

Interactive comment on “Ideas and Perspectives: On the emission of amines from terrestrial vegetation in the context of atmospheric new particle formation” by J. Sintermann and A. Neftel

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We are very grateful for the comments of both reviewers, which we regard as very useful to improve our manuscript. We are glad about the generally positive perception of the text. In the following we present a point-to-point reply to the raised questions from both reviewers.

Anonymous Referee #1 Reviewer: 1) as the vegetation source of amines might be important but measurements are lacking, can the authors make some recommendations about conducting measurements in this aspect?

Authors: Amine measurements remain very challenging. The identification of chemical
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compounds is not always feasible. Emission quantification is even more difficult because of the stickiness and low concentrations of compounds and also because of the heterogeneous sources. We propose to focus investigations mainly on two aspects: a) the link between nitrogen turnover and MA emissions in plants in case studies with plants such as *Chenopodium vulvaria*, *Crataegus*, *Mercurialis perennis*, *Sorbus aucuparia* to establish the link between the nitrogen supply and the MA emissions, and b) to survey how decaying organic matter might release amines. Technical measurement solutions have to be tailored to the specific requirements of investigated issues, such as instrument sensitivity and selectivity, time resolution of measurement setup, field or laboratory measurements (e.g. chamber vs. field measurements), etc.

Reviewer: 2) The title include "perspective", however, in my viewpoint, there is now not enough content to recommend how can we close the gap. from both experimental, modeling sides, also, likely some discussions regarding the future directions will be nice.

Authors: We think that the knowledge-base is not sufficient to establish the link between the vegetation-related amine source and NPF in a quantitative way. Neither from the experimental nor from the modelling side. We judge that an increased knowledge about this relationship is important for an increased process understanding of biogenic emissions and NPF, and as better basis for chemistry-transport models. To point towards this relationship and to create awareness in the scientific community was one of the main reasons to write this paper and submit it to the “Ideas and Perspectives” category. The phrase “perspective” is a fixed journal proposition and has to be included in the title. We believe that we have presented practically all relevant available studies regarding modelling and measurements. On this fundament, we add a brief outlook paragraph in the context and conclusions section in which we discuss future directions: The topic of amines and NPF has become more present in current scientific publications. Field studies using techniques with sufficient accuracy, precision and selectivity to resolve the extremely low ambient concentrations at which amines

and NPF begin to interact are rare or almost non-existent (also see Sipilä et al., 2015, Atmospheric Measurement Techniques Discussions, 8, 3667-3696, doi:10.5194/amtd-8-3667-2015). One essential point will be the distinction between MA's in the gas and aerosol phase. A limitation to an experimental assessment of vegetation-related amine emissions and their atmospheric chemistry and transport is the heterogeneity of sources, resulting in very variable emissions over space and time. This makes a confined quantification very uncertain and not feasible beyond the character of local to regional studies. High quality, detailed laboratory experiments and field measurements for NPF have been conducted with acceleration in recent years. It is likely that the understanding of NPF, and the amine's role, will continue with growing progress. New measurement approaches will lead to a better characterisation of airborne amines and their dynamic behaviour at a few sites. Such approaches include on-line analysers with a high selectivity (like time-of-flight mass spectrometers) and high sensitivity (like AP-CIMS) and new developments in ion-chromatography. Ultimately, however, we think that modelling is probably limited by the large variability of conditions in the environment, which is almost impossible to quantify with field experiments.

Reviewer: 3) Although by adding a few ppts of amines to the SA-H₂O system from CLOUD chamber studies, it is able to reproduce the observed NPF rates in remote forested region. However, i feel we have to be careful about over-interpretation of the role of amine in NPF, since there are also CLOUD chamber studies proving the extremely low volatility organic vapors can do the same job as amines, it is somehow not clearly quantifiable the relative contributions of amines and low-volatility compounds in the NPF events probably (or if there is, the authors should mention this). And i think this is worth to be mentioned in the MS.

Authors: Yes. We will state in the introduction, where other VOCs and their contribution to NPF is mentioned, that it is unclear how the relative importance of amines vs. other VOCs acts under field conditions.

