Review of atmospheric dispersion and deposition in fog or 'haar' events and its impact on human health

> **This document is not complete to the satisfaction of the Atmospheric Dispersion Modelling Liaison Committee as a result of the study being suspended due to the contractors' company ceasing to exist. However the Committee recognise the value of the work performed to date and therefore have opted to publish the work in draft form. The Committee remain open to offers to complete this study.**

1. Factors affecting the development and growth of fog and its significance in natural and urban environments and contractors response to ADMLC comments

2. Comparison of the principal ions present in fog water and its ecotoxicological significance in natural environments

3. Draft review of modelling and research studies

4. Draft review of pollution effects on health during fog episodes

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EXECUTIVE SUMMARY (WORK IN PROGRESS)

Fog can have a profound effect on human activity and the physical environment. On national, local and regional scales, its occurrence can have a significant impact on the environment, economics and public safety.

The World Meteorological Organisation (WMO) defines fog as water droplets suspended in the air, reducing visibility at the Earth's surface to less than 1000 m. Here we describe five different types of fog and the environmental conditions that lead to their occurrence. The five fog types described are:

- Radiation fogs including valley fog;

- Advection fogs including sea fogs;

- Upslope or hill fog;

- Steam fog; and

- Frontal or precipitation fog.

The time of day that fog occurs and its optical density are functions of several environmental variables, and are also affected by the physicochemical properties of the particles on which the fog droplets develop and grow. We discuss here the effect of particle size (the Kelvin effect) and chemistry (Raoult's law) on the formation of fog water droplets and discuss how the Köhler theory combines the Kelvin Effect and Raoult's Law to describe the processes by which fog forms.

Fog water can in many regions represent a significant component of the hydrological cycle, and its significance to communities in arid regions as well as its ecological significance in less arid regions is discussed. Much of the environmental burden of sulphates, nitrates, ammonium and hydrogen ions resides in the atmosphere in liquid or solid aerosols and can be accumulated and removed in fog water. To illustrate this we draw attention to the major ions found in fog water downwind of industrial regions and discuss the ecotoxicological significance of fog in natural and urban environments.

CONTENTS

1 FACTORS AFFECTING THE DEVELOPMENT AND GROWTH OF FOG AND ITS SIGNIFICANCE IN NATURAL AND URBAN ENVIRONMENTS

1.1 Introduction

Fog and mist form when water vapour in the air condenses onto particles, cloud condensation nuclei (CCN), to such an extent that visibility becomes affected. The World Meteorological Organisation (WMO) defines fog as:

"A suspension of very small, usually microscopic water droplets suspended in the air, reducing visibility at the Earth's surface to less than 1000 m" (WMO, 1992).

Mist is defined as affecting visibility between 1000 and 2000 m. Haze differs from mist and fog in that it consists of unactivated particles in the atmosphere that affects visibility at greater distances. Cloud condensation nuclei are activated when the equilibrium vapour pressure of the moisture condensing on their surface is lower than the ambient, favouring droplet growth.

The occurrence of fog can have a profound effect on human activity and the physical environment. On national, local and regional scales, its occurrence can have a significant impact on the environment, economics and public safety, and timely and accurate forecasts are necessary for road safety and air traffic management as well as protecting members of the public who belong to critical groups that are acutely affected by adverse air quality. However, due to the complex physical interactions that lead to the formation of fog, predicting its spatial and temporal occurrence is extremely difficult using conventional meteorological instruments.

1.2 Types of Fog

Byers (1959) produced a detailed classification of 11 types of fog according to the processes that lead to their formation, and highlighted that many fog episodes are the product of complex interactions between one or more of the processes described below.

All fogs can be broadly divided into two categories: condensation fog - fogs that form as a result of the condensation of warm, moist air above a cool body; and evaporation fog - fogs that form as consequence of the addition of moisture to air at the Earth's surface. Within these two categories, five different types of fog are usually classified. These are:

- Radiation fogs including valley fog and freezing (condensation fog);

- Advection fogs including sea fogs (condensation fog);

- Upslope or hill fog (condensation fog);

- Steam fog (evaporation fog); and

- Frontal or precipitation fog (evaporation fog).

1.2.1 Radiation Fogs

Radiation fog forms under stable atmospheric conditions over land that is moist, and usually occurs shortly after dusk on long, cool, clear nights. Under such conditions the troposphere is usually characterised by a low, stable boundary layer with light winds (typically 1-5 kmph), which reduces atmospheric mixing. As a result, radiation fogs are most common during late autumn through spring. Under these conditions the infra-red radiation absorbed at the Earth's surface during the day is radiated back into space, and as the Earth's surface cools, it causes the temperature of the overlying air to decrease generating a temperature inversion. Initially, the temperature inversion may be only several centimetres deep, but can deepen throughout the night. Figure 1 shows the results of a vertical sounding of the atmosphere during a radiation fog event. Note the low wind speeds, the temperature inversion and the convergence of the dew point temperature and air temperature in the lower troposphere.

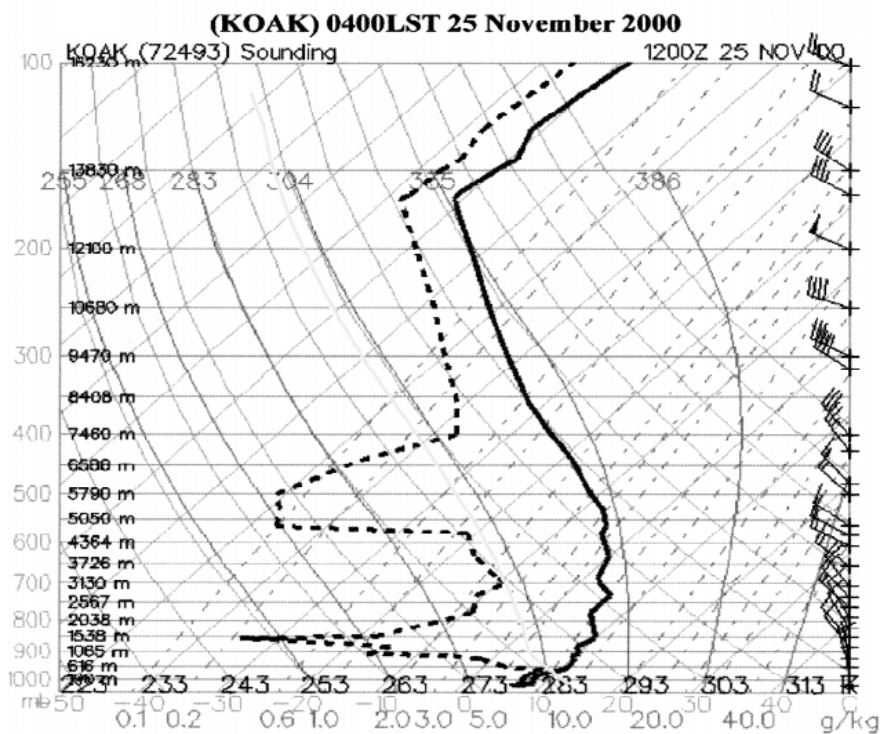**Figure 1   Vertical sounding through the atmosphere during a radiation fog episode. Dashed line is the dew point temperature and the solid line is air temperature. Symbols on the right axis denote wind speed and direction (reproduced from Underwood et al., 2004).**

Shallow radiation fogs are often localised and confined to low ground and troughs in undulating surfaces. These light radiation fogs generally "burn off" the

following morning when incoming solar radiation warms the Earth's surface. This warming generates mixing in the stable layer next to the Earth's surface, which weakens the temperature inversion as a consequence of turbulent lofting of the warming surface air. Also, as the surface air temperature warms, the air temperature and dew point temperatures diverge and moisture on the surface of CCN enters the vapour phase as a result of increases in the vapour pressure of the fog water. However, in mid-winter, at high latitudes where the sun remains low in the sky, radiation fogs may persist for several days, particularly when cooling is sufficiently fast and prolonged to allow a temperature inversion to develop that may be many tens of metres deep. These persistent fogs are often characterised by a very low optical density fog with high liquid water content (LWC) per metre cubed of air. The high LWC of persistent radiation fogs can shield the surface from incoming solar radiation and offer some insulation at the surface and reduce the cooling rate of the surface layers. These fogs tend to persist primarily as a consequence of radiative cooling of the fog top, which in turn sets up gentle convection currents that mixes the sinking cold air throughout the body of the fog. Under these conditions, the troposphere becomes extremely stable and vertical mixing and wind shear are reduced due to a decrease in the flux of heat and moisture from the surface to the overlying air. Any pollutants emitted into this stable layer of air will increase in concentration as a result of a reduction in the height of the boundary layer, reduced advection and a decrease in turbulent mixing. If the air temperature falls below freezing, a freezing fog may result. Freezing fogs occur when fog water becomes supercooled (i.e. remains liquid even though the temperature is below freezing-point). When the supercooled fog droplets deposit to surfaces, a rime (feathery ice crystals) can form. Figure 2 shows a schematic of the formation of radiation fog.
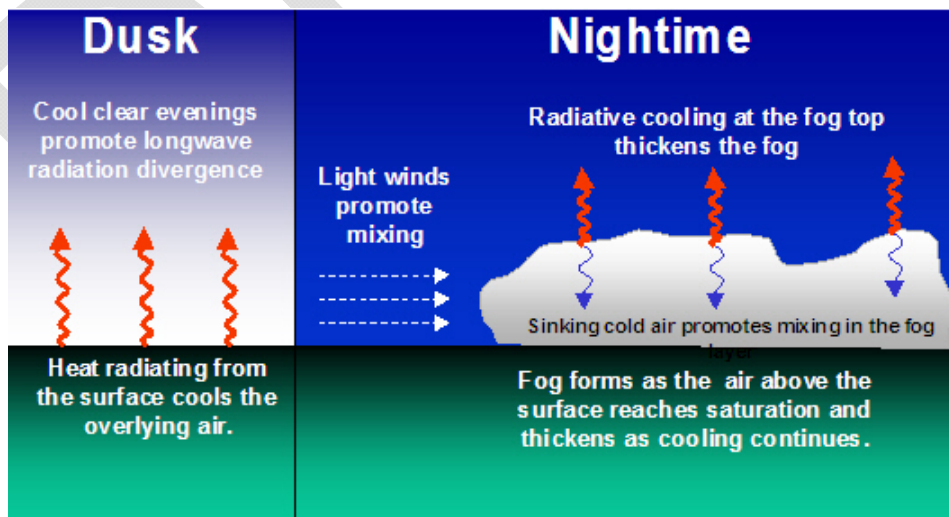

Figure 2   Schematic of the formation of radiation fog.

1.2.2   Valley fog

Valley fogs form when air along the hilltops and valley sides cools after sunset and drains to the valley floor (Figure 3). As the cold air drains down the valley sides the relative humidity in the valley bottom increases and when the dew point temperature and air temperature converge, moisture condenses on CCN. On its own, the temperature of the cold sinking air may not be enough to initiate fog droplet growth. However, on cold clear nights, the temperature of the air mass in the bottom of the valley may continue to fall due to radiative cooling, causing the air to saturate and water vapour to condense on CCN. As the air drains down the valley sides, it can generate gentle katabatic winds that help to stir the fog and increase its optical density by mixing more moisture and CCN in the cold air mass. However, if the air in the valley bottom is chilled below the temperature of the descending air as a result of further radiative cooling, and if the descending air undergoes adiabatic warming, a layer of extremely stable air in the valley bottom may form and persist due to the warmer descending air settling over the cold air mass below. Because valley fogs tend to settle in dips and troughs in the valley floor, they can become very patchy and optically dense, making conditions extremely hazardous for transportation. Moore *et al*. (1987) described the time of day at which a low level temperature inversion occurs in the bottom of a valley, local wind patterns within the valley, and the rate of fog growth as important factors in the development of fog and its persistence in mountain valley systems. Valley fogs may also persist for several days as occurred in the Meuse Valley fog in Belgium in 1930 (Nemery et al., 2001). Here the low wind shear and the presence of a temperature inversion increased the viscosity of the stable boundary layer and allowed the concentration of atmospheric pollutants emitted by local industries to increase to acutely toxic levels which resulted in an increase in mortality of susceptible members of the local community.
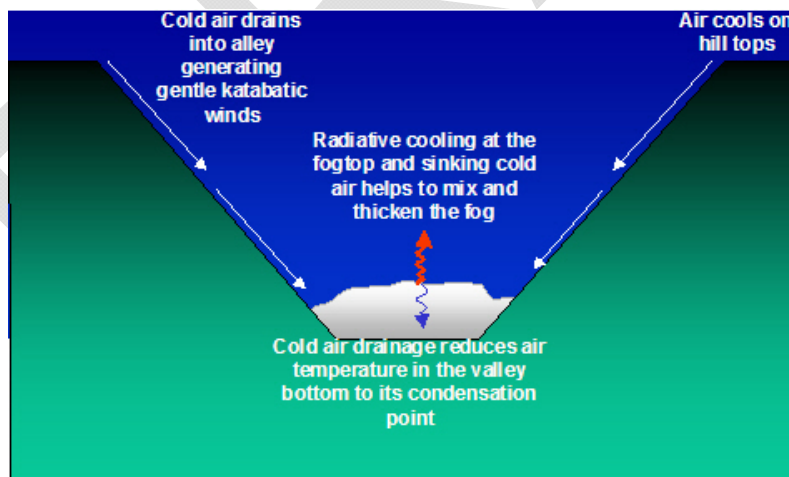

Figure 3   Schematic of the formation of valley fog.

1.2.3   Advection fogs

As the name suggests, advection fog is caused by the horizontal movement of nearly saturated air over cold land or water and can form in cloudy conditions and at wind speeds that would cause radiation fog to dissipate (Figure 4).

1.2.4   Coastal fogs and sea fog

In the mid-latitudes during autumn, winter and spring, weak slow moving synoptic scale weather systems often draw warm moist air from lower latitudes over land where the surface temperature is much cooler than the sea. If the warm air is already near saturation, and the land surface is cold enough, it will quickly cool the warm air to its dew point and fog will form that may be several tens of metres thick. However, the formation of advection fog over land can often be a consequence of both advection and radiative processes (McIlveen, 1992). If the land temperature is not sufficiently low enough to decrease the air temperature to its dew point, fog droplet growth will be suppressed and fog will not form. If warm moist air is advected inland under clear skies, radiative cooling of the land surface below the warmer air aloft may be enough to reduce the air temperature to its dew point and initiate fog droplet growth.

In the UK, coastal advection fogs are most frequent in, but not limited to, spring and early summer. At this time of year, the prevailing wind direction tends to be from the northeast, as opposed to south-westerly winds which prevail across the UK during late summer, autumn and winter (Lapworth and MacGregor, 2008). The north-easterly wind brings moist air off the North Atlantic Ocean and North Sea across cooler coastal waters and cold saturated ground. As the moist air passes over the cold surface, it is cooled to its dew point temperature, encouraging fog formation. In the UK coastal fogs may also occur during the summer months, particularly along the North Sea coastline, when warm moist air from equatorial currents is also carried to cooler more northern coastal waters, which chill the moist air to its dew point temperature. The offshore fog may be carried inland on sea breezes when the land surface warms during the day.
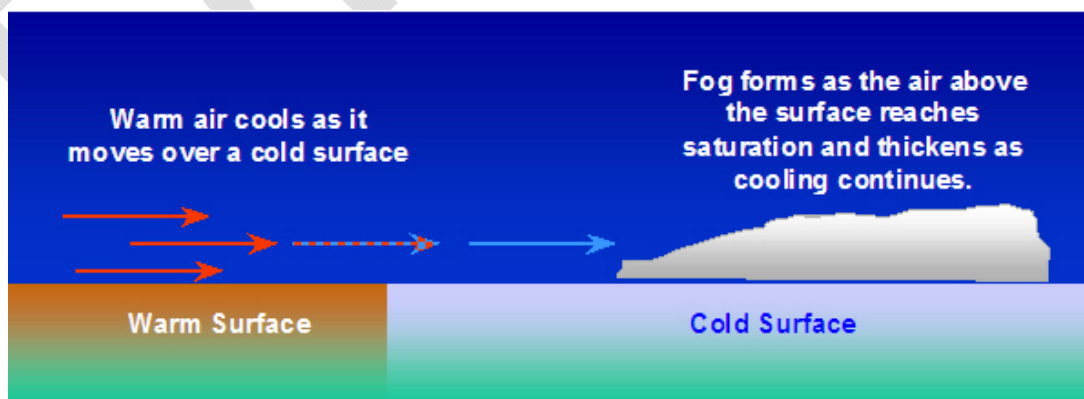
Figure 4   Schematic showing the formation of advection fog when warm moist air moves over a cold land surface.

Sea fogs may also arise as a consequence of the gradual cooling of a warm moist mass of air moving across a large fetch of gradually cooling water. These fogs

can be widespread and are characterised by low wind speeds and calm seas. The boundaries of these fog regions are often misty, caused by the condensation of moisture on extremely hygroscopic maritime CCN at relative humidity below saturation.

Sea fogs also occur at the boundaries between ocean currents of different temperature (Figure 5), as occurs along the Grand Banks off the coast of Newfoundland, Canada. The Grand Banks are one of the foggiest regions on the planet and experiences over 200 foggy days per year. Here fog forms as a consequence of warm moist air flowing northward from tropical waters along the Gulf Stream converging with the much colder Labrador Current flowing south from arctic waters. At the interface between these two waters, the cold air mixes with the warm air and the dew point temperature and air temperatures converge, encouraging the condensation of moisture on the surface of marine CCN. The resulting sea fogs can persist for many days.
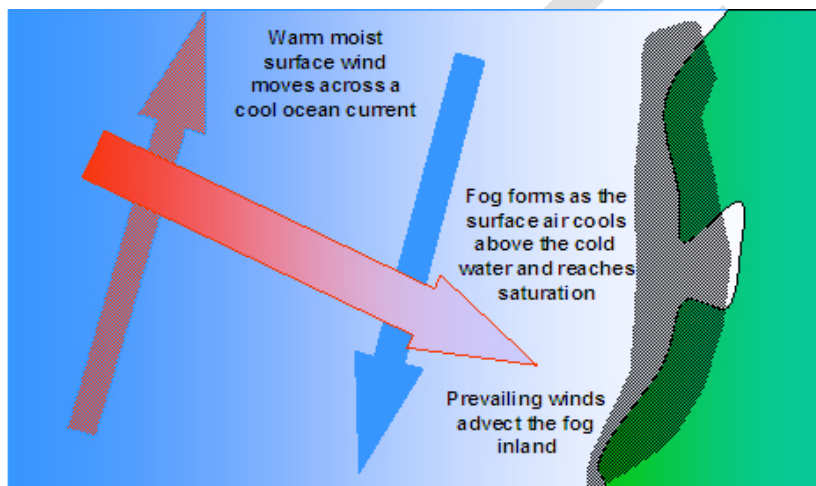
Figure 5   Schematic of the formation of sea fog.

1.2.5   Upslope or hill fog

Upslope fog or hill fog is also formed as a consequence of advection. It forms when mild, moist air undergoes orographic uplift (Figure 6). As air is forced to ascend the windward side of a mountain range or protracted slope, it undergoes adiabatic expansion. As the air expands, it may cool to its dew point temperature causing an increase in the liquid water content of the air nearest the ground.
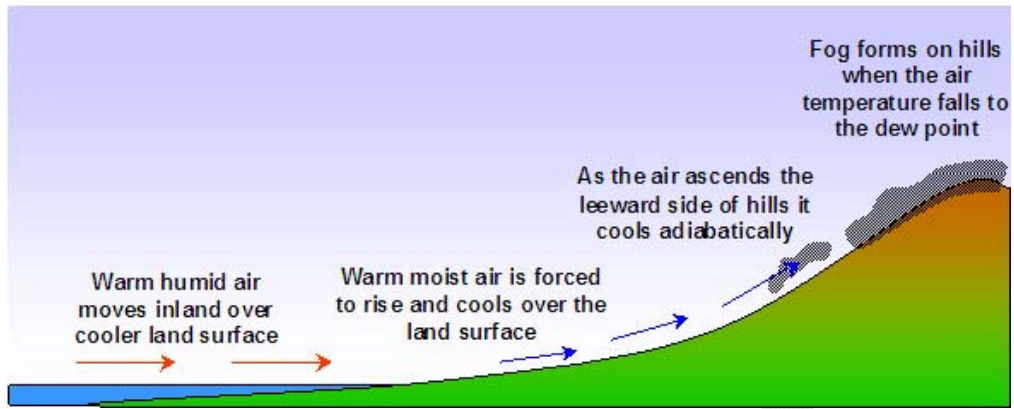
Figure 6 Schematic of the formation of upslope or hill fog.

1.2.6 Sea smoke and steam fog

As a consequence of the heat capacity of water, sea surface temperatures may be higher than the overlying air temperature. If cold air moves across warm water, the lowest layer of air is warmed slightly and mild convective currents are established that mix the air (Figure 7). As the warmer air rises, it gets chilled to saturation by the overlying cold air giving the impression of steam rising from the water surface. Sea smoke is most common at high latitudes and off the coast of cold land masses such as Antarctica, where a high proportion of fog events recorded by the British Antarctic Survey at Halley Research Station are attributed to weak convective air currents being established above open water when strong katabatic winds drive freezing air off the frozen land and ice shelves (Anderson, 1993).
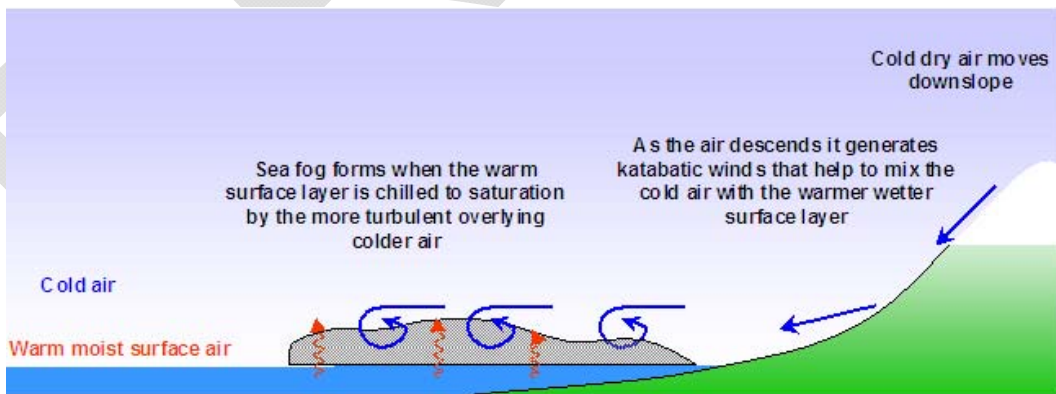
Figure 7 Schematic of the formation of steam fog.

1.2.7 Frontal fog or precipitation fog

Frontal fog (sometimes called precipitation fog) tends to occur in low and mid latitudes and forms when light rain falls through a layer of cool dry surface air. As the rain falls through this layer, it evaporates and increases the humidity of the surface air. If the air saturates, fog will form (Figure 8). As the rain evaporates, the air temperature cools and the dew point temperature and air temperatures converge, favouring the condensation of moisture on CCN and an increase in the liquid water content of the lowest layers of the troposphere. Frontal fog is likely if the air near the ground is near saturation, as evaporation of rain water from surfaces quickly saturates the layer of air closest to the ground.
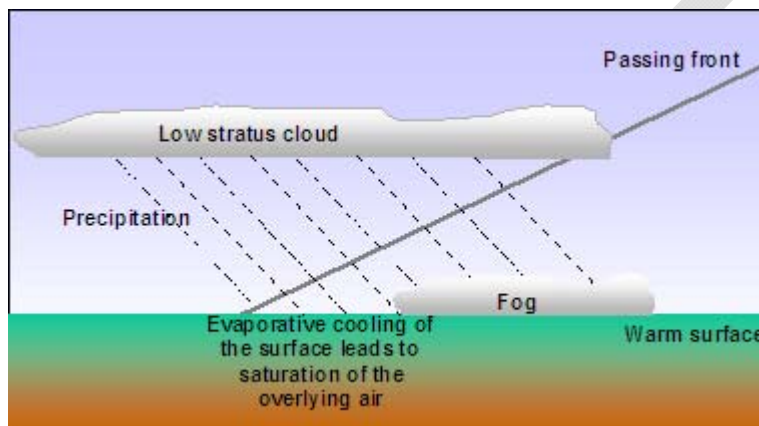
Figure 8 **Schematic of the formation of frontal fog.**

1.3. FACTORS AFFECTING FOG DEVELOPMENT, GROWTH AND DISSIPATION

1.3.1 The Kelvin effect

When relative humidity is at saturation and water condenses on a flat surface, evaporation and condensation are in equilibrium, with equal amounts of moisture entering as leaving the liquid phase. The water molecules in the condensate are bound to each other through electrostatic forces that establish a surface tension across the surface of the liquid. However, CCN are not flat, and as a consequence of the radii of the smallest CCN, each water molecule at the surface of the particle is less tightly bound because it has a lower number of attracting neighbouring water molecules than on a larger sphere. As a result, water on the surface of a particle of small radius has a higher vapour pressure than water on the surface of particles of large radius. Consequently, on small particles, competition between evaporation and condensation proceeds in favour of evaporation and higher degrees of saturation are required to maintain water in

the liquid phase. This is known as the Kelvin Effect, (named after Thomson, Lord Kelvin), which relates surface tension and aerosol growth (Equation 1):

$$\frac{p}{p_{eq}} = \exp\left(\frac{2\,\gamma\,V_m}{r\,R\,T}\right)$$

(Equation 1)

where: p is the vapour pressure of the particle; p_{eq} is the equilibrium saturation vapour pressure; γ is the surface tension; V_m is the molar volume; r is the particle radius; R is the universal gas constant; and T is the absolute temperature.

It can be seen from Equation 1 that as a particle radius decreases to a finite size, constrained by the size of gas molecules, increasing values of supersaturation will be required to initiate fog droplet growth. When considering water vapour in the atmosphere, its transition to the liquid phase in the absence of CCN would not occur until the ratio of p/p_{eq} approached 4 (i.e. 400% relative humidity) (McIllveen 1992). This is much larger than the supersaturation (relative humidity greater than 100%) values encountered in the atmosphere (at most 1% to 2% above saturation) and illustrates the importance of aerosol surfaces for condensation in the formation of fog water droplets.

1.3.2   Raoult's law

The Kelvin effect describes the effect of particle size on droplet formation, but doesn't take account of the chemical properties of particles in the atmosphere, which can be grouped according to their hygroscopic nature. For example: extremely hydrophobic aerosol will not activate to form water droplets in the atmosphere, even under extreme supersaturation values; other aerosol may be water insoluble but contain some hydrophilic sites that allow water to condense on the surface at supersaturation; and some aerosol may be extremely hydrophilic and have been reported to grow as a result of water uptake at relative humidity as low as 70% (Martikainen, 2005). Therefore, the chemical composition of CCN has considerable effect on fog formation and the effectiveness of an aerosol particle to act as CCN depends not only on its size but on its chemistry (Figure 9a). Raoult's Law states that:

"the vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component multiplied by the mole fraction of the component present in the solution".

