Measurement and modelling concentrations and dry deposition of ammonia: methods and challenges

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and many other colleagues

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OVERVIEW

- Modelling of dry deposition of NH_3
- Measurement of dry deposition of NH_3
- Current NH_3 monitoring in the UK
- Challenges in quantifying NH_3 deposition
- Ammonia as a future fuel: some considerations

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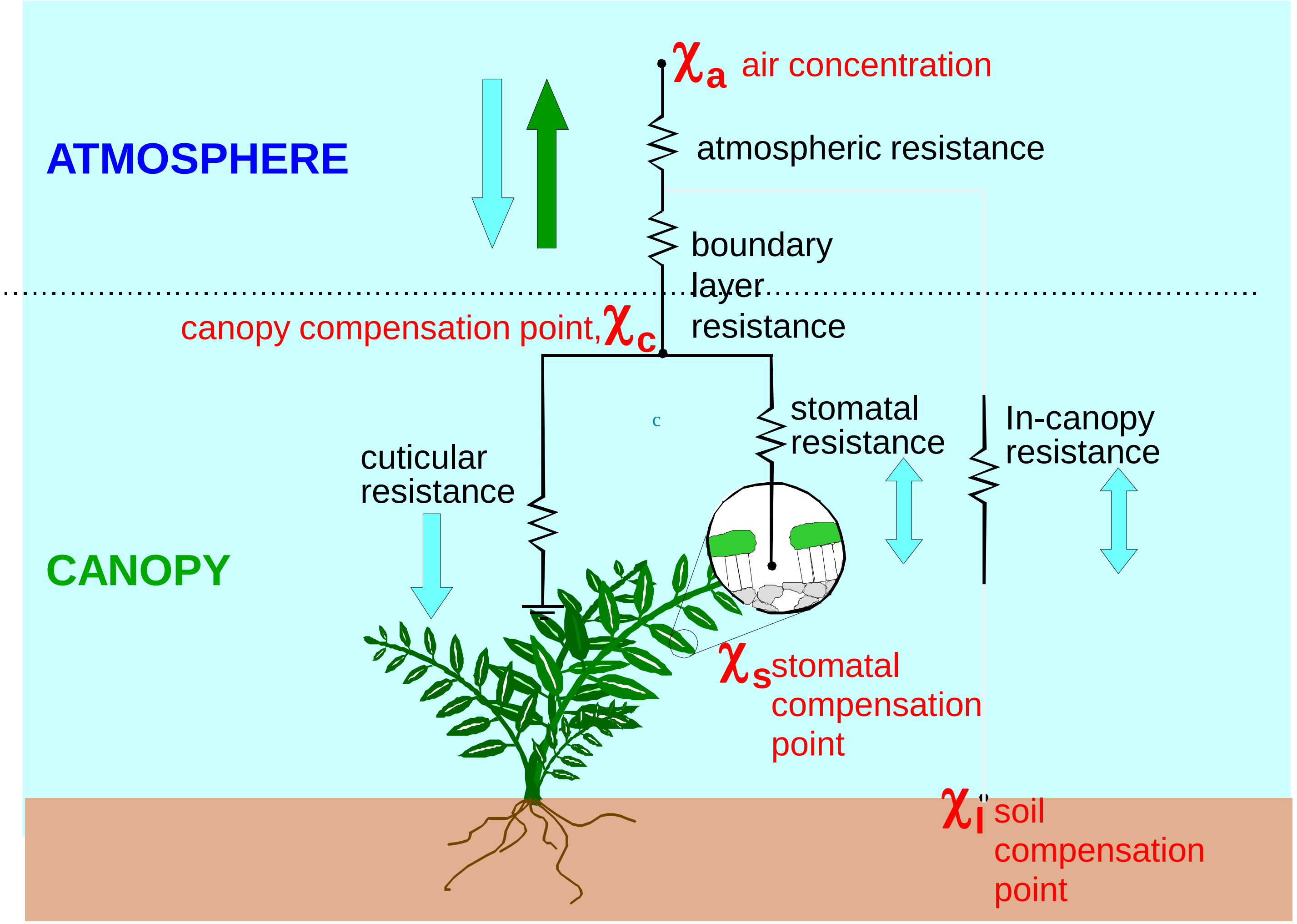
Canopy Compensation Point Model

$$\chi_s = f(T, \Gamma)$$

$$\Gamma = \frac{[NH_4^+]_{apo}}{[H^+]_{apo}}$$



Nemitz, Milford & Sutton (Quart. J. Royal Meteor. Soc. 2000)

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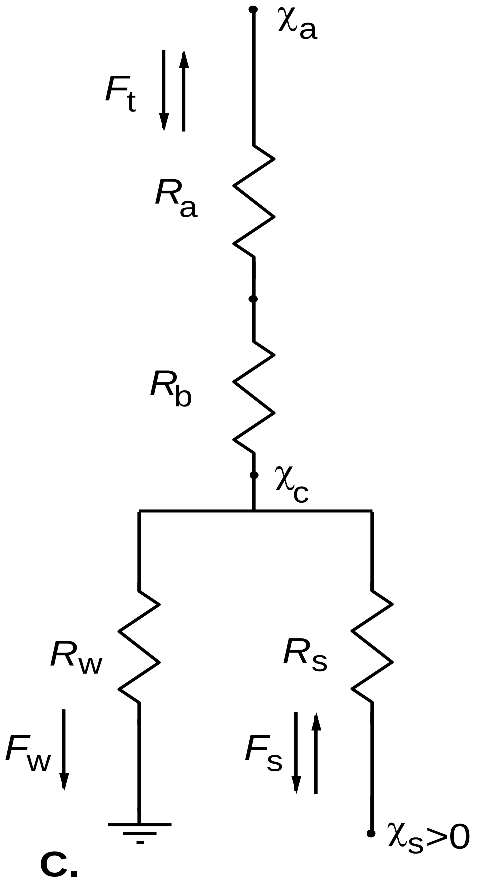
Key Parameters of the Canopy Compensation Point Model



- Atmospheric resistances: easy! from micromet parameters (u_*, U, L, z_0)
- Stomatal resistance R_s: function of radiation (St, PAR), leaf water potential, RH/VPD, temperature
- Cuticular resistance R_w: function of leaf wetness (RH, VPD, leaf wetness measurement), leaf water composition (pH), temperature?, LAI?
- Dimensionless stomatal emission potential Γ_s = $[NH_4^+]/[H^+]$; function of N status, plant type

$$\chi_s = NH_{3(g)} = \frac{161500}{T}\exp\left(-10{,}378\ T^{-1}\right)\frac{[NH_4^+]}{[H^+]} = \frac{161500}{T}\exp\left(-10{,}378\ T^{-1}\right)\Gamma_s$$

$$F_t = -\frac{\chi_a - \chi_c}{R_a(z-d) + R_b}$$

$$\chi_c = \frac{\chi_a (R_a(z-d) + R_b)^{-1} + \chi_s R_s^{-1}}{(R_a(z-d) + R_b)^{-1} + R_s^{-1} + R_w^{-1}}$$

