MODELS FOR TRANSPORTATION AND DEPOSITION
OF ATMOSPHERIC POLLUTANTS

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ABSTRACT

We review some of the scientific background needed to enable the modelling of atmospheric transportation and removal of pollutants, particularly sulphuric compounds, which are major factors in the acidification of lakes. Long range transportation models are particularly important in this context. These models are inherently stochastic in nature, although much work has been done on deterministic models for yearly averages over large regions. We present some different approaches to the modelling problem, and discuss briefly some data and estimation problems.
1. Introduction

Since the early 1960's, there has been increasing concern that acidic precipitation is causing severe damage to the natural environment. The recent dramatic forest dieback in Germany, and the severe acidification of many lakes in Sweden emphasize the potential acuteness of the problem. During the last decade large research efforts have been directed towards understanding the mechanisms of acid rain.

Pure water in equilibrium with atmospheric CO₂ has a pH of about 5.6. In unpolluted areas, rain is slightly more acidic, with a pH of about 5.0 to 5.4. The term acid rain is now commonly used to denote precipitation with high concentrations not only of hydrogen ions, but also of sulphate or nitrate. Anthropogenic (i.e. man-made) release of sulphur oxides and other pollutants may alter biochemical cycles with serious consequences for the biota. There is ample evidence of such effects on water and soil, see e.g. Overrein et al. (1981). It therefore becomes important to study the transportation and deposition of sulphuric and nitric oxides. In this paper we will review some of the scientific background needed to model the deposition of sulphur and nitrogen compounds. We will also discuss some of the deterministic and statistical models suggested for long range transportation and deposition of these compounds, and propose some new approaches to this modelling problem.

Section 2 contains material related to the emission of atmospheric pollutants. In section 3 we study the concept of a mixing layer. Chemical transformations during transportation are described briefly in section 4, and the main mechanisms of deposition are presented in section 5. The EMEP (Co-operative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) model of long range transportation of sulphuric oxides is described in section 6, while section 7 describes various stochastic variants of the deposition models used in EMEP and other deterministic models. In the final section we outline some new approaches to the modelling of transportation and removal of atmospheric pollutants.

We have made no effort to review the vast acid rain literature in detail, and references are not necessarily given to the paper containing the original presentation of the result under discussion. Rather, we often refer to review papers, where the reader can find more detailed references. In 1980, a major international conference on acidic precipitation was held in Sandefjord, Norway, and in 1985 a similar conference was held in Muskoka, Canada. The Proceedings of these two conferences contain much of the material discussed here.

2. Emission of sulphur and nitrogen compounds

The most important ingredients of what is usually called acid rain are sulphur and nitrogen compounds. There are both natural and anthropomorphic sources for these pollutants. In the case of sulphate, man-made and natural sources are about equal in magnitude on a global scale. In Europe and North America, however,
the natural sources are only about 10% of the total emissions (Overrein et al., 1981; this review paper is the source of much of the material in this section). Among natural sources of sulphur compounds are volcanic eruptions, seaspray and, most importantly, biological reduction processes in mudflats, marshes, swamps and oceans. The main anthropomorphic source is combustion of fossil fuels, yielding sulphur dioxide. The main culprits are power plants. Another important source is smelting of sulphur-rich mineral ores. Moller (1984a,b) discusses anthropomorphic and natural sulphur emissions in some detail.

Since heating and energy production are among the most important sources of sulphur compound emissions, there can be substantial seasonal variation in the emissions. In Europe, sulphur emissions peak in January and February, with low values during the summer. The seasonal variation amounts to about 30% of the mean emissions. In North America, the use of air conditioners complicates the picture somewhat, and the seasonal variation is less pronounced. In the case of nitrogen compounds, the natural sources appear to dominate. Ammonium (NH₄) is released to the atmosphere from biological decay processes and from fertilisers. These emissions occur close to the ground, and plant uptake removes them effectively. Natural emissions of nitrogen oxides (NOₓ) come from biochemical processes in soil. The man-made nitrogen oxides are obtained from combustion of fossil fluids, mainly from cars and power plants. There seems to be a continuing increase in the emissions of nitrogen oxides, and nitric acid is responsible for an increasing proportion (currently about 1/3) of the H⁺-ions in acid precipitation (Likens et al., 1979). Conversely, the SO₂-emissions in Europe have been reduced by about a quarter over the last decade (Semb and Dovland, 1986). An ECE (United Nations Economic Commission for Europe) agreement requires a 30% reduction in SO₂-emissions relative to 1980 emissions was signed in 1985 by most major sulphur-emitting nations with the exception of Great Britain, Poland and the United States.

