

FOREST FUELS, PRESCRIBED FIRE, AND AIR QUALITY

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PREFACE

Forest fires and accompanying wood smoke were common components of the earth's environment long before the advent of modern man. Since the dawn of civilization fire has been regarded as friend or enemy, depending on how it served man--a threat to his home, heat for warmth and cooking, a destroyer of game, a screen from his enemies, a creator of desirable habitat for himself and his food.

The bad and good of fire in the forest continues to this day. The havoc of wildfires is almost beyond description. At the same time, the benefits of fire to the ecology of most forests is well known. Foresters have learned to harness and "prescribe" fire as a management tool for many purposes--to establish favorable seedbeds, to remove competing underbrush, to speed up nutrient cycling, to control tree pests, to establish desirable animal browse, to incinerate debris after harvest and thinning operations, and many others.

But prescribed fire, like wildfire, creates smoke, and smoke is regarded in varying degrees as a pollutant. Public pressures and needs are causing laws and regulations such as the Air Quality Act of 1967 and the Clean Air Act of 1970 to be enacted with increasing frequency. Adequate technical information often is not available to determine the extent to which pollution controls are needed, and, if so, in what form. Such is the case with wood smoke from prescribed forest burning--a forestry practice that is being subjected to increasing questioning.

The purpose of this publication is to present the known information on the physical and chemical properties of smoke resulting from burning of forest fuels, primarily wood. To do this job, we have called on the talents and knowledge of a long-time researcher in wood and plant chemistry and a forest research administrator of broad experience. This is Dr. J. Alfred Hall, retired Director of the U. S. Forest Service Forest Products Laboratory at Madison, Wisconsin, and former Director of the Pacific Northwest Forest and Range Experiment Station. We believe that Dr. Hall, a Ph. D. chemist; has provided an authoritative evaluation of the significance of wood smoke in the present day environment and that such information will be of value to foresters, air quality officials, health protection agencies, and the informed public.

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ABSTRACT

The combustion products (smoke) from forest wildfires or prescribed burns are often considered on a par with any other emission that might affect air quality. But enough is known about smoke from woody fuels to indicate that its importance is limited almost entirely to visibility obstruction, an effect that can be minimized by proper timing and preparation for burning. Much of the organic matter in smoke from forest fuels is similar to material normally entering the atmosphere from vegetative life or from the decomposition of vegetative matter. Fire compresses these processes into a shorter time. The environmental effects of prescribed burning are far more than compensated by great reduction in danger of disastrous forest conflagrations.

INTRODUCTION

It took many years, a great deal of research, and much money to arrive at our present position in management of forest lands, but no competent forester would contend that the present position is satisfactory. The dynamics of conversion from a predominantly rural, agricultural society to a predominantly urban and industrial structure have generated a host of still unanswered questions that are basic to working out successful forest management policies for the future.

Fire in the woods has been and continues to be one of management's severest problems and is a major deterrent to: wood production, wildlife habitat, recreation, and water quality and yield. All these uses are limited and sometimes destroyed over vast areas by wild, uncontrollable fire. Thus, the huge group of problems, generally lumped together under the term "fire protection," has always been a major significance in the total task of managing the forests. A powerful element in fire protection is "prescribed burning" for abating the danger of wildfire.

No part of the national heritage of forest wealth is exempt, but the nature of fire problems varies widely between forest regions. They are perhaps most onerous, costly, and sometimes puzzling in the West and South, but the Northeast and Lake States are by no means free of them. Nor do the hardwoods of the Central States escape problems of fire damage and control.

Although wood smoke has always been an important part of man's environment since he learned to use fire, the present crusade to abate air pollution levels an accusing finger at all burning, including forest fuels. The general public believes that anything in the air except air is pollution, dangerous, and must be prevented. The more visible it is, the more dangerous, and smoke from the burning of forest fuels is certainly visible, especially to the city man who is driving through the forested country.

In this publication we shall explore what we know, think we know, and ought to know about the products of combustion of forest fuels. In order to assess the relative importance of the matters to be considered, it will be necessary to evaluate some phases of the total air pollution crisis. We shall find our ignorance far greater than our knowledge.

There are no simple, direct, and rapid solutions to air pollution. But with much work and money, they can be achieved, provided there is time permitted.

This report is a briefed summation of my conclusions drawn from an extensive survey of the literature. It is not meant to be definitive because it deals with a field in which much work is currently being performed and conclusions are subject to change as new results of research appear.

I have taken the liberty of being critical in some matters dealing with abatement of air pollution in general. I have also dared propose the existence of some gaps in our knowledge in the field with which we shall deal.

WHY "PRESCRIBED BURNING"?

We know a great deal about fire behavior in the woods, the relation of weather, moisture, terrain, and fuel supply to how a fire spreads and how to attack it. The record of reduction in acreage burned by wildfires over the past 20 years is excellent, but we still have disasters such as those in eastern Washington in 1970. These teach us that the prevention of all wildfires or stopping them with small damage still elude us. Despite all our advanced technology, aerial attack, and rapid mobilization of men and machinery, when a conflagration is created by a combination of natural forces like those of 1970, it is stopped or controlled only by these things:

1. Change in weather,
2. Running it into natural areas with low concentration of fuel or backfiring from such areas,
3. Creation of areas of low or no fuel into which to head the fire or from which to backfire.

It will be noticed that, as far as man's ability to control fire is concerned, lessening or elimination of fuel is his most important tool,

"Prescribed burning" means that the required burn is to be executed with certain definite objectives and will be carried out under conditions of fuel moisture, weather, and fuel arrangement that will achieve a major objective of the burn, fuel reduction, and do minimum damage to the surrounding forest and the general environment.

Thus, in the South, prescribed burning is intended to reduce the fuel supply on the floor of the pine forests by burning such cover as saw palmetto, dry grass, ty-ty, gallberry, and smaller pine reproduction in order to create areas of low fuel to prevent crown fires and into which a crown fire can be headed and brought to earth where it can be controlled. Anybody who lived in the South through the dry mid-1930's remembers the disastrous wildfires in "rough woods" that brought realization of the utter necessity of prescribed burning.

In the West, a different method is dictated by rugged terrain, prevalence of fires started by lightning, and the nature of the forest. The West is still largely in the process of converting virgin stands to managed forests; a task already in the past in the South. In much of the West, production of our most important species calls for clear areas in which the seedlings can get full light. Thus, clearcutting in small blocks has become general practice. This generates, in old-growth and also second-growth country, huge amounts of residue on the cut areas; cull logs, limbs, tops, foliage, and brush.

Many years ago, most of the Western States required the lowering of fire hazards by removal of slash or burning it. Over the years, increasingly close utilization has caused the bringing of more of the tree out of the woods for conversion to products. But we are still far from the economic possibility of full use of the tree. Certainly, the technology exists by which we can make useful products from the whole tree, but the financial losses incurred would be very large and, under our system, industry cannot bear them. In short, if it were to be attempted, the burden would fall very heavily on the consumer and taxpayer.

As of now, there is no alternative to burning much of the slash and the fuel produced in the woods. It is well recognized that the burning process can be improved by developing more advanced techniques and close cooperation between meteorologists and forest managers. In some States, this process is already working well. Burning can be accomplished with greatly lessened damage to the atmosphere, especially with respect to municipalities near the forests where reduction in visibility is sometimes an important problem.

The objectives served by reduction of fire hazard by burning the slash are important ones. The methods used vary widely according to the forest type and specific situations. All these are subject to analysis and decision by professional foresters trained for the job. This whole subject is treated well by Davis (1959). It is unfortunate that this lucid, excellent treatise has not been revised into a form more understandable to the general public.

The uses of fire in forestry go far beyond reduction of fire hazard. Natural fires over the ages did much to create and maintain our most valuable forests, and we had learned much about the use of fire as a tool in managing the ecological complexes of forest systems. These subjects are covered well by Roe et al. (1971), Wilson and Well (1971), and Taylor (1971).

In general, it has been found that the wise use of fire in prescribed burning is of importance in many fields:

Improved regeneration in some forest types.

Recycling and making available certain nutrients, e. g.
potassium, phosphorus, calcium.

Control of endemic and epidemic diseases, e. g. brown spot
and mistletoe.

Improvement of some brushland and grassland areas for better
browse and forage.

Management of park and wilderness areas.

WHAT DO WE BURN IN "PRESCRIBED BURNING"?

The answer to the above question is complicated by these factors among others:

1. Timber type, age and density of stands.
2. Nature of material and methods and conditions of burning: i. e. ,
old, green, ground cover; broadcast, windrow, piles; fuel density, aspect,
terrain, weather, and wind.

The composition of the fuel actually consumed is determined by such factors, but one thing stands out clearly: the fuel consumed will comprise much material that is not wood itself. How much and what kind? There are no firm answers.

Regarding old-growth Douglas-fir, recent data are given by Morris (1970). He discussed types of burn related to regeneration, and brush invasion, but had few quantitative measures of types of fuel consumed:

Slash fires greatly reduce probable rate of spread and resistance to control of subsequent fires for 5 years and significantly reduce rate of spread alone for 15 years
Fires that we studied consumed virtually all fine twigs supported above the litter but scarcely affected the quantity of wood more than 11 inches in diameter. More intense slash fires would have decreased rate of spread in the first several years and appreciably decreased resistance to control ...
and obviously would have consumed more wood. (Italics mine.)

Broadcast burns in the old-growth Douglas-fir of the West, therefore, may be considered to consume small limbs, twigs, foliage, bark, some wood in tops and limbs, ground cover, and duff, but little in the way of large, cull logs or tops and limbs. More wood might be consumed in piles or windrows but less duff and ground cover. In second-growth Douglas-fir, one might expect the fuel to include higher proportions of foliage, bark, twigs, small limbs, and partially decayed remnants of the preceding stand.

In the South, the situation would be just as variable with respect to fuel composition but might run more to foliage and ground cover.

The percentage of bark with respect to total available fuel is widely variable. Some information of interest was published recently by Harold Young (1971). This article gives the percentages of bark in the whole tree for red spruce, balsam fir, hemlock, white pine, northern white cedar, white birch, red maple, and aspen in Maine. Values are calculated on the dry weight basis, and exclude leaves or needles and branches less than one-fourth inch in diameter. Bark contents for branches and unmerchantable top are:

	<u>Percent</u>		<u>Percent</u>
Red spruce	14	Northern white-cedar	40
Balsam fir	29	White birch	24
Hemlock	15	Red maple	32
White pine	10	Aspen	25

Young's report apparently deals with second growth. He finds that the merchantable bole contains about half the bark of the whole tree and the wood to bark ratio is about 4.6:1.

