Atmos. Chem. Phys. Discuss., 10, C8156–C8162, 2010
www.atmos-chem-phys-discuss.net/10/C8156/2010/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Anthropogenic influence on biogenic secondary organic aerosol" *by* C. R. Hoyle et al.

B. Bonn (Referee)

Bonn@iau.uni-frankfurt.de

Received and published: 30 September 2010

General comments:

This study by Hoyle et al. investigates the very complex system of anthropogenic influences on biogenic secondary organic aerosol formation both in number and mass. This topic is highly complex and includes a variety of Earth science areas with unfortunatley a multitude of gaps in knowledge. Because of that the manuscript is focussed on the gas-phase influence of mankind emissions on the biogenic secondary organic aerosol (SOA) production, which is known to be the dominant (ca. 90% of all SOA) out of anthropogenic and biogenic sources. However, any effects affecting the biogenic emissions themselves such as the stress behaviour and the distribution are treated to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

be constant.

For the purpose of this study the authors perform a good general review on the current knowledge and state of the art of organic aerosol classification. Subsequently they separate different organic aerosol types systematically and clearly identify different ways of anthropogenic modifications of biogenic SOA production, including the anthropogenic organic aerosol (OA) mass that is able to uptake semi-volatile material subsequently and the strong NO_x effect of the gas-phase chemistry of potential precursor species. This study discusses a variety of atmospheric and chamber investigations seeking for a hint for rising or declining biogenic SOA production in the presence of anthropogenic impacts. As a major tool although kept rather short in this study they apply global chemistry transport models such as of Hoyle et al. (2009) to allow turning anthropogenic VOC and NO_x emissions on and off and look for the changes.

The whole study is certainly very relevant for climate studies as well as health effects and can be seen as a review paper without the final two sections. However, some further aspects I'd like to see at least mentioned in the text or spared by a modified title to give the study a more concise focus: As stated previously the authors only investigate the gas-phase chemistry changes by mankind and the effect of a changing preexisting organic particulate matter mass for partitioning but not of the emissions and of temperature. Certainly if we turn anthropogenic emissions on and off, the temperature and humidity might tentatively be similar but not identically due to diverse feedback cycles such as CCN concentrations and the NO and PM mass effects will dominate the resulting effects. But when investigating the general effects and citing studies on climate studies, i.e. pre-industrial, present and projection temperature and weather pattern will change altering the emission intensity, the distribution of biotypes and potential feedback cycles of the biosphere as emitter of biogenic VOCs. The latter include humitity, ozone, cO_2 and NO. I am sure the acid rain period caused effects on the SOA production too. When reading the excellent list of authors such as Alex Guenther one might expect a comment on that Although the authors mentioned that they do not consider land use change, this is in my point of view a relevant aspect too and should be discussed at least in section 5 on the relevance of the findings. Maybe the title should be changed to "Anthropogenic influence on the gas-phase production of biogenic secondary organic aerosol" to exclude the biosphere effects.

Unfortunately the contribution of organics to particle number and CCN remains rather short compared to the rest of the paper. This is certainly due to the notable lack of understanding of the participating compounds and exact processes, although I am confident that soon progress will be made in this context. Recent measurements in our lab indicated a NO derived new particle number formation decrease at very low NO values changing to a gentle increase subsequently until finally suppressing nucleation completely at high NO values. Thus no simple parameterisation seems plausible and might be one of the reasons the authors kept that point only as a side effect. This however has significant impacts on local CCN production, cloud formation, radiation balances and thus surface temperature and VOC emissions.

Altogether this study is well written although the number related subsection is somewhat apart of the rest. The findings are important and open aspects worth consideration and study are named.

Therefore I suggest to publish this paper in *Atmos. Chem. Phys.* after some minor changes.

Specific comments:

1 - Introduction:

p. 19518: The different types of OA are named. Please note that definitions and results mainly depend on the technique applied, i.e. if the aerosol is collected on a filter with continuous exposure to air etc. Thus, any improvement of measurement methods usually results in a newly defined sub-OA definition. Since not all organics can be detected and analysed by the different methods the current estimates are still not final and will be revised in the near future.

p. 19518: It's being stated that POA have somewhat higher volatility than SOA (Huffmann et al., 2009; Robinson et al., 2007). I think that is caused by the mixture of primary mass and volatile material ad- or absorbed on the surfaces. Because of the large size of primary particles the surface is sufficiently large and the partitioning notably enhanced. Heating up of SOA might result partially in polymerization etc which is not the case for POA compounds. However this does not necessarily mean that the originating compounds are less volatile.

p. 19518: I guess the separation into biogenic and anthropogenic SOA is mainly for mitigation purposes.