A large proportion of the man-made emissions come from tall smoke stacks. There is an inverse relation between the height of the smoke stack and the amount of local deposition. A large portion of the emissions are in gaseous or sub-micron particulate (i.e. particles with diameter < 1μm) form (Sheih et al., 1983). A more detailed description of sulphuric aerosols is found in Charlson et al. (1978).

The effect of sulphur and nitrogen compounds on the environment is only partially understood. It appears that sulphuric acids are the main cause of acidification of lakes. In Sweden, about 20% of all lakes are injured by acidity. A quarter of the injured lakes are so severely damaged that only a thick blanket of algae covers the bottom, instead of the diversity of biological forms normally present in lakes. By liming acidic waters and streams, the deterioration of the aquatic environment has been reversed. Currently controlled experiments to monitor both deterioration and reversal are being carried out in cooperation between Norway
and Canada (Wright et al., 1986).

The rapid dieback of German forests has been attributed partly to nitrogen emissions, either directly or through an associated increase in ozone production. This kind of deforestation is also appearing in Scandinavia and the United States. One effect that appears to be associated with increasing acidity is a substantial decrease in the growth rate of trees.

3. The boundary layer

After an air pollutant has been emitted into the atmosphere, it is subject to several processes before it is deposited: turbulent diffusion, advection (i.e. horizontal transportation), chemical transformations and various removal processes (Dovland and Semb, 1980). After emission, the plume of pollutants diffuses rapidly through the lower region of the atmosphere, called the boundary or mixing layer. This diffusion tends to mix the pollutants vertically throughout the layer, so that after the first tens of kilometers of downwind transportation, one may think of the pollutants as uniformly distributed throughout this layer. A common assumption is that from this point on, the plume is advected by the mean wind, subject to chemical transformations and removal processes. No further vertical diffusion is assumed to take place. Aircraft measurements (e.g. Isaac et al., 1983) indicate that cloud dynamics may complicate the picture. In addition, clouds may lift pollutants from the boundary layer and leave them in a higher layer after cloud dissipation. Generally, the higher layer would have stronger winds, so the potential for long-range transportation would increase.

The boundary layer is a region dominated by a balance of turbulent energy sources and sinks derived from interactions of the atmosphere with the underlying surface (Smith and Hunt, 1978). It has a variable depth, ranging typically from a few tens of meters in stable conditions to about 2 km in very unstable conditions. The height of the boundary layer is typically smaller at night. It is often quite difficult to determine the upper boundary, except when an inversion puts an obvious cap on the layer. Under very stable conditions, with inversion both at ground level and at the top of the boundary layer there may well be very little mixing. Instead the pollutants concentrate in a fixed air package, which may be transported long distances with very little dilution (Dovland and Semb, 1980).

Measurements of the vertical distribution of pollutants show that they in general are contained within the lowest 2 km of the atmosphere. The maximum concentration is usually a few hundred meters above the ground. Since wind speed and direction is variable in this region, it is clear that the simple model of advection according to a mean wind may be rather misleading. It is also not obvious how to pick the appropriate wind to model the transport of an air parcel. In Europe the 850 mb wind observations, possibly
with a correction factor have been used (Eliassen, 1978), although derived geostrophic winds, calculated from pressure charts, yield similar results over long periods of time. The results for short time periods are rather different (Dovland and Semb, 1980). In 1983 a tracer experiment, CAPTEX-83, was conducted in eastern North America (Summers and Olson, 1986). Tracer was released under favorable meteorological conditions, and the plume was followed using both air and ground equipment. The center line of the plume was found to be well represented by a 925 mb trajectory. The horizontal diffusion was wider in warm than in cold air advection, and in warm air strong directional shear was observed.

4. Chemical Transformations

Sulphur and nitrogen oxides undergo transformations in the atmosphere, producing sulphuric and nitric acid, sulphate aerosols, nitrogen oxide and ozone (see e.g. Bricard, 1977 or Isaksen, 1982). Most sulphur compounds are infused into the atmosphere either in the form of SO\textsubscript{2} particles or as SO\textsubscript{2} gas. The main oxidants in the gas phase are hydroxyl radicals (OH). These are formed from photochemical reactions involving ozone and water vapor. The production of OH varies with the amount of ultraviolet radiation, being quite limited at high latitudes during the winter.

Ultraviolet dissociation of NO\textsubscript{2} is the only known efficient process producing O\textsubscript{3} in the troposphere. In the presence of hydrogen or organic peroxy radicals, the resulting NO can be retransformed to NO\textsubscript{2}.