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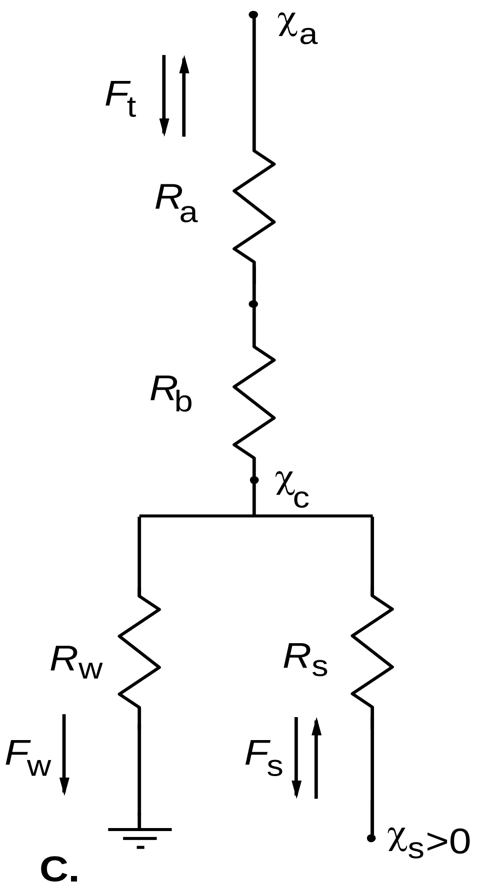

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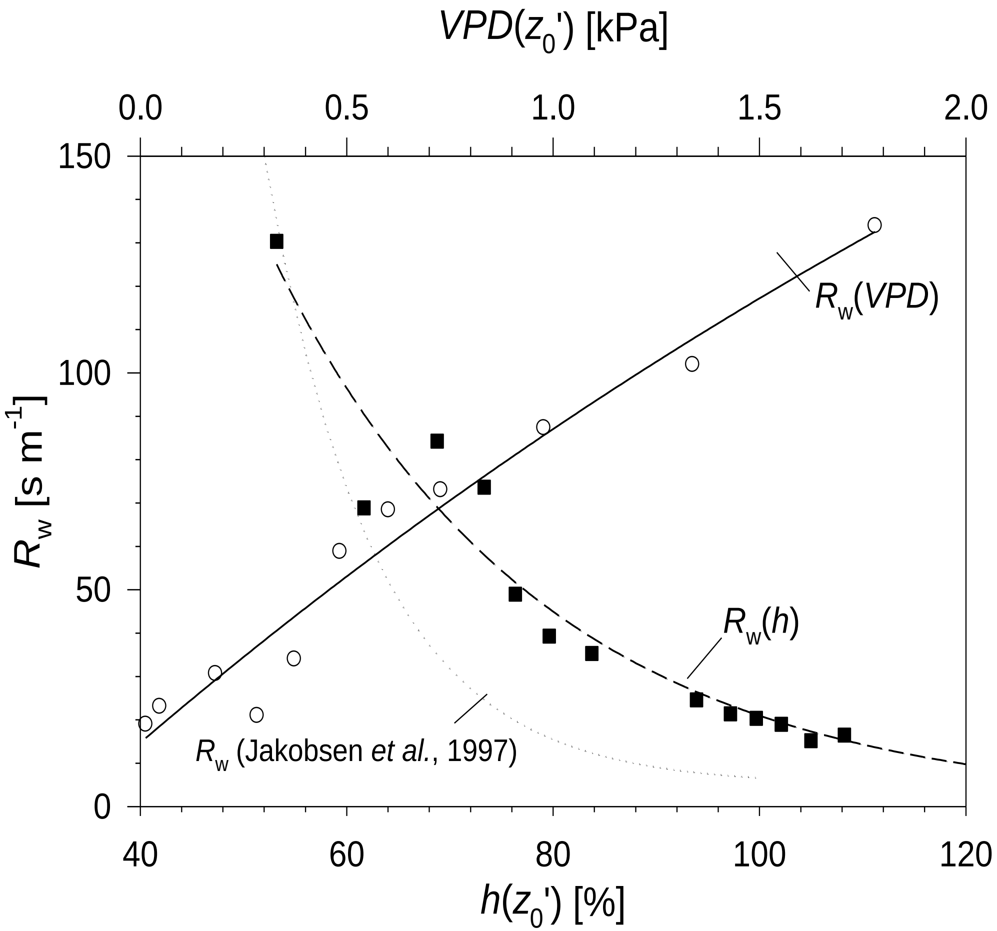
Determination of Cuticular Resistance (R_w)

- Derived as during dark (stomata closed) and windy conditions (e.g. $R_a + R_b < 200$ s m^{-1})