There has appeared recently an excellent series of publications dealing with the literature related to amounts of tree components that should be useful in analysis of forest fuels (Keays 1971a, 1971b, 1971c, 1971d, 1971e). An assemblage of contributions that contain much information useful in studying the physical distribution of fuels on the tree is now available (International Union of Forest Research Organizations 1971).

In burning the fuels in the forest, we are engaged in a very complicated process as far as materials are concerned, and our knowledge of the products of their decomposition by heat and combustion is scarce.

Bark, the outer cortex, varies widely in composition from wood and just as widely among species. Some is on the tree; some has been shed and is on the ground. In some conifers, bark will contain volatile oils and resins; in most it will contain tannins and their relatives, complex coloring materials, the remains of various carbohydrate complexes, some cork in old bark, and so on through a host of compounds.

The phloem tissue and pith are alive, physiologically active, and rich in organic materials that are not wood.

Live needles of conifers usually contain appreciable quantities of volatile oils and resins, usually terpenes and oxygenated relatives. In the pines the content may reach 2 or 3 percent of these highly combustible substances. Some of such materials will persist in the mature, dead foliage of the duff layers, as will the waxy cuticle that coats the needles and leaves, along with bark shed from boles.

In the parenchymatous tissues of foliage, phloem, and pitch varying amounts of reserve carbohydrates, fats, and a small content of protein will be found. The content of such polymers as the hemicelluloses and various gums grouped under the term "polyuronides" will run much higher than in wood. Such materials decompose at elevated temperatures more easily than wood itself and yield different products both in thermal decomposition and combustion.

A great amount of literature deals with amounts and nature of forest fuels as related to rate of spread and control of fires. Much work has been done and is in progress on measurements of relative amounts of various kinds of fuel, a difficult task but one that must be accomplished if contributions of combustion of the vast array of fuel combinations to the atmosphere are to have meaning.

The complexities of sampling are well illustrated in a report on slash burning in the Pack Forest (Fritschen et al, 1970). The project included a number of objectives, some of which will be referred to later. For the moment, data on the nature of material burned in a broadcast slash fire are pertinent. The weights of material on the 7.45-hectare burn were:

	<u>Original in short tons</u>	<u>Remaining after burn</u>
Duff	162.0	79.5
0-1 centimeter	59.7	1.7
1-10 centimeters	97.9	78.1
10 centimeters	326.9	391.4
Brush	5.7	

The increase in larger wood after the burn is explained by difficulties in sampling.

Roughly, the fire consumed about 170 tons of 650 tons of fuel available. Of this:

	<u>Percent</u>
Duff comprised	48
0-1 centimeter (fines) comprised	34
1-10 centimeters (fines) comprised	<u>12</u>
	94

The remainder is attributed to brush and the small amount of larger wood that was burned. The workers estimated an average fire penetration of only 1 centimeter in such material. Clearly, the larger wood pieces contributed little to the total products of the fire, and although the objective of facilitating regeneration by exposing mineral soil was partly achieved, there remained about 52 tons of wood per hectare to interfere with regeneration and management of a second-growth stand of timber.

Similar fuel balances for pile fires were not given, but the description given shows the piles to have been mostly of stacked wood.

The validity of conclusions with respect to atmospheric pollution from various forms of open burning can be judged only if the nature of the fuel and the conditions of burning are known. A good example of the difficulties encountered is given in a comparison of results reported in two publications (Feldstein et al. 1963, Darley et al. 1966). These papers report quite widely different results and interpretations which will be discussed later.

There appears to be general agreement that, in burning forest fuels, the hotter fires with longest possible residence time of combustion products and ample supply of oxygen give most nearly complete combustion. Clearly, over the wide array of fuels available in the procedures of prescribed burning and the wide variation in burning procedures, a very wide range of possible emissions of combustion products will result, both in quality and quantity.

The complexity of the materials burned raises serious questions as to the reliability of the "Emission Factors" and "Inventories of Pollutant Emissions" issued by various bodies in the field of air pollution.

THE PROCESS OF COMBUSTION

Much work has been done on the combustion of solid fuels, especially coal and wood. Perhaps the complex matters involved are best stated in "Encyclopedia of Science and Technology" (McGraw-Hill 1966, p. 306):

First, volatile matter is driven out of the solid by thermal decomposition if the fuel burns in air. At usual combustion temperature, the burning of the hot, solid residue is controlled by the rate at which oxygen diffuses to its surface. The first product of combustion at the surface of char or coke is CO, this burns to CO₂ in the air surrounding the solid, unless it is chilled by some surface.

This description is a bit oversimplified when we deal with wood or the mixture of forest fuels described above. The important variable that has much to do with the process is water content. In old, dry fuels the water content will be low in the smaller material, higher in the coarse. In green slash, the water

content may run high, perhaps exceeding half the weight of the fuel. Much of this water must be evaporated before the fuel actually ignites or before volatile flammable material is evolved in sufficient amounts and of composition that will burn.

A few terms to be used in our discussion should be understood. Pyrolysis" means decomposition means of heat; The process has long been applied to wood for manufacture of charcoal. Often it is referred to as "dry distillation," or "combustion in a deficiency of oxygen." Heat of partial burning of the pile of wood produces products of pyrolysis, the heat of combustion raising the temperature of the wood until it reaches the temperature at which an "exothermic" reaction takes place. This reaction means that chemical materials in the wood are now decomposing with evolution of heat, in contrast to the earlier "endothermic" stage in which heat was being absorbed.

Since we do know much about how wood burns, we shall discuss that process and hope that comparable knowledge may be obtained also for the forest fuels mixtures.

F. L. Browne, of the U. S. Forest Products Laboratory, gave an excellent picture of what takes place in the combustion of wood (1958, p. 1-6). Following is a condensed version of the processes with an occasional comment on my own interjected in brackets.

Pyrolysis

First, the "Course of Pyrolysis." after the surface layer of fuel is dry enough to begin to burn.

Zone A up to 200° C.

A layer of wood at the surface becomes dehydrated and evolves water vapor with perhaps traces of carbon dioxide, formic and acetic acids. [The beginning of thermal decomposition.]

Zone B - 200° to 280° C.

Zone A moves farther into the piece of wood and is succeeded by Zone B, in which pyrolysis remains slow. Water vapor, carbon dioxide, formic and acetic acids, glyoxal, and perhaps a little carbon monoxide are evolved and additional vapors from Zone A pass through. Thus far, the reactions are endothermic and the gaseous products are largely noncombustible. The wood becomes slowly charred.

Zone C - 280° to 500° C.

Zones A and B move inward to be succeeded by Zone C in which active pyrolysis begins suddenly and exothermically. The temperature mounts rapidly unless the heat evolved is dissipated. Combustible gases and vapors (notably carbon monoxide, methane, formaldehyde, formic and acetic acids, methanol, and later hydrogen), diluted with carbon dioxide and water vapor, are enclosed forcibly enough to carry with them droplets of highly flammable tars that appear as smoke. [In a sufficiently hot flame, these will burn. Later work shows production of small quantities of hydrocarbons of low molecular weight that combine intermolecularly and participate in the formation of the tars.]

The primary pyrolysis products undergo further pyrolysis and reactions with one another before they escape [or are burned].

Zone D - Above 500° C.

If the surface temperature continues to rise before carbonization becomes complete, Zone D, composed of charcoal, becomes the seat of still more vigorous secondary reactions in which the gaseous products and tars rising from the zones underneath are further pyrolyzed to more highly combustible products. For example, carbon dioxide and water vapor may react with carbon to form carbon monoxide, hydrogen, and formaldehyde.

These processes must go on to produce combustible gasses which, in mixture with enough oxygen, will sustain combustion. In the absence of a complete oxygen supply, much of the distilled material can be collected and condensed as wood tar and the so-called pyroligneous acid, water-soluble distilled materials.

The Course of Combustion

Zone A - Up to 200° C.

The gases evolved by a very slow pyrolysis are not ignitable. Sound wood does not ignite within Zone A.

Zone B - 200° to 280° C.

Actual ignition of gases may begin but real flaming comes at higher temperatures. [Characterized by intermittent flames in a fireplace.]

Zone C - 280° to 500° C.

The mixture of gases evolved in Zone C at first should be too rich in carbon dioxide and water to sustain flame, but it soon becomes combustible as a result of secondary pyrolysis. At this stage, flaming combustion occurs entirely in the gas phase **outside** the wood because the rapidly emerging gases lack necessary oxygen until they have gone far enough to mix with air in proportions between the upper and lower limits of flammability. [Here, we have a probable explanation of the explosive violence of huge concentrations of evolved gases in massive, wild forest fires.]

The heat of flaming contributes to the speed of combustion, the rate depending on such things as the geometry of fuel arrangement and the available oxygen. A single Log in a fireplace will not keep burning without continuous supply of heat from flaming kindling or hot coals beneath it, but three logs properly placed may keep burning as long as each contributes heat to the others.

In burning wood, all these processes are going on at the same time. Complete combustion is obtained when the hot volatile combustible gases are in contact with sufficient oxygen for sufficient time and the residual charcoal has burned by glowing, until the final residual is inorganic ash, probably 0.2 to 0.3 percent of the original wood.

In prescribed burning, the whole series of the processes in the fine fuels may be almost instantaneous, producing heat to carry them into the coarser fuels which will burn as long as combustion is supported by evolution of sufficient heat.

Recently, I saw demonstrated a multichambered incinerator burning several types of forest fuels, with the finely divided fuels (chips) being fed at a uniform rate after being dried to about 30 percent (dry basis). This process maintained a continuously hot fire (about 1,400° C.) with gases kept hot in abundant air supply while traversing three combustion chambers. The combustion products came out the stack at about 320° C. It is reported that they contained no carbon monoxide, a trace of particulate matter and no hydrocarbons; almost entirely carbon dioxide and water, which did not form a visible plume. The rate of gas flow at the exit was much above the amount of air needed for theoretically complete oxidation. Whether that much more air is needed is not known.

The desert Indian achieves almost this result with his skillfully arranged cooking fire of small, dry sticks, but we cannot with our kinds of fuel and their arrangement in prescribed burning.

Everything in the piles, or in the broadcast spread, or the Southern prescribed fire is combustible to carbon dioxide and water, except for the small

amount of ash. But, because of the necessity for drying the fuel to combustibility and the impracticability of maintaining high temperatures long enough, and obvious insufficiency of mixing with excess air, we get varying degrees of incomplete combustion.

