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Elemental carbon in the atmosphere: cycle and lifetime

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ABSTRACT

Particulate elemental carbon is found in the atmosphere in both urban and remote regions and is often responsible for much of the absorption of solar radiation by atmospheric aerosols. Its atmospheric lifetime is controlled by four factors: the initial size distribution, the concentration of ambient particles, the frequency and duration of precipitation, and the efficiencies of removal mechanisms. A model of the atmospheric cycle of particulate elemental carbon which includes these factors has been used to estimate the range of atmospheric lifetimes expected under various conditions. Calculated lifetimes range from under 40 hours in rainy climates to well over 1 week in clean, dry regions.

1. Introduction

Although particulate elemental carbon (EC) is present as a minor constituent of the atmosphere, and in spite of its being nearly inert, it is of major significance to the atmosphere. EC can comprise a significant fraction of urban aerosol mass (Countess et al., 1980), and has been found in numerous rural and remote areas (see e.g., Wolff and Klimisch, 1982). It is a major contributor to the absorption of sunlight by aerosols (Rosen et al., 1978). This absorption, which has been observed even in very remote locations (Ogren et al., 1981; Waggoner et al., 1981; Heintzenberg, 1982), could alter the Earth's climate by warming the atmosphere while decreasing solar radiation reaching the surface. The probable existence of other important effects of EC, e.g., catalyzing the oxidation of sulfur dioxide in liquid systems (Chang et al., 1981) or decreasing the albedo of snow (Grenfell et al., 1981), suggests a need for understanding both the chemical and physical aspects of its presence in air (Charlson and Ogren, 1982).

The atmospheric cycle of EC provides a framework that simultaneously considers mass continuity, the chemical and physical nature of EC in sources and the atmosphere, aerosol mechanics, meteorological transport (diffusion and advection), and removal processes. In the case of atmospheric EC, no atmospheric chemical reactions or phase changes need to be considered because it is assumed to be inert and non-volatile. In this paper, after describing the properties of EC relevant to its atmospheric cycle, a mechanistic model is presented that integrates them, allows comparison of the pathways by which EC is processed in and removed from the atmosphere, and allows estimation of the temporal and spatial scales of the distribution of EC in the atmosphere and, ultimately, prediction of the response of the system to changes in the controlling parameters.

EC as found in the atmosphere shows only microcrystalline structure (Fig. 1c), and hence the particle morphology does not reflect macroscopic, graphitic crystalline character (Fig. 1a, b). The primary particles tend to be spheres, often agglomerated into chains or clumps (Fig. 1d, f). The physical rigidity and inertness of the solid phase dictate that the surface area per unit mass of EC is maintained nearly constant as the particles agglomerate, resulting in surface/mass ratios up to 1000 $m^2 g^{-1}$ (Donnet and Voet, 1976). Depending on sources, the EC surface may be covered with adsorbed, co-generated substances (often partially-burned, hygrophobic hydrocarbons), or the carbon surface may be exposed to the atmosphere for interaction with other substances. As governed by the physical processes of diffusion and coagulation in the atmosphere, collisions with ambient particles or trace gases can result in hygroscopic coatings

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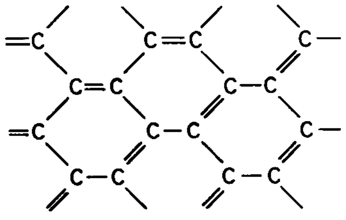
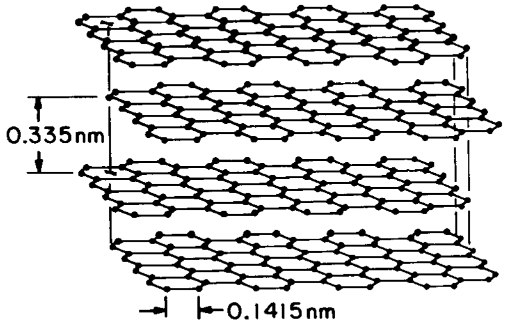
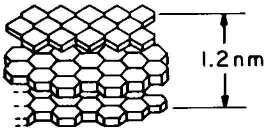


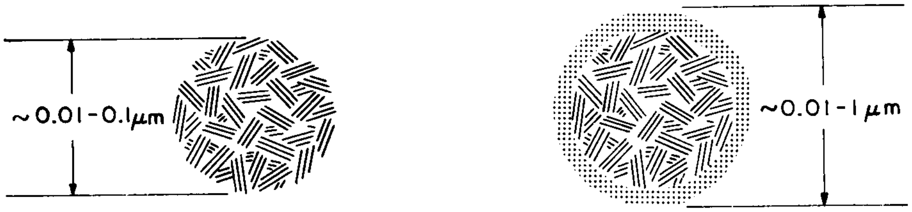
(a) Molecule



(b) Platelet



(c) Platelets



(d) Particle (e) Coated Particle

(f) Chain Aggregate (g) Coated Chain Aggregate

Fig. 1. Structure of elemental carbon in the atmosphere. Particles may be coated with hygrophobic or hygroscopic substances.

(e.g., H_2SO_4) on the surface of the EC. As a result, the coated particles or agglomerates (Fig. le, g) can be expected to display either hygroscopic or hygrophobic behavior.

Graphite is quite inert at ordinary temperatures, is hygrophobic, and insoluble in any solvent. It can be oxidized by air at temperatures above ca. 600 °C or by F_2, and will react in liquid systems of strong oxidizing agents (such as fuming nitric acid, $KClO_4$ or $KMnO_4$). However, such conditions do not normally occur in the atmosphere, and hence EC is assumed to be inert for all practical purposes. Reactions with free radicals (e.g., OH) are not known, but may be important. This inertness dictates that the only modifications and removal processes that exist for EC are physical. In spite of being inert, EC is known to play important chemical roles, particularly its ability to catalyze the oxidation of SO_2 to sulfate in aqueous solution (Chang et al., 1981).

