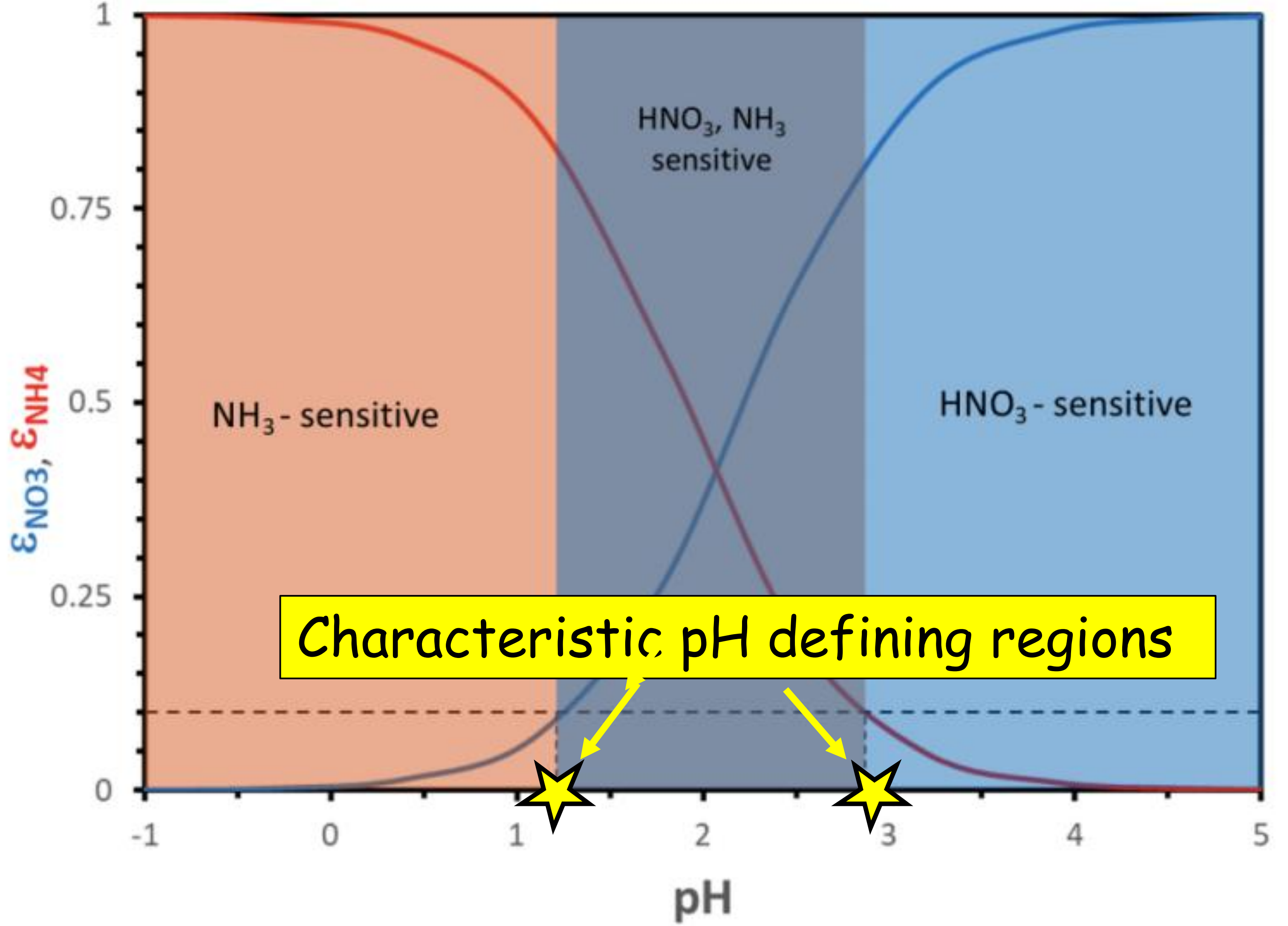
regions of PM sensitivity emerge !



Nenes et al., ACP (2020)

Can pH tell us when PM is sensitive to NH_3 & HNO_3 levels?

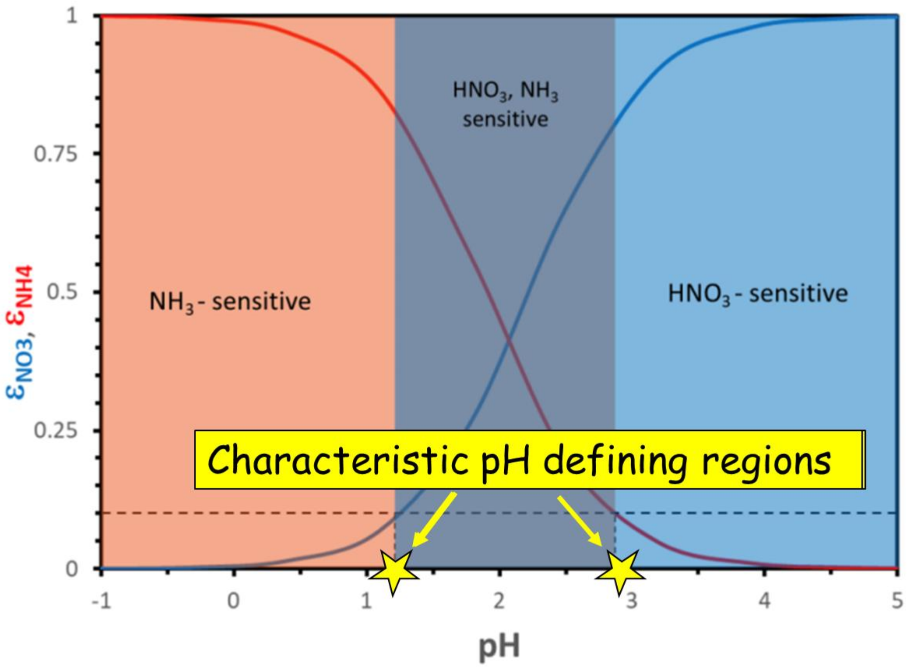
"characteristic" pHs then define regions of PM sensitivity!

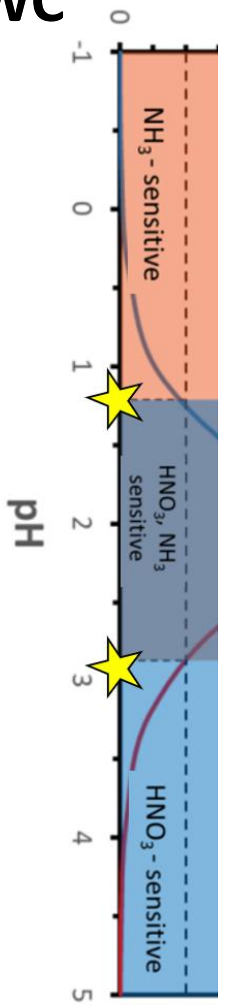


Nenes et al., ACP (2020)

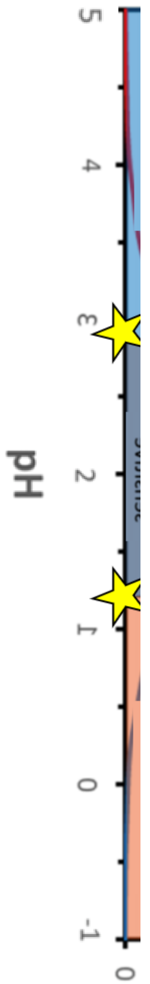
Can pH tell us when PM is sensitive to NH_3 & HNO_3 levels?