Requirements for Complete Combustion

We can calculate the oxygen requirements for wood and assume that these requirements will be near those for the other organic fuels that are in the prescribed burn.

Wood is roughly 50 percent carbon, 6 percent hydrogen, and 43.5 percent oxygen. We may disregard the small amounts of nitrogen and ash.

In the burning of a ton of wood to carbon dioxide and water, there are produced 3,700 pounds of CO_2 and 1,080 pounds of H_2O . The ton of wood contains 870 pounds of oxygen, so 2,790 pounds must be supplied for complete oxidation. Since air is only 20 percent oxygen, just under 7 tons of air must be supplied. Thus, in theory, we need about 174,000 cubic feet of air to burn a ton of fuel. In reality, we need much more. Under our field conditions, a situation capable of supplying that much air is improbable overall, so combustion is incomplete. Burning of gas, suspended solids, and residual solids is going on simultaneously and in varying degrees of combustion.

The original fuel will contain free water in varying amounts. In green slash we may have to evaporate a half ton of water per ton of fuel: a total yield of a ton of water per ton of fuel consumed.

What Temperatures Are Reached?

I mentioned above that, in the multichambered incinerator, temperature of about $1,400^\circ\text{C}$, was maintained continuously in the firebed. Countryman (1964) measured temperature in a mass wood fire. He registered $2,000^\circ\text{F}$. ($1,094^\circ\text{C}$.) for about 10 minutes, 20 minutes after ignition. In the same fire, 15 feet above the fuel bed, he read $2,600^\circ\text{F}$. ($1,420^\circ\text{C}$.) 30 minutes after ignition. Later, Philpot (1965) reported probably higher temperatures in large mass fires. Pie also gave a good review of past work.

Somewhere around $1,420^\circ\text{C}$. may be taken as a maximum temperature achievable in combustion of wood or similar fuels under ideal conditions. Under conditions of prescribed burning, such temperature could only be achieved in rare cases and could only be maintained for a very short time.

Hence, in our prescribed burning, we undoubtedly can measure temperatures from around 300°C . to around $1,400^\circ\text{C}$. with the maximum reached rarely and only for very short times. If the fuel can be piled in such a manner

as to maintain high temperatures for long periods and piled so as to assure a maximum access of air below, around, and above the fire, optimum but not complete combustion may be attained.

I have found no measurements of temperature in a wild forest fire. Under some circumstances, *i. e.*, heavy accumulation of flammable gases, explosive flames may produce such high temperatures for very short intervals.

For purposes of comparison, the temperature of the exploding gas mixture in the automobile cylinder is about 4,500° F. (2,480° C.), far above the maximum obtainable in wood.

WHAT ARE THE PRODUCTS OF COMBUSTION OF FOREST FUELS?

Obviously, the products of combustion of forest fuels are going to range widely from all carbon dioxide and water at complete combustion to the products of straight thermal decomposition or pyrolysis. And the usual fire will have some of all the possible mixtures. Thus, although we can identify many of the components, quantitative measurements can have meaning only if the conditions of burning are described.

Products of Straight Distillation.

Earlier, the fact was discussed of the presence of natural volatile materials, especially in the foliage, conifer needles, bark, and live tissue. Needles of some species contain appreciable quantities of oils that are volatile with steam. The duff, with varying amounts of old needles, would contain some also. In the process of drying, the first stage in the burn, these materials would be in the vapor arising from the burn.

Most of these substances are terpenes or closely related oxygenated compounds. A typical and abundant terpene is α -pinene, familiar as the principal component of turpentine. The odor of conifer foliage is mostly related to such things as borneol, or bornyl-acetate, an ester of borneol and acetic acid. Various aromatic aldehydes will be in the vapor cloud. These first emissions will not be burned unless they are caught in the next phase of the fire.

As the material dries and comes to the point of pyrolysis, the composition of the evolved gases changes and flames begin.

Products of Pyrolysis

In the enormous amount of work done on the wood distillation process for charcoal manufacture, some 230 substances have been identified. These result from thermal breakdown of the complex mixture of fuel materials with which

we deal, wood containing the hemicelluloses, cellulose, lignin, and varying proportions of other chemicals already referred to, lumped as "extractives."

Browne (1963, p. 9) states: "The yield of products when wood has been completely pyrolyzed is about what would be obtained by pyrolyzing separately the proportional amounts of the major wood constituents." I suspect this statement is of doubtful applicability to our mixture of forest fuels with such a diversity of chemical substances.

Much work has been done on pyrolysis of the principal components of wood itself, viz., cellulose and lignin. With the coming of the more sophisticated analytical techniques of recent years, considerable new knowledge is being obtained with regard to the mechanisms of pyrolysis and the reactions that follow among the primary products. These products appear to be highly reactive when first formed in the distillation zone, probably largely in the form of free radicals. These would have very short lives, would not be found free in the condensed products of pyrolysis, and would play a very active part when the vapors from pyrolysis mix with air in the zone of flaming combustion.

The products of pyrolysis of resin-containing conifers differ from those of hardwoods by virtue of decomposition of the resin components.

The origin of the multitude of products of pyrolysis can be traced in part to the intermolecular condensation reactions between such molecules as furfural, formaldehyde, glyoxal, acrolein, a wide variety of phenols and substituted phenols, and various hydrocarbons. Some will be further changed by combustion, but noncondensable organic gases and some CO will escape the combustion process.

It would be fruitless to attempt to review here the wide range of possibilities.

Products of Combustion

Clearly, the complicated processes by which pyrolysis proceeds yield a host of molecular species in the form of gases which, in the presence of air, will burn. If the temperature of the flame is high enough and continues long enough, combustion is complete and the products are CO_2 and H_2O . Whenever the vaporous products are cooled, either in pockets in the burning pile or in diffusion currents around the fire, condensation of vapors will take place and intermolecular reactions will be slowed or stopped. Since unburned carbon particles are omnipresent except in zones of complete combustion, these form the nuclei for adsorption of condensed organic gases and, if the zone is cool enough, water.

To sum up these complex processes, the amounts of substances burned, escaping unchanged, or altered by heat and intermolecular reactions, or by

partial oxidation, present infinite possibilities in the matter of final products. A vast amount of very carefully controlled laboratory work will have to be done, on specific fuels, before definitive statements can be made as to so much of this or that being produced in burning so much wood or forest fuels. Thus, flat statements as to amounts of chemicals or classes of chemicals entering the atmosphere from forest fires or prescribed burning are lacking at this time in specific meaning.

THE ATMOSPHERE AS A DYNAMIC SYSTEM

We speak of "clean air" as an achievable reality, once having existed, fouled by man, and to be returned to its original condition. In truth, our knowledge of geology and biology teaches us that clean air, all made up of nitrogen, oxygen, and rare gases, never existed and probably never will until the ultimate transformation of the earth to a cold body devoid of all life.

We are finding that our atmosphere, overall, is an immensely complex system containing huge amounts of substances that are not "air" at all.

A part of the tasks involved in the analysis of the system has been covered well in the monumental study by Robinson and Robbins (1968). This report was followed by a supplemental report in June 1969.

A quotation from the introduction to the first report is of interest:

There are sources in the natural environment of a wide variety of gaseous and particulate materials which are commonly clas sed as air pollutants when they are emitted by man-made sources. In addition, the atmosphere possesses a number of mechanisms which act to remove, sometimes at a quite rapid rate, most, if not all, of the materials emitted into On a much smaller scale, the air pollution problems in major urban areas are examples of situations where the pollutant emission rate seriously overburdens the scavenging processes for significant but limited periods of time within the confines of the urban area It is also often assumed, apparently, that commonly identified pollutants are uniquely related to man's activity and that pollutant emissions constitute a permanent and ever-worsening burden for our atmospheric environment. These assumptions are drastic oversimplifications and can lead their proponents far from reality.

Thus, the frightening episodes of heavy pollution from coal smoke and sulfur dioxide in Donora, Pa., New York, London, and the Ruhr have been equated in many instances with all particulate and gaseous pollution. In reality, these are special cases of limited applicability outside of the regions directly involved and the necessity for abatement there of the known causes is not open to disputation.

In a similar vein is a recent article by J. E. Lovelock (1971).

Quoting Lovelock:

The atmosphere should therefore be regarded as a biological contrivance whose constituents are in a state of dynamic balance with the biosphere.

The possibility then arises that, even over industrial regions, a large amount of the haze is associated with plant growth, although proof of this requires detailed analysis of the aerosol which are lacking.

Los Angeles smog may be, nevertheless, a special case; it is undoubtedly the result of urban activity -- the interaction between the hydrocarbon emissions of the gasoline engine and other reactive species produced by the action of sunlight. The combination of car population, climate, and geography that is needed to produce this smog is not at present reproduced anywhere else in the world.

In spite of this, there are general attempts to equate all hydrocarbons in the "ambient air"¹ with Los Angeles type of photochemical smog (more on this under "Hydrocarbons").

Lovelock points out that the evidence from satellite photographs shows that the industrial regions of North America and western Europe contribute much less to haze in the northern hemisphere than do tropical forests and deserts. The desert regions are often covered with an aerosol of soil particles.

A different point of view is presented by W. T. Pecora, Director of the U. S. Geological Survey (1970a, 1970b). Assuming that man has developed nearly all of his influence on ecological matters in the last 10,000 years, mostly in the last 200, Dr. Pecora makes the following statement:

Some myths need to be destroyed. Let me cite a few that demonstrate that natural processes are by far the principal agents in modifying our environment. This is not to excuse or put aside what man does, but rather to put man's actions in proper natural perspective.

It has been calculated that more than 100 million tons of fixed nitrogen in the form of ammonia and nitrates are annually transferred from the atmosphere to the surface of the earth as

¹I have not found a satisfactory definition of "ambient air." The Oregon Department of Environmental Quality defines it as "the air that surrounds the earth, excluding volume of gas contained within any building or structure." I interpret this as meaning anywhere in the open, but the definition seems to have little meaning in interpreting the actual influence of a source of pollutant on the "ambient air."

The Federal Environmental Protection Agency has recently defined "ambient air standards" for some pollutants and uses the term as though it were generally understood, but it is still undefined.

a part of a natural precipitation process. In the United States alone there falls upon the face of our land annually more than 4 million tons of table salt, 2.5 million tons of sodium sulfate, and 36 million tons of calcium compounds--all in rain water.

