Atmos. Chem. Phys. Discuss., 12, C9099–C9109, 2012
www.atmos-chem-phys-discuss.net/12/C9099/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Are black carbon and soot the same?" *by* P. R. Buseck et al.

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Received and published: 7 November 2012

Interactive comment on "Are black carbon and soot the same?" *by* P. R. Buseck et al.: Disagreement on proposed nomenclature

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Buseck et al (2012) raise important issues of terminology in dealing with light-absorbing carbonaceous aerosols. Although some might argue that the points raised by Buseck et al. are "only" terminology or nomenclature, not science, we would respond that terminology is essential to doing and communicating and advancing science. A rose by any other name would smell as sweet, but still it useful to have a mutually agreed on definition of "rose." So, although, as elaborated below, we disagree with the nomenclature suggested by Buseck et al., we applaud them for raising an important issue. We wholly concur with their statement that "confusion can be avoided if terms are defined and widely understood," and it is for that reason that we submit this Interactive Comment.

The principal issue raised by Buseck et al. is the distinction among substances that have been variously called "soot," "elemental carbon," and "black carbon." Other terms are used as well, often associated with particular instruments or measurement techniques, such as "refractory back carbon," "brown carbon," and "absorbing aerosol," and amounts of substances so named are often reported quantitatively. This profusion of names and the resultant need for precise definitions has been noted previously by Bond and Bergstrom (2006) and Andreae and Gelencsér (2006), both of which studies provided extensive reviews of the various types of light absorbing carbonaceous substances and associated terminology. Both sets of investigators used, and to some extent advocated the use of, the term "light absorbing carbon" as a general term to avoid confusion with various definitions that are operationally based on specific measurement techniques.

As widely recognized, light-absorbing carbonaceous substances in atmospheric aerosols absorb shortwave (solar) radiation and thus exert a direct radiative influence on climate and climate change and also various indirect effects through modification heating rates and atmospheric stability and modification of the cloud nucleating properties of aerosol particles. It is important therefore in the context of understanding the influences on climate change and representing them in models that there be accurate understanding of the physical, chemical, and optical properties of atmospheric aerosols containing these substances and the processes that control these properties and the amounts and distributions of these aerosols. Characterization of these substances and understanding these processes are important as well from perspectives of visibility degradation, impairment of health through inhalation, and degradation of materials through deposition. Numerous methods have been developed and employed over the years to characterize and quantify these substances, but as these methods exploit different properties of these substances and thus do not necessarily measure the same thing, differences arise among quantities, which may even have the same name, when determined by different methods. This is very cross-disciplinary science, which, to some extent, contributes to divergent terminologies but is all the more reason for consistent terminology across disciplines, the better to enhance communication and understanding.

In their discussion paper Buseck et al. raise several distinct points. First they take issue with the widely employed term "black carbon" (BC) used to denote light-absorbing carbon in atmospheric aerosol particles, arguing that neither reliable samples nor standards exist for such a substance. We agree with this assessment. They observe that BC is not a well defined material and propose that the term should be restricted to light-absorbing refractory carbonaceous matter of uncertain character, an assessment with which we concur. Buseck et al. also consider the term "elemental carbon," which they suggest "should be restricted to describing the high-T[emperature] component of thermal-optical analysis." As a further point Buseck et al. advance the term nanosphere soot, which they abbreviate as "ns-soot," to denote specifically "particles that consist of nanospheres, typically with diameters $<$100 nm, that possess distinct structures of concentrically wrapped, graphene-like layers of carbon and with grape-like (acinoform) morphologies."

We suggest that these are separable concepts, and the failure to realize this has led to much of the confusion in the existing terminology. Perhaps separating them can point to a path toward a broadly acceptable and accepted nomenclature for light-absorbing carbonaceous material in atmospheric aerosols. In brief we suggest that black carbon is a category of substances consisting mostly of carbon and having a very low reflectivity throughout the visible spectrum and thus appearing black. Elemental carbon is a set of substances consisting entirely (or almost entirely) of carbon, not all of which are highly absorbing throughout the visible. Soot, which encompasses a broad set of substances produced by incomplete combustion of carbonaceous fuel, is defined by formation mechanism, not optical properties, composition, or structure. These terms refer, respectively, to optical properties, composition, and formation process, which are independent concepts. We elaborate on these points below.

First, consider the term "black carbon." "Black" means completely absorbing of light, which implies a reflectivity of zero, an absorptivity of unity, and an emissivity of unity. Of course this is an ideal, a Platonic form. An object that has a spectrally uniform absorptivity of 0.95 is still considered "black" even though it is not quite black.

