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**Soot in the Stratosphere:
The Impact of Current and HSCT Aircraft Emissions**

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SOOT IN THE STRATOSPHERE: THE IMPACT OF CURRENT AND HSCT AIRCRAFT EMISSIONS

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Abstract

One of the trace components of emissions from aircraft engines and other combustion sources are soot particles. These particles are strongly absorbing in the visible and IR spectra, may act as condensation nuclei, and may provide a large surface area for the catalytic promotion of gas-phase chemical reactions. Soot is found throughout the troposphere, even at remote locations, and also in the stratosphere. Present techniques do not allow an unambiguous identification of the sources. This paper discusses the emission of soot from existing and proposed aircraft and the contribution of this soot to concentrations observed in the troposphere and stratosphere. We consider the implications of these emissions for issues in stratospheric physics and chemistry.

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Introduction

"Soot" is a ubiquitous component of all combustion emissions. It is usually found as very small particles of complex morphology, containing an underlying structure of carbon in a graphitized form. The particle sizes at the source are frequently measured in hundreds of Angstrom units: after a short residence time in the atmosphere, the elementary particles may have coalesced into agglomerates of typical dimension 0.01 to 0.1 micrometer.⁽¹⁾ Other species may be associated with the soot particle: adsorbed organic compounds, accreted sulfur species, water, etc. The soot particle *per se* does not have a unique composition, size, shape, or other characteristic other than its graphitic carbon core. This core is strongly absorbing in the visible and infrared spectral regions, due to the partially mobile electrons in the carbon ring structure.⁽²⁾ The optical absorption is quantitatively proportional to the number of these carbon atoms, and thus to the mass of carbon present as "soot". A measure of the optical absorption can be converted directly to a mass of carbon present in a chemically identifiable form.⁽³⁾ No other material commonly found in the atmosphere has as large an optical absorption cross-section as that of soot: approximately 10 m² per gram at 550 nm in the visible spectrum. Mineral dust has an absorption cross-section approximately three orders of magnitude smaller than that of soot. Only in the most remote desert environments does the concentration of dust exceed the concentration of soot by factors of 1000 or more: the atmospheric lifetime of dust is relatively short, due to the larger particle size, and dust is more efficiently removed from the atmosphere than soot. The majority of samples show dust-related optical absorptions of less than 5 to 10 percent of the total absorption. Thus, the optical absorption of a sample of atmospheric aerosol, either collected on a filter or measured *in situ*, may be primarily attributed to the soot content of that aerosol sample.

Tropospheric sources of soot

Soot is emitted from all combustion processes known except the burning of non-carbonaceous fuels in CO₂-free air. It results from the reduction and partial pyrolysis of fuel fragments at the periphery of the combustion process. The emission factor for soot may be defined as the mass rate of emission of carbon in a soot particulate form, measured in the exhaust stream, divided by the mass rate of consumption of carbon in the fuel. This emission factor can vary over a very wide range, even for combustors of similar nature: thus, the factor is usually presented on a logarithmic scale. An emission factor of 10⁻³ represents the emission of one gram of carbon as soot, per kilogram of carbon consumed in the fuel. Emission factors range from 10⁻¹, for the conflagration of asphaltic materials, to 10⁻³ to 10⁻⁴ for diesel engines, from 10⁻⁴ to 10⁻⁵ for gasoline-powered automobiles, to less than 10⁻⁶ for the controlled combustion of natural gas in large industrial installations.⁽⁴⁾ The emission factor for soot is a good indicator of the "quality" of combustion: the emission of soot from an acetylene torch may be varied by four orders of magnitude by changing the oxygen supply rate, **without** changing the rate of consumption of carbon in the fixed acetylene flow.

Soot is emitted from essentially all fuel-consuming anthropogenic activities, including point sources (e.g. power stations), ground-level mobile sources (e.g. vehicles), agricultural burning, and aircraft traffic. Natural sources include forest fires and other conflagrations. This soot is dispersed throughout the troposphere, and is eventually removed by wet and dry deposition.^(5,6) There are no known mechanisms for the formation of soot in the atmosphere from gaseous precursors, nor for its effective destruction in the atmosphere by reactions. Oxidative destruction by ozone does occur, and can be simulated in the laboratory: however, the rate under atmospheric conditions is extremely slow. The concentration of soot measured at a remote location is a balance between the upwind source strength, the dispersion in transit, and the rate of deposition.