Particulate matter and natural gases dispersed from the volcanoes is a continuing phenomenon. From three eruptions alone--the Krakatoa eruption in Java (1883), the Mount Katmai eruption in Alaska (1912), and the Hekla eruption in Iceland (1947) -- more particulate matter in the form of dust and ash and more combined gases were ejected into the atmosphere than from all of mankind's activity. Add to known volcanic activity the normal action of winds, forest fires, and evaporation from the sea, and we can readily conclude that man is an insignificant agent in the total picture, although he is becoming an important agent in an extremely local context.

We can glean from the above quotations and others that the local situations are almost entirely urban and that, in the total atmospheric system, they are extremely irritating--albeit temporary--happenings to a lot of people.

DECOMPOSITION OF VEGETATIVE MATTER IN NATURE

The following material has been greatly condensed from "Plant Physiology" (Quastel 1963) .

The natural fate of vegetative growth in the main is decomposition and incorporation into soil. This is a complex process, varying widely in its chemical and physical nature according to temperature, moisture, sunlight, acidity or alkalinity, and a host of other variables. But, it is abundantly clear that if this decomposition did not take place, the surface of the earth would long since have been covered deeply with vegetative refuse.

Clearly, it is impossible and unprofitable to review the enormous literature in the field, but we can draw a few conclusions.

We are dealing with wood, straw, grasses, and herbaceous vegetation as materials that are decomposed. In chemical terms we have cellulose, hemicelluloses, various gums and mucilages roughly grouped as "polyuronides," lignin of various compositions, and "extractive materials" that include a host of coloring matters, tannins, volatile oils, and resins; almost an infinite number of possible combinations and compositions.

From this complex material, the natural processes of an enormous number of species of fungi, bacteria, etc., produce volatile and nonvolatile substances. The latter become the cells of the micro-organisms concerned and soil itself; the former enter the atmosphere.

Not only micro-organisms but a huge variety of insects take part in the processes.

The decomposition of the carbohydrates may produce much carbon dioxide, but also a variety of volatile organic acids (mostly acetic, butyric, and valeric acids), some alcohols, some hydrocarbons (mostly methane), and hydrogen.

Some organisms have been shown to yield about 10 percent of volatile acids from cellulose, in particular acetic and formic, with the former dominant in quantity. Both would appear as "organic acids" in ordinary analysis of air.

The population of anaerobic organisms in soil is said to produce from cellulose: acetic, butyric, and lactic acids; ethyl alcohol; carbon dioxide; and hydrogen.

One of the best known root fungi, growing on wood, produces an oily substance found to be a mixture of esters of cinnamic acid and anisic acid, along with acetaldehyde. The latter would appear in air analyses as aldehydes, and the esters would appear as hydrocarbons.

This complicated natural process explains in part the theme of Rasmussen and Went (1965) that much volatile material is produced in the continuing decay and replenishment of products of plant growth. The dead structures of the fauna and flora that carry out the process eventually contribute their share of building soil and producing volatile matter.

In burning, we of course compress into a short time similar processes of oxidation and chemical transformation with production of some materials that go into the air and are eventually returned to the cycle of life and death of vegetative growth. There is great chemical similarity between the products of combustion of forest fuels and the products of their natural decay.

BURNING OF FOREST FUELS RELATED TO EMISSION FACTORS

Methods of routine measurement for the various types of emanations from fires applied to such fuels as forest fuels leave much to be desired, especially because they must be designed for purposes of continuous monitoring, operate without much human attention, and record automatically.

Two publications on the national air pollution control problem concern us especially in our present task of evaluating emission factors. They are:

1. Public Health Service Publication No. 999-AP-42, "Compilation of Air Pollutant Emission Factors" (Duprey 1968).
2. National Air Pollution Control Administration Publication No. AP-73, "Nationwide Inventory of Air Pollutant Emissions" 1968, (U. S. Department of Health, Education, and Welfare 1970h).

The basis for these two publications is a series of publications by the National Air Pollution Control Administration (NAPCA) dealing with air quality criteria and control techniques.

Doubtless these two documents represent the best that could be produced by competent engineers to meet statutory requirements in a hurry.

But unfortunately, two fallacious impressions have been created in the public mind.

1. Figures given generally carry the idea that all quantities are real. In fact, many are gross approximations.

2. Amounts of organic substances entering the atmosphere from all sources are cumulative and remain as pollutants henceforward.

From "Nationwide Inventory of Air Pollutant Emissions" I have compiled the following tabulation of supposed emissions, nationwide, from burning of forest fuels.

<u>Pollutant from forest fires</u>	<u>Total emissions in millions of tons per year</u>	<u>Percent of national total</u>
Carbon monoxide ^{2/}	7.2	7.2
Particulates	6.7	23.7
Sulfur dioxide	(3/)	
Hydrocarbons	2.2	6.9
Nitrogen oxides	1.2	5.8

We shall proceed to examine materials and groups of materials entering our environment and active atmospheric system as they relate to burning forest fuels and their relative importance in the whole problem.

Carbon Monoxide (CO)

A full coverage of sources, background levels, fate in the atmosphere, physiological reactions, is given in NAPCA Publication AP-62 (U. S. Department of Health, Education, and Welfare 1970a).

Aside from carbon dioxide, not considered a pollutant, carbon monoxide constitutes in tonnage by far the largest percentage of air pollution components.

~~Since its~~ toxic nature has long been recognized and urban concentrations from

²This figure, compiled from NAPCA Publication AP-65, p. 5-4 (U.S. Department of Health, Education, and Welfare 1970d), is given as comprising: 2.48 million tons from prescribed forest burning and 4.74 million tons from forest wildfires.

³Negligible.

Automobile exhausts have long been accepted as dangerous to health, physiological reactions to ambient concentrations have given rise to an enormous literature.

There have always been, until recently, some mysteries of a highly technical nature connected with CO.

It has been known for many years that there are natural sources of CO whose magnitude has been found or estimated to be relatively small when compared to the amounts produced in incomplete combustion, especially of gasoline in motors. The great amounts produced in modern times have been estimated to release into the world's atmosphere about 220 million tons annually, of which the United States contributes about half.

Good reviews of the whole matter are given by Jaffe (1968) and Robinson and Robbins (1968).

Agreement with regard to emission factors is hardly to be expected in dealing with the uncertainties encountered in wild forest fires and prescribed burning. The 7,200,000 tons of CO from these combined sources, often quoted, has as much accuracy as estimates of:

1. Acreages burned;
2. Fuels consumed per acre;
3. Density, character, and arrangement of fuels;
4. Weather factors.

Estimates of 1 and 2 were given to the National Air Pollution Control Administration by the Forest Service. NAPCA applied an "emission factor" of **60** pounds of CO per ton of forest fuels, derived as a general average for "open burning." Reports by Darley et al. (1966) and Gerstle and Kemnitz (1967) apparently formed the basis for this figure. The problems involved in arriving at even an intelligent guess as to tonnages of CO ascribable to burning forest fuels are well illustrated by Feldstein et al. (1963). These workers reported **600** pounds per ton of landscape debris. It is difficult to explain such enormous discrepancies in results by competent workers.

Regardless of these matters, there have not been actual measurements of CO production per ton from forest fires or prescribed burning practices. Attempts have been made to obtain significant figures with respect to CO concentrations in and around fires in forest fuels (Countryman 1964).

Quoted from Countryman's summary: "Some of the data obtained also strongly suggest that conditions may exist in field - scale fires that are not evident in small - scale or laboratory fires." He found, as expected, lethal concentrations of CO in the active part of the fires studied, but the concentrations were much lower toward the edge of the fire. "No significant concentrations of CO were found in the streets of test fire 760-1-64." In this fire, concentrations of CO were measured within the field from piles of fuel arranged in systematical patterns.

In 1970, an important report, concerned especially with various methods of burning logging slash in the Northwest, was issued (Fritschen et al. 1970). With regard to CO, quoting from summary: "High CO and CO₂ concentrations found at the fire site decreased rapidly to ambient conditions in horizontal and vertical directions."

This report embodies work that used airplanes for sampling and advanced methods of analysis, and certainly points the way for further intensive research.

Both the above reports and other work that cannot be covered in this brief review support the desirability of the high-energy fire for prescribed burning.

It is strongly indicated that increased concentrations of CO do not persist for more than short distances from the going fire. Since large fires in forest fuels rarely occur in the vicinity of major urban centers in which local high concentrations of CO are sometimes dangerous, it is not apparent that combustion of forest fuels can be of any significance to the urban problems.

Certainly, firefighting personnel in the forest must be protected against possible high concentrations of CO in terrain where confined gases may build up to dangerous levels.

Fate of CO in the Environment

Reference was made above to perplexing problems connected with CO. Most important of these has been the question of what happens to it in the atmosphere or elsewhere to account for the fact that its concentration in the atmosphere is not found to be increasing at all. This is in spite of the great increase in the amounts put into the air in recent years.

It has long been clear that somewhere is a "sink" for CO, and many theories have been advanced to account for it. It is indicative of the nature of the puzzle that estimated life of CO in the atmosphere, until recently, has varied from about 3 or 4 months to 5 years (Jaffe 1968).

An attempt to explain the short life of CO in the troposphere was recently reported (Dimitriades and Whisman 1971). Using C¹⁴-labeled CO, these workers demonstrated an oxidation rate of CO to CO₂ in the troposphere of about 0.05 percent per hour, day or night. This calculates to a lifetime of 0.3 year. The rate seemed to be independent of CO concentrations.

It has been suggested by several that the soil may be a major sink. Considerable work has been done showing consumption of CO by various species of bacteria and lower fungi,

Perhaps the expected answer to the puzzling questions involved is heralded by a recent report by Dr. Inman and colleagues of Stanford Research Institute (Inman, Ingersoll, and Levy 1971). Various nonsterile soils were exposed to

test atmospheres containing 80 to 130 p. p. m. of CO, under a variety of conditions: "During preliminary experiments, nonsterile potting soil was observed to reduce the total amount of CO in a plastic atmosphere chamber from 1,443 to 47 micrograms within 3 hours. Sterilizing the soil (121° C, for 20 minutes) completely eliminated the activity." The original paper should be consulted for results of this ground - breaking experimentation and the important questions raised. In general, uncultivated soils high in organic matter were most active, but there are as yet unexplained contradictions. After making certain assumptions, Inman has calculated that the total soil surface of the United States is capable of taking up 569 million metric tons per year, nearly three times the estimated world production due to man's activities.

