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SCIENCE

CURRENT PROBLEMS IN RESEARCH

# Air Conservation

With discovery of the sources and chemical reactions of pollutants, the stage is set for conservation.

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Our confidence in the abundance of the four principal elements of our forefathers has been severely shaken in recent times. We have learned that the increasing population will have less and less room in which to grow its crops and keep its cattle. Coal, oil, and gas reserves have definite time limits, and we might have had to face a major war over water rights had our ancestors not been wise enough to create a United States of America. Finally, our supposedly infinite supply of air has turned out to be limited, too. With the advent of atomic energy, many of these problems can be solved, but the universal use of atomic energy will make the problem of keeping our air fit to breathe even more difficult. Now we are concerned with constituents present in concentrations of a few parts per million. The future, and part of the present, generation must worry about the removal of pollutants present in quantities smaller by a factor of many powers of ten. In this more efficient cleaning process, the theoretical knowledge and technical skill required will be far greater than the knowledge and skill available today.

Perhaps we should even be grateful that in recent years air pollution disasters and near disasters have developed on such a scale that they have attracted the attention of the whole world. Such an episode occurred in London, when,

17 OCTOBER 1958

during a black fog period in 1952, some 4000 excess deaths were recorded. Other disasters drawing world-wide attention were those in Donora, Pennsylvania, Poza Rica, Mexico, and the Meuse Valley in Belgium (1). In each of these incidents dozens of people met their death by suffocation.

In recent years, the smog conditions developing in Los Angeles and in other cities on the Pacific Coast have greatly inspired a more intensified effort to clean the air all over our country (2). Keeping the air clean is expensive. In the Los Angeles area alone it is estimated that several hundred million dollars have been spent already to curtail some emissions, and many more will have to be spent before the smog will again be unnoticeable. At the present time the air-pollution-control authorities, working against a 4 percent increase in population, are doing somewhat better than holding the line. Over the whole nation the expense will be staggering and will probably run into billions of dollars.

It is understandable that there has been a great deal of resistance to the installation of costly control equipment which often does not contribute in a direct manner to profits. Some of the objections have been removed in recent years, and it is now generally conceded that damage from air pollution is large and that recovery measures often pay for themselves and in some cases may even make profits. Corrosion due to the emission of various chemicals is a source of

tremendous expense to the public. Recovery methods will reduce this corrosion and will also lower the cleaning bills for the outside, as well as the inside, of our houses. But even if no direct profit is made, the many intangibles make it worth while to improve working conditions. The standard of living of the workers is raised, and possible adverse effects on their health are eliminated. This contributes to an increased efficiency on the part of the worker. It also raises the value of the industrial property and of the surrounding real estate. In many cases, management has gone much further than merely curing existing air pollution problems. At the present time, climatological and topographical conditions are examined carefully in selecting the site for new industry, and in the construction of new buildings the installation of air-pollution-control equipment is considered beforehand, rather than at a time when public relations have suffered a severe setback.

The old slogan, "Prosperity is measured by the number of smoking stacks," is no longer true. Today, prosperity can be gaged by the number of strange-looking bulges protruding from the roofs of the factories. These bulges are dust- and fume-collectors and indicate that the community and its industry have progressed to a standard of living and social consciousness that does not permit objectionable emissions to spread over other peoples' property. Many modern factories and offices have installed in the air-conditioning system air-purification systems as well, since experience has shown that clean air is healthier and leads to less absenteeism and, in addition, keeps cleaning and redecorating costs at a minimum. Scientific laboratories, too, have found that the protection from plant damage, from interference in the sensitive enzyme systems, and from destruction of oxidant-sensitive organic compounds which can be obtained by air purification is worth while.

Less satisfactory, from a hygienic point of view, is the way many of us spend our day undergoing fumigations with tobacco smoke and engine exhaust

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-a combination which for many years has been under suspicion where its effects on health are concerned.

One of the most common forms of air pollution is that caused by smoke. A cross-country trip by airplane should convince anyone that smoke is a problem in every great city from Los Angeles to New York. Large streamers, extending for scores of miles, have their origin in open burning dumps, lumberyards, steel mills, foundries, and power plants, to name only a, few of the multitude of sources. This is an old problem; some 200 years ago laws were passed in England to regulate the burning of certain types of coal. Even today, combustion is still a major source of air pollution.