Use the two "characteristic" pHs to define the sensitivity regions generalize for all LWC





LWC=10



LWC=10

Nenes et al., ACP (2020)

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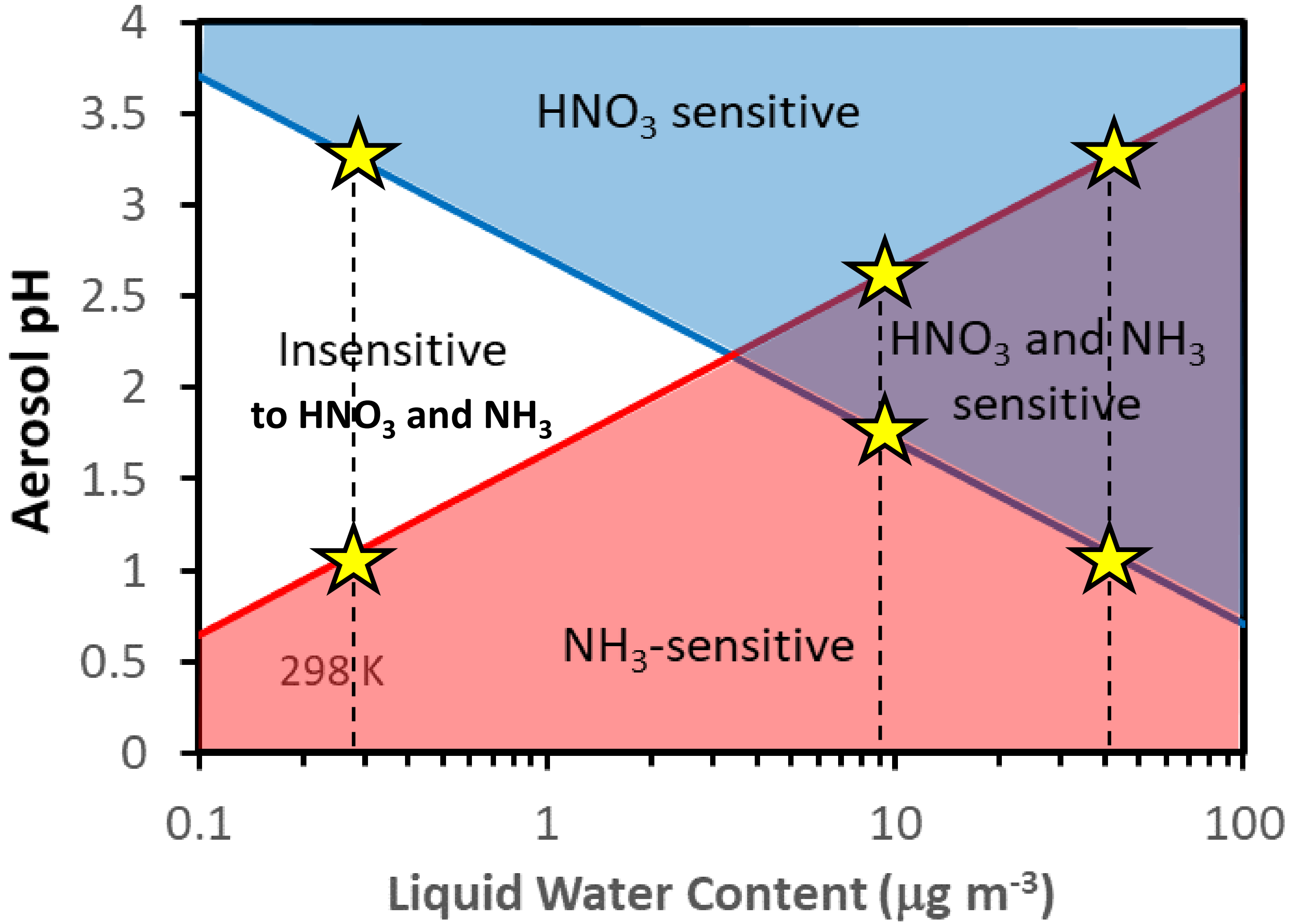
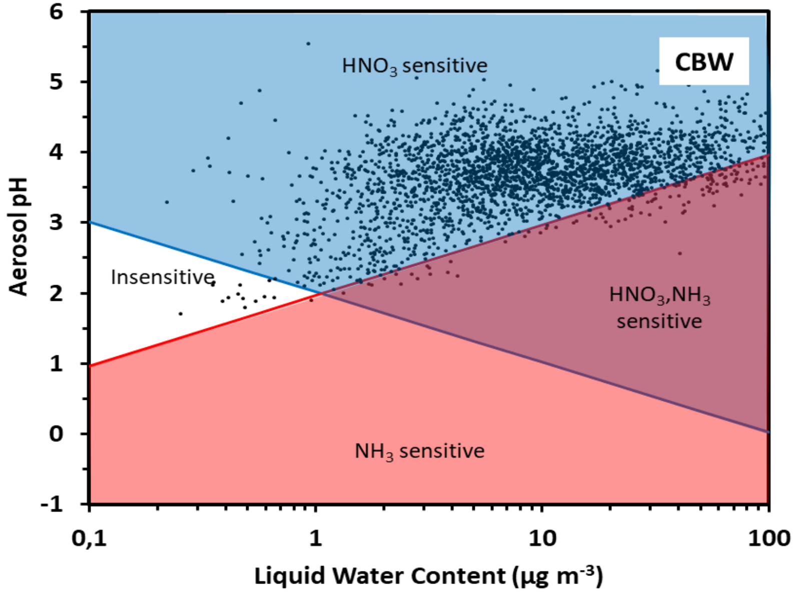


From measurements + thermodynamic model we can determine the sensitivity regimes!

Then determine PM policy for our region

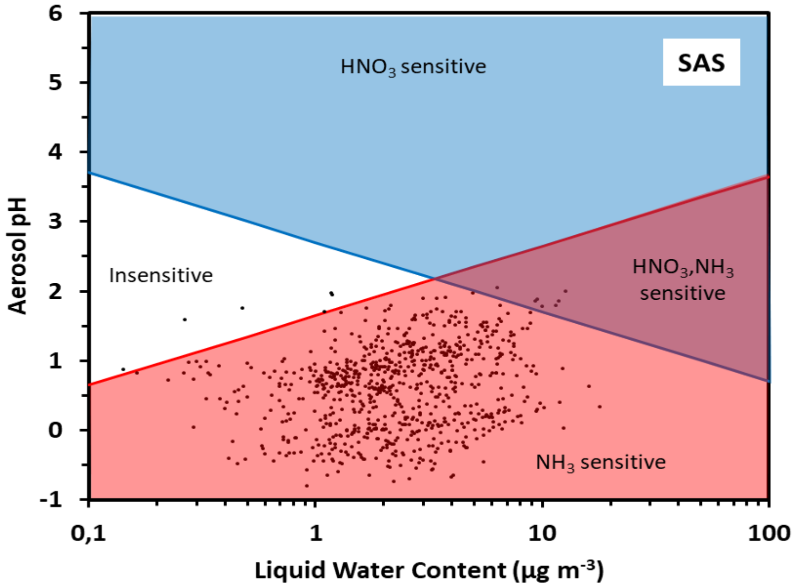
Nenes et al., ACP (2020)

Application of framework to AQ network data



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.



