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## ORGANIC MATTER IN THE ATMOSPHERE, AND ITS POSSIBLE RELATION TO PETROLEUM FORMATION

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The fate of most major plant products, such as carbohydrates, fats, and proteins, is well known. They are synthesized from CO<sub>2</sub>, H<sub>2</sub>O, and mineral compounds, and ultimately are broken down to CO<sub>2</sub> and H<sub>2</sub>O again along well-known biochemical pathways. Only the breakdown of cellulose and lignin to humus products is less well understood.

*Organic Volatile Matter in Atmosphere.*—The fate of one major group of plant products, the derivatives of isoprene (terpenes, including sesqui-, di- and triterpenes, carotenoids, rubber and phytol) is, however, almost completely unknown. In the plant no enzymes are known that are able to break down these hydrocarbons or near-hydrocarbons. Once produced, they remain in the plant until the death of the cell or evaporate into the air. Even after release from the cell, nothing is known about their fate.

In the case of rubber, it is known that with age a certain degree of depolymerization of the long hydrocarbon chains occurs, leading to a sticky resin-like material containing some volatile products. Neither rubber, nor terpenes, nor carotenoids are attacked by any known microorganisms. About carotenoids, we know that when crystalline  $\beta$ -carotene is left exposed to the air it gradually decomposes to a white powder. This is due to autoxidation.<sup>1</sup> Each mole of carotene gives off 0.64–0.85 mole CO<sub>2</sub>. In an earlier paper, Escher<sup>2</sup> showed that in carotene oxidation a catalytic agent is formed which causes it to deteriorate more rapidly once it has started. The O<sub>2</sub> taken up did not agree with the oxygen content of the oxidation product, indicating that part of the carotene had been volatilized during its oxidation. Actually a strong odor of ionone develops upon the autoxidation of carotene (the end-rings of the carotene molecule when split off would produce ionone).

There are indications that in nature this type of decomposition of carotenoids also occurs. An aerial epiphytic alga, *Trentepohlia*, is brilliantly brown-orange in color and is very rich in  $\beta$ -carotene (personal communication of Dr. L. Zechmeister). When these algae are kept dry in the laboratory, they decolorize and turn a grayish white, giving off a strongly aromatic odor. The *Trentepohlia* occurring in Central

Europe is actually called "Veilchen Alge"<sup>3</sup> due to its strong ionone odor, suggesting that there is a continuous carotene-decomposition in the older cells giving rise to volatile hydrocarbons, predominantly ionone.

The carotene, left in the leaves after they have dropped off plants in autumn, is also at least partly decomposed by depolymerization, as the very aromatic odor of the forests in late autumn suggests, when again ionone-like products are released. Therefore the *only known* mechanism by which rubber and carotenoids can disappear after death of the cell is depolymerization and volatilization, which conceivably could lead to complete disappearance of these compounds by evaporation into the air.

It should be mentioned that carotenoids, terpenes, and rubber can also be returned to the carbon-cycle by burning. This has become a major factor in their disappearance since the advent of man; yet, in the over-all balance of nature, burning can account for the breakdown of only a fraction of all plant materials.

With how much organic material are we concerned when considering these non-metabolized plant products? Plant tissues, on a dry-weight basis, contain on the average 0.1 per cent carotenoids. To this has to be added the phytol of chlorophyll, which adds another 0.05 per cent. Since the total dry weight of carbon compounds produced per year by all land plants is  $5 \times 10^{10}$  tons, carotenoids and phytol are formed on earth at the rate of  $7.5 \times 10^7$  tons per year.

Only a very small fraction of all terpenes and resins formed remain in the earth crust, in the form of amber, kauri, or other resins. The rest disappears, again presumably by the only known mechanism—volatilization into the air.

