

Response letter

Dear Editor,

sorry for inconvenience. We added the short discussion about the N fluxes and in the context of yearly N fluxes and N content measured from the studied forest in the manuscript as requested Dr. A. Neftel. We updated the response letter accordingly. These additions are highlighted in yellow.

Best regards,

Antti-Jussi Kieloaho and co-authors

**“The main weakness of the paper is the assumption that the soil solution concentrations of amines are constant over the entire May-Oct period, and representative of the study area. This has a major impact on the quantitative (and possibly qualitative) conclusions and does not seem to have been validated in any way. Is this assumption at least consistent with the magnitude of the emissions estimated for DMA (i.e. are fluxes of the size likely to deplete the soil pool over the measurement period, in the absence of other processes)?”**

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 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.

**“Another drawback of the analysis is that the time resolution of the atmospheric samples (weekly integration) is much lower than the timescale of variability in the conditions that drive the fluxes. Therefore the authors are forced to assume that the average concentration holds throughout the integration period, which is almost certainly not the case. I think one additional sensitivity study would help in assessing how much uncertainty this introduces to the flux estimates. For example, if an artificial diurnal cycle could be imposed on the atmospheric concentration data (giving the same average concentration), with a factor of two difference in concentrations between noon and midnight, how would this affect the calculated fluxes?”**

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 NH<sub>3</sub> 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 ( $\pm 51$ ) nmol m<sup>-2</sup> d<sup>-1</sup> and DEA flux was -1.2 ( $\pm 1.2$ ) nmol m<sup>-2</sup> d<sup>-1</sup> during the study period from May to November. When the artificial diurnal cycles were introduced the DMA flux was 170 ( $\pm 61.8$ ) nmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 1 middle) and DEA flux was -1.12 ( $\pm 2.79$ ) nmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 2 middle) in the first scenario. In the second scenario the DMA flux was 169 ( $\pm 55.8$ ) nmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 1 lower) and for DEA the flux was -1.22 ( $\pm 2.90$ ) nmol m<sup>-2</sup> d<sup>-1</sup> (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 NH<sub>3</sub> 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). Consequently, 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<sup>-2</sup> d<sup>-1</sup> and DEA flux was -1.12 ( $\pm 2.79$ ) nmol m<sup>-2</sup> d<sup>-1</sup>. In the second scenario, which assumes the alkylamines behave as that of monoterpenes, the DMA flux was 169 ( $\pm 55.8$ ) nmol m<sup>-2</sup> d<sup>-1</sup> and for DEA the flux was -1.22 ( $\pm 2.90$ ) nmol m<sup>-2</sup> d<sup>-1</sup>.

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 NH<sub>3</sub> (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.

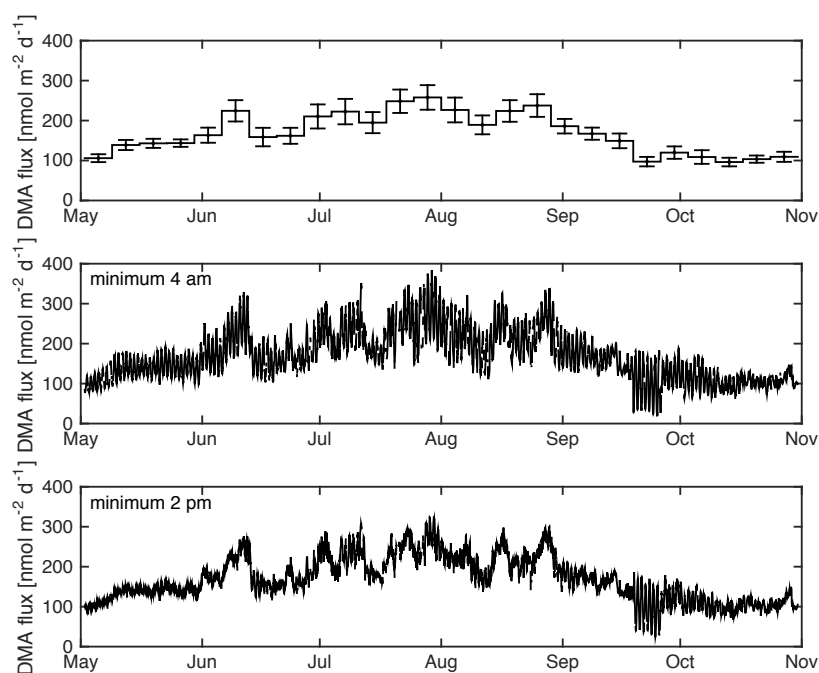


Figure 1. Estimated fluxes for DMA. In the upper panel fluxes with standard deviations as presented in the manuscript, in the middle and in the lower panels fluxes with artificial diurnal cycles at minimum 4 am and 2 pm, respectively.

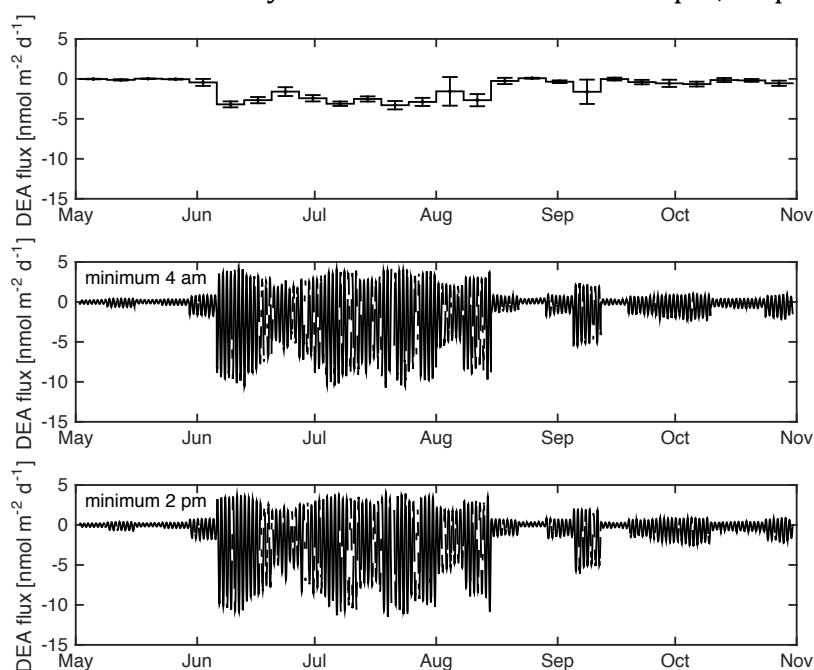


Figure 2. Estimated fluxes for DEA. In the upper panel fluxes with standard deviations as presented in the manuscript, in the middle and in the lower panels fluxes with artificial diurnal cycles at minimum 4 am and 2 pm, respectively.

**“It should be clarified in the abstract that the mixing ratio attributed to DMA could also have contributions from EA.”**

This is now clarified in the abstract and following sentence was added:

Used ambient air concentration of DMA was a sum of DMA and ethylamine.

**“Section 2.3 - What procedures were used to confirm that the target amines were stable in the extraction procedures described? Perhaps more relevant, can you be sure that there’s no contribution from larger molecules degrading to release these simple amines during the extraction procedure?”**

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.

**“Section 2.4 - How reasonable is the assumption that the soil solution concentrations are constant over the entire May-Oct period, and representative of the study area? This has a major impact on your conclusions and does not seem to have been validated in any way.”**

As the consumption and release processes of amines in soils are not well established as stated previously, and to keep the estimation method straightforward the effect of different soil solution levels on the fluxes were studied by sensitivity analysis. Based on the results, one of the main reservoirs of amines in the soil is fungal hyphal biomass and as stated in the manuscript fungal biomass is present in large quantity in boreal forest soil (Wallander et al., 1999). In a square meter scale fungal hyphae are present in an almost evenly distributed throughout the forest soil (Pickles et al., 2010) and this biomass is being constantly renewed (Pickles et al., 2010, Santalahti et al., 2016). However, due to significant methodological challenges, very little is known of the fungal hyphal turnover rates in soils. New developments in methodology, based on the use of molecular biological tools and stable isotopes, and extensive field scale studies are expected to provide more detailed information on fungal hyphal dynamics in boreal forest soils.

To illustrate to complexity of the boreal forest soils, in the Fig. 3 it can be seen how intensively soil is colonized by ectomycorrhizal fungal hyphae. As the turnover rate of this (in the picture mostly white) hyphae may vary from days to months, it is obvious that there are uncertainties related to the assumptions that soil solution concentrations are constant. However, in a stand scale we assume that over any time range, the average amine flux from fungal hyphae to soil may well be rather constant, supporting our assumptions in the manuscript.

