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Atmospheric Effects of Pollutants

Pollutants which affect clouds are most likely to produce modifications in weather and climate.

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In this article we shall consider some of the present and potential future influences of pollution upon the atmosphere, particularly upon the earth's temperatures, clouds, and precipitation. Our concern is with local, regional, and global effects. Included will be a discussion of atmospheric processes that may be affected by pollutants with subsequent impacts on weather and climate along with suggested criteria by which chemicals may be classified according to their effects upon atmospheric processes. We shall also discuss control criteria and monitoring and present summarizing conclusions and recommendations for attitudes toward and questions to be asked regarding possible future air pollutants as they may affect weather and climate.

Atmospheric Dispersion Cycle of Pollutants

The dispersion cycle of a pollutant through the atmosphere depends on the nature of the source, its dilution and dispersion by atmospheric motions, and the removal or scavenging of the pollutant by atmospheric and surface processes. In the evaluation of a new material as a potential source of air pollution one should consider the material at the various stages in its manufacture and disposal. The material may initially reach the atmosphere during production, when, because of a lack of adequate emission control, a significant amount of it may be vented into the atmosphere. The production phase may also be a source of significant by-products which may be important environmental pollutants. In fact, by-product emissions constitute a large fraction of current industrial air pollution problems [for example, sulfur dioxide (SO_2) from smelters or aerosol particles from pulp and paper mills]. A material may also become an air pollutant as a result of its use (for example, solvents or additives in fuel). Usage sources may also be divided on the basis of whether or not combustion is involved, because combustion provides a mechanism for chemical change. The last stage of the usage cycle in which a potential for air pollution is present is in final disposal. Incineration is probably of most concern, but the volatilization of certain materials can also produce air pollutants.

For meteorological purposes, sources should also be classified according to their geometry. An isolated source, such as an industrial stack, is a "point source" and may cause relatively high concentrations of pollutant emissions in local areas downwind from the source. Turbulence in the atmosphere disperses a point source emission both laterally and vertically relative to the average wind, and this causes a relatively rapid dilution of the emission with distance downwind. Another type of source geometry is the "area source" which can be considered to be made up of a large number of small sources distributed more or less uniformly over a large area. Vehicle exhausts or home heating emissions are typical examples of sources that may be considered as components of an area source. Because of the size of an area source, dispersion in a crosswind direction is generally ineffective in diluting the effluent cloud and thus the reduction in concentration downwind must be accomplished by vertical mixing processes. Decisions on whether a given source should be classed as a large point source or a small area source should be made on the basis of whether or not crosswind dispersion is an effective factor in diluting the plume.

Atmospheric diffusion models may be applied to estimate the downwind concentration field of a pollutant (*1*). In areas close to a point source the height of the emission plays a role in the concentration pattern. At distances represented by significant travel times the same diffusion model may be used for both point and area sources, and the long-range wind trajectory becomes the controlling factor in estimating exposure levels. Through the successive application of modeling schemes and with the appropriate climatological data, estimates of global concentration fields can be developed. The simpler modeling schemes can be modified to include various atmospheric processes that tend to scavenge the materials from the atmosphere (*2*).

Temperatures in cities are commonly 2° to 3°C and occasionally as much as 10°C higher than those in neighboring rural areas (*3*). Although this effect, which is referred to as the urban "heat island," is not due principally to chemical emissions, we mention it here because it can play a role in the dispersion of pollutants in cities. The urban heat island is produced primarily by the large areas of concrete and asphalt in cities, which absorb and store heat better than vegetation or soil and which

