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

A.-J. Kieloaho[1,2], M. Pihlatie[1,2], S. Launiainen[3], M. Kulmala[2], M.-L. Riekkola[4], J. Parshintsev[4], I. Mammarella[2], T. Vesala[2,5], J. Heinonsalo[1]

[1] {University of Helsinki, Department of Food and Environmental Sciences, P.O. Box 56, FI-00014, Helsinki, Finland}

[2] {University of Helsinki, Department of Physics, Division of Atmospheric Sciences, P.O. Box 68, FI-00014, Helsinki, Finland}

[3] {Natural Resources Institute Finland, Environmental Impacts of Production, Latokartanonkaari 9, FI-00790, Helsinki, Finland}

[4] {University of Helsinki, Department of Chemistry, Laboratory of Analytical Chemistry, P.O. Box 55, FI-00014, Helsinki, Finland}

[5] {University of Helsinki, Department of Forest Sciences, P.O. Box 27, FI-00014, Helsinki, Finland}

Correspondence to: A.-J. Kieloaho (antti-jussi.kieloaho@helsinki.fi)

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 ±51 nmol m^{-2} d^{-1}) and a sink of DEA (-1.2 ±1.2 nmol m^{-2} d^{-1}). We also

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

1   Introduction

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

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

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

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

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

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

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

2   Materials and methods

2.1   Study site and supplementary measurements

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

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

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

1   (6.4 ± 0.83 nmol m^{-3}) was measured in October. Ambient air concentration of DEA varied

2   from 0.02 to 0.63 nmol m^{-3} the mean being 0.26 (± 0.22) nmol m^{-3} (Kieloaho et al., 2013).

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.

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^{-1} (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 µL 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 µm 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 µL 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 µm, 50 mm x 2.1 mm, Merck, Darmstadt, Germany) was

26 used and the temperature was kept at 40 °C. Ionization parameters were as follows: drying

27 gas (nitrogen) temperature 300 °C, gas flow 7.5 L min^{-1} and nebulizer (nitrogen) 35 psi. MS1

28 and MS2 heaters were kept at 100 °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.

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 µmol L^{-1} and 0.296 µmol 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

11   $R_3N\ (aq) + H^+\ (aq) \leftrightarrow R_3NH^+\ (aq),$ (1)

12   where R_3N 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 (R_3N) and dissociated (R_3NH^+)

16   forms of amines. In the first step, using equilibrium thermodynamic principles, the fraction

17   (f_{R3N}) of total amine concentration present as non-dissociated form can be estimated (Montes

18   et al., 2009), when the activity of R_3N and R_3NH^+ are assumed to be equal. The activity of

19   protons $[H^+]$ in soil solution is based on the measured pH values. Equilibrium dissociation

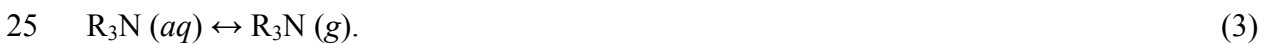
20   coefficients (pK_a) for DMA and DEA are 10.3 and 10.5, respectively, and K_a is a negative

21   logarithm of pK_a,

22   $f_{R3N} = \dfrac{[R_3N]}{[R_3N]+[R_3NH^+]} = \dfrac{1}{1+\frac{[H^+]}{K_a}}.$ (2)

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

24   phases and soil air,

25   $R_3N\ (aq) \leftrightarrow R_3N\ (g).$ (3)

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   $k_H = \dfrac{c_{R3N}}{p_{soil}},$ (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     $$k_{(T)} = k_1 e^{\frac{-\delta H°}{R(T_2^{-1} - T_1^{-1})}},$$ (5)

6   where $k_{(T)}$ is the temperature corrected coefficient, k_1 is the coefficient to be corrected, $\delta H°$ 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 Seinfield and Pandis (2006)

12     $$k_{H(T,pH)} = k_{H(T)} \left(\frac{1 + [H^+]}{K_{a(T)}} \right),$$ (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, nmol m^{-2} d^{-1}) of DMA and DEA were estimated using flux-gradient

21   relationship (Figure 1) as

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

23   where C_s and C_a are concentrations (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} (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.