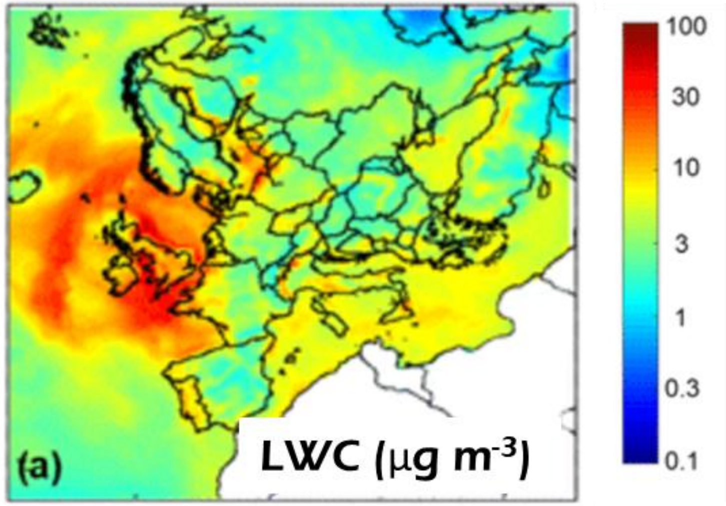
Southeast United States (06/13-07/13):

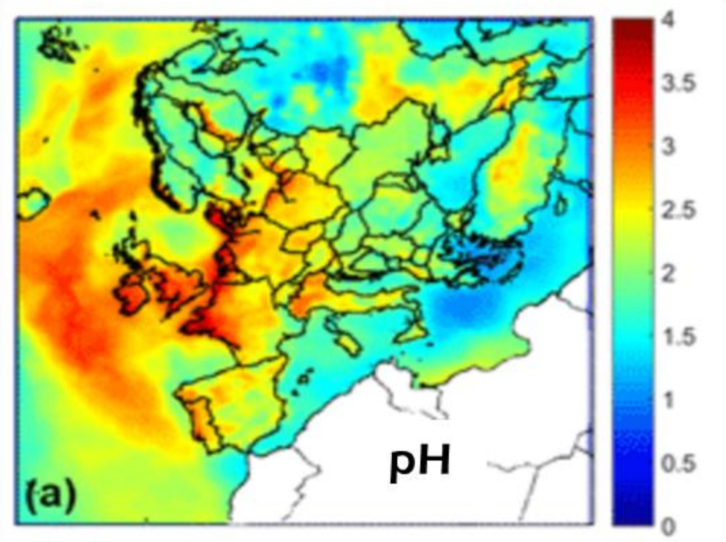
- Aerosol is in the **NH_3-sensitive** regime.
- NH_3 (and SO_4) reduction policies ***efficient*** for PM reduction.
- NO_3 reduction policies ***not efficient*** for PM reduction.

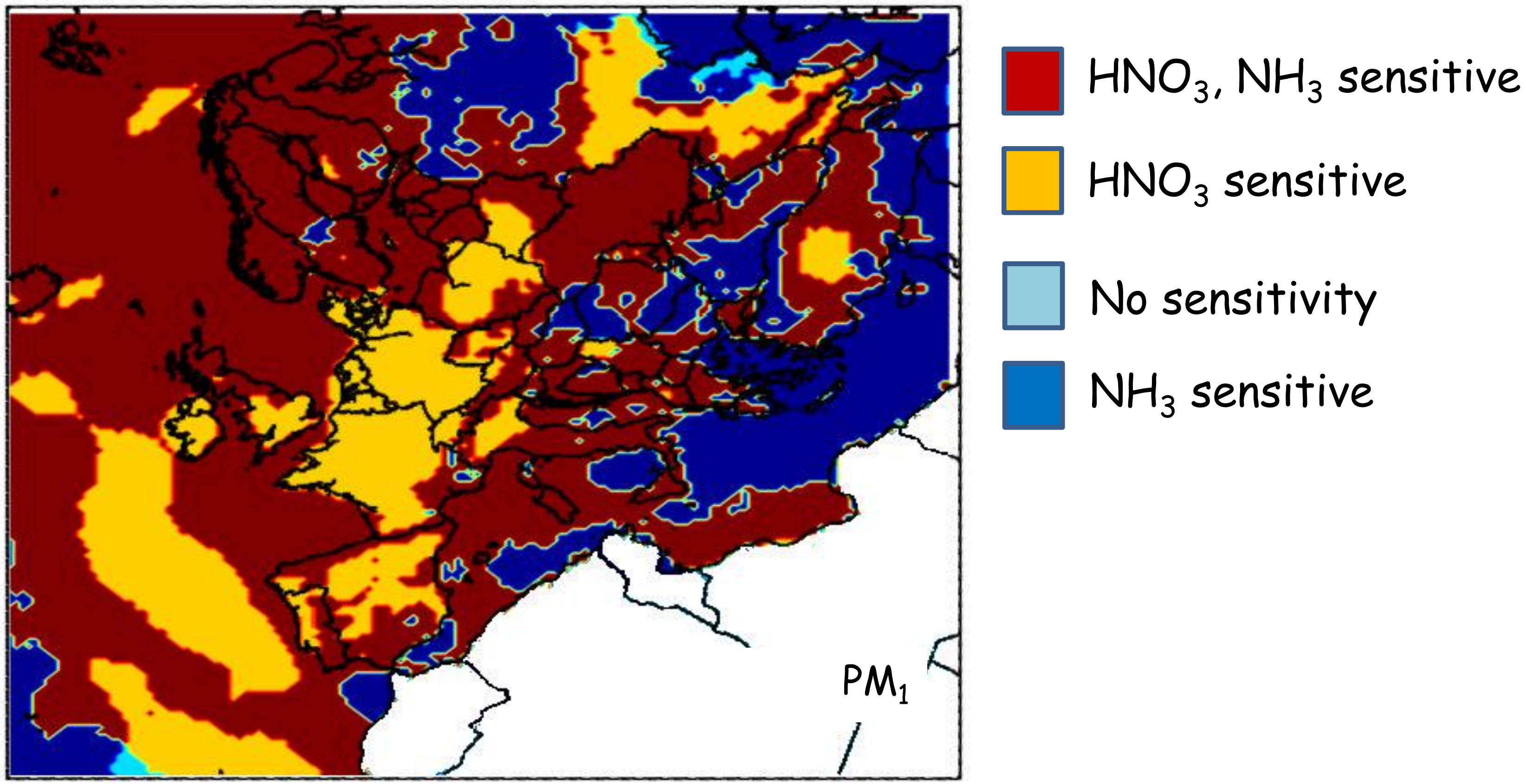
Nenes et al., ACP (2020)

Application to Air Quality simulations

PM-CAMx simulations (May 2008) from Kakavas et al., 2021







East: you become NH_3 sensitive
West: you become NH_3/HNO_3 and HNO_3 sensitive!

Because of its effect on partitioning, acidity impacts even dry nitrogen deposition and the nitrogen cycle!