2 - Mechanisms for an anthropogenic effect on BSOA

In general it would be nice to make a short overview plot or figure of the individual effects and the ones considered in this study.

p. 19519: (2.1 Partitioning) The lower saturation vapour pressure compounds may also form in multiple oxidation steps or by ageing. Here providing ASOA will allow enhanced partitioning and subsequent ageing folwed by a higher total flux towards the condensed phase due to a change in the particle-phase concentration of species. Is this considered in here too?

p. 19520: Problems of the miscibility might depend on the primary organic aerosol structure. This also applies for different mixtures in the atmosphere. So far we treat several species separately in the context of aerosols such as sulphuric acid, nitric acid, ammonia etc but several thousands with a enormous variety of properties as a single

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

class, i.e. organics. This causes problems and maybe these would popp up as well when summing up all inorganics. Second, we need to be carefull about POA. This is essentially a mixture at least in the atmosphere of elemental carbon, oxidized carbon and unburned fuels, which are notably in contribution. This mixture certainly provides multiple ways of restructuration (density change), ageing, revolatilisation etc that EC does not.

p. 19521: Surely the initial stage products of α-pinene oxidation are modest in hygroscopicity (Prisle et al., 2010) because of their oxidation degree increasing with time. This applies to all secondary products. Higher oxidation products such as pinic acid are thought to be formed mainly after multiple oxidation steps partially in the aerosol phase (Kanawati et al., 2007).

p. 19522: The role of NO$_x$ is written excellent. Probably the parameter $\frac{\Delta VOC}{NO_x}$ is even better for parameterisation.

p. 19524: A further explanation concerning the drop in SOA yields at high NO$_x$ not mentioned in here could be: The photooxidation experiments are commonly a mixture of OH and ozone oxidation with the latter leading to less volatile products. Thus increasing NO$_x$ to higher values causes ozone to drop more efficient than OH. This causes the oxidation products to be more volatile and the SOA yield increases, i.e. background atmospheric chemistry.

p. 19525: Sesquiterpenes: Wait! Interpretation might be difficult. The contribution of the ozone-reacion dominates always in contrast to monoterpene oxidation. Thus increasing NO does not affect the primary yield of products. Since those oxidation products are larger NO is expected to be incorporated in the RO$_2$-reaction products without fragmentation. The larger the product and the higher the number of functional groups the lower the vapour pressure and thus the larger the SOA yield. It seems that for monoterpenes NO simply blocks the ozone contribution.

p. 19526: Asmentioned by the authors I would tend to be very carefull in giving exact

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

numbers of anthropogenic contributions to SOA in the Amazon region. The effects are due to a) the tremendous change in the Amazon region during the last years (not considered here) and b) the direct and indirect effects with the latter less obvious. Maybe state ca. 80% in line 20.

p. 19527: (upper paragraph) The emission of Amazonian monoterpenes and NO depends strongly on the conditions of rain, forest fires (natural and anthropogenic ones) dry and humid season and is hard to be state in general with the coarse global models.

p. 19527: New particle formation, organics and CCN - Since we clearly lack in mechanisms and exact products leading to SOA and number concentrations as well as the detailed ageing of several 1000 compounds the difference is apparent. Fortunately it seems that at least currently nature is balancing out some of these problems but not necessarily in a future condition. In the subsection it appearsthat NO would tend to negatively affect the nucleation intensity or occurence. But this is very difficult to say since it can appear vice versa because of aerosol dynamics and radical chemistry playing a crucial and non-linear role. In some conditions number is expected ti rise.

p. 19528: Lack of new particle formation in the Amazon region - The old argument. It might also happen that a nucleation starting compound requiring activation is limiting because of the multitude of reaction partners otherwise suppressing. The activation might occur extremely rapid because of the high VOC loading. Thus a new particle quickly rises to larger sizes 10-20 nm without stabilising inorganic compounds to remove the excess energy produced.

3 - Methods for separating the contributions of different sources to organic aerosol

p. 19530: BVOCs: The regional land use changes are very important on the global scale with respect to future climate projections and mitigation strategies. Since this paper might be used for such purposes this point should be mentioned quite briefly to indicate further important non-negligible effects.

4 - Observational and modelling data

p. 19535: The fraction of ASOA is slighly higher than expected by earlier studies but agrees with the normal assumption of about 10% contribution. However this might be an order of magnitude estimate so far (see comment for p. 19539).

p. 19538: Problems with results from bulk or filter analysis - It is always apparent that partitioning compounds are partially lost by filter sampling in a changing environment. Only the primary fraction remains unmodified. The same is known for mas spectrometry with hundreds of products partially very fragile and partially below the detection limit. However all might add up to a notable mass.

p. Please note that the value of 10.3 Tg(C)/yr of SOA is among the lowest simulated ones! The higher the number of details and the more detailed the chemistry schemes the higher the simulated mass production. Detailed simulations as of Derwent et al. (2003) and others simulated around 60 Tg(C)/yr, hence about six times the value than cited and this is only for monoterpenes. The simplification to the two product schemes seems to fail in getting the number in the same height. With this in mind the increase by a factor of three to about 30 Tg(C)/yr is excellent and worth to postulate but might be in a different intensity with a more complex scheme. And what about considering the aerosol dynamics and size distribution including Kelvin and Raoult effects? Otherwise this is very plausible.

Thanks for the interesting study.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19515, 2010.