$$\boldsymbol{R_c = \chi_a / F_t - R_a - R_b}$$

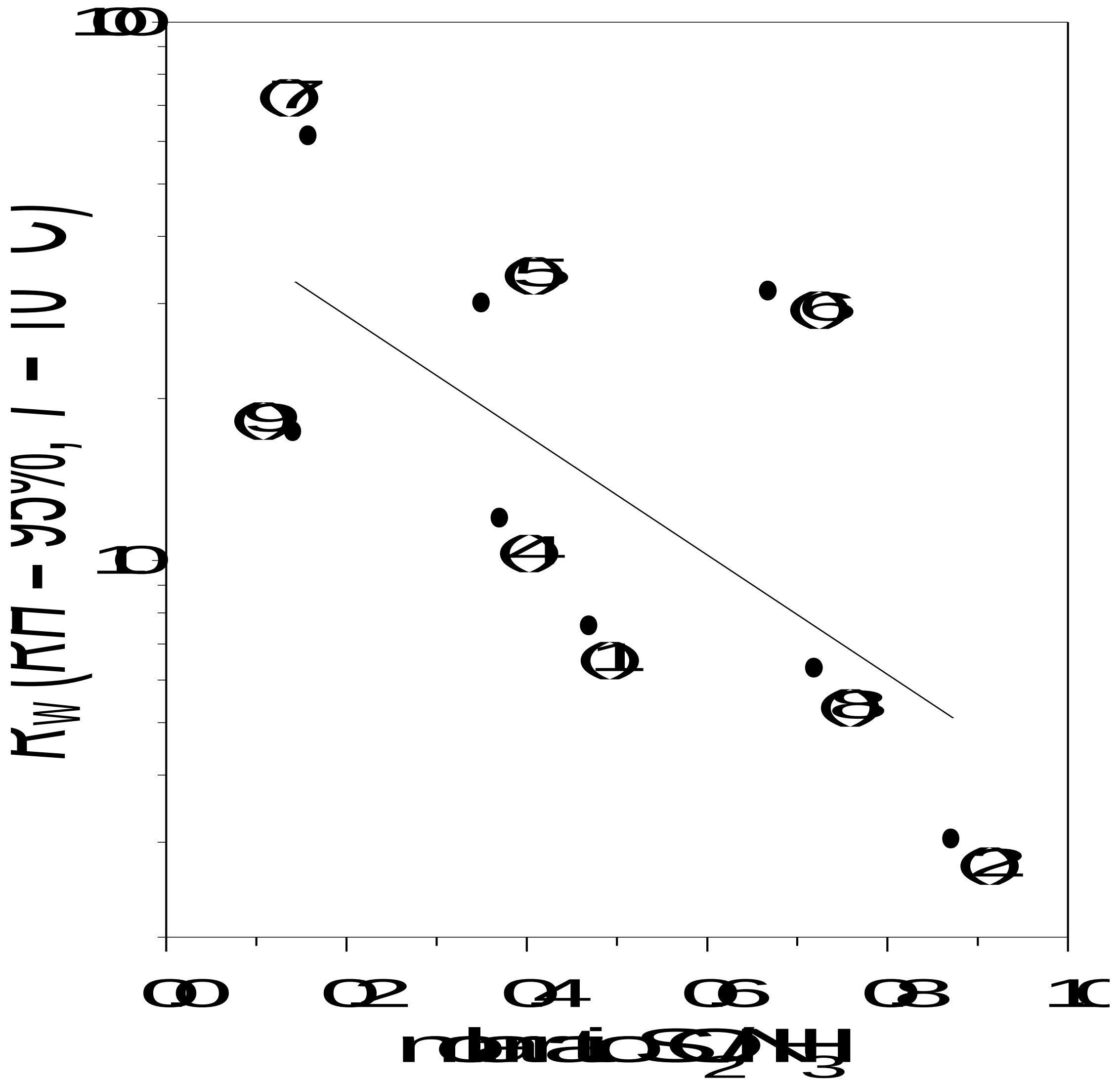
- R_w is a function of chemical properties of cuticle and leaf water layers (Flechard *et al*. 1998).
- Vapour pressure deficit (VPD) or RH is often used to determine the parameterisation of R_w (Nemitz *et al.* 2000).



Taken from Nemitz *et al.* (2004) Surface exchange fluxes of NH_3, SO_2, HNO_3 and HCl over a heathland. Atmos. Chem. Phys. 4, 489 - 1005.

The full squares and open circles represent block-averaged values for 50 sequential 30-min values of R_w values, sorted for h and VPD, respectively. The dashed and the solid lines show the parameterizations used to fit the measurements.

Impact of the chemical climate on cuticular resistance (R_w)



Taken from Nemitz, Milford and Sutton (2000). Quart. J. Royal Meteor:

Compilation of the cuticular resistance (R,) at relative humidity RH = 95%, and temperature, T = 10 "C, parametrized as a function of molar ratio of the mean SO_2 and NH_3 air concentrations. The numbers are those of the datasets used.

Note: a subsequent meta-analysis of Massa et al. (2010) considering a larger showed a more complex picture

SO_2 likely no longer the controlling acid gas. HNO_3 and HCl have risen in relative importance.

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Cuticular uptake resistance (R_w) increases at high NH_3 concentrations (saturation effect)

Ecosystem scale:
Jones et al., 2007; Concentration-dependent NH_3 deposition processes for mixed moorland semi-natural vegetation Atmospheric Environment, 41 (2007), pp. 2049-2060

For individual species response see:
Jones et al., 2007; Concentration-dependent NH_3 deposition processes for moorland plant species with and without stomata. Atmospheric Environment, 41, pp 8980-8994

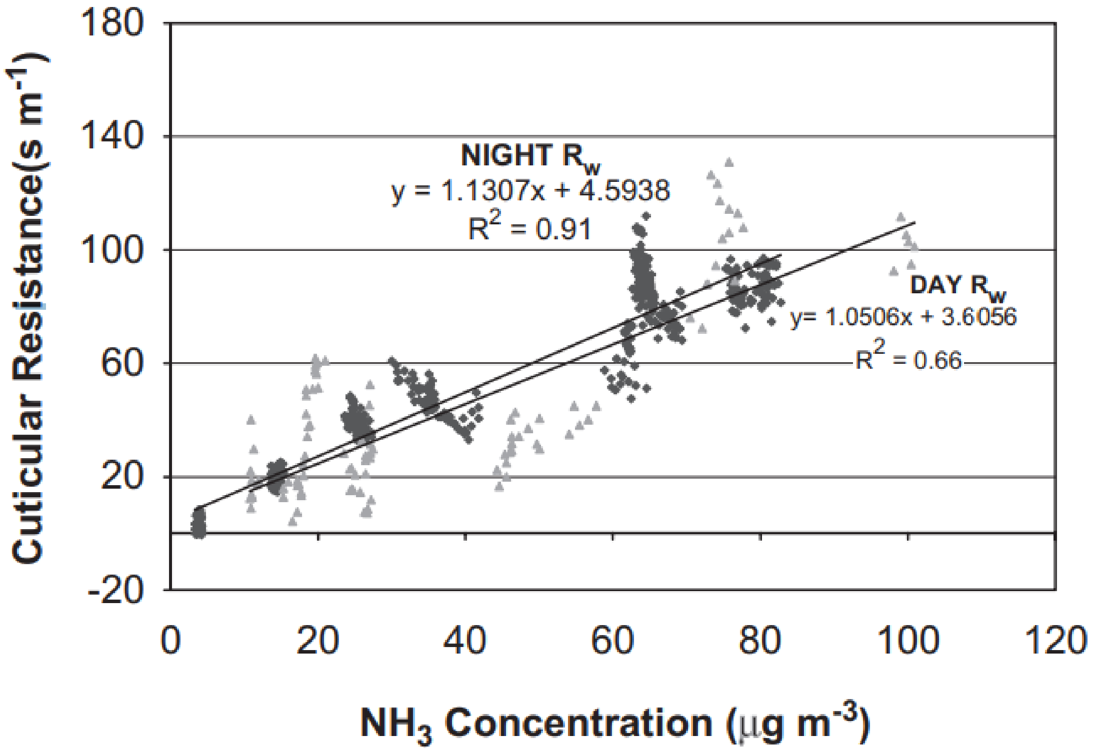
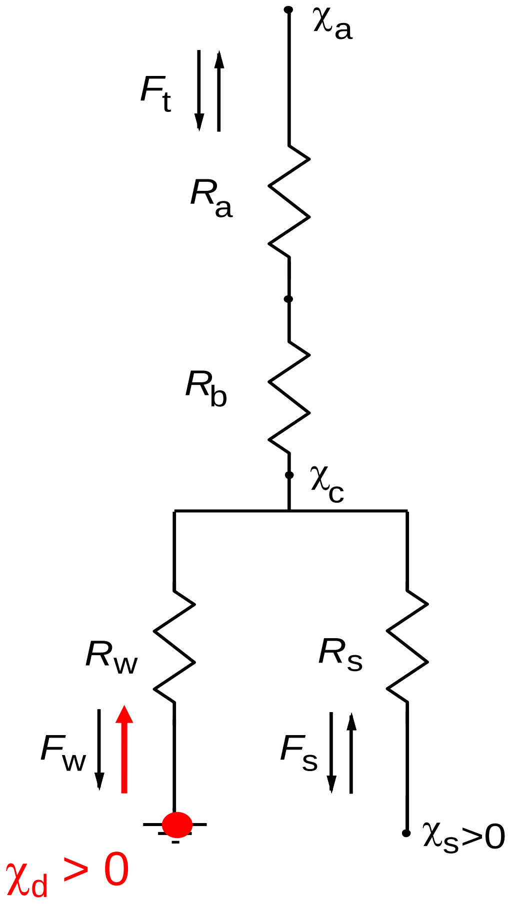