Sources of EC are ubiquitous in both natural and polluted settings, but almost all involve combustion. The major formation mechanisms involve pyrolysis of gas-phase or condensed-phase carbonaceous materials. These processes tend to make primary particles in the radius range from 0.01 to 0.1 μm. Larger carbon particles can be emitted if the residence time or concentration of primary particles is sufficiently large to permit coagulation. Still larger (super-micrometer) pieces of EC can be generated mechanically by the shedding off of carbon layered on the walls of combustion chambers or exhaust systems, or by the physical weathering of graphite-containing sedimentary rocks or exposed charcoal; these large particles are not considered in this paper because of their very short lifetimes in the atmosphere. Measured size distributions of combustion aerosols are often multimodal, and the mean diameters and masses of the modes depend on the combustion source and its operating conditions (Groblicki and Begeman, 1979; Whitby, 1979).

After entering the atmosphere, EC is subjected to the effects of meteorological and aerosol physical factors. Other than mixing fresh EC with ambient aerosols, atmospheric turbulence, advection, and subsidence should have no effect on the physical or chemical nature of EC. However, atmospheric motions can carry EC into clouds, where the behavior of the particles is dictated by the chemical nature of their surfaces. If the surface is hygrophobic, the particle will not grow at high relative humidities and remains inactivated in clouds. On the other hand, if it is hygroscopic it may or may not be activated into a cloud droplet, depending on a complex set of considerations determined by the amount of water soluble material on the particles (Mason, 1957) and on any surface active compounds that might be present (Giddings and Baker, 1977).

Since most clouds or cloud layers do not form precipitation, particles that act as cloud condensation nuclei are usually evaporated. This cycle of cloud droplet formation and evaporation may be repeated 10–60 times before precipitation occurs (Junge, 1964). Chemical reactions within the droplet can produce non-volatile material from gaseous reaction products, such as sulfate produced from SO_2 oxidation (Hegg and Hobbs, 1978; Chang et al., 1981). Hence the repeated cycling of EC into and out of cloud droplets probably builds up the mass of soluble but non-volatile material coated onto or attached to the carbon particles.

2. Integration of controlling factors

To model the various mechanisms affecting EC, a total of six reservoirs (differentiated by size and chemical morphology of the EC-containing particles) are considered (Fig. 2). Referring to Fig. 2, *external mixture* defines EC physically isolated from other constituents, such that the properties of the EC-containing particles with respect to water are determined by EC alone. An *internal mixture* is one where EC is physically in contact with other, perhaps more abundant, hygroscopic aerosol constituents (e.g., sulfates), with the other compounds dominating the physical and chemical properties of the EC-containing particles. *Nuclei mode* and *accumulation mode* refer to the size of the particles, with the nuclei mode including particles smaller than about 0.1 μm diameter and the accumulation mode containing particles from about 0.1 to 1 μm diameter. The *cloud droplet* reservoir includes EC contained in cloud droplets, while the *precipitation* reservoir contains atmospheric EC on its way to the surface in hydrometeors.

The selection of these particular reservoirs reflects the importance of two factors in controlling aerosol cycles: particle size and hygroscopicity. Nuclei mode aerosols have higher diffusion coefficients than those in the accumulation

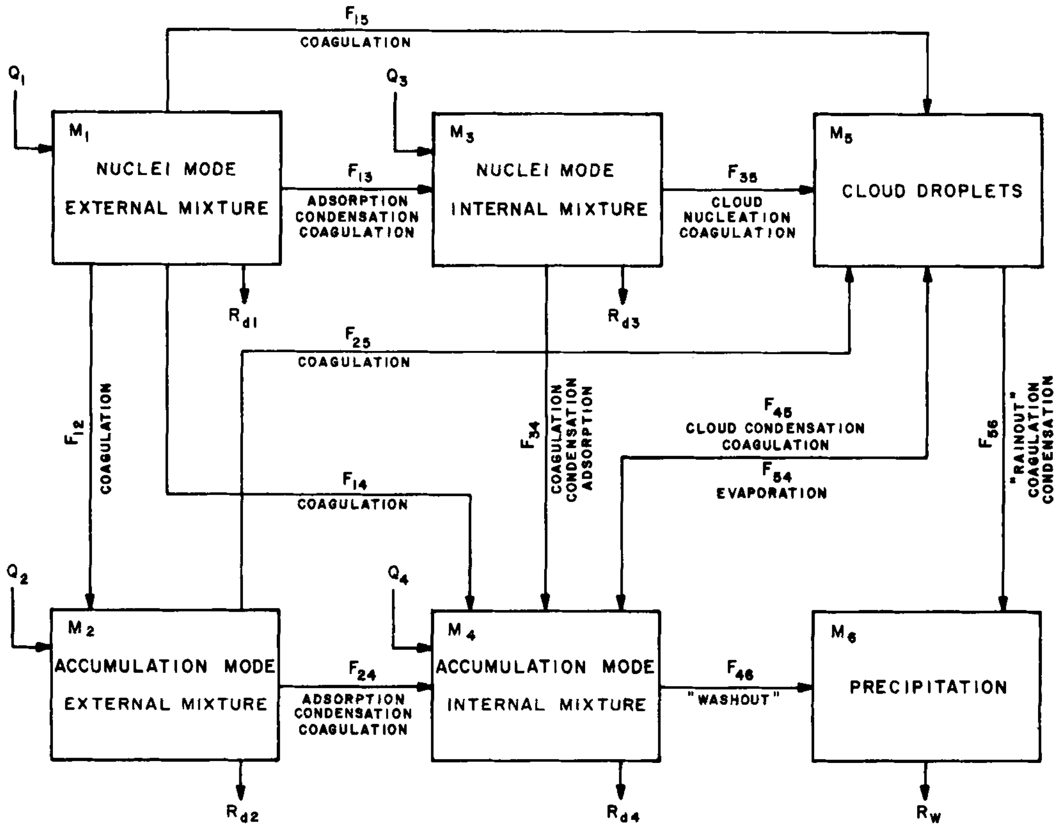


Fig. 2. Mechanistic model of the atmospheric cycle of elemental carbon.