In soil, the gas transport is dominated by molecular diffusion though the air-filled part of soil matrix. The soil resistance (r_g, s m^{-1}) in the organic soil layer of depth Δz_s (here 0.05 m) is estimated as

$$r_g = \frac{\Delta z_s}{D_p} = \frac{\Delta z_s}{D_o \theta_a{}^b}, \tag{8}$$

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

The transport through the quasi-laminar boundary layer at the soil surface is described by the soil boundary-layer resistance (r_b, s m^{-1}) following Schuepp (1977)

$$r_b = \frac{Sc - \ln(\delta_o / z_1)}{k_v u_{*g} z_1}, \tag{9}$$

where Sc is the Schmidt number, k_v (~0.41) is the von Kármán constant, u_{*g} is the near-ground friction velocity, the height above the ground, where the molecular diffusivity and turbulent transport efficiency equal, is $\delta_o = D_o / k_v u_{*g}$, and z_1 is the height below which the wind profile is assumed logarithmic. The model for r_b applied here is identical to that used to compute gas-transfer e.g. in Baldocchi (1988), Nemitz et al. (2001) and Launiainen et al. (2013).

The aerodynamic resistance (r_a) accounts for the turbulent gas transport between the soil surface and concentration measurement height (z_m) in the canopy air space. The r_a is calculated by integrating the inverse of eddy diffusivity (K_s, m^2 s^{-1}) over the layer as in Baldocchi (1988)

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

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

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

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

15   were calculated to compare their atmospheric lifetimes (τ_{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 τ_{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   μmol L^{-1}), as these variable have an effect on dissociation and separation between gas and

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

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

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 amines 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 diurnal amplitude of ambient air concentrations was set to be two times the measured weekly concentration.

3   Results

3.1   Amine contents in soil, soil-derived fungal hyphae, and pure fungal cultures

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

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

3.2   Estimated soil air concentrations

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

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

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

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

to increase rapidly from 10 nmol m^{-3} for DMA and from 0.01 nmol m^{-3} for DEA to soil air concentrations in pH 6.0, 680 nmol m^{-3} for DMA and 0.81 nmol m^{-3} for DEA.

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

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

3.3 Resistances and chemical reaction timescale

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

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

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

3.4 Estimated soil fluxes

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

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

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

Soil temperature increase from 0 to 20 °C increased DMA fluxes from 81 nmol m^{-2} d^{-1} to 255 nmol m^{-2} d^{-1} near-linear manner, and DEA fluxes from -1.1 nmol m^{-2} d^{-1} to 1.3 nmol m^{-2} d^{-1} (Figure 6C) near-linearly. Fluxes decrease near-linearly with increasing soil water content (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 nmol m^{-2} d^{-1} to 122

2 nmol m^{-2} d^{-1} and DEA flux from -1.7 nmol m^{-2} d^{-1} to -0.84 nmol m^{-2} 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 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 (±61.8) nmol m^{-2} d^{-1} and DEA flux was -1.12 (±2.79) nmol m^{-2} d^{-1}. In the second scenario,

15 which assumes the amine concentration behave as that of monoterpenes, the DMA flux was

16 169 (±55.8) nmol m^{-2} d^{-1} and for DEA the flux was -1.22 (±2.90) nmol m^{-2} d^{-1}.

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

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

In both sample types, field collected hyphae and pure fungal cultures, DEA were found in the same range strongly supporting each other, and show that fungi are a reservoir of DEA. DEA concentrations found in the humus soil may reflect concentrations found in fungal biomass and may be of fungal origin. In the pure fungal culture biomass, DMA concentrations were 50 times higher than those measured for DEA. DMA concentrations were also higher than DEA concentrations in the soil used in the greenhouse experiment. 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.

