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Cloud water pH and Sulphate aerosols

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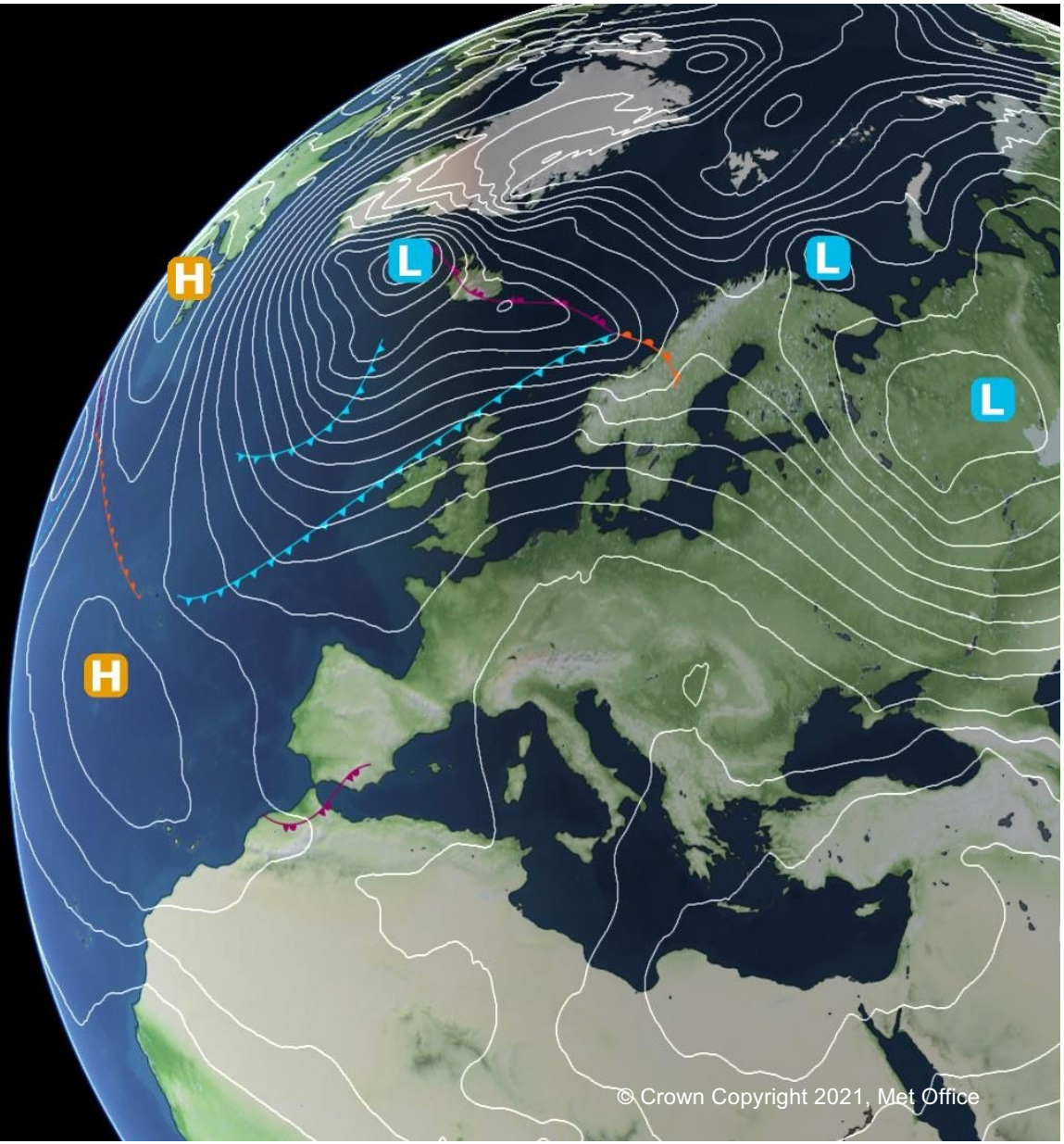
UKESM/UKCA Science advances Workshop

26/03/2021



Why is it important?

