

1. Background

Micrometeorological measurements of ammonia fluxes show that the process is bi-directional, i.e. ammonia can be emitted from the surface, or can be deposited to the surface.

Emission occurs when there is a source of ammonia, either from decaying plant material, or if the equilibrium between ammonium ions in the leaf apoplast and ammonia gas in the surrounding air exceeds the air concentration. Deposition occurs when surface concentrations are less than those in the surrounding air.

The process is dynamic – i.e. it changes with time, on time-scales of minutes, and for a given surface, fluxes may change direction as air concentrations and surface conditions vary.

Wet surfaces provide additional complications, because ammonia will dissolve in any liquid (from rain or dew) on leaves or other surfaces. Although this dissolved ammonia will not usually enter stomata directly (but see papers by Burkhardt et al.), it provides a potential source of ammonia gas for direct uptake by stomata if internal leaf ammonia concentrations are low enough.

Although such dissolution into surface water may be a measured sink for a deposition flux, what happens when surface water evaporates, for example after rain, or as dew evaporates in the morning? There is plenty of evidence that much of the dissolved ammonia is returned to the gas-phase as the water evaporates, in response to changing equilibrium concentrations in the surface solution (e.g. Flechard et al.). Similar behaviour has also been observed for sulphur dioxide.

- Is dissolved ammonia always returned to the gas-phase as surface water evaporates?
- Are there processes operating that would retain deposited ammonia, leading to a net deposition flux?
- If the source of the dissolved ammonia is from inside the leaf, do these processes lead to net retention of nitrogen within the plant-soil system?

This poster explores answers to such questions.

5. Conclusions

Other chemical processes may act to retain ammonium ions on leaf surfaces. For example, the ammonium ions may exchange with other ions held on cation exchange sites at the surface, releasing metal ions such as potassium into solution. Whether the ammonium ions held on exchange sites are released back into solution, and thence to the atmosphere, as surface water evaporates would depend on the relative rates of ion exchange equilibration processes compared with the rate of change of solute concentrations as a water layer evaporated.

Biological processes may also act to retain deposited ammonia – there is evidence from several studies that organic nitrogen compounds are formed on leaf surfaces from deposited ammonia gas. Deposited ammonia may also cross the cuticle and be metabolised by leaves on time-scales similar to those involved in wetting/drying cycles.

However, the key process likely to operate even at the low levels of SO₂ observed in today's atmosphere, is the retention of ammonium ions with sulphate produced from the oxidation of SO₂. The radical decrease in SO₂ concentrations over the past 20 years means that a much smaller proportion of the dry deposited ammonia gas is now retained on vegetation surfaces than would have been the case previously.

One of the effects of the reduction in SO₂ concentrations has been an effective decrease in the long-term dry deposition rate of ammonia from the atmosphere.

This process can be included in deposition/transport models by including a dependence of the deposition velocity for ammonia on the sulphur dioxide concentration (e.g. Smith et al., 2000).

6. References

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- Flechard, C.R., Fowler, D., 1998. Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements. *Quarterly Journal of the Royal Meteorological Society* 124, 759-791.
- Flechard, C.R., Fowler, D., Sutton, M.A., Cape, J.N., 1999. A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere. *Quarterly Journal of the Royal Meteorological Society* 125, 2611-2641.
- Smith, R.I., Fowler, D., Sutton, M.A., Flechard, C., Coyle, M., 2000. Regional estimation of pollutant gas dry deposition in the UK: model description, sensitivity analyses and outputs. *Atmospheric Environment* 34, 3757-3777.

2. Simple ammonia chemistry

The ammonia molecule (NH₃) is highly soluble in water, and solubility increases as temperature decreases, with a 3-fold increase from 25°C to 0°C.

Ammonia reacts with water to give the ammonium (NH₄⁺) ion and hydroxyl (OH⁻) ion, so that solutions of ammonia in pure water are slightly alkaline.

For example, 1 ppb NH₃ in equilibrium with pure water would generate a solution concentration of 1.2 μM NH₄⁺ and a pH of 8.2 at 20°C (Fig.1). Because the dissociation equilibrium is also temperature-dependent, the overall solubility of NH₃ (unreacted and reacted) is less dependent on temperature, with only a 60% increase from 25°C to 0°C.