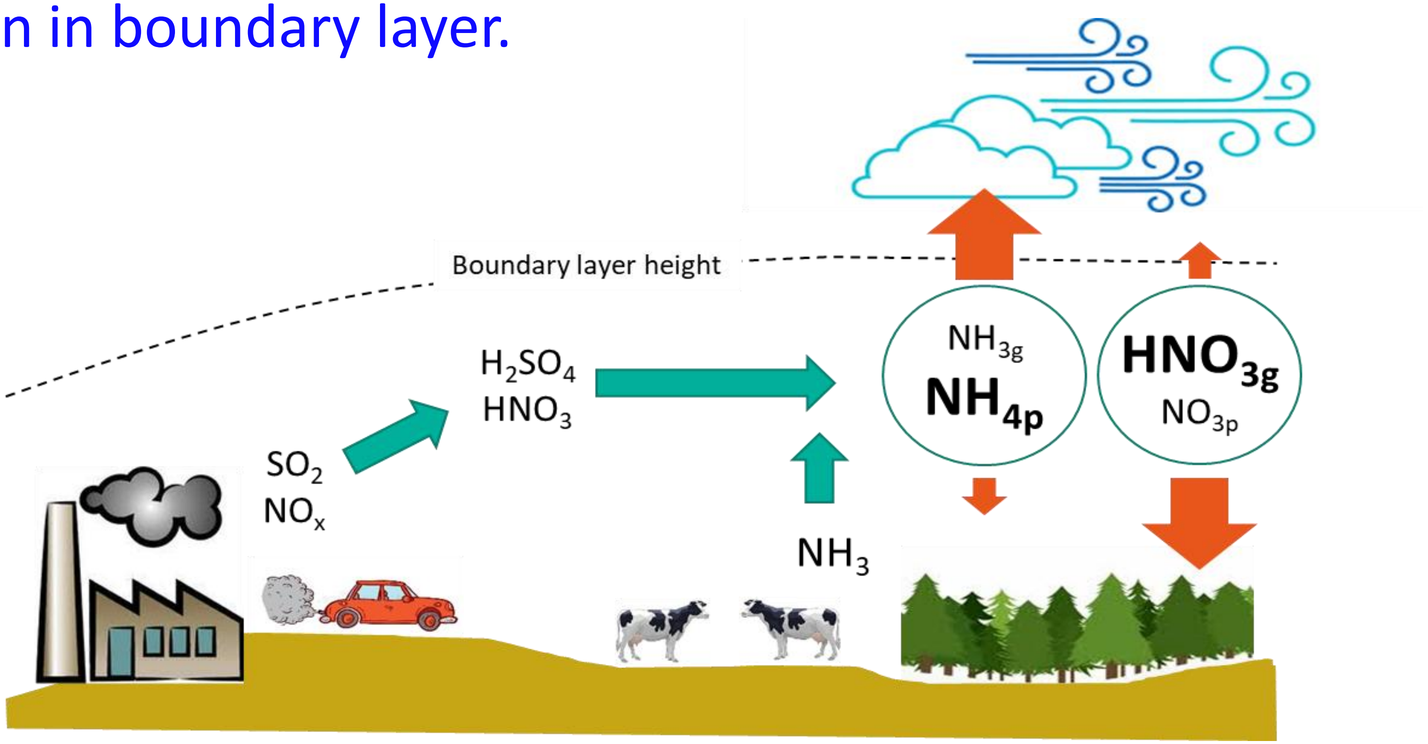
The nitrogen cycle is:

- Dominated by the inorganic reduced (NH_4/NH_3) and oxidized (NO_3/HNO_3) compounds.
- Dry deposition velocity of N species varies *dramatically* if in aerosol or gas form (~10 times).
- Dry deposition controls ***lifetime*** and ***deposition pattern*** of N if there is no wet deposition!
- Lifetime determines concentration in boundary layer.

Realization:

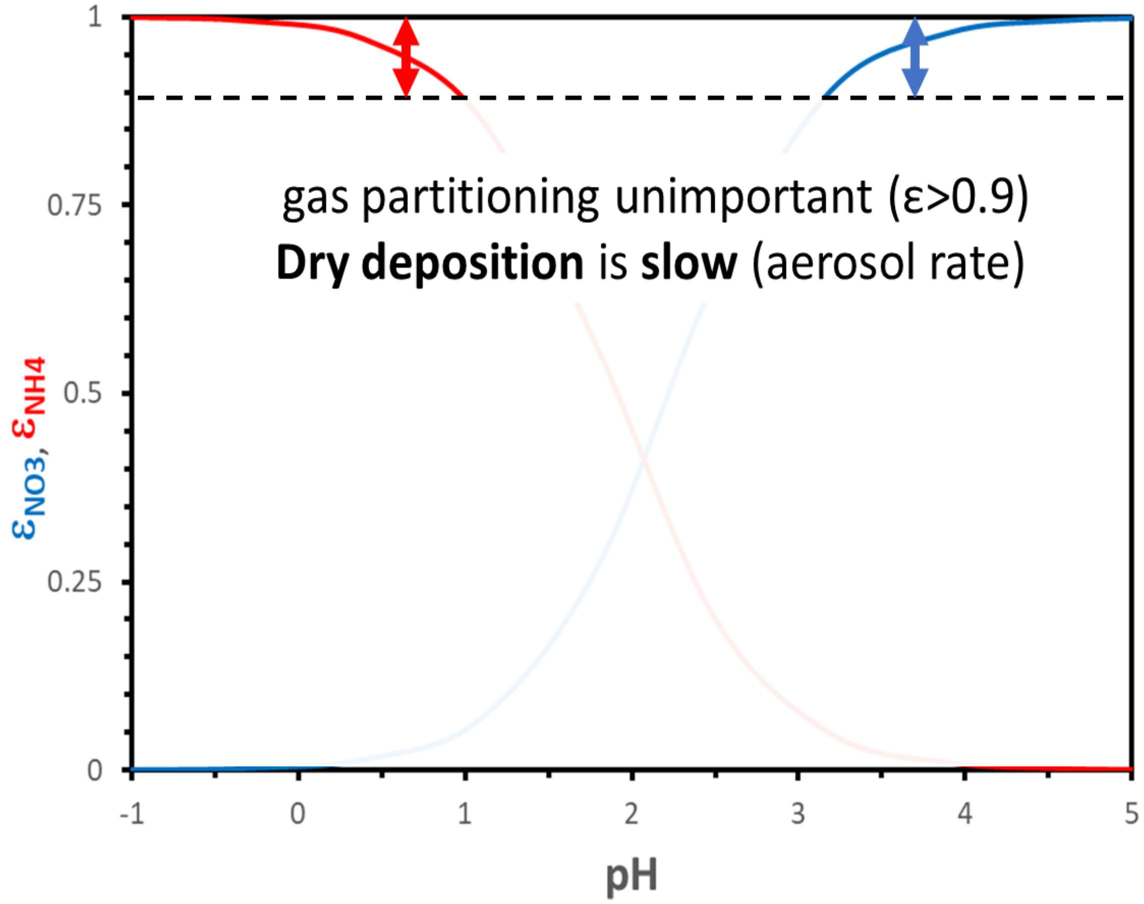
- Acidity affects all the above!

