

PARTICULATE CARBON

Atmospheric Life Cycle

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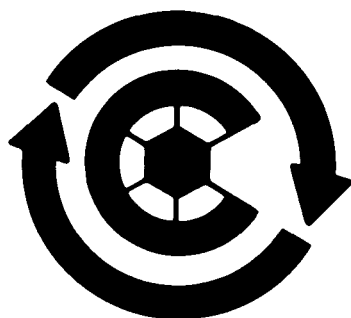
An
International
Symposium
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General Motors
Research
Laboratories



**Edited
by
George T. Wolff
and
Richard L. Klimisch**

PARTICULATE CARBON

Atmospheric Life Cycle



Edited by
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General Motors Research Laboratories

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PREFACE

This book contains the papers and discussions from the symposium, "PARTICULATE CARBON: Atmospheric Life Cycle," held at the General Motors Research Laboratories on October 13-14, 1980. This symposium, which focused on atmospheric particulate elemental carbon, or soot, was the twenty-fifth in this series sponsored by the General Motors Research Laboratories. The present symposium volume contains discussions of the following aspects of particulate elemental carbon (EC): the atmospheric life cycle of EC including sources, sinks, and transport processes, the role of EC in atmospheric chemistry and optics, the possible role of EC in altering climate, and measurement techniques as well as ambient concentrations in urban, rural, and remote areas.

Previous symposia have covered a wide range of scientific and engineering subjects. Topics are selected because they are new or represent rapidly changing fields and are of significant technical importance. It is ironic that the study of particulate elemental carbon or soot should meet the above criteria for selection because soot, especially from coal and wood combustion, has been a recognized air pollutant for centuries. However, since the 1950s, when intense efforts to study air pollution were initiated, to until a few years ago, the role of elemental carbon in the atmosphere was largely ignored. The major reason for this was the lack of a suitable measurement technique. Recently, this situation has changed, and presently there are about 20 different measurement techniques being employed by various research groups. Unfortunately, however, the various techniques appear to give different results, and before the symposium there had been no coordinated effort to compare the various methods. Such an effort was initiated at the meeting and is currently in progress under the coordination of our group.

In addition to the measurement difficulties, this field is further complicated by inconsistencies, redundancies, and contradictions in nomenclature. For example, nearly every measurement method results in unique operational terminology for

elemental carbon. The other descriptors include: apparent elemental carbon, soot, dry soot, black carbon, nonvolatile carbon, nonsoluble carbon, absorbing carbon, residual carbon, and total noncarbonate/nonvolatile carbon. No attempt was made to change the nomenclature used by the various authors in this book so the reader should be aware of these terminology difficulties. Hopefully, a more universal set of nomenclature can be adopted in the near future when the relationships between the results from the various analytical methods become known.

In preparing for the symposium, we discovered that there were a surprisingly large number of researchers engaged in various aspects of research on particulate elemental carbon. We attempted to gather the leading investigators in each area so that a holistic view of the subject could be obtained. We believe that the symposium was successful in accomplishing this and we feel that the papers represent important original contributions to the field.

The efforts of a number of people were responsible for the success of this symposium. The advice and suggestions of Dr. Robert J. Charlson of the University of Washington and Dr. Tihomir Novakov of Lawrence Berkeley Laboratories were especially appreciated. At General Motors Research Laboratories, we would like to thank R. Thomas Beaman for making the symposium arrangements, David N. Havelock for overseeing the manuscript layout and art work, Denise M. Pierson for her assistance in the indexing, and Cheryl Clark for her conscientiousness and skills as a secretary and discussion transcriber.

George T. Wolff and Richard L. Klimisch

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SESSION I
THE IMPORTANCE OF
PARTICULATE ELEMENTAL CARBON

Session Chairman

G. M. HIDY

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THE ATMOSPHERIC CYCLE OF ELEMENTAL CARBON

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ABSTRACT

Four sets of factors determine the overall nature of the cycling of elemental carbon through the atmosphere and thereby determine the concentration fields, and fluxes in and out of the atmosphere. The source factor controls mass emission rates, initial microphysical properties such as size distribution, initial chemical composition, and location of injection into the atmosphere. Aerosol mechanics determine the rate of coagulation of the elemental carbon particles with themselves and with other aerosol particles, the rate of diffusive removal to surface sinks, and sedimentation. Chemical factors, largely the physical and chemical properties of impure graphitic carbon, subsequently govern the refractive indices along with the chemical interaction of the particles with other gas and aerosol constituents and with liquid water. Finally, meteorological factors include mixing in the planetary boundary layer, advection, incorporation into clouds and/or into cloud droplets, chemical processes inside of cloud drops, cloud evaporation and removal by precipitation. These factors may be linked together in a system flow diagram to explain the observed presence and behavior of carbon particles in air.