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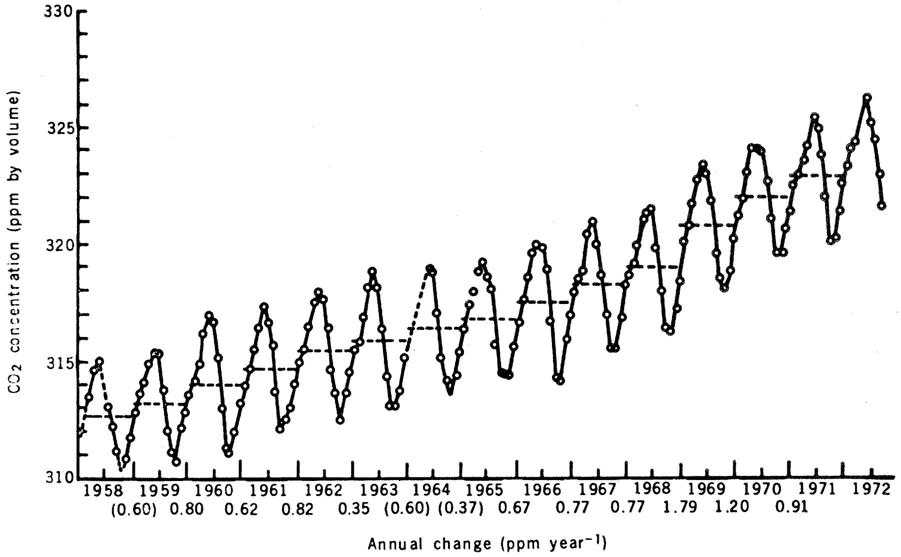

Fig. 1. Mean monthly CO_2 concentrations at Mauna Loa, Hawaii. Horizontal dashed lines indicate average yearly values. Annual changes in parentheses are based on an incomplete record. [Data from Keeling *et al.* (*14*)]

impede transpiration cooling. This effect is compounded by the enormous quantities of heat injected into the air in cities from combustion processes and air-conditioners.

Cities also affect winds by virtue of channeling by streets and the increased "roughness" of the surface topography (*3*). On the average, the winds measured in the downtown area are about 10 percent less than at an airport on the outskirts of a city. However, in light winds (less than about 15 kilometers per hour) the reduction can be as high as 40 percent. Since light winds often accompany synoptic situations conducive to air pollution, reductions in wind speeds caused by buildings in cities can be especially harmful.

Once pollutants are emitted to the atmosphere, transformations and scavenging processes begin to affect them and to act in concert with dispersion factors to increase dilution. These transformation or scavenging processes include both chemical reactions and direct removal mechanisms (*4*).

Precipitation provides the major mechanism by which pollutant materials are removed from the atmosphere. Although gaseous materials may be dissolved in cloud droplets and raindrops, aerosol particles are especially susceptible to precipitation scavenging mechanisms. Small particles can be incorporated into cloud droplets and ultimately into rain if they act as condensation or freezing nuclei. At later stages in the growth processes, particles may be brought into contact with cloud droplets or ice crystals by Brownian motion and thermophoretic and diffusiophoretic effects. If the pollution and precipitation particles are in the proper size range, pollutants may also be captured by precipitation particles as they fall to the ground. Studies of nuclear fallout have shown that precipitation scavenging processes account for about 80 to 90 percent of the atmospheric aerosol removal in regions with moderate rainfall (*4*).

Aerosol Dynamics

Some of the earth's aerosol burden is injected into the air directly (for example, by forest fires, volcanoes, and wind-scoured dust). In addition, however, many complicated processes can generate aerosol gas-to-particle conversions, and the particles can then grow by surface chemistry and physical accretion. Photochemical reactions of gaseous species, especially of the nitrogen oxides, promote oxidative attack upon naturally occurring forest terpenes and waste industrial organic molecules to produce the hygroscopic and polymeric species of smog (*5*). Sulfur dioxide from smelting wastes and fuel combustion oxidizes (in large part heterogeneously but also with the aid of nitrogen oxides) to form sulfur trioxide (SO_3), which hydrolyzes to sulfuric acid (H_2SO_4) mists and ammonium sulfate aerosols. The number density and surface density of the resulting aerosol populations increase markedly at the small end of their size spectra, that is, at radii much less than 0.1 micrometer, which is about the threshold for appreciable interaction of the aerosol particles with light (*6*). Consequently, most of the primary gas-to-particle conversions are also concentrated among the smallest particles. Particles with radii in excess of 1 μm begin to settle out by gravitational sedimentation and, with increasing efficiency, to be washed out by clouds and rain. Intermediate populations are maintained in a quasi steady state by coagulation kinetics.

Particles grow and shrink in response to local humidities, and multiplication processes and chemical reactions may occur in evaporating clouds (*7*). Surface-active chemicals, such as fatty acids and alcohols, alter coagulation kinetics and may "stabilize" the large particles by impeding their growth.

