2.3 Atmospheric Transport of Chemicals

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When the atmospheric transport of polluting chemicals is considered, the problem seems naturally to divide itself into three categories, based largely on the time and distance scales involved. These categories are: (1) local transport, by which we mean distances of up to perhaps 50 km, in which the main phenomena are mixing within the atmospheric boundary layer, prevailing winds, and immediate deposition; (2) mesoscale transport, up to a few hundred kilometres, for which synoptic weather pattern information and knowledge of the rate of photodegradation processes are vital; and (3) global transport, for which major considerations are the balances between the various global sources and sinks involved, as well as understanding of particular transport routes and pathways that may lead to much higher pollutant levels in remote areas than can be understood on the basis of general diffusion phenomena. See Table 2.3.1.

All of these processes are important for the purposes of this volume. However, since in general they have been summarized in many published works, we restrict ourselves to describing each of the phenomena involved only briefly, and then addressing issues which are of particular significance to the often isolated areas considered here, particularly in northern climates. Here, a major concern is the long-range input of pollutants from built-up temperate areas into regions where the prevailing ecosystems are rather delicate. Local pollution generation is limited in magnitude but important over short distances. The main conclusions are that the problem is serious and becoming more so, and that the main source of uncertainty in our conclusions is the lack of monitoring facilities in the remote areas involved, as well as a persistent lack of fundamental understanding of the processes by which these more remote ecosystems do or do not cope with the stresses they suffer.

Table 2.3.1   Features of the three main types of atmospheric transport

	Distance scale	Transport mechanisms	Removal mechanisms	Modelling
Local	0–50 km	Prevailing wind; atmos. stability	Deposition	Wind rose, stability classes
Mesoscale	50–1000 km	Vertical mixing throughout troposphere; weather patterns	Deposition/ resuspension; photochemistry	Trajectory analysis multiple-level models
Global	Global	General circulation	Oceanic and Arctic sinks	General circulation models

2.3.1   INTRODUCTION

The rejection of the old adage that the 'solution to pollution is dilution' is a quite recent phenomenon. Until just a few years ago, once a pollutant was dispersed just enough that its presence was not immediately obvious, it was regarded as no longer any kind of a threat. The same opinion was held for a great many pollutants in the environment and for some persons, indeed, it still is.

Most people now realize, however, that dispersion of a pollutant from a concentrated point source (or a localized collection of point sources) to a level at which it is not an immediate threat to man, his structures, his domesticated plants and animals, or the ecosystem at large, is but a first step. We now know that significant ecosystem effects can be produced by pollutants generated many hundreds of kilometres away (mesoscale pollutant transport). We have even finally come to recognize, alas, that even the vast mass of the atmosphere on a global basis has a very definitely limited capacity to dilute, assimilate and ultimately dispose of the chemicals it receives. It seems clear that cessation or curtailment of input to the atmosphere is the ultimate solution. Until that can be arranged, however, it is vital that we understand the fate of what does get released.

2.3.2   CHEMICAL AND PHYSICAL PROCESSES

When a chemical, in whatever form (gas, particle, aerosol, etc.), is released into the atmosphere, it has only three possible fates in any time period: it must be chemically converted into some other form; it must be effectively removed from the atmosphere, or at least that part of the atmosphere with which we expect to come into contact in the near future; or it must remain in the atmosphere and become part of a general accumulation phenomenon. Which of these happens

depends strongly, of course, on the chemical and physical nature of the substance involved; but relatively few polluting substances (mercury vapour may be a counterexample) travel very far without a chemical transformation or a (perhaps temporary) removal process being effective, and therefore it is appropriate to consider these before discussing details of transport processes. Chemical transformations, particularly photochemical degradation of organic pollutants in the atmosphere, have been extensively dealt with in a previous volume in this series (Korte, 1978).

2.3.3 DEPOSITION AND EXPOSURE CALCULATIONS

Deposition onto ground, water or vegetation is perhaps the most important sink, or removal process, for all atmospheric contaminants that are not chemically degraded in the atmosphere itself. From the point of view of land- or water-based organisms, such deposition is perhaps the most important source. Fortunately, the problem may in most cases be dealt with in a fairly simple way.