Fig. 10. Relationship between NH_3 concentrations ($\mu g\,m^{-2}\,s^{-1}$) and daytime R_w ($s\,m^{-1}$) (light grey triangles) and night-time R_w ($s\,m^{-1}$) (black diamonds) for a mixed vegetation canopy.

Leaf surfaces respond to chemical composition and can saturate at high NH_3 levels



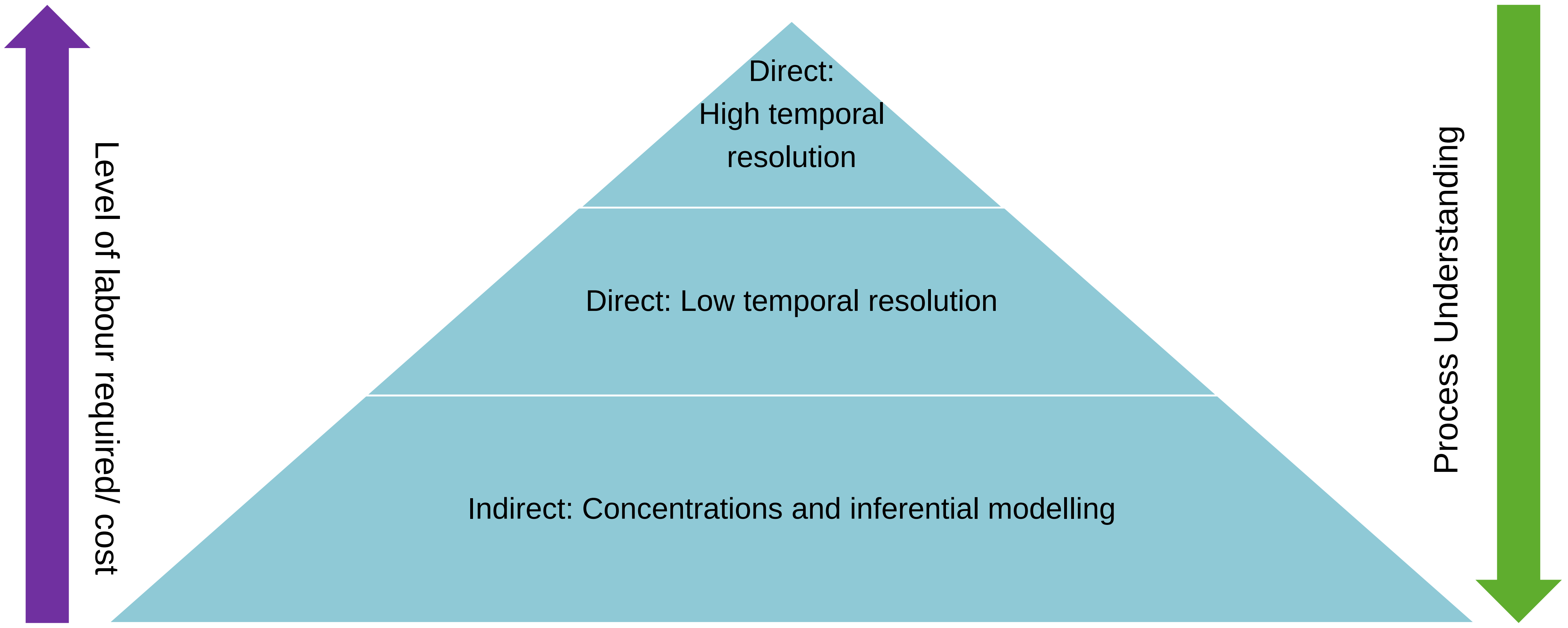
- Increase in R_w or introduction of additional cuticular emission potential (χ_d)

Two examples of approaches to deal with R_w in ACTMs:

- EMEP: R_w function of annual average NH_3/SO_2 concentration ratio in air
- DEPAC (LOTOS-EUROS): R_w as a function of ambient NH_3 concentration (Jones et al., 2007a, b)

➢ In both models only deposition to the cuticle is possible

NH_3 dry deposition measurement approaches



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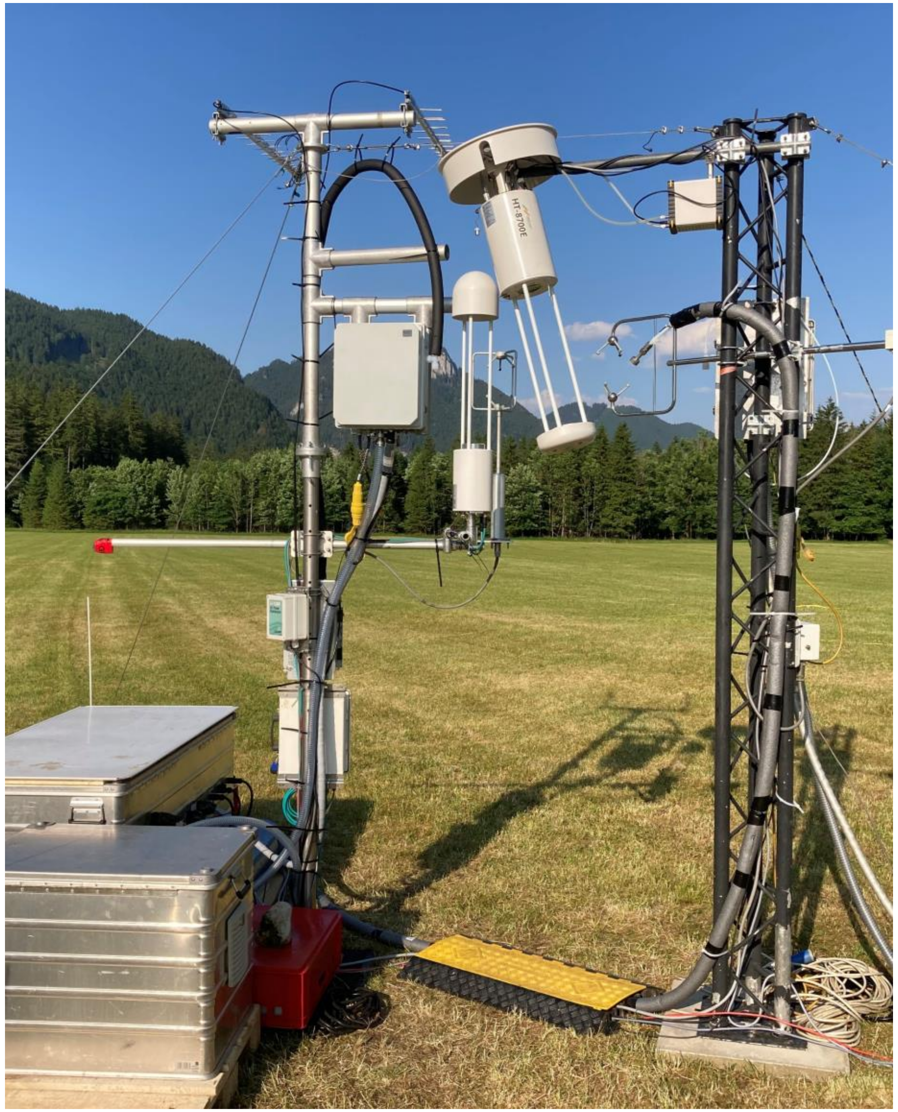
Direct measurements