Soot has been measured at all points in the troposphere at which samples have been taken. Concentrations range from tens of micrograms per cubic meter in polluted cities, to hundreds of nanograms per cubic meter in rural areas, to tens of nanograms per cubic meter at remote loca-

tions, to fractions of a nanogram per cubic meter at the South Pole Observatory.⁽⁷⁾ These results are reasonably well explained on a broad scale by general circulation models incorporating anthropogenic sources, meteorological pathways, and wet and dry deposition terms.

Deep convective storms and other forms of troposphere-stratosphere exchange can transfer some of this tropospheric soot into the stratosphere. The aerosol's lifetime in the stratosphere will be much longer than its lifetime in the troposphere. Thus, another equilibrium will be reached in which the rate of destruction and loss of soot in the stratosphere equals its rate of injection from the troposphere: **in the absence of in-stratosphere sources.**

Stratospheric sources of soot

In addition to the injection of soot from the troposphere, there are source terms for the production of soot in the stratosphere. These are primarily aircraft emissions and the burn-up of infalling meteoritic material. This latter source of stratospheric soot is not well understood at present, and it can be noted that even the so-called 'carbonaceous' chondrites contain only a small fraction of their mass as carbon, and that the fractionation of this during burn-up into particulate soot versus CO₂ is likely to be small. The remainder of this paper will concentrate on aircraft emissions as a stratospheric source of soot, both emissions from existing aircraft and emission scenarios from projected fleets in the future.

Aircraft emissions - present

The emission factors for particulate soot from existing aircraft engines operating under cruise conditions are believed to range from 10⁻⁴ to 10⁻⁵, i.e. emission indices of from 0.1 to 0.01 grams of soot per kilogram of carbon consumed in the fuel. The present fleet of commercial aircraft consumes approximately 1.5 * 10¹⁴ grams of fuel per year⁽⁸⁾, leading to total emissions of soot of magnitude 10⁹ to 10¹⁰ grams of soot per year. Most of these emissions are released at the aircraft cruising altitudes: although the emission factors may be much greater at take-off, the fuel consumed during take-off represents only a small fraction of total fuel consumption.

For many flight routes, the aircraft is operating at all times in the upper troposphere and the emissions are subject to tropospheric removal

processes. However, for some flight routes the aircraft are operating in the stratosphere for a substantial fraction of the time. This is the case for transpolar routes flown in wintertime, when the aircraft may be flying above the tropopause located at some 10 km altitude at far-north latitudes. It has been estimated that approximately 15 percent of present commercial aviation fuel consumption occurs in the stratosphere, defined by a combination of latitude, season, flight altitude, and the low level of the tropopause over the winter Arctic.⁽⁹⁾ Adding emissions from other aviation, we may estimate that the amount of soot emitted directly into the stratosphere is in the range of $2 * 10^8$ to $2 * 10^9$ grams of carbon per year.

Aircraft emissions - future

Various scenarios have been proposed for a fleet of High-Speed Civil Transport aircraft to be deployed in the future. The scenarios depict the majority of aircraft operations to be conducted above the tropopause along the most likely routes: thus, most HSCT exhaust will be emitted directly into the stratosphere. The projected fuel consumption is on the order of $7 * 10^{13}$ grams per year. Considerable attention has been directed towards the needs for reduced exhaust emission indices for critical pollutant species, primarily the oxides of nitrogen. Candidate engines have been designed, but no full-scale prototypes have been constructed and tested as of this date. Emission indices for "major" species (e.g. NO_x) and "minor" species (e.g. soot, or "smoke") have been estimated, based on previous experience. However, the new designs are sufficiently different from existing aircraft engines that one cannot automatically assume an extrapolation of performance in terms of the emission of "minor" species. The production of these pollutants is very much a secondary effect, affecting only one in 10,000 of the fuel molecules, and so a relatively small change in engine design may result in a large change in soot emission without noticeable effects on NO_x production or energy efficiency.