Consequently, the presence of one or more solutes reduces the vapour pressure of an aerosol, which can have a profound effect on fog droplet growth. This was demonstrated by Mattila *et al*. (2000) who showed how, in an atmosphere of high nitric acid concentration, aerosol growth can occur even though relative humidity was below 100% (Figure 9b). This implies that in polluted environments, fogs may occur which contain CCN that start to develop into fog

droplets at relative humidities below saturation, resulting in optically dense fogs that initiate earlier, occur to a greater depth and persist longer than would otherwise occur in clean air. Similar concentration effects are also observed in marine environments where hygroscopic particles dominate CCN spectrum. However, marine aerosol tends to be dominated by large CCN, which have short atmospheric residence times due to gravitational settling.

1.3.3 The Köhler theory

The Köhler theory combines the Kelvin Effect and Raoult's Law to describe the process by which water vapour condenses on, or evaporates from curved surfaces of different chemistry, and can be used to describe fog droplet formation. The Köhler theory is based on thermodynamic equilibrium and describes the activation of fog droplets at different humidities for aerosols of different chemical composition and is calculated using the Köhler equation (Equation 2).

$$\ln\left(\frac{p(D_p)}{p_{eq}}\right) = \frac{4\,M_w\,\sigma_w}{RT\,\rho_w\,D_p} - \frac{6n_s\,M_w}{\pi\,\rho_w\,D_p^3}$$

(Equation 2)

where: D_p is the droplet diameter, p is the droplet vapour pressure, p_{eq} is the saturation vapour pressure, M_w is the molecular weight of water, σ_w is the droplet surface tension, ρ_w is the density of water, n_s is moles of solute, R is the universal gas constant and T is the absolute temperature.

Equation 2 shows how the size and chemical composition of aerosol (a function of their source) can have a profound effect on the ability of CCN to form fog water droplets.
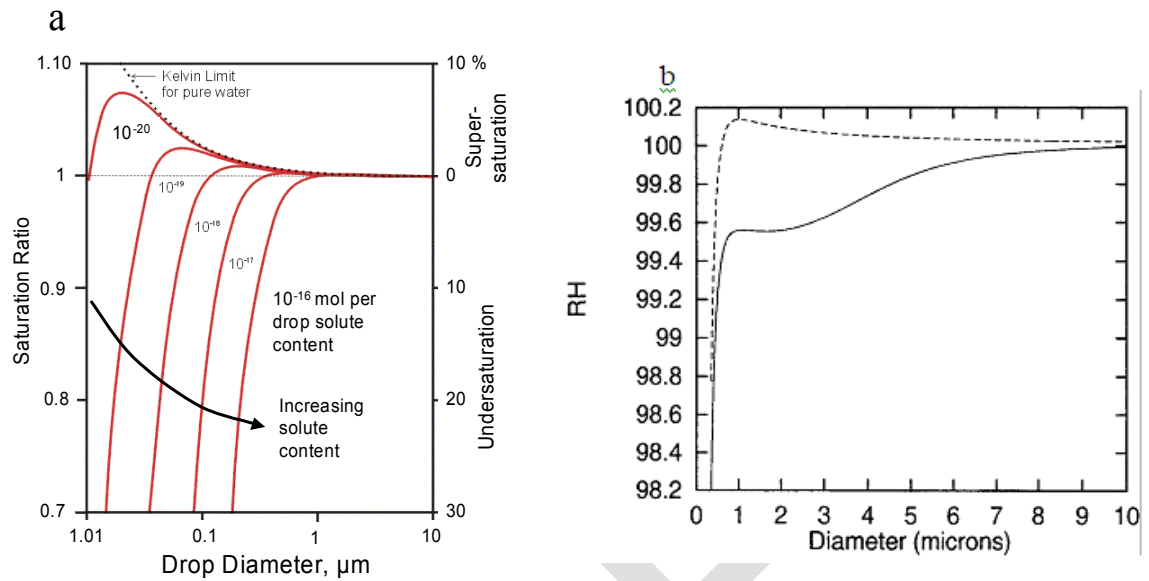
Figure 9 Plots of (a) the equilibrium saturation ratio over droplets of given size and solute content and (b) Köhler curves for ammonium sulfate particles with dry diameter of 0.1 µm. The dashed line is the normal Köhler curve. The solid line shows how the Köhler curve is depressed and droplet growth starts at lower relative humidity due to gaseous nitric acid pollution.
(Panel a from *www.ems.psu.edu/~lno/Meteo437/Figures437.html*; Panel b from Mattila et al., 2000).

1.3.4   The effects of CCN on fog formation and density

Aitken (1888) used a cloud chamber to make the first measurements of aerosol concentrations and surmised that without particles in the atmosphere there would be no clouds and no precipitation. Generally, all fog occurs when the temperature of the air and its dew point become nearly identical, which results in saturation and the condensation of moisture on CCN. However, in extreme circumstances and as a result of the physicochemical properties of cloud condensation nuclei, fog formation can also occur at relative humidities considerably lower than saturation.

The rate at which fog develops and its intensity is controlled to a large extent by the availability of CCN. In atmospheres with low concentrations of CCN, fog onset is often delayed relative to regions of high concentration, which tend to encounter fogs that are not only denser (i.e have a higher LWC per unit volume) but also occur to a higher vertical extent (Bott, 1991). Conversely, areas that have low CCN concentrations exhibit fog layer formation of low optical density that forms later in the night (Figure 10).
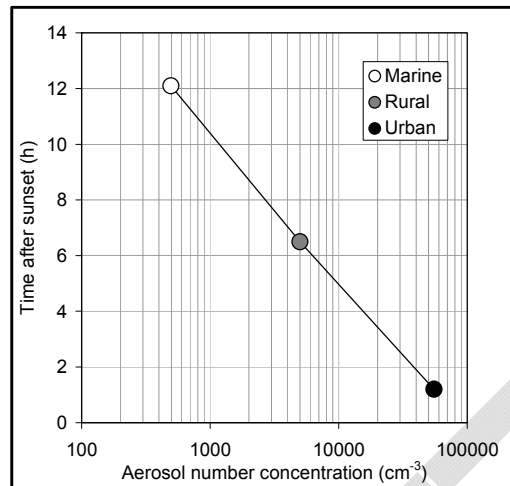
Figure 10   Time after dusk at which a liquid water content of 0.05 gm^{-3} first appeared during simulations of aerosol growth performed with maritime, rural and urban aerosols (adapted from Bott, 1991).

1.3.5   Dissipation of fog

Fog dissipation generally results from multiple processes that occur simultaneously as a result of a wide range of factors that feed back on each other. The processes discussed above in Sections 2 and 3 that govern the formation of fog (thermodynamical, radiative, and microphysical) are equally important for fog dissipation.

Fog can dissipate as a result of many physical and environmental processes that cause the air temperature and dew point temperatures to diverge. For example, advection fogs will dissipate when the fog moves from a cold surface to a warmer one. Also, hill fogs can dissipate as a result of adiabatic warming of the air mass as it descends the leeward side of a slope. In marine environments, fog can lift from the surface so that it forms a stratus deck when it comes into contact with a cold front. As the fog rises above the surface it may break up to form stratocumulus clouds.

As discussed above, radiation fogs and valley fogs usually occur in the evening and can persist through the night as a result of continued radiative cooling of the Earth's surface and as a result of radiative cooling of the fog top. However, during the day, incoming solar radiation may decrease the density of the fog top and penetrate it, warming the Earth's surface and the fog layer in contact with it. As the surface warms, convective currents become established that mix the fog layer with the overlying unsaturated air, and as the air temperature increases, the dewpoint temperature and air temperatures diverge, resulting in a shift in the equilibrium vapour pressure of the fog droplets in favour of the vapour phase. Also, as the air above the fog layer warms, large scale eddies may become established that help to generate wind shear that mix the fog layer with the overlying unsaturated air.

1.4. SOURCES OF CCN IN THE TROPOSPHERE

CCN may be emitted directly to the atmosphere (primary particles) as a result of natural activity (e.g. crustal dust, volcanic activity, biological material, sea spray, etc.) or as a result of anthropogenic activity (burning fossil fuels, biomass burning, etc.). Secondary particles are formed in the atmosphere as a result of physicochemical transformations of primary emissions (e.g. gas to particle conversions). Aerosols exhibit considerable variability in their size and composition with particle diameters (D_p) ranging between several nanometres (nm = 1×10^{-9} m) to several micrometers (μm = 1×10^{-6} m), and are usually classified into two size ranges: the coarse mode (D_p >1μm), and the fine aerosol fraction commonly known as the accumulation mode (D_p < 1μm). Table 1 shows estimated global emissions of major aerosol classes.

Aerosols tend to have the majority of their mass in the coarse mode, except in polluted urban areas where a greater mass of accumulation mode particles are emitted to the lower troposphere (Figure 11a). However, due to gravitational settling, the atmospheric lifetime of the coarse mode is comparatively short resulting in the number concentration of primary aerosol with D_p > 1 μm typically measured in the tens per cm^3 (Figure 11b). In contrast, the number concentration of primary aerosol with D_p < 1 μm typically measures several 10,000s per cm^3 (Figure 11b). Consequently, despite most of the mass of primary aerosol in natural environments being associated with the coarse mode, most of their number density is in the accumulation mode.

The mass of coarse and accumulation mode aerosol also changes on temporal and spatial scales depending on physicochemical properties and ambient conditions. For example, if the aerosol is composed of a large fraction of hygroscopic material and relative humidity increases, the mass of aerosol as well as its size distribution will increase. Also, if the number concentration of primary particles increases, the peak diameter of the accumulation mode will tend to shift to larger sizes as a consequence of coagulation (Porter and Clarke, 1997), and favour gravitational settling.

Table 1   Estimated global emissions of major aerosol classes in the 1980's (reproduced from Seinfeld and Pandis, 1998).

	Estimated Flux (Tg yr^{-1} dry mass)			
Source	Low	High	Best	Particle size category[a]
Natural				
Primary				
Soil dust (mineral aerosol)	1000	3000	1500	Mainly coarse
Sea salt	1000	10000	1300	Coarse
Volcanic dust	4	10000	30	Coarse
Biological debris	26	80	50	Coarse
Secondary				
Sulphates from biogenic gases	80	150	130	Fine
Sulphates from volcanic SO2	5	60	20	Fine
Organic matter from biogenic VOC	40	200	60	Fine
Nitrates from Nox	15	50	30	Fine and coarse
Total natural	**2170**	**23540**	**3120**	
Anthropogenic				
Primary				
Industrial dust etc. (except soot)	40	130	100	Fine and coarse
Soot	5	20	10	Mainly fine
Secondary				
Sulphates from SO2	170	250	190	Fine
Biomass burning	60	150	90	Fine
Nitrates from Nox	25	65	50	Mainly coarse
Organics from anthropogenic VOC	5	25	10	Fine
Total anthropogenic	**305**	**640**	**450**	
Total	**2475**	**24180**	**3570**	

[a]Coarse and fine size categories refers to mean particle diameter above and below 1μm, respectively
Sulphates and nitrates are assumed to occur as ammonia salts
Original source: Keihl and Rodhe (1995)

Secondary aerosol is formed when atmospheric gases enter the liquid or solid phase as a result of changes in ambient temperature, or as a result of gas phase reaction products having a lower vapour pressure than the reactants. For example, volatile organic trace gases contribute significant mass to the global secondary aerosol budget (Table 1) and can be extremely reactive in the atmosphere having atmospheric residence times of several hours to several days (Atkinson, 2000). These emissions may be anthropogenic or biogenic in origin and react with photochemical oxidants to produce particles of lower vapour pressure. These newly formed microscopic particles (Aitken mode or nucleation mode particles) may be too small to allow water to condense on their surfaces under normal environmental conditions but may coalesce due to Brownian diffusion, electrostatic attraction or phoretic effects to form particles of larger D_p. Particle growth as a result of coalescing is enhanced during turbulent mixing which induces faster particle motion and a greater probability of particle collisions.
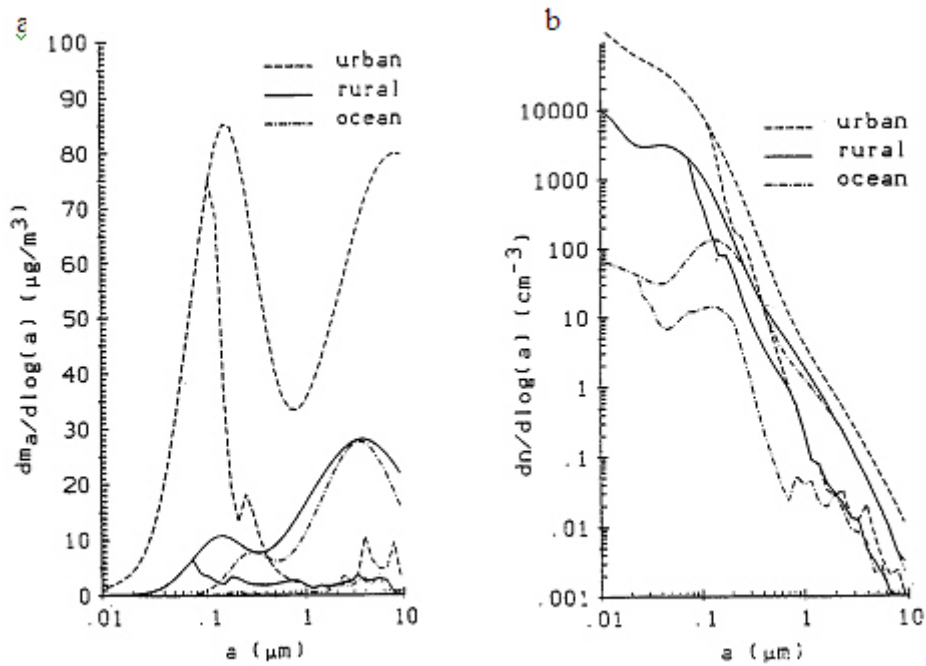
Figure 11   Modelled mass distributions (panel a) and particle number concentrations (panel b) for urban, rural and ocean environments. The upper and lower curves in each panel for the three environmental scenarios represent number concentrations and mass distributions before and after the onset of fog (from Bott, 1990).

1.5. LOCAL ENVIRONMENTAL VARIABLES

If a stable temperature profile is established above the surface, turbulent diffusion in the overlying air mass is weak and the temperature difference between the surface and the air leads to direct radiative cooling of the lower layer of the atmosphere of about 2 K h^{-1} (Turton and Brown, 1987). The presence of vegetation at the surface can influence surface temperature profiles by decreasing surface wind speed and further limiting turbulent mixing between the ground and the overlying air. Duynkerke (1991), measured surface radiation fluxes before, during and after fog formation and recorded that at night-time, surface vegetation temperatures were as much as 10 K lower than the upper soil temperature. Thus vegetation can play an important role in determining the onset of fog formation by helping to establish a sharp temperature gradient between the ground and the overlying layer of air.

The spatio-temporal heterogeneity of fog is not only a product of the difference in heat fluxes between the atmosphere and the surface, but may be regulated to a large extent by the flux of water between the atmosphere and the surface. When the wind speed is zero and the ground is dry, fog onset may be delayed as water vapour within the low level temperature inversion is depleted due to condensation on surfaces when dew forms (or hoar frost when the surface temperature is below -0.5°C). However, in the presence of a light breeze, turbulent mixing can replenish moisture in this layer, and when the air temperature at the surface layer converges with the dew point temperature,

water vapour condenses on CCN forming a shallow layer of radiation fog that may enhance the laminar appearance of the boundary layer. Radiation fogs may increase in optical density throughout the night but may also dissipate and redevelop during the same nocturnal period (Welch and Cox, 1986) as a consequence of the depletion in the liquid water content of the fog in its lower layers due to gravitational settling of fog water droplets, and its later replenishment with moist air. When considering advection fogs, moisture can also be lost from the atmosphere to dry surfaces. However, because of the higher wind speeds associated with advection fogs, turbulent mixing in the moving air mass more readily replenishes lost moisture.

If the land surface is already moist and the vapour pressure of the air is lower than the vapour pressure of the moisture at the wet surface, some of the ground moisture will evaporate into the overlying air, increasing its humidity. Turbulent mixing, nocturnal cooling, or orographic lifting may complete the saturation process and allow moisture to condense on the surfaces of CCN when the dew point temperature and air temperature converge.

Gravitational settling of fog droplets can reduce the lifetime of fog and increase visibility. At the start of fog episodes, the liquid water content of the troposphere can be high and the number of fog water droplets per unit volume large, due to relatively high concentrations of CCN. As more and more CCN become activated and grow due to the condensation of moisture on their surface and due to droplets coalescing in the atmosphere as a result of turbulent mixing and Brownian motion, the droplet size distribution increases and they fall through the boundary layer and deposit at surfaces. As more and more droplets are deposited from the troposphere the liquid water content of the air may decrease.

The LWC of fog can also be reduced due to impaction of fog water droplets on surfaces. Impaction occurs when particles moving in the atmosphere fail to follow their streamline trajectory when they approach an obstacle. If the particle has sufficient inertia, it will leave its streamline and impact on the surface so long as it is able to penetrate the surface boundary layer of the object. Similarly, if the object is of sufficiently small cross sectional area in relation to the droplet diameter, deviations in the trajectory of the air as it passes the object will be small resulting in high impaction efficiency for that object. Impaction is important for the deposition of fog water to vegetation, particularly to conifer needles, where the relatively small cross sectional area of a needle helps to increase the occult deposition of moisture (i.e. deposition of fog and mist by direct contact with surfaces). The effect of gravitational settling and impaction of fog water droplets on local air quality can be observed following fog events when the air is scrubbed clean of pollutants and visibility and air quality is improved.

1.6. ENVIRONMENTAL SIGNIFICANCE OF FOG

1.6.1   Hydrological cycle

Fog water can in many regions represent a significant component of the hydrological cycle, and collecting fog water as an alternative source of water may

be a viable option for many fog prone rural communities that don't have access to municipal water supplies. For example, villagers in the dry hillside community of Belavista, Peru, receive approximately 1.5 cm of rainfall per year (National Geographic, July 2009), and the region receives most of its moisture from fog water. The fog in this region forms when warm moist air flowing inland from the pacific encounters the hilly terrain and is forced to ascend (orographic uplift). As it rises, it cools adiabatically and the moisture it carries condenses, forming the hill fog that regularly enshrouds the region. Historically, the people of Belavista relied on expensive water for domestic use being transported to them from the Peruvian capital, Lima, but are now harvesting hundreds of litres of fog water per day during the fog season. The fog water is collected using fog collectors that use the principles of impaction. The fog collectors are simple, flat, rectangular nylon nets that are supported by posts at either end. The nets are arranged perpendicular to the direction of the prevailing wind and the fog water settles out of suspension onto the fine mesh nets and is collected in troughs or drums. The use of fog collectors by fog prone rural communities is becoming more common and several investigations have taken place to determine its viability. On the island of Tenerife, research was carried out in Teno National Park to investigate the use of fog water for domestic and agricultural use (Jaén, 2002). Results indicated that during fog events and at the highest altitudes in the park, it is possible to collect $4 \, l \, m^{-2} \, day^{-1}$ using fog collectors, with the highest amount water collected in a single day recorded at $51 \, l \, m^{-2}$. Similarly, Shanyengana *et al*. (2002) explored the possibility of rural communities in Namibia collecting fog water. They concluded that harvested fog water could be used to dilute saline bore water, making it potable. It can be seen from these and other examples (e.g. Estrela *et al*., 2009; Olivier and de Rautenbach, 2002; Pandy *et al*., 2007; Sabah *et al*., 2007) that fog water can represent a significant component of the hydrological cycle and its collection can have a positive impact on human activity. However, the concentration of pollutants in fog water can be significant, especially downwind of industrialised regions (discussed below), and care needs to be taken when using fog water for domestic or agricultural activities.

1.6.2   Ecological importance of fog water

As well as a source of water for isolated communities in arid regions, fog water can have considerable ecological significance. In a modelling exercise to determine the importance of fog water to forests in semi arid regions, Katata *et al*. (2010) draws attention to the effects of fog water not only on moisture inputs to soil from gravitational settling, leaf drip and stemflow, but also as a consequence of the direct cooling effects of the evaporation of fog water from the surfaces of heat stressed leaves. Fog water can also be of considerable importance to ecosystem function in less arid regions. For example, Dawson (1998) investigated water inputs into the redwood forests of northern California using hydrogen and oxygen isotopic signatures in fog water to trace its use. He showed that the largest of the redwood trees (*Sequoia sempervirens*) use approximately 20% of the fog water that they intercept (i.e. for transpiration), with the smaller redwood trees using larger volumes. Dawson (1998) also showed that the fog water intercepted by the trees is critical to the maintenance of the redwood forest ecosystem, with intercepted fog water accounting for two-thirds of the water used by many understorey species.

Following its interception by vegetation, the chemistry of fog water can change considerably and may represent an important pathway for the addition of nutrients and pollutants to the soil environment (Norden, 1991). Once intercepted, the fog water can become enriched in nutrients by several processes as discussed by Fisk et al. (2006), including:

- The dissolution of absorbed gaseous chemicals on vegetation being washed from above ground surfaces to the soil;

- The dissolution of solid metabolites on vegetation being washed from above ground surfaces to the soil; and

- Ion exchange or leaching of metabolites from leaves and deposition to the soil.

1.6.3　Ecotoxicological significance of fog

Fog water can bring nutrients and pollutants to fragile ecosystem and research shows that all methods of deposition (dry, wet and occult) need to be accounted for when examining chemical inputs into watersheds as each may dominate over different spatial and temporal scales.

Much of the environmental burden of sulphates, nitrates, ammonium and hydrogen ions resides in the atmosphere in liquid or solid aerosols and can be accumulated and removed in fog water (Pandis and Seinfeld, 1998). The ecotoxicological significance of occult deposition of fog water lies in the elevated concentration of chemical species found in fog droplets in many regions (Table 2).

Nitrogen, and to a lesser extent sulphur, are essential plant nutrients and are deposited to land in fog water. However, their over application can lead to the eutrophication of ground water, its acidification and direct damage to plants and surfaces. Also, essential soil cations such as Mg^{2+} and Ca^{2+} can be leached from the soil matrix and replaced with acidifying H^+ ions. Therefore, the deposition of nitrogen and sulphur are important factors within the concept of critical loads, and because of their elevated concentrations in fog water, occult deposition is particularly important in natural ecosystems which tend to have smaller critical loads than less sensitive agrosystems. The effect of acid fogs and acid rain on ecosystem function has been the cause of much debate surrounding forest decline in Europe, USA and Asia and its effects have been investigated by many researchers (e.g. Bussotti and Ferretti, 1998; Cape, J. N. 1993; Reddy et al., 1991; Longhurst et al., 1993; Larssen et al., 1999).

Table 2　　Comparison of the weighted means of pH and ionic concentrations in rain and fog water collected downwind of an industrial location (from Thalmann et al., 2002).

Ion	pH	H^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	K^+	Mg^{2+}	Na^+
Rainwater	5.3	7.9	5.6	26.9	24.5	36.7	7.6	1.8	1.2	9.9
Fogwater	4.1	123.2	42.6	646.2	437.7	925.5	53.9	12.1	13.2	46.8
Ratio rainwater/fogwater	–	16	8	24	18	25	7	7	11	5

The concentration of trace minerals and dissolved gasses in fog water experienced at a particular location is controlled by the origin of the air mass; with air that has passed over industrial regions having a greater concentration of dissolved chemical species than air that originates from cleaner environments. Figure 12 shows the results of an investigation of ion fluxes in fog water and rain water at two sites in Europe: Kerzersmoos, an arable site in Switzerland; and Waldstein in Germany, a rural site located close to the border with industrial regions in the Czech Republic. Both locations experience fogs with Kerzersmoos prone to radiation fogs, and Waldstein experiencing advection fogs with air masses originating over the Czech Republic being forced to ascend hilly terrain. Figure 12 clearly shows that pollutant concentrations in fog water deposited at these sites are affected by the origin of the air mass.

The flux of chemical species delivered to a specific location is not only a function of their atmospheric concentration, but is also affected by the site elevation. As such, occult deposition fluxes can be important in many upland regions and can vary temporally and spatially, with the greatest fluxes of pollutants tending to occur downwind of source and at elevated sites due to the higher frequency of foggy days experienced at such locations (Zimmermann and Zimmermann et al., 2002)(Figure 13).

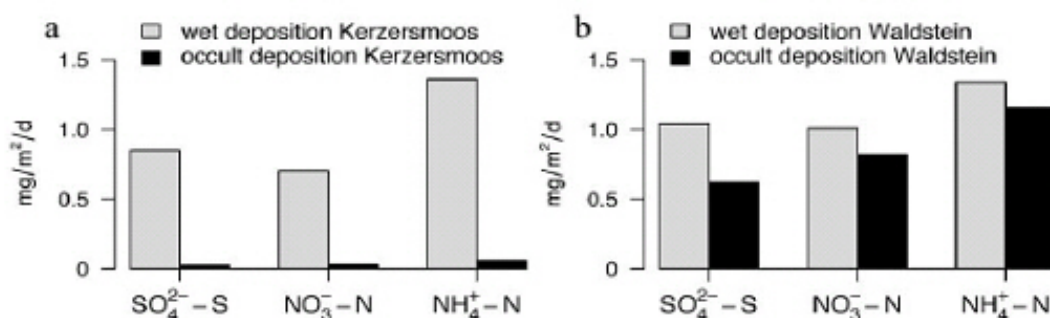**Figure 12.** **Comparison of daily average wet and occult deposition of SO_4^{2-}-sulphur, NO_3^--nitrogen and NH_4^+-nitrogen (in mg m^{-2} day^{-1}) at a) Kerzersmoos in Switzerland and b) Waldstein in Germany (from Thalmann et al., 2002)**
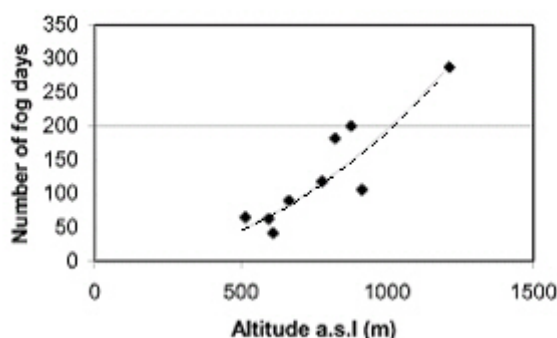
Figure 13 **Altitudinal dependence of fog frequency in Erzgebirge, Germany (from Zimmermann and Zimmermann, 2002)**

The increase in fog frequency at elevation is the result of adiabatic increases in the liquid water content of air as it rises along the windward side of hills, and needs to be considered when calculating the flux of pollutants from the atmosphere at elevated locations. Reynolds *et al*. (1997) investigated the importance of occult deposition of sulphur and nitrogen species to exposed moorland in Wales, and reported that occult deposition accounted for approximately 20% of the wet deposition of sulphur and 10% of the wet deposition of nitrogen. Similar results were observed by Dollard (1983) on Great Dunn Fell in Cumbria. However, Reynolds *et al*. (1997) and other researchers (e.g. Unsworth and Wilshaw, 1989; Vermuelen et al., 1997; Herckes et al., 2002) have also reported increased deposition of fog water for upland forested sites, due to the efficiency of fog water deposition to upland vegetation. Therefore, occult deposition to moorland and upland forests is a potentially important mechanism for the deposition of pollutants and can have potentially adverse effects on ecosystem function, particularly in the UK where many upland regions are enshrouded in cloud and fog for a considerable fraction of the year.