Nenes et al., ACP (2021)

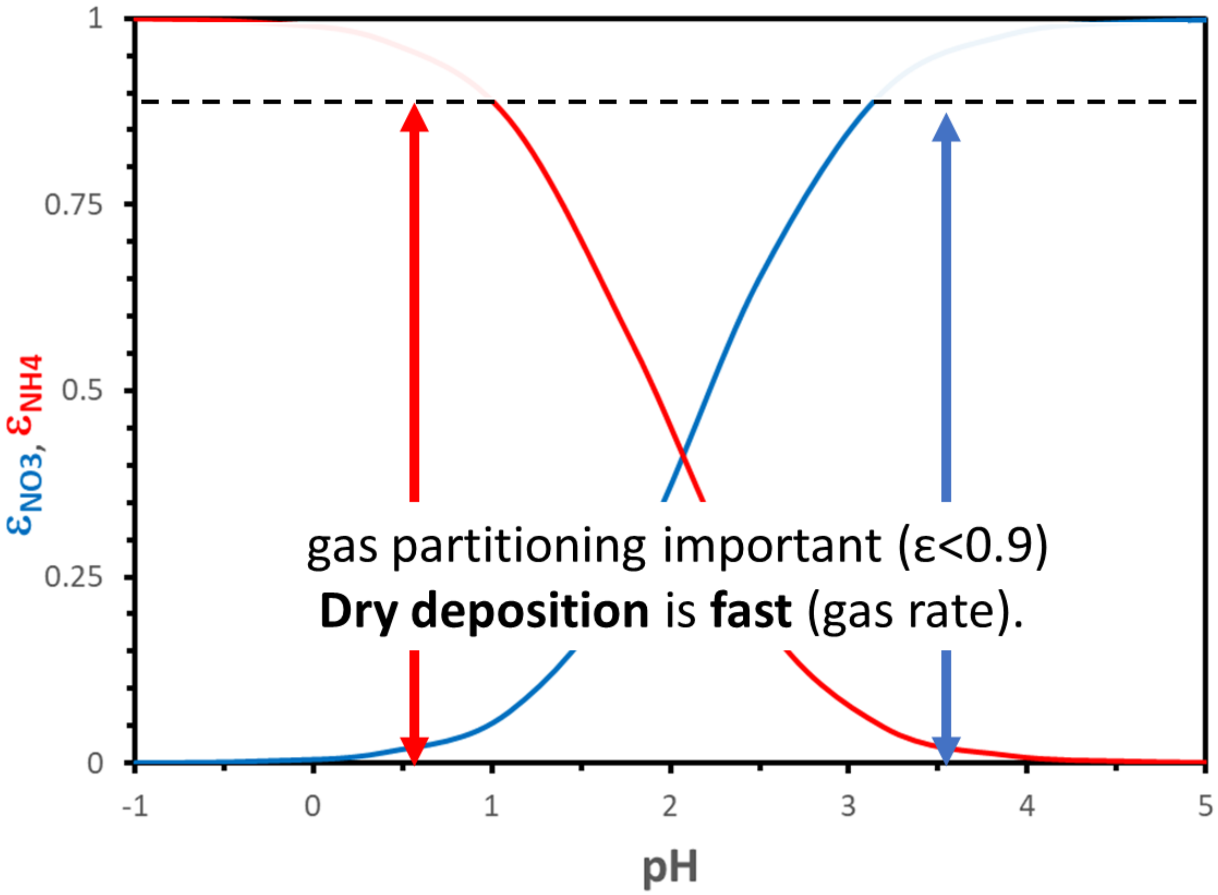


pH affects atmospheric deposition of nitrogen

N in aerosol? It deposits *slowly*

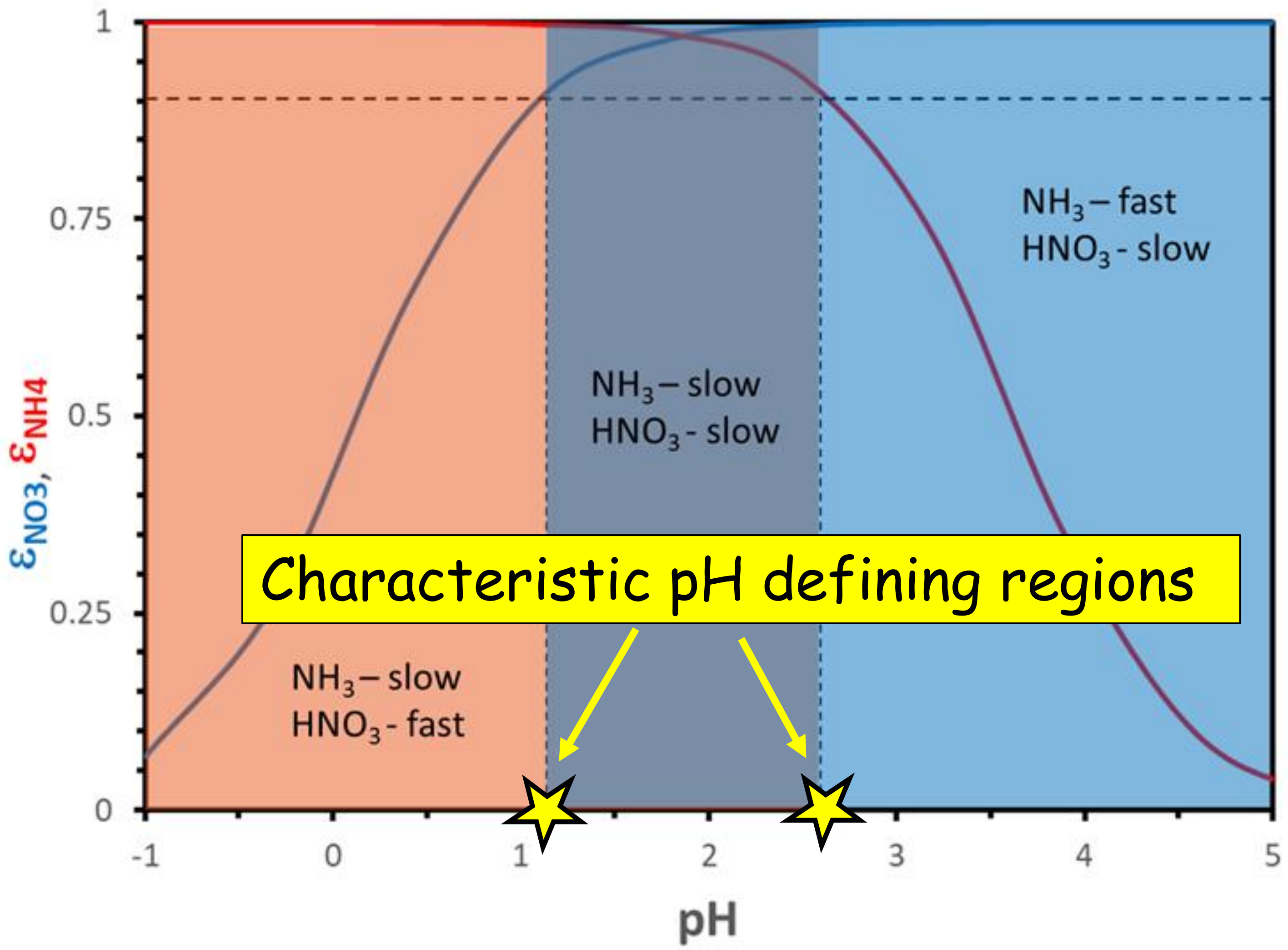


N in gas? It deposits *quickly*



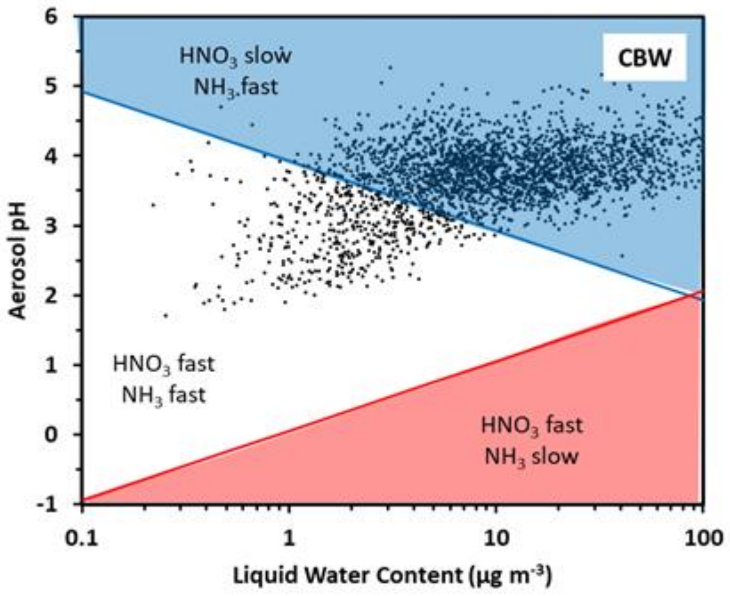
Deposition determines how far emissions travel to affect ecosystems

