The Classification of Pollutants and their Pathways in the Atmosphere [and Discussion]

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The classification of pollutants and their pathways in the atmosphere

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Atmospheric pollutants may damage, directly or indirectly, human life and health, other living organisms and complete ecosystems, human artefacts, and climatic conditions. The development of appropriate policies and methods for control of pollution requires, *inter alia*, an assessment of the routes taken by pollutants or their precursors through the atmosphere. Consideration of these routes leads to a broad classification on a local, regional or global basis associated mainly, but not exclusively, with the terrestrial boundary layer, with the troposphere and with the stratosphere respectively. This may require in some cases the perspective of total biogeochemical cycles, and in any event of the relative importance of man-made and natural sources of materials to be regarded as pollutants.

1. Introduction

Pollution is not a branch of natural philosophy but a social phenomenon to which a scientific approach is mandatory if effective methods of dealing with it are to be found and applied. To pollute, according to Dr Johnson, means 'to corrupt by mixture of ill, either moral or physical', a definition confirmed in the latter, presently relevant sense by the *Oxford English Dictionary* as 'to make physically impure, foul or filthy: to dirty, stain, taint, befoul'. A long-standing result of human activities is the release into the atmosphere of waste products, either accidentally or deliberately, which do just these things with actual or potential consequences of damage.

These consequences may be itemized broadly as follows:

(1) damage to human life or health;

(2) damage to other living organisms, including crops and extending to ecosystems in general;

(3) damage to buildings and other artefacts;

(4) modifications to climate with all the consequential changes which could occur falling under the first three headings.

Two trends have become very apparent in recent years. The first is the vastly increased use of new technologies and associated inroads on the material resources of the planet, with the consequences that there are much greater volumes of waste product, in greater variety, thereby resulting in larger pollution hazards and newer ones. Secondly, social awareness has developed in such a way as to find these hazards variously unacceptable, and to seek to control them by minimizing or eliminating them. The impact of developing technology and the concern about its implications for pollution are, of course, not uniform over the world.

The control of pollution is to be visualized as taking place within a framework of legislation which permits the encouragement of restraint and the curbing of excess. Any such framework implies a philosophy of control and corresponding policies. This is not the place to undertake a review of such matters but current concern with them in the United Kingdom is emphasized by the appearance of two recent reports; one on pollution control in Great Britain and how it works (Department of the Environment 1976*a*); the other on an integrated approach to air-pollution control (Royal Commission on Environmental Pollution 1976) in which recommendations for changes in present methods of handling some of the problems are put forward.

The general issue of control is raised at the outset in order to emphasize that the study of pollution is a practical matter, and that the fundamental objective of any scientific investigation of it must be to assist decision-makers by providing them with the best available information. Such information comprises, for the most part:

(1) estimates on a quantified basis of the actual or potential damage caused by specific pollutants, or combinations of them;

(2) the identification of existing and potential sources of pollutants, and the placing of them in perspective against natural sources;

(3) the relation of sources to effects.

The last of these implies a knowledge of the pathways of pollutants, from identified sources to identified sinks. Together these kinds of information enable an assessment of the total risk situation and the identification of areas where control can best be applied. Further information falls under the headings of practical suggestions for methods of control, and programmes for research into pollution affairs. Authorities may then set up cost/benefit analyses on whatever basis they decide may be appropriate in order to decide on action.

2. The Royal Society Study Group on Pollution in the Atmosphere

The Royal Society Study Group on Pollution in the Atmosphere was set up in 1975 with the principal terms of reference of undertaking an intensive study of the long-range dispersal, absorption and chemistry of pollutants in the atmosphere and their effect on the environment, including man-made ecosystems; and to arrange for a Discussion Meeting on this subject in the 1976/77 session; it is that Discussion Meeting which has given rise to the present series of papers.

The Group was made up of about 25 individuals drawn from universities, government departments and industry, and represented the wide variety of scientific disciplines involved – physics, chemistry, meteorology, chemical engineering, fluid mechanics and biology. It has maintained a working interface with a parallel Study Group on Long Term Toxic Effects – mostly in humans – which held a similar Discussion Meeting shortly after.