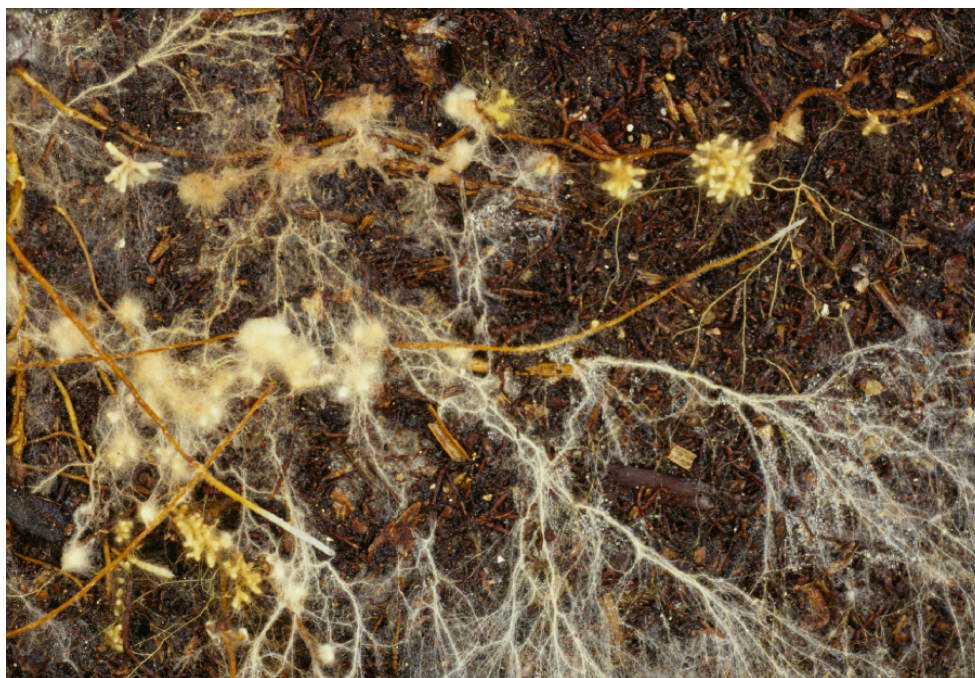


Figure 3. Illustration of Scots pine rhizosphere and mycorrhizosphere on boreal forest humus.

**“Technical comments L24 – atmosphere is misspelled For the Sipila paper, the reference is to the Discussion rather than final version.”**

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

**“The authors discuss the role of boreal forest soil layers as amine source. There is a striking in balance between the apparent importance that amines play in the context of aerosol formation and the knowledge on the emissions. The study focus on fungi as a potential source and presents an estimation of potential exchange fluxes of two amines (DMA and DEA) that have been experimentally accessible. The authors follow a reasonable simple strategy and estimate the fluxes based on a resistance analogy between the concentration in the atmosphere above the soil and the concentration in the open pore space of the soil. The paper is within the scope of BG. An important result is the evidence that fungi in soil are a potential amine source and as fungi are generally part of the organic part of a soil system, soil surfaces can potentially emit amines. Atmospheric concentrations 2m above ground are available with weekly samples. The soil concentration used in the resistance analogy is calculated assuming equilibrium conditions over a water-air interface with given pH and temperature. The aqueous concentration is determined based on bulk extraction techniques of soil samples and in the laboratory grown fungal samples. I haven’t seen from which depth interval the soil samples have been taken. I also cannot judge whether the given values are representative and in the same order of magnitude as what effectively occurs in nature. But the assumption of a single pore space concentration values logically reduces the calculated dynamic of the concentrations in the open pore space over the reported time frame to variability in soil pH, soil water content and soil temperature.”**

Soil samples were collected from 3 to 5 cm depth in the soil from mixed F and O-horizons. As described in the manuscript, small sample set of field samples were collected. At the time of analysis of field samples only standards for DEA was available. When DEA concentration was compared with the concentrations measured from the experiments, we found out that DEA concentrations were in the same order of magnitude or slightly higher in the field samples than in the samples from experiments.

**“The analysis drastically shows that the depth of the humus layer has the strongest influence on the estimated exchange flux (see figure 6E). This is a consequence of the chosen approach as with the resistance analogy the soil source is assumed to take place at the bottom, i.e. the amine molecules must diffuse through a soil layer with a thickness  $\Delta z$  and  $r_g$  sharply increases with increasing  $\Delta z$ . I rather think that potential amine sources are distributed in the humus layer proportionally to the decaying rate of fungi. I can also imagine that there are existing consumption processes of amines, so that most of the amines that enter the open pore space will be consumed before they have the chance to reach the atmosphere. The assumed mean layer of 5cm could be a reasonable compromise to yield numerically good looking fluxes.**

**All in all, I am not fully convinced that the soil in Hyytiälä act as the amine source that drives the measured concentration at 2m in the trunk space. It would be important to directly determine e.g. DMA concentration at the soil surface to give evidence for an emission gradient. The new generation of “ptr-qitof” systems promises to have sensitivities below 1 ppt that should be sufficient to detect a gradient. But of course this is a recommendation for future work and I am also aware tat this systems are very expensive.”**

We agree with You that method we used has drawbacks and it leaves room for discussions. To overcome the restrictions of our straightforward method, we did sensitivity analysis to identify major sources of uncertainties rising from the used estimation method, e.g. we studied effect of depth of amine source in the soil profile. At the present knowledge or according to this study, we cannot conclude that soil processes drive ambient air concentrations of amines. Our approach is the first attempt to identify possible sources in a forest environment. As presented in the manuscript, boreal forest soil contains large and renewing pool of amines in hyphal biomass. According to our results, we can say that it is possible that amines can be released from the soil into the atmosphere. As You stated it is of major importance to study the soil-atmosphere amine exchange further by measuring gradient of amines in different compartments of boreal forest ecosystems.

Thank You for the tip of the instrument! At the moment, it seems that the measurement techniques are not developed enough to measure gaseous fluxes of amines due to the problems with proton affinity higher than water of these compounds. Measurement techniques utilizing proton transfer reaction (PTR)

and hydronium ions as ion source are not suitable for primary or secondary amines. In the case of tertiary amines, proton transfer method using hydronium ions can be used with caution. We would like to thank You for an interesting future topic for studying amines in soil-plant systems. We are aware of a modified version of the PTR technique that uses charged oxygen ions instead of hydronium ions (Sintermann et al., 2011). This technique could potentially be used for amine measurements, but in our knowledge, however, to our understanding it is not commercially available. We are looking forward for more advance techniques utilizing chemical ionization methods and new studies utilizing on-line measurements of amines.

**“A last point: I converted the mean DMA flux of 170nm m<sup>-2</sup> and d-1 to roughly 9 gr ha<sup>-1</sup>yr<sup>-1</sup> as I am more used to judge N fluxes per hectare. It would be helpful if this number is discussed in the context of the yearly N turnover in Hyytiälä. I assume that the vegetation at this station is generally N limited and that the biological systems are using N economically. If I assume the typical ratio of /NH<sub>3</sub> of 1% that is found in agricultural systems, total reduced N emissions of the soil compartment would be around 1 kg ha<sup>-1</sup>yr<sup>-1</sup>. Is this plausible?”**

If we use suggested 1% for typical ratio of amines and NH<sub>3</sub> in agricultural systems, and get the total reduced N emissions of 1 kg ha<sup>-1</sup> yr<sup>-1</sup>, the total reduced N emission is slightly higher than the measured N<sub>2</sub>O emissions (0.3 kg ha<sup>-1</sup> yr<sup>-1</sup>) from the studied forest soil (Pihlatie et al., 2007; Korhonen et al., 2013). The total reduced N emission value seems to be in reasonable range or at least a good upper estimate as the soil NO<sub>3</sub><sup>-</sup> content at the site is reported negligible while the reduced N (organic and ammonium) content is markedly higher (Korhonen et al., 2013). The highest nitrogen pool in the studied forest ecosystem is bound to the litter/humus layer (combined F and O horizons; Korhonen et al., 2013), which is approximately 5 to 10 cm thick. In the studied forest site O horizon contained 710 kg N ha<sup>-1</sup> and it is approximately 34% of total N pool in the forest (Korhonen et al., 2013). Unlike in agricultural soils, Korhonen et al. (2013) showed that in the studied forest 98.9% of the extractable N is in the form of organic N (26.8 kg N ha<sup>-1</sup>) and most of the mineral nitrogen is in the form of ammonium (0.31 kg N ha<sup>-1</sup>).

Based on the N pools in the studied boreal forest environment, we know that the organic N pool is the largest in the whole forest. We also know, based on our earlier studies that mycorrhizal fungi are capable of degrading and utilizing organic N compounds as nutrient source (Talbot and Treseder, 2010). Hence, we hypothesize that soil fungi could also release amines into the soil solution as we demonstrated that they contain high quantities of amines. At the moment the knowledge about the soil solution concentrations of amines (especially in natural systems) are scarce and we cannot say in which ratio amines are present in the soil respect to ammonium or do the amines and ammonium share similar release and consumption processes. Equally likely as assuming a fixed ratio of amine and NH<sub>3</sub> emissions, it is possible that fixed ratio with NH<sub>3</sub> does not exist. This is topic clearly calls for further studies.



We added following paragraphs in the discussion section (P19 L7-L19) and added Korhonen et al. (2013) in the reference list.