In the liquid phase, either when droplets form around particles or when gaseous SO\textsubscript{2} dissolves in water, ozone is an important oxidant. SO\textsubscript{2}-oxidation by O\textsubscript{3} is highly dependent on the pH in the droplets, and is inefficient below pH of 4.2. However, the presence of ammonium species increases the pH and thereby the oxidation rate even in heavily polluted air masses. H\textsubscript{2}O\textsubscript{2} is another oxidizing agent, which is independent of pH (Anlauf et al., 1986). Oxidation rates are higher near the source, and higher in urban than in rural areas (Davies, 1979), because of the local presence of catalyzing metallic ions.

The transformation of nitric species is not very well understood, but it seems likely that most of the oxidation of NO\textsubscript{x} takes place in the gas phase, partly due to inefficient absorption of gaseous NO\textsubscript{x} in droplets. The most efficient oxidation of NO\textsubscript{2} is by hydroxyl radicals, as mentioned above. The resulting gaseous nitric acid can be dissolved in droplets, where it dissociates into H\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} ions, thereby affecting the pH, and thus the oxidation rates of SO\textsubscript{2}.

Different sources of pollutants yield different kinds of high pollution episodes. For example, Brosset (1978) reports two kinds of events, white and black. The white events are times of high sulphate concentration but low soot content and usually low nitrate concentration. A possible explanation for these events is that dry air with relatively low concentration of gas phase SO\textsubscript{2} is photochemically oxidized, and brought to
equilibrium with NH$_3$. On the other hand, the black events, characterized by large soot content and high nitrate concentrations, would arise from hot flue gas emitted from a smoke stack. This contains soot, manganese, sulphur dioxide particles, carbon dioxide etc. In the cooling process, first manganese and then water condenses on the particles. SO$_2$ dissolves on the water film, oxidizes to H$_2$SO$_4$ and dissolves the Mn-film. There are now ideal conditions for catalytic oxidation of SO$_2$: high concentration of sulphur dioxide, high humidity and a good catalyst (Mn) spread over a large area.

5. Wet and dry deposition

There are two different mechanisms for removal of pollutants from the atmosphere: wet and dry deposition. Wet deposition is the transfer of a substance from the atmosphere to the surface of the earth within or on the surface of a hydrometeor (snow, hail or rain), whereas dry deposition is the direct transfer to and absorption of gases and particles by natural surfaces such as vegetation, soil, water or snow (Fowler, 1980).

The main mechanism by which particulate or gaseous compounds may be captured by cloud or rain drops is called the cloud condensation nuclei (CCN) pathway. Simply, particles between 0.1 $\mu$m and 1 $\mu$m function as nuclei around which water vapor can condensate to form raindrops. Fowler (1980) estimates this mechanism to account for about 60% of the sulphur and nitrogen in rain. The second most important mechanism is solution and oxidation of gaseous SO$_2$ to SO$_4^{2-}$ and NO$_2$ to NO$_3^-$, accounting for about 20%. Since the CCN pathway dominates wet removal, the more rain that falls, the more sulphur and nitrogen is deposited. However, the concentration of sulphur decreases with rainfall amount. Hicks and Shannon (1979) suggest that concentration is inversely proportional to the square root of rain volume (in the case of convective rainfall), though their data seem rather limited. Different meteorological conditions are likely to yield different such relations.

The processes described above are known as rainout mechanisms, i.e. mechanisms in which material is transferred to cloud droplets before they start their descent. Processes transferring material to falling raindrops are known as washout mechanisms. The distinction between rainout and washout is not universally accepted, but is nevertheless often used to help focus attention on meteorological and geographical differences that can be quite important. The main source for washout is impaction and interception, where a rain particle accumulates particles in the layer below the cloud on its way down to the ground. When the rainfall is heavy, this mechanism quickly ceases to be effective, so that this mechanism probably accounts for the enhancement of sulphur and nitrogen concentrations at the beginning of some periods of rain. Snow has a much higher washout scavenging efficiency than rain (Raynor and Hayes, 1983).

Another kind of wet deposition is called occult deposition, and occurs when an area is immersed in
fog or low clouds. This is quite important at high elevations. Lovett (1986) reports that 60-80 % of the wet deposition at 1200 meters is direct uptake from clouds. Hydrogen ion concentrations are higher in cloudwater than in rainfall, with pH values of 2 not uncommon. Both turbulence and gravity contribute to the deposition. Deposited cloud water may evaporate on leaf or needle surfaces, leaving quite high acidic concentrations. This deposition occurs only at about one percent of the area affected by acidic depositions, but this area contains a large proportion of the spruce forests.

The particles between 0.1 μm and 1 μm are mainly removed by wet deposition. Larger and smaller particles are subject to dry deposition. Dry deposition is governed both by transfer in the gas-phase and by sorption at the surface (Garland, 1978). The rate of sorption is proportional to the surface concentration. A very important dry deposition effect is deposition on snow cover in the winter, leading to a spring shock of high acidity when the snow melts.