The Group held its first scientific meeting in September 1975, and since then has had a further 12 such meetings. At a very early stage it adopted a method of approach which was essentially that of the present Discussion – that of pathways of pollutants. Early meetings were given over to general considerations of the transport of matter through the atmosphere, of the kinds of chemical change which are important during that transport, and of deposition or absorption from the atmosphere, drawing examples from the behaviour of various pollutants. This laid a foundation within which it was possible to discuss particular problems relating to the total behaviour of specific pollutants. Meetings were held on the impact of supersonic flight on the stratosphere, the impact of fluorocarbons, the transport of sulphur compounds in northwest Europe, airborne heavy metals, carbon dioxide in the atmosphere, and the philosophy and practice of air pollution monitoring. Finally, the Group gave consideration to transient pollution: that resulting from accidental release into the atmosphere of more or less toxic substances.

3. Pathways in pollution: general

The total amount of a pollutant released depends on the number and size of its sources. Its capability of doing damage is conditioned by the amount of it available at the place where it is taken up from the atmosphere. Consequently it becomes important to know the pattern of its dispersal from the original sources, the way in which chemical change may occur during its migration, and the efficiency of the sinks through which it is finally removed from the sphere of effective action. That action may be of course be direct, as in inhalation or in deposition on the surface of an organism or material which as a result suffers harm; or it may be less direct, as for example with acidified rain which may induce changes in the character of soils or watercourses to which it penetrates.

The shortest known pathway of atmospheric pollution is almost certainly that between the burning tip of a cigarette and the lungs of the smoker. It has been treated extensively elsewhere and is outside the present terms of reference. Similarly, indoor pathways have been excluded, although the extensive work that has gone into the rigorous control of atmospheres in places of work where toxic substances may be a hazard has produced many results that are of value in the setting of standards in wider contexts. The quality of domestic indoor atmospheres may sometimes leave much to be desired but is not of great interest in considering atmospheric pollution in general.

The atmosphere proper which is our concern may be divided roughly into three zones. The uppermost is the stratosphere, which extends to a height of some 50 km above the surface from about 8 km above the poles to about 16 km above the equator, subject to seasonal and other fluctuations. It is bounded by temperature inversions and is characterized by rising temperature with increasing height. The pressure at the lower bound is of the order of one-tenth that at the surface, and at the upper bound about one-thousandth of that pressure. It is generally calm because of its temperature gradient, which limits convection, free of cloud except for a little near its base, and free of precipitation. Regions above the stratosphere do not appear as yet to have produced issues important for pollution.

Below the stratosphere is the troposphere, extending downwards almost to the Earth's surface, and with a temperature gradient in the opposite direction. The upper interface, called the tropopause, is not readily crossed by diffusing gases, and our understanding of transfer across it is incomplete, especially in middle latitudes where it is ill defined, being spread over an extent of a few kilometres called the tropopause gap in which the temperature gradient is indeterminate. In terms of motion the troposphere is relatively violent, since it responds vigorously to the uneven heating of the land masses and the oceans with the production of winds. It is associated with cloudiness, often extreme, and with the precipitation of rain or snow. The troposphere is very important in determining general patterns of climate.

Close to the surface of the Earth the troposphere is modified in a boundary layer, very roughly defined, extending vertically a kilometre or so. In this region the atmosphere is responsive to detailed features of the surface such as mountains, valleys, coastal littorals, conurbations or even large individual buildings. At times its upper bound may be associated with a temperature inversion, providing a region from which the upward escape of air is difficult. A useful account of the physics of planetary atmospheres, and the terrestrial one in particular, has recently been given by Houghton (1977).