- Sulphate aerosol is primarily formed from the oxidation of SO_2 in the atmosphere (S(IV) to S(VI)) from anthropogenic and natural (e.g. Volcanoes, DMS) sources
- Oxidation can occur in the **gas phase** via reaction with OH

Overall $SO_2 + OH + M \rightarrow H_2SO_4 + M$ H_2SO_4 vapour can lead to particle formation

- SO_2 also dissolves in water and oxidation can also occur in the **aqueous phase** via reaction with H_2O_2 and O_3

H_2O_2 $HSO_3^- + H_2O_2 + H^+ \rightarrow 2H^+ + SO_4^{2-} + H_2O$ **pH independent**

O_3 $HSO_3^- + O_3(aq) \rightarrow SO_4^-(+ H^+ + O_2)$

O_3 $SO_3^{2-} + O_3(aq) \rightarrow SO_4^{2-}(+O_2)$

Reactions with O_3 are highly sensitive to pH

Globally, Gas-phase accounts for **15-35%** of tropospheric sulphate formation whereas **aqueous phase 60-80%** so an important pathway to consider

The problem is UKCA uses a fixed global value for cloud water pH of 5

- pH also important in calculating the amount of SO_2 dissolved for reactions and wet deposition

Why is this a Problem?

pH is important for reaction rates

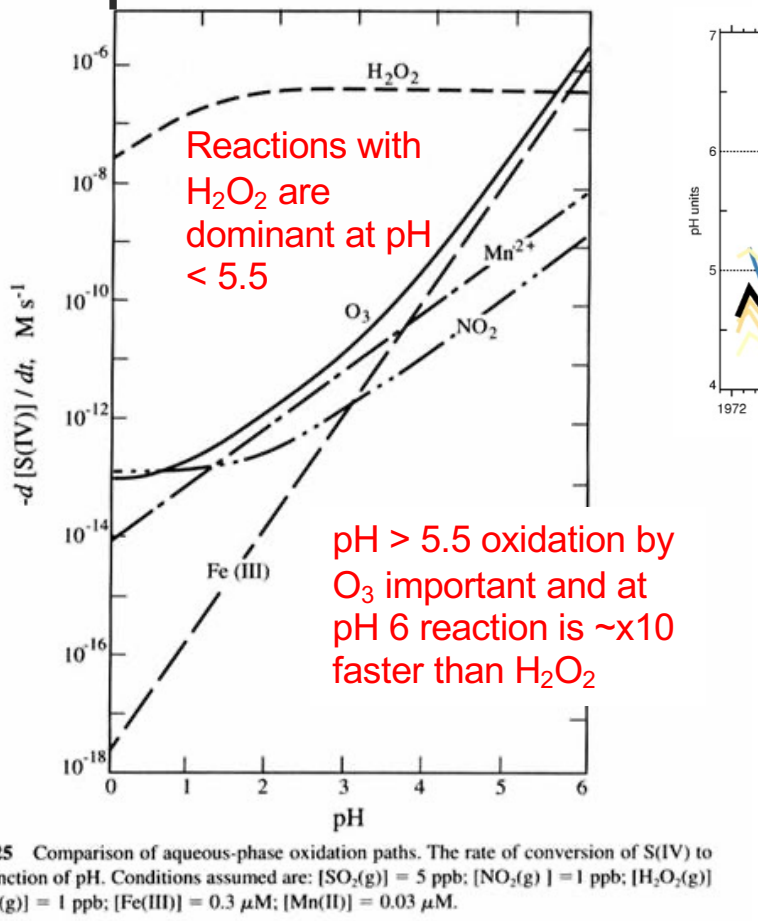
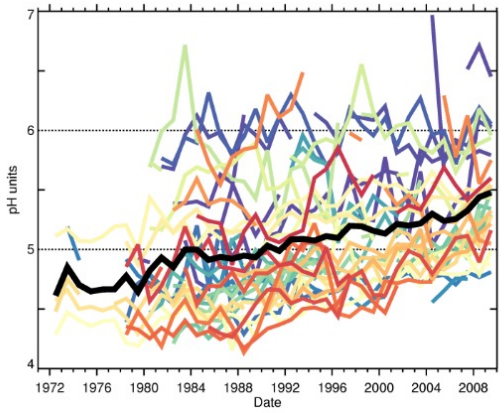


FIGURE 6.25 Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are: $[SO_2(g)] = 5$ ppb; $[NO_2(g)] = 1$ ppb; $[H_2O_2(g)] = 1$ ppb; $[O_3(g)] = 1$ ppb; [Fe(III)] = 0.3 μM; [Mn(II)] = 0.03 μM.