The mean DMA flux of  $170 \text{ nmol m}^{-2} \text{ d}^{-1}$  is approximately  $9 \text{ g ha}^{-1} \text{ yr}^{-1}$  and the annual flux is slightly higher than that of nitrous oxide ( $\text{N}_2\text{O}$ ,  $3 \text{ g ha}^{-1} \text{ yr}^{-1}$ ) measured from the studied forest (Pihlatie et al, 2007, Korhonen et al., 2013). It is likely that soil fluxes of reduced N are higher than those of oxidized forms (e.g. HONO and  $\text{N}_2\text{O}$ ) due to higher dissolved organic nitrogen and  $\text{NH}_4^+$  concentrations in soil solution (Korhonen et al., 2013). Unlike in agricultural soils, Korhonen et al. (2013) showed that in the studied forest 98.9% of the extractable N is in the form of organic N ( $26.8 \text{ kg N ha}^{-1}$ ) and most of the mineral nitrogen is in the form of ammonium ( $0.31 \text{ kg N ha}^{-1}$ ). In the studied forest site O horizon contained  $710 \text{ kg N ha}^{-1}$  and it is approximately 34% of total N pool in the forest being the highest nitrogen pool in the studied forest ecosystem (Korhonen et al., 2013). Mycorrhizal fungi are capable of degrading and utilizing organic N compounds in soil as nutrient source (Talbot and Treseder, 2010). Hence, we suggest that soil fungi could also release amines into the soil solution as we demonstrated that they contain high quantities of amines.

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# Soil concentrations and soil-atmosphere exchange of alkylamines in a boreal Scots pine forest

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## Abstract

Alkylamines are important precursors in secondary aerosol formation in the boreal forest atmosphere. To better understand the behaviour and sources of two alkylamines, dimethylamine (DMA) and diethylamine (DEA), we estimated the magnitudes of soil-atmosphere fluxes of DMA and DEA using a gradient-diffusion approximation based on measured concentrations in soil solution and in the canopy air space. Used ambient air concentration of DMA was a sum of DMA and ethylamine. To compute the amine fluxes, we first estimated the soil air space concentration from the measured soil solution amine concentration using soil physical (temperature, soil water content) and chemical (pH) state variables. Then, we used the resistance analogy to account for gas transport mechanisms in the soil, in soil boundary layer and in the canopy air space. The resulting flux estimates revealed that the boreal forest soil with a typical long-term mean pH 5.3 is a possible source of DMA ( $170 \pm 51 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) and a sink of DEA ( $-1.2 \pm 1.2 \text{ nmol m}^{-2} \text{ d}^{-1}$ ). We also

1 investigated the potential role of fungi as a reservoir for alkylamines in boreal forest soil. We  
2 found high DMA and DEA concentrations both in fungal hyphae collected from field humus  
3 samples and in fungal pure cultures. The highest DMA and DEA concentrations were found  
4 in fungal strains belonging to decay and ectomycorrhizal fungal groups, indicating that boreal  
5 forest soil, and in particular, fungal biomass may be an important reservoir for these  
6 alkylamines.

7

## 8 **1 Introduction**

9 Aerosols are important in cooling the atmosphere through increasing the scattering of sunlight  
10 and increasing albedo through cloud formation. In boreal forests, volatile organic compounds  
11 emitted from the biosphere largely drive aerosol formation, and aerosol growth to cloud  
12 condensation nuclei (Kulmala et al., 1998; Kerminen et al., 2010; Riipinen et al., 2012).  
13 Amines have been suggested to be one of the key compounds in the aerosol formation process  
14 (Angelino et al., 2001; Silva et al., 2008; Kurtén et al., 2008; Smith et al., 2009; Yu et al.,  
15 2012; Almeida et al., 2013).

16 Amines are nitrogenous organic molecules in the form of  $NR_3$ , where R denotes hydrogen or  
17 alkyl or aryl group. Low-weight alkylamines, which have one to six atom carbon chains  
18 bound to a nitrogen atom, are known to be degradation products of amino-acid-rich  
19 substrates, such as dairy or fish (Ge et al., 2011a). However, the origin of these amine  
20 compounds in natural environments is poorly understood. Sintermann and Neftel (2015)  
21 concluded that flowering of vegetation especially in springtime, and non-flowering vegetation  
22 during growing season are potential sources of alkylamines. Sintermann and Neftel (2015)  
23 suggested that the contribution of fungal sporocarps and decomposing organic matter as  
24 amine sources increases towards the autumn.

25 Low-weight alkylamines may be produced in soils during the degradation of organic N  
26 compounds, especially amino acid decarboxylation (Yan et al., 1996; Xu et al., 2006). Kim et  
27 al. (2001) and Rappert and Müller (2005) showed that quaternary ammonium compounds  
28 (e.g. carnitine, choline and betaine), often present in soil solution (Warren et al., 2013;  
29 Warren, 2014), could be degraded to alkylamines (trimethylamine, dimethylamine and  
30 monomethylamine) by the soil microbial community using both aerobic and anaerobic  
31 pathways. Sintermann and Neftel (2015) stated that decaying organic matter contains elevated

1 levels of precursor substances for alkylamine production, hence indicating that decaying  
2 organic matter may be a source of alkylamines.

3 Concentrations of alkylamines in atmospheric particles and in gas phase are rarely reported  
4 from boreal ecosystems, despite the importance of amines in aerosol formation processes  
5 (Mäkelä et al., 2001; Smith et al., 2009; Kieloaho et al., 2013), mostly due to challenges in  
6 detecting these compounds. Mäkelä et al. (2001) reported elevated concentrations of  
7 dimethylammonium (protonated dimethylamine) during particle formation periods in boreal  
8 forest. In our previous study (Kieloaho et al., 2013), we found the gas-phase alkylamines in  
9 boreal forest air, and we concluded that the seasonal variations in the atmospheric amine  
10 concentrations is linked to vegetation dynamics and soil activity.

11 Direct flux measurements of alkylamines are difficult to perform and are very rarely made  
12 (Sintermann and Neftel, 2015) due to the high reactivity of amines and lack of suitable  
13 measurement techniques and instrumentation. However, the magnitude of fluxes can be  
14 indirectly estimated if the concentrations of the target compounds in different reservoirs (e.g.  
15 vegetation, soil and atmosphere) are known. In general, the fluxes are driven by a  
16 concentration gradient between the reservoirs, such as ambient air and an aqueous solution.  
17 As follows, gas-phase concentration in soil air can be calculated by assuming equilibrium  
18 between the aqueous solution and the gas-phase above the solution (Farquhar et al., 1980;  
19 Nemitz et al., 2000). Furthermore, the fluxes through a soil-atmosphere boundary can be  
20 estimated using a gradient-diffusion approximation, often presented by an electrical resistance  
21 analogy (Hicks et al., 1987; Seinfeld and Pandis, 1998; Sutton et al., 1998).

22 In this study, we used three layers to estimate the potential exchange of two alkylamines,  
23 dimethylamine (DMA) and diethylamine (DEA), between soil and the atmosphere (Figure 1).  
24 Amine concentrations in boreal forest soil and in fungal hyphae were measured, and used to  
25 estimate potential fluxes of the selected alkylamines from a boreal Scots pine forest soil to the  
26 atmosphere. We hypothesize that by using soil amine concentration data and the resistance  
27 analogy, it is possible to estimate the potential sources and sinks of alkylamines in the soil.

28

## 1 2 Materials and methods

### 2 2.1 Study site and supplementary measurements

3 Study site is a Scots pine forest at the SMEARII station (Station for Measuring Forest  
4 Ecosystem – Atmosphere Relations) at Hyytiälä (61°84'N, 24°26'E, 180 m a.s.l.) in southern  
5 Finland (Hari and Kulmala, 2005). The forest stand at the SMEARII station is approximately  
6 50 years old and dominated by Scots pine (*Pinus sylvestris* L.) with Norway spruce (*Picea*  
7 *abies* (L.) H. Karst.), birch (*Betula* L. spp.), and European aspen (*Populus tremula* L.), found  
8 occasionally in the understory. The most common plant species at the ground level are  
9 bilberry (*Vaccinium myrtillus* L.), lingonberry (*Vaccinium vitis-idaea* L.), wavy hairgrass  
10 (*Deschampsia flexuosa* (L.) Trin.), and heather (*Calluna vulgaris* (L.) Hull.). The most  
11 common mosses are Schreber's big red stem moss (*Pleurozium schreberi* (Brid.) Mitt.), and a  
12 dicranum moss (*Dicranum* Hedw. sp.) (Ilvesniemi et al., 2009). The soil at the site is Haplic  
13 podzol on glacial till, with an average depth of 0.5-0.7 m.

14 A half hour average of soil water content (at 0.05 m), soil temperature (at 0.05 m) and above  
15 canopy (at 23 m) friction velocity was used in the calculations of DMA and DEA equilibrium  
16 gas-phase concentrations in soil air, and to calculate DMA and DEA soil-atmosphere  
17 exchange. Soil temperature was measured using PT-100 resistance thermometers, and soil  
18 water content was measured with a time-domain reflectometer (TDR 100; Campbell  
19 Scientific Inc., Logan, UT, USA). A mean pH-value of 5.3 measured over 14-years, and  
20 sampled once per month during snow free period from three replicate suction cup lysimeters  
21 at 2 cm depth in the mineral soil was used. The 10 and 90 percentiles of the soil pH were 4.5  
22 and 6.0, respectively.

