Biogeosciences Discuss.,
doi:10.5194/bg-2016-363-AC3, 2017

Biogeosciences Discussions
Open Access
EGU

Interactive comment on "Soil concentrations and soil-atmosphere exchange of alkylamines in a boreal Scots pine forest" *by* A.-J. Kieloaho et al.

A.-J. Kieloaho et al.

antti-jussi.kieloaho@helsinki.fi

Received and published: 6 January 2017

You are right; one clear weakness in our study is the assumption that the soil solution concentrations of amines are constant. We had discussion on that issue already when we started to work with this project, and we acknowledge that this assumption simplifies the true condition. However, as the amine concentration measurements in any media (atmosphere, soil, vegetation, fungi) are very rare or nonexistent, and as our study is the first to present amine concentrations in fungal biomass and in boreal forest soil, we decided to keep the estimation scheme simple and approach straightforward. This decision is based on the lack of knowledge in production and consumption processes of amines in the soil-plant systems – as clearly mentioned in the manuscript.

It should be noted that our study is the first one where amine concentrations in fungal

Printer-friendly version

Discussion paper

biomass and in boreal forest soils are presented. It is possible that soil solution of amines follows same kind of seasonal pattern as Pajuste and Frey (2003) have suggested for ammonium. In the case of amines, it is known that plants are able to take up at least monomethylamine (Kielland, 1994; Wallender and Read, 1999, and Javelle et al., 1999), however use of amines as a source of nitrogen for plants is not well established (Shiraishi et al., 2002; Vranova et al., 2011). One main result of our study was that we could clearly identify gaps in the knowledge concerning amines exchange between biosphere and the atmosphere and suggest future work to better understand the role of amines in soil-atmosphere exchange. As addressed here, assuming the constant soil concentration is not a weakness but also one of the main results of this study. This issue needs to be studied further in future projects.

What comes to the concerns about depletion of amine pool in soil, the ratio of amines in soil solution vs. in volatile form in ambient air is in our study 100 to 1 for DMA and 1 to 1 for DEA. This means that the pool of DMA in the soil matrix does not change very rapidly due to volatilization, while there seem not to be significant of pool of DEA in the studied soil. In addition, as the fungal hyphae was found a significant pool of amines in our study, based on recent studies on renewal of the fungal hyphae (Pickles et al., 2010; Santalahti et al., 2016), we can be quite confident that the renewal of the fungal hyphal biomass in soil is fast enough to release amines into the soil throughout the growing season. Also if amines are released from soil decomposition processes as suggested by Sintermann and Neftel (2015), we can be confidently assume that amines are released into the soil throughout the growing season in a rate that outcompetes the loss to the atmosphere. In addition, our data suggests that there seems to be hot periods (e.g. autumn) when even more amines as discussed in this manuscript are released into the soil solution and potentially emitted to the atmosphere. But naturally, this should be validated in future studies, when we have better understanding of soil processes involved in amine exchange, and a longer time series of the soil amine concentrations. We did, as suggested, additional sensitivity analysis by introducing artificial sinusoidal diurnal cycle into the weekly ambient air concentrations. As the diurnal

cycles for studied amines are not yet fully understood, we introduced two scenarios based on current knowledge. In the first scenario we set ambient air concentration minimum at 4 am assuming that diurnal cycle follows that of air temperature. You et al. (2014) observed temperature dependent diurnal cycle for NH3 and trimethylamine in their measurements in a forest site in Alabama (US). In the second scenario we set minimum at 2 pm assuming amine concentrations behaves as observed for monoterpenes in the studied forest environment by Hakola et al. (2012). In the both scenarios, amplitude of ambient air concentrations was set to be two times the measured ambient air concentrations as suggested.

In the manuscript, the estimated mean DMA flux was 170 (±51) nmol m-2 d-1 and DEA flux was -1.2 (±1.2) nmol m-2 d-1 during the study period from May to November. When the artificial diurnal cycles were introduced the DMA flux was 170 (±61.8) nmol m-2 d-1 (Fig. 1 middle) and DEA flux was -1.12 (±2.79) nmol m-2 d-1 (Fig. 2 middle) in the first scenario. In the second scenario the DMA flux was 169 (±55.8) nmol m-2 d-1 (Fig. 1 lower) and for DEA the flux was -1.22 (±2.90) nmol m-2 d-1 (Fig 2. lower) during the study period. In the case of DMA diurnal cycle did not have as great effect on the fluxes estimated in the manuscript. It did however increase the variability as you suspected if minimum is at 4 am. In the case of DEA, diurnal cycle has greater effect on flux estimates. Based on the artificial diurnal cycle it can be that soil can act as a source for DEA. However, at the current knowledge diurnal cycle of the amines is not known and this should be studied further as soon as there is possibility to measure amines more frequently than in weekly concentration measurements conducted by Kieloaho et al. (2013).