The complexity of processes affecting aerosol kinetics and the resulting populations of particle sizes and types enhance the possibilities for minor atmospheric constituents to amplify effects. For example, aerosols may influence the vertical temperature structure of the atmosphere, which in turn influences mixing and dispersion and the buildup of aerosols.

Cloud and Precipitation Processes

Perhaps the most sensitive atmospheric processes which can be affected by air pollutants are those involved in the development of clouds and precipitation. The structure of clouds with temperatures below 0°C (that is, cold clouds) can be modified, and under certain conditions precipitation from them altered, by particles which are termed ice nuclei (*8*). The concentrations of natural ice nuclei in the air appear to be very low (about 1 per liter, therefore only about 1 in 10^8 airborne particles are ice nuclei). Consequently, even very few particles which are effective as ice nuclei at temperatures above about -15°C have the potential for modifying the structure of clouds and the development of precipitation. If the concentration of the anthropogenic ice nuclei is about 1 per liter, the result may be an enhancement of precipitation; however, if the concentration is greatly in excess of 1 per liter, the result will be a tendency to "overseed" cold clouds and reduce precipitation. Certain steel mills have been identified as sources of ice nuclei. Also of concern is the possibility that emissions from automobiles may combine with trace chemicals in the atmosphere to produce ice nuclei.

Precipitation from clouds that have temperatures above 0°C (that is, warm clouds) may be modified by particles which serve as cloud condensation nuclei (CCN). Efficient CCN are hygroscopic particles with sizes in excess of a few tenths of a micrometer. A source that produces comparatively low concentrations of very efficient CCN will tend to increase precipitation from warm clouds, whereas one that produces large concentrations of somewhat less efficient CCN might decrease precipitation. Modifications in the structure of clouds and precipitation have been observed many miles downwind of fires (*9*) and pulp and paper mills (*10*), both of which emit CCN into the air.

Apart from effects on precipitation processes, inadvertent modification of the microstructure and distribution of clouds will affect radiative properties. Such changes could have profound effects on atmospheric temperature distributions and global climate (*11*).

Radiation Balance

Many molecules absorb strongly in limited parts of the spectrum, particularly in the infrared region; for example, water vapor (H_2O), carbon dioxide (CO_2), and ozone (O_3) each significantly affect the heat transfer of outgoing thermal radiation from the earth's surface (*12*). The infrared radiation is a minor part of the incoming solar power, however, which peaks at wavelengths near 0.5 μm. Around this wavelength only two atmospheric molecules normally occur in concentrations sufficient for their molecular absorptions to significantly affect the atmospheric heating rate, namely, O_3 and nitrogen dioxide (NO_2).

The O_3 absorbs strongly in the ultraviolet, with a maximum cross section of 10^{-21} square meter at 0.25 μm. At longer wavelengths absorption by O_3 is weaker, and near the earth's surface the normal background concentrations of O_3 produce average heating rates less than 10^{-3} °C per day; in dense urban smog, O_3 concentrations occasionally approach 1 part per million (ppm), with the result that direct heating rates may approach 0.1°C per day. Even the larger of these rates is negligible by comparison with advective heat transfer upward from the hot surface of the earth. Therefore, O_3 is not a significant direct agent for energy input to the lower atmosphere. However, O_3 is intimately associated with aerosol formation in photochemical smogs and may, therefore, indirectly affect the radiation balance.

The NO_2 absorbs strongly in the visible, with a richly structured spectrum of mean cross section 2×10^{-23} square meter between 0.30 and 0.55 μm. Integrated over the solar spectrum, the mean mixing fraction of NO_2 (that is, the number of moles of NO_2 divided by the total number of moles in the air) in the remote troposphere is 3×10^{-9}, and this mixing fraction produces a heating rate of 0.06°C per 12-hour day at the earth's surface. Mixing fractions of NO_2 greater than 10^{-6} have been observed in Los Angeles, and NO_2 with mixing fractions greater than 0.5×10^{-6} and 0.25×10^{-6} occurs there for short time periods with an average expectancy of 3 and 29 days per year, respectively. The greater of these values results in heating rates of 1°C per hour, a very significant contribution (*13*).