1.7. FOG IN URBAN ENVIRONMENTS

Brimblecombe (1981) examined the frequency of fog in London, UK, using several hundred years of historical observations. He reported that in the 17th Century there was a relatively high frequency of Fog episodes in London (twenty per year), likely due to the climatic conditions of the "Little Ice Age". Fog frequency then decreased during the 18th Century and early 19th Century before increasing to approximately 70 episodes per year during the late 19th Century. This increase in fog frequency was attributed to the distribution and strength of London's air pollution sources. Since the late 19th Century, fog episodes in London have been decreasing; however several notable fog episodes have occurred in London in the 20th Century. For example, January 1924 and December 1925 witnessed two fog events that effectively paralysed the city due to extremely low visibilities, and in November 1948, fog is reported to have contributed to the deaths of between 700 and 800 people. These deaths were caused by the interaction of smoke and fog, giving rise to the term "smog".

Smog forms when emissions from burning fossil fuels mix with water droplets in the fog generating a highly concentrated cocktail of pernicious compounds that when inhaled results in severe respiratory problems. The effect of smog on human health is probably best illustrated during what has been termed the "Great Fog" in London in 1952. Medical records for the week ending the 13th December 1952 suggest that 4,000 excess deaths occurred as a result of this fog, with a further 8,000 excess deaths over the next two and a half months. Medical records also suggest that a further 10,000 people may have suffered adverse health effects (Bell *et al*., 2003). The intensity of the smog that was generated in London due to its already poor air quality were so severe that the Great Fog led to the introduction of the Clean Air Act (1956), which introduced measures to reduce air pollution in urban areas. Nevertheless, since the introduction of the Clean Air Act (1956), there have still been several notable

smog episodes in the UK. For example, in a newspaper article titled "More smog deaths: rise in Leeds pollution" (Guardian, 7th December, 1962), it was reported that 30 acute respiratory cases had been admitted to hospital in Leeds, where sulphur dioxide concentrations were reported to be an order of magnitude greater than expected due to a widespread temperature inversion that occurred across much of the UK. This nationwide fog episode is also reported to have contributed to: 67 sudden deaths in London; a trebling of pneumonia cases in Glasgow over a four-day period; and three times higher pollution in Manchester relative to December of the previous year. The effects of this fog in the UK in 1962 were widespread as attested by vehicle breakdown recovery services, who reported that severe driving conditions with considerable ice on roads and a reduction in visibility from zero to 50 m were widespread.

A record of the cost of weather related phenomena in the United States is kept by the National Weather Service (NWS), and provides statistical summaries of fatalities, injuries and damages caused directly by weather related hazards including fog (http://www.nws.noaa.gov/om/hazstats.shtml). During the period 1995 – 2005, the NWS attribute 59 deaths, 822 injuries and financial costs of $14.2 million USD directly to fog. However, the NWS records do not include indirect costs (e.g. premature deaths for at risk members of society affected by adverse air quality), which will likely underestimate the true social and economic impact of fog to the American public. For example, in a study of 4018 weather related aviation fatalities, Pearson (2002) summarised a five year dataset between 1995 and 2000 for the USA and concluded that in 63% of cases, poor visibility including fog, was a contributing factor. Such indirect effects associated with adverse weather are not included in the NWS records.

1.8. SUMMARY

Generally the formation and dissipation of fog can be reduced to three principle processes: cooling of air and surfaces, moistening of surfaces and the mixing of air parcels of different temperature and humidity. However, this is an oversimplification of what is an extremely complex phenomenon, borne out by the difficulties facing meteorologists when attempting to forecast fog episodes. This was highlighted by Pagowski *et al*. (2004) who pointed out the highly variable nature of fog due to the complex interactions between physical processes occurring during a fog episode. Indeed, the occurrence of "clouds" at ground level where CCN concentrations are high and surface characteristics are diverse, suggests that complex interactions exist between heat, water, and chemical fluxes during the development, growth and dissipation of fog (Rangognio *et al*., 2009).

The development, growth and dissipation of fog can have a profound effect on our environment and its occurrence is not only a product of the micro-physical properties of CCN and synoptic scale meteorology, but is also heavily influenced by local environmental factors. As a result, the spatial and temporal heterogeneity of factors that contribute to fog formation make forecasting its occurrence, depth and optical density extremely difficult. For example, night-

time radiation fogs form when the ground emits more longwave radiation than it receives from the atmosphere, which may be balanced temporarily, by the upward movement of heat through the soil to the surface. Also, the deposition of dew on surfaces can delay the onset of fog by reducing relative humidity in the lowest regions of the troposphere.

The extent to which visibility at the Earth's surface is affected as a consequence of moisture condensing on CCN depends on many factors including, but not limited to:

- Cooling of warm moist air;

- Vertical mixing;

- Surface type;

- Advection and convection process;

- Heat and moisture transport in soil;

- Topography;

- Longwave radiative cooling at the fog top;

- Deposition;

- Shortwave radiation; and

- CCN size distribution and their physicochemical properties.

2   COMPARISON OF THE PRINCIPAL IONS PRESENT IN FOG WATER AND ITS ECOTOXICOLOGICAL SIGNIFICANCE IN NATURAL ENVIRONMENTS

Introduction

As a consequence of the small radius of fog water droplets and their occurrence at the Earth's surface where the atmospheric concentration of pollutants is high, the concentration of ions in fog water can be significant and is usually higher than in rainwater (Sigg et al., 1987; Burkard et al., 2003). As a result of the scavenging efficiency of fog water, the rate of removal of pollutants from the atmosphere on foggy days has been estimated to occur 5 to 20 times faster than on non-foggy days (Waldman and Hoffmann 1987). Occult deposition can therefore contribute significantly to pollutant deposition at the Earth's surface in areas prone to high incidence of fog (Weathers et al., 1986; Hameed et al., 2000; Wrzesinsky and Klemm, 2000; Thalmann et al., 2002). As the fog water droplets coalesce in the atmosphere, they combine the chemistry of their waters and reactions occur in the liquid phase (Dentener and Crutzen, 1993). Also, the chemical constituents of fog water may combine to form agglomerates (Schumann, 1991) that may undergo repeated cycling through several fog events where they undergo heterogeneous (liquid and solid phase) reactions or coalesce leading to CCN of mixed chemical composition that shift the aerosol size distribution to the coarse mode and increase deposition rates. Factors that affect the chemical composition of fog water include: the history of the air mass; homogeneous (gas phase) nucleation; surface condensation reactions; coagulation; and scavenging of atmospheric aerosol. According to Raoult's law, particles of increasing solute concentration can act as CCN at lower water vapour saturation than the original aerosol.

Many researchers have described a strong inverse relationship between the ionic strength of fog water droplets and the liquid water content of the fog (e.g. Waldman et al., 1982; Munger et al., 1983; Führer, 1986; Fuzzi, 1986; Gervat et al., 1988; Capel et al., 1990; Elbert et al., 2000 and others), which was described by Junge (1963) using:

$$B'(m_B) = \mathcal{E} \ C_a L^{-1} \qquad \text{(Equation 3)}$$

where $B'(m_B)$ is the molality of a chemical in fog water, $\mathcal{E}$ is the scavenging efficiency, C_a is the concentration of the chemical in air (liquid or gaseous) and L is the liquid water content of the fog. The term molality describes the number of moles of solute per kilogram of solvent and is often used when describing the concentration of ions in solution as it is independent of physical conditions. Figure 14 shows the sum of the molalities of the anions in fog water samples collected in orographic cloud at a maritime and continental site plotted against liquid water content. This relationship between liquid water content of the fog

water and its ionic strength explains why solute concentrations are sometimes high at the beginning of a fog event when the fog liquid water content is low and decreases as the fog increases in intensity. As the fog begins to dissipate the solute concentration increases again as liquid water enters the vapour phase.

a   b
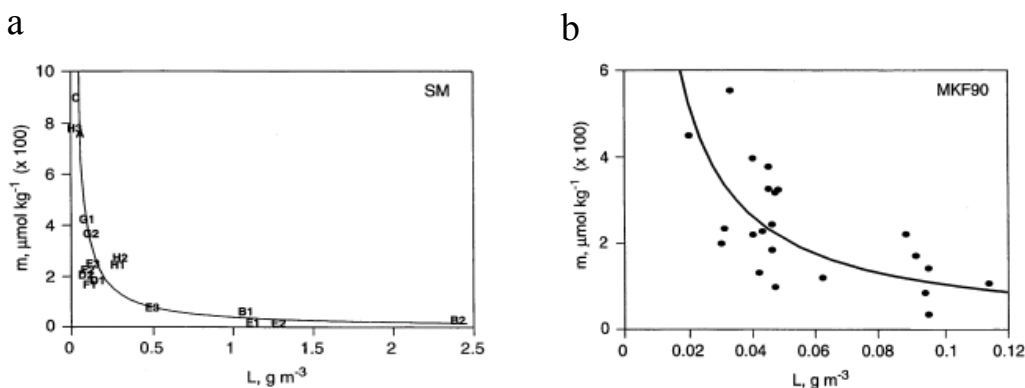
Figure 14   Sum of the molalities for anions (Cl^-, NO_3^- and SO_4^{2-}) collected at: a) a marine site in the Azores; and b) a continental site in Germany and plotted as a function of liquid water content (from Elbert et al., 2000).

Composition of fog water

Given that pollutants are accumulated in fog water and that many regions are subject to high fog frequency, an understanding of the chemistry of fog water is of paramount importance when considering the ecotoxicology of fog in different environments. In marine environments, the chemical composition of fog water generally reflects that of the oceans but can vary considerably as a result of a number of different processes including: long range transportation of continental air; aerosol production as a result of bursting whitecap wave bubbles; and particle removal by deposition and precipitation (Fitzgerald, 1991). Biological activity in the ocean can also affect the chemistry of marine fog water. For example, marine fogs above plankton rich waters are likely to be high in SO_4^{2-} relative to less productive regions as a result of dimethylsulphide (DMS) emissions and its subsequent oxidation. The chemical composition of sea fog recorded over the north Pacific is provided in Figure 15 and shows that marine fog water chemistry is dominated by sodium (Na^+) and chloride (Cl^-) ions, but that the concentration of the various chemicals present in the fog water can vary spatially and temporally. Also worthy of note is the contribution of anthropogenic emissions (i.e. non-sea salt sulphate, termed nss-SO_4^{2-}; nitrate, NO_3^-; and ammonium, NH_4^+) in the fog water samples (Sasakawa and Uematsu, 2005). Similar results have been reported by other researchers (e.g. Sasakawa et al., 2003; Narita et al., 2007)
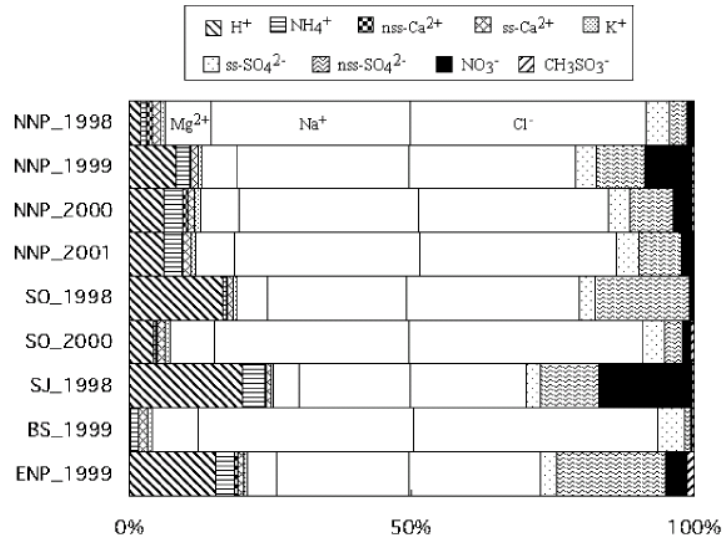
Figure 15   Mean chemical composition of fog water collected over different years at different locations in the North Pacific (north-western North Pacific, NNP_1998 to 2001; Sea of Okhotsk, 1998 and 2000; Sea of Japan, SJ_1998, Bering Sea, BS_1999; and north-eastern North Pacific, ENP_1999) (from Sasakawa and Uematsu, 2005).

The effect of anthropogenic activity on the chemistry of fog water has also been observed in more remote marine environments. For example, Rice and Chernyak (1997) reported the occurrence of pesticides in polar marine ecosystems and evaluated the importance of fog in the transport of these chemicals. They found the concentration of pesticides in fog water were much higher than adjoining compartments of snow, ice, air or water.

In less remote marine regions, the concentration of pollutants routinely measured in coastal fogs increases with the length of time the fog has travelled along the coast. Klemm et al. (1994) examined the concentration of fog water at New England on the east coast of the USA. The chemical composition for the six fog events investigated by Klemm et al. (1994) is provided in Table 3 and shows that the fog water at this measurement site was strongly influenced by sea salt (Na^+ and Cl^-). Air masses that travel along the coast (i.e. from the south, events 2, 3 and 5), showed concentrations of pollutants such as ammonium (NH_4^+), nitrate (NO_3^-), sulphate (SO_4^{2-}) and ambient SO_2 volume mixing ratios that were higher, and had lower pH values lower than air masses that had more maritime easterly trajectories (e.g. fog event 4). It is worthy of note that the fog event with the lowest wind speed, and hence least mixing (i.e. fog event 1), had the lowest pH value recorded for these six fog events and the highest SO_2 volume mixing ratio.

Table 3   Physical and chemical characteristics of 6 coastal fog events at the same site in New England, USA (LWC is liquid water content and LWA is liquid water acidity). Rreproduced from Klemm et al., 1994.

Event No. Date	1 15 Mar	2 16 Apr	3 15 Jun	4 17 Jun	5 24 Jun	6 27 Sep
Observed physical and air chemistry parameters						
Wind speed (m s^{-1})	Calm	1	2	0.5	1.5	1
Wind direction	(W)	S	SE	E	SE	W
Temperature ($^\circ$C)	4	7	13	13	15	15
LWC (g m^{-3})	0.065	0.050	0.032	0.065	0.099	0.086
SO$_2$ (ppb)	5.6	2.5	4.9	1.5	2.6	2.1
Fog water chemical analyses						
pH	2.74	3.06	3.04	4.37	3.19	3.94
NH$_4^+$ (10^{-6} eq. ℓ^{-1})	454	240	224	135	782	101
Na$^+$ (10^{-6} eq. ℓ^{-1})	558	817	1934	577	318	142
K$^+$ (10^{-6} eq. ℓ^{-1})	13	19	49	17	16	6
Ca^{2+} (10^{-6} eq. ℓ^{-1})	15	18	53	13	12	5
Mg^{2+} (10^{-6} eq. ℓ^{-1})	62	94	345	83	39	17
Cl$^-$ (10^{-6} eq. ℓ^{-1})	940	1021	2437	665	453	190
NO$_3^-$ (10^{-6} eq. ℓ^{-1})	1149	1167	720	96	615	143
SO$_4^{2-}$ (10^{-6} eq. ℓ^{-1})	678	159	428	63	446	54
Analytical acidity computations						
LWA (ppb)	2.8	0.9	0.7	0.1	1.3	0.2
LW-nss-SO$_4^{2-}$ (ppb)	0.91	0.11	0.22	0.04	0.70	0.08
LW-NO$_3^-$ (ppb)	1.62	1.21	0.48	0.13	1.02	0.27
LWA/(2·LW-nss-SO$_4^{2-}$ + LW-NO$_3^-$)	0.82	0.63	0.74	0.30	0.53	0.47

The chemistry of fog water in terrestrial environments is also highly variable. In remote background sites, the relative contribution of base cations such as Mg^{2+}, K$^+$ and Ca^{2+} can be significant, but in agricultural areas the chemical composition of fog water tends to be dominated by NH$_4^+$. In urban environments and downwind of industrial regions, the atmospheric concentration of SO$_2$ and NO$_X$ (NO + NO$_2$) can be several orders of magnitude higher than in more remote regions and dominate fog water chemistry.

Emissions of pollutants can increase the frequency of fog events and lower the pH of fog water. As fog becomes more acidic it can result in significant environmental costs on local, regional and continental scales. Elevated concentrations of inorganic nitrogen in fog water also have implications for the eutrophication of natural waters and species diversity in terrestrial environments. The chemistry of fog water in three distinctly different regions; tropical rainforest, a European upland conifer forest and urban site is provided in Table 4 and shows that the concentration of ions in fog water of polluted environments can be several orders of magnitude greater than in more remote regions and that in polluted regions and less remote rural sites, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ concentrations tend to dominate fog water chemistry.

Table 4   Concentration of anions, cations and pH values in fog at a tropical rainforest at Xishuangbanna, SW China (Liu et la., 2008) a forested region in central Europe (Thalmann et al., 2002) and an urban site in Strasbourg, France (Millet et al., 1996).

| | Tropical rain forest | | European forest | Urban | |
| | Xishuangbanna, SW China | | Kerzersmoos, Germany | Strasbourg, France | |
Ion	Min	Max	----	Min	Max
LWC (gm^{-3})	0.15	0.12	----	0.002	0.05
pH	5.71	7.92	4.1	2.9	5.8
Cl^- ($\mu eq\ l^{-1}$)	n.d.	59.4	43	500	13540
SO_4^{2-} ($\mu eq\ l^{-1}$)	n.d.	59.3	438	860	21620
NO_3^- ($\mu eq\ l^{-1}$)	6.7	68.7	646	400	17270
Na^+ ($\mu eq\ l^{-1}$)	11.9	57.4	47	0	2990
K^+ ($\mu eq\ l^{-1}$)	8.2	69.8	12	n.d.	1260
Ca^{2+} ($\mu eq\ l^{-1}$)	9.4	107.1	54	n.d.	7086
Mg^{2+} ($\mu eq\ l^{-1}$)	7.5	97.6	13	n.d.	1457
NH_4^+ ($\mu eq\ l^{-1}$)	n.d.	74.2	926	n.d.	12640

n.d. = below limit of detection

Fog water chemistry

The chemical composition of fog water is highly variable on both spatial and temporal scales and as such, a complete description of the aqueous phase chemistry would be prohibitive. This discussion is therefore limited to the aqueous phase chemistry of the main anthropogenic pollutants. The chemical species that will be discussed here in relation to fog water chemistry are SO_2 and oxidised and reduced nitrogen (NO, NO_2 and NH_4^+).

2.3.1   Aqueous phase chemistry of sulphur dioxide

The primary sulphur containing compounds in the atmosphere are hydrogen sulphide (H_2S), dimethyl sulphide (DMS; CH_3SCH_3), carbonyl sulphide (OCS) and SO_2, the variety of which reflects the diversity of their source.

H_2S arises from the breakdown of sulphur containing organic matter in the absence of oxygen and can also be emitted to the atmosphere as a consequence of volcanic activity.

DMS is the principle sulphur containing compound emitted from the Earth's oceans and is produced by benthic and surface organisms.

Carbonyl sulphide is the most abundant sulphur containing compound in the background atmosphere and is emitted from the marine environment and as a consequence of volcanic activity. Carbonyl sulphide is of low reactivity in the troposphere and has correspondingly long residence times.

Reduced sulphur compounds such as H_2S and DMS are readily oxidised in the gas phase by the hydroxyl radical (OH•) and nitrate radical (NO_3•) and have relatively short atmospheric lifetimes (a few days). Sulphur dioxide is the major

sulphur containing anthropogenic emission. It has an atmospheric mixing ratio of around 20 parts per trillion (ppt) (in the background marine atmosphere), which may increase by several orders of magnitude in polluted urban areas (Table 4).

Sulphur dioxide oxidises in the atmosphere to H_2SO_4 via either gas phase chemistry or aqueous (heterogeneous) chemistry. The gas phase oxidation is predominately driven by the reaction with the OH radical as follows:

$OH\bullet + SO_2 \rightarrow HSO_3^-$ (Reaction 1)

$HSO_3 + O_2 \rightarrow HO_2 + SO_3^{2-}$ (Reaction 2)

$SO_3 + H_2O \rightarrow H_2SO_4$ (Reaction 3)
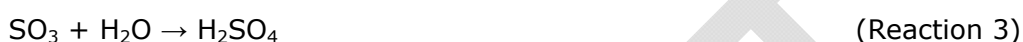
H_2SO_4 is extremely soluble in water and as such, atmospheric aerosol containing H_2SO_4 readily lend themselves to act as cloud condensation nuclei. Gaseous SO_2 is also readily soluble in water at pH >1. In the presence of moisture, including fog, rain, snow and hygroscopic aerosol, SO_2 hydrolyses in a series of pH dependent equilibrium reactions:

$SO_{2(g)} + H_2O_{(l)} \leftrightarrow SO_2 \cdot H_2O_{(aq)}$ (Reaction 4)

$SO_2 \cdot H_2O_{(aq)} \leftrightarrow HSO_3^- + H^+$ (Reaction 5)

$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ (Reaction 6)

The sensitivity of these equilibria to pH is illustrated in Figure 16 and shows that under environmentally realistic pH values, the bisulphite ion (HSO_3^-) dominates fog water. However, as the acidity of the water decreases, equilibrium of reaction 5 shifts in favour of gaseous SO_2 (out gassing).

As SO_2 enters the aqueous phase, the dissolved sulphur ($SO_2 \cdot H_2O$, HSO_3^-, SO_3^{2-}) becomes oxidized to the more stable SO_4^{2-} ion with the consequent formation of sulphuric acid (H_2SO_4). The most important oxidation reactions to form SO_4^{2-} are with ozone (O_3), hydrogen peroxide (H_2O_2) and molecular oxygen (O_2). The reaction of SO_2 with oxygen is catalyzed by iron and manganese present in the cloud droplets. The oxidation of SO_2 by NO_X may be important in heavily polluted environments.
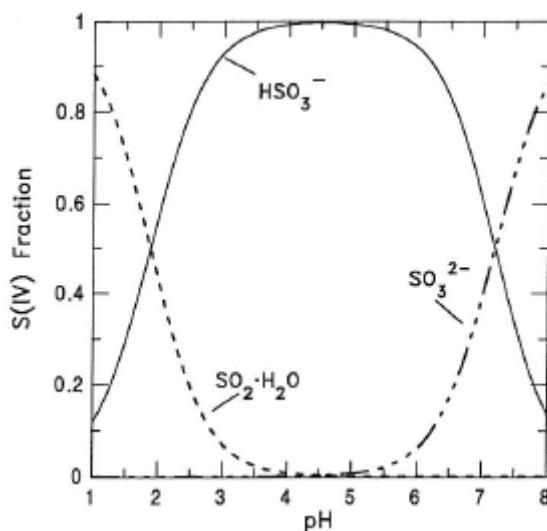
Figure 16   Concentration of S(IV) ($SO_2 \cdot H_2O$, HSO_3^-, SO_3^{2-}) species in water expressed as mole fractions (from Seinfeld and Pandis, 1998)

2.3.1.1   Oxidation by dissolved O_3

Aqueous phase reactions of SO_2 with O_3 are significantly faster than gas phase reactions (Seinfeld and Pandis, 1998). Consideration of the nucleophilic activity of S(IV) compounds (i.e. their ability to readily donate electrons) and the electrophylic properties of O_3 (i.e. its ability to accept electrons) suggests that reaction rates with S(IV) compounds should increase from $SO_2 \cdot H_2O$ to HSO_3^-, with reaction rates being fastest for SO_3^{2-}. Consequently, an increase in the pH value of a solution will increase the overall reaction rate of O_3 as a result of pH dependant increases in the equilibrium concentrations of HSO_3^- and SO_3^{2-} (Reactions 4, 5 and 6 and Figure 16).

$$S(IV) + O_3 \rightarrow SO_4^{2-} + O_2 \qquad \text{(Reaction 7)}$$

2.3.1.2   Oxidation by hydrogen peroxide and organic peroxides

Hydrogen peroxide (H_2O_2) is formed via photochemical reactions in the atmosphere. It is extremely soluble in water and its aqueous phase concentration in fog water is several orders of magnitude greater than that of O_3. Hydrogen peroxide is one of the most effective oxidants of S(IV) ($SO_2 \cdot H_2O$, HSO_3^-, SO_3^{2-}) in fog water (Seinfeld and Pandis, 1998). The reaction of H_2O_2 with SO_2 is independent of pH and extremely fast, such that H_2O_2 and SO_2 rarely exist together in fog water. Consequently, the species with the lowest concentration before the onset of fog is the generally the limiting reactant.

$$HSO_3^- + H_2O_2 \leftrightarrow HSO_4^- + H_2O \qquad \text{(Reaction 8)}$$

$$HSO_4^- + H^+ \rightarrow H_2SO_4 \qquad \text{(Reaction 9)}$$

Organic peroxides may also contribute to the oxidation of SO_2 in fog water. For example:

$$HSO_3^- + CH_3OOH + H^+ \rightarrow SO_4^{2-} + 2H^+ + CH_3OH \qquad \text{(Reaction 10)}$$
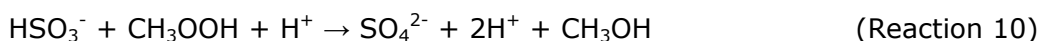
where CH_3OOH is the organic methyl peroxide and reaction product CH_3OH is methanol

2.3.1.3   Iron and Manganese catalysis of SO_2 oxidation by O_2

The oxidation of SO_2 by O_2 in fog water in the absence of a catalyst is negligible (Huss et al., 1978). However, ferric iron, (Fe^{3+}) and manganese (Mn^{2+}) are effective ca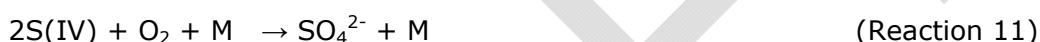talysts of the oxidation of SO_2 by molecular oxygen and are generally present in fog water as a result of the incorporation of airborne crustal material. Fe^{2+} does not catalyse the reaction. The oxidation of SO_2 by O_2 in the presence of Fe^{3+} and Mn^{2+} proceeds as follows:

$$2S(IV) + O_2 + M \rightarrow SO_4^{2-} + M \qquad \text{(Reaction 11)}$$

where M denotes the catalyst. As well as either of these minerals being capable of acting as catalysts, the presence of iron and manganese together in fog water has a synergistic effect on the reaction rate, increasing it by 3 to 10 times faster than when each of the metals are present on their own.

2.3.1.4   Oxidation of SO_2 by NO_2

NO_2 reacts with the bisulphite ion as follows:

$$2NO_2 + HSO_3^- \xrightarrow{H_2O} 3H^+ + 2NO_2^- + SO_4^{2-} \qquad \text{(Reaction 12)}$$

However, nitrogen dioxide is of only limited solubility in water and aqueous phase reactions with SO_2 to form SO_4^{2-} should be of only minor importance. However, the reaction rate increases with pH, and as such the oxidation of SO_2 by NO_2 may be of significance during fog events in heavily polluted agricultural areas where there are large emissions of soluble ammonia (Pandis and Seinfeld, 1989).