At first sight this problem of controlling the emission of smoke appears quite simple-just wash it out! But we have only to think how tobacco smoke from a Turkish pipe bubbles, seemingly undisturbed, through water, to realize that perhaps this problem is not so easily solved after all. Large particles of soot and dust can readily be removed in settling chambers, or in cyclones, where gravitational or centrifugal forces are used to separate the particles by weight. Other methods consist in filtering out the dust through cloth made of cotton, woven plastics, or even glass fibers, in structures known as baghouses. For very fine dust, of the order of from 0.5 to 1.0 micron.

we have to apply processes whereby the electrically charged particle is removed by electrostatic forces by passage between electrodes kept at a potential difference of 15,000 to 40,000 volts. A comparison of particle size of effluents and the means of their recovery is shown in Fig. 1. By catching the particles of a size close to the wavelength of light, an important fraction of the dust responsible for the scattering of light is removed, and therefore the probability of visible plume formation is substantially decreased. The process is attractive to industry because of the low cost of maintenance and the negligible drop in pressure, and it is commonly used in open-hearth furnaces in steel mills and in coal-burning plants (Fig. 2). Recently its use was extended in Los Angeles to the control of stack emissions from oilfired boilers in power plants. Each one of these dust-collection processes has found wide application in industry, but even today systematic studies to increase their efficiency would be most welcome.

The dust present in fuel is not the only agent responsible for an objectionable plume from smokestacks. Virtually all other constituents of flue gas—water, carbon monoxide, and oxides of sulfur and nitrogen—play some role. It is interesting to watch this plume formation take place in a long glass tube through which the hot stack gases are led. As



Fig. 1. Particle size chart illustrating relative size of well-known particulates and the effective range of various control methods. [H. P. Munger, "The spectrum of particle size and its relation to air pollution," in L. C. McCabe, *Air Pollution* (2, chap. 16)]

soon as the gases cool below the dewpoint range, we see a deposition of metal salts, largely in the form of sulfates, along the side of the tube. Next we find a region of droplets, containing insoluble dust embedded in an acid solution of metal salts. Finally, on further cooling, the bulk of the water, containing some sulfuric acid and sulfur dioxide, condenses. When the gas stream, cooled to outside temperature, leaves the experimental stack, it escapes largely as a plume of water vapor containing trace amounts of sulfuric acid, and nearly all the sulfur dioxide and nitrogen oxide, in gaseous form. In this passage very little sulfur dioxide has been converted to sulfuric acid. The dew point of the outlet is close to that of the outside temperature, and only slight heating is required to cause the visible plume to disappear. This practice is followed in many installations where weather conditions are conducive to plume formation.

We expect that phenomena similar to those observed in the glass tubes take place when the gases are released from the stack, with the droplet size adjusting itself to the outside temperature and humidity. This is an important factor in the variability of plume density observed in otherwise identical combustion conditions. The formation of droplets by condensation is not the end of plume formation, for both sulfur and nitrogen oxides, as well as metal salts, participate in a series of reactions leading to a gradual oxidation of sulfur dioxide into sulfuric acid, and of nitric oxide into higher oxides and nitric acid.

Laboratory investigations by Johnstone and Coughanowr (3) have shown that oxidation of sulfur dioxide takes place slowly by photochemical action. These authors estimated that about 1 percent would be oxidized per hour in intense sunlight. This would indicate that in an atmosphere containing 0.1 to 1.0 part per million of sulfur dioxide, about 100 hours of sunlight would be required to decrease visibility to about 1 mile. In continuation of these experiments it was found that oxidation occurs much faster in water solution under the influence of metal salts. Such conditions could conceivably occur in droplets present in the stack plume. The suggestion has been made that it is this reaction which is responsible for the haziness observed at considerable distance from industrial establishments. Evidence that such oxidations do take place when the gases have left the stack is found in an interesting pollution balance made at one time by