- Micrometeorological methods have to fulfil requirements
  - homogenous flat terrain
  - sufficient turbulence
  - Eddy covariance ‘ideal method’ requires sampling of up ≥10 Hz
- Challenging under ambient conditions due to ‘sticky’ nature of NH_3
- Recently there now open path systems on the market to undertake direct flux measurements
- Not applicable near point sources (due to advection errors)



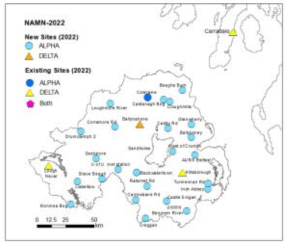
Indirect measurements

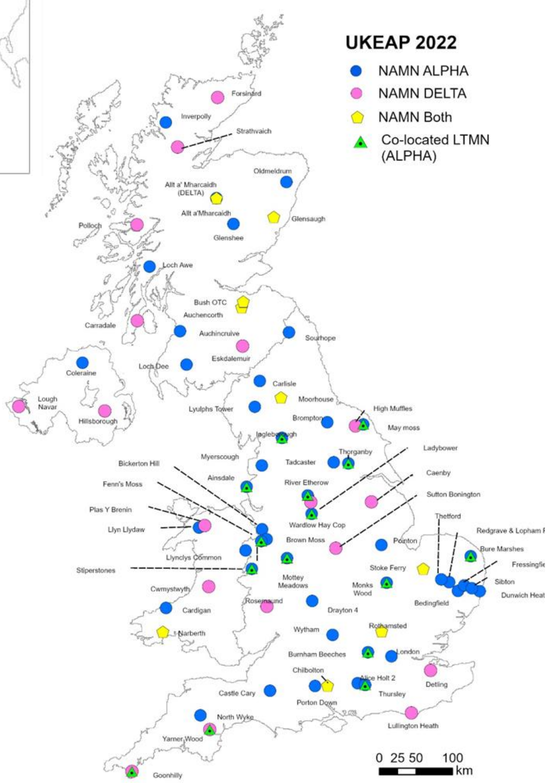
- Two types of concentration measurements:
  - State-of-the art high temporal resolution (20 Hz to 1 hour) at 1 location
  - Multiple sensors with low temporal resolution covering a spatial area (daily to monthly average)
- Data from the measurements are then used to inform models:
  - Measurement model fusion approach (Concentration Based Estimate Deposition Model, CBED[1])
  - Calibration of an atmospheric chemistry transport model (UK: EME4UK)[2]
  - Use similar parameterisations as previously shown

[1] Smith *et al.* (2000) Regional estimation of pollutant gas dry deposition in the UK: model description, sensitivity analyses and outputs. Atmospheric Environment 34, 3757-3777

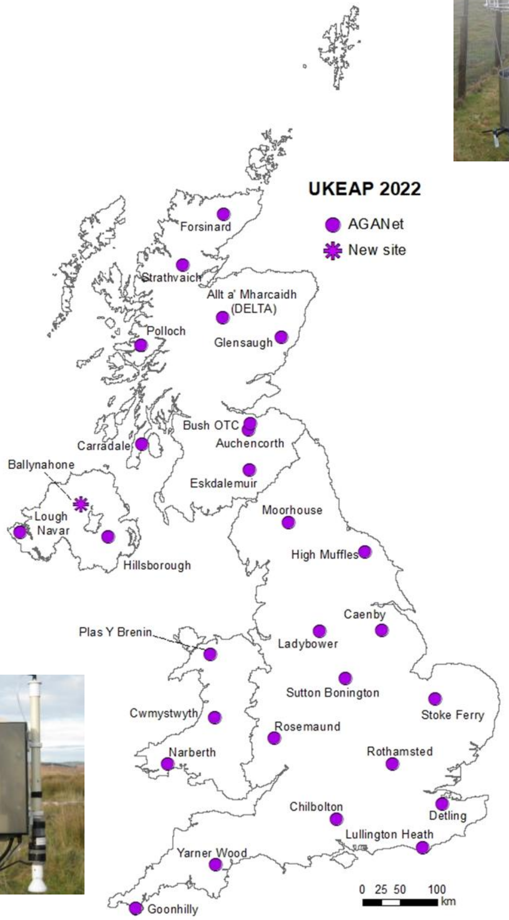
[2] Rowe *et al.* (2022) Trends Report 2022: Trends in critical load and critical level exceedances in the UK. Report to Defra under Contract AQ0849