There are several ways in which an estimate can be made of the amount of volatile organic matter which may be emitted into the atmosphere. The most accurate estimates can be based on actual measured emissions. Haagen-Smit (personal communication) analyzed air which had passed over shrubs of *Artemisia tridentata* and found a release of organic carbon (absorbed as  $\text{CO}_2$  after combustion) which amounted to about 50 kg per day per  $\text{km}^2$  of vegetation. This figure is reasonable if we assume that similar vegetation would produce about 1000 kg dry matter per  $\text{km}^2$  per day. This would mean that about 5 per cent of all photosynthates formed would be released as hydrocarbons in the highly aromatic sage brush vegetation. By assuming that on the average these sage brushes would produce these terpenes at the measured rate for 100 days/year (which is about their period of active vegetation), then sage brush would produce 5 tons of volatile organic matter per  $\text{km}^2$  per year. This particular type of vegetation covers approximately  $2 \times 10^6$   $\text{km}^2$  in the Western United States, and would therefore account for  $10^6$  tons of volatile organic matter per year.

It is likely that coniferous forests produce at least as much volatile matter per  $\text{km}^2$ . With a total area of  $10^7$   $\text{km}^2$  on the whole earth surface, they would account for  $5 \times 10^7$  tons of terpenes released into the atmosphere per year. Adding to this an equal amount of volatile hydrocarbons for all the rest of the vegetation of the earth ( $3 \times 10^7$   $\text{km}^2$  hardwood forests,  $3 \times 10^7$   $\text{km}^2$  of cultivated land, and  $3 \times 10^7$   $\text{km}^2$  of steppes) we arrive at a conservative figure of  $10^8$  tons of volatile organic matter released into the atmosphere per year.

When we add now to these  $10^8$  tons of volatile hydrocarbon-like compounds synthesized by plants, the  $7.5 \times 10^7$  tons of volatile products presumably formed

from carotenoid decomposition, then we arrive at a total of  $1.75 \times 10^8$  tons of volatile organic materials released each year into the air. This does not take into account the materials, presumably volatile too, which come from decomposition of rubber and resins (world production approximately  $2 \times 10^6$  tons/year), and all other similar products not harvested in the natural vegetation (e.g., resins in northern coniferous forests).

There are several other volatile organic compounds, such as simple acids, alcohols, esters, amines, etc., which have not been considered since they have known biochemical pathways for their decomposition.

*Fate of Molecularly Dispersed Organic Matter in Atmosphere.*—We come now to the question—what happens to the  $1.75 \times 10^8$  tons of terpene-like hydrocarbons or slightly oxygenated hydrocarbons once they are in the atmosphere? They persist for some time after their release, as the pungent smell of steppes and semi-deserts, the sweet odor of meadows, or the aromatic smell of pine forests, indicate. Yet, they do not accumulate in the atmosphere, since we do not smell or analyze them in air samples taken some distance away from the vegetation. Besides, in case they persisted, such quantities of combustible material would, in the course of a million years, accumulate to an explosive mixture. Therefore, mechanisms must exist by which this volatile material is removed from the air, similar to the disappearance of smog. The following possibilities of removal of these organic materials from the air exist:

(1) Decomposition to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This is possible only at high temperatures (burning); otherwise these compounds are completely stable, as storage of terpenes in bottles indicates.

(2) Such decomposition is theoretically possible at lower temperatures with the aid of catalysts. However, no plant enzymes are known which break down terpenes, carotenoids, skatol or mercaptans, and none could be expected in the air.

(3) Only few inorganic catalysts are present in the air. Of these the nitrogen oxides are probably the most important, but they are unable to cause complete oxidation either.

(4) Adsorption of these compounds on surfaces might be considered, but the only available surfaces would be leaves and branches, from which they were released in the first place. Besides, such surfaces do not acquire an aromatic odor.

(5) Condensation and precipitation of these terpenes is a possibility to remove them from the atmosphere. It is believed that in conjunction with mechanism 6 this is the only feasible pathway.