In addition to direct heating by molecular absorption, the radiation balance of the atmosphere is affected by aerosol absorption and scattering. Heating rates are especially sensitive to the imaginary part of an aerosol's index of refraction and to the particle size distribution. In the troposphere, remote from large cities and industries, an aerosol burden of about 10^{-8} kilogram per cubic meter of air produces a heating rate corresponding to 0.5°C per 12-hour day (*14*). In urban areas, on the other hand, the heating rate may exceed 1°C per hour, although this neglects multiple scattering. Such a heating rate will profoundly influence the vertical temperature distributions and stabilities above smoggy cities.

In the troposphere, the main mechanism by which a parcel of air cools is by adiabatic expansion during lifting. The predominant mode by which a parcel loses energy is by infrared radiation in the numerous molecular bands of H_2O vapor and CO_2, and by graybody thermal emission from water clouds. Atmospheric constituents with mixing fractions less than 10^{-6} are unlikely to contribute significantly to cooling the air by direct molecular emissions, and even in dense aerosols near cities cooling by graybody radiation can be neglected. Thus, any trace chemical introduced into the atmosphere is unlikely to affect the heating or cooling of the air through direct molecular contributions. However, since aerosols and NO_2 are significant contributors to the heating of the air and since these substances and O_3 interact chemically, any trace chemical which interacts with these constituents has the potential for altering the radiation balance of the earth.

Of great interest and importance to the problem of predicting the effects on atmospheric motions is the observation that, for aerosol spatial distributions which are initially more or less uniform below a critical altitude (as is frequently the case below inversions), heat deposition by aerosol absorption may be concentrated just below that critical altitude with the result that the inversion may be intensified. The converse may also occur when an initial vertical distribution of aerosol burden diminishes exponentially with height, as is frequently the case in unstable air. Incoming radiation may then penetrate the upper and more tenuous aerosols without much heat deposition and instead heat the air at lower altitudes. In this case, the added heating rate at low altitudes may enhance vertical mixing so as to reduce low-level pollution, which then in turn reduces the radiation heat input. Thus, radiation heating by aerosols may operate either to intensify periods of pollution or to speed their dispersal, depending upon the vertical distribution of the aerosols (*13*).

Global Effects

Like the weather, the climate of the earth fluctuates with time but on a longer time scale. Prior to the industrial revolution, changes in climate were almost certainly unrelated to human activity. However, in recent years the question has arisen whether the activities of man might be changing world climate (*8, 11*).

The atmospheric constituent most often mentioned in this regard is CO_2. The concentration of CO_2 in the air has increased by about 10 percent since the beginning of the industrial revolution (Fig. 1). This increase is attributed to the consumption of fossil fuels. Simple theoretical models predict that increases in the concentration of CO_2 in the air should result in increases in temperature at ground level as a result of the "greenhouse" effect. Climatological data indicate that the earth's average annual surface temperature did, in fact, increase by about 0.6°C from 1880 to 1940. Since 1940, however, this temperature has been decreasing and is now about 0.3°C lower than in 1940.

Table 1. Estimated particle production in units of 10^6 metric tons per year due to natural phenomena in all countries. [From Peterson and Junge (*18*)]

Source	Particle diameter	
	$>5\ \mu m$	$<5\ \mu m$
Direct particle production		
Sea salt	500	500
Windblown dust	250	250
Forest fires	30	5
Meteoric debris	10	0
Volcanoes (highly variable)	?	25
Total	790^{+}	780
Particles formed from gases		
Sulfates	85	335
Hydrocarbons	0	75
Nitrates	15	60
Total	100	470

Table 2. Estimated particle production in units of 10^6 metric tons per year due to human activities in all countries. [From Peterson and Junge (*18*)]

Source	1968		2000, $<5\ \mu m$
	$>5\ \mu m$	$<5\ \mu m$	
Direct particle production			
Transportation	0.4	1.8	
Stationary sources (fuel combustion)	33.8	9.6	
Industrial processes	44.0	12.4	
Solid waste disposal	2.0	0.4	
Miscellaneous	23.4	5.4	
Total	103.6	29.6	100
Particles formed from gases			
Converted sulfates	20	200	450
Converted nitrates	5	35	80
Converted hydrocarbons	0	15	50
Total	25	250	580

The changes in temperature in recent years raise the question of possible climatic effects attributable to increased particulate loading. There are some indications that there is an upward trend in the concentrations of particles in the air in the Northern Hemisphere and also at some locations in the Southern Hemisphere which are close to large cities or industrial areas. Estimates of the contributions to particles in the atmosphere due to natural and anthropogenic sources in 1968 and the year 2000 are given in Tables 1 and 2.