It is clear that much is opened up by this work that can only be explained by more work. Dr. Inman informed me that expanded fieldwork was in progress during the summer of 1971 (personal communication).

An observation may be permitted that we now have an additional strong reason for avoiding practices that destroy the microflora of the soil. The role of forest soils in reducing CO concentrations in the troposphere may be of high importance in the general processes of cleansing the air.

In summary, the amount of CO estimated as produced in the combustion of forest fuels, in locations mostly quite remote from the cities, cannot be considered significant in the buildup of local, high concentrations.

In any case, the impression in the public mind, that the highly toxic carbon monoxide accumulates in the atmosphere, should be allayed. It is only dangerous under conditions of stagnant air being continuously fed products of incomplete combustion of organic fuels.

Particulates

Water vapor alone is not visible, but there is a huge cloud of "smoke" in early stages of a fire. SO, the visible water vapor evolved has been adsorbed on fine particulate matter to form a large part of the visible cloud. Whence comes the particulate matter and how much is produced in the fire?

At this point we get into considerable trouble, trying to arrive at something resembling accurate determination of yield of "particulate" from burning wood. Part of the difficulty arises from matters of definition. In "Air Quality Criteria for Particulate Matter," NAPCA Publication AP-49 (U. S. Department of Health, Education, and Welfare 1969a), p. 1- 5, is given the following:

The term "particle" is used to mean any dispersed matter, solid or liquid in which the aggregates are larger than a single small molecule (about 0.0002 micron in diameter) but smaller than 500 microns. Particles in this size range have a lifetime in the suspended state varying from a few seconds to several months,

Further, on page 1-11: "Since particulate matter may consist of such a wide variety of substances, a discussion of chemical properties cannot be "specific."

Obviously, this definition covers an enormous range of sizes and properties, up to windblown sand and inorganic dusts such as windblown soil and even some species of insects. In actual practice, standards exclude such materials.

Byram and Jemison (1948) compiled a table of sizes for atmospheric "suspensoids" that is of interest:

<u>Suspensoid</u>	<u>Diameter in microns</u>
Smokes	0.002 to 0.3
Dust causing lung damage	0.5 to 1.0
Bacteria	1.0 to 15
Plant spores	10 to 30
Pollens	20 to 70
Fog or cloud	5 to 50
Mist	50 to 100

The methods for determination of "particulate" in air are quite adequately described in Chapter 1 of "Air Quality Criteria for Particulate Matter" (U. S. Department of Health, Education, and Welfare 1969a) and leave no doubt as to why such wide variations occur in results reported for comparable situations. Unless methods of measurement can be better standardized, not much reliance can be placed upon references dealing with amounts of particulate emitted from specific sources.

The whole matter of methods of measurement and their significance was well treated by W. L. Faith in 1968. Perhaps it is for reasons pointed out by Dr. Faith that in both AP-49 on criteria and AP-51 on control techniques, one seeks in vain for data that deal with wood.

The closest reference to prescribed burning comes out in "Compilation of Air Pollutant Emission Factors" (Duprey 1968). In table 9, page 11, appears:

Emission Factors for Open Burning

<u>Pollutant</u>	<u>Landscape and agricultural refuse (b)</u> (Pounds per ton of refuse)
Particulate	17
Aldehydes (HC HO)	0.01
Carbon monoxide	60.1
Hydrocarbons (methane)	12
Nitrogen oxides	2
Organic acids (acetic)	13

(Note: b factor can be used for leaves, grass, barley, rice, cotton, fine tree prunings, and brush.)

References upon which the table is based are Gerstle and Kemnitz (1967) and Darley et al. (1966).

Only Gerstle and Kemnitz report any figures on particulate yield. Both groups were dealing with small, controlled fires, under about as good laboratory conditions for measurement as could be devised. But, necessarily, samples were taken only a few feet above the flames. Therefore, the data cannot represent changes that took place in the smoke plume after the samples were drawn.

Note the supposed broad applicability of the selected emission factors to the assortment of fuels which obviously must include all conditions of moisture content, mixture, and packing. The reports given as reference offer a very thin basis for acceptance of these "factors" as having much application to emissions from prescribed burning as practiced.

More significant data about broadcast slash fires and piled slash fires were obtained by Bovee et al, (1969). Particulate figures are reported in micrograms per cubic meter, and no yield per ton can be so derived nor can such data be related to emission factors. However, this report gives excellent support to the value of the high-energy fire, and makes valuable contributions to the general factors that must be considered to obtain best slash or fuel clearance with least harm to the environment. "Concentration of gases and hydrocarbons diluted rapidly to ambient or background values. Particulate emissions in the smoke plume were high but decreased in 20 km to values found over the Seattle area."

It may be expected that work in progress on actual conditions within burning slash and in the ambient air will produce valuable results. But, as of this time, data on actual emissions from burning wood, forest fires, slash, or prescribed burning are lacking. Statements with respect to so many millions of tons of this or that as a result of fires of various kinds have little validity.

Coming back to particulates, or more specifically aerosols, we must consider several matters. From the results reported by Went (1960a and 1960b) and also by Vincent Schaefer (1970), it appears that unsaturated hydrocarbons emitted from a forest fire or prescribed burning very probably combine with each other, formaldehyde, furfural, and oxygen within a short time to form particulate material, probably as liquid aerosols. These would be of a size less than 0.5 micron and unlikely to be measured by the usual methods. These aerosols appear to aggregate promptly to larger particles, contributing to the bluish smoke from a fire after most of the water has been evolved. Thus, more study of plumes by airplane sampling may produce data which, correlated with data near the fire, will show the actual fate of hydrocarbons transformed into particulate matter.

There is much evidence that such material is the basis for a large proportion of the condensation nuclei in the air at all times.

In burning coniferous material, whether in wildfire or prescribed burning, there is bound to be considerable emission of terpenoids in the early stages of the fire arising from the needles and the small wood. Needles may contain up to 2 or 3 percent volatile oils. Heartwood of Douglas-fir and yellow pines will

contain more, but not much heartwood is burned except in good, hot-burning pile of slash.

The visible plume of smoke contains a lot of water and these originally very small aerosols of organic material plus some unburned carbon in finely divided form. When the fuel is damp, the column immediately above the fire may be dense and white because the evaporated water plus the water from combustion soon produce a supersaturated condition in the rising column, depending on temperature. The water condenses on the particulate, forming what amounts to a cloud of water droplets. As the smoke column rises, it continues to cool but also draws in and mixes with considerable outside air. If the air is dry, the droplets evaporate leaving only the particulate visible. A high - rising column may cool enough in its upper portions for water condensation to occur forming a spectacular white cap which usually also dissipates as the cloud top mixes with the surrounding drier air, again leaving the less dense particulate cloud. If the smoke column is within existing clouds, the droplets will not evaporate and, in a precipitating cloud system, will grow along with the cloud drops and tend to fall out.

On a dry day this cloud disperses rapidly; with high relative humidity, it persists longer.

Particulate and liquid or semiliquid aerosols result from oxidation and intermolecular polymerization reactions of burned and unburned hydrocarbons, plus reactions with formaldehyde and furfural. These latter will also react in the vapor phase with polyphenolic substances from pyrolysis of lignin to form resinous materials.

But, with all this probably going on, the total accumulation of particulate or aerosols from burning wood is very small in comparison with that emanating normally from the forest and the forest floor.

I suspect that, in the long run, the total yield of particulate from fires in forest fuels is higher than the emission factor estimated by NAPCA. But, obviously, such material does not remain suspended indefinitely; the smaller particles agglomerate, forming large particles which fall out in a relatively short time. In a moist airmass, they serve as condensation nuclei, forming droplets of moisture that fall out. More are removed by snow or rain. Obviously, such material has a limited time suspended in the air. The first rain will wash most of it to the ground.

I most conclude, therefore, that the principal valid objection to the results of prescribed burning rests on temporary interference with visibility (largely from fog produced in the early stages of the fire, and from smoke particulate in dry air, particulate that tends to take on the optical properties of fog at higher humidities).

The various methods for measuring amounts of particulate probably do not account for a large proportion of suspended material below 0.1 to 0.5 micron

in size. Such very fine particles are probably present in wood smoke in very large numbers, agglomerating and growing as has been suggested above. It may be possible to measure the number of particles in the smoke column, both near the fire and further above it or downwind, in order to find out something about the true situation. At present, most estimates of amount and number leave much to be desired.

These extremely fine particulates probably enter the alveolar tissues in the lungs. Coarse particulate is well taken care of by the mucociliary system in the respiratory tract. The medical profession is well aware of this fact, but there is a question not very well answered: Since the alveoli cannot expel the extremely fine particulate, what is its fate and why have we not all succumbed to the obvious continual breathing of the fine organic particulate constantly emitted by the plant world, as well as from fire and automobiles?

Several conferences with medical men bring out the general opinion that such materials are probably rendered soluble by enzymic action, enter the walls of the alveolar tissues in soluble, small molecules, enter the blood stream, and are eliminated.

Sulfur Dioxide (SO₂)

We can dismiss sulfur and its compounds rather quickly because sulfur is almost entirely absent from forest fuels. Earlier emission factors, compiled by poorly informed workers, included SO₂ as coming from burning wood, but this practice has been discontinued.

Certainly, if a heavy load of suspended particulate matter from a forest fire blanketed a site having a heavy concentration of SO₂ during a long-continued temperature inversion and high relative humidity, there would be trouble. The chances for such an occurrence are extremely remote, but there is no argument about achieving low concentrations of SO₂ in urban air.

Hydrocarbons

In chemical terms, hydrocarbons are compounds composed only of carbon and hydrogen. In the language of the workers in air pollution, the term includes oxygenated derivatives. There are thousands of such compounds, and by use of modern techniques, new ones can be synthesized almost at will.

Hydrocarbons are extremely widespread in the plant world in volatile oils, waxes, and resins. Their close relatives, hydrocarbons partially oxidized or synthesized by the plant in partially oxidized form, are familiar to us in thousands of plant odors, perfumes, and a host of pharmaceutical preparations. One need mention only a few: turpentine, pine oil, peppermint oil, oil of bay, citronella oil, oils of lemon and orange, oil of rose, violet, geranium, and so through a host of hydrocarbons and relatives that are quite familiar to us all.

So, it comes as a surprise to a chemist that "hydrocarbons" are reported in various tables of publications on emissions factors and inventories as all lumped together and carrying the implied label of being generally harmful.