In order for a particle to be deposited e.g. on vegetation, it first must be brought to close contact with the depository site. Usually, this is achieved by the turbulence in the boundary layer. The site is surrounded by a laminar layer, where turbulence is reduced. The particle must pass through this rather thin layer. Heavy particles just fall through it, and very small particles diffuse through it by Brownian motion. The intermediate size particles are unable to penetrate this layer. The main part of the uptake of particles in vegetation is through cuticles in leaves or needles.

Removal of gas confined to a layer of height h, in the absence of other removal processes, is frequently modelled to proceed exponentially, with mean residence time $h/u_v(z)$, where $u_v(z)$ is the deposition velocity at height z. Water is a particularly effective sink for gaseous SO$_2$. The fraction of dry deposition is higher in source areas, and substantially lower in areas far removed from sources. It is quite difficult to measure the dry deposition accurately Hicks (1986). Also, the complicated shape of, say, the canopy of a forest, makes exact physical description of the deposition process very hard. Garland (1978) suggests that about half of the SO$_2$ emitted to the atmosphere is removed by dry deposition. The remainder is oxidized to particulate sulphate and removed in precipitation. The average atmospheric residence time for sulphur is about 5 days.

The data available for model fitting typically consists of wet deposition samples together with (at best) monthly emission estimates and relatively detailed meteorological data. There is substantial measurement error problems with many wet deposition collection programs. For example, if a bucket is open to the air during dry periods, there will be problems with dry deposition, which may lead to overestimates of the wet deposition of, say, sulphate of up to 35% (Fowler and Cape, 1984). It is generally agreed that collectors that only open during rain are preferrable, and many new monitoring programs use event-based data only.
In order to measure dry deposition it is not sufficient to use artificial collectors, since the deposition on actual surfaces will have quite different characteristics. Therefore dry deposition is generally just assumed to depend linearly on the concentration in the air. Again, this concentration cannot be monitored easily, and has to be inferred (cf. Hicks, 1986).

A further problem is inter-laboratory variability. This is discussed by Eliassen and and Saltbones (1984). The discrepancies are most important for sulphates. In the European routine monitoring of sulphuric deposition, described in detail in the next section, it was found necessary to apply a laboratory correction factor to the precipitation chemistry measurements before accepting them as "true" data values.

6. Long range transportation models

There are several different reasons for constructing long range transportation models. The scientific reason, viz. testing our understanding of the basic mechanisms underlying long range transportation, may be the most important. Public health and ecology dictate the importance of predicting extreme episodes of air pollution. From a legal-political point of view the most important reason may be to assess the contribution to deposition from different sources, particularly foreign sources. These three modelling goals are listed in order of required precision. At the current time, only yearly, spatially averaged data can be reproduced by models in a consistent way.

The United Nations' Economic Commission for Europe (ECE), together with the World Meteorological Organization is maintaining a routine program for calculation of long range transport of sulphur in Europe, called EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe). The model used grew out of an earlier modelling effort (see Eliassen, 1978), sponsored by OECD (the Organization for European Co-operation and Development). The goal is to provide the participating governments with information about transboundary fluxes of pollutants.

The model is described in Eliassen and Saltbones (1983). It is a deterministic model, based on the assumption of a stable, well-mixed boundary layer of constant height h, taken to be 1000 meters. Europe is divided by a 150 km grid. Emissions are determined at each of the about 650 grid points by allocating yearly emissions to 6 hour periods, and allowing for a 30% sinusoidal seasonal variation. The air package containing the emissions are transported along trajectories that are determined every six hours from 850 mb wind data. The advection follows the mean 850 mb wind, slowed down and turned appropriately to represent the boundary layer movement. Each emission is tracked for 96 hours, i.e. 16 steps. The deposition at each of 720 receptor points (grid centers as well as the circa 70 chemical measurement stations) is taken proportional to the sum of all remaining amounts in air packages carried to the station by those trajectories.
passing the station at the given point in time. The concentrations \( s \) of \( \text{SO}_2 \) and \( q \) of sulphate are assumed to follow the equations

\[
\frac{Dq}{dt} = -\left(\frac{u_d}{h} + k_t + k_w\right)q + (1 - \alpha - \beta) \frac{Q}{h} \quad (1a),
\]

\[
\frac{Ds}{dt} = -\chi s + k_t q + \beta \frac{Q}{h} \quad (1b).
\]

Here \( D/dt \) is the total derivative along the trajectory. \( Q \) denotes the sulphur emission, \( u_d \) the rate of dry deposition of \( \text{SO}_2 \), \( k_t \) the transformation rate of \( \text{SO}_2 \) to sulphate, \( k_w \) the rate of wet deposition of \( \text{SO}_2 \) and \( \chi \) the deposition rate of sulphate. The parameter \( \alpha \) represents an increased rate of local deposition, here taken to be 15\% in the emission cell. \( \beta \) is the proportion of sulphur emitted directly as sulphate (5\%).