INTRODUCTION

The presence in the atmosphere of particulate elemental carbon (PEC) is a generally accepted fact. This presence can be deduced from any of several points of view. First, sources of PEC exist chiefly in the form of combustion of carbon-based materials and fuels. Second, under atmospheric conditions, PEC is inert to oxidation and modification of its usual graphitic molecular structure. As a result, once it is injected into the atmosphere it must necessarily reside there for some time until aerosol scavenging processes can remove it. Third, and perhaps most commonly, it is observed that filter samples of air are grey or black in color. This observation of

References pp. 15-16.

blackness has been used for over 70 years as a gross indicator of the amount of air pollution (see e.g., Hill [1] and Waller [2]).

The rationale for studying and understanding the presence of PEC in the atmosphere stems from a desire to understand and predict its effects. In general, these effects can be organized into four categories.

1. Effects which are functions of *concentration*, such as atmospheric heating rate due to absorption of sunlight or such as the amount of adsorbed, cogenerated organic matter.
2. Effects which are functions of *dosage* or a product of concentration and time of exposure. The accumulation of carbon in human lungs might serve as an example.
3. Effects depending on a *column burden*, such as the influence on visibility along a sight path or on the optical depth of the atmosphere.
4. Effects depending on a *flux density* such as the rate at which carbon is deposited on windows.

In order to explore and understand the relationship of effects such as these to the sources of PEC, a number of questions may be asked. Among the more important ones are:

- What are typical concentrations and how do they vary with time, over a region, and vertically?
- How do these concentrations compare (magnitude, time and space variation) with other important aerosol constituents?
- What are the major sources and what factors control the source strengths?
- What fraction of the atmospheric burden is due to natural processes and what is due to human activities?
- What are the dominant removal mechanisms, their magnitudes, and controlling factors?
- What are the residence times and how do they compare with those for other aerosol constituents?
- What are the magnitudes of the effects (e.g., on climate, visibility, and the chemistry of other aerosol constituents)?

APPROACH — THE CYCLE CONCEPT

An integrating framework for addressing this family of questions is found in the concept of the atmospheric cycle of PEC. A cycle involving sources, transport, physical transformation and removal can be represented in a variety of different flow schemes or box models.

A simple representation of the cycle is a gross, one-box model of the atmospheric cycle of graphitic carbon aerosols, as illustrated in Fig. 1. This model, which is defined over a specific region, consists of a spatially uniform source, sink, and burden (volume integral of concentration). Such a model is clearly a simplistic representation of cycling through the atmosphere, but it is nevertheless useful because it forces study of the cycle as a whole rather than just one or a few of its aspects. This approach is based on the principle of conservation of mass, which

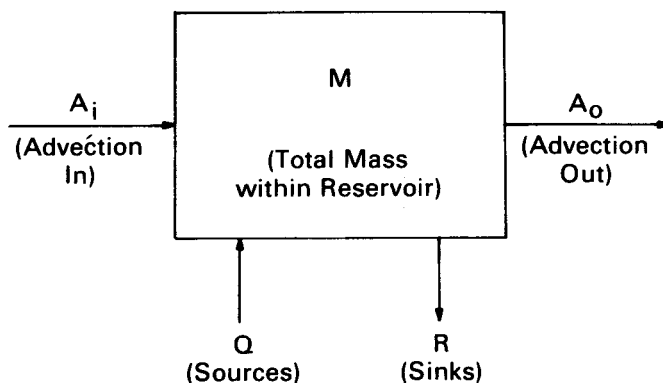


Fig. 1. Gross box model of the atmospheric cycle of particulate elemental carbon (PEC).

requires that the magnitudes and time variation of the sources, sinks, and burden must be consistent. If an internally consistent model can be constructed, then it is likely that all the major fluxes (chemical and physical) have been identified. The important point is that an overall model of the cycle, no matter how simple, is needed in order to interpret measurements or predict effects of atmospheric graphitic carbon.

A major weakness of the gross model is that it does not include any mechanisms for physical and chemical transformations, such as coagulation with other particles or adsorption of trace gases. One way to include these processes is to incorporate a system flow diagram (mechanistic model) within the gross model, as illustrated in Fig. 2. Each of the "mechanistic" reservoirs are characterized by specific transformations of the original particles, and these transformations (fluxes) and reservoirs can be studied independently of the gross model. Eventually, the gross and mechanistic models need to be combined into a complete description of the life cycle, although it is not clear that the measurements needed to effect such a merger are presently available, or even possible.