The suggestion that the rate of deposition should be proportional to the concentration in the atmosphere at any given point or time, although it may seem an obvious hypothesis today, was actually made fairly recently. Credit may be given to Gregory (1945) for the observation, and to Chamberlain (1953) for the subsequent formulation (Yamartino, 1985). In any case, if the rate of deposition, in terms of mass per unit area per second, say F, is proportional to the concentration in the atmosphere, C, in terms of mass per unit volume, so that

$$F(g/cm^2/s) = v/C(g/cm^3)$$

then the proportionality constant, v, obviously has the dimensions of a velocity. The interpretation that one may imagine is that the entire concentration of a pollutant in the atmosphere is settling at a uniform velocity onto the surface of the earth (and simultaneously being uniformly remixed in the atmosphere). Although it is clear that the actual processes at work are much more complicated than that, the term 'Deposition velocity' has gained a popularity in the literature that is not to be challenged.

Realistically, one would expect that for large particles (say, exceeding a few micrometers), the deposition velocity would be something like the terminal, sinking velocity given by Stokes's law. For very small particles (say, less than 1 μm), on the other hand, Brownian movement would maintain a uniform mixture in the lower layers of the atmosphere. Thus, a minimum deposition rate would be expected for particles around 0.1–1.0 μm. This is, indeed, observed.

2.3.4 MECHANISMS OF TRANSPORT

The mathematical equations governing the behaviour of fluids were formulated around 1850, in essentially the same form as we know them today. They are

described in detail in many texts, and we see no reason in the present work to make any more than a brief mention of their general characteristics.

Briefly, the equations are fourth-order time-dependent partial differential equations which are strongly nonlinear. They describe a slightly viscous compressible fluid subject to very complicated driving forces, including differential heating, very much modified by Coriolis forces on a global basis. The boundary condition at the lower edge is quite difficult to prescribe due to the highly variable nature of the terrain over which the air flows.

Once the velocity field, temperature distribution, and so forth for the air itself are known, either by calculation or from very detailed observations in the field, the movement of a pollutant is a further problem involving convection (or advection) and diffusion, generally of a complicated form (see below), as well as deposition and chemical transformation.

Not surprisingly, exact analytical solutions for such an array of equations are not generally available. Indeed, they exist only for a small number of highly specialized and geometrically rather artificial situations. The full-fledged numerical solution in any given case is theoretically possible, but it is extremely expensive in terms of computer time.

The whole subject, therefore, becomes a matter of making approximations that allow one to obtain quantitative information but are still realistic for the particular problem under consideration. Naturally, there is a considerable literature about various possible simplifying techniques. We will leave to other sources the discussion of techniques for solving the fluid mechanical equations themselves, and start from the assumption that we have information (or will be willing to make simplifying assumptions) about the velocity field, and discuss the issue of how to calculate the pollutant distribution starting from that point.

2.3.5 TYPES OF APPROXIMATION

Generally, what kind of approximation is appropriate depends on the time and distance scale of the problem. To begin with, although the equations involve diffusion, what the theoretician regards as (molecular) diffusivity as might be measured in the laboratory, is quite inappropriate. Small- and large-scale eddies and circulation patterns caused by general turbulence, wakes behind objects, rotations induced by low- and high-pressure weather patterns, and so forth produce much more mixing in most situations. The standard response is to replace the molecular value of diffusivity with a much larger value, often itself a function of time and/or distance, determined empirically to make the solution match reality in some sense. Other approximations are made in similar ways.

Environmentally significant modelling studies of pollutant behaviour seem naturally to divide themselves into three levels, for a variety of reasons.

At the strictly local level, most pollutants are after all produced close to the ground, and their effect upon anything in the immediate vicinity will depend

strongly on vertical movement of the chemical within the atmospheric layer closest to the earth, the so-called meteorological boundary layer. This is best understood in terms of stability classes, inversion layers, and the like. Lateral transport depends largely on the prevailing winds at the time, and short-range deposition is reasonably well understood.

