Response to reviews for “Isoprene in poplar emissions: effects on new particle formation and OH concentrations” by Kiendler-Scharr et al.

Reviewer #1

- **Please compare VOCs, O3 and OH concentrations in the chamber during the experiments with typical values observed in the atmosphere. How reasonable are values? Generally, VOC emissions can be very high after biotic or abiotic stress.**

Ozone concentrations in the reaction chamber were around 90 ppb when the UV light was off and dropped to around 40 ppb when the UV light was on. Hence O_3 *concentrations were comparable to those in the atmosphere. VOC and OH concentrations were much higher compared to atmospheric conditions. Due to the high ozone photolysis frequency (*$J(O^1D) \approx 2.9\ 10^{-3}\ s^{-1}$*) the OH production rate was high and OH concentrations ranged between* $5x10^6$ *to* $7.6x10^7$ cm^{-3}*. This is roughly an order of magnitude higher than atmospheric OH concentrations. VOC concentrations at the inlet of the reaction chamber ranged between 5 ppbC for non-isoprene emitting mutants under conditions of low stress up to 450 ppbC for stressed plants. In particular the latter is quite high compared to atmospheric concentrations in the remote atmosphere but low compared to most other laboratory studies. The following text was added to “section 2.1 Set-up” (page 4) to set the used concentrationsinto context:*

“O_3 concentrations were around 90 ppb when the UV light was off and dropped to around 40 ppb when the UV light was on. Hence O_3 concentrations were comparable to atmospheric concentrations. Note that the OH concentration ranged from $5x10^6$ to $7.6x10^7$ cm^{-3} which is roughly one magnitude larger than typically observed in the atmosphere. Also VOC concentrations ranged from 5 ppbC for non-isoprene emitting mutants under low stress conditions to 450 ppbC for stressed plants. While this is quite high compared to atmospheric observations in the remote atmosphere, the VOC concentrations used here are low compared to most other laboratory studies.”

- **It is stated in MS that isoprene suppresses new particle formation but not growth in the present experiments. What are (possible) reasons that isoprene inhibit nucleation but not growth of particles? (page 22429, line 23)**

The likely reason for the observed effect of isoprene on nucleation and not growth rate is, that different (classes of) oxidation products contribute to nucleation and growth, respectively. While nucleation is observed only in the presence of OH radicals and therefore assumed to involve OH oxidation products of BVOCs and/or ozonolysis products, the growth itself may well be dominated by ozonolysis products. The presence of isoprene in our experiments significantly changes the production rate of OH oxidation products from other BVOCs. The change will depend on the relative reaction rates of isoprene with OH and other BVOCs with OH. The presence of isoprene on the other hand does not interfere with the production rate of ozonolysis products of BVOCs.

- **Could you clarify why isoprene is less efficient in quenching new particle formation when emissions contain sesquiterpenes and aromatic VOCs compared to monoterpenes? (page 22431, line 9-16)**

As the suppressing effect of isoprene on nucleation is related to the suppression of OH concentrations it is to be expected that the impact of isoprene on nucleation will scale with

the relative OH reactivity of isoprene compared to OH reactivity of all other VOCs involved. However, rate constants for reactions with OH are unknown for several of the VOCs emitted from poplar. Therefore the fraction Isoprene / (Sum of all VOC- Isoprene) is expressed in units of masses instead of units of OH-reactivities. It might well be, that relating the effect of isoprene on nucleation to the relative OH-reactivities of the BVOC emissions and isoprene may unify the picture regardless of detailed emission pattern of the tree species studied. We would like to point out, that it was also observed that isoprene is more efficient in suppressing nucleation when α-pinene only is studied compared to MT-dominated BVOCs (Kiendler-Scharr et al., 2009). It seems the more efficient a system nucleates new particles, the less the disturbance by isoprene matters, as one might expect for a threshold process such as nucleation. Or in other words: a good nucleator produces higher supersaturations of nucleating vapors, that will persist despite the competition about the OH.
The following text was added to the manuscript (page 8, 3rd paragraph) to clarify this point:

"Note that while the detailed mechanism by which isoprene suppresses nucleation remains unclear, the impact that isoprene has on nucleation in a given BVOC mixture is larger for BVOCs with low nucleation efficiency and high nucleation threshold. Most probably the suppression is related to the relative OH reactivities of isoprene and the sum of all other BVOC emissions. For several BVOCs emitted from stressed poplar OH reaction rate constants are unknown, making a more detailed comparison of emissions with different BVOC classes impossible at this point."

