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Uncertainties in data on organic aerosols

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ABSTRACT

Organic aerosols are gaining increasing attention because of their importance in studies of radiative forcing of climate. However, there is a potential for large and unquantified biases in most of the published data, which has been derived using variations on the evolved gas analysis method (EGA). We argue that the magnitude of these putative uncertainties makes it impossible both to test hypotheses concerning the variation of organic carbon (OC) with altitude and to develop realistic models of radiative climate forcing.

1. Introduction

Sampling and analysis of carbonaceous aerosols is one of the most difficult challenges facing atmospheric chemists (Hering et al., 1990; Jacobson et al., 2000). Our inability to measure and characterize carbonaceous aerosols without artifacts currently prevents us from realistically modeling their impact on direct and indirect climate forcing by aerosols (NRC, 1996). In fact, the most widely-used method, evolved gas analysis (EGA, which we use here to include all thermal methods that measure an evolved gas; Cadle et al., 1980; Chow et al., 1993) has never been adequately characterized using model compounds nor has it been optimized for its current uses. Much exploratory, if qualitative, information was derived from early use of EGA on atmospheric aerosols (especially when used alongside MS and GCMS) (Schuetzle et al., 1975; Simoneit et al., 1977; Rogge et al., 1993). However, the demands on the technique have become much more quantitative as it has become necessary to assess organic aerosol impacts on atmospheric optics, cloud physics, and climate forcing. We are writing to emphasize that there are very large uncertainties in all of the published EGA data and most especially that climate modelers must be wary of using these data without adequate caveats. As we will point out, the uncertainties are so large in some data sets that organic aerosols could range from totally insignificant to absolutely dominant.

A useful case in point is Putaud et al. (2000), who seek closure between gravimetric, chemically-derived, and size-based (OPC) estimates of particulate mass for ACE-2 surface samples. They used a single quartz filter, that was analyzed via EGA. Samples were heated from 80 to 120, 120 to 220, and 220 to 340°C in a $He:O_2$ mixture, then from 340 to 650°C in pure helium to estimate 4 types of OC. Finally, to estimate black carbon, 10% oxygen was added to the helium at 650°C. Evolved gases were converted to CO_2 catalytically and detected by non-dispersive IR. The accuracy of the chemical approach depends on the accuracy of a variety of chemical analyses, including the EGA method for estimating organic carbonaceous material (OC) within particles. They derive analytical uncertainties for OC for their average marine boundary layer (MBL, -99, $+80\%$) and free tropospheric (FT, $\pm 68\%$) samples. (The asym-

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metry in the OC uncertainty derives from sampled volume measurements on parallel samplers and not from the OC analysis itself.) Although the authors present one of the most complete discussions to date of uncertainties for EGA analyses, we argue that the final uncertainties they assign to the mean fraction of OC are unrealistically low ($\pm 7\%$ and $\pm 13\%$ for the MBL and FT, respectively). We note that numerous other authors have given no estimate *at all* of the overall uncertainty (Malm et al., 1994; Liousse et al., 1996; Novakov et al., 1997, 2000; Hobbs, 1999), making it even more difficult to realistically apply their data sets.

Putaud et al. (2000) state, "In the unperturbed MBL, the aerosol composition ($\pm$the absolute uncertainty in the contribution) was ... $20(\pm 7)\%$ OC. In the unperturbed FT, OC ... accounted for $43(\pm 13)\%$ ...." We do not believe their results could be accurate to the $\pm 30\%$ of mean OC that these numbers imply. At issue is their "assumption that the uncertainties were random and thus add quadratically," since the part of their uncertainty due to purely random errors might be reduced by increasing the number of samples. The standard error of the mean of a population decreases as $N^{-1/2}$, but only if the assumption of randomness is fulfilled. Statistical treatments cannot reduce the uncertainty due to systematic errors or biases.

