

Fig. 6. Accelerating use of fossil fuels may result in 50% rise in amount of CO_2 in the air by year 2000. If not absorbed by sea and plants this could raise temperatures several degrees by enhanced "greenhouse" effect, enough perhaps to melt glaciers and flood coastal cities.

THE SUDDEN PEAKING OF POLLUTANTS

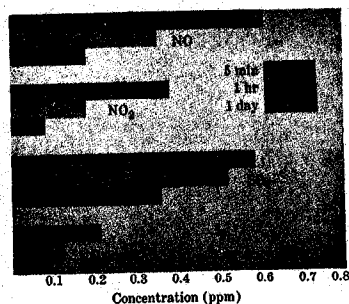


Fig. 7. Importance of continuous monitoring of pollutants—now being done by the Public Health Service's automated equipment in only nine cities—is emphasized by frequently observed higher short-time peaks such as these, which reveal inadequacy of using lower long-period averages in many medical studies.

tons in the blue and near ultraviolet. This dissociation produces nitric oxide and atomic oxygen $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$. The atomic oxygen thus formed combines with atmospheric oxygen molecules to form ozone (O_3).

Other photochemical reactions that contribute to the stew form excited oxygen molecules. These and ozone, perhaps aided by atomic O present in some dynamic equilibrium concentration, attack organic materials, probably by removing hydrogen atoms from the hydrocarbons. This oxidizing assault forms reactive intermediate substances such as alkyl and acyl radicals. These radicals can unite with oxygen to form still more reactive peroxy

radicals. And these, in turn, can react with oxygen to form more ozone, with NO to form larger quantities of chain-initiating NO_2 , and with NO_2 to produce short-lived but plant damaging peracylnitrates (usually abbreviated to PAN) and an abundance of more stable oxidation products such as eye-irritating formaldehyde.

Bewildered? Let's go over it again with reference to Fig. 8. The pivotal group of oxidizing substances consists of atomic oxygen (from dissociation of NO_2), excited molecular oxygen (from solar irradiation of the atmosphere's abundant molecular oxygen), peroxy radicals (from the action of other oxidants on hydrocarbons), and ozone (formed as a by-product in several of the photochemical reactions). During the daylight hours all of the oxidants contrive to react with the original starting materials—hydrocarbons (particularly unsaturated, olefinic ones and some aromatics) and nitrogen oxides—as well as with their reaction products. Thus at any particular time, the air is filled (relatively speaking—remember the troublesome concentrations are down at or below the part per million level) with a very complex mixture of intermediate oxidation and reaction products.

Unquiet controversy in California

A vast amount of experimental and theoretical photochemistry remains to be done at the low concentrations and low temperatures which characterize polluted atmospheres before we completely understand these processes. In the laboratory (Fig. 9, 10) symptoms of photochemical smog can be produced by irradiating with mock sunlight suitably low concentrations of hydrocarbons in the presence of oxides of nitrogen. But considerable controversy exists among both atmospheric chemists and simulators of smog about the precise course and time constants of each of the innumerable reactions occurring in polluted atmospheres. Not all such disputes are academic; indeed one such controversy is particularly instructive. It illustrates in a simple way the difficulty of understanding what our pollution problems really are and casts a long shadow over approaches to controlling photochemical pollution.

Although nitrogen oxides and hydrocarbons are the essential starting ingredients, only hydrocarbons are now being controlled in California, as was mentioned. This also is the control approach called for in a recent bill proposed to Congress and aimed specifically at the motor vehicle pollution problem. It should work; according to the tenets of the familiar chemical law of mass action this should inhibit formation of even the minute concentrations of final photochemical reaction products. Indeed, the consensus among pollution experts in Washington, Detroit and California is that by reducing hydrocarbons enough now,