The solubility of S-compounds increases with oxidation state and is variable according to ambient conditions. When the liquid water content of the atmosphere is low (i.e. RH $\leq$ 75%), the gas phase reaction of SO_2 to sulphate is the dominant oxidation mechanism, and can be approximated to a conversion rate of $\sim$ 5% SO_2 per hour, but at higher relative humidities such as those that occur frequently over the UK, aqueous phase oxidation is likely to be the dominant process. The aqueous phase oxidation rate is highly variable and can be up to 30% per hour under polluted urban conditions. However, a more generally applicable oxidation rate is $\sim$ 12% per hour downwind of source.

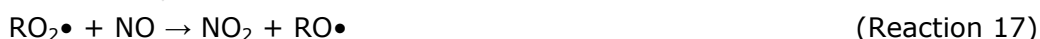# Aqueous phase chemistry of inorganic nitrogen

2.4.1 Oxides of Nitrogen

The atmospheric chemistry of NO_X is more complex than that of SO_2 and as such, it is necessary to first understand the principle gas phase reactions of NO and NO_2 before examining its aqueous phase chemistry. Atmospheric concentrations of NO_X arise as a result of anthropogenic activity and natural processes. Fossil fuel consumption and biomass burning are the major anthropogenic activities that lead to increased atmospheric concentrations of NO and NO_2, and are estimated to be responsible for 75% of the atmospheric burden of these compounds (van den Hout et al., 1990). Natural processes including: lightening; ammonia oxidation; microbial processes in soil; stratospheric input; and marine photolytic and biological processes contribute to the remainder.

In the background atmosphere away from anthropogenic sources, daytime NO_X chemistry is dominated by photo-oxidation processes. In these reactions, NO reacts rapidly with O_3 to form NO_2, which photo-dissociates to regenerate NO and O_3 in a series of cyclic reactions.

$NO + O_3 \rightarrow NO_2 + O_2$ (Reaction 13)

$NO_2 + hv \rightarrow NO + O$ (Reaction 14)

$O + O_2 + M \rightarrow O_3 + M$ (Reaction 15)

(M = a third inert molecule required to dissipate the energy generated by the reaction)

Thus, in the absence of perturbations, a gas phase equilibrium exists in the atmosphere with equal amounts of NO_2 being generated as being consumed. However, deviations from this reaction pathway occur in the presence of free radicals. For example:

$HO_2\bullet + NO \rightarrow NO_2 + HO\bullet$ (Reaction 16)

$RO_2\bullet + NO \rightarrow NO_2 + RO\bullet$ (Reaction 17)

$XO\bullet + NO \rightarrow NO_2 + X$ (Reaction 18)

where $HO_2\bullet$ is the peroxy radical, $RO_2\bullet$ is an organic peroxy radical and X is a halogen such as Cl or Br.

As a result of these reactions, the atmospheric burden of NO_2 increases, particularly in polluted areas and downwind of their source, where the

atmospheric concentration of chemically reactive precursors can be high as a result of anthropogenic activity.

Although these reactions occur in the gas phase, they are important for aqueous phase NO_X chemistry as NO and NO_2 are only slightly soluble in water, and the major sink for NO_2 in the atmosphere is its reaction with OH•. The importance of these gas phase reactions arises from their reaction product nitric acid (HNO_3), which is one of the most soluble atmospheric gasses and may enter solution on the surface of aerosol even at low relative humidity.

$$OH•_{(g)} + NO_{2(g)} \rightarrow HNO_{3(g)} \qquad \text{(Reaction 19)}$$

$$HNO_{3(g)} \leftrightarrow HNO_{3(aq)} \qquad \text{(Reaction 20)}$$

During the night, there is no photolysis of NO_2 and no generation of OH•. Consequently NO_2 oxidation proceeds via reaction with O_3 to create a nitrate radical ($NO_3•$) (as long as there are appreciable concentrations of O_3 present). The nitrate radical reacts with NO_2 producing dinitrogen pentoxide (N_2O_5), which produces nitric acid in the presence of moisture.

$$NO_{2(g)} + O_{3(g)} \rightarrow NO_3^-{}_{(g)} + O_{2(g)} \qquad \text{(Reaction 21)}$$

$$NO_3^-{}_{(g)} + NO_{2(g)} + M \leftrightarrow N_2O_{5(g)} \qquad \text{(Reaction 22)}$$

$$N_2O_{5(g)} + H_2O_{(l)} \leftrightarrow 2HNO_{3(aq)} \qquad \text{(Reaction 23)}$$

The reaction step involving water is the rate limiting step and is slow at low relative humidities, contributing approximately 0.3 ppb HNO_3 per hour (Finlayson-Pitts and Pitts Jr., 1986), but may become increasingly important at high relative humidity (Harrison, 1996)

A second night-time reaction pathway for the production of HNO_3 is by the reaction of $NO_3•$ with hydrocarbons:

$$NO_3^-{}_{(g)} + RH_{(g)} \leftrightarrow HNO_{3(g)} + R \qquad \text{(Reaction 24)}$$

$$HNO_{3(g)} \leftrightarrow HNO_{3(aq)} \qquad \text{(Reaction 25)}$$

Where RH is a hydrocarbon

As such N_2O_5 and NO_3^- are important for the night-time chemistry of fog water, especially in the early evening before the onset of radiation fog, as they not only increase the solubility of NO_X emissions but may also react with and increase the solubility of other organic compounds, increasing their concentration in the liquid phase. Choularton et al. (1992) and Colville et al. (1994) illustrated the behaviour of N-species in orographic cloud on Great Dunn Fell in the northern

Pennines in England. Choularton et al. (1992) recorded increasing concentrations of aerosol NO_3^- in fog water as air moved over the hill during the night and attributed the increase in concentration to the dissolution of N_2O_5 (Reaction 23). Similar results were reported by Colville et al. (1994), who measured higher concentrations of NO_3^- in cap cloud than at their upwind valley site as a result of Reactions 21 and 22. Clearly, when considering the efficiency of occult deposition to vegetation, these reactions have implications for the addition of nitrogen to sensitive habitats in upland regions that are generally nutrient poor.

The liquid water content of fog is approximately 0.05 gm^{-3} (Thompson, 2007), although there is much variability surrounding measurements. When the liquid water content of the atmosphere is greater than 0.01 gm^{-3} and its pH is greater than 1 (i.e. when the pH of cloud water is of environmental interest), nitric acid at equilibrium is completely dissolved and its gas phase concentration in the interstitial air spaces between fog water droplets is negligible. Once in solution, HNO_3 completely dissociates to nitrate ions:

$$HNO_{3(aq)} \leftrightarrow H^+ + NO_3^-$$ (Reaction 26)

Thus the dissolution of aerosol HNO_3 and the hydrolysis of N_2O_5 can contribute to nitrogen deposition as well as the acidity of fog water.

2.4.2 Ammonia

Natural sources of ammonia (NH_3) in the UK have been reviewed in detail in Sutton et al. (2001) and include:

- Direct emissions from humans (sweat, breath, excretion from infants that doesn't enter the sewage system, etc);

- Emissions from domesticated animals (horses, dogs and cats);

- Emissions from wild animals and sea birds; and

- Emissions as a result of biomass burning.

However, anthropogenic activity greatly contributes to atmospheric concentrations of ammonia. Table 5 gives the principle sources of anthropogenic ammonia in the UK between 1990 and 1999 and shows that ammonia emissions are dominated by agricultural sources, in particular livestock management which accounted for approximately 75% of ammonia emissions in 1999.

Table 5   UK emissions of anthropogenic ammonia (kt-N) (reproduced from NEGTAP 2001)

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	%1999
Agriculture (cultivation with fertiliser)	41	44	34	30	29	25	20	23	22	25	9%
Agriculture (livestock)	223	214	212	214	215	211	211	213	217	215	75%
Combustion (stationary)	5	6	5	5	5	4	4	4	3	4	1%
Combustion (road transport)	1	1	1	3	5	7	10	12	14	16	6%
Fertiliser production	4	4	4	4	4	4	5	3	5	2	1%
Other industrial processes (coke, paper, sugar beet, chemicals)	2	2	2	2	2	2	2	2	2	2	1%
Landfill	4	4	4	4	4	4	4	4	4	4	1%
Other (waste burning, pets, market gardens)	16	16	15	14	14	14	14	14	14	14	5%
Sewage sludge disposal	5	5	5	6	6	6	7	6	6	6	2%
Total	301	296	283	283	284	278	276	281	288	287	

As ammonia mixes throughout the troposphere it readily reacts with acidic compounds such as H_2SO_4, HNO_3 and HCl, neutralising their acidity and forming ammonium ions (NH_4^+) in the process.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad \text{(Reaction 27)}$$

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3 \qquad \text{(Reaction 28)}$$

$$NH_3 + HCl \leftrightarrow NH_4Cl \qquad \text{(Reaction 29)}$$

These reactions often result in low fog water acidity in areas of high ammonia emissions. Csequently, because the uptake of SO_2 in water droplets is inhibited at low pH, the neutralising capacity of ammonia on acidified droplets encourages the dissolution of SO_2 (Figure 16 and reactions 4, 5 and 6) and the formation of volatile ammonium sulphate salts (($NH_4)_2SO_4$; reaction 27). However, the deposition of $(NH_4)_2SO_4$ in fog water and its subsequent oxidation can yield significant concentrations of acid downwind of sources of ammonium and SO_2 under conditions of decreasing humidity such as during the dissipation of fog (Reaction 30).

$$(NH_4)_2SO_4 + 4O_2 \rightarrow H_2SO_4 + 2HNO_3 + 2H_2O \qquad \text{(Reaction 30)}$$
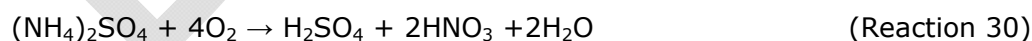
Discussion

The atmospheric burden of SO_2, NO_X and NH_3 has been greatly affected by their emission in industrial and agricultural regions where concentrations are routinely measured several orders of magnitude greater than in regions far removed from such sources (Schulze, 1989 and Table 4). The emission of SO_2 and NO_X in the atmosphere has a considerable influence on fog water acidity, reducing its pH from 5.6 (maintained by the dissolution of CO_2) (Charlson and Rodhe, 1982) to levels that are detrimental to the effective functioning of acid sensitive natural

systems. Chemical analyses of fog water routinely show that the concentration of pollutants are higher in fog water than rain water and that pH values are generally significantly lower than rain water (Igawa et al., 2002; Thalmann et al., 2002; Chernyak et al., 1996; Gordon et al., 1994 Weathers et al. 1986; Dasch, 1988; Fuhrer, 1986). Research shows that all methods of deposition, including occult deposition, need to be accounted for in order to quantify the effects of pollutants into fragile ecosystem as different deposition processes dominate over different spatial and temporal scales.

Occult deposition can contribute to the acidification of standing surface waters that are low in acid neutralising capacity (Skjelkvale et al., 2001). When acid enters water, the acidity is usually buffered by reactions with the bicarbonate ions (HCO_3^-). However, in waters with a low acid neutralising capacity (i.e. waters low in HCO_3^-), the mobility of potentially toxic trace metals such as aluminium, cadmium, copper, lead and zinc increases as a result of higher dissolution rates and lower sedimentation rates (Bache, 1986; Borg et al., 1989; Nelson and Campbell, 1991) caused by acidification. Consequently, small decreases in the pH of fresh water systems can have a profound effect on biodiversity, witnessed by depletions in fish stocks and invertebrate levels.

Nitrogen plays an important role in net primary productivity and its over application in natural environments has considerable implication for ecological community structure. In freshwater environments, phosphorous is typically the limiting nutrient, though nitrogen may also be important for net primary productivity in lakes and streams where low N:P ratios exist (Smith, 2003). Generally aquatic biota are adapted to living in nutrient poor waters where the concentration of inorganic nitrogen is low (Wetzel, 2001; Jensen, 2003).

As discussed, atmospheric pollutants can be elevated in fog water, and as such the deposition of nutrients to sensitive aquatic systems, especially standing water (e.g. lakes and tarns) can lead to their eutrophication. The symptoms of eutrophication include: shifts in phytoplankton composition to toxic and bloom forming species; changes in community structure of benthic organisms, with mass mortality events; changes in fish communities and increased fish mortality; and changes in food web structures that affect every trophic level. NH_4^+ and $NO3^-$ deposition in aquatic environments may also indirectly result in the release of phosphate from sediments which reinforces eutrophication. For a more complete discussion of the effects of inorganic nitrogen on the function of aquatic systems the reader is directed to Camargo and Álonso (2006) and references therein.

The concentration of pollutants in fog water is a function of their atmospheric concentration and time, and as such, fog water chemistry can be extremely variable and is dependant on many factors. Upland areas are generally sensitive to acid and nutrient deposition as their soils and waters are generally nutrient poor and of low acid neutralising capacity. This was highlighted in the Federal Republic of Germany in the 1980's, where it was reported that large stands of spruce and fir trees began to shed their needles and die. The symptoms of the die back was a yellowing (or chlorosis) of the needles, attributed to deficiencies in magnesium caused by acid leaching on nutrient poor soils. In extreme cases, whole stands of trees were affected and died. The cause of the acidification of

the rain and fog water at the time was attributed primarily to high SO_2 emissions upwind of the site, which caused valuable positively charged minerals (cations) to be leached from soils that have a poor cation exchange capacity (CEC). Soil becomes acidified when base cations such as Mg^{2+} and Ca^{2+} in the soil are replaced by hydrogen ions (H^+) from acids such as H_2SO_4 (reaction 9) and HNO_3 (reactions 20, 25 and 26). The NH_4^+ can also act as a H^+ donor (reaction 32). The acidification of soils has also been reported in other areas. For example, the Swedish Environmental Agency reported that in 1985 more than 40% of the soils in southern Sweden were acidified (Figure 18), but have since improved as a result of international legislation to limit SO_2 emissions. The relative decrease in SO_2 emissions in the UK between 1970 and 2007 is illustrated in Figure 19. In contrast, NO_X and NH_3 emissions have declined much more slowly (Figure 19).

Over time, occult deposition may contribute significant quantities of NH_4^+ and NO_3^- to sensitive habitats on local and regional scales, especially in areas of high fog incidence such as upland areas of the central and western UK (Figure 17). For example, Crossley et al. (1992) showed that cloud water deposition to a forest situated at 600m above sea level at Dunslair Heights in Scotland exceeded precipitation inputs by a factor of three. Similar results have been reported by other researchers (e.g. Dollard, 1983; Unsworth and Wilshaw, 1989; Reynolds *et al*., 1997; Vermuelen et al., 1997; Herckes et al., 2002).
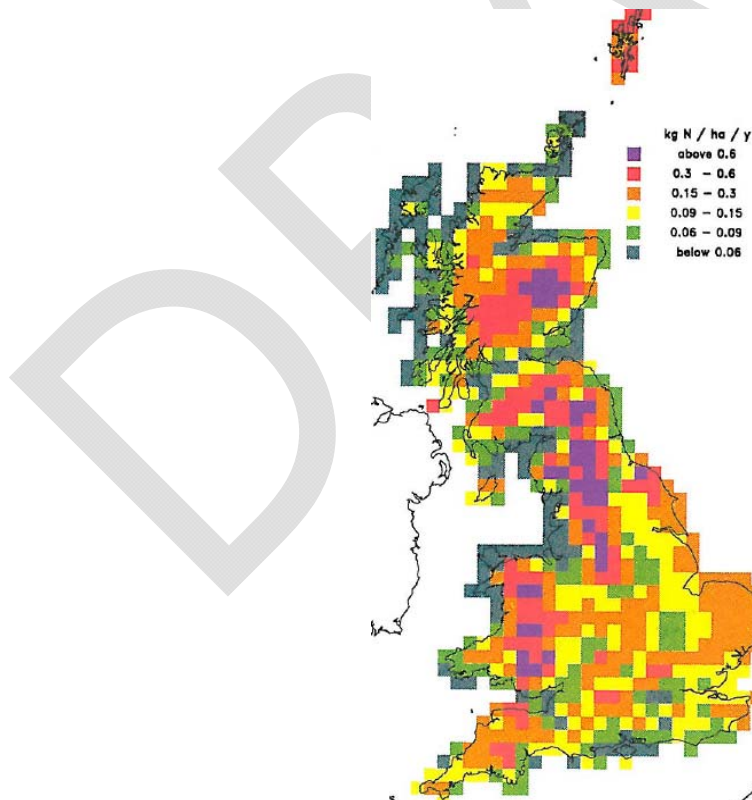

Figure 17   Cloud water deposition of total nitrogen (kg N ha-1 yr-1) in the UK 1989-92 (Source: Department of the Environment, 1994)
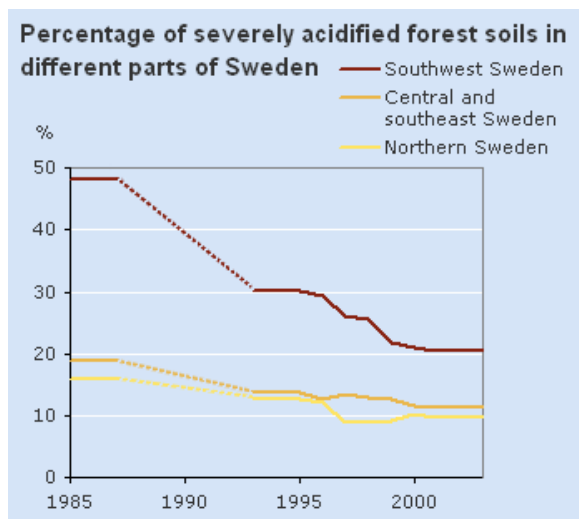
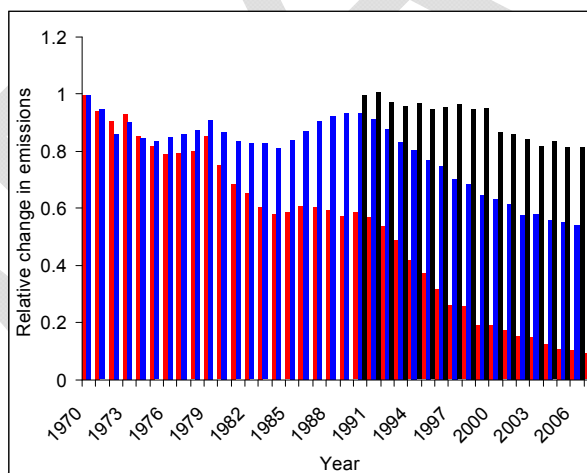**Figure 18** **The percentage of severely acidified forest soils in Sweden (Swedish Environmental Protection Agency).**

Figure 19 **Relative change in SO$_2$ and NO$_X$ emission between 1970 and 2007(red and blue bars respectively) and NH3 emissions (1990 to 2007 – black bars) for the UK (source: http://www.naei.org.uk/).**

The effects of occult deposition of inorganic nitrogen in terrestrial environments are equally complex as those for aquatic systems and have implications for plant biodiversity. Research suggests that long-term chronic nitrogen deposition can lead to loss of plant species in grasslands (Stevens et al., 2003; Clark and Tillman, 2008) and forests (Strengbom et al., 2003; Hurd et al., 1998). The effects of nitrogen deposition on tree species growing at elevation was demonstrated by McNulty et al. (1996) who reported that growth of red spruce and balsam fir declined, and mortality increased due to nitrogen addition. Similar

results have been reported for red pine (Magill et al., 2004) and oak (Wallace et al., 2007). Chronic addition of nitrogen to forest habitats may also affect the species composition of mosses and lichens, fungi, detritivores and canopy insect populations. Given that nitrogen concentrations are normally elevated in fog water, the chronic addition of nitrogen in fog prone regions as a result of occult deposition can have significant implications for community structure. For a review of the effects of nitrogen deposition on forest biodiversity the reader is directed to Xiankai et al. (2008) and references therein.

The effect of acid deposition directly onto plant surfaces is also complex. The pH of unpolluted water is typically 5.6 and research suggests that damage to vegetation doesn't usually occur until the acidity of water on leaves and needles falls to a pH of approximately 3.0 (Evans et al., 1982). The pH of fog water in polluted environments is routinely measured approaching this level (e.g. Zimmerman and Zimmermann, 2002, Colett et al., 2002; Burkard et al., 2003; Klemm et al., 1994; Raja et al., 2008; Millet et al., 1996) and can be significantly lower on surfaces, at least for short periods of time during the dissipation of fog when evaporation from surfaces results in an increase in the ionic strength of the thin film of water on surfaces. Shigihara et al. (2008) exposed seven-year-old beech trees (*Fagus crenata*) to a solution of HNO_3, $(NH_4)_2SO_4$, and $NaCl$ for approximately two years. The trees that were subjected to a pH 3.0 solution had reduced growth (measured as tree height, stem diameter, number of leaves, and dry matter production) and starch levels in stems when compared to trees growing in control plots that were misted with a pH 5.0 solution. Results of laboratory experiments showed that the amount of base cations leached from the beech leaves increased with decreasing pH suggesting that chronic acid fog exposure suppresses growth and physiological activity of beech seedlings.

Summary

The chemistry of fog water is extremely variable on spatial and temporal scales. It is affected by natural processes, although anthropogenic activity has a profound effect on its chemical composition. As a consequence of the small radius of fog droplets, they are able to accumulate pollutants at concentrations greater than in rain water. In areas that are prone to fog events, such as elevated sites or coastal regions, occult deposition of fog water may represent a significant deposition pathway for pollutants. The mass of pollutants deposited in this way is generally less than in wet deposition from precipitation, but concentrations in fog droplets can be very high leading to direct impacts.

3 MODELLING OF FOG

3.1 Fog prediction

It has been known since the end of the 19th century that aerosol particles in a humid atmosphere act like 'seeds' that initiate and accentuate the formation of water droplets, a phenomenon commented on by Mensbrugghe (1892) who wrote that, "aqueous vapour condenses in the air only in the presence of solid particles around which the invisible vapour becomes a liquid." The formation of such tiny droplets at ground level gives rise to the presence of fog, although this process (as well as the decay thereof) is not simple, being governed by a complex set of thermodynamic and micro-physical processes (Gultepe *et al.*, 2007). Of these, Duynkerke (1991) considered the most important to be:

♦ radiative cooling of moist air,

♦ mixing of heat and moisture,

♦ winds (both horizontal and vertical),

♦ heat and moisture transport within soil,

♦ horizontal advection &

♦ vegetation/topographic effects.

In addition, he noted that atmospheric stability, location and season all affect the contributions from each factor.

A considerable body of research exists into observations of fog, with numerous field studies having been conducted worldwide (e.g. Gallagher *et al.*, 1992; Fuzzi *et al.*, 1992; Gultepe & Milbrandt, 2007). Data from such field studies have been used in order to improve the understanding of fog physics and assist in the development of models to simulate the formation, development, transport and dissipation of fog. However there are still difficulties associated with such modelling. In an ideal situation, any modelling of the dispersion of airborne pollutants during the occurrence of fog should be linked with modelling of the aerosol chemistry. Therefore, to examine whether or not this occurs, a review of fog modelling is presented.

3.2 Sensing where fog forms

Remote sensing of fog using satellites is very useful for gathering information about its spatial distribution, properties thereof and rates of growth/dissipation. Several such studies have been undertaken. Underwood *et al.* (2004) investigated the parameters governing radiation fog development in the central valley of California during the Winter months from 1997 to 2000. The study used data from the Geo-stationary Operational Environmental Satellite (GOES) system, using sensors that allowed estimates of the vertical depth and spatial coverage of the fog to be estimated as illustrated in Figures 20 and 21.