(6) Short wavelength radiation can impart enough energy to any organic compounds to make them reactive, as will be discussed at greater length. Studies carried out during the last 10 years, and spearheaded by the work of Haagen-Smit, have acquainted us with the chemical reactions of very low concentrations of olefins in the atmosphere. Ultraviolet light, or visible light in the presence of nitrogen oxides, will cause the formation of peroxides and ozonides of these olefins. These decompose then under ozone production.<sup>4</sup> At the same time condensation occurs, causing the formation of a blue haze due to larger molecular aggregates.

These phenomena, formation of peroxides, ozonides, ozone, and blue haze, are typically associated with Los Angeles (and other metropolitan areas) smog, due to release of olefins and nitrogen oxides from petroleum products and combustion,

all corollaries of human activities. In the Los Angeles area, as much as 1500 tons of volatile organic compounds are released daily into the atmosphere. This amounts to  $5.5 \times 10^5$  tons per year, or for all human activities on earth about  $2 \times 10^7$  tons/year, which is about one tenth of all volatile organic material released into the air all over the world, and compares with the  $5.7 \times 10^{15}$  tons of air in the atmosphere. Therefore, each year the whole atmosphere receives about one thirty-millionth of its weight in extraneous volatile material.

The break-through of our understanding of the nature of smog came as Haagen-Smit demonstrated that oxidation of olefins with ozone produced a blue haze, with a typical smog odor, causing eye irritation, and inducing plant damage,<sup>5</sup> in all details like city smog. This ozonization causes addition of ozone to the double bond of olefins, or breakage of the molecule at the double bond, and condensation of the ozonides or peroxides formed (as mentioned under the nitrogen oxides-catalyzed light-oxidation of olefins). Therefore ozone treatment of olefins serves as a convenient experimental model of what happens in the atmosphere with olefins.

For this reason similar experiments were performed with ozone and volatile plant products. To this end, jars were filled with dilute ozone and placed against a black background. A strong light placed along the side of the jar showed up haze formation. As soon as slightly crushed pine or fir needles were dropped into the jar, a blue smoke started to envelop the needles and slowly filled the jar. Crushed oak or maple leaves did not produce the blue smoke, whereas leaves of Rutaceae and other families with essential oils produced the blue smoke. A spectacular display of smoke streamers in the jar was caused by twisting an orange peel inside: every ejected oil droplet left a trace of blue smoke, like high-energy particles in a Wilson cloud chamber. These experiments show that plant parts, rich in volatile oils, produce a bluish smoke around them upon ozone oxidation, whereas other plants, without oil, do not.

Not only through ozonization are blue hazes formed with organic vapors, but this happens quite generally when the latter are exposed to strong light, rich in actinic rays. This was demonstrated in 1869 by John Tyndall in his well-known experiments, producing the Tyndall-effect, as it was later called. He showed that almost any organic vapors present in air will condense to submicroscopic particles when a strong beam of light passes through it.<sup>6</sup> Independent of its chemical identity (amyl nitrite, benzene, carbondisulfide, butyl nitrite, allyl iodide, isopropyl iodide), a "blue cloud" formed when strong light passed through a sufficiently diluted vapor. This "blue cloud" consisted of particles of less than  $0.1 \mu$  diameter, which reflect predominantly blue light. The fact that this is reflected light is demonstrated by its polarization.

The more dilute the organic vapor is the deeper blue the haze formed in the light beam, and the longer it takes to be formed. This means that the low concentrations of organic matter emitted into the atmosphere might take hours to produce a haze. Tyndall also observed that the longer the organic vapors were subjected to light, the whiter the haze became, because gradually also the longer wavelengths were reflected. This indicated that in light the haze particles gradually grew to a size of about  $1 \mu$ .

From these model experiments with ozone and light we can conclude that partial oxidation, followed by condensation to macromolecular aggregates and submicro-

scopic particles, is the only demonstrable and conceivable fate of the bulk of the volatile matter produced by plants. In this respect they behave like olefins released by man, and resulting in smog. We can therefore ask, to what extent observations in nature support this conclusion.