Fig.1. Concentration (M) of NH₄⁺ in pure water as function of NH₃ concentration and temperature

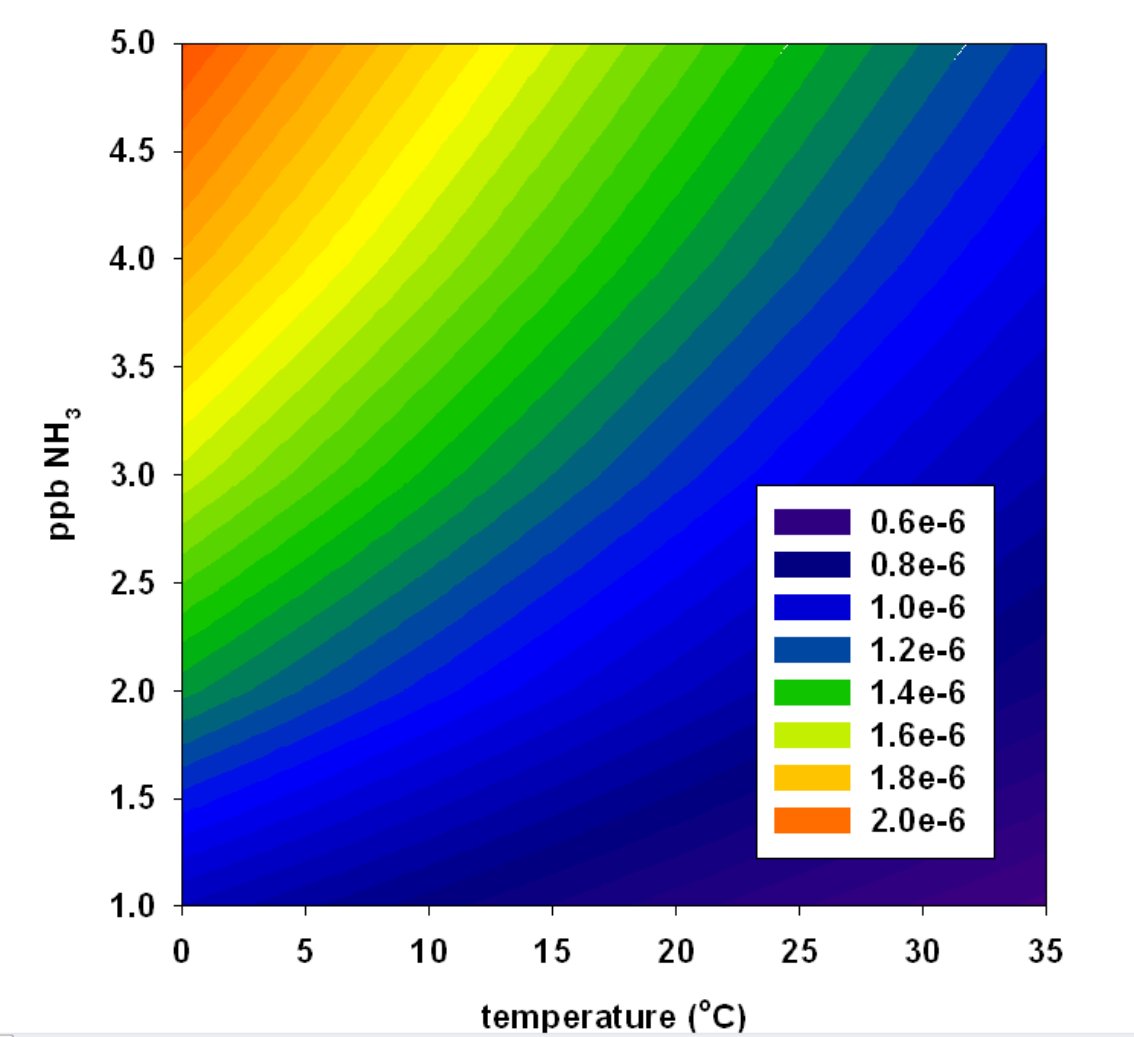
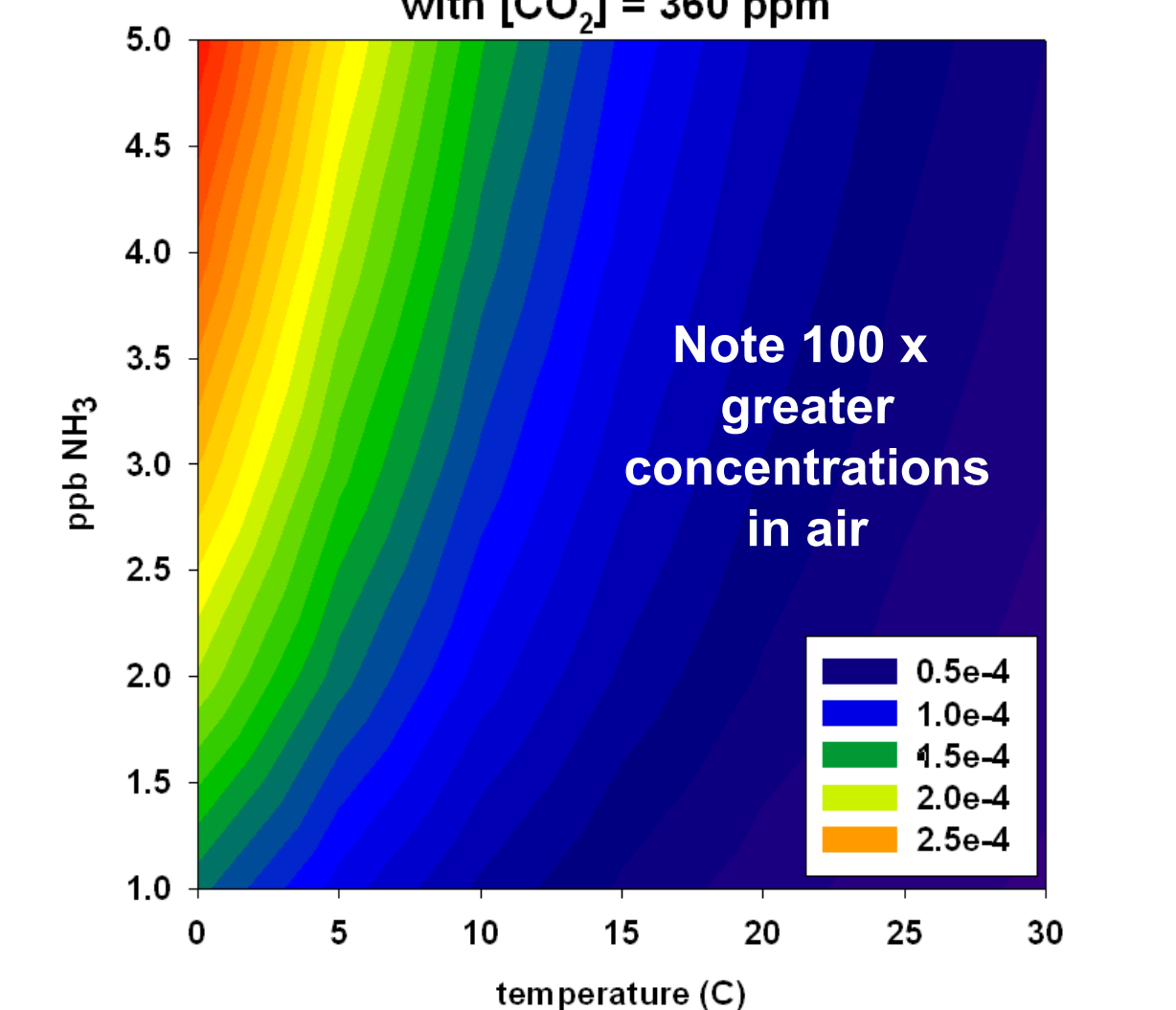