However, Underwood *et al.* (2004) did caution that these sensors were susceptible to spurious signals from dust.
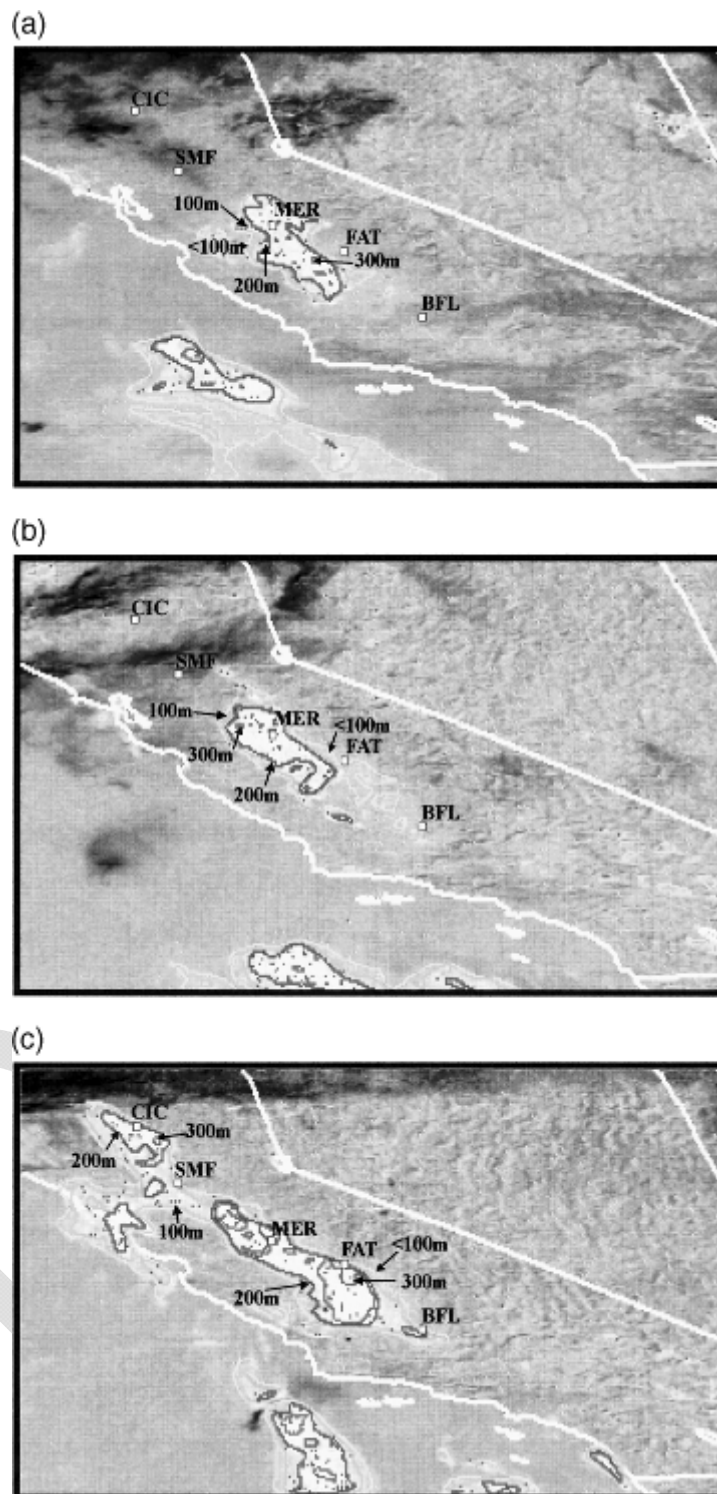

Figure 20. G.O.E.S. satellite images of developing radiation fog in the central valley of California (from the study of Underwood *et al.*, 2004). The contour lines represent fog depth. Image (a) is at (a) 18:00 local time, 24th of Nov. 2000, (b) is at 00:00 on the 25th of Nov. 2000 and (c) is at 06:00 on the 25th Nov. 2000.
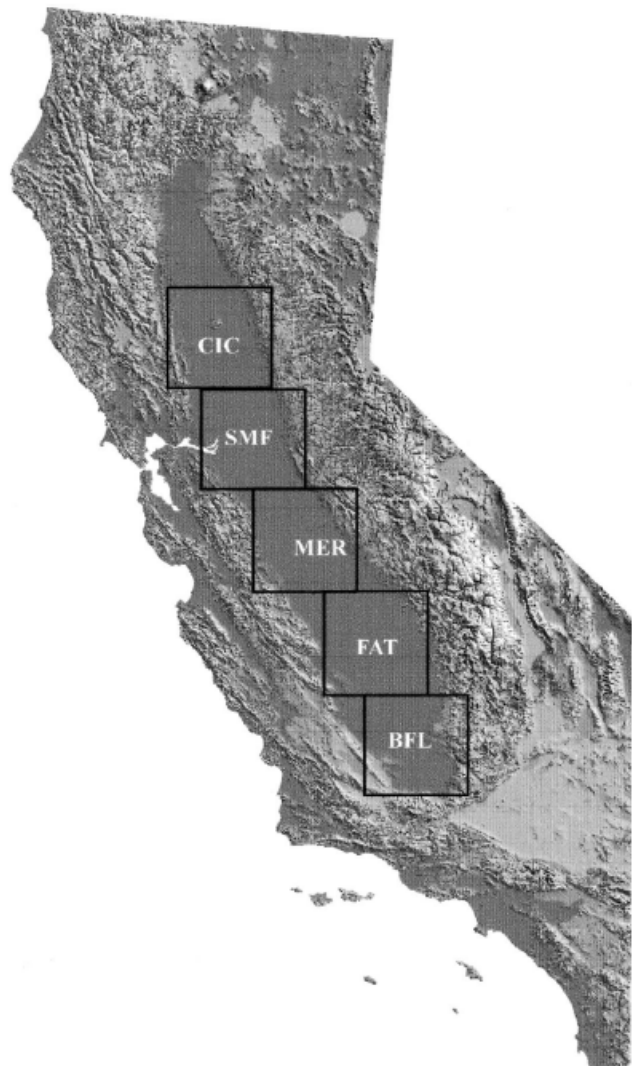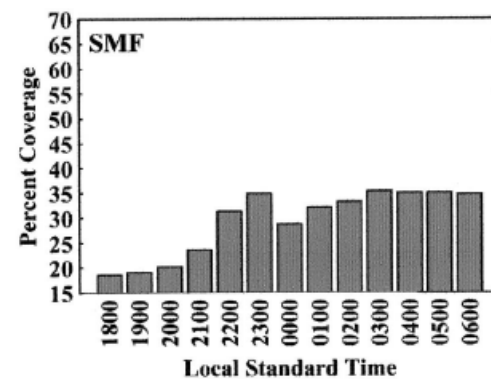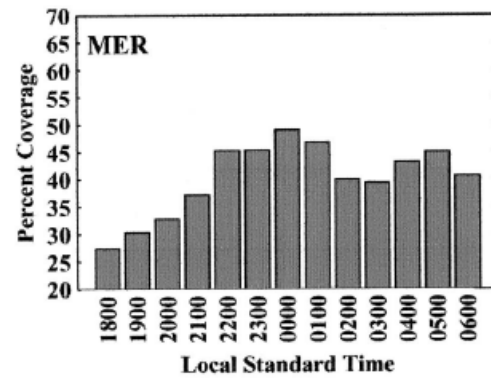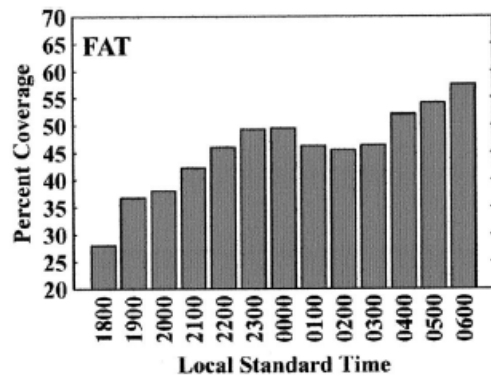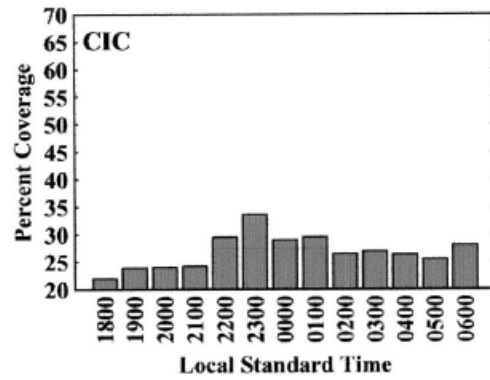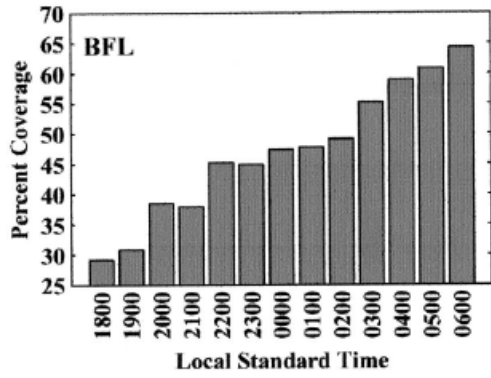
Figure 21. Percentage of ground area covered by fog (*Cp*) for five sub-divisions of the central valley of California (adapted from Underwood *et al.*, 2004). The *Cp* values were calculated based on the maximum observed coverage of fog for each area.

The study of Underwood *et al*. (2004) was driven by the desire to provide accurate data with which models could be initialised. The spatial variability in model results existed due to:

♦   local topography

♦   availability of moisture and soil conditions.

Overall fog development in the horizontal and vertical directions (including so-called 'bursts' of fog) followed temporal trends in relative humidity and surface/dewpoint temperatures. In addition, Underwood *et al*. (2004) concluded that their work confirmed the relationship between the development of nocturnal fog and the temperature conditions prior to sunset, trends in relative humidity in the evenings and surface wind speed (Fitzjarrald & Lala, 1989; Guedalia & Bergot, 1994). In addition, the precision required for diagnosing humidity levels, condensation rates & radiative exchanges are demanding from a forecasting viewpoint.

The main benefit of the work described above, in terms of operational use, is in (a) the provision of data with which models can be compared and (b) the timing of fog forecasting, as the results show that any assumptions made about the extent of fog and how it changes with time could lead to spurious forecasting. Field observations of fog are, by their nature, at discrete locations and hence the formation of fog in certain areas may well be missed depending on the resolution of the observation network. Satellite detection can reveal the full spatial distribution of fog banks as they form or dissipate and the usefulness of this has been acknowledged by others, e.g. Gultepe *et al.* (2007). However improvements in detection algorithms were considered necessary by Ellrod & Gultepe (2007). For this, more spectral channels over and above what was in current use were required, a desire expressed also by Bendix (2002) in his study of satellite-base climatology of fog in central Europe (see Figure 22). He considered that the use of geo-stationary satellites would provide better resolution and illumination. However the European *Meteosat* system then in use lacked non-absorbing-VIS and absorbing-MIR channels. Systems have been improved since then, an example of such by Bendix *et al.* (2006) is shown in Figure 22.

3.3   Modelling fog occurrence

Much work on the modelling of fog and its climatology has been concerned with forecasting the growth of fog and its associated visibility hazard. This presents a formidable challenge to numerical weather prediction models due to the often small spatial and temporal scales of fog formation (Clark *et al.*, 2008). In order to cover the wide spectrum of processes involved in shaping the complexity of fog formation and evolution, carefully designed high-resolution three-dimensional fog models are required. However they are not used extensively because of the computational cost involved in producing operational forecasts (Müller *et al.*, 2007).
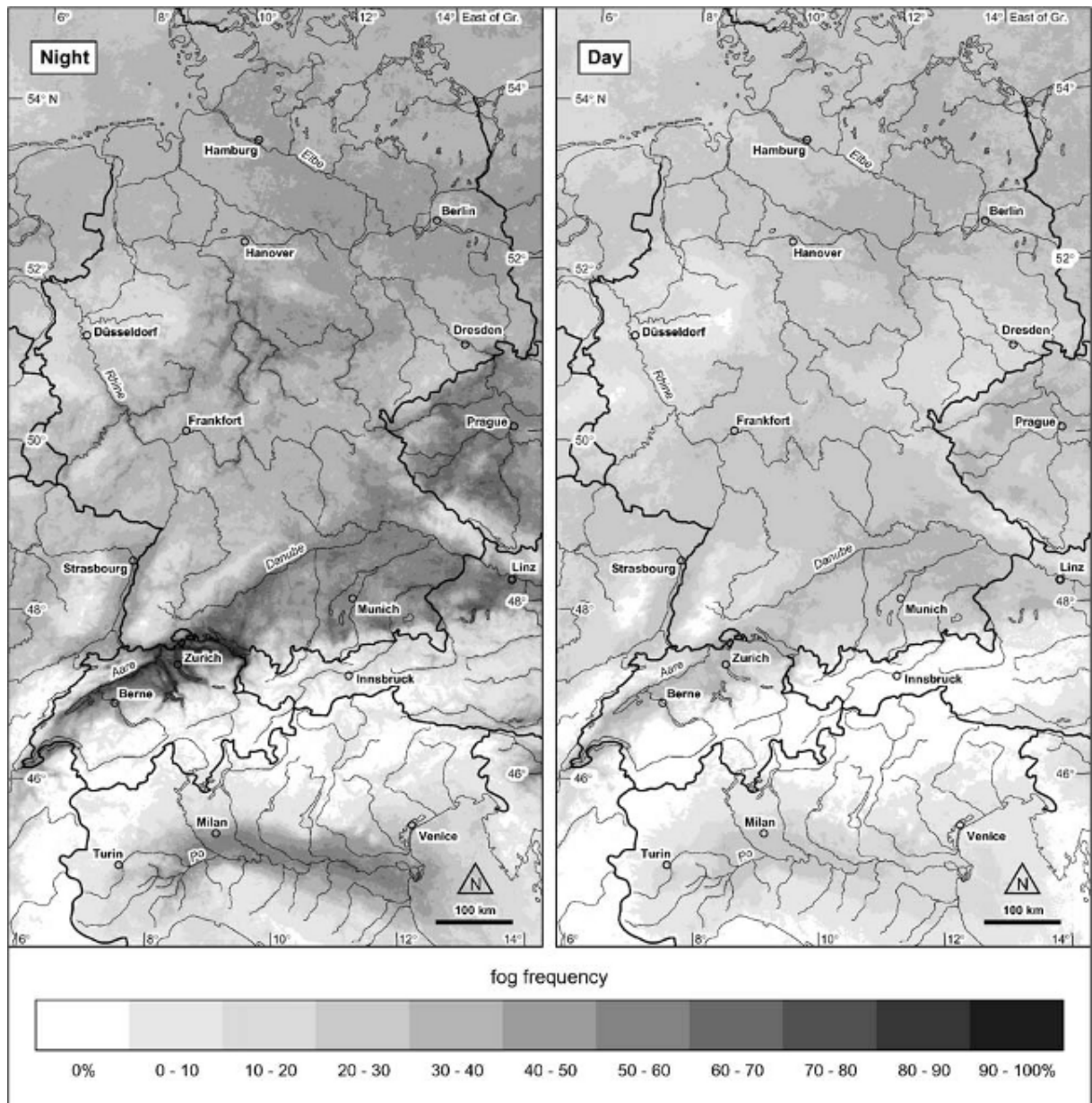
Figure 22. Maps of fog frequency over central Europe for day and night, 1989-1999, from Bendix (2002). The maps are based on 102 satellite image pairs (left: 22:00-09:00; right: 09:00-22:00).

Certain fog models are referred to as one-dimensional in that they model vertical fog development on a very localised scale (*e.g.* Duynkerke, 1991; Bott & Trautmann, 2002; Tardif, 2007). They require data from sources such as observations or larger-scale, three-dimensional models in order to provide the initial conditions, but have relatively high vertical resolution and are less demanding on computational resources in comparison with the latter models. One consequence of this is that ensemble predictions using one-dimensional models are possible, due to the need to ascertain the effects of uncertainties in initial conditions and physical parameterisations.

From the numerical modelling point of view, important issues are the horizontal and vertical resolutions, examples of such issues being provided by Pagowski *et*

al. (2004) and Tardif (2007) respectively. In addition, the methods by which physical variables are incorporated into models are of major importance as incomplete treatment of the physics and chemistry of fog can lead to major errors (*e.g.* Gultepe *et al.*, 2009).

In some situations, where forecasts are required for specific sites and updated frequently (*e.g.* airports), ensemble forecasting using one-dimensional models may be suitable, particularly if local observations are available with which the model can be initialised (*e.g.* Bott & Trautmann, 2002; Tardif, 2007). However, it should be borne in mind that ensemble forecasting does not necessarily provide an accurate forecast, rather it provides a probable likelihood of fog occurring. Additionally, Müller *et al.* (2007) cautioned that the use of such models becomes less appropriate as the complexity of the terrain increases.

Gultepe *et al.* (2007) considered the applicability of the different modelling strategies for fog forecasting and various parameterisations required extensive research: modelling did not provide a clear answer about the role of radiative processes and turbulence, especially as the latter tended to be parameterised. Basic research was still needed with respect to:

♦ the role of turbulence

♦ interactions between the atmosphere and an underlying complex surface, particularly during the stable regime in the nocturnal boundary layer.

♦ data from recent or upcoming field experiments

♦ the use of results from a wide range of models (direct numerical simulation, large-eddy simulation, one- and three-dimensional models)

♦ fog formation in the turbulent high wind conditions should be investigated

♦ large-scale systems that give rise to fog, e.g., frontal systems

3.4 Forecasting Models

Models that are capable of handling the processes within clouds do exist currently. One such example is the model *MIFOG* (Bott *et al.*, 1990). This is a two-dimensional model in which the evolution of and micro-physics of fog are modelled on a spectral basis. Hence it is possible to describe the interaction between the atmosphere and the earth's surface covered with different types of vegetation. However, due to its complexity, the coupled fog-vegetation model cannot be used for routine fog forecasts. Therefore Bott & Trautmann (2002) developed the one-dimensional parameterised model *PAFOG* from *MIFOG*. The main difference between *PAFOG* and *MIFOG* is that the latter's spectral cloud module has been replaced by a parameterisation scheme. This simplification rendered it possible to obtain forecasts for a particular location, for up to thirty-six hours ahead, in a matter of minutes using a typical desktop computer. Sensitivity studies showed that fog evolution was relatively sensitive to the choice of the parameters however. An example of this is shown in Figure 23. Although the physical assumptions of a one-dimensional model imply no vertical motion, it was necessary to include large-scale subsidence in the model

equations in order to obtain a reasonable time evolution of the cloud. In addition, problems arose sometimes if the temperature of the soil and its volumetric moisture content were unknown.

Prediction uncertainties, due to the choice of initial conditions, for one-dimensional modelling were discussed by Clark *et al.* (2008), Müller *et al.* (2007) and Rémy & Bergot (2009). One-dimensional models are unable to simulate horizontal velocity gradients and cannot cope with advection. Such models do not consider changes in humidity, temperature and wind caused by advection and the possibility exists that large errors will develop over time. In addition, if ground-level observational data are used to initialise the model, their predictions at altitude are questionable. Rémy & Bergot (2009) found that, for one-dimensional models, the most crucial observations to help with initialising and forecasting fog were ones that provided an estimate of the initial height of the cloud. Müller *et al.* (2007) claimed that it was possible to compute, on a hourly basis, a fog forecast for the next 18 hours using a single workstation; examples of the ratio of correct:incorrect forecasts are shown in Figure 24. In addition, they suggested that, on balance, a coupled one-dimensional ensemble seemed to be better than a three-dimensional forecast in simple terrain, whereas in complex terrain a three-dimensional forecast could be more accurate.

The vertical resolution of models affects the forecasting accuracy, as found by Tardiff (2007) and Clark *et al.* (2008). Using the *COBEL* fog model, Tardiff (2007) considered that, overall, using a higher vertical resolution improved the model predictions, although certain features were represented better by a low-resolution model. The former was more accurate in its representation of the initial formation and ground-fog phases, especially the first few metres above the ground. Clark *et al.* (2008) appreciated that numerical models required appropriate vertical resolution near the ground in order to resolve the evolution of the near-surface layers of the atmosphere in stable conditions and to estimate local vertical gradients. Fine horizontal resolution was needed to represent the local orography, soil, water and vegetation properties that influence fog formation.

One-dimensional models have the high vertical resolution required to predict fog formation, but need larger-scale input from a three-dimensional model to capture the role of horizontal advection. Alternatively, the use of monitoring data (*e.g.* radiosondes) to initialise a model (*e.g. PAFOG*, Bott & Trautmann, 2002), was considered suitable only for cases with negligible advection. Clark *et al.* (2008) described the use of the United Kingdom Meteorological Office's three-dimensional, *Unified Model* in predicting fog/aerosols and visibility, with detailed descriptions of how the model treats them in a non-linear fashion. This is a weather prediction model capable of modelling weather systems on international scales. Results from case studies have shown that the assimilation of observational data improved the prediction significantly (Figure 25). It should be borne in mind however, that the horizontal resolution used was 4 × 4 km. If modelling a point release from a stack however, such resolution is likely to be too coarse.
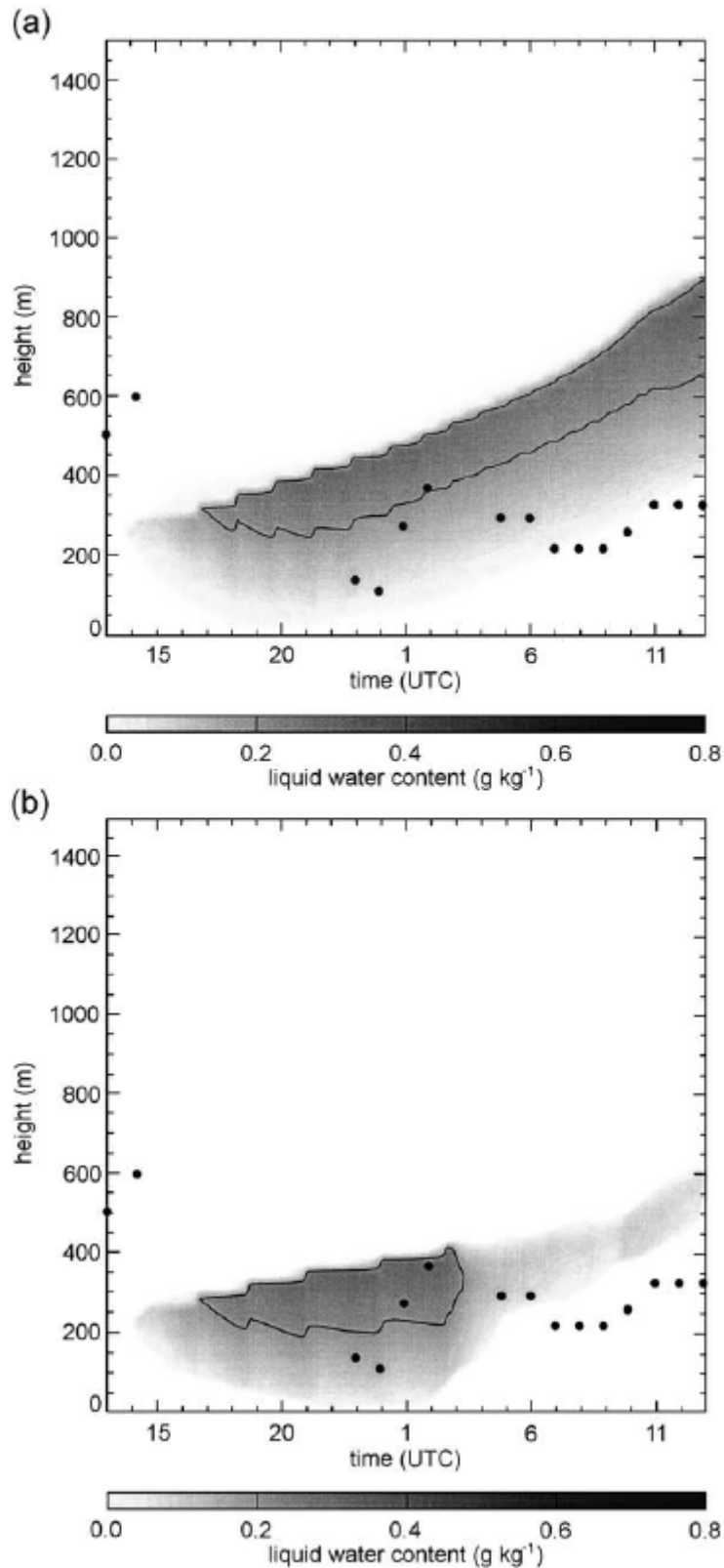
Figure 23. Contour plot of the liquid water content above Lindenberg observatory, Germany on the 21st of November 1998, computed by Bott & Trautmann (2002). Image (a) shows the result without large-scale cloud subsidence in the model's equations, whereas image (b) presents results with the inclusion of this.
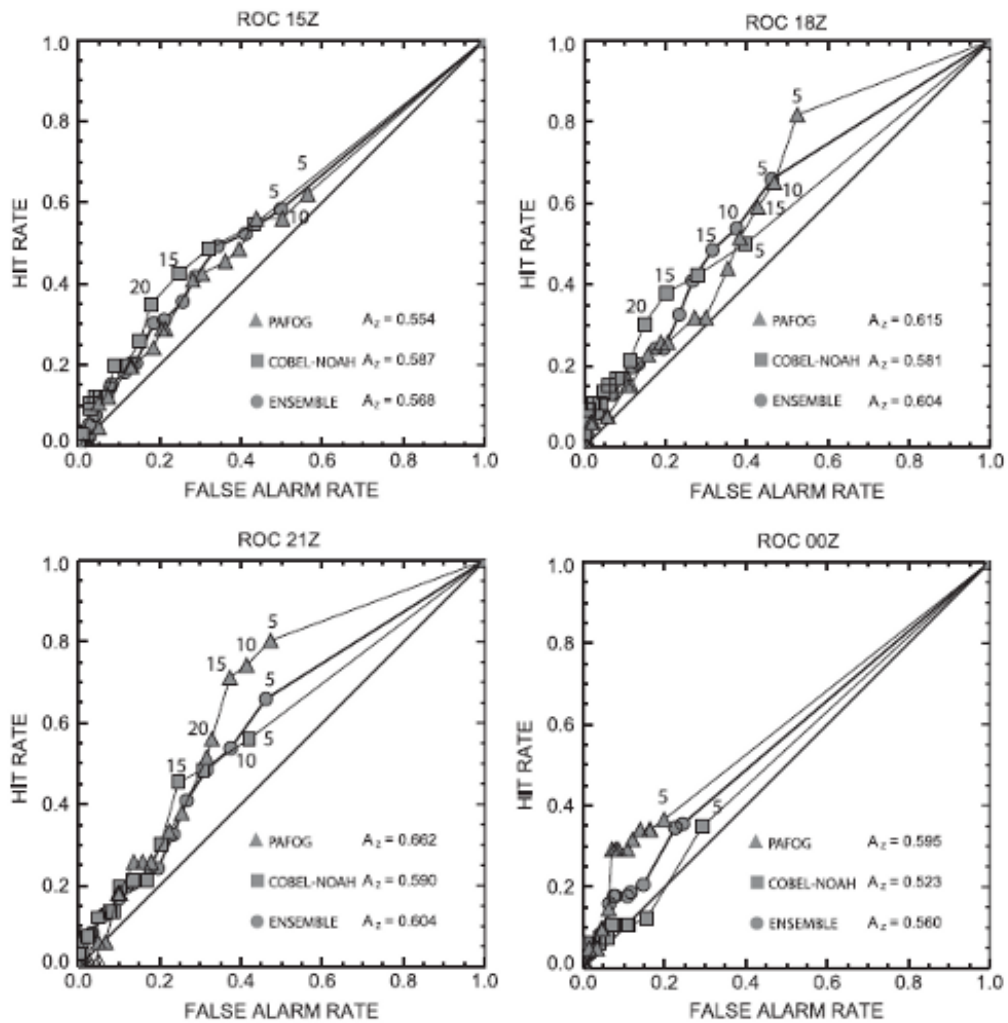
Figure 24. Ratio of correct:false predictions of fog at Zürich airport using *PAFOG*, *COBEL-NOAH* and the multi-model ensemble at different initialisation times (15:00, 18:00. 21:00 & 00:00). Numbers above the symbols indicate the ensemble forecast probability in percent that has to be exceeded in order for the a prediction to be classified as a modelled fog event. Taken from Müller *et al.* (2007).

The body of work discussed above is concentrated on modelling the occurrence of fog. The aqueous chemistry of fog and how particles of pollutants are scavenged/dispersed under foggy conditions remains of interest however. The remainder of this section will concentrate on the possibility of using dispersion models and, in addition, how other researchers have approached the subject of modelling the dispersion and deposition of pollutants in fog.

3.5   Modelling fog/surface interaction

Some of the earliest studies of the interaction of clouds, water droplets and ground vegetation were conducted during the 1980's, *e.g.* Milne *et al.* (1986) and Fowler *et al.* (1988). Following on from such studies, Gallagher *et al.* (1992) studied cloud droplet deposition at a forested site at Dunslair Heights near Peebles and fluxes (differentiated by drop-size) on the open moorland of Great Dun Fell near Penrith. From the observations, Gallagher *et al.* (1992) concluded

that cloud water fluxes could be calculated adequately using parameterised deposition velocities.

Figure 25. Forecasts of fog probability at 12:00 on the 22nd of December 1998 from Clark *et al.* (2008). The shaded regions of images (a) and (b) indicate a probability greater than 0.4. Image (a) includes the assimilation of visibility observations into the model, whereas they were excluded from the trial in image (b). Image (c) shows where observations of visibility at 12:00 were made: shaded / open circles show visibility reports of less than / greater than 1 km respectively.

In California, Lurmann *et al.* (1997) examined the performance of a three-dimensional gas/aerosol air-quality model (known as the *UAM-AERO* model). The model was capable of resolving particle sizes and chemical composition and its results were compared with a comprehensive database from a 2-day long

period of fog in southern California. The *UAM-AERO* model was designed to simulate the relationships between emissions and ambient concentrations of gaseous and aerosol species. However, it did not simulate the formation of fog. Instead banks of haze or fog were incorporated into the model from surface observations and their effect on gas and aerosol species were computed in an empirical manner. The time and locations of haze and fog were input to the model hourly, using the conditions: no-fog, haze and fog as gridded fields. Lurmann *et al.* (1997) showed that improvements in the modelling would be required to predict air quality in fog to a reasonable degree of accuracy.

A thorough review of meteorological modelling of fog cloud / aqueous chemistry for air quality assessments was published by Seaman (2000), discussing fog, soil hydrology and numerical differencing techniques. Seaman (2000) acknowledged fog's effect on air quality, but considered that such conditions had been treated rather crudely. In particular the treatment of the presence of particulate matter, because of its influence on chemical reaction rates, secondary aerosol formation and deposition rates was poor. The ability of a model to simulate fog formation depends heavily on other components of the water cycle:

♦ soil hydrology

♦ evapo-transpiration

♦ vertical transport of eddies in the earth's boundary layer

♦ rainfall

Soil hydrology is important, as fluxes of heat and moisture at the soil surface are related to the radiation flux divergence at the surface, although Seaman (2000) recognised that the moisture content of soils was difficult to measure and that many models use averages related to land use. The more-complex models use temporal variability as a function of rainfall, run-off, evapo-transpiration, *etc*. but require detailed initial information. In addition, small errors due to numerical differencing schemes are potentially serious, as water vapour is important in many chemical reactions.