*Blue Hazes in Atmosphere.*—In nature we find that blue haze formation is very common during daytime, and everywhere over vegetated areas this haze, which is often called summer haze, or heat haze, can be seen, except during or immediately after storms which have brought in clean, completely colorless, and transparent air.

The formation of this blue haze can often be observed directly. In the early morning, after a warm, windless night, visibility at ground level near the vegetation may be very high. Almost as soon as the first sun rays hit the ground, a more or less dense blue haze appears. This haze is also formed under dry conditions, and is *not* a mist or a dust, as its bluish color indicates. It is apparently due to the partial oxidation of the organic vapors which accumulated during night in the thin air layer below the night inversion. During day the vertical mixing of the air usually makes it difficult to identify the vegetation cover as the source of the haze, but occasionally, on a windless day, a slightly denser haze can be observed just above the ground, and in mountainous areas the densest haze on calm days is seen in the valleys, whereas the mountain tops and ridges are always much clearer.

Leonardo da Vinci, who very clearly described this bluish haze, also noted that exhalations of plants were its source, only he believed that it was the moisture given off by them. But water vapor cannot possibly be the basis for this haze for (1) it occurs predominantly in a dry atmosphere; (2) its bluish color indicates submicroscopic size of the particles, whereas the smallest mist droplets, which are more or less stable, have a diameter of  $5 \mu$ ; (3) clouds and steam exhaust remain clearly distinct in an atmosphere of bluish haze, and do not blend with the haze; and (4) over oceans no such blue hazes occur, but light white hazes apparently due to microscopic salt particles are frequent.

In the preceding paragraphs the fate of the volatile organic materials given off by plants was shown to be a bluish haze, and conversely the bluish heat haze hanging especially during summer and fall over continents was identified with these plant emanations. This heat haze is *not* due to human activities, and regularly occurred in previous centuries (before industrialization) as indicated by landscape paintings, especially since the 17th century (e.g., Albert Cuyp, Turner, Monet), and by Leonardo da Vinci's descriptions in his notebooks. Tyndall, in his lecture on "New chemical reactions produced by light,"<sup>6</sup> also suggests that most of the blue color of the sky is due to reflection of light by particles.

These hazes, in a very dense form, can be seen over uninhabited areas (jungles of N. Colombia, the Amazon basin, the Gran Chaco) and therefore are not due to fires or dust. They are completely uniform in intensity and therefore are not traceable to point sources of emission. Smoke from factories or large forest fires can be traced for dozens of miles, and always remains as a band of pollution which never completely blends with the surrounding air. The haze occurrence over jungles also excludes dust as their source. Since these hazes always are restricted to the air below the main temperature-inversion layer, their source has to be terrestrial, and, neither cosmic dust nor long-range transport through the upper atmosphere can account for them.

In view of the extraordinary toxicity of smog products, the question is pertinent whether the hazes due to natural vegetation have a deleterious effect on plants. In the case of smog, it was shown<sup>7</sup> that, whereas high concentrations cause both lesions on leaves and growth retardation, lower concentrations may be symptomless, but they reduce growth rates of even rather smog-insensitive plants (tomatoes). A physiological disturbance of sensitive tobacco varieties—the so-called “weather fleck”—occurs under conditions that dense heat hazes are produced, well away from human activities. It should be attributed to the toxicity of the heat haze, resulting from emanations of plants. If such leaf lesions can be produced by heat haze, it is likely that they reduce growth of the natural vegetation as well. It is therefore suggested that in nature a certain growth control of other plants is exerted by partial oxidation of volatile products of neighboring plants.

The molecularly dispersed organic gases are gradually condensed to haze particles, and thus the air is swept clean of these gases. But what happens to these haze particles?

A newly formed haze is light blue in color, indicating that particle size is well under that of the wavelength of light, and probably  $< 0.1 \mu$ . Chemically they can be expected to be of asphaltic or bituminous nature, with complicated and unpredictable ring structures. All double bonds can be expected to be saturated, first by addition of oxygen, and then by condensation. It is also possible that the ultraviolet rays produce free radicals which react with each other without any intermediate peroxide formation.