Fig. 2. Before the installation of smoke-control equipment, the normal operation of the open-hearth furnaces at Kaiser Steel Corporation's Fontana, California, plant produced smoke which was released directly into the atmosphere. These two pictures, taken within minutes of each other, graphically demonstrate the effectiveness of the electrostatic precipitator on top of the building. (Left) Picture taken with all the units temporarily shut off. (Right) Picture taken a few minutes later with the equipment back in operation, showing clear sky. [Kaiser Steel Corporation]

the Los Angeles County Air Pollution Control District (4). The amount of emission of sulfur dioxide from all sources-refinery operations, oil burning, and gasoline consumption-is well known. We also know the area in which this emission is dispersed, as well as the height of the inversion layer which limits its upward movement. From these data we are able to calculate the expected sulfur dioxide concentration and compare this with the actual observed average concentration. We find, in making up this balance, that about half of the sulfur dioxide is lacking, as is shown in Table 1. This missing sulfur dioxide is found mostly as calcium and ammonium sulfates in dust settling over the country. Free sulfuric acid, except in close proximity to the stack, is virtually absent.

Research work on the effects of stack gas constituents on plants and animals is still an important field of environmental hygiene. Only recently some interesting data were revealed on the synergistic effects of aerosols and oxides of sulfur on physiological responses such as flow resistance in the respiratory system (5). This specific air pollution problem illustrates how much work has to be done before we can really understand the phenomena connected with the emission of dust and fumes. Some of this work is in the field of engineering, and other aspects deal with inorganic, physical, physicochemical, and photochemical processes. Finally, we have problems in physiology and pathology of plants and animals, as well as legal and economic problems.

#### Los Angeles Smog

Notwithstanding its many facets, this control problem is simple compared with a more recently discovered air pollution problem which threatens to affect all metropolitan areas. It is an oxidized hydrocarbon type of pollution, better known as Los Angeles smog, from its place of discovery (Fig. 3).

was suddenly surprised to find itself engulfed in an eye-irritating cloud of chlorine-like odor. This incident lasted about a year and was generally attributed to the emissions from a synthetic-rubber plant. After the control of these emissions, complaints stopped, only to be resumed after the war. The rubber plant could not be blamed this time, for it was closed, nor could sulfur dioxide and soot be blamed for the severe eye irritation. As a matter of fact Los Angeles is a very clean city in this respect, with a dustfall of only 20 to 30 tons per month per square mile, as compared with several times this quantity in other industrial cities. There is no resemblance at

During the war years, Los Angeles

Table 1. Comparison of measured and calculated concentrations of pollutants in downtown Los Angeles (4, p. 41).

Clear day* (parts per million by vol.)		Day of sr (parts p by	Day of intense smog† (parts per million by vol.)	
Measured	Calculated	Measured	Calculated	
3.5	3.5 <b>t</b>	23.0	23.0‡	
0.08	0.10	0.4	0.6	
0.05	0.08	0.3	0.5	
0.2	0.40	1.1	2.6	
0.07	0.02	0.4	0.1	
0.07	0.03	0.4	0.2	
	Clear (parts p by v Measured 3.5 0.08 0.05 0.2 0.07 0.07	Clear day* (parts per million by vol.)           Measured         Calculated           3.5         3.5‡           0.08         0.10           0.05         0.08           0.2         0.40           0.07         0.02           0.07         0.03	$\begin{array}{c} Clear day^{*} & Day of sr \\ (parts per million \\ by vol.) & by \end{array} \\ \hline \hline \begin{tabular}{lllllllllllllllllllllllllllllllllll$	

\* Visibility, 7 miles. † Visibility, less than 1 mile.

The method defines the calculated value as the same as the measured value for CO. Calculated as hexane.

Preliminary values.



Fig. 3. Dense smog over Los Angeles Civic Center. Note how the buildings project above the base of the inversion layer, while pollution remains below. [Los Angeles County Air Pollution Control District]

all to the problems of cities in the eastern part of the United States, where coal is the major source of energy and where, consequently, soot blackens all buildings. The eye-irritating clouds in Los Angeles are accompanied by complaints from farmers about crop damage (Fig. 4) and, strangely enough, from rubber manufacturers, who observed that their products cracked more heavily in this area than in other sections of the country (Fig. 5). Control of dusts and sulfur dioxide did not help, for the phenomena are due to an effect quite different from the more old-fashioned, reducing type of air pollution. Los Angeles smog, contrary to this type of pollution, is typified by its strong oxidizing action (6, 7).