The meteorological effects of airborne particles depend on their optical and chemical characteristics, as well as on their sizes. Most important are the optical absorption and scattering properties of particles, about which very little is known. At the present time, it is not possible to predict with certainty even the sign of the ground-level temperature change that would accompany an increase in the concentration of atmospheric particles. Increases in particulate loading could increase the amount of solar energy reflected back into space, so that the atmosphere would be cooled (*15*). This might be the reason for the observed decreasing temperatures in recent years. However, if the particles had an absorption-to-backscattering ratio greater than a critical value, the lower atmosphere would be warmed by an increase in particulate loading. Moreover, the sign of the effect depends on the distribution of the particles between and above cloud layers. The weight of arguments at this time probably favors cooling rather than warming as a direct effect of increased particulate loading. It is our opinion, however, that coupled effects between particles and clouds are likely to outweigh direct albedo effects from the particles themselves.

The earth's stratosphere, which is situated between 10 and 50 kilometers above the surface of the earth, is particularly sensitive to pollutants because the residence time of gases and submicrometer sized particles is 1 to 3 years (by comparison, the residence time in the troposphere is 1 to 2 weeks). Photochemical processes occur in the stratosphere, especially O_3-forming reactions, and the dominant heating results from the absorption of solar energy by O_3. Moreover, O_3 absorbs solar radiation at wavelengths shorter than about 0.3 μm and thereby provides a protective shield for protoplasm in the troposphere. These considerations have stimulated concern over possible modifications in stratospheric chemistry that might be caused by supersonic aircraft (*8, 11*). In particular, it appears that nitrogen oxides released in the stratosphere by such aircraft could lead to a significant reduction in the O_3 content if the mixing ratio of the natural nitrogen oxides in the stratosphere is significantly less than 10^{-8} (*16*). Unfortunately, good measurements of the concentrations of nitrogen oxides in the stratosphere are not yet available. The destruction of atmospheric O_3 through "wet photolysis" might also be important (*17*).

Criteria for the Classification of Potential Air Pollutants

In order for a chemical to affect the atmosphere significantly, it must have a physical state compatible with residence in the atmosphere. In principle, any chemical with a finite vapor pressure can become airborne and exist in the atmosphere at concentrations up to an equilibrium value. For example, a chemical compound with a vapor pressure of only 10^{-6} torr ($760\ \text{torr} = 1$ atmosphere) can reach its equilibrium concentration of approximately 1 part per billion (ppb) in the air. Similarly, a chemical with a vapor pressure higher than the ambient pressure boils in the atmosphere and may be present in the atmosphere at any mixing fraction.

For species that are molecularly dispersed, the requirement for appreciable vapor pressure immediately sets upper limits upon molecular weights and dipole moments. For nonpolar molecules (for example, alkanes) vapor pressures at 10°C correspond approximately to mixing fractions of 1 ppm of $H_2(CH_2)_{16}$ and 1 ppb of $H_2(CH_2)_{22}$, which have molecular weights of 226 and 310, respectively. For increasingly polar molecules the lower the molecular weight, the less may be the volatility. Thus, nitrobenzene ($C_6H_5NO_2$) has a mixing fraction at room temperature near 10 ppm, despite the fact that its molecular weight is only 123. Therefore, for chemical species with molecular weights substantially higher than 200 to 300, molecular residence in the atmosphere is incompatible with appreciable mixing fractions. Nevertheless, many of these heavy species can and do significantly affect the atmosphere, but they exist as aerosols rather than as dispersed molecules.

Molecular dipole moments not only affect vapor pressures but also act to enhance solubility in polar fluids, such as water. Similarly, strongly ionic crystals dissolve more readily than covalent or metallic substances. Consequently, polar and ionic species which may enter the atmosphere are preferentially absorbed, dissolved, and concentrated in aqueous clouds. This process facilitates both heterogeneous and aqueous chemistry, which may transform the chemical nature of the original tracer species, and precipitation washout, which may remove these species from the atmosphere entirely.

We have noted that one of the most profound potential effects of extraneous material added to the atmosphere is its possible action as ice nuclei or CCN. The effectiveness of any such agent is related largely to its physical properties, for example, a crystal structure resembling that of ice in the case of ice nuclei and high solubility in the case of CCN. Therefore, these physical properties are signals that may be used to warn of the need for cautionary action.