Gross Model Description — The gross model consists of source and sink strengths, average concentration (and thus burden), and advective transport into the region. One derived quantity of particular interest is the average residence time (or turnover time), defined as the burden divided by sink strength. This quantity can be defined for a particular sink or for the sum of all sinks. Earlier studies [3] of the atmospheric cycle of sulfur aerosols indicated that a spatial scale of the order of several thousand kilometers is appropriate for this type of model. This scale is based on a desire to have source and sink strengths that are large compared with advective fluxes into and out of the region. An alternate approach is to choose a smaller region and include advection terms in the model.

As its name implies, this model can be used to study some of the gross features of the atmospheric cycle of graphitic carbon aerosols, such as the relative importance of advective transport versus local sources and sinks, the average lifetime in the

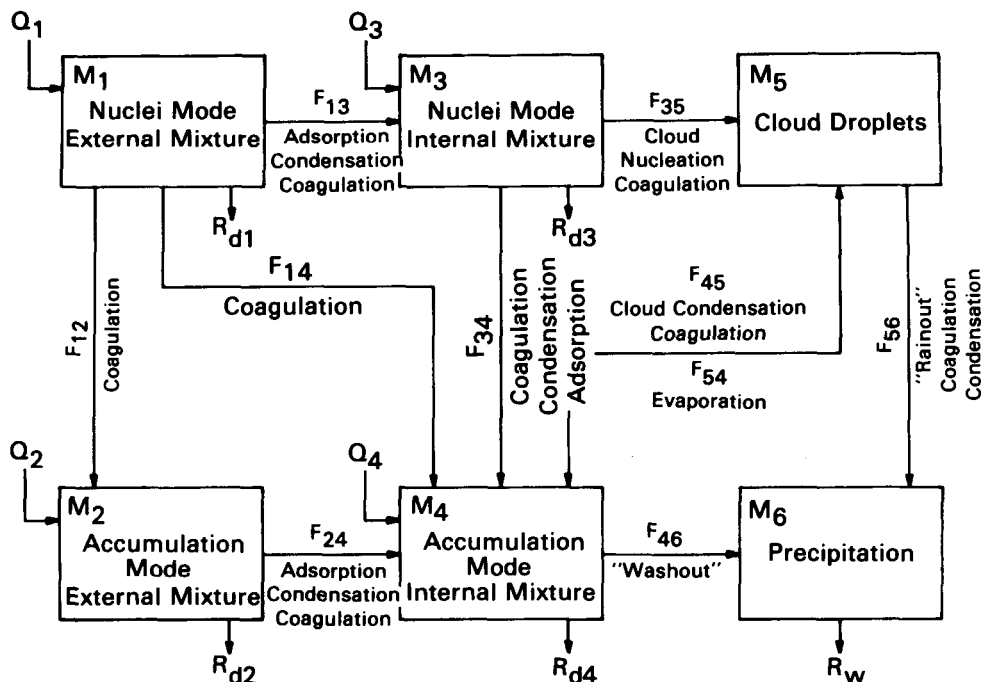


Fig. 2. Mechanistic model of the atmospheric cycle of particulate elemental carbon (Q denotes sources; F is a flux between reservoirs; R_W and R_D are wet and dry removal, respectively; and M denotes the mass or burden of elemental carbon in each reservoir).

atmosphere, and the area influenced by a given source region. By comparison with other aerosol constituents (notably sulfates), the relative importance of graphitic carbon aerosols to atmospheric visibility and radiative climate can be calculated. Comparison of residence times for different aerosol constituents can be used to determine if they have similar removal mechanisms.

Mechanistic Model Description — A total of six reservoirs, differentiated by size and chemical composition of the graphitic carbon-containing particles, are included in the mechanistic model (Fig. 2). Defining the terms used to identify these reservoirs, *external mixture* means that PEC is physically isolated from the other aerosol constituents as individual particles. Thus the properties of the graphitic carbon-containing particles with respect to water are determined by PEC. An *internal mixture* is one where other compounds are physically attached or coated on PEC and hence may dominate the physical and chemical properties of the graphitic carbon-containing particles. *Nuclei mode* and *accumulation mode* refer to the size of the particles, with the nuclei mode including particles smaller than about 0.05-0.1 micron diameter and the accumulation mode covering the particle diameter interval from about 0.1 to 1 micron. The *cloud droplets* reservoir includes graphitic carbon contained in cloud droplets (or ice particles), while the *precipitation* reservoir

contains atmospheric graphitic carbon on its way to the surface in rain, snow, or hail (wet removal).