We argue that these assumptions cannot be supported for their version of the EGA analysis of organic aerosols. There are likely to be sampling and analytical biases (even the sign of which cannot be specified) that cannot be reduced by statistical methods. Among these systematic errors are their assumptions about relationships between evolution temperature and species, the molecular mass/C ratio, charring (not mentioned), and sampling artifacts (which we believe were greatly underestimated). Errors due to the EGA analysis itself, blank variability, and air volume should all be random and could contribute to reducing the uncertainty of the mean. We attempt below to estimate bounds for these systematic uncertainties.

The sampling problem (which is analogous to that for nitric acid and nitrate aerosol) involves the difficulty of separating organic vapors from particles (McDow and Huntzicker, 1990; Turpin et al., 1994). Filter media that collect particles can and do adsorb organic vapors during sampling (a *positive* artifact), after which the former vapor is indistinguishable from material that was actually particulate in the atmosphere. Some media are more prone to this positive artifact than others. Conversely, aerosol species with a modest vapor pressure can evaporate once on a filter (a *negative* artifact), thereby causing an underestimate of the true atmospheric concentration. Some authors, e.g., Novakov et al. (1997, 2000) have used a second filter (in series behind the particle filter) to estimate the positive artifact, on the assumptions that (a) the first filter did not deplete these vapors and (b) the thermodynamic conditions on the second filter are sufficiently similar to those on the first filter that their vapor collection efficiencies will be identical.

2. The evolution temperature/species relationship

While these assumptions are assailable, we note that Putaud et al. (2000) did not use a second filter, either in parallel (as described in Jacobson et al., 2000) or in series. Instead they relied on assumptions that after blank correction (a) all material evolving below 120°C was *not* from particles; (b) half of that evolving between 120 and 220°C was *not* from particles; and (c) all material evolving above 220 °C *was* from particles. Examination of Fig. 1 from Novakov et al. (1997) suggests that these assumptions are shaky at best. Novakov et al. (1997) used stacked quartz filters and subtracted the amount of evolved C on the backup filter from that on the front filter, doing so as a function of the temperature at which the C was evolved.

Three features of these thermograms should be noted. (1) Carbonaceous material begins to evolve well below 100°C, peaking at about 150°C, with substantial, unexplained differences (15–20% in area and 10–15C in peak temperature) between the prefilter and backup filter. It is not clear whether vapor collection alone is responsible for the differences, but the temperature shift suggests that different compounds are evolving from the two filters. Furthermore, particulate organic species that are in dynamic equilibrium with vapors (Pankow and Bidleman, 1991) would be driven off in this temperature range and dismissed as non-aerosol carbon (Coutant et al., 1988). (2) Between 200°C and 300°C there is sometimes a large peak from the backup filter that does not

appear on the prefilter. It accounts for roughly 50% of the carbon evolved in this range. It is conceivable that this peak is due either to evaporation of relatively volatile aerosol OC (a negative artifact) or to actual organic vapor that collected only on the second filter, due to its different thermodynamic state (P and/or T). This excess on the backup filter calls into question the very basis of the serial filter approach, and further emphasizes the difficulty in defining exactly what temperature ranges to assign to vapor-derived artifact and particles, respectively. (3) Above 220°C, as much as half the evolved C from the prefilter is also present on the backup filter and thus apparently was not derived from particles. The shape of the backup-filter thermogram in this range varied widely from sample to sample, suggesting that it was also not a pre-exposure blank. The presence of clear peaks in the backup thermogram that do not appear on the front filter calls into question the assumption by Putaud et al. that everything above this temperature on their single filter was from particles.

While we commend Novakov et al. (1997) for clearly presenting their thermograms, we must note that they provided no estimate of overall uncertainty. Their statement of the accuracy of the CO_2 analyzer ignores all other uncertainties, including the classically difficult problem of taking a small difference (the presumed OC aerosol) between two large numbers (the prefilter OC and the backup filter OC). However, the presentation of the thermograms at least allows the reader to consider the consequent uncertainties in qualitative terms. Putaud et al.'s assumptions and their single-filter sampling strategy make it possible to avoid taking the difference between two large numbers, which obviously would have revealed large uncertainties. However, it is not possible to reduce uncertainties by replacing measurements with assumptions. Based upon comparisons with the thermograms in Novakov et al. (1997), the assignment of temperature regions to vapor, OC, or EC could easily be in error by 30–50%.