mode, resulting in higher rates of coagulation and of collision with the surface (dry removal). However, pure elemental carbon is insoluble and hygrophobic, suggesting that wet removal may not be very efficient for externally-mixed EC. In contrast, accumulation mode sulfate aerosols are hygroscopic and thus are readily incorporated into cloud droplets. By defining the reservoirs in terms of both particle size and hygroscopicity, the mechanisms which transfer EC among the reservoirs are highlighted.

Many of the mechanisms are irreversible, and eventually most of the particles are expected to reach the internally-mixed accumulation mode. From there, the particles are removed by precipitation or dry deposition, but are not expected to return to the other reservoirs. Assuming the fluxes are first-order processes, then there are corresponding rate constants for each process. Alternatively, the reciprocal of a first-order rate constant may be called the turnover time with respect to a particular process, defined as the ratio of the mass in the reservoir to the flux out of the reservoir by a particular pathway. These turnover times can be combined to yield an average residence time (lifetime) for EC, defined as the mass in all reservoirs divided by the total removal flux.

3. Evaluation of turnover times

Coagulation is the predominant mechanism for transferring EC among the various reservoirs, while wet and dry deposition are the only removal mechanisms considered. Condensation of gas-phase reaction products (e.g., H_2SO_4) may serve to speed up the transfer of EC into the internally-mixed accumulation mode, but is omitted in the present study.

3.1. *Coagulation*

Calculation of coagulation rates for bimodal aerosol size distributions follows the approach of

Whitby et al. (1978) which treats each mode as single-sized particles lumped at the mean size of the mode. The intermodal coagulation constant is based on the surface geometric mean sizes of the two modes, while the intramodal coagulation constant is twice the monodisperse value based on the number geometric mean size of the mode. Whitby et al. (1978) showed that this approach agrees closely with a complete numerical calculation of the total number concentration of a coagulating, bimodal aerosol.

Collisions between modes decrease both the number and mass of particles in the nuclei mode, but add only mass to the accumulation mode. The rate of change of the number concentration of externally-mixed, nuclei mode EC (N_1) caused by coagulation can be written as

$$\frac{dN_1}{dt} = -K_{nn}N_1^2 - K_{nn}N_1N_3 - K_{na}N_1N_2 - K_{na}N_1N_4 \qquad (1)$$

where N_2, N_3, N_4 are the number concentrations of externally-mixed accumulation mode EC, internally-mixed nuclei mode particles, and internally-mixed accumulation mode particles, respectively; K_{nn} is the intramodal coagulation constant for the nuclei mode; and K_{na} is the intermodal coagulation constant between the nuclei and accumulation modes. Similar equations may be written for the other reservoirs.

The second-order term on the right-hand side of eq. (1) prevents the treatment of coagulation as a first-order process when N_1 is high. However, rapid dilution upon emission into the atmosphere almost immediately reduces source concentrations by factors of up to 10^4 (Whitby, 1979), and further reductions of one or more orders of magnitude by turbulent mixing occur within a few hours (Pasquill, 1974). As a result, the second-order term in eq. (1) soon becomes insignificant, allowing treatment of coagulation as a first-order process.

The large number of collisions required for nuclei mode particles to grow in size up into the accumulation mode suggests that any self-coagulation which does occur affects only the number concentration of the nuclei mode, and not its mass concentration; in other words, self-coagulation does not provide a significant flux of particles from the nuclei mode into the accumulation mode once the particles enter the atmosphere. In addition, Whitby (1978) has shown that coagulation rates between the nuclei and accumulation modes generally exceed those for coagulation within the nuclei mode, and that coagulation of the submicrometer particles with coarse particles (diameters > 1 μm) is negligible. As a result, the coagulation turnover time of EC is expected to be primarily a function of the accumulation mode number concentration.

Characteristic coagulation turnover times for EC coagulating with accumulation mode particles are shown in Fig. 3 as functions of the number concentration of accumulation mode aerosols. The results are presented as ranges of values because of variations in measured size distributions for combustion sources and ambient aerosols (Whitby, 1978, 1979). Additional abscissae are shown in Fig. 3 for accumulation mode volume, mass, and light scattering coefficient using approximate conversion factors of $N/V = 500\ \mu m^{-3}$ (Whitby, 1978), $M/V = 1.5\ g\ cm^{-3}$ (Junge, 1963), and $\sigma_{sp}/M = 3.3\ m^2\ g^{-1}$ (Waggoner et al., 1981). Also