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

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

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

monoterpenes (Hakola et al., 2006). In this study, the estimated soil air concentrations of DEA were smaller than the measured ambient air concentrations, which suggest that the soil is not necessarily a source of atmospheric DEA. The soil air concentrations are based on limited data of soil solution concentrations, and the results serve as the first estimates for both soil air concentrations and soil fluxes for DMA and DEA. DMA and DEA were assumed to have similar exchange processes with NH_3, having both sink and source behavior between the soil and the atmosphere

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

Flux estimates were found to be sensitive to soil temperature, soil pH and soil water content, and soil resistance had a major effect on transport, while aerodynamic and quasi-laminar resistances had only minor effects on the fluxes of DMA and DEA. We found that DMA and DEA flux estimates were especially sensitive to change in soil pH. Flux estimates were calculated based on three pH values, mean pH (5.3) and 10 and 90 percentiles (4.5 and 6.0, respectively). The pH, in which the mean flux estimate is zero, is a compensation point with respect to soil pH. Below the compensation point pH, direction of alkylamine flux is into the soil and soil is a sink of alkylamines. The compensation point pH occurred for DMA at pH 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 NH3 (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_3 in total agricultural emissions as a proxy for

17   agricultural alkylamine emissions. TMA emissions were 0.3% from NH_3 emissions from

18   livestock farming and it can be partly explained by the same formation pathway of

19   alkylamines and NH_3 (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_3

21   emissions for both livestock farming and vegetation. Mineral soils have been found to be a

22   sink for atmospheric NH_3 while litter of organic layer may act as a source of NH_3 (Neftel et

23   al., 1998; Schjoerring et al., 1998; Nemitz et al., 2000).

24   It has been proposed that NH_4^+ 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_3 in the laboratory (Schjoerring et al., 1998) and in the field (Nemitz et al.,

28   2000). Previously Hansen et al. (2013) observed NH_3 emissions after a litterfall in a

29   deciduous forest in Denmark, indicating that changes in nitrogen inputs may influence NH_3

30   dynamics. The ambient air measurements of NH_3 in boreal forest air indicate that NH_3 may be

31   emitted from the ecosystem in the summer and in autumn as the concentrations of NH_3 in

32   boreal forest air peak during this period, and remain lower in the spring and in winter months

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

The mean DMA flux of 170 nmol m^{-2} d^{-1} is approximately 9 g ha^{-1} yr^{-1} and the annual flux is slightly higher than that of nitrous oxide (N$_2$O, 3 g ha^{-1} 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 N$_2$O) due to higher dissolved organic nitrogen and 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 kg N ha^{-1}) and most of the mineral nitrogen is in the form of ammonium (0.31 kg N ha^{-1}). In the studied forest site O horizon contained 710 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.

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

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

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

5   Conclusion

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

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

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1 Table 1. The mean dimethylamine and diethylamine concentrations (µg g^{-1} fresh weight) and their standard deviations in the field samples,

2 different fungal functional groups and in the humus soil in a greenhouse experiment.

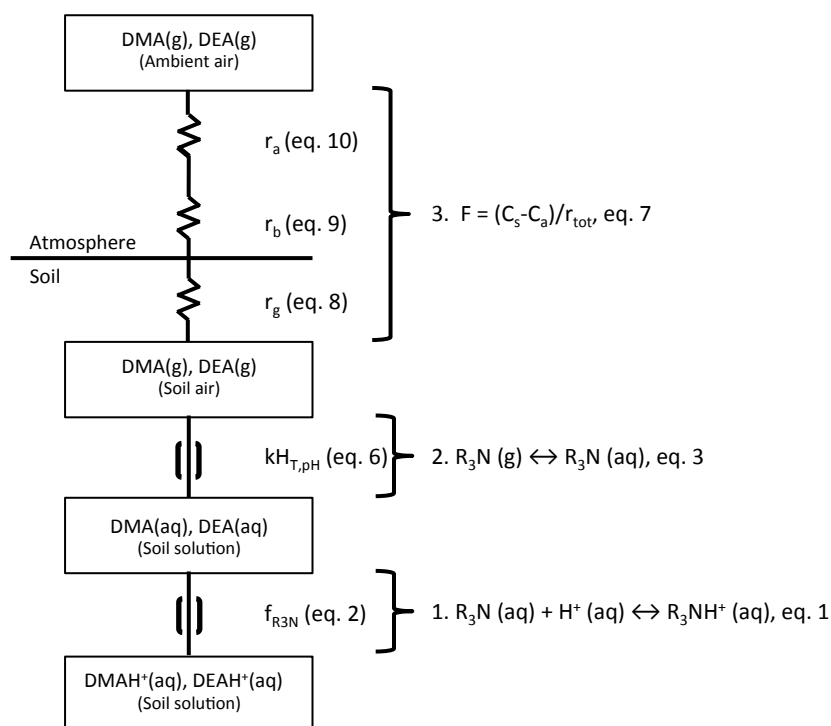
	Dimethylamine (DMA)	Diethylamine (DEA)
Field samples	µg g^{-1} FW	µg g^{-1} FW
Soil fungal hyphae	n.m.	2.9
Humus soil	n.m.	0.3
Mineral soil	n.m.	<0.01
Pure culture samples		
Ectomycorrhiza	116 (±34)	2.5 (±0.9)
Ericoid mycorrhiza	80 (±18)	1.9 (±0.5)
Endophyta	25 (±12)	0.49 (±0.23)
Decay fungi	360 (±320)	6.8 (±5.9)
Control agar media	4.3	0.13
Experimental samples[a]		
Humus soil (with plant)	4.3 (±3.9)	0.03 (±0.02)
Humus soil (without plant)	6.7 (±2.2)	0.02 (±0.01)
Mean of humus soil	4.6 (±3.2)	0.02 (±0.02)