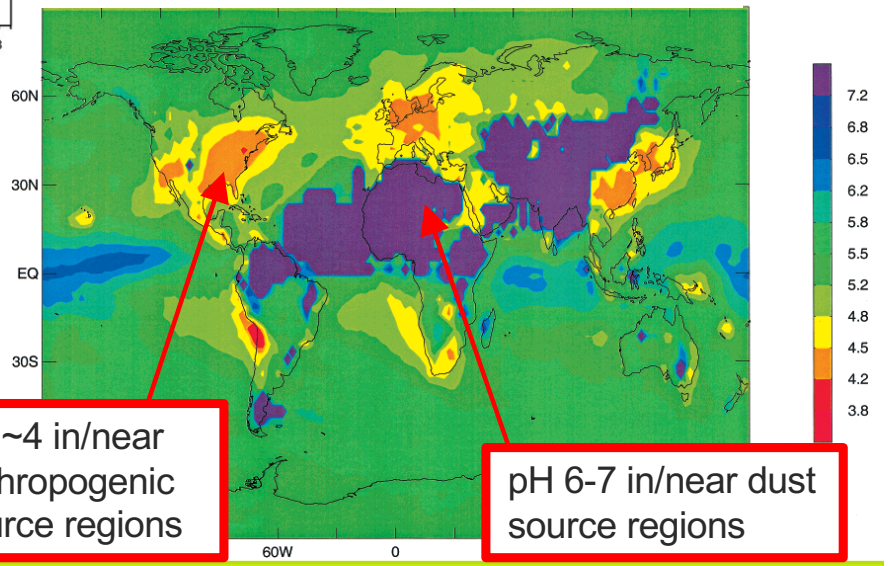
Seinfeld and Pandis, 2006

pH is both spatially and temporally variable



Changes to European Rainwater pH already observed, ~↑1 pH unit since 1980

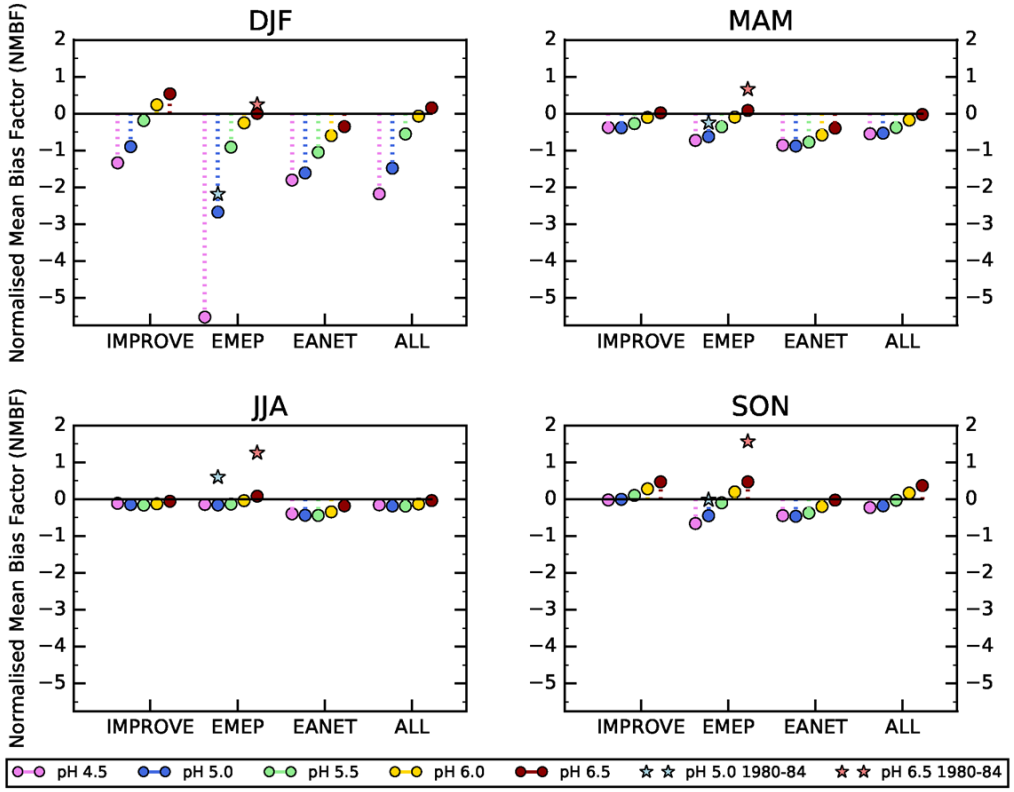
Spatial variability in rainwater pH



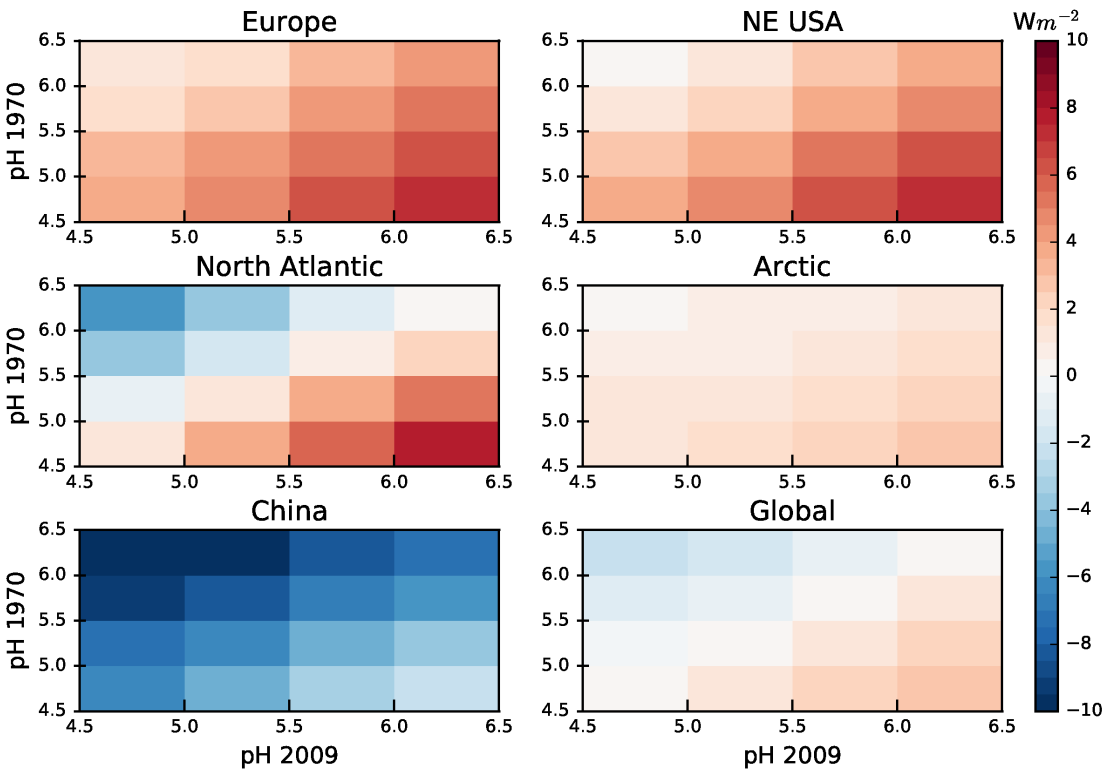
Reproduced from Rodhe et al., 2002 – Global distribution of pH in rainwater from model

Previous Results

Surface SO4 bias affected by pH



Recent Aerosol Radiative Forcing affected by pH



Turnock et al., (2019) GRL – The Impact of Cloud Water pH on Aerosol Radiative Forcing (10.1029/2019GL082067)

Initial development

- A new development branch implemented previous approach that was in GLOMAP to change pH based on SO_2 concentrations (representative of polluted and non-polluted conditions)