- **Geoengineering is nowadays a very interesting topic in the atmospheric science. I feel that genetically modified trees and plants could be used to increase emissions of reactive VOC (or decrease isoprene emissions) to the atmosphere and hence increase SOA loading which can lead to an increase in cloud condensation nuclei concentrations, etc. Could you speculate the use of genetically manipulated trees in the field of geoengineering?**

While we agree that the topic of geoengineering is receiving increasing attention, we think that the level of understanding of changed BVOC emissions and their potential impact on atmospheric chemistry and climate is far from sufficient at this point. Moreover, trees need to grow for some ten years, so the engineering effect is shifted to a far future. We pointed this out in the original manuscript and extended the respective text to now read (page 10, second to last paragraph):

"A recent long-term outdoor study (Behnke et al. 2011) with non-isoprene-emitting poplars - the same lines used in the present work - in the moderate climate of Central Europe revealed no remarkable difference between emitting and non-emitting trees with respect to plant growth and wood quality. However, and in addition to the social and political decision for the cultivation of GM plants, more real-field trials under strongly contrasting climatic and soil conditions are needed to clarify conclusively whether isoprene-free poplars are an option for the second generation of biomass plants, either generated by genetic manipulation or classically by selection of low emitting phenotypes.
Keeping in mind that all fast growing tree species (poplars, willows, eucalypts) are among the strongest emitters of isoprene and monoterpenes (Kesselmeier and Staudt, 1999) the large scale extension of woody biomass plantations expected in future might change the relative abundance of isoprene in VOC mixtures with implications for both gas phase oxidation capacity and the nucleation potential. A decrease in new particle formation potential from VOC emissions from a given land area constitutes the change of an essential element in

biosphere atmosphere climate feedback mechanisms. Further research is needed to fully understand the driving mechanisms in this suppression of new particle formation and its potential change and impacts under future climate scenarios."

Specific comments:

- **In the second sentence, there is mentioned a high nucleation rate observed in the experiments. However, it is not clearly indicated is the results from high or low concentration isoprene experiments. The better place of information of nucleation rates would be later in the abstract. Also, values (or magnitude) of nucleation rates for high isoprene concentration experiments should be also mentioned in the abstract and/or in the text later. Furthermore, VOCs, O3 and OH concentrations during the high nucleation rate experiment should be mentioned in the MS.**

The highest nucleation rates observed in our experiments were observed in the case of transgenic poplars i.e. in the absence of isoprene. The sentence on nucleation rate was moved in the abstract as suggested by the reviewer. The concentrations of VOCs, O3 and OH are now explicitly discussed in section 2.1 (see answer to point 1 above).

- **Introduction: Page 22421, line 6-: Please specify how common species are poplars in globally. Are they globally important trees?**

The use of poplar in our investigations was motivated by both the increasing attention that poplar receives from its potential use as source of bioenergy and the availability of mutants that are modified in their BVOC emission pattern. We extended the respective text in the manuscript (page 3 last paragraph) to now read:

"We investigated the new particle formation and secondary organic aerosol mass formed from poplar emissions. Poplars are not only among the strongest emitters of isoprene (Kesselmeier and Staudt, 1999) but as a fast growing pioneer tree, also these plants receive enormous attention due to increasing demand of renewable bioenergy (Schnitzler et al., 2010). World-wide poplar plantations represent 5.3 million ha with an increasingly positive trend in many countries (International Poplar Commission, Synthesis of Country Progress Reports 2008). Wiedinmeyer et al. (2006) developed expected land use changes in model-based estimates of future changes in global isoprene emissions. Their simulations revealed that the conversion of natural vegetation to plantations (poplar and others, e.g. oil palm and eucalypts) could substantially increase global isoprene flux up to 37 % compared with the current situation. Moreover, the potential of genetic manipulation offers the opportunity to analyze poplar mutants with different VOC emission pattern."

- **Experimental: Page 22424, line 2: Acronym GC-MS is not explained.**

done

- **Please clarify or insert an appropriate citation how emission rates (µg(C)/m2s), number efficiencies and incremental particle mass yield have been calculated.**

The description and reference for calculation of the emission rate was introduced on page 7 (discussion of figure 1) to now read:

"Figure 1 shows the temporal evolution of emission rates of isoprene (red triangles), sum of all monoterpenes (MT, green triangles), sum of sesquiterpenes (SQT, green circles), and sum of aromatic compounds (brown circles) at the example of an isoprene-emitting poplar. Emission rates were determined from the measured VOC concentrations at the plant chamber outlet using the one-sided leaf area as reference for the biomass as described in e.g. Heiden et al. (2003). As depicted in Fig. 1 isoprene emissions were quite constant whereas other VOC emissions increased over time, causing systematic changes of the emission pattern with decreasing contribution of isoprene to the total VOC emissions. "

The procedures to calculate number efficiencies and incremental mass yields from comparison of consumed BVOC mass to particle number and particle mass are described in detail in Mentel et al. (2009). This was added to the experimental section 2.3 Instrumentation:

"From these data together with BVOC consumption, number efficiencies and incremental mass yields were calculated as described in detail in Mentel et al. (2009)."