Another important issue concerning computer modelling of multi-phase chemical systems (*e.g.* water droplets, particles and gaseous compounds) in air quality models was discussed by Müller (2001). This issue is termed 'operator splitting', the basis of which is the use of separate time-integration solvers designed specifically and efficiently for single processes such as advection, diffusion and chemistry. This is largely for historical reasons, based on limited computing resources and was accepted widely for many years. In addition, it is possible that physical processes such as condensation, evaporation or coagulation may each be treated by a separate sub-solver. However, the method has an inherent disadvantage: the creation of concentrations of material, distributed across the domain that are removed from the equilibrium at the beginning of each 'chemical' time step.

Other research has been conducted into aqueous chemistry, wet deposition and the role of cloud water. Shimshock (1986) and Shimshock & de Peña (1989) have presented investigations of the chemistry of ammonia in the atmosphere,

including solubility in water, multi-component aqueous chemistry and possible interactions between gaseous ammonia molecules and water droplets. In addition a detailed review of current knowledge of aqueous ammonia chemistry and the in-cloud scavenging of ammonia was presented by Renard *et al.* (2004). Their review included a section on factors that influence deposition velocities, one of which was humidity. Although this seemed to be more relevant to scenarios after a rain shower, this could apply to fog and its deposition to surfaces.

Several field studies on fog deposition and aerosol growth under humid conditions have been reported in the literature (for example Moore *et al.*, 2004; Holwerda et al. (2006); Kim *et al.*, 2006; Biswas *et al.*, 2008 and Haywood *et al.*, 2008) and it has been shown that gravitational settling is an important feature. Settling and wet removal of solutes dissolved in the drops is a very important atmospheric loss mechanism. Moore *et al.* (2004) warned also that typically, in the past, investigators have measured the water flux and multiplied that by bulk cloud composition. However, the removal rate increases with increasing droplet size (Choularton *et al.*, 1992) and if the composition of the drops varies also with size, this may yield misleading results (Moore *et al.*, 2004). The use of eddy-covariance techniques to try and match patterns of water collection from field measurements with atmospheric conditions and flux of liquid water (*i.e.* the product of wind speed and fog liquid water content) was considered to be promising by Holwerda et al. (2006). The significance of ionic concentrations in fog water droplets and implications for acid deposition was pointed out by Kim *et al.* (2006), using a study of fog / low cloud over a mountain ridge in South Korea. The research highlighted the transport of pollutants from polluted areas in North-east Asia and the deposition thereof in fog. Haywood *et al.* (2008) reported airborne measurements of pollution plumes and compared them with predictions using numerical weather prediction models by Clarke *et al.* (2008), however no deposition out of the atmosphere was calculated/modelled.

Information concerning the modelling of fog formation, *followed by deposition*, is very sparse. Published studies on the three-dimensional modelling of fog deposition are especially so. Klemm *et al.* (2005) used a modified version of one-dimensional model developed initially by Lovett (1984) for forested mountainous areas. In such areas, hill fog is common and deposition of water on the canopy is driven by turbulence rather than sedimentation. Klemm *et al.* (2005) considered that eddy-covariance was a suitable method to derive estimates of turbulent fog water exchange above the top of the canopy. They did acknowledge concern over the fact that they were using a one-dimensional model for what was akin to advection fog and found that the modelled deposition was greater than that measured.

Deposition of aerosols to canopies was studied also by Petroff *et al.* (2008), although their study was concerned with dry deposition, rather than foggy conditions. They did however raise the point that modelling of the collection of particles by vegetation tends to be based on theory or experiment, based on deposition on filtration media or isolated surfaces. It was put forward that this

was questionable, as canopies tend to present a variety of surfaces to the flow, with differing orientations, shapes and sizes, all in motion due to flow turbulence.

One of the most relevant works published on the simulation of radiation fog and the deposition and removal of pollutants is that by Lillis *et al.* (1999). They used a modified version of a model from Pandis & Seinfeld (1989) that was capable of modelling the radiation physics of air cooling, chemical kinetics and parameterisations of the processes of droplet deposition.

Other seemingly useful studies are those by Shimadera *et al.* (2008 & 2009), who simulated transport of pollutants and fog formation in and around the Yodo river basin and Kinki regions of Japan. The model used was the *MM5* meso-scale model (see Section 3.7.5), hence the resolution was relatively coarse for modelling localised dispersion. However they were able to compute concentrations of pollutants, including the presence of fog and some of the comparisons of their predictions are shown in Figure 26. The authors discussed briefly some ways of improving the model also. They regarded the land surface data used to have been inadequate and improving this may help.

Besides the specialised models discussed above, there are other, more generic, models that are used for weather prediction and are capable of modelling the formation of fog. In addition, there are simpler models that are used for modelling of pollutant dispersion. How these might be suitable for modelling fog dispersion is discussed next.

3.6   Dispersion models

A variety of models exist for the transport, dispersion and deposition of pollutants. These range from simple parameterisations such as the R91 model by Clark (1979), through large-eddy simulations of pollutant dispersion, to operational models (such as the *NAME* model created by the United Kingdom's Meteorological Office) capable of predicting pollutant transport over international boundaries.

Current regulatory models are based on advanced Gaussian Plume formulations, using Monin-Obukhov boundary layer scaling and incorporating modules to account for building affected dispersion and complex terrain. The two principle models used in the UK are *ADMS* (*A*tmospheric *D*ispersion *M*odelling *S*ystem), developed by Cambridge Environmental Research Consultants (CERC) and *Aermod*, developed by the United States Environmental Protection Agency (USEPA) and the American Meteorological Society (AMS).
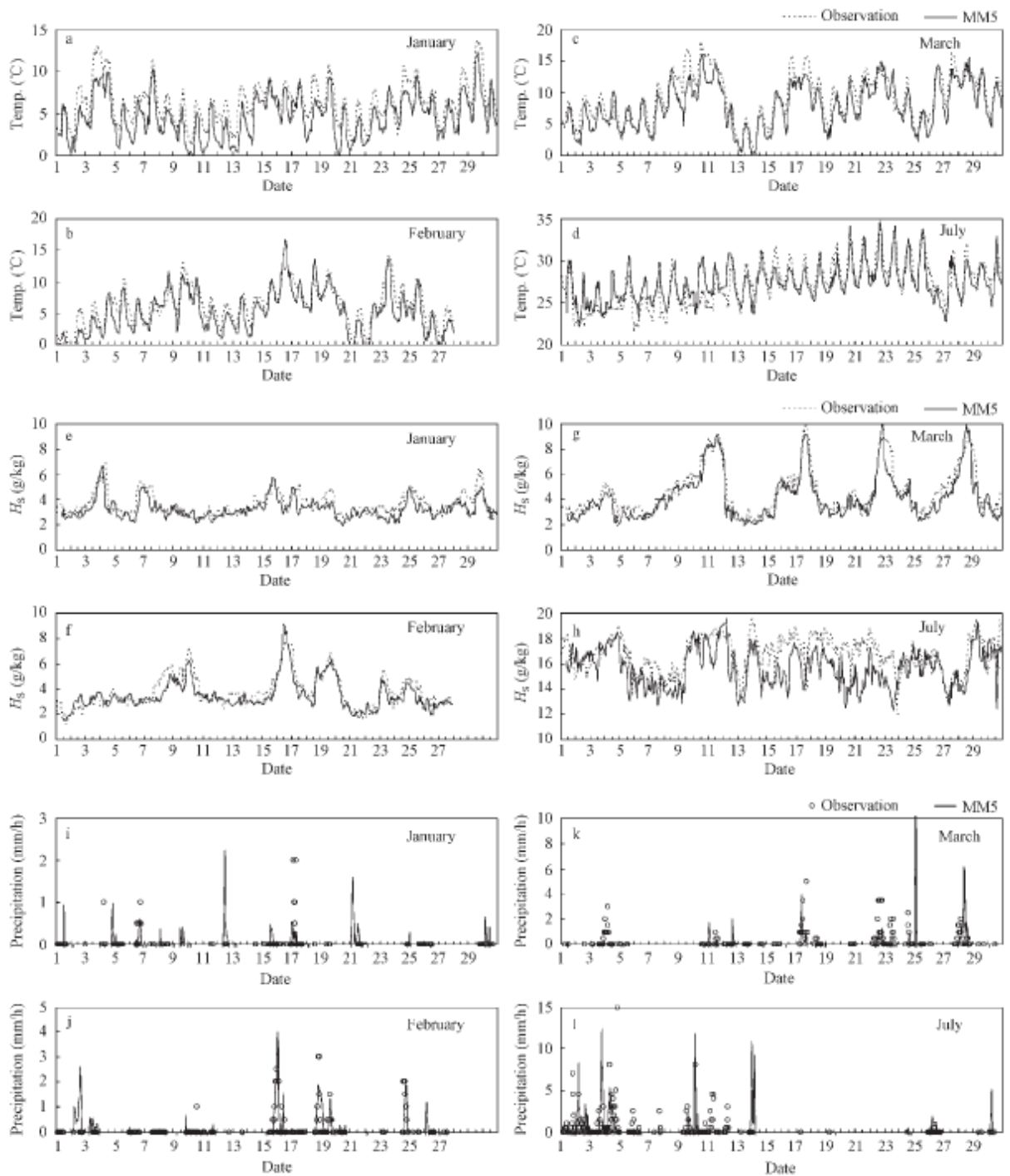
Figure 26. Comparisons of time series of observed and simulated hourly temperature, specific humidity (*H*s), and precipitation at the Kobe Marine Observatory in January, February, March, and July 2005, with *MM5* model predictions. Images from Shimadera *et al.* (2008).

3.6.1   *ADMS*

The most recent major release of *ADMS* is version 4.2 (CERC, 2007). The model includes the *FLOWSTAR* module to determine airflow and turbulence over complex terrain based on the theory that flow perturbations induced by terrain features are relatively small. By applying a small perturbation to the airflow, the Navier-Stokes equations can be linearised, whereby the non-linear terms are

replaced either by constants or defined as simple functions of the mean flow. Small perturbation theory can only be applied to model flow over terrain when the topographical features are low and of moderate slope (often cited as being less than approximately 1:3). Flow velocities at a particular point can be determined from the upstream flow plus a perturbation (or change) term that accounts for the effects of the terrain. There is a limit to the lowest wind speed that can be modelled however, below which the model will treat the meteorology as calm conditions.

3.6.2 Aermod

Like *ADMS*, *Aermod* is a steady-state plume model, designed for modelling the dispersion of air pollutants over ranges up to 50 kilometres from stationary industrial sources (Cimorelli *et al.*, 2004). A terrain pre-processor exists for the purpose providing a physical relationship between terrain features and the behaviour of air pollution plumes. It also provides information that allows the dispersion model to simulate the effects of air flowing over hills or splitting to flow around hills. Although the model's formulation is relatively simple, plumes of material are modelled as impinging on and/or following the terrain as appropriate. The approach was designed to be realistic, but simple, while avoiding the need to distinguish among simple, intermediate and complex terrain as required by other regulatory models. In addition, a pre-processor of meteorological data (*Aermet*) is incorporated. This accepts surface meteorological data, upper air soundings and (optionally) data from on-site instruments. It then calculates atmospheric parameters needed by the dispersion model, such as

♦ atmospheric turbulence characteristics,

♦ mixing heights,

♦ friction velocity,

♦ Monin-Obukov length and

♦ surface heat flux.

Similarly to *ADMS*, *Aermod* uses a minimum wind speed setting when using observed meteorological data. Any wind speeds less than this threshold are treated as calm conditions and are not included in the dispersion calculations.

3.6.4 *NAME*

The Numerical Atmospheric Modelling Environment (*NAME*) model was developed by the United Kingdom's Meteorological Office, originally for the modelling of material released from nuclear accidents. However, subsequent development has enhanced *NAME's* capabilities and it is now used in a wide variety of situations. It is a Lagrangian particle model, in which emissions from pollutant sources are represented by parcels released into a model atmosphere driven by meteorological data that are either input from local observations or three-dimensional data from the Meteorological Office's *Unified Model*.

3.6.4   *Fluidyn*-PANACHE-PANEIA

Panache, developed by *Transoft International*, is an example of a Eulerian Computational Fluid Dynamics code designed specifically for the simulation of atmospheric flows and pollutant dispersion over short and medium ranges. It uses a finite-volume-based approach, in which the governing differential equations for mass, momentum and heat transfer are solved in 3-dimensional space and time. The model allows the input of the terrain, including location, orientation and topography, building features, pollutant types and sources thereof and meteorological data. The computational mesh can be generated either uniformly, which maps obstacles approximately, or non-uniformly in which the grid wraps around any specified obstacles.

3.7   Suitability of the various models for modelling dispersion in fog

The *NAME* model uses wind field data from a numerical weather prediction model which is demanding in terms of computing power. However an advantage of using *NAME* is that it is able to treat temporal and spatial variations in the wind field and model how the motion of any particles is affected by them. In running the *Panache* model, the meteorological conditions can be specified as either a constant wind direction and wind speed profile with height, or using a wind rose. However using the former option, it can take several hours for one run to be completed on a desktop computer. Where the *ADMS* and *Aermod* models are concerned, they are capable of being run on a desktop computer also and treat individual or groups of sources, such as industrial stacks. For a domain size of a few kilometres square, both *UK-ADMS* and *Aermod* take considerably less time than *Panache* in completing simulations. However, for wind speed below certain thresholds, conditions are treated as calm with no definite wind direction and the simulation skips the relevant lines of meteorological data.

3.6.7   Use of Gaussian dispersion models for radiation/advection fog

As mentioned, for the conditions under which radiation fog is formed, wind speeds and hence turbulence, are very low. A review of models for use in low wind speeds was performed by Lines and Deaves (1996, in National Radiological Protection Board, 1999), who made suggestions for techniques for use when modelling low wind speeds. Since the wind speed term in the Gaussian plume equation is part of the denominator, as it tends to a very small / zero value, the concentration value approaches infinity. This is the reason behind the minimum wind speed thresholds that programmes such as *UK-ADMS* and *Aermod* employ. However, these thresholds can be set as low as *e.g.* 0.1 m s^{-1} (in *ADMS*) and the models will still perform the dispersion calculation for speeds above the value set, but ignore data for calm conditions. As meteorological conditions will be stable or very stable during nocturnal fog episodes, a positive value for the Monin-Obukhov length needs to be entered as an input parameter. *UK-ADMS* also incorporates the facility for modelling the ionic concentration of droplets (specifically for SO_2 and HCl).

As advection fog forms under conditions of moving air, then the use of models such as *UK-ADMS* or *Aermod* is considered to be valid for obtaining estimates of

pollution dispersion in such cases. In particular, the presence of incoming sea fog, or haar, is one such situation. In summer, haar forms when warm, moist, stably-stratified air flows over relatively cold water, usually onshore in the afternoon. In the fog bank, the air temperature will have reduced to the dew point temperature. Over the land, atmospheric stability may be likely to be convective due to daytime solar heating. *UK-ADMS* is able to treat coastlines in this way, with the development of a boundary layer over land into which a plume can be entrained. In such cases, *ADMS* requires meteorological data in a file that includes either the sea and land surface temperatures, or the temperature difference between the two. However, coastlines are treated as very simple straight lines and the module within the whole model has not been validated yet. *Aermod* does not have a module written specifically for treating the development of boundary layers inland from coastlines, this would require the user to specify this. Therefore *UK-ADMS* would seem to be the better choice for modelling transport of pollutants in haars where the superposition of boundary layers may be of significance.

3.7 Summary

In essence the formation of fog is governed by many factors and forecasting fog formation places demands on the ability of a model to treat or parameterise them accurately. Satellite observations have proved useful in providing data concerning spatial extents and depths of fog, with which models can be evaluated. Fully three-dimensional models are complex and expensive to run however; several one-dimensional models have been developed for local forecasting on a frequent basis. Although such models are not capable of handling advective conditions, they may be used for radiation fog modelling.

Numerical weather prediction models such as the *Unified Model* and *MM5* are able to handle fog formation, pollution and aqueous chemistry. However the horizontal resolutions at which they operate currently (of the order of a few kilometres) may be too coarse for the modelling of aerial releases from (effectively) point sources such as stacks. Until such time as the operational resolution of numerical weather models reduces to tens of metres, for such sources, the use of the Gaussian dispersion models such as *UK-ADMS* and *Aermod* would seem to offer the best method of modelling plume dispersion in fog.

In terms of modelling releases in radiation fog conditions, both *UK-ADMS* and *Aermod* would not model winds less than their respective calm conditions thresholds. However, it is possible to set these thresholds at extremely low windspeeds (of the order of tenths of metres per second) although this would be likely to significantly increase the uncertainty in the modelling predictions. Where possible, estimates of boundary layer height, surface temperature and relative humidity should be obtained and used as inputs into the model.

For advective fog, in particular haar off the sea, the coastline option in *ADMS* provides a method for modelling releases in such conditions. However it is advised that, as this module has not been validated, any results should be used with caution. It is recommended that validation of the coastline module be performed. The use of *ADMS* for modelling hill fog is not recommended as

orographic enhancement of the airflow will be modelled as rainfall rather than fog and further work is required in modelling this aspect of fog formation.

4 POLLUTANT EFFECTS ON HUMAN HEALTH DURING FOG EPISODES

4.1 Introduction

During the London fog of 1952, 4000 people are reported to have died over four days as a direct result of the physiochemical interactions of smoke and fog (smog) (Figure 27). As a consequence of the scale of this disaster, the "Great Fog" has become a landmark in air pollution epidemiology. This event helped to focus public and scientific attention on air quality issues and allowed researchers to do the first detailed analysis on the relationship between levels of air pollutants and increased morbidity and mortality (Brimblecombe, 1988). Prior to the mid 20th Century, suitable methods of exposure measurements were not available, and the study of air pollution and mortality was limited to observations of increased mortality during specific episodes. Monitoring of air pollutants is now part of many national regulatory programs and epidemiological studies on mortality and morbidity are the cornerstone of our understanding of adverse health effects from air pollution.
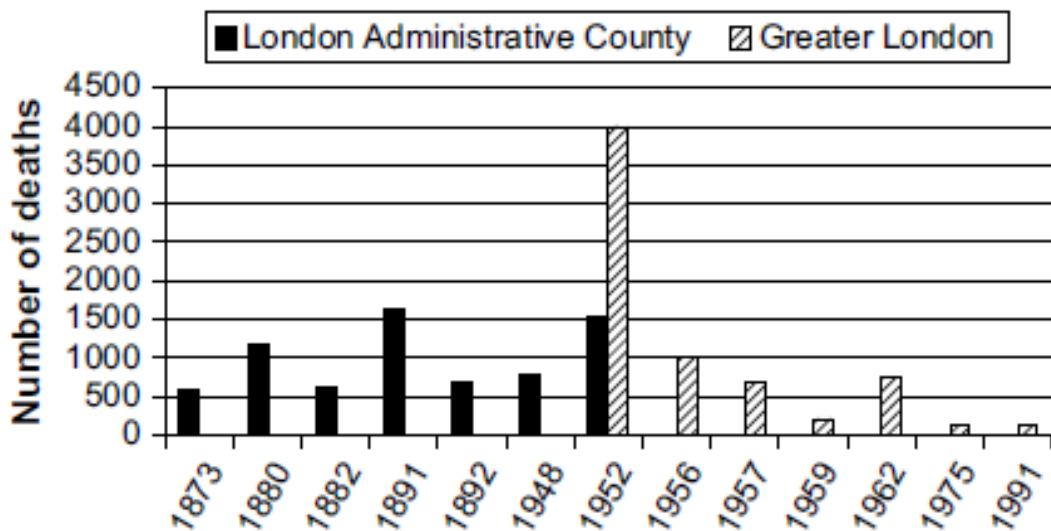
Figure 27   Estimated excess deaths in London fogs 1873-1991 (taken from Anderson, 2009).

In the UK, the principle measured air pollutants in regulatory programmes are PM_{10}, SO_2, NO_x and O_3, which are all associated statistically with daily mortality. However, it has proved very difficult, to disentangle their independent effects. Furthermore, it is suggested that detailed information on the speciation of particles needs to be linked with feasible epidemiological study design to quantify the effects of air pollution on health (Anderson, 2009). This will be even more of

a challenge for fog droplets since their chemical composition can be extremely variable on spatial and temporal scales depending on, e.g., the history of air mass, homogenous nucleation, surface condensation reactions, coagulation and scavenging of atmospheric aerosol, not to mention variations in environmental factors such as temperature and relative humidity.

Establishing a causal relationship between exposure and health during fog episodes is complex, and as with air pollution, research suggests that the health effects may be acute for susceptible members of the public and more chronic for less at risk members of the public. The argument is that as a result of the physiochemical properties of fog water and fog-pollutant interactions, fog water may act as an additional stressor in critical groups who are already at risk as a result of advanced chronic disease or a life threatening acute illness (Anderson et al., 2003). The causes of the conditions that are responsible for this vulnerability are multifactorial. This concept of multifactorial causation has lead to a shift in thinking with the acceptance that air pollution can cause adverse effects beyond the lung, for example, on the cardiovascular system (Donaldson et al., 2001) and on reproductive and perinatal outcomes (Lewtas, 2007).

This chapter focuses on epidemiological and laboratory studies related to adverse health effects as a result of fog episodes. Such studies have been employed not only to evaluate the effects of historical air pollution disasters such as the London fog in 1952 (Logan, 1956; Waller and Lawther, 1957; Black, 2003), the Meuse Valley fog of 1930 (Nemery, 2001), or the Donora fog of 1948 (Ciocco, 1961), as addressing some of the health risks from acid-polluted natural fog. Closely related to this issue is the influence of droplet size on deposition of inhaled acid (and other pollutants contained in fog water) within the respiratory tract and thus its influence on toxicity.

4.2   Acute health effects of smog events

A correlation between air pollution and mortality was first revealed in the Meuse Valley (Belgium) fog episode in December 1930. The area of Liège on the River Meuse, was once one of the most heavily industrialised areas of continental Europe. Between Dec 1 and Dec 5, 1930, a thick fog covered a large part of Belgium. It has been reported that hundreds of people in villages situated in the narrow portion of the Meuse Valley between the towns Huy and Liège started to exhibit severe respiratory symptoms. In those with chronic cardiorespiratory problems there was a worsening of their clinical state. During the fog episode there was ten times the expected number of deaths. Autopsies showed that many of the dead had suffered acute irritation on the respiratory tract (Nemery, 2001).

A similar episode occurred in Donora, Pennsylvania (USA) in 1948 (Ciocco and Thompson, 1961), where an estimated 5000 to 7000 persons in a town of 140000 residents became ill. Four hundred people required hospitalisation, and 20 people died before rain dispersed the smog. Autopsy results showed fluorine levels in victims in the lethal range and were as much as 20 times higher than normal. Evidence suggests that fluoride gas produced by zinc smelting processes was trapped in the fog and was responsible for the increased death rate (Hopey,

2008). As in the Meuse Valley episode, the fog occurred during a temperature inversion in a small industrial town situated in a river valley.

Both the Meuse Valley and Donorra fog episodes had a strong industrial element, whereas the London fog episode in December 1952 differs from these events in that the pollutants responsible for the reported adverse health effects and fatalities were emitted as a result of burning coal in domestic grates. The "Great Fog" was the product of a prolonged temperature inversion that allowed pollutant levels to increase to dangerous levels. Deaths in the London fog were mainly due to chronic bronchitis and emphysema exacerbated by chemical irritants (SO_2 and possibly sulphur trioxide, SO_3) and particulate matter (smoke). It has been reported that a further 8000 deaths above that expected occurred during the 10 weeks following the fog, with the cause of these deaths being attributed to any or all of: a delayed effect of the air pollution episode on human health; an effect of a further increase in pollution in January and February; and the coincidence of an influenza epidemic (Wilkins, 1954). Reports of the London fog by the Ministry of Health noted morbidity and mortality in Greater London remained elevated for three to four months following the fog episode, which was attributed to an influenza epidemic at the time. However, Wilkins (1954) suggested that the smog episode may have caused a decrease in resistance to illness, causing higher rates of morbidity and mortality at the time. No follow-up work was done to clarify this idea at the time, and official estimates attributed lingering increased rates of illness and death to influenza. More recently, Schwartz (1994) reported that the relative risk of mortality increased during the London smog relative to the preceding four days due to elevated ambient concentrations of particulate matter. Although further winter episodes associated with increases in mortality occurred in London, air pollution concentrations in London and most other major western cities have fallen significantly compared to historical levels (Anderson, 2009).

4.3   Chronic health effects of smog events

Each of the three smog episodes described above have helped to drive public health research into the impact of air pollution on public wellbeing and the mechanisms by which smog might be linked with increases in morbidity as well as mortality. However, the quantification of chronic effects of smog events is extremely difficult illustrated by:

- Spatial and temporal variations in the emission of different pollutants emitted from industry and domestic properties during fog events;

- Differences in the physicochemical properties of these pollutants (Chapter 1 and 2); and

- Spatial and temporal variations of different environmental variables responsible for fog formation (Chapter 1).

Nevertheless, since the smog events in the Meuse Valley (1930), Donora (1948) and London (1952) researchers have provided extensive documentation that exposures to acutely elevated pollutant concentrations also causes chronic public health effects (Pope, 2000). For example, Bell and Davis (2001) undertook an

assessment of the acute and chronic effects of the 1952 London Fog using novel indicators and reported that as many as 12,000 excess deaths were caused by persisting health effects following the fog event (not the 4000 originally reported). The indicators used by Bell and Davis (2001) in drawing their conclusions included:

- Minimum and maximum environmental variables;

- Analysis of weekly mortality and air pollution data including several weeks before and after the smog event;

- Analysis of indirect indicators of morbidity: insurance claims, hospital admissions, and notifications of pneumonia from November 1952 to January 1953 with comparisons for previous years;

- Assessment of the potential role of influenza in accounting for elevated rates of morbidity and mortality during the 3 months after the smog episode and calculation of the excess deaths due to the smog; and

- Examination of levels of key pollutants during the fog event compared to modern-day standards and to levels encountered currently in some rapidly developing regions.

Wichman et al. (1989) also used novel indicators to determine the effect of pollutant concentrations on the local population during fog episodes. They examined indicators of mortality and morbidity for a polluted area relative to an unpolluted area during the same fog episode. The test area and control area were both located in the Rhine Valley and had six million inhabitants in each area. Data for mortality (24,000 death certficates), morbidity in hospitals (13,000 hospital admissions, 5400 outpatients, 1500 ambulance transports) and consultations in doctors' offices (1,250,000 contacts) were analysed spanning a six week period prior to, during and after the fog event. Wichman et al. (1989) reported that during the fog event, mortality and morbidity in hospitals increased in the polluted area, but there was no substantial increase in the control area. Regression analysis showed there was a moderate influence of temperature, but a strong influence of ambient air pollution. The work of Wichman et al. (1989) illustrates that the effects of elevated pollutant concentrations such as acidifying emissions, particulate metals and black smoke are responsible for the increase in morbidity and mortality, but it is not clear if these effects were exacerbated by the fog.