The model does not account for horizontal diffusion beyond the size of the grids. Johnson et al. (1978) present a model (quite similar to the EMEP model) that includes a diffusion of an emitted puff of sulphur at the rate \( O(z^{1/2}) \). In the Johnson et al. model, the wet deposition is taken to be proportional to the precipitation intensity. This is not the case in the EMEP model, partly because of the limited understanding of the physical process of wet deposition. A constant rate of wet deposition is assumed whenever measurable precipitation is observed anywhere in the receptor cell. However, this leads to a geographic distribution of wet deposition that does not properly reflect the distribution of precipitation concentrations. The concentration, \( c \), of sulphate in precipitation is therefore computed as \( c = az + b \), where \( a \) is the scavenging ratio for anthropogenic sulphate, and \( b \) is a background value, so that precipitation may contain sulphate even when there is no trajectory passing through the receptor cell. As may be expected, this yields a very poor day-to-day estimate of wet sulphate deposition, but works reasonably well for long term averages. Since precipitation is not uniform over a receptor cell, stochastic models for rainfall may improve model performance. We will see examples of such models in later sections of the paper.

The EMEP model predictions of two year averages at 40 stations correlate relatively well with the observed averages. Daily values are not well predicted: for \( \text{SO}_2 \), 28 out of 40 stations have correlations between predicted and observed values "significantly different from zero at the 1\% level" (Eliassen and Saltbones, 1983).

An experimental model that allows for varying \( h \), loss of material to the troposphere above the boundary layer, and a seasonally varying rate of chemical transformation, improves the monthly predictions, in particular for sulphate in the summer.

The evaluation of this kind of model frequently concentrates on the correlation between observed and predicted deposition. Since the predictions typically do not track the extreme values very well, even a highly linear relation between observations and predictions may not mean that the observations are well tracked.
In North America, modellers are working towards increasingly complex deterministic models where detailed chemistry, meteorology and cloud physics is included. For example, the Canadian ADOM/TADAP model (Acid Deposition and Oxidant Model, Venkatram et al., 1986) is a 12 layer model, studying 43 species of gas pollutants, 90 gas phase reactions, 25 aqueous phase reactions, etc. Preliminary calibration results for simplified versions of this model are not very impressive. For general reviews of different modelling efforts, see Eliassen (1980) and Fisher (1983).

7. Stochastic models

Rodhe and Grandell (1972) study the removal time of aerosol particles from the atmosphere by precipitation scavenging. They assume that the removal process is a doubly stochastic Poisson process with intensity process \( \lambda(t) \) which takes on two values, \( \lambda_d \) or \( \lambda_w \), according to whether or not it rains. The intensity process is also assumed to be Markov. This process is also a renewal process, and is used by Smith and Karr (1983) to model rainfall. The removal time \( T \) of a particle is simply the time to the first event in the removal process, and it is straightforward to derive its distribution function.

Grandell and Rodhe (1978) generalize this model. Here the precipitation and dry periods are random variables \( \tilde{T}_w \) and \( \tilde{T}_d \), respectively. The scavenging intensity \( \lambda(t) \) is a stochastic process which, during a precipitation period, takes on a random value \( \bar{\lambda} \), only dependent on \( \tilde{T}_w \), and during a dry period takes on the fixed value \( \lambda_d \). Relatively straightforward algebra enables the computation of expected removal time, at least if \( \lambda_d = 0 \), i.e. when dry deposition is ignored. The result is

\[
E(T) = \frac{1}{\tau_d + \tau_w} \left( \frac{\sigma_d^2 - \tau_d^2}{2} + C + \frac{(B + \tau_d)^2}{1 - A} \right)
\]

(2)

where

\[
\tau_d = E\tilde{T}_d,
\]

\[
\tau_w = E\tilde{T}_w,
\]

\[
\sigma_d^2 = \text{Var}\tilde{T}_d,
\]

\[
A = Ee^{-\bar{\lambda}\tilde{T}_w},
\]

\[
B = E\left(\frac{1 - e^{-\bar{\lambda}\tilde{T}_w}}{\bar{\lambda}}\right),
\]

and

\[
C = E\left(\frac{e^{-\bar{\lambda}\tilde{T}_w} - 1 + \bar{\lambda}\tilde{T}_w}{\bar{\lambda}^2}\right).
\]
In the special case treated in Rodhe and Grandell (1972), $\hat{T}_w$ and $\hat{T}_d$ are exponentially distributed, and $\lambda$ is the constant $\lambda_w$. Then

$$T_0 = \frac{\tau_d^2}{\tau_d + \tau_w} + \frac{\tau_d + \tau_w}{\tau_w \lambda_w}.$$  

(3)

The authors also give asymptotic expressions for the survival function of $T$.