3. Positive sampling artifacts

The utility of the dual-filter approach for assessing the positive artifact depends heavily on the nature of the vapor/filter interactions. One can imagine a scenario, for instance, in which strongly-adsorbing vapors are depleted by the first filter, so none adsorbs on the second. The dual-filter method would not correct for that artifact. One could also hypothesize that the quartz has a limited number of active sites; when they are saturated by the most strongly-adsorbing vapors, all the rest would pass through to the second filter. This could explain the appearance of large peaks on backup filter thermograms at different temperatures from those on the front filter. This could also explain the observation of Novakov et al. (2000) that for all but the most lightly-loaded samples, the backup filter held 20–30 ug C, regardless of the loading on the front filter. It is likely in this case that the positive artifact on the first filter would depend to some extent on the nature of the strongly-absorbing species. Finally, one could imagine that all vapors adsorb equally on both filters, so the backup is a good correction for the positive artifact on the first. That is the fundamental assumption of the dual-filter approach.

We believe that this last assumption is a risky one, at best, because the thermodynamic state of the second filter can be and often is very different from the first. It has long been recognized that pressure drops in samplers can significantly change the thermodynamic conditions therein (Junge, 1952; Biswas et al., 1987; Berner et al., 1998; McDow and Huntzicker, 1990). With low pressure impactors for instance (Biswas et al., 1987), large pressure drops result in large changes in the temperatures in the high velocity flow and lower pressures at the sampling surfaces that can cause some impacted materials to evaporate. Unfortunately, only McDow and Huntzicker (1990) address the issue of the analagous pressure changes within the matrix of filters, and none discuss possible temperature changes. It is difficult to estimate the decreased temperatures as well as the pressure drops for the tiny, irregularly shaped regions of high velocity within a quartz fiber filter.

Two simple cases can be described that bound the problem: isothermal pressure change and adiabatic expansion. If the thermal conductivity of the filter and its support are high and the air flowing through the filter is kept at ambient temperature, the only change is the pressure drop across the filter. However, if there is no heat exchange (which is unrealistic, but is a definable limiting case),

adiabatic cooling occurs. In both instances, the index needed for estimating the magnitude of the changes in thermodynamic conditions is the pressure drop. Unfortunately, none of the cited papers reporting concentrations of OC aerosol provide data on the pressure drop. In the TARFOX experiment (Novakov et al., 1997), two Pallflex 2500QAT-UP filters were used in series with the second filter providing a basis for estimating the positive artifact. The total pressure drop (D. Hegg, personal communication) was on the order of 250 mb, or 125 mb per filter. The potential for substantial cooling exists: for comparison, the pressure drop in many CN counters is around 250 mb, which yields an increase in RH to around 300%.

The consequences of this large pressure drop are hard to quantify, especially those caused by cooling; however, the direct influence of pressure drop alone can be assessed. Presumably, particles were caught close to the front face of the first filter, and, if so, suffered only small evaporative losses due to slightly decreased pressure. Meanwhile, vapors of organic constituents were adsorbed throughout both filters, with less and less being adsorbed as the partial pressures of the vapors diminished along with the total pressure. This means that the amount of vapor adsorbed on the back filter should have been less than on the front filter. If there was no enhancement of vapor adsorption caused by a temperature decrease, the use of the back filter to correct for the "positive artifact" in the front filter would actually underestimate the artifact amount and correspondingly overestimate the mass concentration of organic aerosol particles. It is clearly impossible to be quantitative in this estimate because of a lack of analysis of the dynamic temperature changes within the filter matrix; however, the magnitude of the underestimate of artifact could easily be proportional to the corresponding pressure change, meaning that the amount of artifact on the front filter could have been underestimated by some tens of percents, depending on exactly where in the second filter the material is adsorbed. A single-filter method could underestimate the positive artifact by roughly 30%, based on the variability of the second-filter carbon Novakov et al. (1997) found in this temperature range. Overall, the positive artifact could contribute 30–50% uncertainties.