For practical measurement of the typical oxidizing effect of Los Angeles smog, liberation of iodine from potassium iodide, oxidation of phenolphthalin to phenolphthalein, and many other oxidation-reduction reactions can be used. For an explanation of the effect of oxidizing smog on living tissue, its demonstrated action on amino acids such as cysteine, tryptophan, and histidine, as well as on glutathione and lysozyme, is significant and might well account for the irritating symptoms. The measured oxidant action is caused by an excess of oxidizing over reducing components in the polluted air. In Los Angeles smog the concentration of sulfur dioxide, a reducing substance, is low, and its effects are usually negligible. In other areas, the presence of the oxidizing pollutants may

well have escaped attention because of the masking effect of an excessive amount of reducing substances. It is quite possible that the oxidizing pollutants which characterize Los Angeles smog are of more frequent occurrence than was originally suspected.

The concentration of the oxidant varies during the day, increasing toward noon and decreasing to virtual absence during the evening and night hours. The time of increased concentration of the oxidant is invariably correlated with eye irritation and haze. The type of damage to plants from oxidizing pollutants is readily distinguishable from damage from other types of pollutants, such as sulfur dioxide or fluoride. Sensitive plants-spinach, sugar beets, alfalfa, endive, oats, and pinto beans-are used extensively to gage the spread of the pollution (Fig. 6). A major part of the oxidant consists of ozone, which is directly responsible for the excessive rubber cracking observed in the Los Angeles area. Spectrographic, as well as chemical, methods have definitely established the presence of ozone concentrations 20 to 30 times higher than those found in unpolluted air, where the normal concentration amounts to 1 to 3 parts per hundred million.

A simple and inexpensive method of measuring ozone involves the use of bent pieces of antiozodant-free rubber as indicators (Fig. 7) (8). The time necessary for the appearance of the cracks is directly related to the ozone content of

the air. At night, and on smog-free days, it may take as long as an hour for the first cracks to appear; on a smoggy day, cracks are often evident in a matter of a few minutes, under the conditions of the test. During heavy smog periods the total oxidant concentration is higher than can be accounted for on the basis of the presence of ozone alone when determined by spectrographic methods. This excess oxidant, corrected for the action of oxides of nitrogen, consists mainly of peroxidic material formed by the atmospheric oxidation of organic material. These organic peroxides are held to be responsible for eye irritation and plant damage resulting from smog. In the atmosphere over a city it is to be expected that the reactive ozone will enter into reactions with a number of other pollutants. Among the most prevalent of these groups are olefins, present in gasoline; fumigation experiments with gasoline fractions, and also with pure olefins which have been allowed to react with ozone, led to a reproduction of the typical plant-damage symptoms and to eye irritation, haze formation, and typical smog odor, as well. These experiments strongly indicated that the irritating materials were intermediate oxidation products of hydrocarbon oxidation and are of peroxidic nature, since the usual end products-aldehydes, ketones, and organic acids-are inactive in the concentration range used.

Most organic compounds are relatively stable against oxidation, when completely pure, but the presence of peroxides speeds the auto-oxidation considerably through a chain reaction initiated by hydrogen removal from the hydrocarbon chain. This effect can be accomplished also through the action of light on either the hydrocarbon or the oxygen molecule. In the latter case, the excited oxygen may remove hydrogen. Most hydrocarbons do not have absorption bands in the wavelength region of sunlight for a direct photochemical reaction. Similar reactions can be accomplished in a roundabout way by having a substance present which accepts the light energy and subsequently transfers it to the compound to be oxidized. In nature we find such substances in chlorophyll and other photochemically active pigments. In polluted atmospheres nitrogen dioxide functions as an oxidation catalyst in this way. Strong absorption of light by nitrogen dioxide occurs from the near ultraviolet through the blue part of the spectrum, and, upon irradiation, nitrogen dioxide splits into atomic oxygen and nitric oxide. Fumigation experiments with gasoline or olefin in the presence of oxides of nitrogen resulted in eye irritation and the same type of plant damage that was previously obtained with ozone acting on the olefins directly. In this case, too, we are able to calculate the concentration of hydrocarbon which should be present in a certain area and compare this with the actually observed concentration, just as we have done with the sulfur oxides. We find that the hydrocarbon concentration in the air is less than it had been calculated to be; on the other hand, the concentrations of the oxidation products-aldehydes and acidsare considerably higher than had been calculated, as is shown in Table 1. All these observed facts are in harmony with an explanation of Los Angeles smog as an oxidation phenomenon of organic material.