In a different vein, Baker et al. (1979) start from the conservation equation for concentration

$$c'(t) = -\nabla \cdot (uc) + q - s,$$  

(4)

where $u$ is the wind velocity, $q$ is the infusion and $s$ the removal process. This equation (equivalent to (1a) and (1b)) states that the concentration in a given volume increases with the infusion of new material and decreases with deposition of existing material and transportation out of the given volume. They investigate cases where the transport term $\nabla \cdot (uc)$ can be ignored. There are two situations in which this may be reasonable. First, all variables may be measured in a system travelling with an air parcel of velocity $u$. $q$ and $c$ are then relative to the air parcel. This is natural when thinking about the deposition, $c$, but the infusion $q$ becomes a function of the actual path of the air parcel. The other possibility is to study infusion and removal from a moving air parcel relative to a fixed frame of reference, but averaged over large areas.

In the case of industrial sulfate particles, they assume simply that $q(t)$ is a constant $Q$, and that removal is by dry deposition or rainout, with $s(t) = c(t)/T_w$ when it is raining and $s(t) = c(t)/T_d$ when it is not. They, like Rodhe and Grandell (1972), model the rain process as a two-state Markov process, with rainy periods of length $\hat{T}_w$ and dry periods of length $\hat{T}_d$, both having exponential distributions with parameters $\lambda_w$ and $\lambda_d$, respectively. The particular case of $\hat{T}_w = 0$ simplifies many formulae. If we let $p_w(c, t)$ be the density of concentration if it is rainy at time $t$, and $p_d(c, t)$ be the corresponding function if it is dry, we get the partial differential equations

$$\frac{\partial p_w(c, t)}{\partial t} = -\frac{p_w(c, t)}{\lambda_w} + \frac{p_d(c, t)}{\lambda_d} + \left( \frac{c}{\lambda_w} - Q \right) \frac{\partial}{\partial c} p_w(c, t)$$  

(5a)

and

$$\frac{\partial p_d(c, t)}{\partial t} = -\frac{p_d(c, t)}{\lambda_d} + \frac{p_d(c, t)}{\lambda_d} + \left( \frac{c}{\lambda_d} - Q \right) \frac{\partial}{\partial c} p_w(c, t).$$  

(5b)

By integration it is easy to get expressions for average concentration. Letting $t \to \infty$, the average concentration converges to $QT_0$, where $T_0$ is the average residence time for a single particle, as given above in (3). Baker et al. (1983) indicate how to take the transportation term in (4) into account, under some simplifying assumptions.

Grandell (1982) assumes a constant infusion rate and that wet deposition is proportional to the rainfall intensity $R(t)$. Then

$$c'(t) = Q - aR(t)c(t).$$  

(6)
Grandell computes first and second order moments for some simple models of $R(t)$. The expected values are all decreasing in $a$, so the limit as $a \to 0$ can be thought of as a model for long-lived particles. Provided that the cumulative rainfall process

$$h(t) = \int_0^t R(s)\,ds$$

is mixing, the properly normalized concentration process converges to an Ornstein-Uhlenbeck process (i.e. a Gaussian stationary Markov process). The models are fitted to empirical data, but the fit is not very good.

In the models discussed above, the deterministic rate equations have been taken as given, with randomness added in only through the rain process. Stein (1984) generalises equation (4) further, again in the case where transportation can be neglected. He further assumes that the removal rate $d(t)$ is independent of the concentration, so that

$$c'(t) = q(t) - d(t)c(t). \quad (7)$$

The random processes $q(t)$ and $d(t)$ are allowed to change each time rain stops or starts, but they remain otherwise fixed. Allowing the infusion process, $q$, to depend on rainfall allows, for example, the study of air parcels relatively high up in the atmosphere, for which pollution emitted from the ground may be partly eliminated by washout on its way up. A rather general formula for expected long-run concentration specializes to the results of Baker et al. (1979) and Grandell and Rodhe (1978). In particular, allowing for random wet and dry removal rates increases the asymptotic expected concentration. In Stein’s work the rainfall process is assumed to be a binary alternating Markov renewal process, i.e. the lengths of time spent in the wet state are i.i.d. random variables, independent of the lengths of time spent in the dry state, which in turn are i.i.d. with a different distribution.