Sources of pollution are located almost exclusively at or very close to the surface of the Earth, aircraft providing the exception. By far the commonest pollutants are the combustion products of fossil fuels. The major products are carbon dioxide and water, the latter of which can hardly be regarded as a pollutant because of the much larger amount of water vapour deriving from natural sources. Carbon dioxide merits consideration, however, because the amount currently being emitted is sufficient to cause some increase in the total atmospheric content. Carbon dioxide is important in photosynthesis and in the absorption of infrared radiation. It is dealt with in one of the later papers in this volume. The combustion products also constitute the major source of man-made sulphur oxides, derived from sulphur compounds in the fuel, extreme refining of which is prohibitively expensive. They are further the major source of nitrogen oxides – nitric oxide and nitrogen dioxide – which are formed by the fixation of atmospheric nitrogen during the combustion process. Automotive fuels also yield unburnt hydrocarbons and related substances – some of which may be carcinogenic – as well as carbon monoxide and compounds deriving from anti-knock additives, predominantly of lead. Another product, black smoke, has largely been eliminated in recent years because of the application of official policies about industrial and domestic effluents.

Direct industrial emissions of other, potentially toxic materials are minimal because of careful control of stacks, as they are in general domestic emissions. A recent important exception to this is the recent widespread dissemination of chlorofluoromethanes from refrigeration devices and aerosol sprays. Agriculture provides sources of pollution. Denitrifying bacteria in the soil provide a source of nitrous oxide which may become a source of concern with the increasing use of nitrogenous fertilizers. Not all gaseous pollutants are associated with modern technology: primitive slash-and-burn agriculture contributes to the emission of chlorine compounds. Finally the possibility exists of the accidental discharge, in single incidents, of significant amounts of substances which may be of high toxicity, such as radioactive materials and industrial products and intermediates.

Particular pollutants may have many and varied pathways from source to sink, both in atmospheric trajectory and in chemical change along the path. Thus, nitrogen oxides released from an automobile exhaust may react, via rather complicated chemistry, with other emission products to give lachrymatory substances in aerosol form such as peroxyacetyl nitrate (PAN), which make up photochemical smog – a *local effect*. If emitted from a high stack, a proportion of such oxides may escape from the boundary layer into the troposphere generally, and appear as nitrous or nitric acids in precipitated rain several hundred miles away, in which case there is an example of *regional* pollution. Because of their reactivity or solubility they are most unlikely to reach the stratosphere. If they are actually emitted there, however, from the exhaust of a supersonic aircraft they will be disseminated round it fairly quickly (a few months) with small chance of escape downwards and only slow upwards migration; they will then engage in the complicated, partially cyclic sets of reactions which can result in a decrease in the amount of stratospheric ozone until they form nitric acid which eventually reaches the troposphere and is rained out. This provides an example of *global* pollution.

The practical object of any study of the pathways of a pollutant is the construction of as complete an inventory as may be possible of the substance concerned, so that the contribution of a particular source or group of sources to the various sinks can be estimated. This requires more or less extensive measurement or monitoring of the substance, as well as substances with which it may react in the atmosphere. It also tends to need the construction and application of an appropriate model of the situation.

As atmospheric pathways become longer in space and in time, the more blurred and difficult to unravel they tend to become. Part of this difficulty stems from the more extensive sampling and modelling required, the latter of which can be a burden on even large computer systems. Part of it arises because the paths themselves intersect and overlap. Increasingly it becomes necessary to take into account a wider range of sources, including natural ones. Ultimately there may be significant impact on the total biogeochemical cycle of one or more elements. In this respect the work which is being done under SCOPE auspices (Svensson & Soderlund 1976) on the global cycles of nitrogen and sulphur is of great importance, as well as work currently proceeding on the carbon cycle.

4. LOCAL POLLUTION

In the local situation, sources are usually clearly defined and are almost exclusively man-made. Pathways in the atmosphere lend themselves to representation by sophisticated techniques of modelling, and monitoring is a relatively straightforward affair. A typical very localized situation is the deposition of lead compounds from automobiles close to highways and road junctions. Materials emitted from high stacks can be dealt with by using modelling techniques associated with the cases of representative weather conditions proposed by Pasquill (1961) which allow estimates to be made of the amount of pollutant retained in the boundary layer and the amount taken up into the troposphere. Effective times from emission to deposition range from a few minutes to a day or two. This applies to both steady or intermittent emissions and to near instantaneous accidental releases.