UK Monitoring Networks

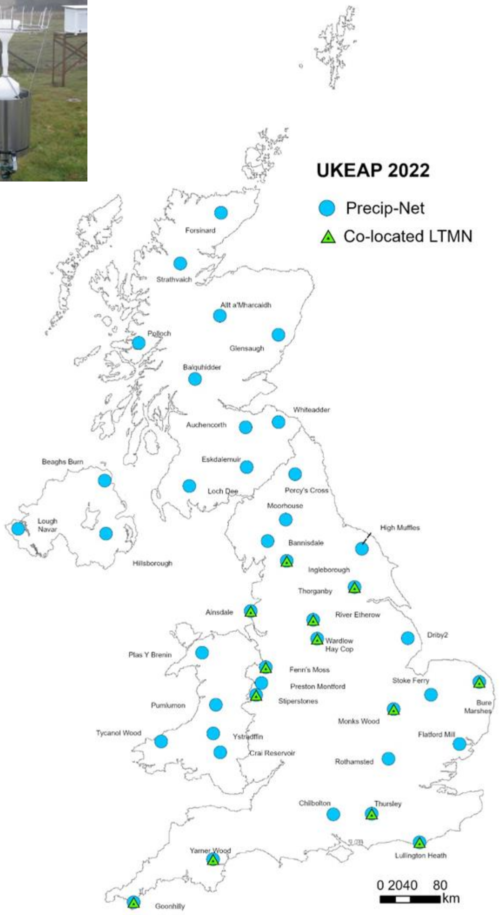




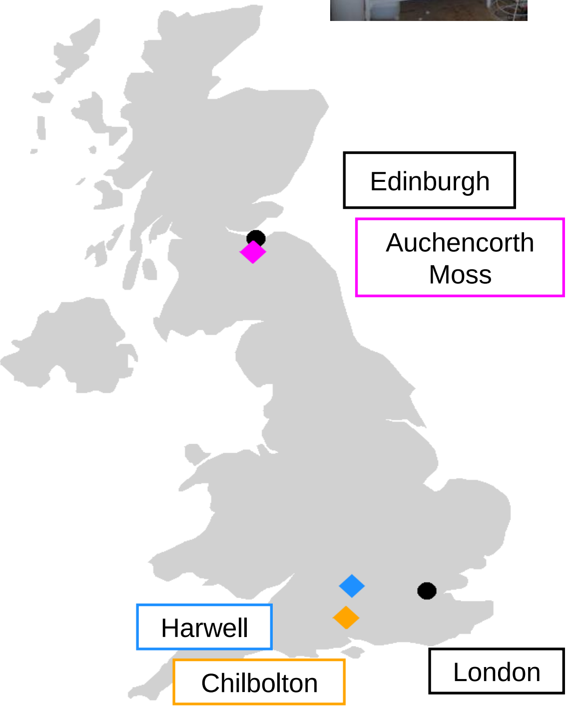
National Ammonia Monitoring Network *(112 sites)*



Acid gases and Aerosols Network *(28 sites)*



Precipitation Network *(41 sites)*



EMEP supersites *(2 sites)*

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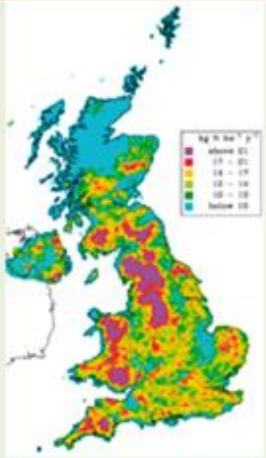
UK Monitoring Networks



Modelling and mapping pollutant concentrations and deposition

National and international assessments atmospheric pollution and deposition to the environment

Critical Loads and exceedance mapping

National Ammonia Monitoring Network (112 sites)

Acid gases and Aerosol Network (28 sites)

supersites sites)

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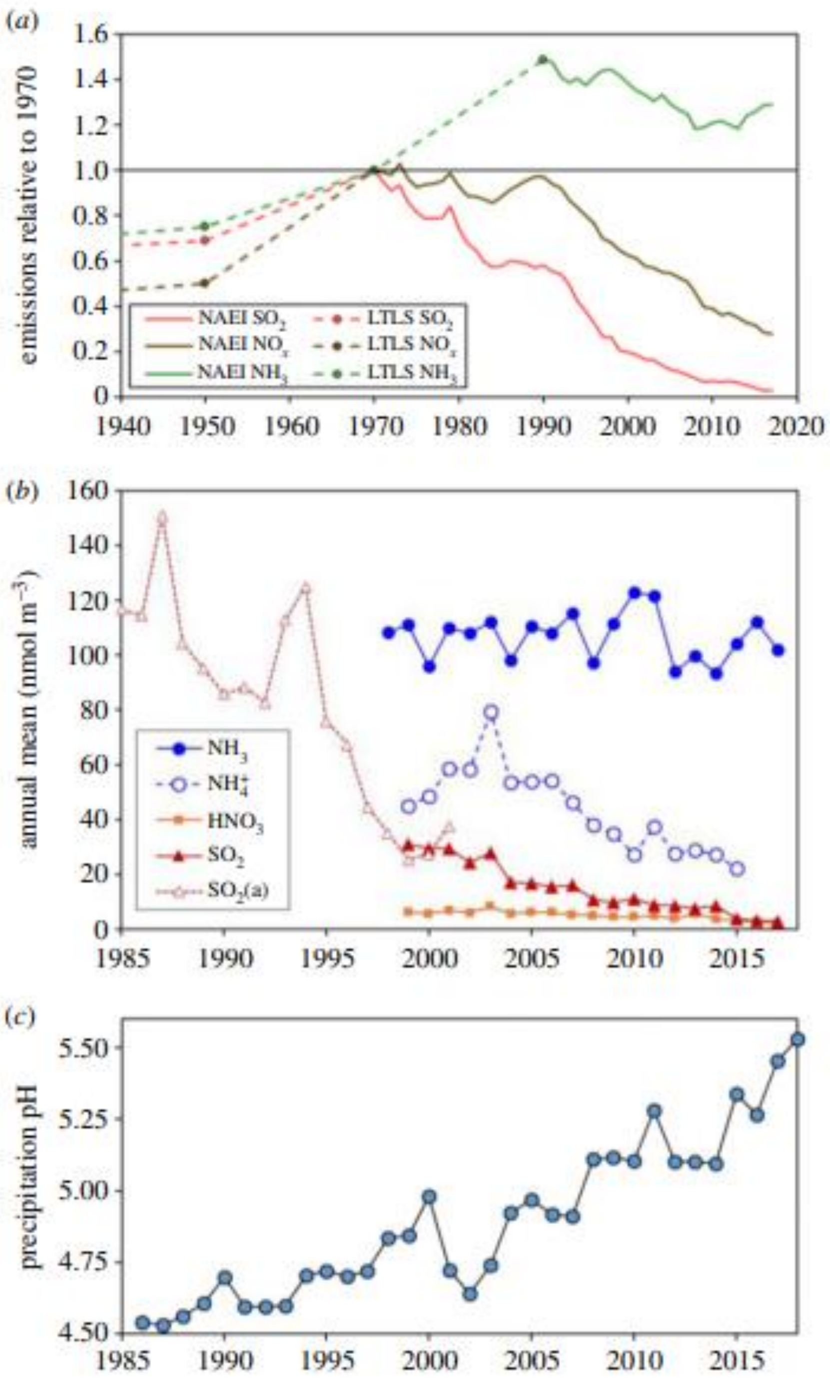
Current status of NH_3 in the UK

- Decrease in NH_3 emissions is not reflected in NH_3 concentrations
- UK moving from an acidic towards an alkaline environment
- Likelihood that R_w is increasing and more potential for desorption from the cuticle



Taken from Sutton, M.A. *et al.* 2020. Alkaline air: changing perspectives on nitrogen and air pollution in an ammonia-rich world. Philosophical Transactions of the Royal Society A, 378(2183), p.20190315.