pH affects atmospheric deposition of nitrogen



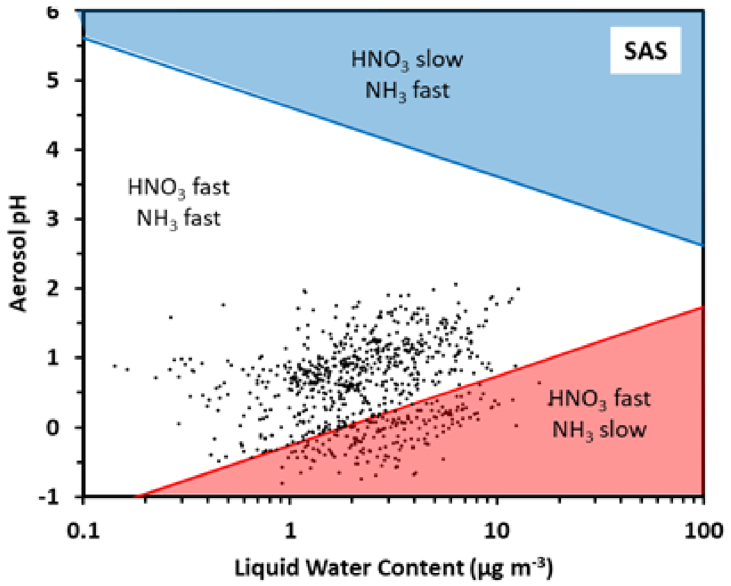
Nenes et al., ACP (2021)

Deposition regime maps: effects of pH and aerosol water



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., *ACP* (2021)

ReCLEAN

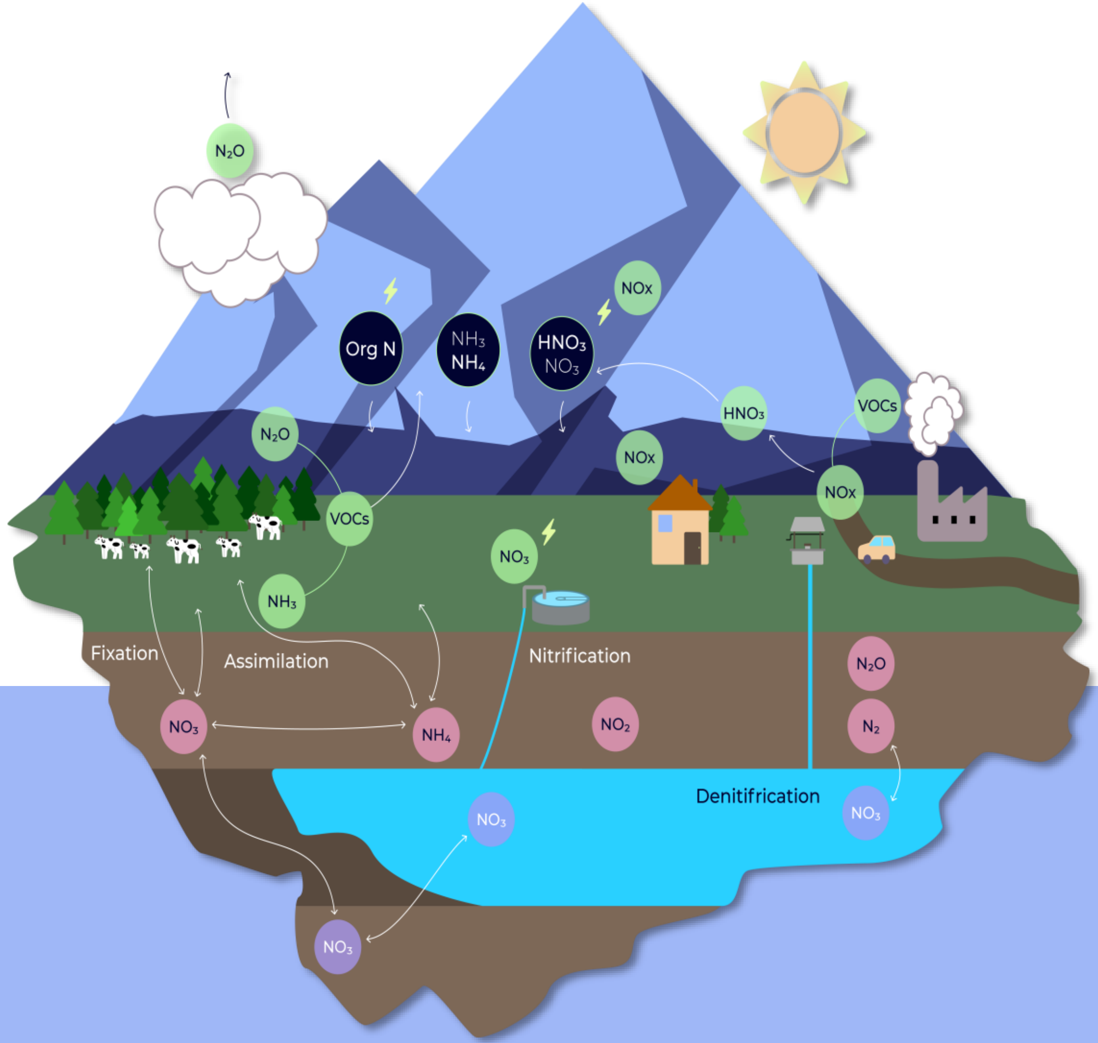
ETH BOARD EPFL PSI ETH zürich WSL eawag aquatic research

ETH Domain Joint Initiative:

Reactive nitrogen at the **CL**imate, **E**nergy, **A**griculture, water and health **N**exus

Main aims :

- Understand & quantify N fluxes across and within compartments.
- Assessing the impact of the energy transition and climate change on Switzerland's nitrogen cycle.