Statements have been made that the proposed engine designs for the HSCT fleet will achieve soot emission indices of 0.01 grams soot per kilogram of fuel, i.e., an emission factor of 10^{-5} . This would result in the net emission of approximately $7 * 10^8$ grams of carbon per year from these fleet scenarios.

Note, however, that the HSCT emissions are released in the stratosphere: an estimated HSCT fleet emission of $7 * 10^8$ g/yr may be compared with the estimate of present emission from existing aviation in the range of 2 to $20 * 10^8$ g/yr of soot directly emitted in the stratosphere. HSCT emissions will probably have a significant impact on the budget of soot in the stratosphere.

Another factor in comparing the impact of HSCT emissions with existing inputs of pollutants is that the HSCT exhaust is fresh at the point of injection into the stratosphere. Although optical and bulk-compositional properties are generally unaffected by aging in the atmosphere, the surface properties are definitely modified following exposure to oxygen, adsorbable organics, water, sulfur and other species in the ambient atmosphere. Thus, soot from tropospheric sources that is gradually mixed into the stratosphere may have quite different behavior than fresh engine exhaust in terms of acting as a cloud condensation nucleus, catalytically promoting reactions between gas-phase species impinging on its surface, etc. For this reason, the relationship of **quantity** of soot between existing sources and HSCT emissions may be less important than the **relative activity or effect**.

Measurements of soot in the stratosphere

A small number of measurements of soot concentrations in the stratosphere have been made, and this work is ongoing. The samples are collected by impaction onto a substrate exposed to the ambient air stream on an aircraft wingtip, and are returned to the laboratory to measure the optical absorption. Due to the very low concentrations of soot in the stratosphere, long exposure times are necessary in order to collect enough material for analysis. The optical absorption is due to the presence of both soot and mineral dust. In the troposphere, optical absorption due to dust is usually small compared to that of soot except in remote desert environments. In the stratosphere, this may not necessarily be the case. Dust injected into the stratosphere by volcanic eruptions may have a long residence time, and its concentration may be sufficiently large relative to the concentration of soot that the two species' contributions to optical absorption may be comparable. While it is difficult to separate these contributions based solely on a "macroscopic" measurement of absorption, it is easy to distinguish these two materials microscopically. The size of soot particles is usually smaller than 0.1

micron, with a characteristic agglomerate morphology, while volcanic dust particles are usually larger than 1 micron in size, with a mineral-crystal appearance. In addition, microprobe XRF techniques can identify the chemical composition of individual particles, and can distinguish carbon-rich particles from silicon-rich particles. However, these microscopic techniques are only semi-quantitative in terms of estimating the concentration of material in the sampled air stream, and they must be used in conjunction with total aerosol analyses.

Because of the uncertainty in the assignment of optical absorption to a particular species, the stratospheric measurements may be reported as a measurement of an absorption coefficient. This data may subsequently be converted to a species mass concentration if the absorption cross-sections are known, and the fractional contributions of the various species are determined from microscopic examination of a representative population of collected particles.

The measurements performed before the eruptions of Mount St. Helens and El Chichon^(10,11) yielded an estimate of the optical absorption coefficient of $5 \pm 4 \times 10^{-9} \text{ m}^{-1}$. This result was obtained from the analysis of impactors flown on the wingtip of the NASA ER-2 high altitude research aircraft. Sampling was resumed in 1990, using a similar technique, and the results to date indicate an absorption coefficient of $2 \pm 0.9 \times 10^{-9} \text{ m}^{-1}$. The earlier data had estimated uncertainties of almost 100 percent for each measurement: the samples were collected over short periods of time, and the small amount of material produced an extremely small change in the transmission of light through the sample. The current samples are collected for periods of 30 to 40 hours: being exposed, sealed, and then re-exposed from one flight to the next until sufficient sampling time has accumulated. Each measurement has an uncertainty of from 20 to 40 percent, which is smaller than the spread in results from one sample to the next. Thus, we feel that the present results are consistent with the earlier data, and indicate that the general scale of optical absorption coefficient in the stratosphere at altitudes from 18 to 21 km is approximately $2 \times 10^{-9} \text{ m}^{-1}$, under conditions not substantially perturbed by volcanic eruptions.