Much more remains to be found out about deposition itself, and about the subsequent pathways in targets of pollution to the point where actual damage is induced. The hazards to people, vegetation or artefacts are not easy to estimate because of the problems of getting valid information about the effects of long duration of exposure at low levels of concentration. The situation is quite different when dealing with a single accidental release of quantities of a substance which may be acutely toxic. The techniques of control are also quite different, being related to design to prevent mechanical failure of plant rather than with the establishment of permissible low levels of emission.

5. REGIONAL POLLUTION

Regional pollution, occurring at up to a few hundred miles from sources, is rare because of the relatively wide spread from the source and consequent high dilution of the pollutants. For a given type of environment the local effects would be expected to much more severe and demanding of attention. The exception is found where for some reason the remoter target is particularly vulnerable.

The most characteristic example of this is the deposition of acid rain, deriving from the sulphur and nitrogen oxides of combustion products, falling on soils which are weakly buffered. This can result in damage to vegetation, and to animal life in rivers and lakes which become too acid.

The analysis of pathways in such cases tends to be a matter of great complication in part because of the wide range of sources of pollution which can contribute and the possible intervention of effects from natural sources. A further source of complication lies in the complexity of the atmospheric trajectories, which take a few days to traverse, in the rather violent motions of the troposphere. Extensive monitoring, including aerial observations, must be used in conjunction with the modelling. A recent study in this category is the intensive work sponsored by O.E.C.D. on the transport of sulphur compounds across North-West Europe (see, for example, Department of the Environment 1976*b*).

6. Global pollution

Global pollution is largely synonymous with stratospheric pollution. Mixing times there are in the region of a few weeks in the E–W dimension, a few months in the N–S dimension, while vertical motion is generally much slower in the lower parts of the stratosphere, with characteristic times of a few years. Transfer to and from the troposphere and between hemispheres is also slow. The result is a global, or at least hemispheric distribution of pollutants. Chemically stable substances which are not readily rained out of the troposphere can also achieve world-wide distribution.

The pathways of stratospheric pollution start from two kinds of source: direct injection into the stratosphere and penetration of the tropopause by substances released at a lower level which are stable enough to survive upward transfer from the surface. Attention has been focused very heavily on the effects of pollutants on the ozone in the stratosphere because of its efficiency in filtering out potentially harmful ultraviolet radiation.

In the upper parts of the stratosphere, radiation of wavelength below about 220 nm is removed by absorption by diatomic oxygen molecules, which are in consequence dissociated to free atoms. These atoms can combine with further diatomic oxygen to form ozone (O_3), which can then be destroyed by a variety of further reactions. The result is to give a near steady state amount of ozone. Ozone itself is a very effective absorber for radiation up to a wavelength of about 290 nm, its effectiveness then falling rapidly to zero at about 320 nm. It is the absorption of this radiation and its ultimate degradation to heat which is largely responsible for the temperature distribution of the stratosphere (and therefore for the stratosphere itself).

The narrow band of radiation between 290 and 320 nm, known as u.v.-B, appears to be particularly biologically active. This is perhaps not very surprising in that the quanta concerned are equivalent to about 400 $\mathrm{kJ\,mol^{-1}}$, which is near the threshold of breaking many of the chemical bonds found in organic materials. There is, for example, a damaging action on DNA. More especially, there is a significant correlation between exposure to u.v.-B and non-melanoma skin cancer, a relatively frequent condition of low mortality to which some groups of white-skinned people are particularly prone. There is also evidence that some cases of the much rarer, but much more dangerous, melanoma skin cancer are induced by exposure to u.v.-B.

Absorption of u.v.-B by ozone in the stratosphere is such that a decrease of 1 % in total ozone lets through about 2 % more u.v.-B, with consequent and not necessarily linear effects on skin cancer incidence; hence the major part of the current concern. There may also be consequences for other animals and for vegetation, etc., but little useful evidence is available. A sufficient change in ozone and its distribution might also affect the atmospheric heat balance in ways which are difficult to predict with accuracy.

Anxiety has stemmed from three main types of source of pollution:

(1) the injection of nitrogen oxides directly into the stratosphere from the exhausts of supersonic aircraft;

(2) the penetration from below of the very stable chlorofluoromethanes, used as refrigerants and aerosol sprays, in increasing amounts;

(3) the penetration of nitrous oxide, released by denitrifying bacteria, and its potential increase through increased use of nitrogenous fertilizers.