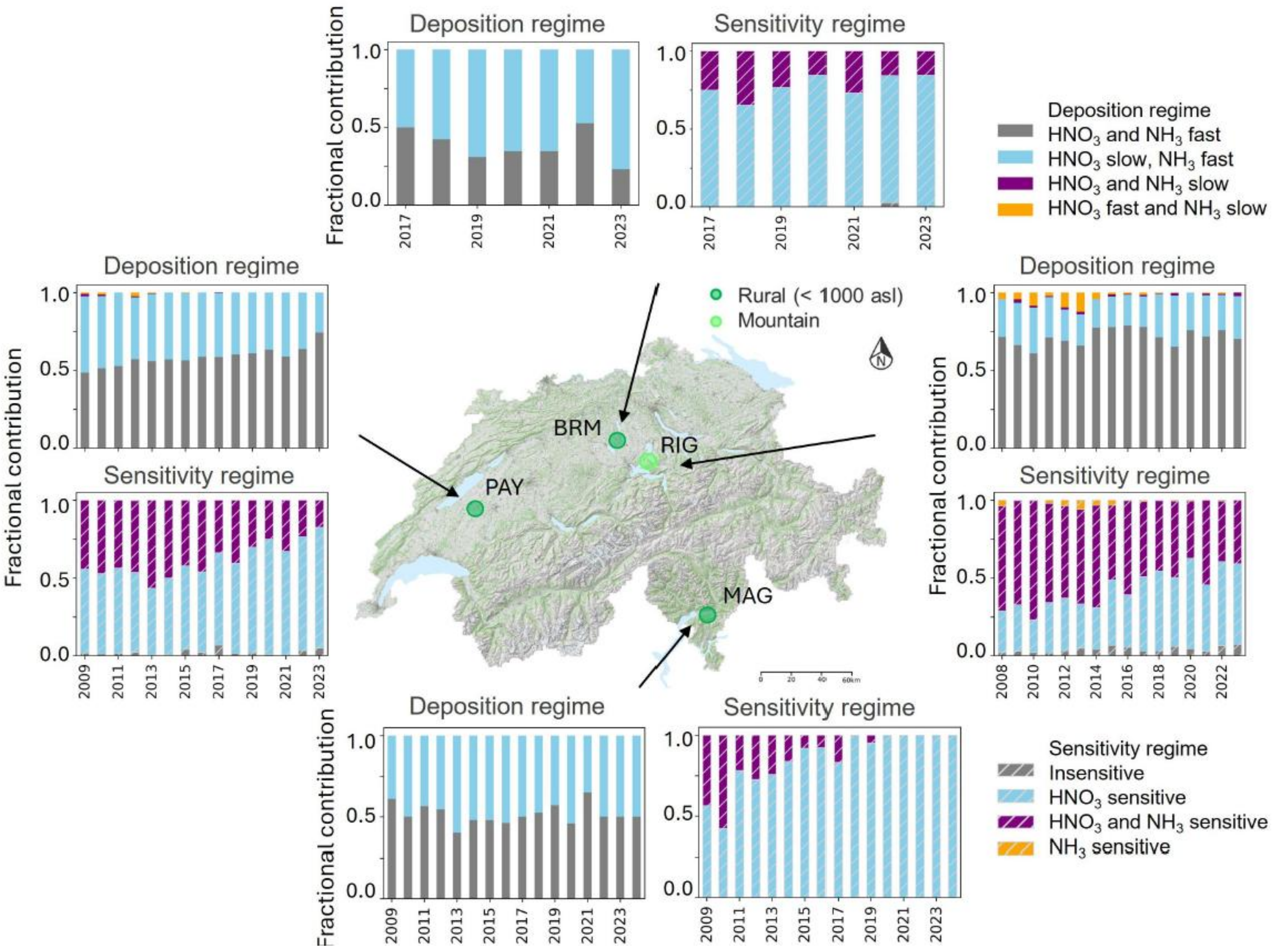


Website
http://reclean.epfl.ch

LinkedIn
@ReCLEAN

Newsletter

N deposition & sensitivity regimes for Switzerland



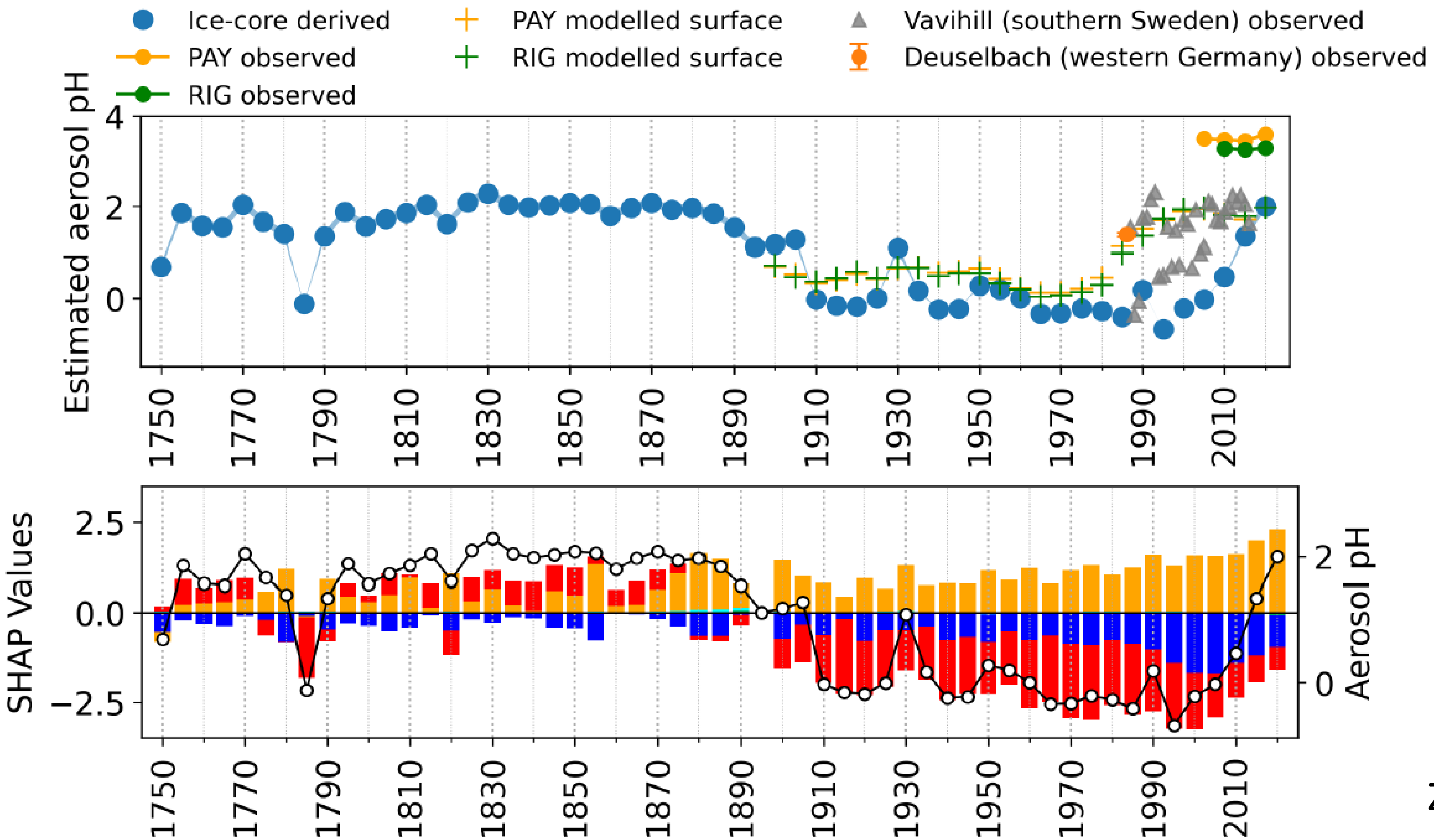
NH_3 deposition mostly fast, suggesting emissions redeposit near sources;

PM sensitivity to HNO_3 is increasing, indicating NO_x reduction would be an effective strategy for mitigating PM levels in Switzerland.

