

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

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Thank You for great comments!

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.

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

C1

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.

If we use suggested 1% for typical ratio of amines and NH₃ in agricultural systems, and get the total reduced N emissions of 1 kg ha⁻¹ yr⁻¹, the total reduced N emission is slightly higher than the measured N₂O emissions (0.3 kg ha⁻¹ yr⁻¹) 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 NO₃⁻ content at the site is reported negligible while the reduced N (organic and am-

C2

monium) 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⁻¹ 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⁻¹) and most of the mineral nitrogen is in the form of ammonium (0.31 kg N ha⁻¹).

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 NH₃ emissions, it is possible that fixed ratio with NH₃ does not exist. This is topic clearly calls for further studies.

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C3

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C4