23 The ambient air concentrations of DMA and ethylamine (EA), and DEA were measured at 2  
24 m, below the overstory canopy (Kieloaho et al. 2013) and used in the flux estimation. The  
25 analytical procedure was incapable to resolve DMA and EA, and therefore only the sum of  
26 these compounds is reported, and later referred as DMA concentration. The DMA+EA and  
27 DEA air concentration measurements were conducted from May 2011 to October 2011 by  
28 collecting weekly air samples into phosphoric acid impregnated glass fiber filters described in  
29 detail in Kieloaho et al. (2013). Measured ambient air concentrations of DMA+EA varied  
30 from 0.49 to 6.4 nmol m<sup>-3</sup>, and the mean observed air concentration with standard deviation  
31 was 1.7±1.2 nmol m<sup>-3</sup> (Kieloaho et al., 2013). The highest concentration of DMA+EA

1 (6.4±0.83 nmol m<sup>-3</sup>) was measured in October. Ambient air concentration of DEA varied  
2 from 0.02 to 0.63 nmol m<sup>-3</sup> the mean being 0.26 (±0.22) nmol m<sup>-3</sup> (Kieloaho et al., 2013).

### 3 **2.2 Soil and fungal hyphae samples**

4 Soil samples were collected at same time in May 2011. The first soil samples were used to  
5 screen the concentrations of amines in the humus layer, mineral soil and visible fungal  
6 hyphae. A 10-liter sample of the humus layer (F/H-horizon) and a 5-liter sample from the  
7 underlying mineral B-horizon were collected. The soil was homogenized and stored at +4°C  
8 (for about day) until three 2 mL samples of mineral soil, humus layer, and visible fungal  
9 rhizomorphic hyphae were collected.

10 The second soil samples were stored at +4°C until used in the greenhouse experiment where  
11 the effects of soil organic matter decomposing enzymes on nitrogen turnover processes were  
12 studied (Kieloaho et al., 2016). The soil samples were extracted with 1 M KCl, and analyzed  
13 for low molecular weight amines as described in chapter 2.3.

14 In total 19 different fungal strains, representing 14 different Ascomycete and Basidiomycete  
15 fungal species were grown one by one for six weeks in LN-AS media containing axenic liquid  
16 cultures (Bäck et al. 2010). The strains were divided into four functionally distinct groups:  
17 ectomycorrhiza, ericoid mycorrhiza, endophytes and decay fungi based on their sequence  
18 identification. Individual strains used in this study are listed in Table C1.

19 Fungal biomass was collected from the liquid cultures using a Miracloth filter, rinsed with  
20 distilled water and stored at -20°C until extracted and analyzed for amines. Agar plugs and  
21 the growth media, used for fungal inoculation in flask cultures, were analyzed separately for  
22 amine concentrations as negative controls.

### 23 **2.3 Low molecular weight amine analysis**

24 Fungal biomass samples and the first set of soil samples were extracted by dynamic  
25 sonication assisted extraction for 20 minutes with flow rate of 0.5 mL min<sup>-1</sup> (1% aqueous  
26 acetic acid – acetonitrile, 1:1). Samples inserted in extraction chambers made of polyether  
27 ether ketone (PEEK, 5 cm length, i.d. 7.5 mm) equipped with screw caps. After extraction,  
28 samples were filtered through the 0.45-µm syringe filters. Extraction solvent was pumped  
29 through the extraction chambers, which were immersed in ultrasonic bath (Branson Sonifier

1 S-250 A, Branson, Danbury, CT, USA) using Jasco PU-980 HPLC pumps (Jasco Corp.,  
2 Easton, MD, USA).

3 The samples were statically extracted for 30 minutes. Mineral and humus soil samples, 21.8 g  
4 and 16.2 g of fresh weight, respectively, were extracted by sonication with 40 mL  
5 dichloromethane-methanol (1:1) together with 1 mL 1M HCl for 30 minutes. Also, 700 mg  
6 fresh weight of fungal hyphae samples was weighed and extracted with 10 mL of the  
7 extraction solvent with addition of 100  $\mu$ L 1M HCl. After the extraction, the fungal and  
8 mineral soil samples were evaporated to 5 mL and humus soil sample to 15 mL, and then  
9 filtered through 0.45  $\mu$ m acetyl cellulose syringe filters.

10 Low molecular weight alkylamines in extracts from soil, soil fungal hyphae and fungal pure  
11 cultures were analyzed with the analytical method introduced by Ruiz-Jiminez et al (2012).  
12 Soil extracts and cultured fungal biomass extracts were first dansylated. Since dansylated  
13 amines are relatively unstable, derivatized samples were analyzed immediately or within 24  
14 hours. Acetaminophen was used as an internal standard (the final concentration of the  
15 standard was 1 ng at the detector). The derivatization procedure tends to overestimate amine  
16 concentrations but the estimations of the relative amounts to the internal standard of amines  
17 are presumed to be accurate (Ruiz-Jiminez et al (2012).

18 Analysis of the samples was performed with an Agilent 1260 Infinity liquid chromatograph  
19 coupled via electrospray ionization to an Agilent 6420 triple quadrupole mass spectrometer  
20 (Agilent Technologies, Santa Clara, CA, USA). The initial mobile phase was a mixture of  
21 50% A (water acidified with 1% acetic acid) and 50% B (acetonitrile). Sample volume of 20  
22  $\mu$ L was injected and a linear gradient to 100% B in 10 minutes was applied. After 7 minutes  
23 in 100% B, mobile phase was decreased to 50% B in one minute. The column was let to  
24 equilibrate before the next injection for 7 minutes in 50% of B. A Hibar HR column  
25 (Purosphere, RP-18, endcapped, 2  $\mu$ m, 50 mm x 2.1 mm, Merck, Darmstadt, Germany) was  
26 used and the temperature was kept at 40  $^{\circ}$ C. Ionization parameters were as follows: drying  
27 gas (nitrogen) temperature 300  $^{\circ}$ C, gas flow 7.5 L min<sup>-1</sup> and nebulizer (nitrogen) 35 psi. MS1  
28 and MS2 heaters were kept at 100  $^{\circ}$ C. The dynamic multiple reaction monitoring acquisition  
29 method was applied. MassHunter Quantitative Analysis software B.04.00 was used for data  
30 processing.

31 To identify amines in the samples the following external standards were used:  
32 isopropylaniline, tripropylamine, 2-amino-1-butanol, DL-2-aminobutyric acid and



1 diethylamine for the first field soil samples and the soil fungal hyphae, and methylamine,  
2 dimethylamine, ethanolamine, diethylamine, dibutylamine, and *sec*-butylamine for the second  
3 soil samples (Kieloaho et al., 2016) and for pure fungal culture strains.

#### 4 **2.4 Concentrations of DMA and DEA in soil air**

5 The concentrations of DMA and DEA in soil solution (aq.) are obtained from the  
6 measurements in the greenhouse experiment on boreal forest soil (Kieloaho et al., 2016), and  
7 assumed to be constant during the whole study period. The DMA and DEA concentrations in  
8 soil solution were  $92.3 \mu\text{mol L}^{-1}$  and  $0.296 \mu\text{mol L}^{-1}$ , respectively.

9 The concentrations of non-dissociated DMA and DEA are calculated from the measured soil  
10 solution concentrations based on reversible acid-base reaction



12 where  $\text{R}_3\text{N}$  is non-dissociated amine molecule and R denotes either methyl or ethyl organic  
13 side group or hydrogen atom. The dissociation reaction reaches a temperature dependent  
14 equilibrium, which is independent of reactant and reaction product concentrations.

15 A concentration in soil solution is a sum of non-dissociated ( $\text{R}_3\text{N}$ ) and dissociated ( $\text{R}_3\text{NH}^+$ )  
16 forms of amines. In the first step, using equilibrium thermodynamic principles, the fraction  
17 ( $f_{\text{R}_3\text{N}}$ ) of total amine concentration present as non-dissociated form can be estimated (Montes  
18 et al., 2009), when the activity of  $\text{R}_3\text{N}$  and  $\text{R}_3\text{NH}^+$  are assumed to be equal. The activity of  
19 protons  $[\text{H}^+]$  in soil solution is based on the measured pH values. Equilibrium dissociation  
20 coefficients ( $\text{pK}_a$ ) for DMA and DEA are 10.3 and 10.5, respectively, and  $K_a$  is a negative  
21 logarithm of  $\text{pK}_a$ ,

$$22 f_{\text{R}_3\text{N}} = \frac{[\text{R}_3\text{N}]}{[\text{R}_3\text{N}] + [\text{R}_3\text{NH}^+]} = \frac{1}{1 + \frac{[\text{H}^+]}{K_a}} \quad (2)$$

23 In the second step, the non-dissociated DMA and DEA are partitioned between aqueous  
24 phases and soil air,



26 According to Henry's law, the solubility of non-dissociated gas in a solution is directly  
27 proportional to the partial pressure of the gas above the solution

$$28 k_H = \frac{c_{\text{R}_3\text{N}}}{p_{\text{soil}}}, \quad (4)$$

1 where  $k_H$  is Henry's law coefficient,  $c_{R3N}$  is non-dissociated aqueous phase concentration and  
 2  $p_{soil}$  is a partial pressure of alkylamines in soil gas phase. Due to temperature dependence,  
 3 acid dissociation ( $K_a$ ) and Henry's law coefficients were corrected for temperature by Van  
 4 t'Hoff equation

$$5 \quad k_{(T)} = k_1 e^{\frac{-\delta H^\circ}{R(T_2^{-1} - T_1^{-1})}}, \quad (5)$$

6 where  $k_{(T)}$  is the temperature corrected coefficient,  $k_1$  is the coefficient to be corrected,  $\delta H^\circ$  is  
 7 the enthalpy change in reaction or phase transition,  $R$  is the molar gas constant, and  $T_1$  and  $T_2$   
 8 are temperatures in Kelvins. To take into an account the effect of acid dissociation on the  
 9 partitioning of DMA or DEA between the aqueous and gas phases, a temperature corrected  
 10 acid dissociation coefficient was used to calculate the effective Henry's law coefficients  
 11 according to Seinfeld and Pandis (2006)

$$12 \quad k_{H(T,pH)} = k_{H(T)} \left( \frac{1+[H^+]}{K_{a(T)}} \right), \quad (6)$$

13 where  $k_{H(T)}$  is the temperature corrected Henry's law coefficient,  $[H^+]$  is measured proton  
 14 concentration of aqueous phase and  $K_{a(T)}$  is the temperature corrected acid dissociation  
 15 coefficient.