This implication arises probably from the following facts. Unsaturated hydrocarbons are produced by incomplete combustion of organic fuels, especially petroleum fuels and coal. By unsaturated, we mean the absence of hydrogen atoms in the molecule from adjacent carbon atoms, so situated that the hydrocarbon has high affinity for oxygen or other elements in order to saturate itself. If such substances, usually small molecules, are formed in the presence of much sunlight and materials capable of giving off oxygen easily, we get "photochemical oxidation" and much trouble in cities.

An excellent report by the American Chemical Society (1969, see especially p. 35-39) explains the complex chemistry involved in the Los Angeles-type photochemical smog. It was apparently the discovery of the basic reason for this irritating type of pollution and its relation to certain unsaturated hydrocarbons of low molecular weight that brought about the general erroneous accusation of "pollutant" against all hydrocarbons.

Full analysis of the atmospheric gases produced in combustion of any fuel is a **troublesome**, expensive, and time-consuming task, requiring equipment and techniques. Due to the need for rapid and continuous methods of analysis to apply to monitoring urban atmospheres heavily polluted by automobile exhaust, a method was developed that gave a less exacting figure for "total hydrocarbons."

sophistica

The method is called "the flame ionization technique." A sensitive instrument detects the increase in ion intensity that results when a sample of air containing any organic compound is introduced into a hydrogen flame. It responds to carbon atoms in proportion to the number in the sample, except that those bound to oxygen, nitrogen, or the halogens do not respond. Thus, it measures as hydrocarbons the very numerous species of compounds containing oxygen also; i. e., alcohols, acids, aldehydes, ketones, ethers, and esters. Thus, those carbon atoms in such oxygenated compounds, that are attached only to other carbon atoms and hydrogen, will appear as hydrocarbons in such analyses. It is clear, therefore, that the data obtained are misleading. In urban atmospheres, heavily laden with automobile exhaust, the method is a valuable tool. But, in many other instances, it fails to distinguish between those specific compounds involved in photochemical smog of the Los Angeles type and the hundreds of compounds, including natural emanations from plants, that are quite harmless. Sophisticated and costly methods are available for making such distinctions, but they are not very practical for continuous monitoring.

A further error arises when, e. g., tons of hydrocarbons, aldehydes, organic acids, "other organics" are reported as classes in "emission inventories," then added together for a huge sum of "total pollutants." It is quite evident that the tonnage of "hydrocarbons" includes most of the carbon content of the other classes, and adding all classes together is duplication and gives a false result.

The simplest and most abundant hydrocarbon in the air is methane, often called "marsh gas," the principal component of natural gas. It has been estimated that the amount of methane in the atmosphere at one time is 310 million tons, but Robinson and Robbins (1968, p. 101) think this far too low and estimate 1,600 million tons with residence time of 4 years and a constant background of about 1.5 p. p. m. Quite obviously, there is also a still undiscovered "sink" for methane, which most scientists believe to be in the biosphere.

Fortunately, in hydrocarbon determinations, technicians have learned to account for the methane content by appropriate reductions. However, it should be pointed out that, in many instances, it is quite probable that the methane content is much higher than the background figure.

Actual data on emissions of hydrocarbons from combustion of forest fuels are scarce. There are plenty of yields of "total hydrocarbons" per ton from backyard burning, single-chamber incinerators, etc., where little regard is given to what is burned.

Darley et al. (1966) calculated their yield of total hydrocarbons as C and reported:

<u>Fuel</u>	<u>Pounds per ton</u>	
Native brush		
dry	4.7 ± 2.5	} San Joaquin Valley
dry and green	15.2 ± 4.3	
green	27.4 ± 8.8	
Fruit prunings (M. C.		
11 $\pm$ 4 percent)	4.2 ± 1.3	} Bay Area
Native brush (M. C.		
5 $\pm$ 1 percent)	4.7 ± 2.1	
Fir chips	2.8	
Redwood chips	2.2	
Fruit prunings (M. C.		
35 $\pm$ 15 percent)	9.7 ± 4.2	
Native brush (M. C.		
13 $\pm$ 7 percent)	4.4 ± 2.3	

One can derive from these figures:

1. The yield is low compared with that reported for the gasoline engine (130 pounds per ton).
2. The fruit prunings with higher moisture content gave about double the yield for that with low MC.

In table III, page 688, of the same publication, an attempt is made to assess the yield of ethylene, olefines, and "saturates plus acetylenes" in pounds per ton.

In the woody materials concerned, the ethylene yield is about two-thirds that of olefines. The ratio of olefines to saturates varies from 2 to 5. "Thus, among the hydrocarbons measured, the photochemically active olefines predominated." This is a statement that can be interpreted in various ways.

Aside from that, the authors submit a summary statement as follows: "Thus, the annual yield (of hydrocarbons) from agriculture (burning) approximates the daily yield from automobiles in this area." (San Francisco Bay area.)

The report on modeled slash fires by Fritschen et al, (1970) gives quite a lot of data on chromatographic analysis of samples taken in or around going fires, but interpretation is difficult in terms of what is actually produced with respect to reactive versus nonreactive substances. On page 33, a table of combustion products is presented for Douglas-fir, western hemlock, and western redcedar slash burned in the laboratory. Yields of hydrocarbons (as C) are given, varying from 1.2 to 2.2 grams per kilogram of fuel; moisture contents, 7.2 to 8.4 percent.

This amounts to from about 2.4 to 4.4 pounds per ton, which is consistent with the yield reported by Darley et al. (1966) for fir and redwood chips. It is of interest that carbon balance here varied from 79 to 110 percent, a matter that is not explained.

The composition of the hydrocarbons collected in bag samples in various positions related to active fires indicated very small quantities of a number of potentially photochemically reactive hydrocarbons. But, doubt is thrown on these results by the authors because of probable contamination of samples by materials from sources other than the fires.

Table 14, page 36 (Fritschen et al. 1970), gives gas chromatographic analyses of smoke from laboratory fires. Procedures followed those given in Darley et al. (1966), but no attempt was made to estimate yields per unit of fuel. The unsaturated hydrocarbons known to be photochemically reactive were present but, with the exception of ethylene, in very small amounts.

It may be expected, again, that the hotter fires yield fewer total hydrocarbons than the cooler ones. Undoubtedly, the unburned hydrocarbon content of the plume contains methane, ethylene, and traces of other unsaturated hydrocarbons. But good quantitative data are lacking.

Also lacking are data on the action of oxygen and light on these olefinic components during the periods of time between sampling and analysis.

Hydrocarbons in the Atmosphere Emitted by Vegetation

Only part of the hydrocarbons in the atmosphere are products of combustion. I have already referred to the general occurrence of hydrocarbons and their near relatives in the plant world.

Analyses of the "ambient atmosphere" at Point Barrow, Alaska, have shown the presence, among other compounds, of ethane, ethylene, butane, acetaldehyde, acetone, methyl and ethyl alcohol, and methane. Of this array, only ethylene is regarded as having significant photochemical activity. Evolution of ethylene in the ripening of fruit has been known for many years. In fact, its use in giving ripe color to oranges and lemons was introduced about 45 years ago by Dr. Frank Denny.

Dr. R. A. Rasmussen, now at Washington State University, has informed me that he has also confirmed emission of ethylene in the ripening of leaves, especially at the time of abscission. He has made no estimate of the amounts thus contributed to the atmosphere.

Rasmussen also reported in 1970 the emission of isoprene from a large number of plant species, under natural conditions, and from the intact, living foliage. This discovery is particularly exciting because isoprene itself has been regarded as not being produced in plants, although its skeleton occurs in all the terpenes and polyterpenes; e. g., rubber. Since α -pinene is the most abundant terpene (principal constituent of turpentine), it is striking to find Rasmussen's report showing isoprene being emitted from foliage in almost as much amount as α -pinene.

Isoprene is 2-methyl-1,3-butadiene and thus closely related to the photochemically active 1,3-butadiene, a known component of automobile exhaust. Rasmussen points out that the biological fate of foliage emissions is poorly understood but observes that organic volatiles emanating from tropical foliages can be utilized by wild populations of fungi as the sole carbon source for growth. It will be seen that the tonnages of these materials are enormous. Some such sinks must exist in the biosphere.

Rasmussen was a student of Dr. F. W. Went, who, in 1960, had announced the occurrence in the atmosphere of very large quantities, in toto, of organic materials as natural products of the plant world (Went 1960b).

Went has since published extensively on the relationship of these materials--largely hydrocarbons, terpenes, especially, and their derivatives--to atmospheric phenomena, such as Aiken nuclei and submicroscopic aerosol particulates. Of particular interest was his article in Nature in 1960 (Went 1960a). After discussion his work showing the great emanation of volatiles from forest vegetation (100 million tons per year); Went proceeded to demonstrate convincingly the relation of the terpenes, sunlight, and oxygen to the omnipresent blue haze always observable over forests, especially in still, hot weather. He also discussed the formation of particulate matter by intermolecular union of oxidized molecules and theorized about the ultimate fate of such very small particles.

In 1965, Rasmussen and Went published experimental evidence of unequivocal nature on the general subject. In this important paper, they estimated the world production of plant volatiles released into the atmosphere to be 438 million

tons per year, giving an average concentration of about 1 p. p. m., higher in summer, lower in winter. Compounds identified were mostly terpenes and, surprisingly, large emissions were measured from dead hardwood leaves. Rasmussen demonstrated the origin of terpenoids from decomposition of the carotenoid family of compounds. Much of the fine basic work involved is covered in Rasmussen's Ph. D thesis (1964).

Combustion of Forest Fuels. Related to "Hydrocarbons"

In accordance with the practice of the various Air Pollution Control Authorities, perhaps it will be well to use the term "hydrocarbon" as including the wide assortment of compounds being measured and reported thus. (This will include volatile acids, aldehydes, ketones, ethers, esters, and mixed molecules with mixed properties.)

Also, we shall have to speak of those special classes of hydrocarbons especially abundant in the plant world, the terpenes (C_{10}), sesquiterpenes (C_{15}), diterpenes (C_{20}), and polyterpenes of higher molecular weight, and include them and their oxygenated derivatives in the loose term "terpenoids." Perhaps someday, intensive application of known analytical methods to the wide variety of forest fuels will give us accurate measures of the actual fate of these substances when involved in fires.