#### Formation of Ozone

When all the typical symptoms of smog had been reproduced, the problem remained of accounting for the relatively high ozone content in the polluted atmosphere. It is now well established that the generation of ozone is intimately connected with the same photochemical reaction of organic material and oxides of nitrogen which causes eye irritation and plant damage. The formation of ozone is apparently a general phenomenon and is observed with many types of hydrocarbons, as well as with alcohols, ketones, aldehydes, and acids. The production of ozone has been attributed to the intermediate formation of peroxide radicals. This hypothesis is supported by the behavior of a model substance, biacetyl, upon irradiation. Years of photochemical research have shown that this diketone dissociates predominantly into acetyl radicals, which are further decomposed into methyl radicals and carbon monoxide. In most of these photochemical experiments the presence of oxygen is rigorously excluded to avoid complication. When oxygen is admitted, the free radicals will form peroxy radicals, and these apparently react with more oxygen to yield ozone:

$$H_{3}C - C \xrightarrow{H_{1}}{\stackrel{H_{2}}{=}} C - CH_{3} \xrightarrow{h_{1}}{\stackrel{h_{2}}{\longrightarrow}} H_{3}C - C \xrightarrow{-o_{2}}{\stackrel{H_{3}}{=}} H_{3}C - CO^{-} + O_{2}$$

This rather surprising result can readily 17 OCTOBER 1958



Fig. 4. Severe damage on the under side of spinach leaves caused by Los Angeles smog. [Los Angeles County Air Pollution Control District]

be verified by a simple lecture experiment in which a drop of biacetyl is introduced into a Pyrex flask. Next, a small piece of rubber with the ends tied together to form a loop is suspended in the flask. After exposure for an hour to sunlight, the rubber is heavily cracked, due to ozone attack. The rubber used should not contain antiozodants, of course. Infrared investigations have confirmed the chemical analysis and indicate that we are really dealing with ozone. Another well-known instance of radical formation is the irradiation of alkyl nitrites whereby an alkyl radical and nitric oxide are formed. When irradiation is carried out in air or oxygen, the alkyl radical forms a peroxide radical and ozone formation can readily be established. This reaction is similar to that postulated in the formation of smog of the Los Angeles type. The starting products in that case are nitrogen dioxide and hydrocarbons or their derivatives. We may visualize, first, a light-activated dissociation of nitrogen dioxide to nitric oxide and atomic oxygen, followed by a reaction of the atomic oxygen with a molecule of oxygen to form ozone. Atomic oxygen may also abstract a hydrogen from a hydrocarbon, with formation of an alkyl radical. This, in turn, can form ozone, as shown previously in the case of biacetyl. Also, reactions between nitric oxide and alkyl and alkylperoxy radicals may take place. Representatives of such combinations have been found in long-path infrared studies conducted by workers at the Franklin Institute (9). Especially interesting is the formation of a peracylnitrite, a direct combination product of the photochemically produced nitric oxide and peroxy radical. This compound appears in smog atmospheres as well as in irradiation of synthetic mixtures of hydrocarbons and nitrogen oxides. It is postulated that these types of compounds play an important role as intermediates in the reoxidation of the nitric oxide to nitrogen dioxide.

A systematic study of the area of concentrations of hydrocarbon and oxides of nitrogen where ozone formation takes place showed that the reaction is limited to quite low concentrations of the reactants, as is shown in Fig. 8. Experiments of this type have focused attention on the circumstances peculiar to the problem of air pollution—that is,



Fig. 5. Severe rubber cracking observed in Los Angeles area. [J. W. Haagen-Smit]



Fig. 6. The effect of air pollution control in the Los Angeles area for the period 1956-57. The intensity of eye irritation (top) has decreased, as has the area over which eye irritation is observed. Reported plant damage (bottom), too, has been less severe. [Los Angeles County Air Pollution Control District]

the extreme dilution. A chemist referring loosely to slow and fast reactions has in mind the conditions in laboratory synthesis, where concentrations of about 10 percent are most commonly used. In atmospheric reactions the concentrations are in the order of 0.00001 percentabout one millionth as much. As a result, reactions which under the usual laboratory conditions are considered fast become very slow. For example, when a bimolecular reaction with participants in the concentration range of 10 percent (100,000 parts per million) requires 0.0036 second to go halfway to completion, it takes 106 times as long, or a whole hour, to reach the same point with a concentration of 0.1 part per million. Under the latter circumstances, not only can ozone survive attack by reducing agents but even free radicals have a far better chance of survival. It took many years to unravel relatively simple reactions such as the photodecomposition of acetone, biacetyl, and other compounds. In the air these reactions are complicated by the presence of oxygen, water, carbon dioxide, and an almost infinite variety of organic compounds from the evaporation and combustion of gasoline and from the burning of trash in its many forms.