Mari Pihlatie (Referee2): Reviewer: In order to further improve the paper, and to make
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a more balanced picture of the current understanding of different terrestrial sources of amines, I suggest, despite the uncertainties, that more space is given to discuss potential for amine emissions from soils and fungi. This can be done by reorganizing the chapter 3 (Vegetation as a potentially significant source . . .) so that all the other sources of amines (soils, fungi etc) are presented in the end, or preferably so that a new chapter is added (e.g. 4: soils and fungi as other potential sources for amines) to discuss amine concentrations and potential for emissions from fungi and soils. These issues are already shortly discussed in page 3221, rows 21-26 (fungi) and pages 3222-3223 (soils), and could now be given a bit more attention and deepness. Despite the fact that these topics are very little studied and the discussion may remain speculative, they may be equally important sources of amines, and hence should not be left out from the discussion.

Authors: We fully agree with this statement. We re-arrange section 3 (dividing it into two subsections: 3.1 Amines from living plants, 3.2 Amines from organic matter and in fungi) in order to include a new subsection 3.2 discussing the other sources (soil, fungi, organic residues) as already incorporated in the present section 3. These processes are very little studied. Their contribution to gas phase amines is an interesting scientific topic of high potential importance due to the ubiquitous presence of heterotrophic processes. To pronounce the potential relevance of amines from soil a little more, we slightly adjust this part from the abstract: "In addition, vegetative plant tissue exhibiting high amounts of MAs might potentially lead to significant emissions, and the decomposition of organic material could constitute another source for airborne MAs." into "In addition, vegetative plant tissue exhibiting high amounts of MAs might potentially lead to significant emissions. The decomposition of organic material constitutes another, potentially ubiquitous, source for airborne MAs."

Reviewer: ...This is also closely related to the aspects of the potential impact of increased reactive nitrogen (Nr) load onto terrestrial ecosystems, as it is clear that an increase in Nr will certainly influence soil N turnover processes, which may stimulate

also amine formation and emissions.

Authors: We also think that accelerated N turnover could have an increasing effect on amine formation and discuss the impact of Nr deposition on biomass turnover on p.13, l.10-20. We extend this statement with the link to the new subsection on organic matter sources to highlight their role: "In principle, accelerated amine formation from decaying organic matter (Sect. 3.2) might co-vary with an accelerated biomass turnover".

Reviewer: Specific comments...

Authors: All specific comments, raised by Mari Pihlatie, are addressed in the final manuscript, following the suggestions.

Additional author's comment not related to the reviewer's comments:

Very recently, another manuscript dealing with state-of-the-art ambient amine measurements (bisulphate-cluster based AP-CIMS) at the Hyytiälä site has been published (Sipilä et al., 2015; Atmospheric Measurement Techniques Discussions, doi: 10.5194/amtd-8-3667-2015). During May 2013, the authors found negligible amounts of DMA without relationship to NPF, but they detected TMA + PA and a C4-amine (unquantified). These data represent a useful addition to the measurements presented in our manuscript (p.7), since they are 1) from the comparatively most investigated site Hyytiälä, 2) seem to have unmatched low detection limit for DMA, and 3) the authors criticise and discuss the reliability of measurements in former studies, also presented in our manuscript. We add the study by Sipilä et al. at p.7 and modify the conclusion (at the bottom of p.7 and top p.8): "Despite high measurement uncertainties (Freshour et al., 2014), such elevated MA concentrations and higher ratios to NH₃ in comparatively remote situation compared with agricultural environments, could point towards vegetation as another source for MAs". It now reads: "The uncertainties of measured gas-phase amines are substantial due to uncertainties in relation to calibration, instrument drift, inlet absorption, gas-to-particle partitioning, and detection interference with other gas species (Freshour et al., 2014; Sipilä et al., 2015). Elevated MA concen-

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trations and higher ratios to NH₃ in comparatively remote situation, compared with agricultural environments, could point towards vegetation as another source for MAs. Yet, the topic has to be further investigated." For the sake of completeness, we also add one sentence at p.7, referring to a recent contribution (Hemmilä et al., 2015; Geophysical Research Abstracts, 7) with amine determination in 2014 at Hyytiälä: "Recent measurements continued to find airborne amines at that site (Hemmilä et al., 2015)".

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