When considering atmospheric acidity, Kigawa (1984) identified H_2SO_4 as the cause of respiratory disease in 600 individuals over a 10 year period in Yokkachi, Japan. Kigawa estimated that peak concentrations of H_2SO_4 in the town may have been as high as 1600 µg m^{-3} prior to electrostatic precipitators being installed to reduce the emissions of sulphate aerosol from a local factory. Following installation of the pollution abatement technology, the number of new cases of "allergic asthmatic bronchitis" steadily decreased. The importance of Kigawas research was the clear identification of H_2SO_4 as cause of morbidity in the absence of confounding factors. In another study Schenker et al. (1983) studied the influence of pollutants emitted as a result of coal combustion on rural populations in Pennsylvania, US. They reported a greater risk of "wheeze most

days or nights" in non-smokers living in high SO_2 areas relative to low SO_2 areas. The risk associated with the pollutant increased significantly for those individuals living in the same area for more than 5 years.

However, many of the studies conducted to determine the effects of air pollution during fog events, including those discussed above, do not address the question of whether the effects of elevated pollution are exacerbated during fog events. Nevertheless, in light of research such as that undertaken by, for example, Kigawa (1984) and Schenker et al. (1983), it is plausible that as a result of the elevated concentrations of pollutants in fog water, and the size distribution of fog water droplets (between 1 µm to greater than 10 µm; i.e. the same size range for respirable and inhalable particulate matter) people living in areas prone to high pollution may receive a greater dose of pollutants during foggy days than during non-foggy days. This could prove particularly important following an accidental release of chemicals during a fog event. Indeed, people residing in areas prone to more regular fog events such as haar, may witness a greater degree of chronic symptoms as a result of repeated exposure to the higher concentration of pollutants in fog water.

4.4 Epidemiological studies

Epidemiological studies have provided convincing evidence for a relationship between exposure to ambient particulate matter (PM) and increased mortality and morbidity (e.g., Dockery et al., 1993; Pope et al., 1995; Schwartz, 2000). As a result, the UK has set an air quality objective of 40 µg m^{-3} for PM_{10}. However, the chemical composition of particulate matter is extremely variable and the exact physiochemical nature of the component or components of the ambient particulate mix responsible for the adverse health effects remains uncertain. As a result, the USEPA has revoked the annual PM_{10} air quality standard, because they suggest that "available evidence does not imply a link between long-term exposure to PM_{10} and health problems". However, they have retained the existing 24-hour PM_{10} standard of 150 µg m^{-3}. Since fog development and intensity are controlled by the concentration of aerosols and particles, adverse health effects caused by PM and its chemical constituents may basically be projected to fog episodes. For example, Figure 11 shows that in urban areas after the onset of fog both particle number and mass distributions of aerosols have their maximum in the fine range < 0.1 µm which is respirable into the deep lung (see, Figure 29).

Current standards for air pollution in the UK and elsewhere in Europe relate to PM_{10}, SO_2, NO_x and O_3, which as a result provides the vast majority of data against which adverse health effects have been quantified. However, fog episodes and the chemistry of fog water droplets have characteristics, particularly their elevated acidity, that has resulted in several epidemiological and laboratory studies specific to fog which are discussed here.
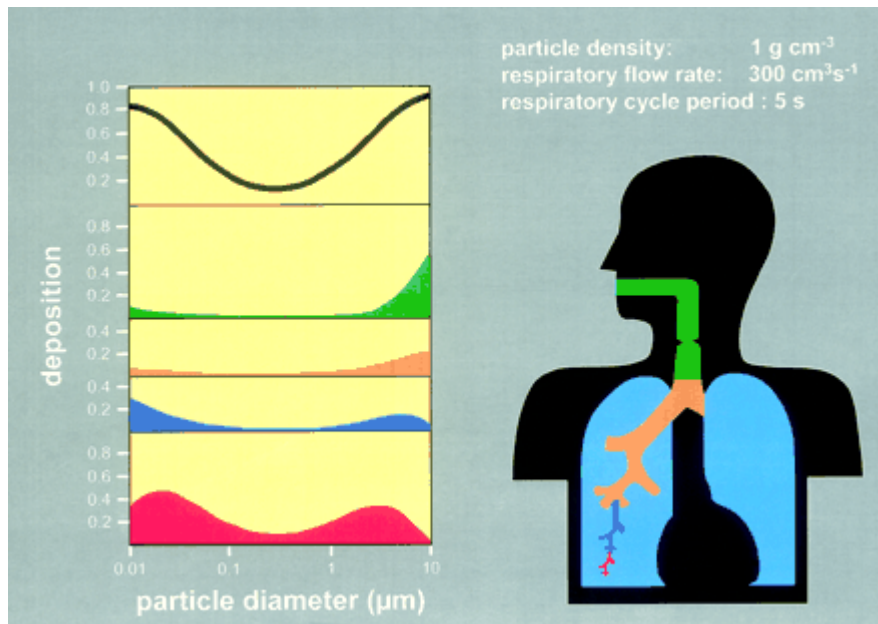
Figure 29   Total and regional deposition of unit-density spheres in the human respiratory tract predicted by the ICRP deposition model for oral inhalation at rest (taken from Heyder, 2004).

Several lines of epidemiologic evidence suggest that ambient acid aerosol pollution may represent a respiratory health hazard (Lippmann, 1985, 1989). Of possible concern is also the fact that historical air pollution episodes with documented increases in death and illness rates occurred during foggy weather (e.g., London, 1952). However, evidence from historical incidents is uncertain and modern pollution episodes are less severe, resulting in large uncertainties of the effects of fog on human health. In an attempt to address some of these uncertainties, Tanaka et al. (1996) examined the relationship between meteorological conditions and hospital visits for 102 asthma sufferers over a two-year period in Kushiro (Japan), a city of 200,000 residents with little industry. Based on a significant increase in hospital visits of adult asthma patients they concluded that inhalation of naturally occurring acid fog may have adverse effects on the respiratory tract of the asthmatic patient. However, it is uncertain if the water droplets alone contributed to respiratory conditions in asthmatic patients or if the accumulation of chemical species in fog water, even in relatively clean environments, contributed to their symptoms. In a separate study, Kashiwabara et al. (2002; 2003) reported a high frequency of emergency visits by asthmatic children was related to mist or fog, average atmospheric temperature, and barometric pressure. They reported that: 1) the average number of emergency department visits was higher on misty or foggy nights than on clear nights in each season; 2) that the average atmospheric temperature on misty or foggy nights with a high incidence of hospital visits was higher than that on misty or foggy nights without any visits; 3) asthmatic children frequently visited the emergency department on misty or foggy nights, especially during midnight to dawn periods with relatively high atmospheric temperature. They suggest that mist and fog may be a stimulus for constriction of the airways because a higher atmospheric temperature on misty or foggy nights indicates a larger saturated amount of airborne water droplets. However, they did not measure the liquid water content of the fog directly or conduct a

chemical analysis of the fog water so it is not clear if the fog water, its chemistry or meteorology is responsible for the asthma attacks.

4.5 Acid fog

Aerosols with droplets of a mean aerodynamic diameter of 1 µm or less have received most attention in health studies because they are typical of acidic ambient urban pollution (Figure 11) and are respirable into the deep lung. In polluted fog, however, the majority of the particle mass is in droplets 10 µm or larger in diameter (Hackney et al., 1985) and do not have the same pattern of deposition in the respiratory tract, which might change their health risk (Leduc et al., 1995). Figure 28 summarises the results of numerous deposition studies with monodisperse particles of varying size and density. The particles are inhaled through the mouth or the nose under different breathing patterns for a particle diameter range between 0.01 and 10 µm. The data was compiled using the International Commission on Radiological Protection's deposition model for inhalation at rest. This figure shows that total deposition can be partitioned into four regions of the respiratory tract (extrathoracic, upper bronchial, lower bronchial and alveolar region) and has been used to develop and a semi-empirical model to predict regional deposition for particles larger than 0.01 µm (Heyder et al., 1986; ICRP, 1994). According to this model, fog droplets with a diameter smaller than 10 µm have the potential of being deposited into the lower bronchial and alveolar regions and may be biologically active in susceptible individuals. Particles of 10 µm or larger may only deposit in the extra-thoracic and upper bronchial regions of the respiratory tract.

Water collected from naturally-occurring fogs is often found to be contaminated by acidic air pollutants (Waldman et al., 1982, Klemm et al., 1994; Millet et al., 1996; Zimmerman and Zimmermann, 2002; Colett et al., 2002; Burkard et al., 2003; Raja et al., 2008). The pH of fog water may be as low as 2 (Waldman et al., 1982; Hoffman, 1984; Jacob et al., 1985), whereas a pH near 5.6 is expected in pure water in equilibrium with atmospheric CO_2. Sulphuric acid and HNO_3 are the most common acid air pollutants. Acid fogs are formed via heterogeneous phase reaction of SO_2 or NO_x with atmospheric water droplets (Chapter 2). Controlled exposure studies of healthy human adults to H_2SO_4 in the fine particle mode (0.1 – 1 µm diameter) have shown no consistent effect on pulmonary function or respiratory symptoms following acute exposures to sulphuric acid aerosols at concentrations ≤ 1000 µg/m³, even with exercise (Avol et al., 1988, Linn et al., 1994). On the other hand, there is some evidence that asthmatics may be more sensitive than healthy individuals to the effects of acid fog water on lung mechanical function. It has been suggested that they may experience some constriction of the bronchial passage following exposure to sulphuric acid particles at concentrations < 1000µg/m³ (Avol et al., 1988; Linn et al., 1989). Avol et al. (1988) conducted a laboratory study of healthy and asthmatic volunteers on short-term respiratory effects of H_2SO_4 in fog. Responses were measured in terms of forced respiratory function, airway resistance and irritant symptoms. Following exposure to concentrations between 0 and 2000 µg/m³ H_2SO_4 in light fogs (~0.1 g/m³ liquid water content, 10 µm median droplet diameter, 10°C), and following periods of exercise, both asthmatics and healthy volunteers are reported to have exhibited no more than a

slight effect on pulmonary function as a result of H_2SO_4, even at the highest concentration. In contrast, there was a modest increase in respiratory symptoms (coughing) with increasing acid, suggesting that acid fog effects occur via a mechanism somewhat different to those that govern responses to irritant gases like SO_2 or O_3.

Linn et al. (1989) utilized a similar exposure protocol to specifically examine the effects of particle size on health. Healthy and asthmatic adults were exposed for 1 h to a pure water aerosol or approximately 2000 μg/m³ H_2SO_4 at three difference droplet sizes: 1, 10, and 20 μm. Healthy subjects showed increases in lower and upper respiratory irritant symptoms when exposed to the acid fog (10-20 μm particle diameter), but not adverse effects when exposed to 1-μm acid aerosol. In contrast, lung function change in asthmatics tended to vary with exposure time and was not statistically related to aerosol diameter: four of the 19 asthmatic subjects were unable to complete one or more exposures because of respiratory symptoms. The authors reported significant decrements in lung function in these subjects, requiring administration of a bronchodilator. As stated by the authors, "the pattern of these appreciable clinical responses by asthmatics suggests a causal relationship to acid exposure, without obvious dependence on droplet size". These more dramatic responses to acid aerosols are not reflected in the mean responses of other research studies, and suggest the existence of a few particularly susceptible individuals.

Naturally occurring fog water tends to be hypo-osmolar (i.e. has an osmotic pressure greater than that of the solution it's being compared to) with respect to body fluids (Balmes et al., 1988); most acid fogs have an osmolarity of <30mOsm (milli osmole[1]). Inhalation of hypo-osmolar aerosols is a well-established stimulus to bronchoconstriction (Schoeffel et al., 1981). Therefore, the effects of hypo-osmolarity of fog may enhance the effects of acidity on the respiratory tract. To test the effects of varying osmolarity of acidic aerosols, Balmes et al. (1988) administered aerosols of NaCl, H_2SO_4, HNO_3, or a mixture of H_2SO_4 plus HNO_3 to 12 asthmatic subjects via a mouthpiece. All solutions were prepared at an osmolarity of 30 mOsm, and delivered at doubling concentrations until specific airway resistance increased by 100%. An additional series of experiments with H_2SO_4 at 300 mOsm was performed. The 12 subjects were selected from a group of 17 asthmatics on the basis of their responsiveness to hypo-osmolar saline aerosol. Aerosol particle size was similar to coastal fogs, with mass median aerodynamic diameter (MMAD) ranging from 5.3 to 6.1. Delivered nebulizer output during exposure ranged from 5900 to approximately 87000 μg/m³, which is not representative of foggy conditions (≤ 500 μg/m³; see, also below the study from Leduc et al., 1991). All hypo-osmolar aerosols caused bronchoconstriction. Lower concentrations of hypo-osmolar acidic aerosols were required to induce bronchoconstriction than with NaCl, and there was no difference between acidic species. No bronchoconstriction occurred with iso-osmolar H_2SO_4, even at maximum nebulizer output (estimated H_2SO_4 concentration greater than 40000 μg m⁻³). The authors concluded that acidity can enhance bronchoconstriction caused by hypo-osmolar aerosols. However, these exposures did not represent environmental conditions. In a separate study,

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[1] In chemistry, the osmole (Osm or osmol) is a non-SI unit of measurement that defines the number of moles of a chemical compound that contribute to a solution's osmotic pressure.

Leduc et al. (1995) concluded that short-term exposure to acid fog at environmentally realistic hypo-osmolarity and H_2SO_2 concentrations of 30 mOsm and 500 µg m^{-3} respectively, does not induce bronchoconstriction and does not change bronchial responsiveness in asthmatics.

Aris et al. (1991) examined the effects of H_2SO_4 fogs (droplet size approximately 6 µm) of varying liquid water content (LWC) on airway resistance. Ten subjects were exposed for 1 h with intermittent exercise to H_2SO_4 and NaCl at low (LWC=0.5 µg/m³) and high (LWC=1.8 µg/m³) liquid water content. The mean sulphate concentrations were 960 µg/m³ for low water content fogs and 1400 µg/m³ for high liquid water content fog. Surprisingly, specific airway resistance decreased slightly with most exposures, with no significant difference among the four atmospheres. The authors speculated that the decrements in pulmonary function following exposure to acid aerosols in previous studies may have been due to increases in airway secretions or effects on the larynx rather than bronchoconstriction.

4.6 Summary

There are two major arguments that have lead to the assumptions that human health may be adversely affected during fog episodes. These are: (1) Water droplets in fog may concentrate soluble toxic air pollutants. When inhaled, these droplets are deposited preferentially at airway bifurcations, which receive disproportionately high local doses of toxicants; and (2) Nitrate and sulphate are usually the predominant anions in acidic fog water. Nitric and sulphuric acids are potent respiratory irritants at high doses (e.g. in accidental exposures), even for healthy people.

Epidemiological studies on mortality and morbidity are the cornerstone of our understanding of adverse health effects from air pollution. However, studies relating air pollution during fog episodes to adverse health effects are lacking. This review has shown that only a limited database exists regarding health effects and foggy environments. All of the clinical studies reviewed here involved acute exposure, and the majority of these involved exposure levels above those that would be encountered during a typical fog event. The available evidence suggests that the minimally effective concentration of sulphuric acid required to alter pulmonary mechanical function in healthy humans following acute exposure is >1000 µg m^{-3}, but in asthmatics it may be significantly less. On the other hand, epidemiological studies have provided no clear evidence that natural occurring acid fog has a bronchoconstrictive effect in asthmatic patients. Instead, these studies tend to suggest that a combination of airborne water droplets in fog or mist, coupled with other pollutants and meteorological factors may contribute to adverse health effects in susceptible members of the public.

While unabated emissions have undoubtedly contributed to significant increases in mortality, during non-fog episode periods (e.g., Waller & Lawther, 1957), evidence for worsening health as a result of fog pollutant interactions is less clear. Moreover, limitations of statistical methods at the time of historical fog episodes, and confounding and serial correlation of data processing has prevented analysis that could separate the effects of air pollution from those of confounding factors such as temperature (Anderson, 2009). Now that emissions

of the major pollutants in the UK and elsewhere have fallen due to Air Quality Standards and technical pollution abatement strategies (e.g. exhaust treatments, flue gas desulphurisation technologies) it is unlikely that such acute responses to fog episodes could be repeated where such strategies have been implemented. Nevertheless, chronic effects of fog-pollutant interactions cannot be discounted due to the delivery of pollutants in the respirable and inhalable size fraction of fog water droplets at potentially toxic levels.

5 REFERENCES

Aitken, J. (1888). On the number of dust particles in the atmosphere. Transactions of the Royal Society of Edinburgh 35:1-19.

Anderson, P. S. (1993). Evidence for an Antarctic winter coastal polynya. Antarctic Science 5: 221-226

Anderson, H.R., Atkinson, R.W., Bremner, S.A. and Marston, L. (2003). Particulate air pollution and hospital admissions for cardiorespiratory diseases: are the elderly at greater risk? Eur Respir J Suppl 40,

Anderson, H.R. (2009). Air pollution and mortality: A history. Atmospheric Environment 43(1), 142-152.

Aris, R., Christian, D., Sheppard, D., Balmes, J.R. (1991). Lack of bronchoconstrictor response to sulfuric acid aerosols and fogs. Am Rev Respir Dis. 143, 744-750.

Atkinson, R. (2000). Atmospheric chemistry of VOCs and NOx. Atmospheric Environment 34: 2063-2101

Avol, E.L., Linn, W.S., Wightman, L.H., Whynot, J.D., Anderson, K.R. and Hackney, J.D. (1988). Short-term respiratory effects of sulfuric-acid in fog - a laboratory study of healthy and asthmatic volunteers. Japca-The International Journal Of Air Pollution Control And Hazardous Waste Management 38(3), 258-263.

Bache, B.W. (1986) Aluminium mobilization in soils and waters. J Geol Soc (Lond), 143: 699-706.

Balmes, J.R., Fine, J.M., Christian, D., Gordon, T. and Sheppard, D. (1988). Acidity potentiates bronchoconstriction induced by hypoosmolar aerosols. Am Rev Respir Dis 138(1), 35-39.

Bell, M. & Davis, D. (2001). Reassessment of the Lethal London Fog of 1952: Novel Indicators of Acute and Chronic Consequences of Acute Exposure to Air Pollution. Environmental Health Perspectives, 109: 389-394.

Bell, M.L., Davis, D.L., Devra L., Fletcher, T. (2003) A Retrospective Assessment of Mortality from the London Smog Episode of 1952: The Role of Influenza and Pollution. *Environmental Health Perspectives* (http://ehp.niehs.nih.gov/members/2003/6539/6539.pdf)

Bendix J. (2002). A satellite-based climatology of fog and low-level straus in Germany and adjacent areas. Atmospheric Research, 64, pp. 3-18.

Bendix J., Thies B., Nauß T. & Cermak J. (2006). A feasibility study of daytime fog and low stratus detection with TERRA/AQUA-MODIS over land. Meteorological Applications, 13, pp. 111-125.

Bianco L., Tomassetti B., Coppola E., Fracassi A., Verdecchia M & Visconti G. (2006). Thermally-driven circulation in a region of complex topography: comparison of wind-profiling radr measureements and MM5 numerical predictions. Annales Geophysicae, 24, pp. 1537-1549.

Biswas K.F., Ghauri B.M. & Husain L. (2008). Gaseous and aerosol pollutants during fog and clear episodes in South Asian urban atmosphere. Atmospheric Environment, 42, pp. 7775-7785.

Black, J. (2003). Intussusception and the great smog of London, December 1952. Archives Of Disease In Childhood 88(12), 1040-1042.

Borg, H., Andersson, P., Johansson, K. (1989). Influence of acidification on metal fluxes in Swedish forest lakes. Science of the Total Environment, 87/88: 241-54.

Bott A., Sievers U. & Zdunkowski W. (1990). A radiation fog model with a detailed treatment of the interaction between radiative transfer and fog micro-physics. Journal of Atmospheric Science, 47, pp 2153-2166.

Bott, A. (1990). On the influence of the physico-chemical properties of aerosols on the life cycle of radiation fogs. Journal of Aerosol Science, 21: 279-282.

Bott A. & Trautmann T. (2002). PAFOG – a new efficient forecast model of radiation fog and low-level stratiform clouds. Atmospheric Research, 64, pp. 191-203.

Brimblecombe, P (1981) Long term trends in London fog. *The Science of The Total Environment,* 22: 19-29

Brimblecombe, P. (1988). The big smoke: a history of air pollution in London since the medieval times. Routledge, London & New York, 1-185.

Bussotti, F., Ferretti, M. (1998) Air pollution, forest condition and forest decline in Southern Europe: An overview Environmental Pollution 101: 49-65

Burkard, R. Bützberger, P., Eugster, W. (2003). Vertical fogwater flux measurements above an elevated forest canopy at the Lärgeren research site, Switzerland. Atmospheric Environment, 37: 2979-2990

Byers, H. R. (1959). General Meteorology, 3rd Edition, McGraw Hill Book Co., Inc.

Camargo, J.A., Alonso Á. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic systems: A global assessment. Environment International, 32: 831-849.

Cambridge Environmental Research Consultants Ltd. (2007). User's guide to the Atmospheric Dispersion Modelling System, version 4. Cambridge, U.K.

Cape, J. N. (1993) Direct damage to vegetation caused by acid rain and polluted cloud: Definition of critical levels for forest trees Environmental Pollution, 82: 167-180

Capel, P.D., Gunde, R., Zürcher, F., Giger, W. (1990). Carbon speciation and surface tension of fog. Environmental Science and Technology 24: 722 – 727.

Charlson, R. J., Rodhe, H. (1982). Factors controlling the acidity of natural rainwater. Nature, 295: 667–673.

Chernyak, S.M., Rice, C., McConnell, L. (1996). Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. Marine Pollution Bulletin, 32:410 – 419.

Choularton, T.W., Wicks, A.J., Downer, R.M., Gallagher, M.W., Penkett, S.A., Bandy, B.J., Dollard, G.J., Jones, B.M.R., Davies, T.D., Gay, M.J., Tyler, B.J., Fowler, D., Cape, J.N., Hargreaves, K.J. (1992) A field study of the generation of nitrate in a hill cap cloud. Environmental Pollution, 75: 69-74

Cimorelli, A. J., Perry, S. G., Venkatram, A., Weil, J. C., Paine, R. J., Wilson, R. B., Lee, R. F., Peters, W. D., Brode R. W., & Paumier, J. O. (2004). AERMOD: Description of model formulation, U. S. Environmental Protection Agency, EPA Rep. 454/R-03-002d, 85 pp.

Ciocco, A. and Thompson, D.J. (1961). A follow-up of Donora ten years after: methodology and findings. Am J Public Health Nations Health 51, 155-164.

Clark (1979). The first report of a working group on atmospheric dispersion: a model for short and medium range dispersion of radionuclides released to the atmosphere. National Radiological Protection Board Report NRPB-R91.

Clark P.A., Harcourt S.A., MacPherson B., Mathison C.T., Cusack S. & Naylor M. (2008). Prediction of visibility and aerosol within the operational Meteorological Office Unified Model. I: model formulation and variational assimilation. Quarterly Journal of the Royal Meteorological Society, 134, pp 1801-1816.

Clark, C.M, Tilman, D. (2008). Loss of plant species after chronic lowlevel nitrogen deposition to prairie grasslands. Nature, 451: 712-715.

Colville, R.N., Choularton, T.W., Gallagher, M.W., Wicks, A.J., Downer, R.M., Tyler, B.J., Storeton-West, R.L., Fowler, D., Cape, J.N., Dollard, G.J., Davies, T.J., Jones, B.M.R., Penkett, S.A., Bandy, B.J., Burgess, R.A. (1994) Observations on Great Dunn fell of the pathways by which oxides of nitrogen are converted to nitrogen. Atmospheric Environment, 28:397-408

Crossley,A., Wilson, D.B., Milne, R. (1992) Pollution in the upland environment. Environmental Pollution, 75: 81 – 88.

Dasch, J.M. (1988). Hydrological and chemical inputs to fir trees from rain and clouds during a 1-month study at Clingmans Peak, NC. Atmospheric Environment, 22: 2255–2262.

Dawson, T.E. (1998. Fog in the Redwood Forest: ecosystem inputs and use by plants. Oecologia 117: 476-485.

Dentener, F.J., Crutzen, P.J. (1993). Reaction of N_2O_5 on tropospheric aerosols: impact on the global distributions of NO_X, O_3 and OH. Journal of Geophysical Research 98: 7149-7163.

Dockery, D.W., Pope, C.A., Xu, X.P., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G. and Speizer, F.E. (1993). An association between air pollution and mortality in 6 United-States cities. New England Journal Of Medicine 329(24), 1753-1759.

Dollard, G. J., Unsworth, M. H., Harvey, M. J. (1983). Pollutant transfer in upland regions by occult precipitation. Nature, Land. 302: 241-243.

Donaldson, K., Stone, V., Seaton, A., MacNee, W. (2001). Ambient particle inhalation and the cardiovascular system: Potential mechanisms. Environmental Health Perspectives, 109, 523-527.

Duynkerke, P.G. (1991) Radiation fog: A comparison of model simulation with detailed observations. Monthly Weather Review, 119, pp. 324-341.

Duyzer J.H., Verhagen H.L., Weststrate J.H. & Bosveld F.C. (1992). Measurement of the dry deposition flux of NH_3 on to coniferous forest. Environmental Pollution, 75, pp. 3-13.

Elbert, W., Hoffmann, M.R., Krämer, M., Schmitt, G., Andreae, M.O. (2000) Control of solute concentrations in cloud and fog water by liquid water content. Atmospheric Environment 34: 1109-1122

Ellrod G.P. & Gultepe I. (2007). Inferring low cloud base heights at night for aviation using satellite infra-red and surface temperature data. Pure and Applied Geophysics, 164, pp. 1193-1205.

Evans, L.S., Lewin, K.F., Cunningham, E.A., Patti, M.J. (1982). Effects of simulated acidic rain on yields of field grown crops. New Phytologist, 91: 429-411.

Estrela, J.M., Valiente, J.A., Corell, D., Fuentes, D., Valdecantos, A. (2009) Prospective use of collected fog water in the restoration of degraded burned areas under dry Mediterranean conditions. Agricultural and Forest Meteorology. 149: 1896-1906.

Finlayson-Pitts, B.J., Pitts Jr., J.N. (1986). Atmospheric Chemistry, Wiley, New York.

Fišák, J. Skřivan, P., Tesař, M., Fottová, D., Dobešová, I., Navrátil, T. (2006). Forest vegetation affecting the deposition of atmospheric elements to soils. Biologia, Bratislava. 61: 255-260.

Fitzjarrald D.R. & Lala G.G. (1989). Hudson valley fog environments. Journal of Applied Meteorology, 28, pp. 1303-1328.

Fitzgerald, J.W. (1991). Marine aerosols: a review. Atmospheric Environment, 25A: 533 – 545.

Fowler D., Cape J.N., Leith I.D., Choularton T.W., Gay M.J. & Jones A. (1988). The influence of altitude on rainfall composition at Great Dun Fell. Atmospheric Environment, 22, pp. 1355-62.