- **Results and discussion: Are errors/deviations indicated after number values, e.g. 1.6 (±0.6), standard deviations, standards errors or something else. Please clarify.**

Standard deviations are reported throughout the manuscript, which is now explicitly stated (page 7, last paragraph).

"Note that if not stated otherwise standard deviations are reported."

- **Page 22428, line 12, eq. 1: Please clarify a meaning of the coefficient 1.5 in the equation.**

The coefficient 1.5 is a fitting parameter that was derived from MCM calculations for the system α-pinene + isoprene (see supplementary material to Kiendler-Scharr et al., 2009). We have no unambiguous explanation of the physical/chemical meaning of this fitting parameter and treat it as empirical parameter here. To clarify this in the manuscript we added the following text:

"The coefficient 1.5 is a fitting parameter that was derived from MCM calculations for the system α-pinene + isoprene (see supplementary material to Kiendler-Scharr et al., 2009)."

- **References: There are Atmos. Chem. Phys. Discuss. papers that have already been published in Atmos. Chem. Phys. (Kanawade, Whalley).**

The respective reference was updated.

- **Figures: Fig. 1. For comparison, similar plot for transgenic line poplar would be nice to see, too.**

As mentioned in the text and discussed in detail in Behnke et al. (2009), the emissions from transgenic and wild type poplar are very similar after ozone stress. The only difference is the emission of isoprene from wild type poplar. See figureR1 below for illustration. We think the manuscript would not profit from adding this figure and therefore keep referring to the very similar emissions and Behnke et al reference only in the manuscript. Note that as also discussed in Behnke et al. (2009) the detailed temporal behaviour of stress induced emissions *shows a significant variability also for individuals of the same line. The differences in temporal behaviour of emissions between those shown in figure 1 of the manuscript and the ones shown here are therefore not regarded as representative of a difference between transgenic and wild type poplar.*

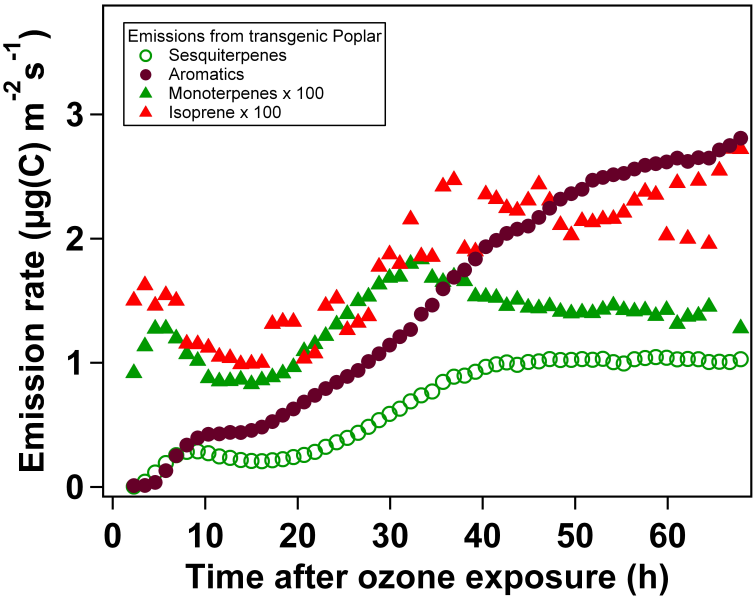

Figure R1: Emission rate of sesquiterpenes (green open cycles), aromatics (dark red cycles), isoprene (red triangles), and monoterpenes (green triangles) for a transgenic poplar as function of time after ozone exposure. Note that for visualization purposes monoterpenes and isoprene were scaled by 100.

- **Fig. 1. Concentration of MT is so low that the changes cannot be seen. Multiply it by 10 or insert secondary y-axis for MT.**

done

- **Fig. 3. Purple shaded area is not explained in the figure caption.**

done

references:

Behnke K, Grote R, Brüggemann N, Zimmer I, Zhou G, Elobeid M, Janz D, Polle A, Schnitzler JP (2011) Isoprene emission-free poplars – a chance to reduce the impact from poplar plantations on the atmosphere. New Phytologist. Published online, early view

IPC (2008) Report of the 23nd session of the international poplar commission. Beijing, China, ftp://ftp.fao.org/docrep/fao/011/k3380e/k3380e.pdf

Anonymous Referee #2

General comments:

This manuscript discusses the results of laboratory experiments to study the effect of isoprene on new particle formation from VOCs emitted by a wild type (WT) Grey poplar and a mutant type (MT), in which isoprene emission was suppressed. The authors found that isoprene suppresses particle formation rates and OH concentrations.