The models described above are discussed further in the monograph by Grandell (1985). In a different vein, Egbert and Baker (1985) use a fairly general Markovian model which can incorporate several layers, correlation between vertical transport and removal, etc. Assume that a (generalised) particle can exist in any of $n$ states. In the simplest model $n = 2$, and the states correspond to survival and removal. In a more general situation, modelling wet removal of sulphur in a region of convective precipitation, there are six states: the particle may be either in a dry region or a storm region. The dry region has an upper and a lower state, whereas the storm region has states corresponding to particles in, near, or below a cloud. Finally, a particle may be removed. A particle can, for example, move from the in-cloud storm state to the upper dry state when the cloud evaporates. Chemical transformations may be included by increasing the number of states.
The trajectory of a particle is described by

\[(X(t), Z(t), t \geq 0),\]

where \(X(t)\) is the location and \(Z(t)\) the state of the particle at time \(t\). Given the trajectory \((X(t), t \geq 0)\), the state process is assumed to evolve according to the transition probability

\[Pr\{Z(t + dt) = j | Z(t) = i, X(t) = x\} = \lambda_{ij}(x, t) dt.\]

A Markovian model for the transportation completes the model. Egbert and Baker develop equations for the two first moments in some cases, assuming temporal stationarity and spatial homogeneity.

This model is amenable to several generalizations. For example, the transition probabilities for the state process may be made to depend on the previous trajectory rather than the current location. The state process can be generalized to incorporate more accurate meteorological models. Also, wind conditions may be included as covariates, affecting the velocity of horizontal transportation. From a statistical point of view, the estimation of the model parameters may be a restrictive problem.

8. A stochastic differential equation model

In this section we will present another model derived from (4), but assuming a different kind of random variability. We assume that the removal rate depends on rainfall intensity, but also incorporates randomness derived from other sources, such as intracloud dynamics, geographic features etc. We will take the infusion process \(q(t)\) as given. Let \(R(t)\) be the intensity of rainfall, so that the amount of rain from all storms in the time period \((t_1, t_2)\) is \(\int_{t_1}^{t_2} R(u) du\). The model is then the Itô stochastic differential equation

\[dc(t) = (q(t) - d(t)c(t)) dt + \sigma c(t) dB(t)\]

where

\[d(t) = \begin{cases} \lambda_d & \text{if } \int_{t_1}^{t_2} R(u) du = 0; \\ \lambda_w g(\frac{1}{r} \int_{t_1}^{t_2} R(u) du) & \text{if } \int_{t_1}^{t_2} R(u) du > 0, \end{cases}\]

\(B(t)\) is a Brownian motion process, \(\lambda_d\) is the dry deposition rate, \(\lambda_w\) is the rate of wet deposit per unit of precipitation, \(r\) is a lag parameter, allowing for non-instantaneous deposition, and \(g(\cdot)\) is the functional relation between wet deposition rate and rainfall amount. As mentioned above, Hicks and Shannon (1979) suggest that \(g(x) = x^{1/2}\). This model has instantaneous variability of the order of magnitude of squared concentration, as found in the European LRTAP data analyzed by Baker et al. (1984). It is not strictly a mass balance equation, since concentrations may increase without an increase in \(q(t)\).
Conditional on $R(t)$ and $q(t)$, and assuming that $\tau$ is known, standard results (cf. Arnold, 1974, Theorem 8.5.5) show that the expected concentration $m_t$ at time $t$ satisfies

$$m'_t = d(t)m_t + q(t),$$

and the expected squared concentration $P_t$ satisfies

$$P'_t = (2d(t) + \sigma^2)P_t + 2q(t)m_t.$$

The statistical properties of the rainfall process $R(t)$ are not specified in the above model. For a discussion of various attempts at rain process modelling, see Waymire and Gupta (1981). Conditional on $q$ and $R$, the process (5) is similar to the diffusion population models studied by Guttrop and Kulperger (1984). The present model can be extended to the multivariate situation with several interdependent pollutants. Models for trajectories and for the corresponding infusion can also be constructed. The general form for these models will be of the semimartingale type, combining point processes and processes of diffusion type.

Below we will derive maximum likelihood estimates (with respect to an appropriate dominating measure) of the parameters $\lambda_d$ and $\lambda_w$. The variability parameter $\sigma$ is conveniently estimated by the squared variation of an observed path, since $\int (dc(t))^2 = \sigma^2 \int c(t)^2 dt$ a.s.