All of these provide sources of materials which can take part in an extensive and complicated scheme of chemical reactions in which ozone is concerned, and which can result in a net decrease of total ozone. There have been very extensive and sophisticated modelling studies of the stratospheric oxone situation, which is a difficult one because of the linking of the chemistry with transport in the stratosphere and because of uncertainties about whether the chemistry is complete and about the values of some critical rate constants.

The supersonic flight problem is probably the most tractable in that direct injection will produce relatively immediate effects – within a few years. The predictions made in a National Academy of Sciences Report (Booker 1975), given the expected low rate of growth of supersonic transport, give no cause for alarm in that ample time is available for improvements in engine design to limit emissions.

The other two sources listed above provide more serious problems because of the size of the potential effects and of the delay in their appearance associated with the delays in the penetration to the stratosphere of the original emissions. To quote from a recent report (Tukey 1976) on the environmental effects of chlorofluoromethane (CFM) release: 'If CFM uses were to continue at a constant rate, the ozone reduction and consequent u.v.-B increase would flatten out gradually, approaching a steady state. To reach half of this value would take roughly 50 years.'

Consequently one may be concerned about the later developments from pollutants which may already be launched. Fortunately, the work which has already been done (Gutowsky 1976), within 4 years of the recognition of the problem, indicates that there is here effectively an early warning situation: 'It appears that the continued release of CFMs at the 1973 production rate would cause the ozone to decrease steadily until a probable reduction of about 6–7.5 % is reached, with an uncertainty range of at least 2–20 %, using what are believed to be roughly 95 % confidence limits.' Given the time scale and the potential magnitude of the effect there is thus a period of a few years which will enable production to be eased, less potentially harmful substitutes sought, and the predictions sharpened up by improved modelling coupled with direct observations.

It deserves to be emphasized that it is u.v.-B which is likely to have the harmful consequences, and the amount of this which reaches the surface of the Earth now is some ten times greater than the increase which would result from a decrease of 5 % in stratospheric ozone. This could point up the need for a present effective campaign against exposure to sunlight in appropriate areas, of which there is little indication.

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Discussion

S. W. Radcliffe (*Room* 708 *B*, *Scientific Branch*, *Greater London Council*, *The County Hall*, *London SE*1 7*PB*, *U.K.*). In the early part of his paper Dr Sugden has classified the effects of pollution according to physical damage to living organisms, material and climate. I think that the changes which pollution can make to amenity should also be included. For about 20 years the inhabitants of London and other large cities have been enjoying the cleaner air brought about by smoke control. I believe this would rank in their minds as just as great a benefit as any mitigation of physical damage. Airborne pollutants that have important amenity effects are still common nowadays; there are, as examples, the stench and dirtiness of road traffic, the smells of food processing and chemical plant, and the noise and vibration of traffic and aircraft. Amenity effects are even more difficult to deal with quantitatively than physical effects, and are therefore possibly less attractive subjects for scientific investigation. I feel, however, that they should always be kept in mind in general discussions about pollution and its control.

T. M. Sugden. Many of the benefits stemming from smoke control in London and other large cities are directly physical in nature, both in improved health of people and in reduction of damage to artefacts. I agree that amenity aspects of atmospheric pollution are important: in general they are local in nature, arise from well-known sources and therefore in principle are not difficult to control.

B. A. Thrush, F.R.S. (*University of Cambridge*, *Department of Physical Chemistry*, *Lensfield Road*, *Cambridge CB*2 1*EP*, *U.K.*). One positive aspect of the release of anthropogenic compounds into the atmosphere is that, unlike natural substances, they can provide atmospheric tracers with accurately known source strengths. A familiar example is the rate of redistribution of chlorofluoromethanes, which are released mainly in northern temperate latitudes. The determination of the atmospheric lifetime of methyl chloroform probably provides the most straightforward method for determining the globally averaged tropospheric concentration of hydroxyl radicals, which are believed to provide the main atmospheric sink for many hydrocarbon derivatives.