They also studied the SOA formation potential of isoprene, using deuterated isoprene to be able to separate the isoprene SOA from SOA formed from other VOCs. The authors used novel methods and present interesting and important results which are relevant to the community and within the scope of ACP. The manuscript is well written, and I recommend its publication in ACP after my comments below have been addressed.

Specific comments
1. p. 22426, lines 3-4: The SOA from deuterated isoprene most likely composes more than the ten ions mentioned by the authors. The isoprene SOA constitutes only a small fraction of the total SOA (1.6%, p. 22430), and other deuterated ions could be in the mass spectrum, located in the "shoulders" of larger peaks corresponding to non-deuterated ions. The mass of deuterium is very close to twice the mass of hydrogen, so deuterated and non-deuterated ions might be very close to each other, and the signal from some of the non-deuterated ions could mask the signal of the deuterated ions. If there are other deuterated ions in the mass spectrum which the authors have not identified, their estimate of isoprene SOA yield would be biased low. One way to check for additional deuterated ions would be to conduct an SOA formation experiment with only the deuterated isoprene as VOC precursor and to analyze what fraction of the isoprene SOA mass is due to the ten ions identified here. The isoprene SOA mass found in the mixture experiments could then be scaled according to this fraction.

In any case, the reported uncertainty in the SOA mass yield (2.3+/- 0.3) seems optimistic considering the uncertainties in trying to quantify the amount of isoprene SOA when it constitutes only such a small fraction of the total SOA.

No single VOC experiment was performed in the present study which makes the suggested approach impossible for us. Reasons not to perform such an experiment are that we expect large thresholds for new particle formation from isoprene alone. The experiment would either require the use of large concentrations or the use of inorganic seed aerosols. In either case the question on comparability and representativeness would arise.
Note that the stated errors derive from to the observed standard deviations of organic mass and deuterated mass and do not include systematic errors such as a potential underestimation of deuterated mass due to limitations in mass resolution.
We nevertheless agree with the reviewer that the ion signals used to calculate the deuterated mass likely represent a lower limit of deuterated mass and thereby a lower limit of the SOA yield from isoprene. We therefore added the following sentence to the manuscript (page 9 discussion of figure 4):

"Note that the list of ions used was defined by those peaks unambiguously separated from neighbouring non-deuterated ions. Likely the sum of these ions' signals represents a lower limit for the SOA mass from isoprene oxidation products in the particles. The yield calculated here therefore is a lower limit of SOA yield from isoprene.*"*

2. p. 22430, lines 16-23: I recommend that the authors explain in more detail how they deduce the isoprene SOA mass yield from the total SOA mass yield. It appears that their estimate might require the assumption that all VOCs react at the same rate. If this is the case, this assumption should be stated and justified.

No assumption on the VOCs reaction rate is made for determination of the mass yields. Yields are derived from observed particulate mass versus consumed VOC mass in steady state as *described in more detail in Mentel et al. 2009. This means as long as the fraction of VOC that reacted is known (100% for isoprene and MTs, ~60 % for MeSa), the isoprene mass yield can be derived from the fraction of deuterated mass in SOA. We clarified this by adding the following sentence to the description of yield determination (page 9, last paragraph):*

“This calculation is based on the known isoprene consumption in the reaction chamber and measured deuterated mass in the particles.”

3. The authors find that isoprene suppresses new particle formation (nucleation) rates, but it does not affect particle growth rates. The suppression of nucleation will mainly affect climate through the particles’ role as cloud condensation nuclei (CCN). Particle growth rates are an important determinant of whether freshly nucleated particles grow to “CCN size range” (roughly 100 nm and larger). It is therefore important for the implications of this work that the authors comment on the extent to which isoprene suppresses the formation of particles in the CCN size range.

The net effect of a suppression of nucleation on the number and properties of CCN is difficult to assess based on our experiments alone. While obviously the maximum number of CCN is reduced at lower nucleation rates, constant growth rates could lead to larger CCN. For simplicity lets assume that OH is essentially driving nucleation, while ozonolysis is dominating the condensational growth. Reducing the number of particles will then grow them to relative larger sizes – since the amount of condensing material should be roughly the same. If and to what extent this would affect the CCN properties of particles depends on the size distribution and composition of the new and the pre-existing aerosols. A full description of the effects on CCN availability and properties would require a modelling approach that takes into account aerosol dynamical and atmospheric chemical aspects and is beyond the scope of this paper. We therefore leave the paper as is in this respect.

Technical corrections
p. 22429, line 20: “strenght” should be “strength”

Done

Figures 1 and 3: the time-dependence of the monoterpenes (MTs) is not visible using the scale of these figures. I recommend scaling the MTs.

Done (see also answers to reviewer 1)