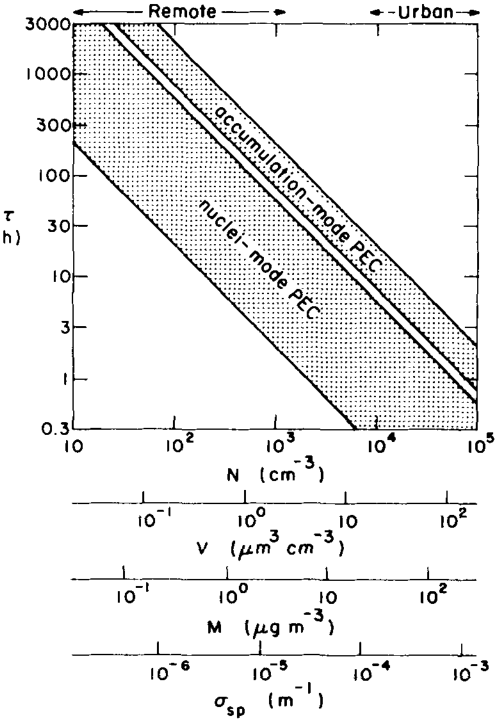


Fig. 3. Coagulation turnover time of externally-mixed elemental carbon as a function of accumulation mode particle number concentration.

shown in Fig. 3 are typical ranges of accumulation mode concentrations reported in the literature (National Research Council, 1979).

As is evident in Fig. 3, externally-mixed, nuclei mode EC has a short coagulation turnover time in urban areas. In rural locations, coagulation turnover times of up to 1 day are expected, while in remote locations, nuclei-mode EC can exist as separate particles for up to 2 weeks. Coagulation turnover times for accumulation mode EC, with its lower coagulation constant, are about a factor of 10 greater than for the nuclei mode. As a result, EC in the accumulation mode can remain externally mixed for a half day or so in urban areas, and over 1 month in clean locations. Two important factors are thus seen to control the time that EC can exist as separate, distinct particles: the initial size distribution of EC, and the ambient concentration of accumulation mode particles.

Externally-mixed EC can also enter the internally-mixed accumulation mode by coagulating with cloud droplets that subsequently evaporate, leaving the EC attached to or coated with the original cloud condensation nucleus. This mechanism can be modelled as a Markov process, using the same approach as Rodhe and Grandell (1972) used to model precipitation scavenging. The turnover time for this mechanism can be written as:

$$\tau_c \approx (1-\alpha)T_{\text{clear}} + \frac{1}{\alpha}\tau_D \qquad (2)$$

where T_{clear} is the average time interval for an air parcel between aerosol-cloud interactions, α is the fraction of the time the particles are within a cloud, and τ_D is the turnover time for particles coagulating with cloud droplets. The relative importance of this mechanism can be evaluated from estimated bounds on the poorly-known statistical parameters T_{clear} and α. Assuming that the particles are imbedded in clouds 5–20% of the time, that the average time spent in cloud-free air is 10–50 h, and that the clouds have a mean droplet diameter of 15 μm and liquid water content of 0.5 g m^{-3}, the coagulation turnover times for this mechanism are 10–60 h and 200–1000 h for nuclei-mode and accumulation-mode EC, respectively. Comparing these estimates with Fig. 3 indicates that this mechanism is likely to be important in remote areas, where it could account for as much as 90% of the transfer of externally-mixed EC into the internally-mixed accumulation mode.

3.2. *Dry deposition*

The major barrier to dry deposition is usually the layer within a few centimeters of the surface. A commonly used parameterization for the flux through this layer assumes that it is proportional to the atmospheric concentration at some reference level, generally 1–10 m above the surface. The dry removal flux, R_d, is written as

$$R_d = V_d M, \qquad (3)$$

where M is the atmospheric concentration and V_d is called the deposition velocity. There is a minimum in the deposition velocity for particles with both low Brownian diffusivities and low settling velocities, typically in the 0.1–1 μm diameter interval.

Although measurements of EC deposition velocities have not been reported, an estimate of the range of values expected can be obtained from theoretical calculations and from measurements of deposition velocities for other species in the same size range as EC. For dry deposition to a smooth surface in moderate winds (5–10 m s^{-1}), Slinn (1977) calculated deposition velocities of 0.002–0.03 cm s^{-1} for 0.02–0.2 μm diameter particles, with the smallest values occurring for accumulation mode particles. Electrical effects were neglected for the calculation, under the assumption that Brownian diffusion is the dominant mechanism for particles smaller than 0.2 μm diameter if water vapor condensation or evaporation are not intense. Measurements of deposition velocities to a water surface reported by Sehmel and Sutter (1974) and Möller and Schumann (1970) yielded results similar to the calculated values.

A range of dry deposition turnover times may be obtained from this range of deposition velocities by considering the simplest case of a uniformly mixed layer of height H. For this case, the column burden is MH and the removal flux is $V_d M$; the corresponding dry deposition turnover time, defined as the column burden divided by removal flux, is H/V_d. No data are available on the vertical distribution of EC, but values for H of the order of 10^3 m are likely (see e.g., Holzworth, 1967; Trägårdh, 1982), assuming that the lifetime of EC is sufficiently long that it can be mixed throughout this layer (ca. 1 day), and that the same processes control the vertical mixing of EC and other submicrometer particles. This assumption is consistent with the lifetimes calculated below, except, perhaps, for the special case of nuclei mode EC emitted at the surface into stable air outside of urban areas. For the case of H in the range 0.5–1.5 km and V_d in the range 0.01–0.05 cm s^{-1}, the turnover time with respect to dry deposition of nuclei-mode EC is expected to be in the range 300–4000 h. An accumulation mode particle with V_d in the range 0.001–0.01 cm s^{-1} would have a corresponding dry deposition turnover time in the range 1400–40,000 h.

3.3. *Wet deposition*

The ability of EC to act as a cloud condensation nucleus (CCN) is dependent on the size and the chemical nature of the surface of the particle. The usual small size (less than a few tenths of one micrometer) and hygrophobic nature of freshly-emitted EC suggest that it is not likely to act as a CCN. After the EC has had adequate time to coagulate with other particles and trace gases, its cloud nucleating properties should be controlled by the chemical composition of the coagulated mixture. For example, collisions of EC with sulfuric acid or ammonium sulfate particles in the accumulation mode should result in a mixed aerosol with cloud nucleating properties similar to those of sulfate aerosols alone.