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Impact of NH_3 currently in the UK

- Critical levels (annual)
  - >1 & ≤ 3 µg m^{-3} (lichens and byrophytes exceeded)
  - > 3 µg m^{-3} (vascular plants)

- 69% of the UK is currently exceeding the critical levels for NH_3 set for lichens and byrophytes
- Areas of high concentrations of NH_3 often associated with local intensive agricultural areas

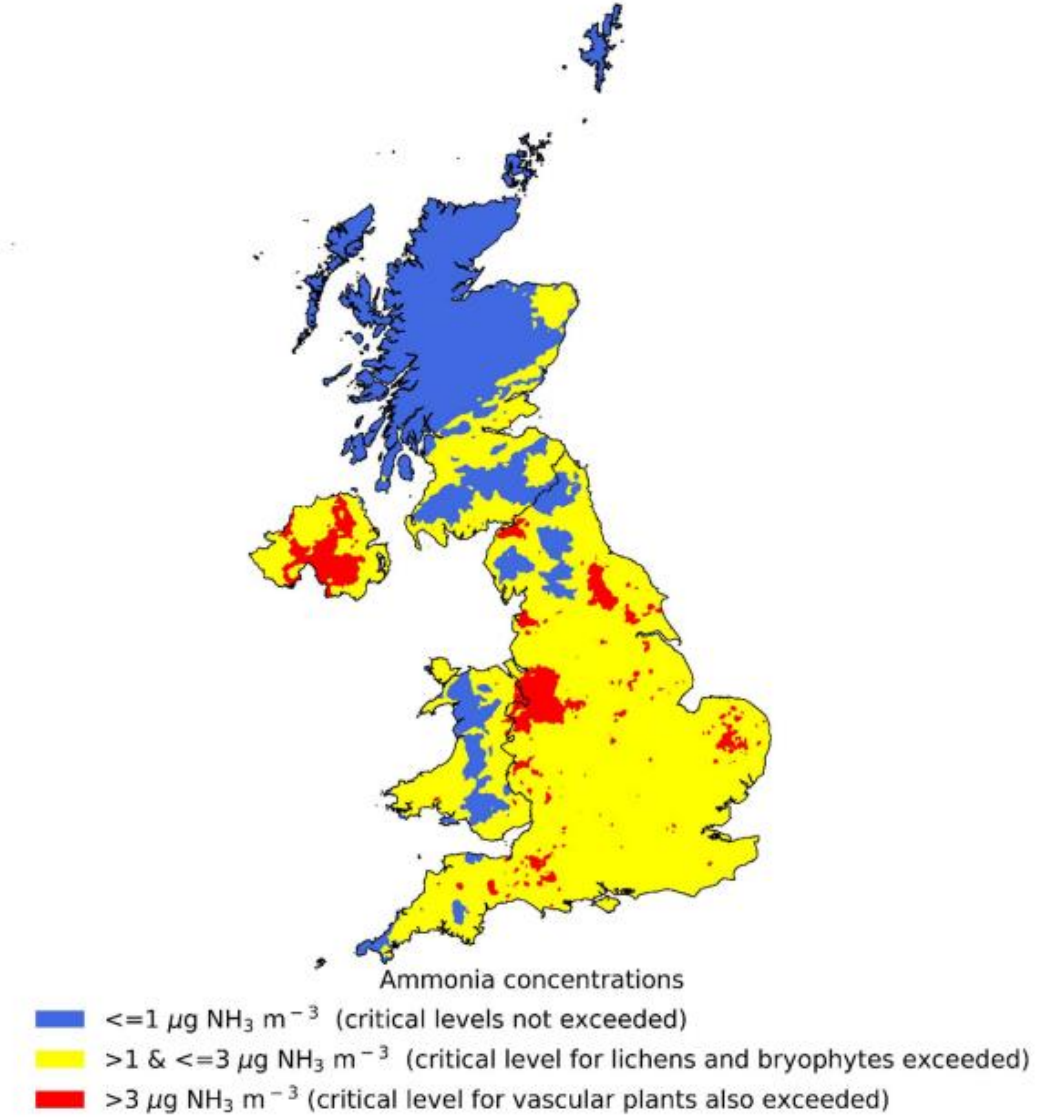


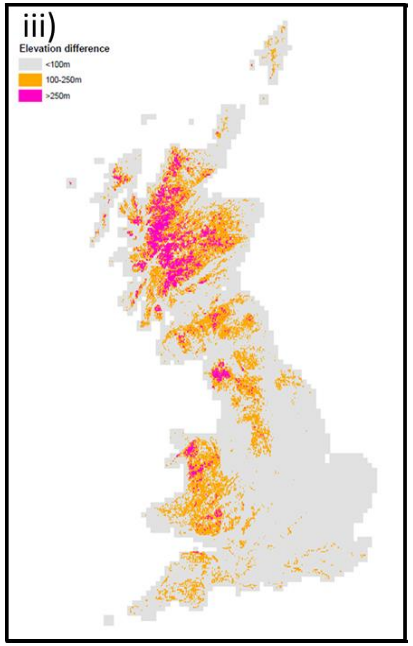
Figure 4.1: EMEP 1 x 1 km mean ammonia concentrations for 2017-19.

Map from: Rowe *et al.* (2022) Trends Report 2022: Trends in critical load and critical level exceedances in the UK. Report to Defra under Contract AQ0849

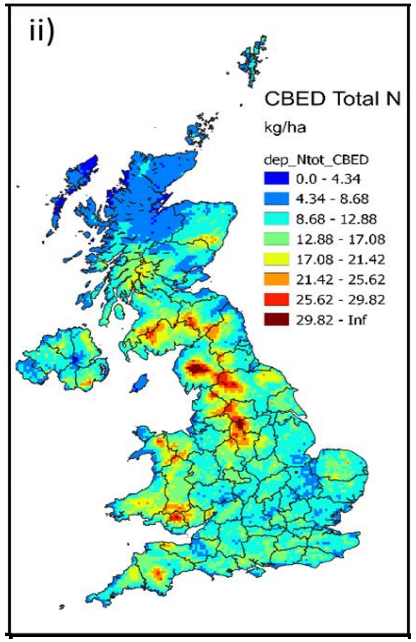
Challenges: quantifying dry deposition to complex terrain

- Dry deposition parameterisations derived for homogeneous, flat surface
- Micrometeorological methods not applicable
- Models currently do not agree the deposition rates to complex terrain
- Expected enhancement of deposition rates to complex terrains
  - ➢ Vulnerable ecosystems to N deposition are at risk