Among many others, the following kinds of molecules are likely in various ways to interact strongly with photochemical oxidation sequences in the air: (i) photoactive molecules which may form O, OH, H, or halogen atoms in ultraviolet or visible radiation; (ii) free-radical scavenging molecules (these first two kinds of molecules will be especially active if any mechanism exists for a regenerating chain); (iii) molecules with double bonds, –C=C–, especially conjugated double bonds, –C=C–C=C–; (iv) molecules with aromatic and heterocyclic rings, especially adjacent to vinyls, nitrates, sulfates, and amines; (v) molecules that form long-lived triplet states by absorption near 3000 to 4000 angstroms (substituted naphthalenes, anthracenes, and similar species); and (vi) molecules with strained rings (that is, three-, four-, or seven-membered rings).

Control Criteria

Table 3. Approximate minimum concentration thresholds for atmospheric effects due to minor constituents.

Species	Effect	Threshold	
		Volume per unit volume of air	Kilograms per cubic kilometer of air
Ice nuclei	Cloud structure and precipitation	10^{-18}	10^{-6}
CCN	Cloud structure and precipitation	10^{-15}	10^{-3}
Aerosols	Visibility and heating rates	10^{-12}	10^{0}
HCl, H_2SO_4	*p*H of rain	10^{-11}	10^{-2}
Aerosols	*p*H of rain	10^{-10}	10^{2}
NH_3	*p*H of rain	10^{-10}	10^{-1}
SO_2	*p*H of rain	10^{-8}	10^{1}
NO_2	Visibility and heating rates	10^{-7}	10^{2}
O_3	Heating rates	10^{-6}	10^{3}

The most elementary precautionary criterion of possible disturbance to the atmosphere of a chemical discharge is that of amount. For each possible chemical constituent, a concentration exists below which the effect of a chemical on the atmosphere will either not be measurable or will be of less significance than natural atmospheric constituents. However, our experience with the difficulties associated with defining any acceptably "negligible" background of radioactive wastes must be taken as a warning that similar difficulties are likely to arise in efforts to determine future control concentrations for many other chemical discharges into the atmosphere. Nevertheless, we can suggest certain concentrations of chemical contamination below which it is increasingly improbable that "significant" atmospheric effects can be expected. We do this by looking at present minor atmospheric species and noticing the concentrations at which we begin to call them to account in explaining atmospheric phenomena.

Table 3 illustrates some of these species and their associated thresholds for affecting particular processes. The direct influences of certain trace gases upon state variables, such as temperature and wind velocity, can be expected at concentrations as low as 10^{-2} kilogram per cubic kilometer of air. Owing to the great variety and complexity of measurable effects in the atmosphere, we judge it likely that most chemicals will measurably affect one process or another when their concentrations approach or exceed 10^3 per cubic kilometer of air (or mixing fractions near 1 ppm). We judge it unlikely that any added chemicals will "appreciably" affect atmospheric processes at concentrations near to or below 1 gram per cubic kilometer of air (or 10^{-3} ppb), except those which act as ice nuclei or CCN and modify the structure of clouds.

Perhaps next in order of elementary criteria to assist one in judging possible mischief to the atmosphere induced by added chemicals is the question of the rate of discharge. Since the concentration of a tracer chemical on any scale, from microclimate (tens of meters or less) up to global systems ($\simeq 10^4$ kilometers), results from the time-dependent interplay of sources, transport, and sinks, the rates of each of these processes must be considered in estimating both the concentrations and the spatial distributions which may be attained by atmospheric chemicals. Upper limits in acceptable concentrations imply upper limits in acceptable input rates.

Since the transport of chemicals in the atmosphere and the sinks for the chemicals are not constant, an acceptable source rate may be difficult to specify. As an example of what is probably an excessive rate, we are familiar with a single source of SO_2 of 5 kilograms per second from a copper smelter which has the effect of reducing the mean *p*H of rainfall, measured at 70 kilometers downwind, one *p*H unit below its normally CO_2-buffered value of 5.6. This example illustrates a condition in which the sources and sinks are rather large, yet the concentrations of ambient SO_2 and sulfate aerosols remain fairly low (5 to 20 ppb) by comparison with other localities which enjoy comparable input but less active transport and washout. For this circumstance a control limit on the input flux of chemicals to the atmosphere would probably be more sensible than a limit on ambient concentrations. The determinations of which of these alternate control criteria will best suit any particular chemical depends principally upon the nature of the sink.