Collisions of EC with existing cloud or rain drops are controlled by many of the same factors controlling dry deposition. Slinn's (1977) calculated collision rates display a minimum at about 0.2 μm diameter for the same reason that deposition velocities have a similar minimum: both Brownian diffusion and inertial effects are weak near this size. Electrical attractions between charged particles and cloud (or rain) droplets may play a role in determining collision rates, but this effect has not been quantified.

A frequently reported parameter for studies of wet deposition is the washout ratio (dimensionless), defined as a particular species' mass mixing ratio in precipitation divided by its average near-surface mass mixing ratio in air. Wet deposition rates are influenced by the physical properties of the precipitating clouds, e.g., temperature, droplet number and size distribution, rainfall intensity and duration, and entrainment rate of ambient air into the cloud. Although the washout ratio parameterization does not explicitly account for these properties, it does provide a means for obtaining rough estimates of expected ranges of wet removal rates. For internally-mixed, accumulation mode EC, washout ratios should be comparable to those for the hygroscopic compounds coating the surface. Washout ratios for ammonium, sulfate, and nitrate (which often are major constituents of the water-soluble, submicrometer aerosol) range from about 200–3000 (Cawse, 1974; Scott, 1981; Duce, 1982). These values are consistent with the notion that these compounds are scavenged with essentially complete efficiency by clouds with liquid water contents of a few tenths to a few grams of liquid water per cubic meter of air (Junge, 1963; Charlson and Rodhe, 1982; Duce, 1982).

Nuclei mode EC, whether internally- or externally-mixed, exhibits a very high coagulation rate with cloud droplets. For example, in a cloud with a liquid water content of 0.5 g m^{-3} and mean droplet diameter of 15 μm, the turnover time due to Brownian diffusion, τ_D, for 0.02 μm diameter particles is 0.8 h. Because clouds often have droplets smaller than 15 μm and liquid water contents larger than 0.5 g m^{-3}, both of which decrease the turnover time with respect to Brownian diffusion, and because the particles typically cycle through several clouds before they are washed out (Junge, 1964), nuclei mode EC is expected to be removed with the same efficiency as water-soluble, submicron aerosols such as sulfates.

Externally-mixed, accumulation mode EC is not expected to be incorporated into cloud droplets as efficiently because it has a much lower diffusion coefficient, and because it is not expected to act as a CCN. The washout ratio due to the Brownian diffusion of these particles to cloud droplets can be written as

$$W = \frac{\rho_a (1 - e^{-t_s/\tau_D})}{L}, \tag{4}$$

where W is the washout ratio, ρ_a is the density of air, L is the cloud liquid water content, and t_s is the in-cloud scavenging time. Assuming values for t_s in the range 0.3–3 h, L in the range 0.3–3 g m^{-3}, and mean cloud droplet diameters in the range 10–20 μm, the washout ratio for externally-mixed, accumulation mode EC is estimated to be 4–400.

Following the approach used in the previous section, the turnover time with respect to wet deposition while it is raining can be written as

$$\tau_p = \frac{\text{Burden}}{\text{Flux}} = \frac{X_a \rho_a H}{X_p p} = \frac{H \rho_a}{W p}, \tag{5}$$

where p is the precipitation rate, and X_a and X_p are the mass mixing ratios of EC in air and precipitation, respectively. For typical cases with $\rho_a = 1$ kg m^{-3}, $p = 0.5$–5 kg m^{-2} h^{-1} (corresponding to rainfall rates of 0.5–5 mm h^{-1}), and $H = 500$–1500 m, τ_p is calculated to be 0.03–10 h for nuclei mode and internally-mixed, accumulation mode EC, and 0.3–800 h for externally-mixed, accumulation mode EC.

The effects of intermittent precipitation on the wet deposition turnover time, τ_w, can be represented as

$$\tau_w \approx (1-\beta)\, T_{dry} + \frac{1}{\beta}\tau_p \tag{6}$$

where β is the fraction of the time that a particle is in a precipitating cloud and T_{dry} is the average length of dry periods encountered by an air parcel (Rodhe and Grandell, 1972; Baker et al., 1979). The values of β and T_{dry} depend on the location and time of year. For illustrative purposes, the values calculated by Rodhe and Grandell (1972) from 1 year of measurements in Stockholm, Sweden can be used to estimate wet deposition turnover times in a climate similar to that of Northern Europe. These values for winter are $\beta = 0.18$ and $T_{dry} = 40$ h; corresponding values in the summer are 0.042 and 92 h. For the range of values of τ_p estimated above, τ_w in the summertime is calculated to be in the range 90–300 h for internally-mixed, accumulation mode EC and nuclei-mode EC, and 100–20,000 h for externally-mixed, accumulation mode EC. The corresponding values for wintertime conditions are 30–90 h and 30–4000 h. Differences between internally- and externally-mixed, accumulation mode EC are lower for the case of effective wet removal (low τ_p) because the wet deposition turnover time is dominated by the length of dry periods. Turnover times with respect to wet deposition in the winter are less dependent on τ_p because the precipitation events are longer. Other regions are likely to have different rainfall statistics, but the values used here can be used to compare climates with frequent and long precipitation events ("winter") to those with characteristically shorter and less frequent events ("summer"). Regions with very different climates (e.g., tropical, arctic, or desert) might be evaluated in the extreme as cases where it either rains always or never.