16 Henry's law coefficient, the acid dissociation coefficient, the acid dissociation reaction and  
 17 phase change energies were retrieved for DMA and DEA from National Institute of Standards  
 18 and Technology Chemistry WebBook (Linstrom and Mallard, 2014).

## 19 **2.5 Estimation of soil-air fluxes of DMA and DEA**

20 The soil-air fluxes ( $F$ ,  $\text{nmol m}^{-2} \text{d}^{-1}$ ) of DMA and DEA were estimated using flux-gradient  
 21 relationship (Figure 1) as

$$22 \quad F = \frac{C_s - C_a}{r_{tot}}, \quad (7)$$

23 where  $C_s$  and  $C_a$  are concentrations ( $\text{nmol m}^{-3}$ ) in the soil air space and in the atmosphere at  
 24 2.0 m above the forest floor, respectively, and  $r_{tot}$  ( $\text{s m}^{-1}$ ) is the total gas transport resistance,  
 25 which includes soil resistance ( $r_g$ ), quasi-laminar boundary layer resistance ( $r_b$ ) and  
 26 aerodynamic resistance ( $r_a$ ) in series.

1 In soil, the gas transport is dominated by molecular diffusion through the air-filled part of soil  
 2 matrix. The soil resistance ( $r_g$ , s m<sup>-1</sup>) in the organic soil layer of depth  $\Delta z_s$  (here 0.05 m) is  
 3 estimated as

$$4 \quad r_g = \frac{\Delta z_s}{D_p} = \frac{\Delta z_s}{D_o \theta_a^b}, \quad (8)$$

5 where the molecular diffusivity in soil  $D_p$  is computed from the molecular diffusivity in free  
 6 air ( $D_o$ ), using air-filled porosity ( $\theta_a$ ) to account for the reduced cross-sectional area and  
 7 increased path length in the soil relative to free air. The parameter  $b = 1.1$  as reported for  
 8 humus layer in Glinski and Stepniewski (1985).

9 The transport through the quasi-laminar boundary layer at the soil surface is described by the  
 10 soil boundary-layer resistance ( $r_b$ , s m<sup>-1</sup>) following Schuepp (1977)

$$11 \quad r_b = \frac{Sc - \ln(\delta_o/z_l)}{k_v u_{*g} z_l}, \quad (9)$$

12 where  $Sc$  is the Schmidt number,  $k_v$  ( $\sim 0.41$ ) is the von Kármán constant,  $u_{*g}$  is the near-  
 13 ground friction velocity, the height above the ground, where the molecular diffusivity and  
 14 turbulent transport efficiency equal, is  $\delta_o = D_o/k_v u_{*g}$ , and  $z_l$  is the height below which the  
 15 wind profile is assumed logarithmic. The model for  $r_b$  applied here is identical to that used to  
 16 compute gas-transfer e.g. in Baldocchi (1988), Nemitz et al. (2001) and Launiainen et al.  
 17 (2013).

18 The aerodynamic resistance ( $r_a$ ) accounts for the turbulent gas transport between the soil  
 19 surface and concentration measurement height ( $z_m$ ) in the canopy air space. The  $r_a$  is  
 20 calculated by integrating the inverse of eddy diffusivity ( $K_s$ , m<sup>2</sup> s<sup>-1</sup>) over the layer as in  
 21 Baldocchi (1988)

$$22 \quad r_a = \int_0^{z_m} \frac{1}{K_s(z)} dz. \quad (10)$$

23 The profile of  $K_s(z)$  within the canopy and the value of  $u_{*g}$  needed for computing  $r_a$  and  $r_b$ ,  
 24 are provided by a first-order closure model for momentum exchange within the canopy as in  
 25 Launiainen et al. (2013, 2015). As shown in Supplement B, the model computes mean  
 26 velocity, momentum flux ( $\overline{u'w'}$ ) and  $K_s$  profiles from local balance of momentum absorption  
 27 and canopy drag neglecting the effects of atmospheric stability. The latter have been shown  
 28 modest for below-canopy flow statistics at the SMEAR II –site (Launiainen et al., 2007).

1 For DMA and DEA flux estimates, the measured weekly mean ambient air concentrations and  
 2 their standard deviations (Kieloaho et al., 2013) were used. Soil air concentrations and total  
 3 resistances were obtained from the calculated half-an-hour values and averaged to weekly  
 4 means and their weekly standard deviations. Gaussian error propagation was used to estimate  
 5 the error of flux estimate with an assumption that errors of concentration gradient ( $C_{gr} =$   
 6  $C_s - C_a$ ) and total resistance ( $r_{tot}$ ) are independent from each other. The error, expressed as  
 7 standard deviation of soil flux ( $F_{std}$ ), was calculated from normalized standard deviations of  
 8  $C_{gr}$  and  $r_{tot}$

$$9 \quad F_{std} = F \sqrt{\left(\frac{C_{gr, std}}{C_{gr}}\right)^2 + \left(\frac{r_{tot, std}}{r_{tot}}\right)^2}. \quad (11)$$

## 10 **2.6 Chemical reaction and turbulent transport timescales**

11 Ratio between turbulent transport timescale and chemical reaction timescale (Damköhler  
 12 number, DA) is a measure of flux divergence due to chemical reactions occurring in the  
 13 ambient air. As DMA and DEA are reactive gases, their respective

$$14 \quad DA = \frac{\tau_{tr}}{\tau_{ch}} \quad (12)$$

15 were calculated to compare their atmospheric lifetimes ( $\tau_{ch}$ ) to characteristic turbulent  
 16 timescale  $\tau_{tr} = r_a/z_m$  which are associated to transport between the soil and the atmosphere,  
 17 in this case the within-canopy measurement height. DMA and DEA mainly react in the  
 18 atmosphere with hydroxyl (OH) radicals, and the chemical timescales  $\tau_{ch}$  for DMA and DEA  
 19 are 3.2 h and 2.6 h, respectively (Héllen et al., 2014). DA smaller than unity indicates that  
 20 chemical reactions play a minor role in linking measured flux at a given height to  
 21 sinks/sources below the measurement height (Rinne et al., 2012). When DA is smaller than  
 22 0.1, the role of chemical reactions is typically neglected in flux estimates (Rinne et al., 2012).

## 23 **2.7 Sensitivity analysis**

24 The sensitivities of the calculated resistances and estimated soil air concentrations and soil  
 25 fluxes were assessed by one-at-a-time method by studying the effect of the measured variable  
 26 on the calculated variable. In case of soil air concentrations, the studied variables were pH  
 27 (from 4.0 to 6.0), temperature (from 0 to 20 °C) and soil solution concentration (from 0 to 100  
 28  $\mu\text{mol L}^{-1}$ ), as these variable have an effect on dissociation and separation between gas and

1 aqueous phases of DMA and DEA. The measured soil solution concentrations were based on  
2 1 M KCl extractions. The soil solution concentration of DMA was used as the upper limit for  
3 the soil solution concentration range.

4 The effects of environmental variables on resistances were assessed separately for  $r_g$ ,  $r_b$ , and  
5  $r_a$ . In case of the  $r_g$ , effect of soil water content (from 0.1 to 0.45 m<sup>3</sup> m<sup>-3</sup>) was assessed due to  
6 its effect on soil spore space continuum. In addition, soil temperature (from 0 to 25 °C) and  
7 soil depth (from 0 to 0.15 m) were studied as they affect diffusion and the length of the  
8 diffusion pathway. For  $r_b$ , the effects of temperature (from 0 to 25 °C) and friction velocity  
9 (from 0.1 to 0.15 m s<sup>-1</sup>) were assessed as they have effects on diffusion and thickness of  
10 quasi-laminar layer, respectively. In case of  $r_a$ , the effect of friction velocity (from 0.1 to 0.15  
11 m s<sup>-1</sup>) was studied as it determines the effectiveness of turbulent transport.

12 The weekly ambient air concentration measurements neglect potential diurnal variation of the  
13 studied alkylamines. To assess whether this significantly affects the estimated DMA and DEA  
14 fluxes, two different sinusoidal diurnal cycles were introduced. The first scenario assumes the  
15 diurnal cycle follows that of air temperature, as suggested for NH<sub>3</sub> and trimethylamine in a  
16 forest site in Alabama (US) (You et al., 2014). The second scenario assumes that diurnal cycle  
17 of amines behaves as observed for monoterpenes at the site of our study (Hakola et al., 2012).  
18 Consequently, the minimum concentrations were assumed to occur at 4 am and 2 pm,  
19 respectively, and the diurnal amplitude of ambient air concentrations was set to be two times  
20 the measured weekly concentration.