We turn now to several specific suggestions on control criteria.

1) We believe that the influences of chemical wastes on weather and climate are likely to be greatly amplified if they affect clouds. The presence or absence of clouds and their nature can have dramatic effects, as can small changes in their frequency or placement. Therefore, changes in clouds produced by aerosols generate enormous relative differences per unit of aerosol mass. Consequently, control attention should be directed especially to a chemical's prospective effects on cloud modification and aerosol dynamics.

2) Regenerating chains of chemical interactions, for example, those involving OH and the oxides of nitrogen, are especially sensitive to modification by additional chemicals which may compete for the chain-carrying radicals. We particularly emphasize the importance of OH and the need to develop and deploy analytical **techniques to**

measure its role in photochemical smogs.

3) We believe that present control criteria for many constituents based on ambient concentrations might profitably be reexamined to determine whether they might better be based upon area flux levels, or throughput. Variable emission licensing, adjusted to the local dispersive capacity of the air, might be explored. However, care must be taken that acute local problems are not converted into chronic regional or global problems.

4) In conventional monitoring for toxic materials, the risk function is usually assumed to be an increasing function of concentration multiplied by the exposure time. With monitoring for meteorological disturbances, similar risk functions may not be appropriate. Thus, risks may often maximize during periods which do not coincide with exposure levels (for example, clouds might be particularly susceptible to modification during periods of high humidity and moderate supercooling). In this case, a monitoring program geared to peak concentration episodes may be seriously misleading. In general, each postulated contaminant must be considered in the light of a likely contaminating mechanism or impact, and control schedules and risk functions defined accordingly.

5) Listed in Table 4 are some pertinent questions and comments on atmospheric pollutants.

Summary

We have argued that aerosols are probably the principal agents by which pollutants may affect weather and climate. They are most likely to act by influencing the structure and distribution of clouds. On the local scale, the effects of pollutants on some aspects of weather are unmistakable. The effects of man-made pollutants on global climate are a matter of debate, but they may already be significant.

Table 4. Some questions and comments on atmospheric pollutants.

Question	Comments
1. What atmospheric process is the discharge likely to affect?	Controls should be based on known or postulated effects of the pollutants (see Table 3).
2. Is the discharge large or small relative to the concentration of the same or other agents in the atmosphere which act similarly?	A discharge must cause an appreciable change in the concentration of the same or similar agents in order to affect an atmospheric process.
3. Are all the constituents of the effluent known?	Trace substances might have more impact on the atmosphere than the primary constituents.
4. Will any of the chemicals in the discharge react with atmospheric constituents?	Beware of regenerating chemical chains, especially those known to involve OH and nitric oxide (NO). Small influences on these two species may have large secondary effects (for example, photochemical reactions leading to smog formation).
5. Can chemicals in the discharge interact in the atmosphere to amplify their effects?	If so, beware! [For example, the reaction between SO_2 and ammonia (NH_3) in the gaseous phase is slow, but in the presence of cloud droplets it is accelerated enormously to produce sulfates.]
6. Is the discharge concentrated (a point source) or diffuse (an area source)?	The first may stimulate more complaints, but the latter more damage.
7. What concentrations are to be expected downwind from sources of pollutants?	Simple model calculations can be used to estimate these concentrations. (The results are not always reliable.)
8. Is the weather stagnant or dispersive?	Controlled emissions are generally best vented in dispersive conditions. However, in some cases discharges in dispersive conditions might produce more total damage by being distributed over a wider area.
9. What are the lifetimes and sinks of the pollutants?	Rapid sinks depress concentrations, but the throughput may remain high and the deposition concentrated.
10. Are the pollutants water-soluble or hygroscopic?	If so, they will concentrate in clouds, will be potentially active in modifying warm clouds, and will experience relatively short residence times in the atmosphere with possibly large local deposition.
11. Are the pollutants surface-active?	Surface-active molecules may coat cloud droplets and affect cloud and aerosol evaporation and coagulation.
12. Do the solid pollutants have crystal structures and dimensions similar to those of ice (that is, hexagonal) and are they insoluble?	If so, beware! They may nucleate ice in cold clouds and affect precipitation processes, even at very low concentrations.
13. Do the chemicals interact with visible light?	If so, they may contribute to atmospheric heating.
If so, (i) Do they photodissociate? (ii) Do they form reactive fragments such as free radicals and metastable atoms? (iii) Do they sensitize other chemicals?	Affirmative answers to these questions imply activity in photochemical processes affecting smog.
14. Do the chemicals interact with infrared radiation?	If so, they will affect radiation transfer, especially if they absorb between the strong lines of H_2O and CO_2. Absorption at these wavelengths will cause warming near the earth's surface but cooling in the stratosphere.
15. Most critical of all, do the pollutants affect aerosols which play a role in cloud processes?	If so, the structure and distribution of clouds may be affected by the pollutants, thereby causing changes in precipitation and optical scattering. Research priority should be given to this area.