4. Overall lifetime of EC in the atmosphere

A number of simplifications can be made to Fig. 2, resulting in a model that can be solved analytically. This simplified model can be used to evaluate the range of lifetimes expected for EC and the relative importance of the various controlling factors. Two questions of particular interest are "which sets of conditions yield short lifetimes", and "which yield long lifetimes".

The cloud droplet and precipitation reservoirs may be eliminated from the mechanistic model and replaced with wet removal from the remaining reservoirs, with fluxes that are based on the wet deposition turnover times estimated above. Coagulation between the externally-mixed reservoirs and the cloud droplet reservoir, followed by cloud evaporation, can be incorporated into the coagulation turnover time between the externally-mixed reservoirs and the internally-mixed accumulation mode. Coagulation between the two externally-mixed reservoirs can be neglected because it takes hundreds of collisions of nuclei mode particles to make an accumulation mode particle, during which time it is highly likely that a nuclei mode particle will collide with an internally-mixed accumulation mode particle. The two nuclei mode reservoirs can be combined because they coagulate with the accumulation mode at the same rate, and because both are expected to be removed at similar rates by rain or clouds. Finally, the source is assumed to be entirely externally-mixed, with a time-invariant distribution of the emissions between the nuclei and accumulation modes.

This approach yields a simplified model (Fig. 4), which can be solved analytically for the steady-state fluxes and burdens in each reservoir. These can be combined to yield expressions for the overall wet and dry turnover times, and hence the atmospheric lifetime (Appendix B). The input parameters required to evaluate the atmospheric lifetime of EC can be grouped into a set of four controlling factors:

(1) Size distribution at the source, parameterized by the mass fraction of the EC emissions that go into the accumulation mode, f_a. Values of f_a can be almost as low as zero or as high as one (Groblicki and Begeman, 1979; Whitby, 1979);
(2) Number concentration of ambient, ac-

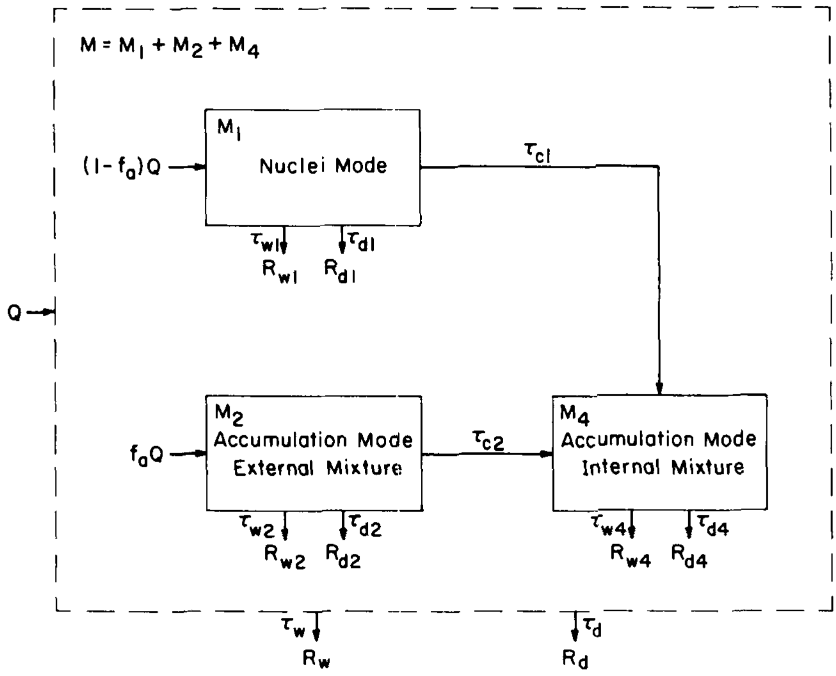


Fig. 4. Simplified mechanistic model of the atmospheric cycle of elemental carbon.

cumulation mode particles (assumed to be hygroscopic);

(3) Time of year and geographical region, parameterized by average time between and duration of precipitation events;

(4) Effectiveness of removal mechanisms, parameterized by the washout ratio, precipitation rate, dry deposition velocity, and mixing height.

The expected ranges of values for the latter three factors, in terms of turnover times, were discussed earlier. Values near the extremes of these ranges were chosen to study both the range of values of the overall lifetime of EC and its sensitivity to the controlling factors; the values chosen are listed in Table 1. For each combination of input parameters, the overall lifetime was calculated, along with the individual fluxes and burdens for each reservoir. The results of these calculations are represented in Fig. 5, and can be summarized as follows:

1. Calculated lifetimes range from less than 1 day to over 1 month.
2. The time interval between precipitation events is the dominant factor for cases with effective wet removal mechanisms.
3. In urban and rural areas, most of the variability in lifetime is due to variations in the wet sink.
4. In remote areas, lifetimes have the greatest variability and are more sensitive to the initial size distribution and the effectiveness of dry removal mechanisms.
5. If the estimated dry deposition velocities are appropriate, then dry deposition is relatively unimportant. Comparisons of calculated removal rates show that only in remote areas do dry processes contribute more than one-third of the total removal flux.
6. With one exception, short lifetimes (<2 days) occur only if the wet removal mechanisms are effective and operate frequently ("winter"). The exception is the situation where nuclei-mode EC is emitted into clean air with highly effective dry removal mechanisms, which allows dry deposition to become important.
7. Long lifetimes (>1 week) occur if wet removal mechanisms are ineffective and precipitation