It is clear that, in the initial phases -- the driving out of free water, bound water, and perhaps some water produced by thermal decomposition -- materials volatile in steam will be evolved. The proportions of those normally present in the fuel that are evolved will vary according to the moisture content. The substances evolved will include a wide assortment of terpenoids. They will, according to the work of Rasmussen and Went (1965), be rapidly oxidized and polymerized to quite small particulate matter behaving as aerosol which scatters light. The aerosol particles in this phase will probably be carried in water droplets.

There is no way of predicting the amounts involved unless we know the amounts present, their nature, physical properties, and the amount of steam distillation to which they are subjected. But we do know a few things.

For example, coniferous foliage of many species contains appreciable quantities of terpenoids, up to 2 or 3 percent. Some species are much lower. Bark, especially the phloem tissue which forms a larger proportion of the twigs and small branches than of the big limbs and trunk, usually has appreciable amounts of similar materials. Similarly, pith, also constituting a high proportion of the smaller woody parts, contains these materials,

In the flaming stage, accompanied by higher temperatures in the now dry, or nearly dry, fuel, all such compounds will be volatilized since they boil below 250° C. Higher polymers, such as polyterpenes, resins, and resin acids, will

probably decompose and be evolved as hydrocarbon fragments of unknown properties. All of them, if enough oxygen is present, will burn to CO_2 and water; but since this will not be true in most situations, they will be only partly oxidized. The resulting substances, undoubtedly including unburned carbon, may enter the atmosphere as vapors, aerosols, or particulates of larger size. Until accurate measurements are made upon fuels of known composition under well-controlled conditions of combustion, products from flaming foliage can be only speculative.

It seems fairly certain that the materials of the nature discussed cannot exist in the smoke column above the fire in the vapor phase for very long. α -pinene, the most abundant terpene, boils at 156°C . and most of the others will be higher. It seems that we need more knowledge of actual conditions within the smoke plume. This cannot be obtained from wild forest fires and will be difficult even with small model fires. It seems to me that more thought should be given to laboratory studies of relatively small scale in which conditions can be measured and controlled with reasonable accuracy and reproducibility.

It should be noted that various aldehydes, notably furfural and formaldehyde and oxymethyl-furfural, will be evolved along with a wide variety of phenolic decomposition products of the flavonoids, lignin, various tannins, etc. In such a milieu, undoubtedly intermolecular condensations take place, rates depending on temperatures and concentrations. Resultant materials will probably appear and be estimated as the larger particulates; larger, that is, than the aerosols produced in the earlier, cooler stages of the fire. Aldehydes stay uncombined for only a very short time.

All things considered, it seems to me that the probable total evolution of hydrocarbons from burning forest fuels is probably higher than values reported. But the relative importance of this matter, as far as photochemical smog is concerned, seems to be very small.

(Treatment of "polynuclear hydrocarbons" thought to be related to incidence of some types of cancer in humans is not given, as might be expected, in NAPCA Publication AP-64 on hydrocarbons (U.S. Department of Health, Education, and Welfare 1970b), but is given in AP-49 (U.S. Department of Health, Education, and Welfare 1969a).

Polynuclear Hydrocarbons (Carcinogenic Substances) (PNH)

These compounds consist of polymers of benzene, joined in various patterns, of high molecular weight and high boiling points. Several such substances have been shown to produce cancer in susceptible strains of experimental animals and naturally are gravely suspected of causing human cancer.

Early observations connected the tar in London chimneys with prevalence of scrotal cancers in the chimney sweepers. Later work showed the presence of these compounds in coal tar. For example, phenanthrene has long been a product of coal tar manufacture for which little use has been found.

The most discussed of these materials has been 3-4 benz-pyrene (often written benz-a-pyrene) because it is the most active one observed in causing incidence of cancer. Its presence is usually considered as indicative of the presence of other high polymers of benzene. In the midfifties, the presence of the polynuclear hydrocarbons was demonstrated in coal and uncracked petroleum.

Up to now, their presence in coal tar, coal smoke, and products of combustion of petroleum fractions had been attributed to incomplete combustion; and by extension, formation of PNH came to be accepted as the characteristic result of incomplete combustion of organic materials in general. There seems little question that they are formed in reactions of free radicals in the general processes of burning solid, liquid, and gaseous fuels. (A good review of this point of view is given by Tebbins, Thomas, and Mukai (1956).

As mentioned, it had been found that PNH were present in crude petroleum and coal. This suggested to German chemists the possibility that they were normal components of the plant and animal world, since geological theory has it that coal and oil are of organic origin, the fossil remains of plant and animal life. An excellent review of the resulting work is given by Graf and Diehl (1966). The authors present unequivocal evidence of the presence of polynuclear carcinogenic hydrocarbons widely spread throughout the plant world. 3-4 benz-pyrene was found to be omnipresent. Leaves of a wide variety of tree species as well as numerous vegetables serving human nutrition contain a normal amount of these substances in the order of 1 to 2 micrograms per 100 grams of dry substance, calculated as 3-4 benz-pyrene. The content of the PNH compounds increases threefold to fivefold in the dying process; that is, when the chlorophyll-containing parts of the plant become yellow. Seeds, fruits, and bulbs containing relatively high amounts of reserve carbohydrates contain only 1 to 10 percent of the quantities found in green plants.

The authors showed that in germination of maize, wheat, and lentil seeds, all containing PNH, further quantities were synthesized during germination and growth of the plant. The evidence is that the process takes place independently of photosynthesis, even in the absence of light. Thus, PNH are apparently produced in the process of respiration. The authors conclude that "a natural amount of these substances ... has always existed in our environment."

In the same volume, Graf and Nowak (1966) present evidence that PNH are natural growth stimulants. The following tree materials were analyzed with positive results: leaves of beech, oak, pear, linden, maple, poplar, and needles of fir and pine.

Quantitative results were reported for green and yellowed leaves of beech, oak, and tobacco for six PNH. In general, the content of PNH increased from the green to yellow stage about twofold to sixfold. (It is of interest to note that the amount of 3-4 benz-pyrene was about the same in tobacco and oak leaves.)

More recently, further important evidence of normal biosynthesis of PNH in green plants has appeared. Borneff and coworkers published results of work on algae (1968). A summary is quoted:

Algae (*Chlorella vulgaris*) grown in C^{14} -acetate medium synthesized benz-pyrene and other polycyclic aromatic hydrocarbons with 10 times higher specific activity than algae from a control batch without the isotope. This observation confirms earlier results and seems to show unequivocally the biochemical synthesis of carcinogens in plants. The results of the experiments offer an explanation for the occurrence of benz-pyrene in vegetables, vegetable fats and oils, in the soil and ground water.

Also, an important contribution was made in 1970 by workers at Texas A.&M. University (Hancock, Applegate, and Dodd 1970). Careful experimentation was carried out on vegetation remote from a railroad right-of-way running diesel engines.

The workers analyzed leaves of little bluestem and post oak in the remote control area and by the railroad. Five PNH were identified and determined: anthracene, fluoranthene, pyrene, benz(a) anthracene and benz (a) pyrene. Contents ranged from 5 to 110 micrograms per kilogram of dry material. In most instances, samples from the control area had higher concentrations than samples by the railroad. Individual and total concentrations were highest on dormant plants and lowest during periods of active plant growth.

A comparison of pyrene to benz(a) pyrene ratios suggested that most of the PNH found on the leaves were products of plant biochemical synthesis and not products of locomotive exhaust.

I have not been able to find evidence of the actual occurrence of PNH in wood; but in view of the report just discussed, a strong presumption is established that they are present in wood, bark, needles, and leaves.

There are available three comparatively recent reports on products of pyrolysis of hardwoods: Jahnsen (1961), Porter (1963), and Lustre and Issenberg (1969). Jahnsen gives no evidence of the presence of PNH in the smoke from burning hickory sawdust at temperatures below 400° C. Two references given by the author are of interest:

1. Anonymous: Great Britain, Department of Scientific and Industrial Research. Report of the Food Investigation Board. For the year 1949, this report denied the presence of fused ring compounds (PNH) in smoke. (Reference not verified.)
2. D. J. Tilgner (1958); Production and utilization of smoke for the purpose of smoking food products. (Reported the presence of three carcinogens on the walls of a smokehouse in use for 6 months.)

Porter reported on the probable presence of 3-4 benz-pyrene contaminated with anthracene. Evidence was presented of the probable presence of other species of PNH, none of which could be isolated but, by chromatographic analysis, appeared to be present.

It may be concluded that PNH compounds are probably present in wood smoke from burning forest fuels. Whether they are products of combustion or residuals from incomplete combustion is not clear. It seems probable that the latter is more likely the case in view of the generally low temperatures prevailing during periods of high production of smoke in fires burning forest fuels. (These compounds boil at high temperatures and are low in chemical reactivity, but there is clear evidence of their destruction by soil microflora (Poglazova et al, 1968 -- from Air Pollut. Abstr. Aptic 29160, July 1971.)

It is of interest to note the greater incidence of lung cancer in urban areas than in rural areas (Kotin and Falk 1959).

Of interest is the following table from page 10- 21 of NAPCA Publication AP-49 (U. S. Department of Health, Education, and Welfare 1969a):

Benzo(A) Pyrene Concentrations in Several
Urban and Nonurban Areas

State	Micrograms BaP/1000 m ³ air	
	Urban	Nonurban
Alabama	24	0.076
Indiana	39	1.8
Maryland	14	0.70
Missouri	54	0.025
North Carolina	39	0.25
Oregon	8	0.01
Pennsylvania	61	1.9
South Carolina	24	1.1

Table 10-3, page 10-22 in the same publication, shows the fraction of the total aromatic hydrocarbon content in some urban atmospheres represented by benz-pyrene. Low fractional contents are reported in Los Angeles and San Francisco, communities burning very little coal. High figures are reported for others listed with Nashville having near 10 times the content reported for Los Angeles.

Firm conclusions cannot be drawn but it appears from the reported data that:

1. Urban communities have much more PNH in the atmosphere than rural areas, with the highest figures reported from coal-burning cities.
2. PNH result from combustion of fossil fuels, either as residual particulates or as products of vapor phase reaction of free radicals.
3. PNH are probably released in relatively small amounts in the pyrolysis and combustion of forest fuels.
4. PNH occur widely spread in the plant world, including many items of human diet.
5. We are, have been, and always will be exposed to PNH.

It is difficult indeed to envision any significant increase in urban exposure to PNH attributable to burning forest fuels.