At somewhat larger distances, however, of the order of 50 km or more, the prevailing wind is likely to have changed in direction by the time the pollutant has travelled that far, and the speed and direction of the prevailing winds at a point are no longer accurately predictive of the pollutant's fate. For such cases, real-time consideration of weather patterns and of their changes in space and time are required, and much more complex models are needed. Also, the times involved allow photochemical reactions to proceed, which must therefore be considered in considerable detail.

Finally, at the global level, the overall efficacy of mechanisms for final removal of chemicals from the atmosphere must be considered, and although general circulation models are critically important in particular cases, the overall holding and disposal capacities of the atmosphere are perhaps the dominant considerations.

2.3.6 THE GAUSSIAN PLUME

The direct analytical solution of the governing equations under a number of simplifying assumptions (uniform wind field, including close to the ground, wind uniform over time for a long period, constant diffusion coefficients, no up- or downstream diffusion, etc.) leads to what is usually called the Gaussian Plume Model, for which an explicit formula for the pollutant density as a function of position can be written. A slight generalization which allows spatially varying diffusion coefficients is called the Gradient Transport or the K-model, and is conceptually quite similar. One or the other of them is used very widely in formulating models of air pollutant transport (Hanna, 1985).

The Gaussian plume approach is a very convenient way of handling air pollution estimation problems as far as it goes. However, the assumptions are very often not valid; the most important of these, perhaps, is the idea that the air is moving past the pollutant source essentially as a solid, and that lateral and vertical diffusion are the only mechanisms by which pollutants can be distributed. Even if the numerical values are increased to reflect the existence of eddy diffusivity, the results suffer because of larger-scale instabilities connected with buoyancy, stability, and other phenomena.

To make this general approach more realistic, Pasquill (1961) devised the concept of Stability Classes. The idea was to classify meteorological situations into a number of categories that influenced the speed at which vertical movement, particularly movement from the height at which the pollutant was released down to ground level, can take place. The results of the study were called

Pasquill Stability Classes, and are now more often known as Pasquill–Gifford, or even Pasquill–Gifford–Turner Stability Classes, to reflect further work (Gifford, 1961, 1976; Turner, 1970). These classes are very widely used to evaluate and predict short-range short-term air pollution events.

2.3.7 AVERAGE EXPOSURE: THE WIND ROSE

The basic Gaussian and Pasquill approaches deal, fundamentally, with situations where the wind is in a constant direction. We know, however, that it varies in direction and in speed, and we should consider the modifications needed to deal with these cases. The first situation one must consider is the problem of predicting or evaluating the long-term average pollution levels that will result from a given source, considered first to be emitting uniform amounts of material over a long period of time. For this purpose the so-called Wind Rose was developed. This is a pictorial representation of the magnitude and direction of prevailing winds at a geographical location, information which is typically available from existing records (or which can be recorded automatically for a relatively low price).

The application of this concept is simple enough. One imagines preparing a sort of map, by superimposing a Gaussian-type plume on each of a number of direction vectors around the compass circle presented on a wind-rose diagram, noting how much pollution (on a long-term average) results from each one, and adding the results for a fairly fine grid or network of points on the resulting two-dimensional map. The process may sound laborious, but it can easily be computerized, and a readily understood result, such as a contour map, can be produced. Again, this approach is widely used for localized pollution problems.

The main drawback to the wind-rose concept is that it is severely limited in terms of distance from the source. This is especially true in directions other than that of the prevailing wind. Even for locations where the wind is almost always in one direction, there will be (perhaps brief) periods when the wind direction is quite different. A Gaussian plume approach applied to these directions will lead to the incorrect conclusion that some pollution will travel 'upstream', as it were, for unlimited distances. In fact, the time over which the wind continues in such a direction may be quite limited and the polluting material may virtually never have the opportunity to travel any great distance. Thus, the wind-rose approach will overestimate the amount of pollution that will be felt in an 'upstream' direction and, for that matter, will give incorrect results for larger distances in all directions from the source. In practice, this limits the distance over which the approach can be used to something between 30 and 50 km.