21

## 22 **3 Results**

### 23 **3.1 Amine contents in soil, soil-derived fungal hyphae, and pure fungal** 24 **cultures**

25 Concentrations of DEA in humus soil and in fungal hyphae restricted from the humus were  
26 0.3 µg g<sup>-1</sup> FW and 2.9 µg g<sup>-1</sup> FW (Table 1), respectively. Amine concentrations in the mineral  
27 soil were below the detection limit of 0.01 µg g<sup>-1</sup> FW. DMA was not measured from field  
28 samples, as it was not included in standards used for the first soil samples. The results for  
29 other amine compounds (2-amino-1-butanol and DL-2-aminobutyric acid) analyzed from  
30 field samples are presented in the supplementary material (Table A1).

1 The highest DMA and DEA concentrations in the fungal pure cultures were measured in the  
2 decay fungi (Table 1). DMA concentrations were much higher than those of DEA throughout  
3 the all functional groups, and concentration of DMA varied from  $25 \mu\text{g g}^{-1}$  FW in endophytic  
4 fungi to  $360 \mu\text{g g}^{-1}$  FW in decay fungi. Three out of four most amine containing fungal strains  
5 belonged to ectomycorrhiza. DEA concentrations in soil fungal hyphae ( $2.9 \mu\text{g g}^{-1}$  FW),  
6 ectomycorrhiza ( $2.5 \mu\text{g g}^{-1}$  FW) and ericoid mycorrhiza ( $1.9 \mu\text{g g}^{-1}$  FW) were in similar  
7 range, while the concentrations in humus and mineral soil were markedly lower (Table 1).  
8 Amine concentrations of DMA and DEA and other measured amines (methylamine,  
9 ethanolamine, *sec*-butylamine, and dibutylamine) of individual strains, as well as the mean  
10 amine concentrations of ecological fungal groups, are shown in supplementary material  
11 (Table C1 and Table C2, respectively).

### 12 **3.2 Estimated soil air concentrations**

13 Over the study period, the estimated mean soil air concentrations of DMA and DEA with  
14 standard deviation, at mean soil pH (5.3), were  $27 \pm 5.1 \text{ nmol m}^{-3}$  and  $0.032 \pm 0.006 \text{ nmol m}^{-3}$ ,  
15 respectively. The effect of soil temperature, soil pH and soil solution concentration on amine  
16 concentrations in soil air are shown in Figure 3. The soil air concentration follows the  
17 seasonal trend in soil temperature (Figure 2). For DMA, the mean soil air concentration was  
18 higher than the measured mean ambient air concentration ( $1.7 \text{ nmol m}^{-3}$ ) during the study  
19 period. For DEA, the mean soil air concentration was lower than the measured ambient air  
20 concentration ( $0.26 \text{ nmol m}^{-3}$ ).

21 Sensitivity of estimated soil air concentration to soil solution concentration was assessed  
22 using a soil solution concentration range from 0 to  $100 \mu\text{mol L}^{-1}$ . Soil air concentration  
23 changed linearly in the studied range  $29 \text{ nmol m}^{-3}$  for DMA and  $11 \text{ nmol m}^{-3}$  for DEA (Figure  
24 3A).

25 Soil air concentrations of DMA and DEA are highly sensitive to soil pH. The non-linear  
26 relationship is caused by pH-dependency of dissociation of an alkylamine in soil solution (Eq.  
27 2), and partition of an alkylamine between aqueous solution and gas-phase (Eq. 6).

28 In the measured range soil air concentration change was  $680 \text{ nmol m}^{-3}$  for DMA and 0.81 for  
29 DEA (Figure 3C). Soil air concentrations in pH 4.0 were  $0.07 \text{ nmol m}^{-3}$  for DMA and less  
30 than  $0.01 \text{ nmol m}^{-3}$  for DEA. In pH 5.1 soil air concentrations for the both compounds starts

1 to increase rapidly from 10 nmol m<sup>-3</sup> for DMA and from 0.01 nmol m<sup>-3</sup> for DEA to soil air  
2 concentrations in pH 6.0, 680 nmol m<sup>-3</sup> for DMA and 0.81 nmol m<sup>-3</sup> for DEA.

3 Soil temperature had a minor effect on soil air concentrations than pH in assessed ranges. The  
4 concentration change in the temperature range was 24 nmol m<sup>-3</sup> for DMA and 0.03 nmol m<sup>-3</sup>  
5 for DEA (Figure 3B). Sensitivity of soil air concentration was not assessed for soil water  
6 content because it has an effect only to the transport of DMA and DEA through the soil.

7 Estimated soil air concentration did not correlate with measured ambient air concentration in  
8 case of DMA (r=0.09, p=0.68), but it correlated in case of DEA (r=0.67, p<0.01) (Figure 7A  
9 and 7B, respectively).

### 10 **3.3 Resistances and chemical reaction timescale**

11 The mean total resistance for soil-air pathway ( $r_{\text{tot}}$ ) was 13 500 ( $\pm 2300$ ) s m<sup>-1</sup> for DMA and 18  
12 500 ( $\pm 3200$ ) s m<sup>-1</sup> for DEA. The  $r_{\text{tot}}$  was dominated, i.e. the transfer of the studied amines  
13 mostly limited, by slow diffusion of through the soil matrix (soil resistance,  $r_g$ ). The mean soil  
14 resistance of both gases was  $\sim 14\,000$  s m<sup>-1</sup> (Figure 4B) hence being 1 and 2 orders of  
15 magnitude larger than quasi-laminar resistance ( $r_b$ , 1200 s m<sup>-1</sup>) and aerodynamic resistance  
16 ( $r_a$ , 110 s m<sup>-1</sup>), respectively (Figure 4C).

17 Sensitivity of each resistance component to environmental variables (soil water content,  
18 temperature and friction velocities and in case of  $r_g$  organic soil depth) was assessed  
19 separately (Figure D1). In short,  $r_g$  increases linearly with length of the diffusion pathway  
20 ( $\Delta z_s$ ) and non-linearly with increasing soil water content (eq. 8). The temperature sensitivities  
21 of  $r_g$  and  $r_b$  are weak in the studied temperature range, and caused by weak decrease of  
22 molecular diffusivity with temperature. The  $r_b$  (eq. 9) and  $r_a$  both decrease nearly order of  
23 magnitude when the above-canopy friction velocity increases from 0.1 to 1.5 m s<sup>-1</sup>, while the  
24  $r_b$  to  $r_a$  -ratio is quasi-conserved. Most of the non-linear decrease of  $r_b$  and  $r_a$  occurs at  $u_*$   
25 below 0.5 m s<sup>-1</sup> (Figure D1).

26 For DMA, Damköhler number (DA) ranged from 0.013 to 0.026 and having a mean of 0.019  
27 ( $\pm 0.004$ ). For DEA, DA ranged from 0.017 to 0.033 with a mean of 0.023 ( $\pm 0.005$ ). Due to  
28 DA numbers lower than 0.1 the removal of DMA and DEA by chemical reactions in the  
29 canopy air space can be considered negligible for the flux estimates.

### 1 **3.4 Estimated soil fluxes**

2 The mean soil-atmosphere fluxes of DMA and DEA over May to November 2011  
3 measurement period were  $170 (\pm 51) \text{ nmol m}^{-2} \text{ d}^{-1}$  and  $-1.2 (\pm 1.2) \text{ nmol m}^{-2} \text{ d}^{-1}$ , respectively  
4 (Table 2). The DMA flux increased from the spring to summer, and then decreased in the  
5 autumn. Unlike in the ambient air concentrations (Figure 2B), there was no autumnal peak in  
6 the estimated DMA fluxes (Figure 5). The seasonal pattern in DEA flux did not follow the  
7 changes in soil temperature or moisture, and the fluxes were negative most of the  
8 measurement period. Several strong and distinct DEA uptake periods were estimated in June,  
9 August and October (Figure 5).

10 Effects of environmental variables (pH, temperature, soil water content, soil depth, and  
11 friction velocity) on estimated soil fluxes are shown in Figure 6. A linear increase in soil  
12 solution concentration would increase flux from soil to the atmosphere linearly. (Figure 6A).  
13 The pH has strong effect in the partitioning of DMA and DEA between aqueous and gas  
14 phases (Figure 3C), and thus also in the flux estimates (Figure 6B). The fluxes computed for  
15 10 and 90 percentiles of measured soil pH (4.5 and 6.0, respectively) were  $-0.67 (\pm 0.68) \text{ nmol}$   
16  $\text{m}^{-2} \text{ d}^{-1}$  and  $4500 (\pm 1300) \text{ nmol m}^{-2} \text{ d}^{-1}$  for DMA, and  $-1.4 (\pm 1.2) \text{ nmol m}^{-2} \text{ d}^{-1}$  and  $2.7 (\pm 1.0)$   
17  $\text{nmol m}^{-2} \text{ d}^{-1}$  for DEA, respectively (Table 2).

18 According to the sensitivity analysis, both amines reach a zero flux point below which the  
19 emission from the soil will turn into an uptake to the soil in the measured pH range from 4.5  
20 to 6.0. This turning point (compensation point with respect to pH) occurred at pH 5.7 for  
21 DEA and at pH 4.7 for DMA was (Figure 6B). A 10% decrease in soil solution concentration  
22 of DMA increased the turning point pH by 0.1 and similarly an increase in soil solution  
23 concentration of DMA decreased the turning point by 0.1 pH unit. The turning point of DEA  
24 was less affected by the soil solution concentration. A change of 10% in DEA soil solution  
25 concentrations lead to a change in turning point pH of  $\pm 0.06$ . Decrease in pH decreased the  
26 available DMA and DEA concentrations and affected partitioning between soil water and soil  
27 air, but the proton concentration had no influence on the transport processes.