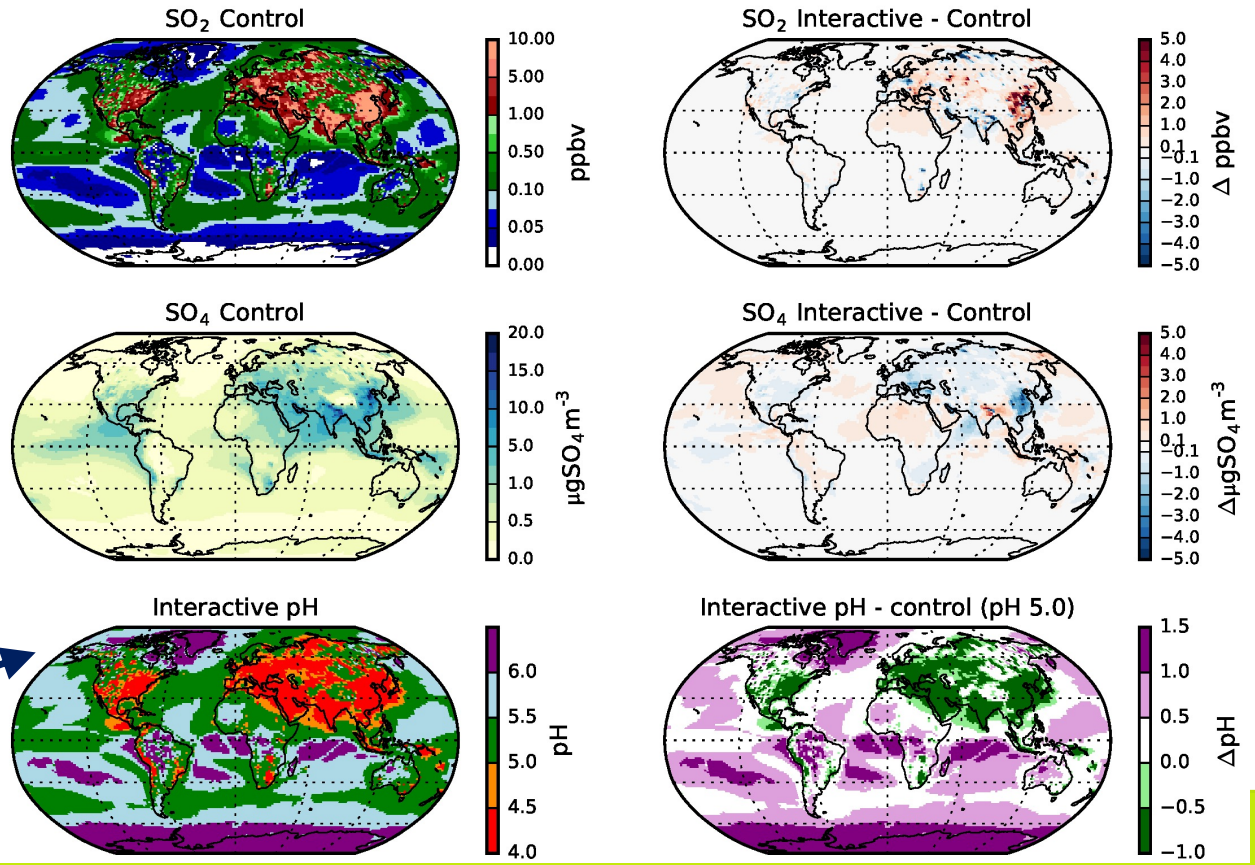
if [SO2(lat,lon)] < 0.05 ppb then pH = 6.0

if [SO2(lat,lon)] > 0.05 ppb and < 0.1 ppb then pH = 5.5

if [SO2(lat,lon)] > 0.1 ppb and < 0.5 ppb then pH = 5.0

if [SO2(lat,lon)] > 0.5 ppb and < 1.0 ppb then pH = 4.5

if [SO2(lat,lon)] > 1.0 ppb then pH = 4.0



Initial results encouraging but need more testing/development

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Future Work

- Look into development branch further:
  - potential of impact of changes in pH on SO_2 and SO_4
  - are appropriate values are being used to set cloud water pH based on SO_2

- Look into developing a more sophisticated approach to calculating acidity/pH based on acid-base balance of SO_2, CO_2, NH_3 concentrations to improve spatial and temporal representation of pH

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Additional Slides

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- Oxidation can occur in the **gas phase** via reaction with OH

$$SO_2 + OH + M \rightarrow HOSO_2 \cdot + M$$

$$HOSO_2 \cdot + M \rightarrow HO_2 \cdot + SO_3$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$$ H_2SO_4 vapour can lead to particle formation

- SO_2 also dissolves in water and oxidation can also occur in the **aqueous phase** via reaction with H_2O_2 and O_3

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How does UKCA treat Aqueous Phase Chemistry?

- Uses equilibrium Henry's law approach to calculate dissolution of SO_2 to cloud droplets
- To calculate the rate of sulphate production uses:
  - Uses cloud fraction
  - Cloud liquid water content of 0.0002 kgm^{-3}, typical of stratocumulus cloud)
  - **Fixed cloud water pH of 5**
- Produced sulphate mass is partitioned into soluble accumulation and coarse modes
- pH also important in calculating the amount of SO_2 dissolved for wet deposition