Similarly we all know what carbon is, the sixth element of the periodic chart, atomic weight 12. Nonetheless there is an inherent ambiguity in what is meant by "carbon" or for that matter any element. The term "carbon" (or hydrogen or silicon, etc.) can sometimes refer to the "elemental" material, that is, not bonded to other elements in compounds, or alternatively to the element within a chemical compound. Hence the term "elemental carbon" is used to denote carbon that is not bonded to other substances. Of course the term "elemental" is also an ideal, a limiting Platonic form. A piece of aluminum, for example, is considered to be elemental, even though it has an oxide layer over its entire surface that passivates it from reacting with oxygen in air. But for a sufficiently small piece of aluminum (nanometer) for which the influence of the surface is significant for the entire material, the question of whether it is still "elemental" needs to be rethought. Examples of elemental carbon are diamond, graphite, amorphous carbon, C_{60} ("buckyballs"), carbon nanotubes, all of which are different allotropes of elemental carbon. Carbon is hardly unique in having multiple allotropes; sulfur and phosphorus, for example, similarly exhibit multiple solid allotropic forms. However, it must be recognized that in addition to this formal definition, there are widely used operational definitions of "elemental carbon" that may not be entirely consonant with it.

Putting these concepts together provides a very good sense of what is meant by "black carbon" and "elemental carbon". Black carbon is carbon that is black. This definition would seem to concur with that of Moosmüller et al. (2009), who operationally defined BC as "carbonaceous material with a deep black appearance, which is caused by a significant, non-zero imaginary part ... of the refractive index that is wavelength independent over the visible and near-visible spectral regions." Neither of these definitions assumes or implies anything regarding the formation process. Black carbon might be formed by incomplete combustion of a carbonaceous fuel. But it can also be formed by pouring concentrated sulfuric acid on sugar, which dehydrates the sugar (extracts the water from the carbohydrate) leaving behind black carbon. It can be made in the kitchen: heat sugar on the stove, again driving out the water and leaving black carbon behind. It can be formed by heating wood in the absence of oxygen, making charcoal. It can be formed by burying vegetation in soil for millions of years, forming coal. All of these substances contain black carbon. If that is *all* that they contain (no appreciable amounts of other elements), they *are* black carbon, and they are also elemental carbon.

Similarly the term "elemental carbon" already has a formal definition; it is a substance containing only carbon, carbon that is not bound to other elements, but which may be present in one or more of multiple allotropic forms. It is thus clear that the term "elemental carbon," like the term "black carbon," denotes a set of possible materials and is not restrictive in specifying a given material with unique, well defined optical, structural, or other properties. This formal definition, which cuts across multiple disciplines, contrasts with the operational definition of "elemental carbon" proposed by Buseck et al. and other such operational definitions.

The formal definitions of black carbon and elemental carbon given above are independent of measurement techniques and formation process. Black carbon absorbs light, and thus measurement of light absorption would seem to be an approach to determination of the amount (mass) of black carbon. But such an approach is fraught with pitfalls, such as the dependence of absorption on particle size, shadowing in the light path, presence and nature of and state of mixing with other material, and the like. Hence the wide (order of magnitude) range of specific absorption coefficients (absorption coefficient per mass, unit $\mathrm{m}^2\ \mathrm{g}^{-1}$) for black carbon reported in the literature (e.g., Liousse et al., 1993; Petzold et al., 1997; Bond and Bergstrom, 2006, Moosmüller et al., 2009). It is clear from this widespread divergence in properties that BC is not, as Buseck et al. note, a substance for which there are reliable standards and samples. Nor does it seem possible, for the above reasons, that a single standard reference "black carbon" could be developed. However, it is clear that black carbon is a concept and a terminology that is useful to retain to refer to strongly light-absorbing material that consists entirely or primarily of carbon. Similarly, because elemental carbon can consist of multiple different kinds of materials (allotropes) that may have widely differing properties (e.g., graphite amorphous carbon, carbon nanospheres), an operational definition of "elemental carbon" such as that proposed by Buseck et al. might lead to a difference between the mass of "elemental carbon" so determined and the actual mass of elemental carbon in a sample.

We turn finally to Buseck et al.'s suggestion to denote as "nanosphere soot" the particles that they have characterized as "nanospheres, typically with diameters $<$100 nm, that possess distinct structures of concentrically wrapped, graphene-like layers of carbon and with grape-like (acinoform) morphologies." These particles have been shown to be present in atmospheric aerosols at a variety of locations and have been identified thus far as having been formed only as the products of incomplete combustion of carbonaceous fuels. However as the defining property of such particles is structural, it seems inappropriate to assign to them a name that implies a formation process. Additionally, incomplete combustion of carbonaceous fuel might under some circumstances produce nanosphere soot particles having composition and structure entirely different from those particles, i.e., concentrically wrapped, graphene-like layers of carbon, to which Buseck et al. would attach the name nanosphere soot. Thus the term "nanosphere soot" is neither comprehensive nor exclusive.

