Atmos. Chem. Phys. Discuss., 13, C9826–C9831, 2013
www.atmos-chem-phys-discuss.net/13/C9826/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Chemical mass balance of refractory particles ($T = 300$ C) at the tropospheric research site Melpitz, Germany" *by* L. Poulain et al.

Anonymous Referee #1

Received and published: 9 December 2013

The manuscript describes a reconstruction of chemical composition of refractory material (RM). RM is defined as the mass remaining in aerosol after passing a thermodenuder (TD) heated to 300°C. The reconstruction is achieved by comparing RM mass estimated using two methods. The first method combines black carbon and TD-DMPS measurements and uses an assumed particle density to arrive refractory mass concentration (RMC). The second method combines black carbon (BC) measurements with an estimate of refractory organic material, which is derived from LVOA factor in AMS measurements assuming that a fixed fraction of LVOA is refractory. The authors argue that RM measured with the TD system is composed practically completely of BC and

refractory organics.

There are several major issues that need to be addressed before this manuscript can be accepted for publication.

The purpose of the presented work and its general usefulness is unclear. The definition of RM is strictly method-specific. A different TD temperature or a longer residence time will produce a different amount of material that remains in particles after passing the TD. Thus, the results presented in this paper are limited only to TD systems that are operated at the same temperature and residence time.

The purpose of reconstructing composition of RM, though not explicitly stated, appears to be to derive the amount of LVOA from measurements of RM with a TD system if BC concentration is known. For example, if 1 ug/m3 of RM is measured with a TD and there is 0.3 μg/m^3 of BC, then, according to the authors, there should be 0.7 μg/m^3 of refractory organics. If one uses a mass fraction remaining (MFR) for LVOA of 50%, the LVOA concentration can be estimated to be 1.4 μg/m^3. This could be useful if one does not have an AMS available. However, as the authors point out in the manuscript, the MFR of LVOA could vary by more than a factor of 1.5 (30% vs. 52%). Thus, such an estimate of LVOA is bound to be highly uncertain, especially if one takes into account uncertainties in measurements of BC, particle density, etc., in addition to the uncertainty in MFR.

If I have misunderstood the authors and the purpose is the opposite, i.e., to derive the amount of RM from the AMS measurements, then it is not clear how useful this information is. The authors seem to equate the observed MFR at 300°C with aerosol volatility (see, for example, the abstract where the authors state that the aerosol was more volatile in summer than in winter). The TD temperature used in this study, however, is more suitable to characterize aerosol stability, not volatility. As the authors correctly point out, many inorganic molecules decompose at temperatures lower than 200°C. The same is true for organic compounds. The TD temperature used in this study is sufficient to break most common organic bonds, see figure 3 in Epstein et al. (Environ. Sci. Technol. 2010, 44, 743–748). Organic RM measured in this study most probably consists of decomposition products of high molecular weight compounds (many of which are admittedly LVOA). The amount of these decomposition products does not say much about aerosol volatility or the amount of low volatility compounds.

The argument that RM is composed of only BC and refractory organics appears to be based on a comparison of two estimates, of which one uses a rather arbitrary assumption that the density of RM is 1.6 g/cm^3, while the other depends on the assumed fraction of RM produced by LVOA. The density of graphitic material is 2.2-2.3 g/cm^3; that of crustal material is similar. Thus, it is not clear why the value of 1.6 g/cm^3 was chosen. If this value was chosen due to the presence of organic material in RM, it must then depend on the mass fraction of organics. This fraction varies not only with location but also with time due to varying contributions of different aerosol sources. As the authors show, even at one measurement location the refractory fraction of LVOA is not constant and can change by a factor of 1.5. The mass closure thus becomes subject to an arbitrary choice of parameters. Even if the conclusions presented by the authors are correct, their general applicability is questionable.

The authors argue that a good correlation between the two estimates indicates that their hypothesis is correct, i.e., that the refractory material consists of BC and refractory organics. However, there could be other components in RM that correlate tightly with either BC or refractory organics. If this is the case (and the authors do not provide any proof that it is improbable), a good correlation between the two estimates would be preserved, but RM would contain other material in addition to BC and organics.

The authors contradict their hypothesis when they discuss marine-influenced air masses. If there was indeed a significant contribution of marine aerosol to the fine fraction, then there should also be a significant contribution of sodium chloride and/or sodium sulfate. The argument that sodium hydrate is volatile is not tenable, because the only part that volatilizes is water, while sodium sulfate remains in the particles (its

melting and boiling points are above 1000°C). Sodium sulfate comprises about 44% of sodium decahydrate mass. Thus, if there was a significant contribution of marine air, there should be a significant contribution of sodium salts to RM. The argument that there was a significant processing of marine aerosol and (probably) a large contribution of highly oxygenated organics is also tenuous – why would this secondary organics differ from other aged air masses that are not marine-influenced?

The calculated MFR is, as the authors admit, overestimated if the same upper size integration limit (800 nm) is used to calculate integrated volume of both original and thermodenuded aerosol. The authors thus propose to use a rather arbitrary boundary of 400 nm. A better method of correcting for the contribution of large particles is to calculate a new upper boundary for TD aerosol as d_{up} =MFR$_{800}^{1/3}$, then integrate TD size distribution to d_{up}, calculate new MFR, and repeat these steps until changes in MFR become negligible with each additional iteration step (Stanier et al., 2004, Aerosol Sci. Technol., 38, 215–228). The authors should recalculate all the MFR data using that method and reanalyze the data.

Minor comments and corrections:

p.26986, l.25: change “transmission” to “transport”

p.26992, l.2: remove “as”

p.26996, l.9-12: One cannot make such a conclusion using the presented data. As Figure 7 shows, dV/dLogD of RM at any size larger than about 200 nm (and probably at smaller sizes too) is smaller than that of the original aerosol. If the aerosol is externally mixed with respect to RM, the measured RM size distribution would remain the same after the TD, but the volatile material would evaporate. The authors do not have enough evidence to prove otherwise.

p.26996, l.13: remove “principally”

p.26997, l.4: replace “more under continental” with “under stronger continental” p.26998, l.2-3: I do not think that a change in VFR from 11

p.26998, l.9: replace “in averaged for” with “on average”

p.26998, l.23-24: Here the authors say that 13% and 4% refer to “the total mass”, while the same numbers were attributed to “the total inorganic mass” on p.26993, l.1. Which one is correct? It should be also noted that the total mass of crustal material is larger than the mass of ions due to the presence of oxygen in oxides of metals and carbonates. Since the authors refer to ions, I assume filters were analyzed using ion chromatography. If this is the case, water-insoluble compounds would not be detected during the analysis.

p.26998, l.15: replace “in opposite” with “in contrast”

p.26999, l.19: “change of”

p.26999, l.23: “upper size cut”

p.26999, l.25: replace “is depending” with “depends”

p.27000, l.3: remove “consequently,”

p.27000, l.13: replace “supplied” with “supplemented”

p.27000, l.14: replace “might be” with “are”

p.27001, l.6: replace “on oxidation states” with “of oxidation state”

p.27001, l.9: replace “on” with “of”

p.27001, l.14: Remove the last sentence because there is nothing in the manuscript that supports it.

Figure 5 caption: “the measured RMC” is confusing because it is not directly measured, it is estimated using an assumed density. I suggest using RMC$_{BC,AMS}$ and RMC$_{DMPS}$ instead of “RMC$_{est}$” and “RMC$_{meas}$” throughout, because both parameters are partly based on measurements and estimates. The estimate based on the DMPS should not

be referred to as “measured” in other parts of the manuscript either.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26981, 2013.