Following text was added in the manuscript (P11 L12-L20): The weekly ambient air concentration measurements neglect potential diurnal variation of the studied alkylamines. To assess whether this significantly affects the estimated DMA and DEA fluxes, two different sinusoidal diurnal cycles were introduced. The first scenario assumes the diurnal cycle follows that of air temperature, as suggested for NH3 and

trimethylamine in a forest site in Alabama (US) (You et al., 2014). The second scenario assumes that diurnal cycle of alkylamines behaves as observed for monoterpenes at the site of our study (Hakola et al., 2012). Consecuently, the minimum concentrations were assumed to occur at 4 am and 2 pm, respectively, and the amplitude of ambient air concentrations was set to be two times the measured weekly concentration.

Following text was added in the manuscript (P15 L12-L16): The flux estimates were modestly sensitive to assumed diurnal cycle of ambient air concentration. Assuming air temperature –dependent diurnal cycle (scenario 1), the DMA flux was 170 ($\pm$61.8) nmol m-2 d-1 and DEA flux was -1.12 ($\pm$2.79) nmol m-2 d-1. In the second scenario, which assumes the alkylamines behave as that of monoterpenes, the DMA flux was 169 ($\pm$55.8) nmol m-2 d-1 and for DEA the flux was -1.22 ($\pm$2.90) nmol m-2 d-1.

Following text was added in the manuscript (P18 L6-L12): The diurnal cycles of ambient air concentrations of the studied amines are still currently unknown. By introducing artificial diurnal cycles as observed for trimethylamine or NH3 (You et al., 2014), and monoterpenes (Hakola et al., 2012), it was found out that the diurnal cycles are not likely to have major effect on estimated DMA flux. However, the unknown diurnal cycle of ambient DEA concentration may significantly contribute of the uncertainty and even to sign of the estimated DEA soil-atmosphere DEA flux.

Analytical procedure was validated elsewhere (Ruiz-Jimenez et al., 2012). Recoveries and stability of the analytes were assessed with standard addition method at two concentrations (0.25 and 10 ng per sample). Addition was performed to a pool aerosol sample. According to the results, the analytes were quantitatively recovered and they were stable for the period of the analysis. However, we can never be sure that the studied amines are not produced from other compounds during the sampling, storage or sample preparation, since no relevant/suitable reference material is available.

The following clarification was added to the paper (P16 L8-L13): There is a possibility that degradation of sample compounds results in formation of the studied analytes

during the sample preparation procedure. This, however, could not be assessed, due to the absence of suitable reference materials, thus increasing the measurement uncertainty. Similarly, some of the studied amines could have degraded into smaller compounds and hence not to detected in our analysis, leading to underestimation of the concentrations of the studied compounds.

The mistakes mentioned in technical comments are corrected into the text.

References

Hakola, H., Hellén, H., Hemmilä, M., Rinne, J., and Kulmala, M. (2012). In situ measurements of volatile organic compounds in a boreal forest. Atmos. Chem Phys., 12:11665-11678.

Javelle, A., Chalot, M., Södeström, B., and Botton, B. (1999). Ammonium and methylamine transport by the ectomycorrhizal fungus Paxillus involutus and ectomycorrhizas. FEMS Microbial Ecology, 30:355-366.

Kielland, K. (1994). Amino acid absorption by Arctic plants: implications for plant nutrition and nitrogen cycling. Ecology, 75:2373-2383.

Pajuste, K. and Frey, J. (2003). Nitrogen mineralization in podzol soils under Scots pine and Norway spruce stands. Plant and Soil, 257:237-247.

Pickles, B.J., Genney, D.R., Potts, J.M., Lennon, J.J., Anderson, I.C., and Alexander, I.J. (2010). Spatial and temporal ecology of Scots pine ectomycorrhizas. New Phytologist, 186:755-768.