The asphaltic products thus formed are almost completely inert chemically, and cannot be broken down. Therefore they can only disappear from the atmosphere by precipitation. This can occur with rain or snow, provided rain droplets or snowflakes form around the haze particles. The number of rain drops or snowflakes is much too small (by a factor of perhaps  $10^5$ ) to precipitate the haze particles. Therefore a further condensation process must occur. This apparently takes place (1) through continued irradiation, as Tyndall had found, and (2) in the inversion layer when cumulus clouds are forming. Whereas normally the haze particles are coalescing at a very slow rate, the mist droplets formed around haze nuclei in the cloud are rapidly coalescing, disappearing and reforming, and during that process the haze particles become concentrated. This results in an accumulation of the haze in the location of cloud formation, or in the inversion layer. It also results in a color change from the indistinct blue of the  $< 0.1 \mu$  particles to yellow, brown, or black particles of  $> 0.5 \mu$  diameter. From a plane flying at the height of these condensed haze layers, they are very distinct, and sometimes several layers, at 200–500 m intervals, can be seen; occasionally as many as seven have been observed one above the other, but the usual number is 0, 1, or 2. These dark haze layers probably coincide with the primary and secondary inversion layers.

When, since the last change of air mass, no cumulus clouds have been produced in the inversion layers, no denser yellow or brown thin haze layers occur. Whereas the diffuse blue heat haze layer only occurs over land masses or immediately adjacent seas, the higher thin yellow or brown haze layers can be seen over oceans as far as 2,000 km away from land (e.g., west of California over the Pacific Ocean, west of Ireland over the Atlantic). Sometimes thin clouds form in the upper haze layers, which then are not white, but gray in color.

When rain or snow originates in these haze layers, the droplets or ice crystals will usually form around the haze particles, which thus become precipitated on the earth. Of all solid material contained in rain over the continental United States, only a quarter is water soluble and consists of NaCl or  $(\text{NH}_4)_2\text{SO}_4$ ; the rest is water-insoluble and a considerable part is combustible. In Swedish rainwater 43, 58, and 71 per cent of the residue was organic.<sup>8</sup> About 70 per cent of the snow-nuclei in Japan disappear upon combustion. Of the solid material accumulating on the Greenland Ice Cap<sup>9</sup> or the floating ice islands in the Arctic Ocean, 5 to 7 per cent is organic. This is not organized matter such as pollen grains, bacteria, spores, or lint, but is a thin coating of oily material, often deep-yellow in color, on dust and clay particles, which makes them stick together and prevents them from displaying Brownian movement. These observations were made on two samples of surface dirt collected by Norman Goldstein on the ice island T-3, floating in the Arctic. One sample was marked as coming from a moraine, but it did not contain larger particles and was doubtless atmospheric dust, like the other sample. Chemical analysis gave:

	Analysis of organic matter	
	Sample 1, %	Sample 2, %
Combustible matter	6.9	6.0
C	35.6	33.5
H	14.3	11.9
N	15.4	11.5
O (by difference)	34.7	43.1

This leads to an approximate composition  $\text{C}_8\text{H}_{26}\text{N}_2\text{O}_5$ , or assuming that the sample was not completely dry,  $\text{C}_8\text{H}_{16}\text{N}_2$ .

On glaciers and permanent snow fields, much solid material accumulates, which is partly dust, partly a brown, or black asphalt.

*Blue Hazes as the Source Material for Petroleum Formation.*—The above observations indicate the probable fate of the haze particles once they have become precipitated with rain. They attach themselves to solid surfaces with which they come in contact, and therefore form part of humus, and of the upper clay layer of the soil. Whereas the cellulose and lignin content of humus and peat gradually decreases with age due to bacterial action, the asphaltic or bituminous materials remain largely unaltered, and thus the caloric value of peat and bituminous coal gradually increases with age. These bituminous deposits in the upper layer of undisturbed soil may account for its low wettability.