Fig.2. Concentration (M) of NH₄⁺ as function of NH₃ concentration and temperature with [CO₂] = 360 ppm



But in the atmosphere, and on a leaf surface, other components are present. Carbon dioxide (CO₂) is an acidic gas, and dissolves in water to neutralise the alkaline solution from the dissolved ammonia.

At an air concentration of CO₂ of 360 ppm, 1 ppb NH₃ in equilibrium at 20°C would generate a solution concentration of 37 μM NH₄⁺ and a pH of 6.8 (Fig.2).

All would disappear back to the gas phase when the water evaporated, unless other chemical reactions occurred on the leaf surface.

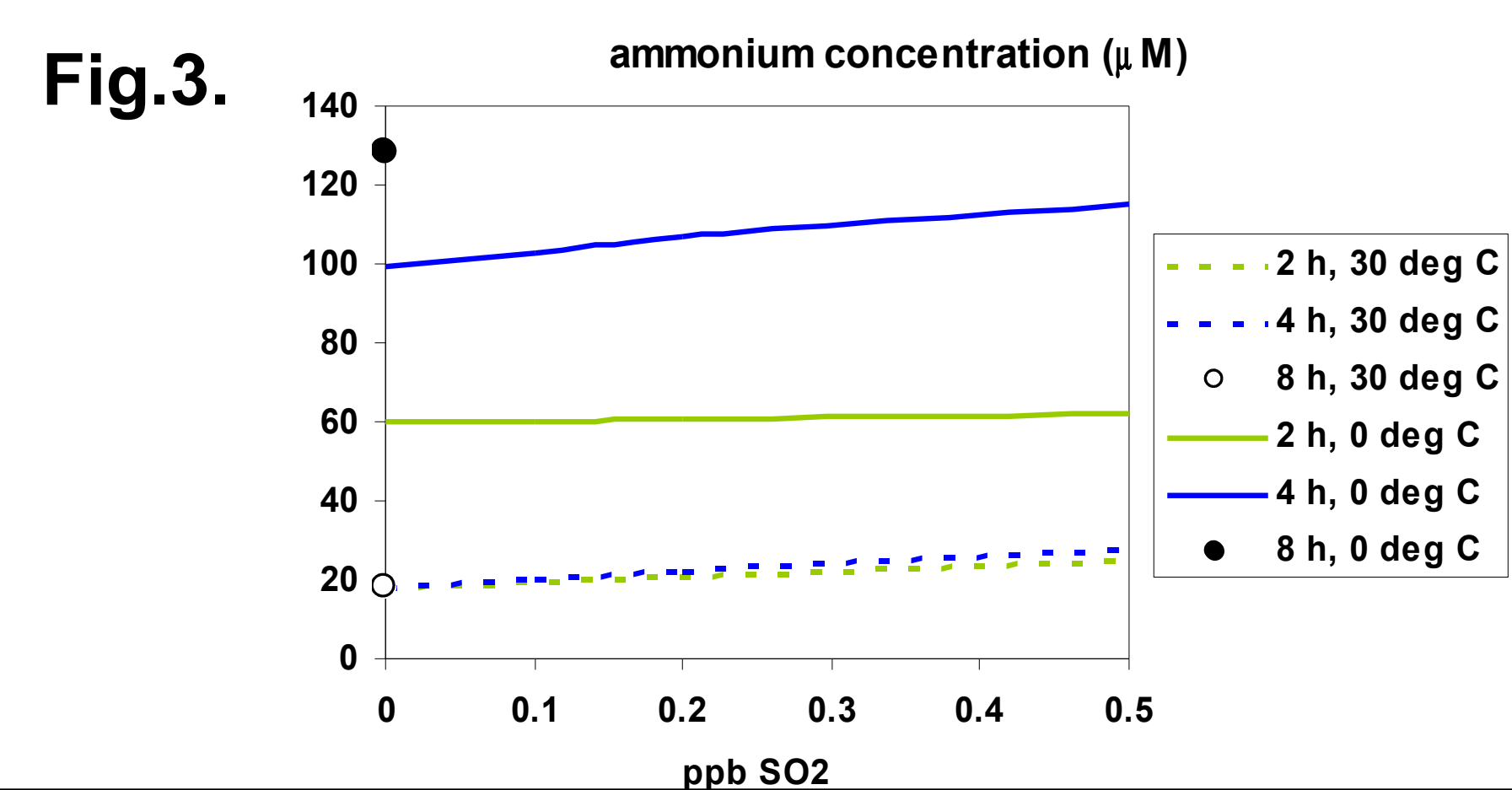
3. Other acidic gases

Just as CO₂ neutralises the alkaline solution, so do other acidic gases such as sulphur dioxide (SO₂).

Air concentrations in the UK are now generally below 1 ppb – how important is its role in affecting the solubility of ammonia?

A dynamic model of gas transfer to a layer of water 0.1 mm deep, constrained by a gas-phase transfer rate equivalent to a deposition velocity of 2 cm s⁻¹, can be used to investigate the importance of SO₂ for NH₃ uptake. As expected, the uptake of ammonia (1 ppb), shown by the NH₄⁺ concentration in solution, is much greater at 0°C than at 30°C (solid line in Fig. 3), and equilibrium is reached much more quickly at higher temperatures. The uptake rate is dictated by the air concentration and deposition velocity, and at its fastest could only generate a solution concentration at a rate of 0.01 μM s⁻¹. The presence of small concentrations of SO₂ makes little difference to the ammonium concentration in solution after 2 h, 4 h or 8 h (Fig. 3).

As with the case of carbon dioxide, when the solution evaporates, all the solutes would return to the gas phase unless other chemical reactions occur.



4. The role of oxidation reactions

Oxidation of dissolved SO₂ in surface water films can in principle occur through reaction with ozone (which is not particularly water soluble), hydrogen peroxide (which is highly soluble, but present at low concentrations), by free radicals (e.g. hydroxyl) formed by light-driven reactions, or by molecular oxygen (particularly in the presence of metal catalysts). Overall reaction rates are not known experimentally, but observed oxidation rates in cloud droplets are in the range 1-10% h⁻¹. As sulphate is produced in solution, acidity also forms, further neutralising the alkali formed as ammonia dissolves.

When the water film evaporates, the sulphate salt (in this case ammonium sulphate) is involatile, and remains on the surface, thereby leading to net deposition and retention of the deposited ammonia. The model can be used to calculate the fraction of the ammonium in solution that is retained through sulphate formation.

The figures below show the % retention for 1 ppb NH₃ deposition to a 0.1 mm thick water layer, as a function of the SO₂ concentration, temperature and oxidation rate.

The fraction increases with oxidation rate, and with time.