The reasons for selection of these particular reservoirs lie with the physical and chemical properties of graphitic carbon aerosols. Nuclei mode aerosols have higher diffusion coefficients than those in the accumulation mode, resulting in higher rates of coagulation and of collision with the surface (dry removal). However, pure graphitic carbon is insoluble and hygrophobic, implying that wet removal is not very efficient for externally mixed graphitic carbon aerosols. In contrast, accumulation mode sulfate aerosols are hygrophilic and thus are readily incorporated into cloud droplets, making removal by precipitation a dominant mechanism for them. By defining the reservoirs in terms of the physical and chemical properties, the mechanisms which transfer graphitic carbon among the reservoirs are highlighted. Some of the mechanisms thought to be most important are included in Fig. 2, although there are probably other important fluxes that are not shown. If these fluxes are thought of as first-order processes, then there are corresponding rate constants (or reciprocal lifetimes) for each process. For any particular source-to-sink pathway, these lifetimes can be combined to yield an overall lifetime, and compared with the lifetimes observed in the atmosphere (e.g., via the gross model). Ultimately, calculation of equilibrium concentration or burden and response times may be accomplished if the coefficients are known via an approach similar to that of Yuen *et al.* [4].

CONTROLLING FACTORS

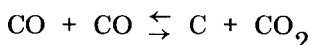
Consideration of the processes involved in the cycling of PEC through the atmosphere results in the definition of four sets of controlling factors:

1. Source characteristics,
2. Aerosol mechanics,
3. Chemical properties of PEC,
4. Meteorological factors.

Source Characteristics — Sources of PEC are ubiquitous in both natural and polluted settings but almost all involve combustion. Small amounts of coarse particle PEC can be generated by the physical weathering of graphite-containing sedimentary rocks or exposed charcoal (e.g., in a forest after a fire has stopped). If we limit our focus to fine (sub μm radius) particles, all PEC is generated by combustion of carbon containing materials.

There are basically two mechanisms by which PEC can be generated, both involving pyrolysis. Gas phase reactions exist by which hydrocarbons are dehydrogenated and the carbon eventually ends up reassembled into a graphitic structure. Such reactions are known for both aromatic [5] and aliphatic compounds [6]. Commercial production of carbon black often utilizes methane, and acetylene flames can be very sooty, demonstrating that even small hydrocarbon molecules can produce graphitic carbon. It is speculated that in the case of such low carbon numbers, droplets of aromatic material may be formed as an intermediate preceding

the final pyrolysis to graphitic structures [7]. Another gas-phase production mechanism involves the equilibrium:



which is shifted to the right at $T \sim 600^\circ\text{C}$ [8]. The other mechanism involves the pyrolysis of a droplet or particle of a carbon containing material. An example of this process may be the production of soot in oil burners or diesel engines.

Both of these processes tend to make primary particles in the radius range from 0.02 to 0.1 μm . Larger carbon particles can be emitted from sources if the residence time and/or concentration of primary particles is sufficiently large to permit coagulation. Fig. 3 shows a few typical size distributions for sources, and includes a freeway distribution [9, 10] showing a probable contribution of direct injection to the atmosphere of primary particles. It thus seems clear that sources control the initial size distribution of PEC and that the initial sizes are considerably, perhaps a factor of ten, smaller than the bulk of the mass of the fine particle, accumulation mode aerosols. This difference in size dictates that the PEC has a factor of ca. 10^{-3} smaller particle mass, decreased Stokes number, and about a factor of 6 increase in Brownian displacement in comparison to the accumulation mode.

The chief consequences of the small initial size of PEC lie in the realm of aerosol mechanics [11], in the morphology of the particles [12] and in the likelihood that light absorption is proportional to the mass concentration [13]. The small initial particle size encourages coagulation, but at the same time the physical rigidity and inertness of a solid phase dictates that the surface area per unit mass of PEC is maintained as the particles agglomerate. Soots may have surface/mass ratios up to 1000 m^2/gm [6]. Depending on the source, this surface area may be covered with adsorbed cogenerated materials, or it may be exposed to the atmosphere for interaction with other substances.

Besides these size-dictated quantities, the source factors determine the initial chemical composition. Some sources produce relatively pure PEC, while others may produce a soot which is only 50% elemental carbon [15], the rest often being organic matter. In turn, the initial chemical composition determines whether the soot is hygroscopic (such as PEC coated with H_2SO_4) or perhaps most often it determines that the PEC is hydrophobic.

Source factors also govern the mass of PEC injected into the atmosphere. The amount of PEC produced per unit of fuel burned varies with the type of source and individual source operating conditions. Table 1 shows some examples to illustrate this variability.

Finally, source factors determine location of injection into the atmosphere. Some, perhaps most, sources are widely distributed and close to the ground and may be called area sources. Others are elevated and isolated point sources, while jet aircraft might be considered as elevated line sources.

Aerosol Mechanics — Due mainly to small initial particle size, PEC has a strong tendency to coagulate, both within the source and in the atmosphere. In the latter case, coagulation ultimately brings the PEC into physical contact with the other