#### **Theoretical Investigations**

The field of atmospheric reactions is now being actively studied by a number of physical chemists and provides an interesting example of the way in which a practical problem has stimulated a number of theoretical investigations. Such study has familiarized a large group of physical chemists with the exciting field of extreme dilution, in which research should prove to be far less disturbed and complicated than research at higher concentrations, where molecules collide all too frequently. In addition, the practical aspects of air-pollution photochemistry have made available the instrumentation necessary to study these phenomena from a theoretical point of view. The purely theoretical physicist and chemist would have difficulty in obtaining the millions of dollars which have gone into the development of these instruments. It is gratifying to find that, as a by-product of the study of an unpleasant problem such as air pollution, a significant contribution to fundamental problems in chemistry could be made.

### **Automobile Exhaust Fumes**

These remarkable reactions have now been confirmed in at least four different laboratories and provide a firm basis for control measures. We know which compounds contribute to these reactions and we know their sources, and now the Air Pollution Control District has only to control hydrocarbons, their oxidation products, and the oxides of nitrogen. Unfortunately, the necessary control equipment cannot be ordered because it still has to be invented. After hydrocarbons at refineries have been recovered, the major remaining source of hydrocarbons is the exhaust of automobiles, which amounts to 1200 tons per day. Direct and catalytic afterburners and deceleration devices are now being developed, but even after a successful device has been produced it will take many years before such devices will be installed on all the cars in the Los Angeles area. Pressing air pollution considerations can now be added to the many other arguments for streamlining our transit systems.

There are other difficulties. The major contributor to the oxides of nitrogen is, again, the automobile, and, apart from injection of water into the cylinders and the combustion of very rich fuel mixtures, no means are yet available for reducing the oxides of nitrogen. Several engineering laboratories are now searching for ways to reduce the nitrogen dioxide content of exhaust gases from gas, oil, and gasoline combustion through studies on the variable combustion conditions which can be obtained through boiler modification or changes in engine design. Often the



Fig. 8. Area of ozone formation with 3methylheptane and  $NO_2$ . Ozone formation takes place only at concentrations indicated by shaded area (10,000 parts per million, volume for volume, is equivalent to 1 percent). [A. J. Haagen-Smit and M. M. Fox, Air Repair (7)]

question has come up, "Can't we do one or the other—hydrocarbon control or nitrogen dioxide control?" The answer, I believe, is "No." Most of the smog reactions are directly dependent on the product of the concentration of both hydrocarbons and oxides of nitrogen.

The private automobile is a major offender in both respects, and there is no reasonable basis for hope that control devices in the hands of the average car owner will give anywhere near the performance they give in an automobiletesting laboratory. Also, changes in gasoline composition could not be expected to have a drastic effect on smog-producing hydrocarbons in the exhaust. The steady increase in population tends to neutralize any control effort, and it is therefore evident that emissions must be controlled wherever possible. Besides be-



Fig. 7. Ozone in air is measured by its effect on rubber under strain. The degree of cracking indicates the concentration. [Los Angeles County Air Pollution Control District]

ing an objectionable factor in the photochemical reactions, the nitrogen oxides are objectionable in their own right and are quite toxic even in low concentrations. Fortunately we have not yet reached anywhere near the lower alert limit of 5.0 parts per million, but the concentration of this pollutant is steadily increasing, and since it appears in all combustions, the increase is practically proportional to the increase in population. Especially in areas of heavy traffic the concentration might at times surpass the safe limits, or, rather, what we now believe are safe limits. Oxides of nitrogen are rather unpleasant compounds. In concentrations of only 25 parts per million they act like war gases such as phosgene and cause lung edema. It is quite possible that, at far lower doses, objectionable damage might occur.