The meaning of the word "soot," which comes from the Old English, has stayed remarkably constant over time. The Oxford English Dictionary (1933), which cites its first use in the eighth century of the common era, defines soot as "a black carbonaceous substance or deposit consisting of fine particles formed by the combustion of coal, wood, oil, or other fuel," a definition that would seem to conform very well to current common and technical usage. The American Meteorological Society Glossary of Meteorology (Glickman, 2000) gives a similar definition: "Fine particulate mass, mostly carbon, that is emitted as a result of incomplete fuel combustion." The Glossary of Atmospheric Terms of the International Union of Pure and Applied Chemistry (Calvert, 1990) offers a similar definition: "Aggregations of black carbonaceous particles formed during incomplete combustion and which are deposited before being emitted from a chimney." A similar definition is offered by Andreae and Gelencsér (2006): A black, blackish or brown substance formed by combustion, present in the atmosphere as fine particles ("soot particles"), or adhering to the sides of the chimney or pipe conveying the smoke. A somewhat more differentiated definition was offered by the participants of the 1994 Dahlem Conference on Aerosol Forcing of Climate (Charlson and Heintzenberg, 1995):

> *Soot particles*: Particles formed during the quenching of gases at the outer edge of flames of organic vapors, consisting predominantly of carbon, with lesser amounts of oxygen and hydrogen present as carboxyl and phenolic groups and exhibiting an imperfect graphitic crystal structure. Soot particles are typically present in the atmosphere as aggregates of platelets having diameters of some tens of nanometers. Depending on the formation process, soot particles can have oily surface coatings or, alternatively, exhibit a high surface density of sites for adsorption of gases; *cf.* Black carbon, Charcoal.

It is clear from these several definitions that an essential feature of the definition is that soot is formed in conjunction with combustion; i.e., that soot is a consequence of a *process*, combustion of carbonaceous fuels. Moreover, combustion of different fuels under different conditions can yield soots with different properties, as opposed to a specific material with certain characteristic structural properties.

It is clear as well from current technical use of the word "soot" that what is denoted as soot does not consist solely of black carbon, or elemental carbon, but can and generally does contain other substances. Thus in a recent study, Vander Wal et al. (2010) write: "Soot is a highly variable material. Physically the nanostructure can range from amorphous to graphitic to fullerenic. Chemically nearly any element may be included, while the surface functional groups are predominantly oxygen-based." These investigators present high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy analyses of soot collected from plant and industrial scale oil-fired boilers, a diesel engine, a jet engine and a wildfire, finding that soots from different sources exhibit different physical and chemical properties. They report that soots from these emission source classes may be differentiated physically on the basis of carbon lamella length, mean separation and tortuosity and chemically by elemental composition and surface functional groups.

A quite differentiated picture of what they refer to as "mature soot" is presented by Cain et al. (2010) who characterize it as a fractal aggregate of small primary particles, mostly spherical, composed primarily of large polycyclic aromatic hydrocarbons with carbon bonded in their aromatic network, and having a typical atomic C/H ratio of 8:1. These investigators note in contrast that nascent soot particles $\sim$10 nm in diameter extracted directly from flames are liquid-like, are far from carbonized, and can have internal structure and compositions notably different from one another, depending on the particle size, age, and the gas-phase chemical environment in which they were formed and grew.

Andreae and Gelencsér (2006) use the term "soot carbon" to refer to "carbon particles with the morphological and chemical properties typical of soot particles from combustion." They characterize these particles as "aggregates of spherules made of graphene layers, consisting almost purely of carbon, with minor amounts of bound heteroelements, especially hydrogen and oxygen." They go on to explicitly distinguish this material from the material commonly denoted as soot by stating that the material so defined "does not include the organic substances (oils, etc.) frequently present in or on combustion particles."

Based on these examples of recent work, and a rich older literature, it is clear that what is referred to in the technical literature as soot can have highly varied physical and chemical properties. Consequently it would seem that a term such as "nanosphere soot" would encompass much more variety of properties and composition than is exhibited by the well defined and exquisitely characterized nanospheres shown by Buseck et al. in their Figure 7. Based on this characterization we suggest that these particles might be denoted much more precisely by a term something like "nested graphitic-like spherical annuli" rather than "nanosphere soot." In principle, as well, such nested graphitic-like spherical annuli might, someday, be produced, or be found to be produced, by some process other than incomplete combustion; should that be the case, characterizing such particles as soot, which term is restricted to material produced by incomplete combustion of carbonaceous fuel, would turn out to be inappropriate on that ground as well.

In summary, we feel that Buseck et al., in their discussion paper, have raised important issues. We concur with them that "black carbon" is not a well defined substance and consequently that this term not be used to refer to a specific substance, although it might usefully be employed to denote substances that are carbonaceous and absorb strongly and uniformly throughout the visible and near visible spectrum, as discussed above. We consider the term "elemental carbon" to be useful in describing material that consists entirely or almost entirely of carbon that is not chemically bonded to other elements; we disagree with the recommendation of Buseck et al. that this term be used

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or restricted to the high temperature component of thermal-optical analysis. Finally, we take issue with the proposal of Buseck et al. to use the term "nanosphere soot" to denote the substance that they have characterized as nested graphitic-like spherical annuli sometimes present in combustion-generated aerosol particles.

To conclude, we agree with Buseck et al. in the importance of precise working definitions of quantities reported. Thus we think it is essential that investigators report precisely the measurement that is being made and the conversion from the measured quantity to the reported quantity. This would allow the measurements to be used by other investigators with confidence in understanding of the reported quantity, irrespective of its name.

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