4. Negative sampling artifact

Eatough et al. (1996) used a multi-channel diffusion denuder sampler to evaluate the evaporative artifact in samples collected at Canyonlands National Park in the southwestern US. This location may be a reasonable analog to that in ACE-2, where urban emissions have had a few days to react before being sampled. They found that on average the negative artifact was 40% of the total organic particles, with as much as 50% being lost in the spring. This was in contrast to earlier measurements in Los Angeles (Eatough et al., 1995), where there was no negative artifact and a large positive one. The commonly-used dual-filter approach offers no way to estimate negative artifacts. Single-filter measurements could thus be in error by somewhere between plus and minus 50%.

5. Charring

Charring can also cause difficulties in interpreting EGA thermograms. These problems arise when some classes of compounds (such as carbohydrates and other modestly high MW oxygenated organic species) char before they evaporate. If the objective is only to determine total aerosol carbon, this problem is inconsequential; however, if the temperature of gas evolution is used as a means for deciding what may have been in (or on) aerosol particles, or worse, if the temperature is used to infer existence of some class of molecular forms, then the amount of charring can influence the resultant quantitative data. Because the charring depends on many factors, including the temperature, the rate of temperature change (Jacobson et al., 2000) and the carrier gas used in the EGA apparatus (He versus O_2, for example), ambiguities arise that make it difficult to compare results from one laboratory with those of another.

6. Converting carbon mass to organic matter mass

Another possible source of systematic error relates to the use of a ratio to convert the measured C mass to a presumed organic material mass. The molecular C mass ratio varies from 1.17 for large

saturated hydrocarbons (such as dodecane) to 1.06 for polycyclic aromatics such as benz(a)anthracene, to 3.75 for oxalic acid, a factor of 3.5 range for known aerosol species. Note that the ratio (and thus the uncertainty from estimating it) rises dramatically as oxidation occurs. Putaud et al. used a value of 1.7 ± 0.3. This problem is even more acute when the estimation of organic mass is based on analysis of hydrogen (Cahill et al., 1989; Malm et al., 1994), since that ratio changes even more dramatically as compounds become oxidized. For the three molecules listed above the molecular H mass ratios are 7, 19, and 45, a factor of 6 range. Since a large fraction of carbonaceous aerosol is water-soluble (Kawamura and Sakaguchi, 1999), it is likely that many organic aerosol molecules are polar and thus lie in a range where the ratios are fairly large. It is easy to imagine that the same amount of carbon in the FT and MBL might be associated with a factor of 2 or more difference in organic matter mass, due to different oxidative environments and aging times.

7. Summary of uncertainties

As noted above, several of the errors considered by Putaud et al. (2000) would not be random. The various systematic errors discussed above could easily be as much as 30–50% for the temperature assignment in the analysis (which may not be totally independent of the following two), 30–50% for positive sampling artifacts, 50% for negative sampling artifacts, and 30–50% for the molecular mass C mass ratio. Thus, systematic errors in the $\pm 80\%$ range are possible, in addition to the 15–20% random errors and the flow rate uncertainties that Putaud et al. (2000) noted.

Even if we apply only a $\pm 60\%$ systematic uncertainty to Putaud et al.'s mean OC percentages (holding the remainder of the mass constant and assuming no uncertainty in the non-C analyses), one is left with 10–29% OC in the unperturbed MBL and 23–55% OC in the unperturbed FT. A major suggestion in their abstract, that "... the source for the FT aerosol could be the transport of continental aerosol through precipitating convective clouds" is based on their deduction that the mean OC fraction is *higher* in the FT than the MBL. However, with what we believe to be a more realistic treatment of uncertainties it is evident that even the sign of the MBL/FT gradient is not known, leaving their conclusion (and similar ones by other authors) without support. The fact that the samplers in the FT and MBL used very different size-selection devices adds further uncertainty to their apparent gradients. OC could indeed be insignificant (as little as 10% in the MBL) or it could be highly significant (29% in the MBL) or even dominant (55% in the FT), based on a conservative estimate of the systematic analytical uncertainties. There is little here to constrain any model of OC behavior in aerosols.