28 Soil temperature increase from 0 to 20 °C increased DMA fluxes from  $81 \text{ nmol m}^{-2} \text{ d}^{-1}$  to  $255$   
29  $\text{nmol m}^{-2} \text{ d}^{-1}$  near-linear manner, and DEA fluxes from  $-1.1 \text{ nmol m}^{-2} \text{ d}^{-1}$  to  $1.3 \text{ nmol m}^{-2} \text{ d}^{-1}$   
30 (Figure 6C) near-linearly. Fluxes decrease near-linearly with increasing soil water content  
31 (Figure 6D). This is due to non-linear increase of  $r_g$  with increasing soil water content (Figure



1 D1). In assessed soil water content range DMA flux changed from 241  $\text{nmol m}^{-2} \text{d}^{-1}$  to 122  
2  $\text{nmol m}^{-2} \text{d}^{-1}$  and DEA flux from -1.7  $\text{nmol m}^{-2} \text{d}^{-1}$  to -0.84  $\text{nmol m}^{-2} \text{d}^{-1}$  (Figure 6D).

3 The estimated soil-atmosphere fluxes are sensitive to the assumed depth of amine  
4 sources/sinks in the soil. Because of the dominating role of soil resistance, the absolute value  
5 of flux decrease with soil depth, and the sensitivity is strongest when soil depth is under 0.03  
6 m (Figure 6C) Increasing friction velocity decreases soil boundary layer and aerodynamic  
7 resistances and modestly affect the flux estimates (Figure 6F). The strongest impact occurs  
8 friction velocity values smaller than  $0.2 \text{ m s}^{-1}$ , and is mostly due to  $r_b$  (Figure D1). It should  
9 be noted that the friction velocity may become an important factor affecting the flux estimates  
10 in calm conditions if the amine sources or sinks are located very close to the surface leading  
11  $r_g$  and  $r_b$  being of same order of magnitude.

12 The flux estimates were modestly sensitive to assumed diurnal cycle of ambient air  
13 concentration. Assuming air temperature -dependent diurnal cycle, the DMA flux was 170  
14 ( $\pm 61.8$ )  $\text{nmol m}^{-2} \text{d}^{-1}$  and DEA flux was -1.12 ( $\pm 2.79$ )  $\text{nmol m}^{-2} \text{d}^{-1}$ . In the second scenario,  
15 which assumes the amine concentration behave as that of monoterpenes, the DMA flux was  
16 169 ( $\pm 55.8$ )  $\text{nmol m}^{-2} \text{d}^{-1}$  and for DEA the flux was -1.22 ( $\pm 2.90$ )  $\text{nmol m}^{-2} \text{d}^{-1}$ .

17

#### 18 **4 Discussion**

19 The results of this study shows that soil is an important reservoir of alkylamines, and our  
20 results suggest that this may be due to high amine concentrations in fungal hyphae in the  
21 boreal forest soil. Furthermore, we show in the flux estimation that these compounds can be  
22 released from the soil into the atmosphere under favorable environmental conditions. The  
23 source-sink behavior was dependent on soil conditions including temperature, soil water  
24 content and pH. Soil was shown to act as a source of DMA and a sink of DEA. The fact that  
25 both the DMA and DEA concentrations were much higher in the fungal hyphae and in fungal  
26 pure cultures as compared to the humus or mineral soil, indicate that the fungal community  
27 may be the primary source of these alkylamines in boreal forest soils.

28 Both the concentrations of DMA and DEA in humus samples from the greenhouse  
29 experiment (Kieloaho et al., 2016) were lower than those of the fungal pure cultures (Table  
30 1). The DMA concentrations were higher than DEA concentrations in the humus samples and  
31 in pure fungal cultures. Overall, the DEA concentration in the humus samples of the

1 greenhouse experiment were lower than those measured from the field humus samples (Table  
2 1).

3 In both sample types, field collected hyphae and pure fungal cultures, DEA were found in the  
4 same range strongly supporting each other, and show that fungi are a reservoir of DEA. DEA  
5 concentrations found in the humus soil may reflect concentrations found in fungal biomass  
6 and may be of fungal origin. In the pure fungal culture biomass, DMA concentrations were 50  
7 times higher than those measured for DEA. DMA concentrations were also higher than DEA  
8 concentrations in the soil used in the greenhouse experiment. There is a possibility that  
9 degradation of sample compounds results in formation of the studied analytes during the  
10 sample preparation procedure. This, however, could not be assessed, due to the absence of  
11 suitable reference materials, thus increasing the measurement uncertainty. Similarly, some of  
12 the studied amines could have degraded into smaller compounds and hence not to detected in  
13 our analysis, leading to underestimation of the concentrations of the studied compounds.

14 Fungal sporocarps were shown to contain of monomethylamine, dimethylamine and  
15 trimethylamine (Sintermann and Neftel, 2015). However, these measurements were based on  
16 fungal sporocarps and not on fungal hyphae, which is the only one form of fungi present in  
17 forest soils. Fungal sporocarps occur seasonally and sporadically mainly in autumn, whereas  
18 fungal hyphae are found throughout the year in forest soil (Santalahti et al., 2016). Therefore,  
19 the sporocarp data does not necessarily reflect the most important fungal contribution as a  
20 source of alkylamines in boreal forest ecosystems.

21 The fungal community of boreal forest soil undergoes seasonal variation. Santalahti et al.  
22 (2016) observed a clear soil fungal community shift in which the ectomycorrhizal fungi seem  
23 to disappear in late autumn while saprotrophic community dominates in the winter. In this  
24 study we show that ectomycorrhizal fungi contain high quantities of DMA and DEA, which  
25 could be released into the soil solution, and subsequently to the atmosphere during their  
26 disappearance in late autumn. In boreal Norway spruce forest in Sweden, Wallander et al.  
27 (2001) estimated that humus contains 700-900 kg ha<sup>-1</sup> ectomycorrhizal hyphae, which is equal  
28 to the amount of fine roots found in humus.

29 The estimated soil air concentrations correlated positively with the measured ambient air  
30 concentrations of DEA, but not with DMA. Kieloaho et al. (2011) found strong correlation  
31 between ambient air concentration of DEA and ambient air monoterpene concentration, and  
32 suggested that the source of DEA might be in vegetation as has been suggested for

1 monoterpenes (Hakola et al., 2006). In this study, the estimated soil air concentrations of  
2 DEA were smaller than the measured ambient air concentrations, which suggest that the soil  
3 is not necessarily a source of atmospheric DEA. The soil air concentrations are based on  
4 limited data of soil solution concentrations, and the results serve as the first estimates for both  
5 soil air concentrations and soil fluxes for DMA and DEA. DMA and DEA were assumed to  
6 have similar exchange processes with  $\text{NH}_3$ , having both sink and source behavior between the  
7 soil and the atmosphere

8 At the end of September and in October, the flux estimates of DMA and DEA did not explain  
9 the elevated atmospheric concentrations of DMA and DEA (Figure 2B). This missing  
10 autumnal peak in the fluxes might be due to a rapid change in soil DMA concentration, which  
11 could not be taken into account in the soil air concentration estimates due to the lack of  
12 continuous soil solution concentration measurements. During the autumn (from September to  
13 October), litterfall provides an input of fresh decomposable material into the soil, which also  
14 has an immediate effect on soil nitrogen concentrations due to the nitrogen rich leachate from  
15 the needle litter (Pihlatie et al., 2007; Starr et al., 2014). It was also recently shown that a  
16 common ectomycorrhizal fungal genus *Piloderma* sp., which also contained the highest  
17 quantities of alkylamines in our study, has a clear seasonal pattern, and it seems to disappear  
18 from the soil in late autumn (Heinonsalo et al. 2015). *Piloderma* sp. was shown to be active in  
19 protease production, protease is an enzyme that facilitates the decomposition of proteins,  
20 possibly due to the protease activity *Piloderma* sp. was also found to be able to obtain N from  
21 organic sources and deliver proteinaceous N to the host plant Scots pine. This involvement of  
22 ectomycorrhizal fungi in soil organic N cycling may make them 'nitrogen hotspots' that  
23 release also alkylamines into soil solution after their death (Heinonsalo et al. 2015).