Nitric Oxide, PAN (Peroxyacetylnitrates) and Photochemical Smog

The famous "smog" of Los Angeles is a highly specialized phenomenon, with little resemblance to the "smogs" of general popular parlance that deal with decreased visibility for the most part. The ingredients in Los Angeles smog are: sunlight (lots of it), nitric oxide (NO), and hydrocarbons of low molecular weight that are components of automobile exhaust. The hydrocarbons of interest in photochemical smog, Los Angeles type, are unsaturated; viz., they have a high capacity to combine with oxygen or ozone, and produce the PAN, eye irritating and injurious to health and vegetation.

The source of the nitrogen dioxide (NO₂) involved is nitric oxide (NO) from automobile exhaust. It has been estimated that, as much as 90 percent of the photochemical smog in Los Angeles arises from automobile exhaust. A footnote in a report by the American Chemical Society (1969, p. 36), referring to photochemical smog, states, "Ironically, if either smoke or fog is present in quantity, this variety of smog cannot occur."

It should be noted that smoke from forest fuels can rarely, if ever, be implicated in the Los Angeles photochemical smog. The larger chaparral fires in southern California occur mostly during periods of high wind; just the reverse of the conditions of dead calm and inversions that generate the smog.

It was stated earlier that, in combustion of wood and similar materials under ideal conditions, a maximum temperature of about 1,420° C. has been attained for very short periods. Under conditions of prescribed burning, the attainment of such temperatures is improbable. Formation of NO falls to near zero at about 1,540° C., according to a graph on page 4-3 of "Control Techniques for Nitrogen Oxide Emissions from Stationary Sources" (U. S. Department of Health, Education, and Welfare 1970g). This temperature is still substantially above the probable maximum in burning wood.

I have found no reported measurement of NO production in forest fires. From results of research in model fires, I find 2-3 pounds per ton of wood reported, doubtful.

However, forest fires are credited with 1,200, 000 tons of NO per year (U. S. Department of Health, Education, and Welfare 1970h). This repeats the statement by the Secretary of Health, Education, and Welfare in Senate Document #91-63 (1970, p. 81).

In the publication on control techniques for NO (U. S. Department of Health, Education, and Welfare 1970g), table 6-3 credits wild forest fires with 800, 000 tons per year of NO, produced in burning 200 million tons of wood. Leaving out the Secretary's figure, the 800, 000 tons result requires production of 8 pounds of NO per ton of wood burned. Thus, the postulated rate of production is about four times the highest probable rate from a pile of wood of quite uncertain size.

Robinson and Robbins (1968) give an excellent review in their Chapter V, "Atmospheric Nitrogen Compounds." The final paragraph in Chapter V, page 92 is: "This cycle does show even in this simplified form that the pollutant emissions of NO and NO₂ are relatively unimportant factors in the total circulation of nitrogen in the atmosphere." They are speaking of total worldwide production of NO₂ of 550 million tons a year, of which 500 million tons are of biological origin. The residence time in the atmosphere is calculated at 3.5 days, so there is an appreciable background value.

It seems inconceivable to me that the slight amounts, if any, of NO from combustion of forest fuels, appearing soon as NO₂, can have any measurable effect on creation of photochemical smog or toxic effect on vegetation of humans,

This conclusion has nothing to do with the necessity for reducing emanations of NO from the combustion of gasoline in the automobile.

BURNING--NECESSITY AND METHODOLOGY

When known and practical procedures are followed in prescribed burning of forest fuels, troublesome pollution in large centers of population can be reduced to a minimum that will not be objectionable. Such procedures involve proper integration of burning schedules with weather reports and handling slash so as to produce as fast and hot combustion as is practicable. Experience in the last few years has demonstrated well the practicability of these procedures when good coordination is established between meteorologists and forestry agencies, public and private (Cramer and Graham 1971)^{4/}.

There is no argument against the fact that most wildfires feed and spread on high accumulations of fuel, either as slash in the West or inflammable under-story in the South. Prescribed burning in the South has done remarkably well

⁴W. R. Beaufait and O. P. Cramer. Principles of smoke dispersion from prescribed fires in northern Rocky Mountain forests. 1969. (In-Service distribution, Forest Service, Northern Region, Missoula, Mont.)

in reducing damage from wildfires. In the West, compulsory disposal of slash has saved many thousands of acres and many billion feet of timber from destruction by wildfires.

Someday, a long time off I fear, we may be able to use the material we now must burn. A part of the necessity that we dispose of forest "waste" is our wealth of forest materials. Technologically, we could undoubtedly now convert all of it to useful materials, but at costs that would exceed returns. Possibly future developments might make such enterprise profitable, but at present the public would have to assume costs in excess of returns. In the meantime, we must burn forest waste in order to lessen the risk of destructive and disastrous wildfires.

In both burning of slash and reduction of fuel by prescribed burning in standing timber, the objectives and procedures by which they are realized must be executed by men trained in forestry and especially in behavior of fire in forested country. The decisions involved require a high type of professional competence in both foresters and meteorologists.

By such cooperation, it has already been amply demonstrated that the smoke nuisance can be significantly reduced. There will still be interference with visibility for brief periods, but this is a small price to pay for the assured saving of immense forest wealth from destruction.

Furthermore, and of overwhelming importance, the blanketing of the Northwest by days of dense smoke from a Tillamook burn, the earlier Yacolt burn, and the more recent Oxbow fire and fires in eastern Washington must not occur again if at all preventable. In the long run, properly conducted prescribed burning of forest fuels can be one of our most powerful tools against some extreme "air pollution" episodes.

CONCLUSION

In the harvest of the forest crop, we still must leave in the woods vast amounts of material, flammable when it dries and a most dangerous contributor to the dreaded wildfire. So, for many years, the cleanup of flammable forest waste has been a required part of the protection phase of the forest management. If the material could be removed economically and processed into consumer goods, the problems arising from burning it would be eliminated. Although the technology currently exists for using timber harvest residues, the costs of collecting, transporting, and processing far exceed possible returns.

These things are true not only of the "prescribed burning" of the fuel left from the harvest, they are equally true of the fuels consumed in the prescribed burning practiced in the South and in other regions in management of second and third crops of pine.

The term "prescribed burning" means that material to be burned is burned under planned conditions that will achieve the objective with minimum damage to the forest and the general environment. It has been amply demonstrated that such desirable results can be achieved by close coordination of those responsible for slash burning with meteorologists. Also, it has been amply demonstrated that programs of prescribed burning have served well the broad objective of reducing damage from wildfires.

But smoke from prescribed burning is visible, and the public generally believes that anything visible in the atmosphere must be dangerous pollution. Hence, this report has tried to bring together our knowledge of the nature of the combustion products of forest fuels and their action in the atmospheric environment.

There are many gaps in our knowledge. In the first place, we do not know the true nature and amounts of the material burned. Clearly, part is wood, but we burn foliage, twigs, old and young bark, brush and grass in the understory. Data are plentiful on products of combustion of wood and so-called backyard trash, of unknown composition and uncontrolled conditions of burning.

Tables of emission factors and emission inventories are of little help with regard to forest fuels because they are made up of guesses at volumes, nature and conditions of burning of fuels and interpretations of results. We need a great deal of carefully controlled work in order to have definitive answers to the questions:

1. What do we burn?
2. Under what conditions should we burn?
3. What are the products under variable conditions with specific classes of fuels?

But, lacking much information, I have put together a great deal of available data and have submitted my conclusions.

Burning of forest fuels is a mixture of the products of distillation, thermal decomposition, and flaming and nonflaming combustion, usually going on all at the same time. Much of the organic matter entering the atmosphere is very similar to material normally entering the atmosphere as the products of vegetative life or decomposition of vegetable matter in normal processes of nature. Fire compresses these processes into shorter time.

The visible cloud of smoke from a slash fire is nearly all water; but since it is visible, we know it consists of water condensed on particulate matter, partly unburned carbon. In the later stages of a prescribed fire, the bluish color is due to unburned carbon and other particulate produced from gas phase reactions of products of dry distillation (pyrolysis), ordinary volatilization, and combustion. The behavior of the cloud and its appearance are functions of air temperature, relative humidity, the size and energy content of the combustion column, and a host of other factors that need study.

The sulfur content of wood is negligible so there is no problem with sulfur dioxide.

The temperatures attained in burning forest fuels are generally too low to permit formation of nitric oxide. Temperatures sufficiently high for formation of nitric oxide may be attained very briefly in explosions of concentrations of flammable gases, especially in wildfires. But, because of the probably negligible amounts of nitric oxide produced in prescribed burns, they cannot be considered as of any importance in production of "photochemical smog" of the Los Angeles type.

As for carbon monoxide, evidence of increased concentrations at short distances from going fires is lacking. The possibility of enhancing dangerous concentrations of carbon monoxide at street level in cities is so remote as to be disregarded. In addition, recently obtained evidence is submitted that the microflora of uncultivated soils provides the long-sought natural sink for carbon monoxide, ample in capacity for all conceivable needs.

Hydrocarbons, a term including the host of oxygenated derivatives that are produced, are in large part similar to or identical with products of nature, omnipresent in the environment. Only small traces of photochemically active compounds of low molecular weight are produced. Even here, isoprene and ethylene are produced in natural emanations from vegetation in amounts that have not yet been estimated, but must be very large in comparison with those produced in prescribed burns.

The "polynuclear aromatic hydrocarbons," supposedly carcinogenic and formerly thought to be produced entirely by incomplete combustion, are now shown to be normal products of photosynthesis, very widely spread in the plant world. Whether they are formed in combustion of forest fuels is unknown. That some may enter the atmosphere in any process of burning vegetable material is to be expected. We always have been exposed to them and always will be. Fortunately, the soil microflora have been found to destroy these materials.

Particulate matter, largely carbon particles, must also contain material of the nature of aerosols, formed by intermolecular condensation of terpenoids, phenols, and reactive aldehydes, partially adsorbed on carbon. In their chemical nature they are probably indistinguishable from many components of the atmosphere, produced in normal natural processes.

We need research aimed at the actual fate of these materials under the widely varying conditions of their liberation and reaction. Very little is known of their behavior in the processes of combustion.

I have found no evidence that involves the combustion products of forest fuels in permanent injury to human health. There are well-known temporary discomforts that arise from heavy exposure, but, as any fighter of forest fires knows, these do not last very long.

In general, the only penalty inflicted upon the environment by prescribed burning is a small and temporary decrease in visibility. This is a slight cost for the rewards obtained in abating wild fires.

With increased cooperation between foresters and meteorologists, even this small penalty will undoubtedly be greatly decreased.

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