[a] Kieloaho et al. (2016)

n.m.: not measured

1 Table 2. Mean soil air concentrations and flux estimates for dimethylamine and diethylamine followed by their standard deviations in different

2 soil pH values measured in lysimeter waters at 2 cm depth at SMEAR II station.

	Dimethylamine (DMA)			Diethylamine (DEA)		
soil pH	4.5	5.3	6.0	4.5	5.3	6.0
soil air conc. [nmol m^{-3}]	0.68±0.13	27±5.0	680±130	8.1×10^{-4}	0.03±0.01	0.81±0.15
flux/ measured air conc. [nmol m^{-2} d^{-1}]	-0.67±0.68	170±51	4500±1300	-0.14±0.12	-1.2±1.2	2.7±1.0

2 Figure 1. Scheme used for soil-atmosphere flux estimation of dimethylamine (DMA) and

3 diethylamine (DEA) from reactions occurring in soil solution to transfer from soil air to

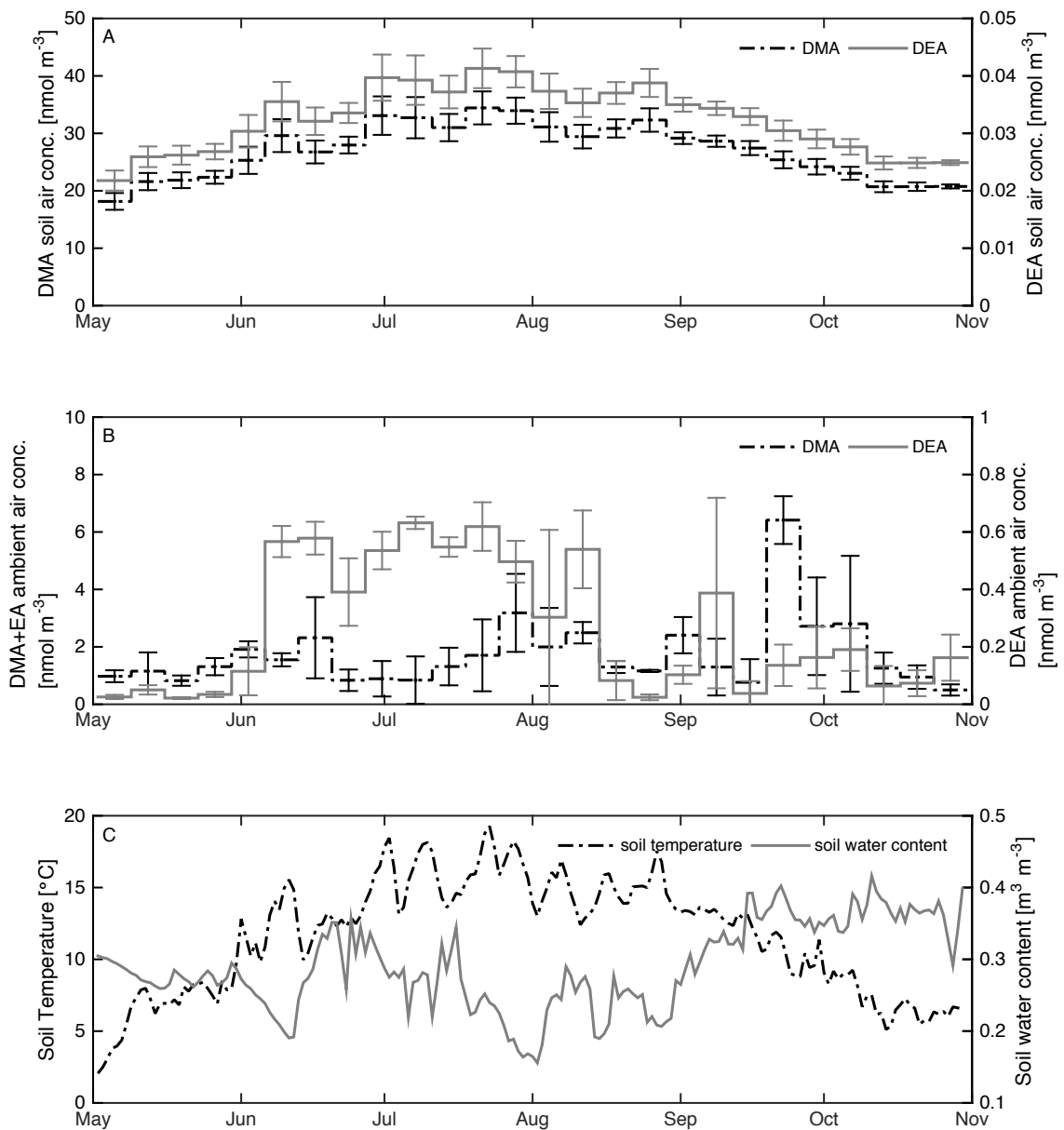
4 ambient air. Boxes denote DMA and DEA concentrations in soil solution, soil air and ambient