Assuming this absorption coefficient to be due only to the presence of soot, then dividing the result by an absorption cross-section of 10

m^2/gram yields an upper bound for the soot concentration of 0.2 nanograms per geometric cubic meter at altitude. At sea level, this would become approximately 3 nanograms per standard cubic meter. This result is comparable with measurements of soot concentrations at remote surface locations. Concentrations of 1-5 ng/SCM are measured over the southern Pacific Ocean: concentrations of 5 ng/SCM are measured at 3 km altitude at the Mauna Loa Observatory, when air mass trajectories do **not** bring emissions directly from industrialized Asia. At the South Pole, concentrations of soot may be as high as 5 ng/SCM during austral summer, but fall to less than 0.1 ng/SCM during austral winter.

The stratosphere sampled over the Northern Hemisphere contains at least ten times more soot than the winter troposphere at the South Pole. The stratosphere is polluted relative to the cleanest portions of the global troposphere.

Modelling

We may construct an extremely simple model to predict concentrations of soot in the stratosphere based on estimates of soot inputs to the stratosphere. This model shows reasonable agreement with the measurements reported above.

The surface area of the planet is approximately $5 \times 10^{14} \text{ m}^2$. A layer in the stratosphere of thickness 4 km contains a volume of approximately $2 \times 10^{18} \text{ m}^3$. If 10^9 grams of soot are dispersed in this layer, the resultant concentration will be 0.5 nanograms per geometric cubic meter. If the aerosol is removed with a mean residence time of one year, an input rate of 10^9 grams of soot per year will maintain the concentration in the layer.

The parameters used in this simple model may be plausibly varied by factors of two, but probably not by factors of ten. The predicted concentration is in the same range as the actual measurements.

Future emission scenarios

Certain projections predict a doubling of fuel use by the subsonic commercial aviation fleet within the next 25 years. It is not clear that substantial improvements in soot emission factor will be required, and thus we may estimate that this scenario would double the subsonic fleet soot injection in the stratosphere from the present value of approximately 1 to 2×10^9 grams per year. The proposed HSCT fleet emissions would

contribute an additional quantity of approximately 1×10^9 grams of soot per year. Thus, the direct emission of soot in the stratosphere would treble under this scenario, and we would predict a trebling of the concentration to a probable value on the order of 10 nanograms per standard cubic meter.

While the direct optical effects of this material may be small, the consequences for heterogeneous physics and chemistry may be substantial. The freshly-emitted soot has a large active surface area that may catalytically promote chemical reactions between gaseous species, and the particles may also act as cloud condensation nuclei. Some fresh combustion soot samples may be measured to have an active surface area of 1000 m² per gram, due to their highly microporous structure. A concentration of 10 nanograms per geometric cubic meter of this material would provide an active surface area of 10⁻² m² per geometric cubic meter of the stratospheric atmosphere. We combine this with a value for the mean free path of air molecules of 2×10^{-5} cm., and a collision frequency of 10⁹ per second: the result is an estimate that this concentration of fresh soot would provide every gas molecule in this region of the stratosphere with a collision on a surface that is possibly catalytically active, at a rate of order 1 per second. This is a result that needs to be input to models of heterogeneous atmospheric chemistry in order to determine the possible impact of soot emissions on the composition of the stratosphere.

Summary

Soot is found in the stratosphere at present in concentrations that are small but measurable. The most probable sources of this material are aircraft exhaust emissions from that portion of flight routes in the stratosphere (e.g. transpolar routes in wintertime); and exchange of polluted air from the troposphere. Since concentrations in the stratosphere exceed those measured in the cleanest regions of the troposphere, it is possible that current aircraft emissions are the dominant source of stratospheric soot. A simple emission/dispersion model yields an estimate of the aircraft contribution that is in agreement with the observations.

The concentration of soot is probably too low to cause any detectable direct optical effects, even though its optical absorption cross-section is large. However, the soot particles may act as

condensation nuclei, and their surfaces may catalytically promote chemical reactions between gas species in the stratosphere.

We estimate that emissions from the proposed fleet of High-Speed Civil Transport stratospheric aircraft would lead to an increase in the concentration of soot in the stratosphere by a factor of two or three.

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