Ruiz-Jiminez, J., Hautala, S.S., Parshintsev, J., Laitinen, T., Hartonen, K., Petaja, T., Kulmala, M., and Riekkola, M.-L. (2012). Aliphatic and aromatic amines in atmospheric aerosol particles: comparison of three techniques in liquid chromatography-mass spectrometry and method development. Talanta, 97:55-62.

Santalahti, M., Sun, H., Jumpponen, A., Pennanen, T., and Heinonsalo, J. (2016).

Vertical and seasonal dynamics of fungal communities in boreal Scots pine forest soil. FEMS Microbiol Ecology, DOI:10.1093/femsec/fiw170.

Shiraishi, T., Kawamoto, Y., Watanabe, T., Fukusaki, E.-I., and Kobayashi, A. (2002). Methylamine treatment changes the allocation of carbohydrate to roots in rice plants. Journal of Bioscience and Bioengineering, 94:460-466.

Sintermann, J., and Neftel, A. (2015). Ideas and perspectives: on the emissions of amines from terrestrial vegetation in the context of new atmospheric particle formation. Biogeoscience, 12:3225-3240.

Talbot, J.M., and Treseder, K.K. (2010). Controls over mycorrhizal uptake of organic nitrogen. Pedobiologia, 53:169-179.

Vranova, V., Rejsek, K., Skene, K.R., and Formanek, P. (2011). Non-protein amino acids: plant, soil and ecosystem interactions. Plant and Soil, 342:31-48.

Wallender, T. and Read, D.J. (1999). Kinetics of amino acid uptake of ectomycorrhizal roots. Plant, Cell and Environment, 22:179-187.

You, Y., Kanawade, V.P., de Gouw, J.A., Guenther, A.B., Madronich, S., Sierra- Hernández, M.R., Lawler, M., Smith, J.N., Smith, J.N., Takahama, S. et al. (2014) Atmospheric amines and ammonia measured with a chemical ionization mass spec- trometer (CIMS). Atmospheric Physics and Chemistry, 14:12181–12194.

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-363, 2016.