### **Cigarette and Cigar Smoke**

Oxides of nitrogen are prominent in a quite different form of air pollution. Cigarette and cigar smoke contains from 300 to 1500 parts per million of oxides of nitrogen, which is completely removed by inhalation, through adsorption in the lungs. No attention has been given to this agent as a causative factor of respiratory ailments in smokers. Its strong toxic action should be an inducement to study more intensely the volatile components of tobacco smoke than has been done in the past, when most attention has been given to nonvolatile tars containing carcinogenic hydrocarbons.

Air pollution control administrations have a difficult task in surviving the years of waiting for engineering to catch



Fig. 9. Hypothetical dispersion of smoke puffs released at two points of the Los Angeles basin at 7 A.M. and 8 A.M., respectively. [F. N. Frenkiel (11)]

up with the demands of the community. Programs for meeting emergency conditions have somewhat contributed to better feelings on the part of the public. It is understandable that most people not accustomed to smelling or inhaling a concoction of ozone, oxides of nitrogen, ozonides, and substances x, y, and z begin to be a little worried. In recent years the medical profession in Los Angeles has set certain levels below which a catastrophe would be unlikely to occur. This is admittedly a very difficult decision to make and it has pointed to a serious deficiency in our knowledge of environmental hygiene.

# **Pollution Levels**

In studies of the health effects of air contaminants it becomes evident that there is a great difference between the industrial and general population levels. The industrial group generally represents a selected group of healthy individuals from which the extrasensitive have been removed, because the working conditions do not agree with them. For the whole population such a selection does not take place to any large degree, and we are dealing with the oversensitives-the sick, the young, and the very old. Public health officers have a most difficult task in establishing pollution levels for such a heterogeneous group, and it is a foregone conclusion that when levels are finally adopted there will be those who will maintain that they are too high, while others will charge persecution of industry because the levels are set too low. Animal experiments, and even experiments with human beings, while indicating some level of toxicity or annoyance, cannot give the answer for a general population. In urban areas we are dealing with several million people, and many would call the death of one or two persons per million, or some 20 for a town the size of Los Angeles, a disaster. The impossibility of approaching this accuracy of prediction in an experimental human, or even animal, colony is evident, for we would have to experiment with a few million individuals to get a statistically valid answer.

We come, therefore, to the conclusion that the only person able to give answers with any certainty about the result of some large-scale fumigation is the epidemiologist gathering data on death rates and general health status. It is, of course, unfortunate that this kind of study comes too late to prevent the disaster; on the other hand, these studies furnish extremely valuable data on ways to prevent recurrence of the same series of events. It is for this reason that the study, such as that by workers at Harvard, of pretoxic effects, consisting in physiological responses warning of the danger ahead, is one of the most promising approaches to the study of pollution levels. These studies deal with the combined and synergistic effects of aerosols and sulfur dioxide. The physiological changes noted are greater flow resistance in the respiratory system, as reported by Amdur and Mead (10). The effects found at lower concentration do not necessarily represent toxic symptoms but may have to be regarded in the same class as sneezing, coughing, or blinking of the eye-therefore as warning signs and pretoxic symptoms.

Air pollution disaster can be prevented. Even nuisance effects can be minimized by planning at the right time. Such planning requires some basic information which can be furnished by the meteorologists. A study must be made of wind trajectories, for the progress of a package of air loaded with pollutants over the area should be known. Also needed are data on the change in concentration in a pollution cloud as it moves across a given area. This change comes about through turbulence and chemical reactions. As in the case in Los Angeles, relatively harmless gases may react to form irritants while moving across the basin. We like to know how long it takes for the pollutants to react sufficiently to give us maximum irritation.

When all these facts, plus the size and nature of the emission, are known, we can begin to think of plotting the trajectories and the isopollution lines for different substances. This kind of calculation has been described by Frenkiel (11) for a hypothetical case in the Los Angeles area. The calculation, which, practically, can be made only by means of electronic calculating machines, shows the fanning out of the emission from a single point of origin and its gradual dilution (Fig. 9). When we are dealing with a diffuse source such as the automobile, we can divide the area into a number of smaller areas for which traffic density, and therefore pollution, are known (Fig. 10). By calculating and integrating each one of these contributions, we arrive at the effect of a multiple source of pollution such as the automobile. This method, more than any other, shows clearly the contribution made by different sources, often miles away, to the pollution at a par-17 OCTOBER 1958

ticular spot. Anyone enveloped by the expanding cloud will experience nuisance effects, regardless of whether or not he is in the exact center. On the basis of this concept, it is possible to express quite clearly how strongly the individual contribution from different sources may vary from one location to another, although both are in the same general area. Almost everyone is aware of this fact. Nevertheless it is quite common to refer loosely to minor and major sources, completely losing sight of the fact that in certain neighborhoods a local nuisance may have a greater effect than larger sources located far away. A great deal of friction could be avoided by recognizing this simple fact, and