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Selenium Biochemistry

Proteins containing selenium are essential components of certain bacterial and mammalian enzyme systems.

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The element selenium was discovered by Berzelius in 1817 and the first organic compound containing selenium, ethylselenol, was prepared in 1847 (*1*). However, for many years few organic selenium compounds were known and, for the most part, these were considered mere chemical curiosities. Eventually, in the 1930's, selenium was identified as a potent toxic substance for cattle and other livestock, and this focused attention on the biochemical properties of selenium compounds. In 1957 selenium was identified as the essential component of a dietary factor that protected rats from severe necrotic degeneration of the liver (*2*). This finding soon led to the recognition by animal nutritionists that several important livestock diseases are actually selenium deficiency syndromes (*3, 4*). Nevertheless, even today the toxicity of selenium and selenium-containing compounds is more generally appreciated than is the essential nature of this micronutrient. It is becoming increasingly evident that animals, bacteria, and possibly higher plants all require trace amounts of selenium, and that when available in the proper amounts the selenium is incorporated in a highly specific fashion into certain functional proteins of the cell. When organisms receive more than micromolar concentrations of selenium, those enzyme systems that cannot distinguish it from its close chemical relative, sulfur (*5*), begin to substitute the selenium indiscriminately for sulfur in many cellular constituents. Because of the greater reactivity and lower stability of selenium compounds compared to the corresponding sulfur compounds, the cell may encounter metabolic problems which eventually can lead to death of the organism. In the present article an attempt is made (i) to discuss briefly those enzymic processes which do not distinguish selenium from sulfur and therefore may be important in selenium toxicity, and (ii) to summarize the current information concerning specific enzymic reactions in which selenium participates as an essential enzyme component.

Although selenium is present in detectable amounts in all soils, it is not usually present in toxic amounts except in semiarid regions in soils derived from cretaceous shales (*6, 7*). In humid climates, or under conditions of irrigation, most of the selenium is leached from soils of this type.

There is a group of plants known as selenium indicator plants that grow in semiarid regions in soils containing large amounts of selenium (*7*). A few of these plants are normally limited in distribution to such areas and, when cultured in the laboratory in solution or moist sand, they exhibit markedly improved growth in response to the addition of selenium (*8*). Selenium indicator plants that have been studied in some detail (*7*) are *Astragalus pectinatus* (narrow-leaved vetch), *A. bisulcatus* (two-grooved poison vetch), and *Stanleya pinnata* (prince's plume). Taxonomic descriptions of these and related species (*9*) usually mention the unpleasant odor of the plants. The bad odor is due to the presence in their tissues of large amounts of various selenium-containing organic compounds which are far more malodorous than their sulfur-containing analogs. In fact the amounts of organoselenium compounds in these plants are often sufficient to cause acute selenium poisoning of grazing animals. Death of the animal may occur within a few hours after ingestion of the toxic plants.

Types of Organoselenium Compounds in Green Plants

Accumulation of the selenium analogs of methionine, *S*-methylcysteine, gamma-glutamylcysteine, and cystathionine appears to account, at least partially, for the high selenium content of some species of selenium indicator plants of the genus *Astragalus*. From specimens of *A. pectinatus* which contained 1500 to 2000 parts per million (ppm) of selenium (1.5 to 2 grams per kilogram of tissue, dry weight) Horn and Jones in 1941 (*10*) isolated a crystalline material that, on the basis of

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