Printer-friendly version

Discussion paper

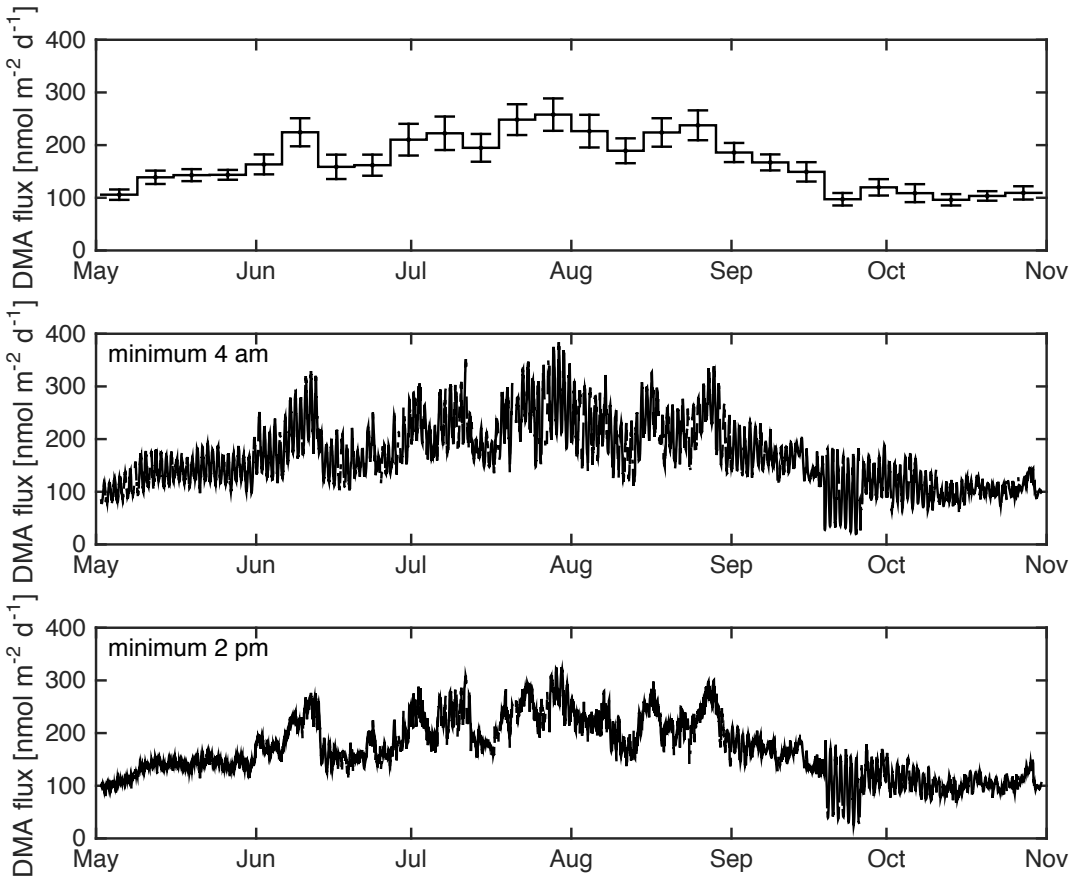

Fig. 1. Estimated fluxes for DMA. In the upper panel fluxes with standard deviations as presented in the manuscript, in the middle and in the lower panels fluxes with artificial diurnal cycles at minimum 4 am

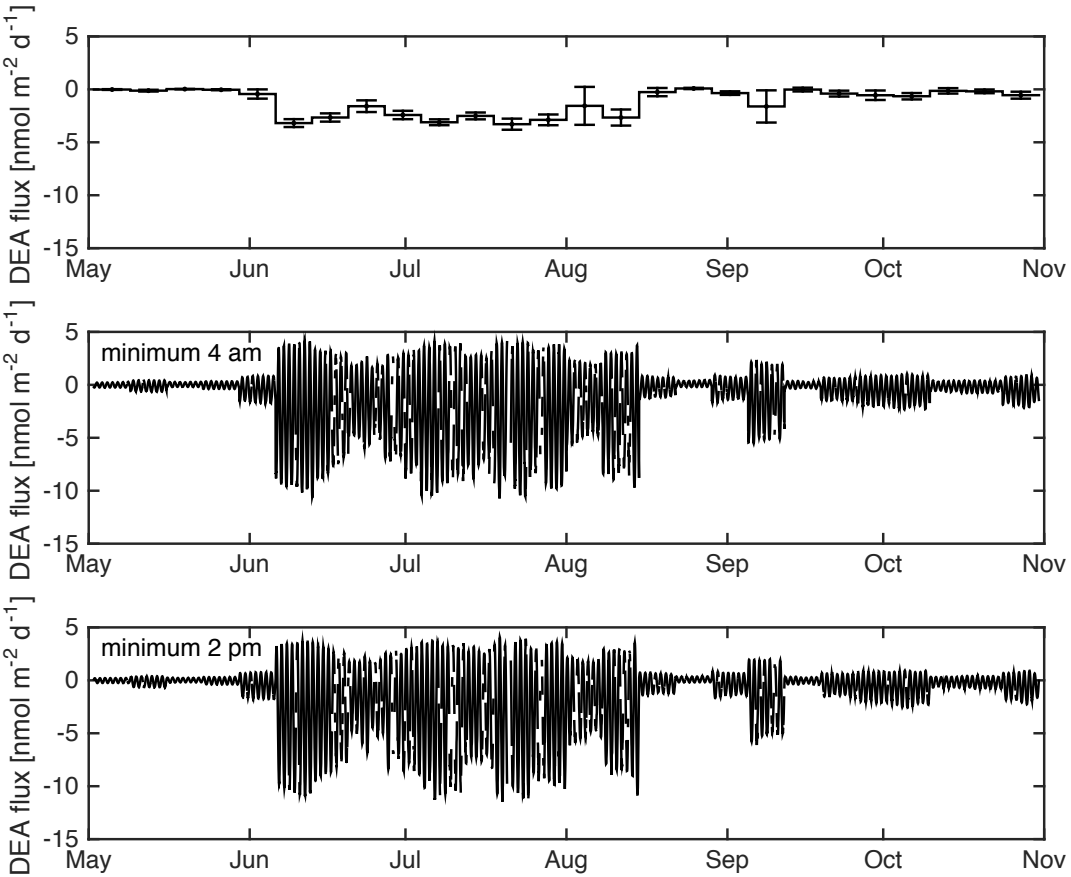

Fig. 2. Estimated fluxes for DEA. In the upper panel fluxes with standard devations as presented in the manuscript, in the middle and in the lower panels fluxes with artificial diurnal cycles at minimum 4 am

Fig. 3. Illustration of Scots pine rhizosphere and mycorrhizosphere on boreal forest humus.

Printer-friendly version

Discussion paper