For simplicity, we will study the instantaneous model, obtained by letting $\tau \to 0$. Let $L(t)$ be the Radon-Nikodym derivative of the probability measure corresponding to the solution of (7) with respect to the probability measure corresponding to the solution of

$$d\xi(t) = \sigma \xi(t)dB(t),$$

for the same Brownian motion $B(t)$. A standard calculation (see e.g. Basawa and Prakasa Rao, 1980, sec. 9.5) yields the estimates

$$\hat{\lambda}_d = \frac{\int_0^T \frac{1}{c(t)}(q(t)dt - dc(t))}{\int_0^T 1_0(R(t))dt},$$

and

$$\hat{\lambda}_w = \frac{\int_0^T \frac{g(R(t))}{c(t)}(q(t)dt - d\xi(t))}{\int_0^T g^2(R(t))dt},$$

where $1_0(z)$ is 1 if $z = 0$ and 0 otherwise. Using Theorem 9.5.1 of Basawa and Prakasa Rao (1980), and assuming that $R(t)$ is an ergodic process, we get uniqueness, consistency and asymptotic normality of the estimates $\hat{\lambda}_d$ and $\hat{\lambda}_w$. Thus it is straightforward to determine the appropriate rates from data. A simple check on the model is to compare the estimated rates with those estimated using other methods. More formally, a goodness of fit test can be obtained by estimating the Brownian increments, as in Guttrop and Kulperger (1984).
A major advantage in this type of modelling is that the uncertainty is explicitly modelled, so that confidence sets for parameters can be determined, as well as prediction intervals for future trajectories.

In most cases we do not have access to continuously observed variates. In fact, the best we can hope for is equispaced observations with discretization interval $\Delta$. Utilizing the results of Le Breton (1976), the discretized estimates

$$
\hat{\lambda}_d = \frac{\sum_{i=1}^{\lfloor T/\Delta \rfloor} I_0(R_i)(\frac{q_i}{c_i} \Delta - 1 + \frac{c_i}{c_{i-1}})}{\#(j; R_j = 0)}
$$

and

$$
\hat{\lambda}_w = \frac{\sum_{i=1}^{\lfloor T/\Delta \rfloor} g(R_i)(\frac{q_i}{c_i} \Delta - 1 + \frac{c_i}{c_{i-1}})}{\sum_{i=1}^{\lfloor T/\Delta \rfloor} g^2(R_i)},
$$

where $R_i = \int_{t_{i-1}}^{t_i} R(t) dt$, $q_i = \int_{t_{i-1}}^{t_i} q(t) dt$, $c_i = c(t_i)$, $t_i = i\Delta$ and $\lfloor \cdot \rfloor$ is the integer part function, will be close to the maximum likelihood estimates based on the discretized data, at least for small $\Delta$.

9. Discussion

Current long range transport models, whose predictions come within a factor of 2 of the observed values, are considered acceptable by the modellers. These models are "statistical" in the sense that they only can predict temporal and spatial averages. A problem is the lack of adequate data for emissions and dry deposition, and the large measurement errors associated with the wet deposition data. There has been no direct modelling of these measurement problems, although e.g. the EMEP model attempts simple corrections to the chemistry data. Another factor limiting the accuracy of the models is the over-simplicity of the approach. While it can be argued that the data do not admit more sophisticated modelling efforts, the model experiments performed on the EMEP model indicate that simple modifications can improve a model substantially.

Among the parts of the model that have a high potential for improvement are: the dry deposition rates, which really should vary with the vegetation present in a receptor cell; the mixing height; the escape of pollutants to the troposphere, yielding a background pollution; and the relation between wet deposition and rainfall amounts, as well as other features of rain cloud dynamics. Most models to date have focused on sulphur. In the future it will be necessary to involve the interaction between sulphur compounds, nitrogen compounds, ozone and maybe even hydroxyl radicals. The resulting nonlinear chemistry could improve models substantially. Also, mounting evidence suggests that sulphur, nitrogen and ozone all are important from the environmental impact point of view, and therefore multivariate models must be developed. The current low quality of data makes it less important to attempt precise modelling of the chemical and meteorological interactions. Simplicity still has a value in model building, especially since the model parameters have to be estimated somehow.
In terms of the modelling goals mentioned in Section 6, the current efforts in the North American modelling community towards very complex models, incorporating many of the known methods, appears to be hampered severely by the lack of adequate data. In order to enhance our understanding of a complex system, the sensitivity of these models to small changes in, say, meteorological conditions, must be studied. The acid rain literature contains little discussion of the problem of predicting extreme episodes. It can be hoped that stochastic models like those discussed above can contribute to the prediction of extreme values. At this time, the EMEP model is used by legislators in Europe to assess contributions to the deposition from different sources. It is not clear that the quality of a model which makes predictions that are correct to within a factor of 2 is sufficient to establish source-receptor relations with sufficient confidence to base legislation upon them.

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