5 air. Numbers denote for steps in the flux estimation. Step 1: acid-base reaction and

6 protonation of alkylamine; step 2: partitioning of non-protonated DMA and DEA between

7 aqueous and gas phases; step 3: flux of DMA and DEA between soil and ambient air in which

8 flux is determined by dividing concentration gradient by sum of component resistances (soil

9 resistance, r_g; quasi-laminar boundary-layer resistance, r_b; aerodynamic resistance, r_a).

2 Figure 2. Estimated soil air concentrations of dimethylamine (DMA) and diethylamine (DEA)

3 with their standard deviations at mean soil water pH of 5.3 (panel A), measured ambient air

4 concentration of DMA + ethylamine and DEA (panel B) with their standard deviations

5 redrawn from Kieloaho et al. (2013). In panel C, measured soil temperature and soil water

6 content from May 2011 to October 2011 are shown.

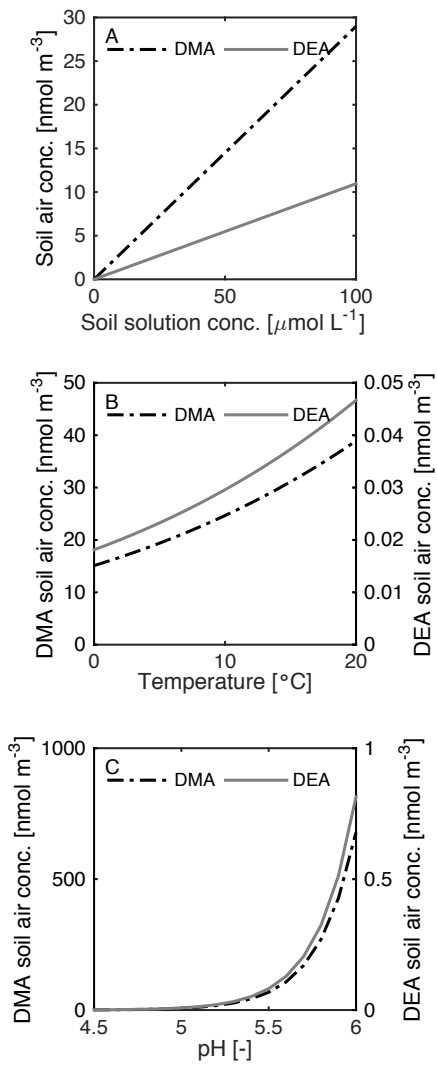



Figure 3. Effects of soil solution concentration (panel A), soil temperature (panel B) and soil
solution pH (panel C) on estimated soil air concentrations of dimethylamine (DMA) and
diethylamine (DEA).