Freiberg J.E. & Schwartz S.A. (1981). Oxidation of SO2 in aqueous droplets: mass-transport limitation in laboratory studies and the ambient atmosphere. Atmospheric Environment, 15, pp. 1145-1154.

Führer, J. (1986). Chemistry of fogwater and estimated rates of occult deposition in an agricultural area of Central Switzerland. Agriculture, Ecosystems and Environment 17: 153 – 164.

Fuzzi, S. (1986). Radiation fog chemistry and microphysics. In: Jaeschke, W. (Ed.), Chemistry of Multiphase Atmospheric Systems. Springer, Berlin, pp. 213 – 226.

Fuzzi S., Laj P., Ricci L., Orsi G., Heintzenberg J., Wendisch M. Yuskiewicz B., Mertes S., Orsini D., Schwanz M., Wiedensohler A., Stratmann F., Berg O.H., Swietlicki E., Frank G., Martinsson B.G., Günther A., Dierssen J.P., Schell D., Jaeschke W., Berner A., Dusek U., Galambos Z., Kruisz C., Mesfin N.S., Wobrock W., Arends B.& Ten B.H. (1998). The Po valley fog experiment 1994 (Chemdrop). Contr. Atmospheric Physics, 71, pp. 3-19.

Gallagher M.W., Beswick K., Choularton T.W., Coe H., Fowler D. & Hargreaves K. (1992). Measurements and modelling of cloudwater deposition to moorland and forests. Environmental Pollution, 75, pp. 97-107.

Gervat, G.P., Clark, P.A., Marsh, A.R.W., Teasdale, I., Chandler, A.S., Choularton, T.W., Gay, M.J., Hill, M.K., Hill, T.A. (1988). Field evidence for the oxidation of SO_2 by H_2O_2 in cap clouds. Nature 333: 241 – 243.

Gordon, C., Herrera, R., Hutchinson, T. (1994). Studies of fog events at two cloud forests at Caracas, Venezuela – II. Chemistry of fog. Atmospheric Environment, 28: 323 – 337.

Guedalia D. & Bergot T. (1994). Numerical forecasting of radiation fog. Part II: a comparison of mode simulation with several observed for events. Monthly Weather Review, 122, pp. 1231-1246.

Gultepe I. & Isaac G.A. (2004). Aircraft observations of cloud droplet number concentration: implications for climate studies. Quarterly Journal of the Royal Meteorological Society, 130, issue 602, pp. 2377 – 2390.

Gultepe I. & Milbrandt J.A. (2007). Micro-physical observations and mesoscale model simulation of a warm fog case during the F.R.A.M. project. Pure and Applied Geophysics, 164, pp. 1161-1178.

Gultepe I., Tardif R., Michaelides S.C., Cermak J., Bott A., Bendix J., Müller M.D., Pagowski M., Hansen B., Ellrod G., Jacobs W., Toth G. & Cober S.G. (2007). Fog research: a review of past achievements and future perspectives. Pure and Applied Geophysics, 164, pp. 1121-1159.

Gultepe I., Pearson G., Milbrandt J.A., Hansen B., Platnick S., Taylor P., Gordon M., Oakley J. P. & Cober S. G. (2009). The fog remote sensing and modelling field project. Bulletin of the American Meteorological Society, 90, pp. 341-359.

Hackney, J.D., Linn, W.S. and Avol, E.L. (1985). Potential risks to human respiratory health from acid fog - evidence from experimental studies of volunteers. Environ Health Perspect 63, 57-61.

Hameed, S., Mirza, M.I., Ghauri, B.M., Siddiqui, Z.R., Javed, R., Khan, A.R., Rattigan, O.V., Qureshi, S., Husain, L. (2000). On the widespread winter fog in northeastern Pakistan and India. Geophysical Research Letters 27: 1891-1894.

Harrison, R.M. (1996). Chemistry of the troposphere, in Pollution: Causes, Effects and Control, 3rd edition. Ed. M. Harrison. The Royal Society of Chemistry.

Haywood J., Bush M., Abel A., Claxton B., Coe H., Crosier J., Harrison M., MacPherson B., Naylor M. & Osborne S. (2008). Prediction of visibility and aerosol within the operational Meteorological Office Unified Model. II: validation of model performance using observational data. Quarterly Journal of the Royal Meteorological Society, 134, pp 1817-1832.

Herckes, P., Mirabel, P., Wortham, H. (2002). Cloud water deposition at a high-elevation site in the Vosges Mountains (France). The Science of The Total Environment. 296: 59-75.

Heyder, J. (2004). Deposition of inhaled particles in the human respiratory tract and consequences for regional targeting in respiratory drug delivery. Proc Am Thorac Soc 1(4),

Heyder, J., Gebhart, J., Rudolf, G., Schiller, C.F. and Stahlhofen, W. (1986). Deposition of particles in the human respiratory-tract in the size range 0.005 - 15 mu-m. J Aerosol Sci. 17(5), 811-825.

Hoffman, M.R. (1984). Acid fog. Engi Sci 48, 5-11.

Holwerda F., Burkard R., Eugster W, Scatena F.N., Meesters A.G.C.A. & Bruijnzeel L.A. (2006). Estimating fog deposition at a Puerto Rican elfin cloud forest site: comparison of the water budget and eddy co-variance methods. Hydrological Processes, 20, pp. 2669-2692.

Hopey, D. (2008). "Museum remembers Donora's deadly 1948 smog", Pittsburgh Post-Gazette, October 21, 2008.

Houssos E.E., Lolis C.J. & Bartzoka A. (2009). The main characteristics of atmospheric circulation associated with fog in Greece. Natural Hazards and Earth System Sciences, 9, pp. 1857-1869.

Hurd, T.M., Brach, A.R., Raynal, D.J. (1998). Response of understory vegetation of Adirondack forests to nitrogen additions. Canadian Journal of Forest Research, 28: 799 – 807.

Huss, A. Jr., Lim, P.J., Eckert, C.A. (1978). On the "uncatalysed" oxidation of S(IV) in solutions, Journal of the American Chemical society, 100: 6252-6253

ICRP – International Commission on Radiological Protection (1994). Human respiratory tract models for radiological protection. Ann. ICRP 24.

Igawa, M., Kase, T., Satake, K., Okochi, H. (2002). Severe leaching of calcium ions from fir needles caused by acid fog. Environmental Pollution, 119: 375 – 382.

Jensen, F.B. (2003). Nitrite disrupts multiple physiological functions in aquatic animals. Comparative Biochemistry and Physiology, 35: 9-24.

Jaén, M (2002). Fog water collection in a rural park in the Canary Islands (Spain). Atmospheric Research 64: 239-250

Jacob, D.J., Waldman, J.M., Munger, J.W. and Hoffmann, M.R. (1985). Chemical-composition of fogwater collected along the california coast. Environmental Science & Technology 19 (8), 730-736

Junge, C.E. (1963). Air Chemistry and Radioactivity. Academic Press, New York.

Kashiwabara, K., Itonaga, K. and Moroi, T. (2003). Airborne water droplets in mist or fog may affect nocturnal attacks in asthmatic children. Journal Of Asthma 40(4), 405-411.

Kashiwabara, K., Kohrogi, H., Ota, K. and Moroi, T. (2002). High frequency of emergency room visits of asthmatic children on misty or foggy nights. Journal Of Asthma 39(8), 711-717.

Katata, G., Nagai, H., Kajino, M., Ueda, H., Hozumi, Y. (2010). Numerical study of fog deposition on vegetation for atmosphere–land interactions in semi-arid and arid regions. Agricultural and Forest Meteorology, 150: 340-353

Kim M-G., Lee B-K. & Kim H-J. (2006). Cloud/fog water chemistry at a high elevation site in South Korea. Journal of Atmospheric Chemistry, 55, pp. 13-29.

Kitagawa, T. (1984). Cause analysis of the Yokkaichi asthma episode in Japan. Journal of the Air Pollution Control Association, 34: 743-746.

Klemm, O., Bachmeier, A.S., Talbot, R.W., Klemm, K.I. (1994). Fog chemistry at the New England Coast: Influence of air mass history. Atmospheric Environment, 28: 1181 – 1188.

Klemm O., Wrzesinsky T. & Scheer C. (2005). Fog water flux at a canopy top: direct measurement versus a one-dimensional model. Atmospheric Environment, 39, pp. 5375-5386.

Larssen, T., Seip, H. M., Semb, A., Mulder, J., Muniz, I. P., Vogt, R. D., Lydersen, E., Angell, V., Dagang, T., Eilertsen O (1999) Acid deposition and its effects in China: an overview. Environmental Science & Policy. 2: 9-24

Larson L.J., Largent A. & Tao F-M. (1999). Structure of the sulphuric acid−ammonia system and the effect of water molecules in the gas phase. Journal of Physical Chemistry A, 103, pp. 6786-6792.

Larson L.J. & Tao F-M. (2001). Interactions and reactions of sulphur trioxide, water, and ammonia: an *ab initio* and density functional theory study. Journal of Physical Chemistry A, 105, pp. 4344-4350.

Leduc, D., Fally, S., de Vuyst, P., Wollast, P. and Yernault, J.C. (1995). Acute exposure to realistic acid fog: Effects on respiratory function and airway responsiveness in asthmatics. Environ Res 71(2), 89-98.

Lewtas, J. (2007). Air pollution combustion emissions: Characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. Mutation Research-Reviews In Mutation Research 636 (1-3), 95-133.

Lillis D., Cruz C.N., Collet Jnr. J., Richard L.W. & Pandis S.N. (1999). Production and removal of aerosol in a polluted fog layer: model evaluation amd fog effect on PM. Atmospheric Environment, 33, pp 4797-4816.

Lines I.G. & Deaves D.M. (1999). Atmospheric dispersion at low wind speed. Annex A to the Atmospheric Dispersion Modelling Liaison Committee Annual Report 1996/7. National Radiological Protection Board report NRPB-R302.

Linn, W.S., Avol, E.L., Anderson, K.R., Shamoo, D.A., Peng, R.C. and Hackney, J.D. (1989). Efect of droplet size on respiratory responses to inhaled sulfuric-acid on normal and asthmatic volunteers. Am Rev Respir Dis 140(1), 161-166.

Linn, W.S., Shamoo, D.A., Anderson, K.R., Peng, R.C., Avol, E.L. and Hackney, J.D. (1994). Effects of prolonged, repeated expsure to ozone, sulfuric-acid, and their combination in healthy and asthmatic volunteers. American Journal Of Respiratory And Critical Care Medicine 150(2), 431-440.

Lippmann, M. (1989). Background on health-effects of acid aerosols. Environ Health Perspect 79, 3-6.

Liu, J.K., Wang, P.Y., Liu, W.Y., Li J.T., Li, P.J. (2008). The importance of radiation fog in the tropical seasonal rain forest of Xishuangbanna, south-west China. Hydrology Research, 39: 79-87

Logan, W.P. (1956). Mortality from fog in London, January, 1956. Br Med J 1(4969),

Longhurst, J., Raper, D., Lee, D., Heath, B., Conlan, B., King, H (1993) Acid deposition: a select review 1852–1990: 1. Emissions, transport, deposition, effects on freshwater systems and forests. Fuel, 72: 1261-1280

Lovett G. (1984). Rates and mechanisms of cloud water deposition to a sub-alpine balsam fir forest. Atmospheric Environment, 18, pp. 361-371.

Lurmann F.W., Wexler A.S., Pandis S.N., Musarra S., Kumar N. & Seinfeld J.H. (1997). Modelling urban and regional aerosols II. Application to California's South coast air basin. Atmospheric Environment, 31, pp. 2695-2715.

Magill A H, Aber J D, Currie W S, Nadelhoffer, K.J., Martin, M.E., McDowell, W.H., Melillo, J.M., Steudler, P. (2004). Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. Forest Ecology and Management, 196: 7-28.

Martikainen, A. (2005) Comparative evaluation of fogging phenomenon in the ramp of three mines in Finland. Eighth International Mine Ventilation Congress.

Mattila, T., Viisanen, Y., Kokkola, H., Laaksonen, A., Kulmala, M. (2000). Enhancement of CCN concentration due to aqueous phase sulfate production in polluted air. Journal of Aerosol Science, 31: 360-361

McIlveen, R (1992). Fundamentals of weather and climate. Stanley Thornes (publishers) Limited.

McNulty, S.G., Aber, J.D., Newman, S.D. (1996). Nitrogen saturation in a high elevation New England spruce-fir stand. Forest Ecology and Management, 84: 109-121.

Mensbrugghe V. (1892). The formation of fog and of clouds (translated from Ciel et Terre). Symon's monthly meteorological magazine, 27, pp. 40-41.

Millet, M., Sanusi, A., Wortham H. (1996). Chemical composition of fog water in an urban area: Strasbourg (France). Environmental Pollution, 94: 345-354.

Milne R., Crossley A. & Unsworth M.H. (1986). Physics of cloud water deposition and evaporation at Castlelaw, S.E. Scotland. *In Acid Deposition at high elevation sites*, Unsworth M.H. & Fowler D. (eds.), pp. 299-308, pub. Kluwer Academic, Dordrecht, The Netherlands.

Moore, G. E., Daly, C., Liu, M. (1987). Modelling of mountain–valley wind fields in the southern San Joaquin Valley, California. Journal of Climate and Applied Meteorology. 26:1230-1242.

Moore K.F., Sherman D.E., Reilly J.E., Hannigan M.P. Lee T-Y & Collet J.L. Jr. (2004). Drop-size dependent chemical composition of clouds and fogs. Part II: relevance to interpreting the aerosol / trace gas / fog system. Atmospheric Environment, 38, pp. 1403-1415.

Müller F. (2001). Splitting error estimation for micro-physical–multiphase chemical systems in meso-scale air quality models. Atmospheric Environment, 35, pp. 5749-5764.

Müller M. D., Schmutz C. & Parlow E. (2007). A one-dimensional ensemble forecast and assimilation system for fog prediction. Pure and Applied Geophysics, 164, pp. 1241-1264.

Munger, J.W., Jacob, D.J., Waldman, J.M., Ho!man, M.R. (1983). Fogwater chemistry in an urban Atmosphere. Journal of Geophysical Research 88, 5109 – 5121.

Narita, Y.; Iwamoto, Y.; Yoshida, K.; Kondo, M.; Uematsu, M. (2007). Scavenging processes of marine aerosols by sea fog over the northern North Pacific. American Geopphysical Union conference presentation (San Francisco). http://adsabs.harvard.edu/abs/2007AGUFM.A33A0832N

National Expert Group on Transboundary Air Pollution (2001). Transboundary air pollution: acidification, eutrophication and ground level ozone in the UK.

Nelson, W.O., Campbell, P.G.C. (1991). The effects of acidification on the geochemistry of Al, Cd, Pb and Hg in freshwater environments: a literature review. Environmental Pollution, 71: 91-130.

Nemery,B., Hoet, P., Nemmar, A. (2001). The Meuse Valley fog of 1930: an air pollution disaster. The Lancet, 357: 704 – 708.

Norden, U. (1991). Acid deposition and throughfall fluxes of elements as related to tree species in deciduous forests of south Sweden. Water, Air and & Soil Pollution, 60: 209–230.

Ocean Research Institute, University of Tokyo/CREST, Japan Science and Technology, Nakano-ku, Tokyo, Japan

Olivier, J., de Rautenbach, C. J. (2002) The implementation of fog water collection systems in South Africa. Atmospheric Research. 64: 227-238

Pandey, A.K., Sanjeev K. Srivastava, S.K., Tiwari, K.K. (2007) Fog water harvesting. Everymans Science. 42: 190-193

Pagowski, M., Gultepe, I., King, P. (2004). Analysis and modeling of an extremely dense fog event in southern Ontario. Journal of applied meteorology. 43: 3-16.

Pandis, S.N. SeinfeldJ.H. (1989). Mathematical modelling of acid deposition due to radiation fog. Journal Geophysical Research, 94: 12911 – 12923.

Pearson, D. C. 2002: "VFR Flight Not Recommended" A Study of Weather-Related Fatal Aviation Accidents. Technical Attachment SR SSD 2002-18.
(http://www.srh.noaa.gov/topics/attach/html/ssd02-18.htm.)

Petroff A., Mailliat A., Amielh M. & Anselmet F. (2008). Aerosol dry deposition on vegetative canopies. Part II – a new modelling approach and applications. Atmospheric Environment, 42, pp.3654-3683.

Pope, C.A., Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E. and Heath, C.W. (1995). Particulate air pollution as a predictor of mortaility in a prospective study of US adults. American Journal Of Respiratory And Critical Care Medicine 151(3), 669-674.

Pope, C.A. (2000). Epidemiology of fine particulate air pollution and human health: biologic mechanisms and who's at risk? Environmental Health Perspectives, 108::713–723.

Porter, J.N., Clarke, A.D. (1997). Aerosol size distribution models based on in situ measurements. Journal of Geophysical Research, 102: 6035 – 6045,

Quackenboss, J.J., Lebowitz, M.D. and Crutchfield, C.D. (1989). Indoor-outdoor relationships for particulate matter: exposure classifications and health effects. Environ Int 15, 353-360.

Rangognio, J., Tulet, P., Bergot, T., Gomes, L., Thouron, O., Leriche, M. (2009). Influence of Aerosols on the formation and development of radiation fog. Atmospheric Chemitry and Physics Discussions. 9: 17963-18019.

Reddy, G. B. Reinert, R. A., Eason, G (1991) Enzymatic changes in the rhizosphere of loblolly pine exposed to ozone and acid rain. Soil Biology and Biochemistry, 23: 1115-1119

Rémy S. & Bergot T. (2009). Assessing the impactof obersvations on a local numerical fog prediction system. Quarterly Journal of the Royal Meteorological Society, 135, pp. 1248-1265.

Renard J.J., Calidonna S.E. & Henley M.V. (2004). Fate of ammonia in the atmosphere – a review for applicability to hazardous releases. Journal of Hazardous Materials, B108, pp.29-60.

Reynolds, B., Fowler, D., Smith, R. I., Hall, J. R. (1997) Atmospheric inputs and catchment solute fluxes for major ions in five Welsh upland catchments. Journal of Hydrology 194: 305-329

Rice, C.P., Chernyak, S.M. (1997). Marine arctic fog: An accumulator of currently used pesticide Chemosphere, 35: 867-878.

Sabah A. Abdul-Wahab, Hilal Al-Hinai, Khalid A. Al-Najar, Mohammed S. Al-Kalbani. Environmental Engineering Science. May 2007, 24(4): 446-456.

Sasakawa, M., Ooki, A., Uematsu, M. (2003). Aerosol size distribution during sea fog and its scavenge process of chemical substances over the northwestern North Pacific. Journal of Geophysical Research, 108: 4120, 9PP doi:10.1029/2002JD002329

Sasakawa, M., Uematsu, M. (2005). Relative contribution of chemical composition to acidification of sea fog (stratus) over the northern North Pacific and its marginal seas. Atmospheric Environment 39: 1357 – 1362.

Schenker, M. B., Speizer, F. E., Samet, J. M., Gruhl, J., and Batterman, S. Health effects of air pollution due to coal combustion in the Chestnut Ridge region of Pennsylvania: results of cross-sectional analysis in adults. Archives of Environmental Health, 38: 325- 330.

Schulze, T.D. (1989). Air pollution and forest decline in a spruce (*Picea abies*) forest. Science, 244: 776-783.

Schoeffel, R.E., Anderson, S.D. and Altounyan, R.E.C. (1981). Bronchial hyperactivity in response to inhalation of ultrasonically nebulized solutions of distilled water and saline. British Medical Journal 283(6302), 1285-1287.

Schumann, T., 1991. Aerosol and hydrometeor concentrations and their chemical composition during winter precipitation along a mountain slope - III. Size-differentiated in-cloud scavenging efficiencies. Atmospheric Environment, 25: 809-824.

Schwartz J. (1994). Air pollution and daily mortality: a review and meta analysis. Environmental Research 64:36–52.

Schwartz, J. (2000). Assessing confounding, effect modification, and thresholds in the association between ambient particles and daily deaths. Environ Health Perspect 108(6), 563-568.

Seaman N. L. (2000). Meteorological modelling for air quality assessments (N[th.] American Research Strategy for Tropospheric Ozone review paper). Atmospheric Environment, 34, pp. 2231-2259.

Seinfeld, J. H., Pandis, S. N. (1998) Atmospheric Chemistry and Physics. From Air Pollution to Climate Change. John Wiley and Sons, New York.

Shanyengana, E. S., Henschel, J. R., Seely, M. K., Sanderson R. D (2002). Exploring fog as a supplementary water source in Namibia. Atmospheric Research 64: 251-259

Shimadera H., Shrestha K.L., Kondo A., Kaga A. & Inoue Y. (2008). Fog simulation using a meso-scale model in and around the Yodo river basin, Japan. Journal of Environmental Sciences, 20, pp. 838-845.

Shimadera H., Kondo A., Kaga A., Shrestha K.L. & Inoue Y. (2009). Contribution of trans-boundary air pollution to ionic concentrations in the Kinki region of Japan. Atmospheric Environment, 43, pp. 5894-5907.

Shimshock J.P. (1986). Proc. 2nd Intl. speciality conference on meteorological of acidic deposition. Air Pollution Control Assoc., Pittsburgh PA, U.S.A.

Shimshock J.P. & de Pena R.G. (1989). Below-cloud scavenging of tropospheric ammonia. Tellus, 41B, pp. 296-304.

Sigg L., Stumm W., Zobrist J., Ziircher F. (1987). The chemistry of fog: factors regulating its composition. Chimia 41: 159-165.

Skjelkvale, B.L., Stoddard, J.L., Andersen, T. (2001). Trends in surface water acidification in Europe and North America (1989–1998). Water Air Soil Pollution, 130: 787-92.

Smith, V.H. (2003). Eutrophication of freshwater and coastal marine ecosystems: a global problem. Environmental Science Pollution, 10: 126-39.

Stone R. (2002). Counting the cost of London's killer smog. Science, 298, pp. 2106-2107.

Strengbom, J., Walheim, M., Näsholm, T., Ericson, L. (2003). Regional differences in the occurrence of understory species reflect nitrogen deposition in Swedish forests. Ambio, 32: 91-97.

Stevens, C.J., Dise, N.B., Owen Mountford, J., Gowing, D.J. (2004). Impact of nitrogen deposition on the species richness of grasslands. Science, 303: 1876-1879.

Sutton M.A., Schjorring J.K., Wyers G.P., Duyzer J.H., Ineson P. & Powlson D.S. (1995). Plant-atmosphere exchange of ammonia (and discussion). Phil. Trans. Royal Soc. of London, series A, 351, pp. 261-278.

Tanaka, H., Honma, S., Nishi, M., Igarashi, T., Nishio, F. and Abe, S. (1996). Two-year follow-up study of the effect of acid fog on adult asthma patients. Internal Medicine 35(2), 100-104.

Tardiff R. (2007). The impact of vertical resolution in the explicit numerical forecasting of radiation fog: a case study. Pure and Applied Geophysics, 164, pp. 1221-1240.

Thalmann, E., Burkard, R., Wrzesinsky, T., Eugster, W., Klemm, O. (2002). Ion fluxes from fog and rain to an agricultural and a forest ecosystem in Europe. Atmospheric Research 64: 147–158.

Thompson, Anne (2007). Simulating the Adiabatic Ascent of Atmospheric Air Parcels using the Cloud Chamber. Department of Meteorology, Penn State.

Turton, J.D., and Brown, R. (1987) A comparison of a numerical model of radiation fog with detailed observations. Quarterly Journal of the Royal Meteorological Society. 113: 37-54

Underwood, S.J., Elrod, G.P., Kuhnert, A.L. (2004) A multiple case analysis of nocturnal radiation fog development in the central valley of California utilising the GOES nighttime fog product. Journal of Applied Meteorology, 43: 297-311

Unsworth, M.H., Wilshaw, J.C. (1989) Wet, occult and dry deposition of pollutants on forests. Agricultural and Forest Meteorology, 47: 221-238

US-EPA (2004). Air quality criteria for particulate matter. Vol. II. U.S. Environmental Protection Agency, EPA/600/P-99/002bF.

Vermeulen, A.T., Wyers, G.P., Römer, F.G., Van Leeuwen, N.F.M., Draaijers, G.P.J., Erisman, J. W. (1997). Fog deposition on a coniferous forest in The Netherlands. Atmospheric Environment. 31: 375-386.

Verwer J.G. & Sportisse B. (1998). A not on operator splitting in a stiff linear case. Modeling, Analysis and Simulation report MAS-R9830, Centrum Wiskunde & Informatica, Amsterdam, The Netherlands.

Waldman, J.M., Munger, J.W., Jacob, D.J., Flagan, R.C., Morgan, J.J., Hoffmann, M.R. (1982). Chemical composition of acid fog. Science 218: 677 – 680.

Wallace, Z.P., Lovett, G.M., Hart, J.E., Machona, B. (2007). Effects of nitrogen saturation on tree growth and death in a mixed-oak forest. Forest Ecology and Management, 243: 210-218.

Waldman, J.M., Hoffmann,M.R. (1987). Depositional aspects of pollutant behaviour in fogs and intercepted clouds, in Sources and Fates of Aquatic Pollutants, Advances in Chemistry Series, No. 216, Edited by R.A. Hites and S.J. Eisenreich. Wiley. New York, pp. 79-129

Waller, R.E. and Lawther, P.J. (1957). Further observations on London fog. Br Med J 2(5059), 1473-1475.

Weathers, K.C., Likens, G.E., Bormann, F.H., Eaton, J.S., Bowden, W.B., Andersen, J.L, Cass, D.A., Galloway, J.N., Keene, W.C., Kimball, K.D., Huth, P., Smiley, D. (1986). A regional acidic cloud/fog water event in the eastern United States. Nature 319: 657-658.

Welch, R.M., Cox, S.K. (1986). Prediction of quasi-periodic oscillations in radiation fogs. Part I: Comparison of simple similarity approaches. Journal of the Atmospheric Sciences. 43: 633–651.

Wetzel, R.G. (2001). Limnology. 3rd edition. New York: Academic Press.

Wexler A.S., Lurmann F.W. & Seinfeld J.H (1994). Modelling urban and regional aerosols I: model development. Atmospheric Environment, 28, pp. 531-546.

Wichmann, H.E., Mueller, W., Allhoff, P. Beckmann, M., Bocter, N., Csicsaky, M. J., Jung, M., Molik, B. & Schoeneberg, G. (1989). Health Effects During a Smog Episode in West Germany in 1985. Environmental Health Perspectives, 79: 89-99.

Wilkins ET. (1954). Air pollution and the London fog of December, 1952. Journal of the Royal Sanitary Institute 74:1–21

World Meteorological Organization (1992). International Meteorological Vocabulary. 2nd ed. Geneva: Publication no. 182.

Wrzesinsky, T., Klemm, O. (2000). Summertime fog chemistry at a mountainous site in central Europe. Atmospheric Environment 34: 1487–1496.

Xiankai, L., Jiangming, M., Shaofeng, D (2008). Effects of Nitrogen Deposition on Forest Biodiversity. Acta Ecologica Sinica, 28: 5532-5548.

Zimmermann, L., Zimmermann, F. (2002) Fog deposition to Norway Spruce stands at high-elevation sites in the Eastern Erzgebirge (Germany) Journal of Hydrology,. 256: 166-175.