The material normally carried away by erosion with river water must contain the bituminous material washed down with the rain, usually attached to the clay particles. Thus it becomes deposited with the fine silts and clays in delta areas. It is suggested that this material is a source material for petroleum formation. This hypothesis, at least partly, replaces the generally rejected hypotheses of fats, oils, bacteria, and products of activities of marine organisms accounting for the source material of oil formation. It involves:

- (1) The distillation of hydrocarbons or slightly oxygenated hydrocarbons produced by land plants into the air.
- (2) Their return to the earth after condensation to large molecular aggregates (bitumens) through rain or snow.

(3) Their accumulation in delta areas in conjunction with silt and clay deposition.

(4) Transformation of the bitumens or asphalts into petroleum hydrocarbons.

This hypothesis accounts for

(a) The largely marine or lacustrine origin of oil.

(b) The constant association of source materials of petroleum formation with fine silts or clays.

(c) The high asphaltic content of young petroleum deposits.

(d) The lack of correlation between predominantly straight-chain fatty acids (or hydrocarbons) with even-numbered carbon compounds produced by living organisms, and the branched-chain odd-numbered carbon chain so common in natural oils. If they have their origin in complicated addition products like bitumens or asphalts, there would be no anomaly.

(e) The  $C^{13}$  content of petroleum is even less than that of land plants, and very much lower than that of marine organisms. This is accounted for by the lower  $C^{13}$  content of fats and other compounds high in H compared with carbohydrates in higher plants,<sup>10</sup> and indicates land-plant origin of petroleum source-materials.

(f) The strong positive correlation between periods of coal formation (land plant predominance) and petroleum source materials.

(g) The failure of microorganisms to destroy the source materials for petroleum formation.

(h) The quantity of oil resources of the world ( $10^{12}$  tons) can be accounted for even if only a small fraction of all organic volatiles return to earth, and if only a small fraction of this material finds its way into petroleum deposits (total volatile material produced during geological ages—over  $10^{16}$  tons, total organic content of rocks perhaps  $10^{14}$  tons, total petroleum reserves  $10^{12}$  tons).

*Meteorological Implications of the Organic Hazes.*—The hypothesis of the heat haze being due to condensation of volatile organic substances produced by land plants, has many meteorological implications.

1. The dense haze layers formed in the primary inversion layer, normally 1,000–3,000 m above the continents, may be structures which absorb sufficient radiation to cause the inversion layer to be warmer than the adjacent layers. Thus the inversion layer would be both a product of accumulation of haze particles and the cause of their accumulation. A layer of air with a higher temperature at a greater height can be accounted for in only 2 ways: (a) by overlaying a cool air mass with a warmer one, or (b) by heat absorption at higher altitudes in the atmosphere, which is only possible in the presence of absorbing materials. As such only dense haze layers can be considered, since other absorbing materials ( $H_2O$  and  $CO_2$ ) change continuously with height, and not discontinuously, like the haze layers. The much warmer ozone layer in the stratosphere owes its existence to U.V. absorption.

2. Cloud formation at intermediate heights in the atmosphere is possible only in the presence of condensation nuclei. As such NaCl particles have been shown to be highly effective. But their concentration decreases rapidly over the continents, as one becomes further removed from seas or oceans. Yet cloud formation is not reduced. Therefore, continents have their own source of condensation nuclei. As such, haze particles might be most effective. This is also suggested



by the fact that the incomplete combustion products of a Bunsen burner are among the most effective condensation nuclei.

3. The often-assumed correlation between vegetation and cloud formation might be a result of condensation nuclei formed from plant emanations. Certain types of vegetation might conceivably be more effective in producing clouds than other types, depending upon production of volatile products.