8. Recommendations

The work done by Putaud et al. reveals the awesome difficulties associated with carbonaceous aerosol analyses. While we note here the incompleteness of their uncertainty analyses, they have done much better than most authors. Their efforts reveal the need for defining the uncertainties in other published EGA data before it can be used to develop OC parameterizations for climate models. Better sampling techniques and other analytical methods may obviate some of the difficulties they have uncovered.

Our intent is not to suggest that EGA and related OC and EC analyses should be abandoned. There is a growing need for this type of information, and few alternative techniques that can be applied routinely. Rather, we seek to alert users of this data to its potential flaws and to encourage authors, reviewers, and editors to insist that such results be accompanied by realistic, comprehensive, quantitative error analyses.

Having emphasized the very large uncertainties associated with analysis of carbon in aerosols by EGA, it would be unsatisfying if we did not indicate remedies for the present sad state of affairs. These suggestions fall into 3 categories: (1) calibration and intercomparison of existing sampling and analysis methods; (2) re-analysis of extant data; (3) development of methods to replace present-day versions of EGA.

The first requisite is to carefully compare the existing sampling and analysis methods to calibrate them and to analyze and understand all the differences between them. This must include a

clear definition of the particle size limitations of the samplers, changes in the thermodynamic state of water and all other species that undergo phase transitions (due to changes in T or P), and the positive and/or negative artifacts that are peculiar to each and every different sampling protocol. Laboratory studies using known organic species are particularly important, to quantify their sampling and analytical behavior. For typical classes of organic vapors, which adsorption model is most appropriate? Laboratory tests of this type could help us decide when and how to use various artifact-correction methods.

Publications should include all details of the sampling, including flow rate, filter type (if a filter is used), pressure drop, substrate pre-treatment, and blanking protocols. Details of the thermal analysis should also be given, including: pressure in the EGA apparatus; gas composition (He, O_2, air, N_2 or other); rate of heating and T-time profile; the gas analysis method, its uncertainties, and interferences (if any); the means by which the split between organic and "black", "elemental", or "light absorbing" carbon is estimated, including the uncertainties resulting from those protocols; and careful determination of all uncertainties of the EGA method itself (independent of sampling uncertainties).

Calibrations and intercomparisons should be performed with *both* a wide range of sampled ambient aerosols (from natural to polluted settings) and a set of pure laboratory mixtures that provide a good representation of mixtures found in the real atmosphere. A key reason for using pure compounds is to be able to simulate situations with substances of known molecular form and vapor pressure.

The diffusion denuder method of Eatough et al. (1993) should be employed where possible to help quantify the sampling artifacts found in a variety of environments. Even if it cannot be used for routine monitoring, occasional measurements alongside a sampler could point to the most likely type of artifact in that location. While there are assumptions in this method as well, those will be tested during the laboratory calibrations we have recommended. The thermal/optical reflectance method of Huntzicker et al. (1982) can be used to reduce the uncertainty in the assignment of total carbon to OC or EC.

Having thus objectively defined the uncertainties caused by the each of the sampling and analysis methods, the second suggestion is to revisit published results (several of which are cited above) and define for each data set the best estimate of *all* uncertainties. These should be published collectively and in summary by the communities of scientists who do EGA so that data users (e.g., modelers) will have a realistic set of numbers to deal with.

Finally, because the scientific questions related to carbonaceous aerosol demand smaller uncertainties as well as more details, new methods should be developed that provide the information necessary for separating anthropogenic and natural aerosols, water solubility, light absorption and appropriate indices of molecular forms. The recent observation that a large fraction (70–80%) of the carbonaceous aerosol is water soluble under atmospheric conditions (Decesari et al., 2000) opens the door for applications of analytical methods based on aqueous-phase methods. Of these, spray ionization mass spectrometry (Kiss, et al., 2000) appears to be particularly well suited. Evolved gas analyses with isotopic information by accelerator mass spectroscopy (14C, 13C and 12C, Klouda et al., 1988) can aid in estimating the fossil fuel and anthropogenic fraction.

However, until all three of these suggestions are fully implemented we can only continue to utter our words of caution to the users of data.

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