Fig. 10. Geographical distribution of traffic in the Los Angeles area. Area of circles is proportional to the number of vehicles; each square represents 16 square miles. [F. N. Frenkiel (11)]



Fig. 11. Relative contributions of the three principal pollution sources to the mean concentration at California Institute of Technology. The effects of topographical features and inversion are taken into account in the mathematical model of Los Angeles County. The relative proportions of the "important" pollutants emitted by the three principal sources are based on recent studies in Los Angeles County. [F. N. Frenkiel (11)]

Frenkiel's "relative contribution charts" for different locations could be of great help in objectively settling some of the hot arguments (Fig. 11). A prerequisite for such calculations is reliable information on wind directions. Tracer studies based on the addition of easily identifiable materials such as fluorescent substances to the stack gases may be helpful. Much cheaper is the tracing of natural components specific to some of the sources. Aerial photography also offers considerable promise, especially at times when plumes 10 to 20 miles in length can be observed. Closer cooperation of other organizations, such as the Air Force and military and civilian groups, would be of great help.

Application of the methods for the calculation of pollutant distribution and movement would allow us to predict the future development of smog at a certain location and to predict what the elimination of certain sources will do as compared with the removal of others. This is especially important for a complicated case such as we find in Los Angeles. Here, most of the hydrocarbon material is emitted by the automobile, but the other components of smog, the oxides of nitrogen, are produced in nearly equal quantities by automobiles and installations burning gas or oil. The stationary installations are usually large, the trail of oxides of nitrogen is well defined, and the concentration of oxides of nitrogen may be higher than could be expected from a pollution cloud from such a diffuse source as the automobile.

Climatological conditions, and therefore air pollution moved by the wind currents, do not respect legal boundaries, nor does the pollution suddenly stop at the shore line, beyond which it is somewhat more difficult to maintain observation posts. In the Los Angeles area basin,

for example, pollution from the southern industrial area can reach the Los Angeles Civic Center by either a land or a sea route. Federal and state testing programs have drawn attention to these wind movements, which cause pollutants to drift as far as islands 50 miles off the Pacific coast. These pollutants can readily be seen from the air and are quite different in appearance from low-lying clouds, due to their lack of structure and often to their characteristic yellowish-brown, off-white color, caused by refraction rather than by any color of specific chemicals.

Earlier in this article I have discussed more or less regularly occurring, or chronic, air pollution problems. There is, however, a more acute type of pollution which occurs when, through accidents such as explosions of tanks of toxic chemicals or through explosion of enemy bombs, large areas may become dangerous. In such circumstances it is of great importance to have the ability and the machinery to push a button on a computer which tells the health authorities in only a few minutes the area to which the poisonous cloud is drifting and what its concentration will be.

#### Conclusion

Air pollution problems are as varied as the activities of people themselves. We have looked in some detail at only two types of pollution. It has been my intent to make it clear that the problems met in air conservation are extremely complex and need the cooperative assistance of many scientific and technical disciplines. There is hardly any field of human endeavor that is not touched. The student of environmental hygiene has, as his laboratory, hundreds of square miles; as his chemicals, about everything a population emits to the air -in other words, a mixture representing a sizable portion of the inorganic and organic chemicals. His accomplishments have to be attuned to a population so varied in reactions and responses that an "average" person has no meaning in his problem. Entering into and often interfering with the normal occupations of the community, he has to be endowed with diplomatic and legal talents. The increased importance of his job in protecting the cleanliness of the air is felt in many quarters, and several universities and federal agencies have started courses in practical and theoretical aspects of air pollution control. Needed, too, are engineering studies to lead to the improvement of existing methods and to the invention of more efficient and economical processes to deal with old and new problems in air pollution.

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