Table 1. *Parameter values used in sensitivity analysis*

Description	Parameter (units)	Values used		
Mass fraction of emissions into accumulation mode	f_a (none)	0	0.5	1.0
		"Urban"	"Rural"	"Remote"
Coagulation	τ_{c1} (h)	0.3	5	50
	τ_{c2} (h)	3	50	500
		"Winter"	"Summer"	
Rainfall frequency	β (none)	0.18	0.042	
Length of dry periods	T_{dry} (h)	40	92	
		"High effectiveness"	"Low effectiveness"	
Wet removal, summer	τ_{w1} (h)	90	300	
	τ_{w2} (h)	100	20,000	
	τ_{w4} (h)	90	300	
Wet removal, winter	τ_{w1} (h)	30	90	
	τ_{w2} (h)	30	4000	
	τ_{w4} (h)	30	90	
Dry removal	τ_{d1} (h)	30	300	
	τ_{d2} (h)	1000	40,000	
	τ_{d4} (h)	1000	40,000	

events are infrequent, but can also occur in remote areas with more frequent precipitation if half or more of the emissions are in the accumulation mode and if condensation of gas-phase reaction products is unimportant.

These features indicate that, except in very clean areas, there are enough ambient, accumulation mode particles present that EC coagulates fairly rapidly with them, after which the EC is removed at the same rate as other constituents of the internally-mixed, accumulation mode. This is not the case in very clean areas, so that EC can remain externally mixed for longer periods. This causes shorter lifetimes for nuclei mode emissions due to dry deposition, because there are no effective mechanisms for transferring the particles to the accumulation mode. EC emitted in the accumulation mode, however, has a longer lifetime in remote areas because both the wet and dry sinks are not as effective for these particles.

Regions where it rains very frequently (e.g., tropical climates) or very rarely (e.g., desert or arctic climates) can be treated as extreme cases of the climates studied. Thus, the lifetime of EC in tropical climates is expected to be as short as 1 day, while in very dry climates, a lifetime of 10 days or more is generally expected.

5. Conclusion

The atmospheric lifetime of EC is expected to be highly variable, particularly in remote locations. Calculated lifetimes range from less than 40 hours to more than 1 month for combinations of input parameters representing the maximum and minimum values expected in the atmosphere. The longest lifetimes, representing dry climates, are sufficiently great that a particle is likely to be transported into a different climatic regime before it is removed. Short lifetimes (<2 days) are predicted only in areas where precipitation is frequent and of long duration, and where wet removal efficiencies are at the high end of the range of expected values; for these conditions, factors such as initial size distribution, concentration of accumulation mode particles, and effectiveness of dry removal mechanisms play a minor role. Conversely, lifetimes of more than 1 week are expected for cases when wet removal is inefficient and precipitation occurs infrequently. Under such conditions, other factors can play a more important role. In most cases, however, dry deposition is not expected to play a major role in the atmospheric cycle of EC.

In general, these lifetimes are sufficiently long to explain the widespread occurrence of EC observed in the atmosphere. Even the shortest lifetimes are

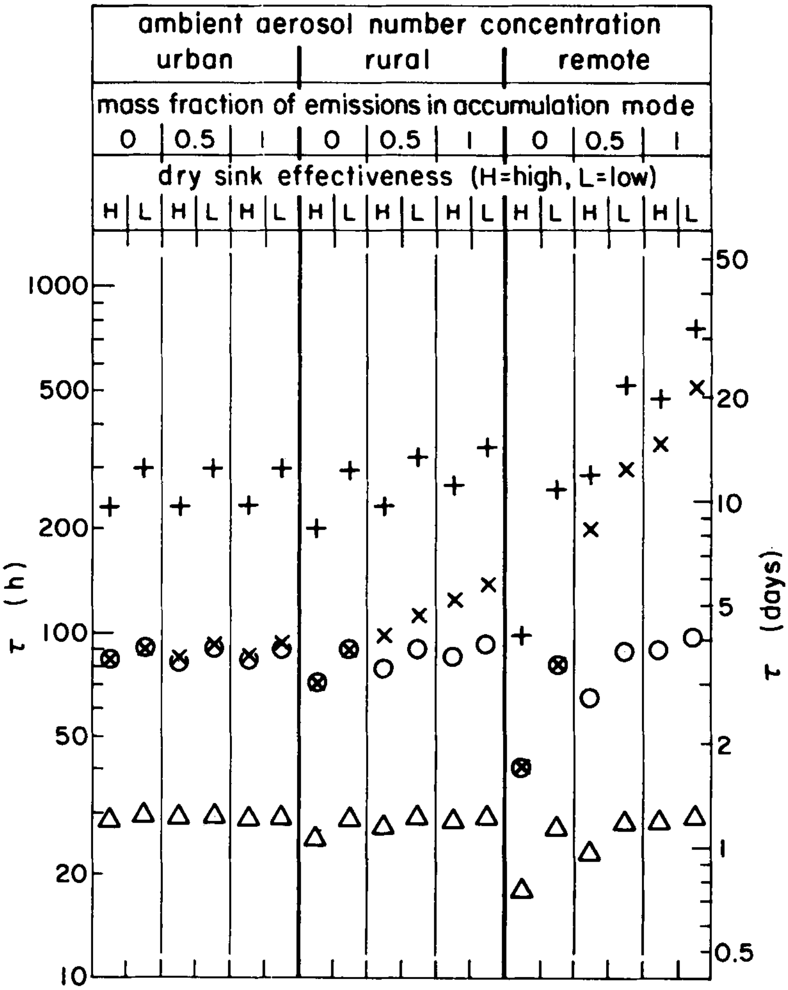


Fig. 5. Atmospheric lifetime of elemental carbon in winter (△,×) and summer (○,+) for effective (△,○) and ineffective (×,+) wet removal.

long enough for urban emissions to be transported out of the cities, while under some conditions EC is predicted to be able to remain virtually undepleted for transport distances of thousands of kilometers.