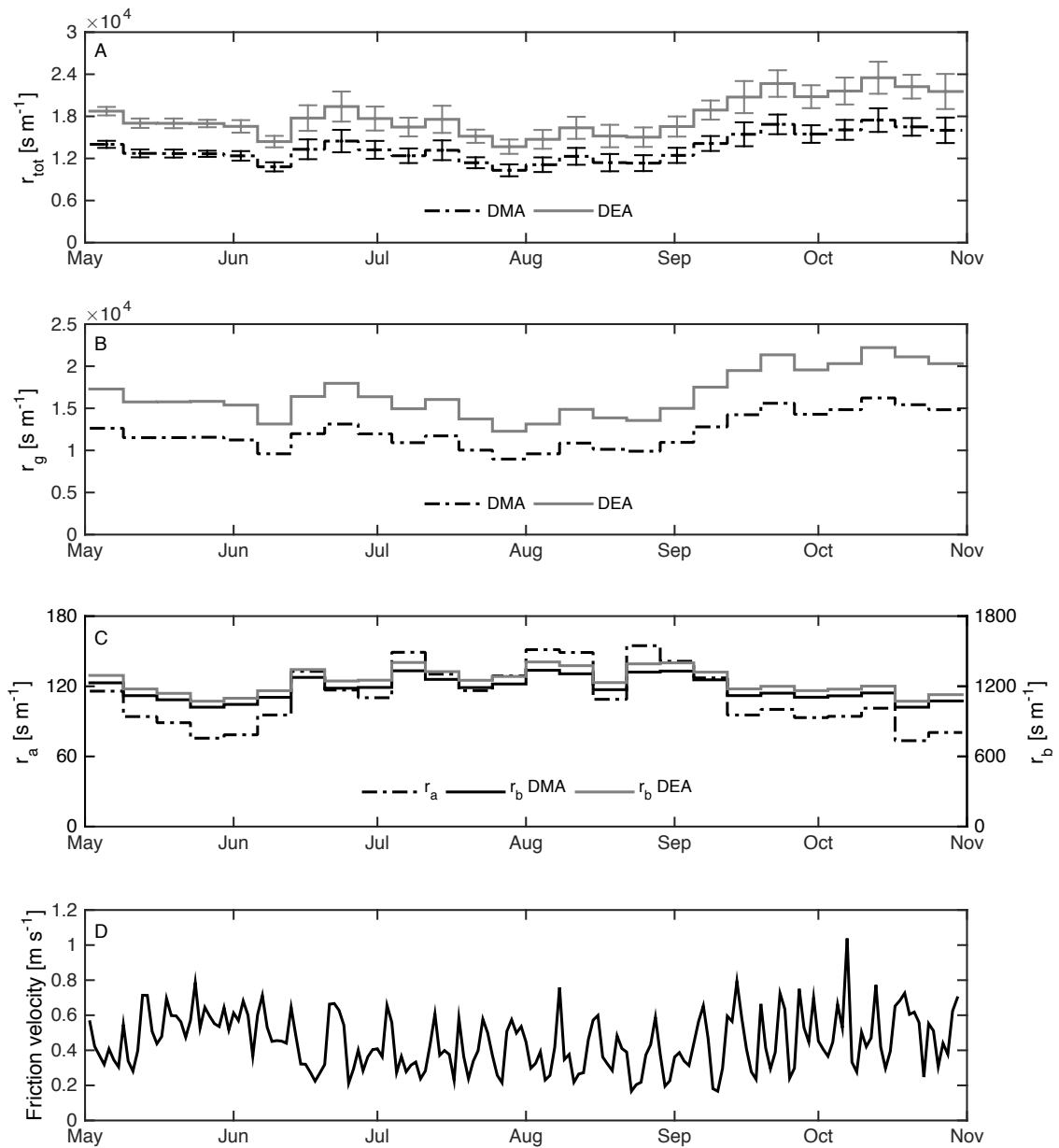



Figure 4. Total resistance (r_{tot}, s m^{-1}) of dimethylamine (DMA) and diethylamine (DEA) and
its components: soil resistance (r_g, panel B) aerodynamic resistance (r_a, s m^{-1}, panel C), quasi-
laminar resistance (r_b, s m^{-1}, panel B). Soil resistance (r_g, s m^{-1}) is calculated using 0.05 m soil
depth. In panel D the daily mean of above canopy friction velocity (m s^{-1}) from May 2011 to
October 2011 is shown. The errorbars in panel A show ± one standard deviation.