4. Certain localities in the world have much lower temperatures than geographical latitude and altitude would make one expect. Lima, Peru, at 12° S.L., and at sea level, e.g., should, according to total sun radiation, have an average temperature of 27–28°C, whereas the actual temperature, throughout the year, is about 19°C. This low temperature (at very low precipitation, 20 mm per year) is apparently due to strong absorption of the sun's radiation by heavy haze layers, which extend to 3,000 m or higher.

5. The organic hazes account for the frequent visibility of sunrays against a partially cloudy sky. This is not due to water vapor, which is strictly invisible until it becomes condensed to a cloud, which then is fully opaque (except at altitudes above 10 km, where the moisture content is so low at the low prevailing temperatures that only transparent cirrus-clouds can exist).

6. Red sunsets and "Alpenglühén" are due to scattering of the blue sunrays by haze, leaving only the yellow and red rays to penetrate the 5–6 air masses at sunset. At sunrise, haze formation is only slight, and therefore sunrises are less colorful than sunsets. Tyndall<sup>6</sup> was the first to suggest this explanation. Yellow or bleak sunsets suggest a high dust content of the air.

7. The light-blue color of the sky at low altitude and especially in vegetated areas is partly due to organic hazes. In deserts and at high altitudes the sky is deep blue or violet, due to a limited molecular scattering of blue light, but without the haze scattering component.

8. In addition to the ozone peak in the stratosphere, there is a secondary peak in ozone concentration near the surface of the earth. The former peak is due to U.V. absorption, the latter can be attributed to ozone liberation upon light oxidation of volatile plant products, much as ozone is liberated during smog formation. The often-claimed high ozone content of the air in coniferous forests can thus be accounted for.

*Conclusion.*—The argument of this paper is built largely on general observations in nature, especially from airplanes, on analogies with smog research, on scattered literature references, and to only a very limited extent on experiment. The argument was gradually developed during the last 6 years, and was occasionally mentioned in semipopular papers.<sup>11, 12</sup> The main reason why it is now presented is that it connects a large number of apparently disconnected facts and phenomena, in many different disciplines. Since the author is unable to carry out work in most of these fields, he could not hope to produce a better documented and experimentally supported paper. Instead of desisting from publishing it, it is now presented in the expectation that future research will either support or discard the main features of the developed hypothesis. As examples of the type of data which would be critical, can be mentioned:

1. Chemical and physical analysis of the heat haze and the thin dense haze layers at higher altitudes, the analysis specifically to take into consideration the

organic chemical composition. Thus far the analysis of particulate matter of the atmosphere has mainly concerned organized or inorganic matter.

2. Carbonisotope analysis of different fractions of natural oil deposits. On the basis of the material presented, it is to be expected that the porphyrins in such oils would have a 1 per cent higher  $C^{13}$  content than the petroleum fractions. For the porphyrins would definitely not be distilled over, as the asphaltic components are, and therefore would have been dissolved out of marine organisms in the sediments into the asphalts or oils of land plant origin.

3. Have the flashes of lightning something to do with the organic content of the air, which is particularly high during thunderstorms, as evidenced by the haze present?

4. To what extent do the organic emanations of plants have to do with cloud formation, especially in cumulus and orogenic clouds?

*Summary.*—It is shown that per year approximately  $2 \times 10^8$  tons of volatile plant products are released into the air. In view of the lack of any mechanism by which these volatile products (predominantly terpenes) can be oxidized to  $CO_2$  and  $H_2O$ , and in view of the fate of gasoline vapors in the air of cities, and based on direct experiments, it is shown that these volatile plant products become particularized in the atmosphere. This condensation process is dependent upon sunlight and partly upon the presence of nitrogen oxides.

This condensation leads to the "heat" or "summer haze" formation present over all vegetated areas. Ultimately the haze particles become precipitated on the earth by rain and snow. It is suggested that this material, bituminous or asphaltic in nature, is a source material for petroleum formation. Also many meteorological facts are explainable on the basis of hazes derived from land plants.

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<sup>12</sup> *Ibid.*, in *Proc. Third Nat. Air Pollution Symp.*, 8-11 (1955).