Regional-scale burdens of EC are most sensitive to accumulation mode emissions outside of urban areas because of the long turnover times with respect to both coagulation and wet deposition in this case. Local deposition rates, on the other hand, are highest for nuclei-mode emissions, particularly in remote areas where the lifetime is most sensitive to the initial size distribution.

These calculated lifetimes are based on three key assumptions for which experimental verification is necessary: (i) that the dry deposition velocities are appropriate; (ii) that collisions of EC with hygroscopic, accumulation mode particles result in particles that are efficient cloud condensation nuclei; and (iii) that collisions between nuclei mode EC and cloud droplets result in coalescence. If true, then clouds and precipitation can be as great a controlling factor in the atmospheric cycles of insoluble, initially hygrophobic particles as they are for hygroscopic compounds.

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7. Appendix A

The following is a definition of symbols used in the text and their dimensions.

f_a = mass fraction of emissions in accumulation mode
F = transfer flux between reservoirs, $ML^{-2}T^{-1}$
H = depth of mixed layer of atmosphere, or scale height, L
K = coagulation constant, L^3T^{-1}
L = cloud liquid water content, ML^{-3}
M = mass concentration ML^{-3}
= column burden, ML^{-2} (Figs. 2, 4; Appendix B)
N = number concentration, L^{-3}
P = precipitation rate, $M^{-2}T^{-1}$
Q = emission rate, $ML^{-2}T^{-1}$
R = removal rate, $ML^{-2}T^{-1}$
t_s = in-cloud scavenging time, T
T_{clear} = average time interval for an air parcel between clouds, T
T_{dry} = average time for an air parcel between precipitation events, T
V = aerosol volume concentration
V_d = dry deposition velocity, LT^{-1}
W = washout ratio = X_p/X_a
X = mass mixing ratio
α = fraction of the time that a particle is in a cloud
β = fraction of the time that a particle is in a precipitating cloud
ρ_a = density of air, ML^{-3}
σ_{sp} = coefficient of extinction due to scattering by particles, L^{-1}
τ = turnover time, residence time, T

Subscripts

n = nuclei mode
a = accumulation mode, air
c = coagulation, cloud
D = diffusion, droplet
d = dry
p = precipitation
w = wet
1 = externally-mixed, nuclei mode
2 = externally-mixed, accumulation mode
3 = internally-mixed, nuclei mode
4 = internally-mixed, accumulation mode

8. Appendix B. Analytical solution of simplified mechanistic model

The differential equations describing the simplified mechanistic model (Fig. 4) can be written as:

$$\frac{dM_1}{dt} = (1 - f_a)Q - \frac{1}{\tau_1}M_1 \tag{B1}$$

$$\frac{dM_2}{dt} = f_a Q - \frac{1}{\tau_2}M_2 \tag{B2}$$

$$\frac{dM_4}{dt} = \frac{1}{\tau_{c1}}M_1 + \frac{1}{\tau_{c2}}M_2 - \frac{1}{\tau_4}M_4 \tag{B3}$$

where

$$\frac{1}{\tau_1} = \frac{1}{\tau_{w1}} + \frac{1}{\tau_{d1}} + \frac{1}{\tau_{c1}} \tag{B4}$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_{w2}} + \frac{1}{\tau_{d2}} + \frac{1}{\tau_{c2}} \tag{B5}$$

$$\frac{1}{\tau_4} = \frac{1}{\tau_{w4}} + \frac{1}{\tau_{d4}}. \tag{B6}$$

The steady-state solutions ($t \to \infty$) to these equations are

$$M_1 = (1 - f_a)Q\,\tau_1 \tag{B7}$$

$$M_2 = f_a\,Q\,\tau_2 \tag{B8}$$

$$M_4 = M_1\frac{\tau_4}{\tau_{c1}} + M_2\frac{\tau_4}{\tau_{c2}} \tag{B9}$$

These equations can be combined to yield expressions for the wet and dry turnover times for the entire system, which can in turn be combined to yield the expression for the overall lifetime, τ:

$$\tau_w = \frac{M_1 + M_2 + M_4}{R_{w1} + R_{w2} + R_{w4}} = \frac{(1-f_a)\,\tau_1 + (1-f_a)\dfrac{\tau_1\tau_4}{\tau_{c1}} + f_a\,\tau_2 + f_a\dfrac{\tau_2\tau_4}{\tau_{c2}}}{(1-f_a)\dfrac{\tau_1}{\tau_{w1}} + (1-f_a)\dfrac{\tau_1\tau_4}{\tau_{c1}\tau_{w4}} + f_a\dfrac{\tau_2}{\tau_{w2}} + f_a\dfrac{\tau_2\tau_4}{\tau_{c2}\tau_{w4}}} \tag{B10}$$

$$\tau_d = \frac{M_1 + M_2 + M_4}{R_{d1} + R_{d2} + R_{d4}} = \frac{(1-f_a)\,\tau_1 + (1-f_a)\dfrac{\tau_1\tau_4}{\tau_{c1}} + f_a\,\tau_2 + f_a\dfrac{\tau_2\tau_4}{\tau_{c2}}}{(1-f_a)\dfrac{\tau_1}{\tau_{d1}} + (1-f_a)\dfrac{\tau_1\tau_4}{\tau_{c1}\tau_{d4}} + f_a\dfrac{\tau_2}{\tau_{d2}} + f_a\dfrac{\tau_2\tau_4}{\tau_{c2}\tau_{d4}}} \tag{B11}$$

$$\tau = \frac{1}{\dfrac{1}{\tau_w} + \dfrac{1}{\tau_d}} \tag{B12}$$

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