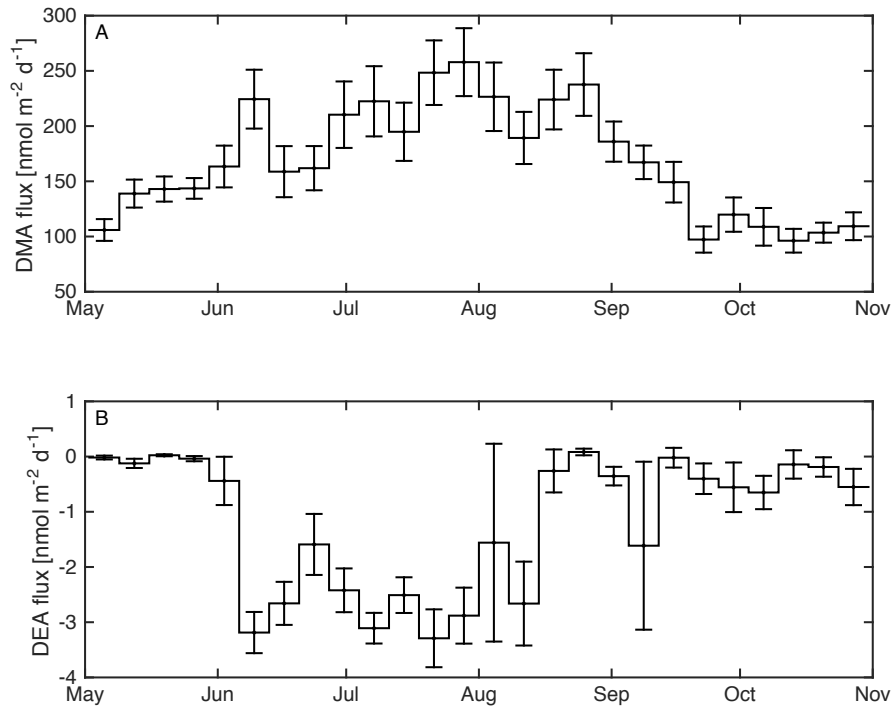



Figure 5. Weekly averages of estimated fluxes of dimethylamine (DMA, panel A) and diethylamine (DEA, panel B) and their standard deviations from May 2011 to October 2011. In emission estimation constant soil solution pH 5.3, average soil depth of 0.05 m and constant soil solution concentrations of DMA and DEA (92.3 μmol L^{-1} and 0.296 μmol L^{-1}, respectively) were used.