24 Flux estimates were found to be sensitive to soil temperature, soil pH and soil water content,  
25 and soil resistance had a major effect on transport, while aerodynamic and quasi-laminar  
26 resistances had only minor effects on the fluxes of DMA and DEA. We found that DMA and  
27 DEA flux estimates were especially sensitive to change in soil pH. Flux estimates were  
28 calculated based on three pH values, mean pH (5.3) and 10 and 90 percentiles (4.5 and 6.0,  
29 respectively). The pH, in which the mean flux estimate is zero, is a compensation point with  
30 respect to soil pH. Below the compensation point pH, direction of alkylamine flux is into the  
31 soil and soil is a sink of alkylamines. The compensation point pH occurred for DMA at pH  
32 4.7, which is lower than the mean measured pH from suction lysimeters, indicating that boreal

1 forest soil can act as a DMA source at least occasionally. In contrary, for DEA the  
2 compensation point with respect to pH was 5.7, which is close to the 90 percentile (pH 6.0),  
3 indicating that soil is a sink of DEA. The compensation point pH is dependent on soil solution  
4 concentration of the amine. Hence, it is clear that even a slight change in soil pH or  
5 alkylamine concentration in soil solution could determine the capability of boreal forest soil  
6 to act as a source or a sink of alkylamines. The diurnal cycles of ambient air concentrations of  
7 the studied amines are still currently unknown. By introducing artificial diurnal cycles as  
8 observed for trimethylamine or NH<sub>3</sub> (You et al., 2014), and monoterpenes (Hakola et al.,  
9 2012), it was found that it the diurnal cycles are not likely to have major effect on estimated  
10 DMA flux. However, the unknown diurnal cycle of ambient DEA concentration may  
11 significantly contribute to the uncertainty and even to sign of the estimated soil-atmosphere  
12 DEA flux.

13 Current understanding of the atmospheric alkylamine sources is mainly from rural areas  
14 where the alkylamine emissions are related to agricultural activities (Schade and Crutzen,  
15 1995; Kuhn et al., 2011). Schade and Crutzen (1995) have suggested using a constant ratio  
16 between trimethylamine (TMA) and NH<sub>3</sub> in total agricultural emissions as a proxy for  
17 agricultural alkylamine emissions. TMA emissions were 0.3% from NH<sub>3</sub> emissions from  
18 livestock farming and it can be partly explained by the same formation pathway of  
19 alkylamines and NH<sub>3</sub> (Kim et al., 2001; Rappert and Müller, 2005). The proxy was, however,  
20 revised by Kuhn et al. (2011), who suggested that TMA emissions are 0.1% from NH<sub>3</sub>  
21 emissions for both livestock farming and vegetation. Mineral soils have been found to be a  
22 sink for atmospheric NH<sub>3</sub> while litter of organic layer may act as a source of NH<sub>3</sub> (Neftel et  
23 al., 1998; Schjoerring et al., 1998; Nemitz et al., 2000).

24 It has been proposed that NH<sub>4</sub><sup>+</sup> is adsorbed onto soil particles in mineral soil, and hence is not  
25 available for gas exchange between soil solution and gas phase (Neftel et al., 1998). On the  
26 other hand, peat soil and litter layer have been shown to be periodically sources of  
27 atmospheric NH<sub>3</sub> in the laboratory (Schjoerring et al., 1998) and in the field (Nemitz et al.,  
28 2000). Previously Hansen et al. (2013) observed NH<sub>3</sub> emissions after a litterfall in a  
29 deciduous forest in Denmark, indicating that changes in nitrogen inputs may influence NH<sub>3</sub>  
30 dynamics. The ambient air measurements of NH<sub>3</sub> in boreal forest air indicate that NH<sub>3</sub> may be  
31 emitted from the ecosystem in the summer and in autumn as the concentrations of NH<sub>3</sub> in  
32 boreal forest air peak during this period, and remain lower in the spring and in winter months

1 (Makkonen et al., 2014). To our knowledge, the only measured alkylamine fluxes from  
2 forested areas are TMA fluxes measured above a Douglas fir forest from June to July in  
3 Netherlands (Copeland et al., 2014). The mean TMA flux during this one-month  
4 measurement period was around zero showing occasional uptake and emission from -192 to  
5  $192 \mu\text{mol m}^{-2} \text{d}^{-1}$ , which is one order of magnitude higher than the DMA flux estimate ( $170$   
6  $\text{nmol m}^{-2} \text{d}^{-1}$ ) in this study.

7 The mean DMA flux of  $170 \text{ nmol m}^{-2} \text{d}^{-1}$  is approximately  $9 \text{ g ha}^{-1} \text{ yr}^{-1}$  and the annual flux is  
8 slightly higher than that of nitrous oxide ( $\text{N}_2\text{O}$ ,  $3 \text{ g ha}^{-1} \text{ yr}^{-1}$ ) measured from the studied forest  
9 (Pihlatie et al, 2007, Korhonen et al., 2013). It is likely that soil fluxes of reduced N are  
10 higher than those of oxidized forms (e.g. HONO and  $\text{N}_2\text{O}$ ) due to higher dissolved organic  
11 nitrogen and  $\text{NH}_4^+$  concentrations in soil solution (Korhonen et al., 2013). Unlike in  
12 agricultural soils, Korhonen et al. (2013) showed that in the studied forest 98.9% of the  
13 extractable N is in the form of organic N ( $26.8 \text{ kg N ha}^{-1}$ ) and most of the mineral nitrogen is  
14 in the form of ammonium ( $0.31 \text{ kg N ha}^{-1}$ ). In the studied forest site O horizon contained  $710$   
15  $\text{kg N ha}^{-1}$  and it is approximately 34% of total N pool in the forest being the highest nitrogen  
16 pool in the studied forest ecosystem (Korhonen et al., 2013). Mycorrhizal fungi are capable of  
17 degrading and utilizing organic N compounds in soil as nutrient source (Talbot and Treseder,  
18 2010). Hence, we suggest that soil fungi could also release amines into the soil solution as we  
19 demonstrated that they contain high quantities of amines.

20 At the moment, ambient air concentration measurements of alkylamines from remote forested  
21 areas are scarce. Recently, there have been several efforts to measure ambient air amine  
22 concentrations using online ion chromatograph connected with quadruple mass spectrometer  
23 (Hemmilä et al., 2014) and CI-API-ToF (Kulmala et al., 2013; Sipilä et al., 2015). However,  
24 they are so far only the first steps in characterizing the amine concentrations and no  
25 continuous datasets are yet available. Flux estimation presented in this study was based on  
26 ambient air concentration measurements conducted by Kieloaho et al. (2013). More recently,  
27 Sipilä et al. (2015) suggested that measured maximum ambient air concentrations of DMA is  
28  $0.06 \text{ nmol m}^{-3}$  in spring and early summer (from May to June 2013), but due to problems in  
29 measurement system, and lack of calibration they advised to take these numbers by caution.  
30 This implies that if the forest soil is a reservoir of DMA, the real fluxes may be higher than  
31 those presented in this study if the atmospheric concentrations of DMA are as low as those  
32 presented by Sipilä et al., (2015). On the other hand, Hemmilä et al. (2014) reported

1 preliminary results of ambient air concentrations of DMA and DEA in summer-time (June-  
2 July) at Hyytiälä Scots pine forest to be  $0.4 \text{ nmol m}^{-3}$  and  $0.08 \text{ nmol m}^{-3}$  for DMA and DEA,  
3 respectively. These results from June to July indicate that the ambient air measurements by  
4 Kieloaho et al. (2013) are in the correct range. The week long sampling time of ambient air  
5 DMA+EA and DEA concentrations (Kieloaho et al., 2013) coupled with the mixing of air,  
6 atmospheric sink processes and deposition of alkylamines onto the surfaces affect the  
7 measured concentrations, and diminish the relationship between source and ambient air  
8 concentrations. Hence, the flux estimates for DMA and DEA in this study can be used as the  
9 first attempts to estimate potential soil-atmosphere exchange in forests.

10 The concentration of ammonium in soil water is expected to change with substrate  
11 availability, environmental conditions, microbial activity, and due to assimilation of nutrients  
12 by either soil microbes or vegetation (Pajuste and Frey, 2003). Assuming that DMA and DEA  
13 share similar formation and consumption processes with ammonium in the soil, as suggested  
14 by Kim et al. (2001) and Rappert and Müller (2005), DMA and DEA concentrations in boreal  
15 forest soil may have two maxima during a year, in early spring and in late autumn (Pajuste  
16 and Frey, 2003). The two maxima are due to the combination of supply and demand of  
17 ammonium from temperature dependent ammonium releasing soil processes (decomposition  
18 and mineralization), and plant and microbial uptake rates. In the spring, the decomposition  
19 produces ammonium while the plant-uptake still remain rather low, whereas towards the late  
20 summer, plant uptake exceeds the mineralization rate leading to minimum concentrations in  
21 the soil. In late autumn, plant uptake decreases faster than the mineralization rate leading to a  
22 slight increase in ammonium concentration in soil (Pajuste and Frey, 2003).

23

## 24 **5 Conclusion**

25 We have shown that boreal forest soil and fungal hyphae in the soil contain alkylamines,  
26 which can be released to the atmosphere in favourable conditions. We hypothesize that the  
27 soil-atmosphere exchange of the studied alkylamines (DMA and DEA) can be estimated based  
28 on soil temperature, soil water content and especially soil pH. Soil was shown to be a source  
29 of DMA, and a sink of DEA at typical soil pH (5.3) levels. The flux estimation method  
30 presented here is a first attempt to quantify the sources and sinks of alkylamines and other  
31 similar compounds that are difficult to measure directly in forest ecosystems. In boreal forest  
32 soil, fungal hyphae seem to form a large pool of low molecular weight amines like DMA and

1 DEA. Therefore, we propose that fungi are the origin of alkylamines in boreal forest soils.  
2 The functional role of boreal forest soil as a source of low molecular weight amines, and their  
3 potential emissions needs to be further investigated in relation to air chemistry and  
4 atmospheric aerosol formation processes. In parallel, more measurements on atmospheric and  
5 soil air amine concentrations are needed to confirm the flux estimates provided in this study.

6

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