Zhang et al., in press

Swiss ice core analysis

ReCLEAN



Zhang et al., in prep

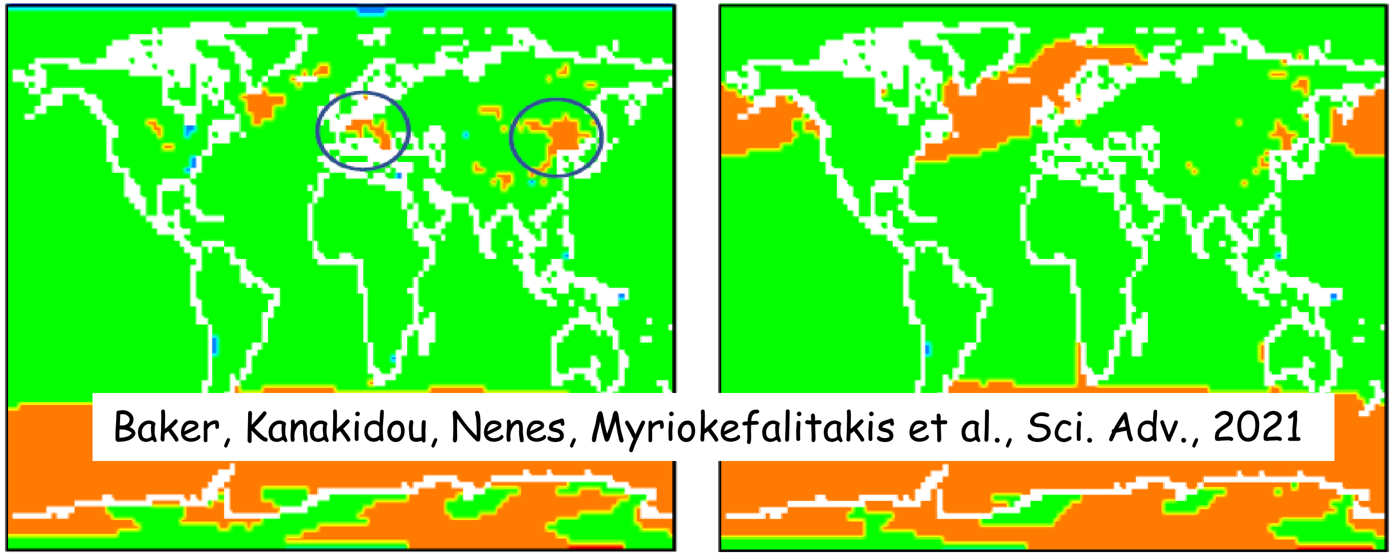
1750–1895 (Natural emissions): Stable aerosol pH (~2); volcanic perturbations; SO_4^{2-} and NO_3^T effects largely offset by NH_3^T.

1900–1990 (Anthropogenic sulfur emissions): Rapid acidification driven by increasing SO_4^{2-} and NO_3^T; NH_3^T insufficience.

1995–2020 (European emission controls): Rapid pH recovery driven by declining SO_4^{2-} and sustained agricultural NH_3 emissions .

Impacts of changing acidity on N deposition

Deposition – 2010 (fine mode)   Deposition – 2100 (fine mode)



Green: nitrate deposits *rapidly* & *does not accumulate*

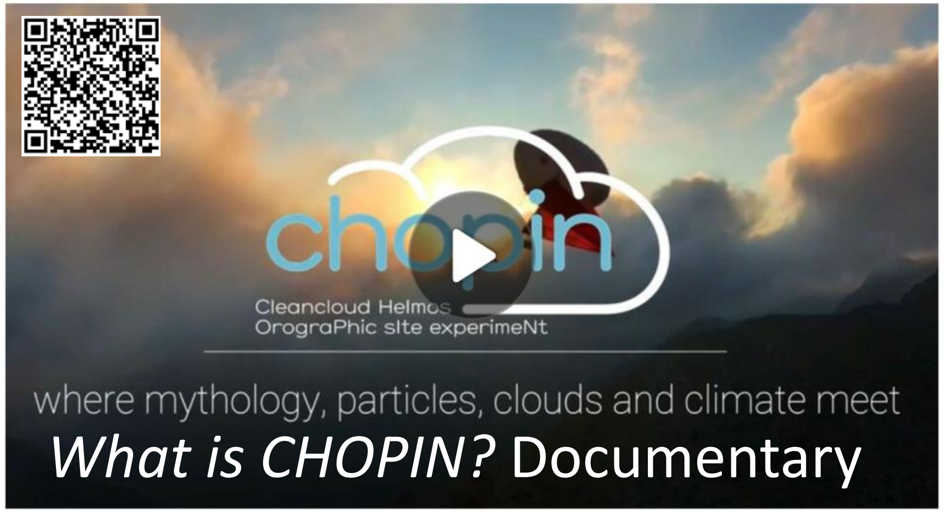
Orange: nitrate deposits *slowly* & *accumulates. Transports across borders*

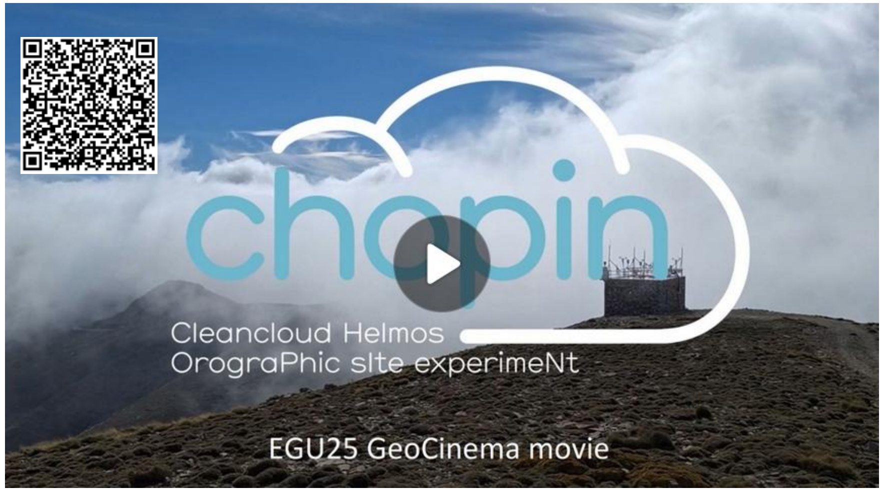
- “Current day” aerosol pH, liquid water favor accumulation of nitrate in Europe and Asia – and increase levels by up to 10x.
- Important for nutrient delivery and radiative forcing.
- Future patterns change drastically - Getting pH right is important!

Some final take-home messages

- As pollution levels change and natural emissions respond to climate change (usually they go up) we need to understand the sources, emissions and impacts.
- Aerosol acidity profoundly impacts processes that relate to aerosol effects on health, climate and marine/terrestrial ecosystems.
- Acidification of dust (mineral, mining, road) has profound impacts on its health effects.
- Aerosol pH determines its “sensitivity regime” to pollution levels. Slow deposition of nitrate **may cause the rapid increase and high concentration of nitrate in many regions of the globe.**
- Regions change acidity and deposition regime over time in with important implications ecosystems. Many regions of the globe need to determined aerosol pH so robust policies and impacts can be understood.
- Acidity impacts on cloud-forming particles, indoor viruses (not shown)....

Check out all the cool outreach videos @ LAPI Channel





https://mediaspace.epfl.ch/channel/LAPI+video+channel

THANK YOU!
Merci! Danke!
Ευχαριστώ!

Special thanks to all the funding sources, countless group members and collaborators that are just too many to show and name here.

I am always grateful to my family and friends.