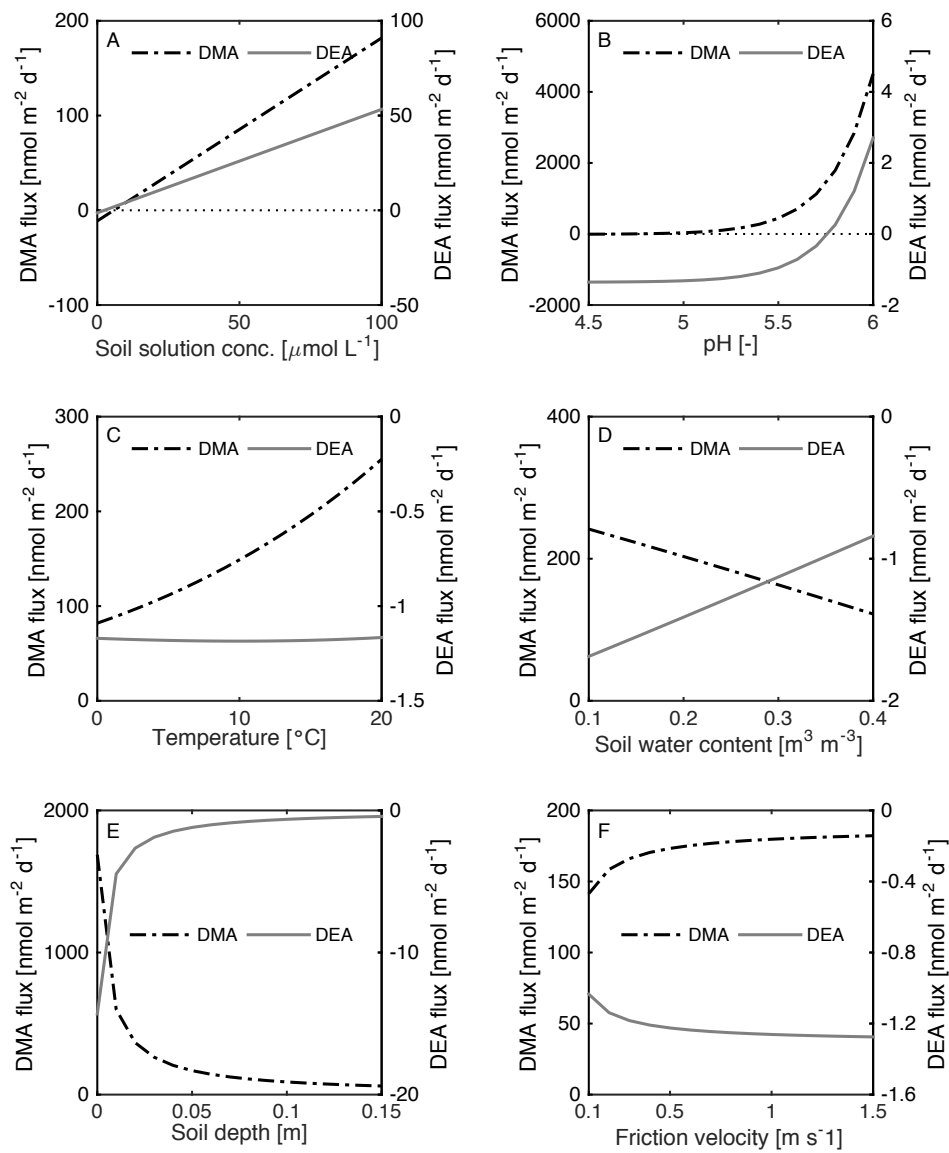
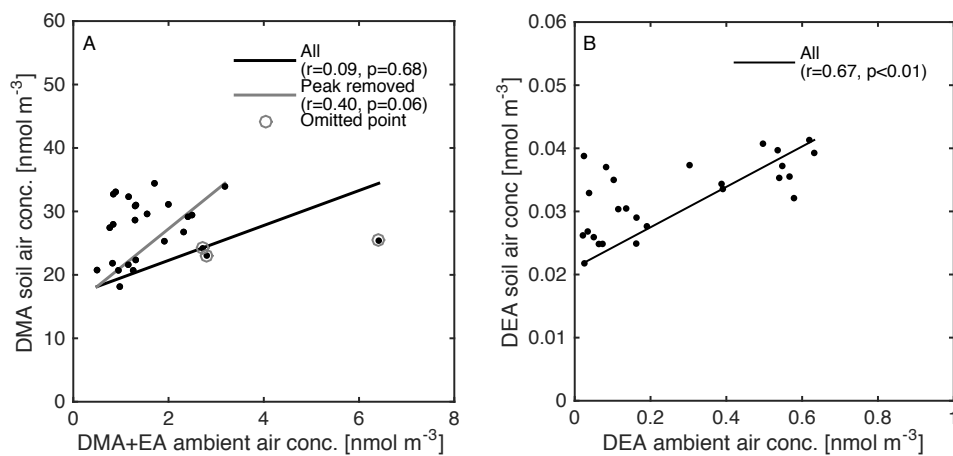



Figure 6. Effect of soil solution concentration (panel A), soil pH (panel B), temperature (panel

C), soil water content (panel D), organic soil depth (panel E), and above-canopy friction

velocity (panel F) on soil flux estimates of dimethylamine (DMA) and diethylamine (DEA).

2 Figure 7. The comparison of measured ambient air concentrations and estimated soil air

3 concentrations of dimethylamine DMA and diethylamine DEA (panel A and B, respectively)

4 with linear least square fits. In case of DMA, three data points from autumn have been

5 omitted (see Sect. 3.3); while also the least square fits without removed points are shown for

6 comparison.