2.3.8 CHANGING WIND PATTERNS: TRAJECTORY ANALYSIS

In order to deal with distances great enough that weather and wind patterns may have changed by the time a packet of air traverses the region considered,

it is necessary to have actual (or simulated typical wind-field information on at least a two-dimensional basis. Then, one can think of a plume with a 'wavy' centre line changing its position and shape with time.

With a reasonable amount of computer time available and a certain amount of care given to the formulations, we may think of integrating the resulting ground-level exposure and deposition to calculate a time-integrated realistic value for both.

Unfortunately, the analytic expression for the Gaussian formulation in any realistic sense breaks down if the centre line of the plume is not straight. What is then needed is a calculation scheme that synoptically takes into account the entire field, incorporating the wind pattern on at least a two-dimensional basis. Two approaches are typically discussed, generally referred to as the Euler and the Lagrange formulations (these have been discussed in many places; see, e.g., Venkatram, 1985). In the Euler approach, one considers dividing the region into cells or subdivisions of some shape, and calculating for each one the inflow and outflow resulting from wind transport and the source and sink (deposition) terms. One can incorporate easily such things as chemical reactions. The drawback is that many numerical problems have yet to be resolved, and inordinate amounts of computer time may be required, even on the largest of modern machines.

The Lagrangian approach is conceptually easier to deal with and, in its simplest form, Trajectory Analysis, permits a number of extremely useful, if approximate, calculations. In a Trajectory Analysis approach (Eliassen and Saltbones, 1975), one imagines a series of 'puffs' to be released from a point, and follows each one across the map using time-dependent information on wind patterns, allowing for a dispersion (which does not have to be isotropic) as it goes. For time-averaged exposure, one keeps track of the accumulated exposure from each puff at each time, a procedure which may sound computationally expensive but in fact is vastly less involved than Euler-type calculations. It is easy to show that, provided the puffs are spaced closely together, the procedure produces results identical to those of the Gaussian plume approach under conditions in which the latter is applicable, so at the very least trajectory analysis may be considered a legitimate generalization of plume-type calculations.

The approach is criticized since it is not clear what wind field should be used. Wind differs in direction and speed at different heights, and so far each such calculation has been produced using what the authors regarded as a 'typical' altitude (such as the wind-field at the 850 mb level) to follow the trajectory, although it is demonstrable that if a different altitude is used for the wind field, the appearance of the trajectory on the map will indeed be noticeably different (Venkatram, 1985). It is interesting to note that all Gaussian plume approaches are subject to the same criticism and more, since they assume the vertical variation does not exist at all, but this drawback is typically ignored.

On the positive side, there are several things one can do with trajectory analysis that are not possible using other approaches. For one thing, it is immediately obvious from short-term simulations that the deposition pattern is naturally extremely 'patchy' for relatively short-term releases (Zuker *et al.*, 1979). This observation seemed nonetheless to come as something of a surprise in, for example, observations of depositions of radioactive materials from the Chernobyl accident (Hohenemser *et al.*, 1986).

Another important application which trajectory analysis makes possible is the investigation of the source of sudden air pollution episodes. The approach allows one to use historic weather pattern information to trace air masses backwards in time to get a rough estimate of where they arose. This has been done in Scandinavian countries, for example, to trace the origins of sudden appearances to locations in other parts of Europe and, indeed, provided one of the first indications of the location, as well as characterizing the type of source, of the Chernobyl incident (Hohenemser *et al.*, 1986).

Finally, an application which is increasingly seen as important is that of tracing a polluted air mass in real time. Incidents such as the accidents at Chernobyl or at Three Mile Island, nonradioactive spills such as Bhopal and elsewhere, and others make it desirable to be able to follow the movement of the main bulk of the polluting substance geographically using an atmospheric model. There is no reason why on-line weather data cannot be combined with existing forecasts for a few hours in advance to provide a quite reasonable prediction of air pollutant movement for even as much as a day before action by regulatory officials, or those in charge of emergency evacuation procedures, for example, might be required. Such on-line modelling systems will inevitably help with decisions concerning evacuation, protective measures, and so forth in case of future accidents which, after all, seem inevitable and ought to be anticipated, if not foreseen.

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