Definition of complex terrain

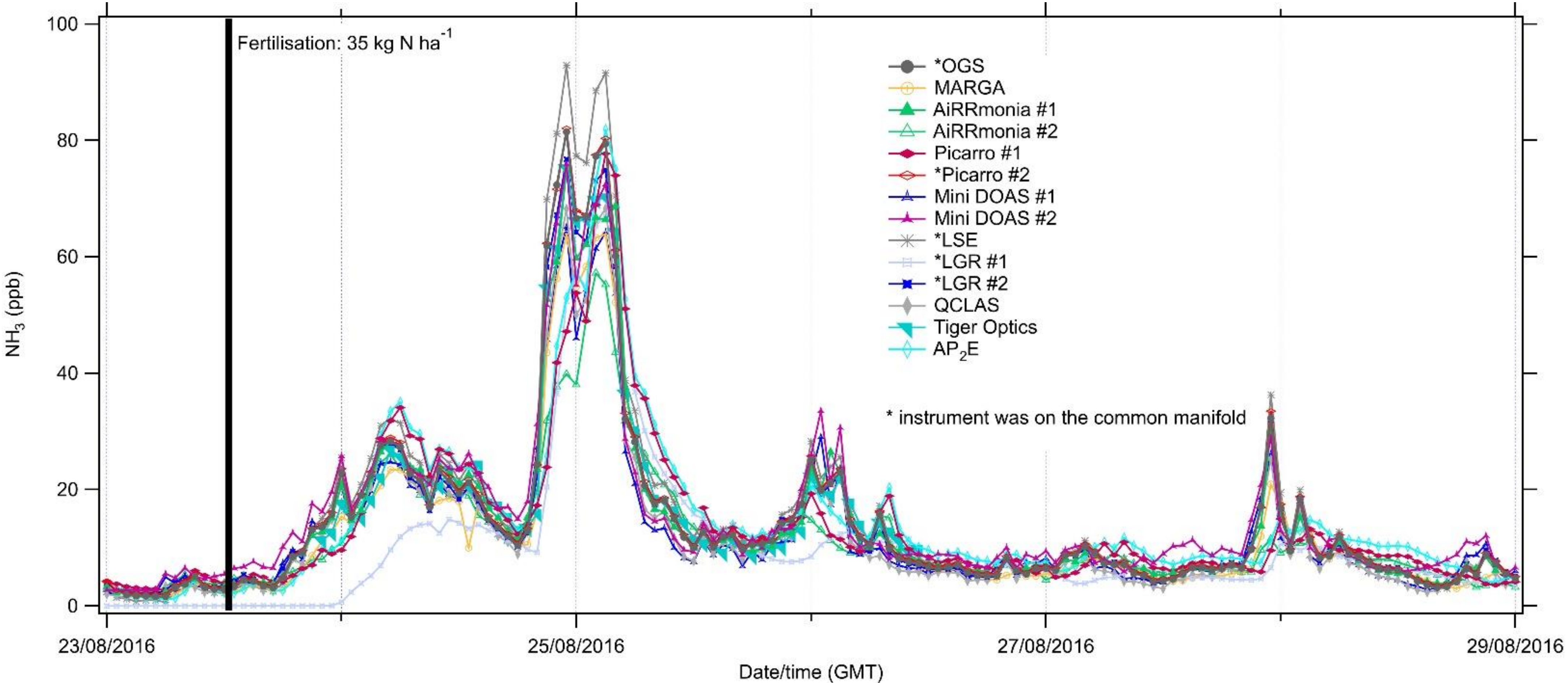


Coincides with large N_{dep}



Taken from: Cowan, N., Nemitz, E., Walker, J.T., Fowler, D., Finnigan, J.J., Webster, H.N., Levy, P., Twigg, M., Tang, S.Y., Bachiller-Jareno, N. and Trembath, P., 2022. Review of methods for assessing deposition of reactive nitrogen pollutants across complex terrain with focus on the UK. *Environmental Science: Atmospheres*.

Challenges: Comparability of NH_3 concentration measurements



Taken from: Twigg *et al.* 2022. Intercomparison of in situ measurements of ambient NH_3: instrument performance and application under field conditions. *Atmospheric Measurement Techniques*, *15*(22), pp.6755-6787.

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MetNH3

Ammonia as a future fuel: some considerations

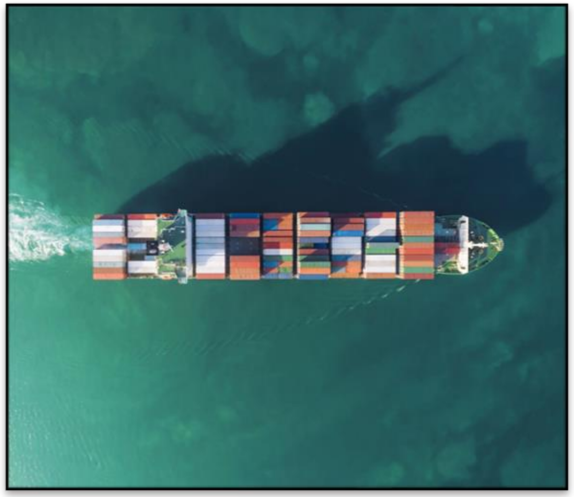

Photo credit: www.faam.ac.uk

- High concentrations are likely to significantly increased the cuticular resistance or introduce a cuticular emission potential (χ_d)

  - Leads to an increase in atmospheric lifetime due to reduction in deposition velocity

  - Further studies are required to determine if an emission potential occurs on the cuticle at elevated concentrations across different environments

Ammonia as a future fuel: some considerations

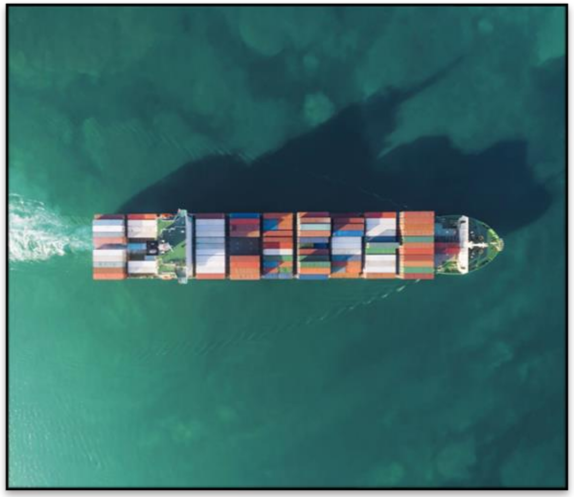

Photo credit: www.faam.ac.uk

- Incident capability in the UK:
  - National monitoring network can help in identify any changes in the state of the UK background concentrations but won't give process understanding
  - A system needs to be developed to quantify dispersion of NH_3 in response to any incident in the future

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Thank you

For more information
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