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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Amine and guanidine emissions from a boreal forest floor" *by* Marja Hemmilä et al.

Anonymous Referee #2

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This manuscript describes a set of measurements made using a MARGA-MS instrument at a boreal forest site during four different months of the year. The MARGA-MS was sampling the outflow of a closed dynamic chamber, which was intended to capture emissions of amines and guanidine from the forest soil. There are relatively few reports of amine emission rates from soil so new information would be valuable. Unfortunately, there are major problems with the experimental design that mean that the data cannot be trusted quantitatively. Some of these issues (described below) even call into question the trends and relative relationships that are reported, meaning that the interpretations are very unreliable. As such, I do not think this paper should be published in ACP.

The authors note very substantial adsorptive and/or reactive losses of the amines dur-

ing quality control tests, even with the best choice of material. The authors make the decision to not account for these losses in calculating the emission fluxes. While this is a questionable decision, it might be overcome if we thought that the losses were consistent over the sampling campaign. The issue is that the losses are likely dependent on ambient conditions (temperature, humidity, insolation) and probably also on the magnitude of emissions. Therefore, it becomes difficult to trust their results, even in a relative or semi-quantitative way. A substantial fraction of the manuscript is devoted to examining how the emissions depend on environmental factors, but it may be that the adsorptive losses are what depends on these factors. From my understanding of the data, there is not way that these issues can be disentangled.

There is another issue in the design of the sampling strategy that undermines the value of the data. The use of amine-free air as the inflow to the chamber means that the emissions of these compounds may not be relevant for ambient conditions. The bidirectional framework that is typically used to explain atmosphere-ecosystem fluxes of ammonia should also apply to bases like amines and guanidine. In this framework, the fluxes are understood to result from the difference between the ambient concentration and the compensation point established by the aqueous (or soil, vegetation) reservoirs of the compound. By setting the initial ambient concentration to zero, the net fluxes are going to be higher (and possibly of a different sign) than they would be in the natural environment. Further, when used for flux measurements, these closed chambers are typically left open for a substantial fraction of each day to ensure that the ground surface enclosed by the chamber has the ability to interact with the overlying atmosphere. Based on the way in which the measurement are presented, it seems that the chamber was closed for many days on end. If this is true, this also undermines the applicability of this system to the natural and undisturbed ecosystem.

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