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Seasonal variations in gas-phase alkyl amines in the ambient air of a boreal Scots pine forest

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Alkyl amines are highly reactive volatile nitrogen compounds that have been suggested to take part in aerosol formation and growth in the atmosphere. Despite this, the sources of these compounds are unknown and there are no long-term measurements available.

We measured alkyl amine concentrations from May to October in 2011 in the trunk space of a boreal forest at the SMEAR II station in Hyytiälä, Southern Finland (61°51'N, 24°17'E, 180 m a.s.l.). The weekly air samples were collected into phosphoric acid impregnated glass fibre filters through PTFE filter and analysed by high performance liquid chromatography electrospray ionisation ion trap mass spectrometer (Agilent 1100 series LC/MSD trap).

Ethylamine and dimethylamine (EA+DMA), propylamine and trimetylamine (PA+TMA) and diethylamine (DEA) were observed on levels above the detection limits. The highest concentrations were observed from September to October for EA+DMA (157$\pm$20 ppt) and for PA+TMA (102$\pm$61 ppt). Mixing ratios of EA+DMA also peaked on weeks 24th, 30th and 35th and TMA+PA on week 36th; however, these peaks were approximately half of those observed in the autumn. DEA annual curve was different than that of the other amines. Instead of the autumn peaks, the highest mixing ratios were measured during the summer (max 15.5$\pm$0.5 ppt , early July). In the autumn the DEA mixing ratios were slightly higher than in early spring, however about half of that measured in the summer.

Amine concentrations were compared to cluster ion and monoterpene concentrations, monoterpene emissions, and to soil and air temperatures and litterfall. Positive and negative cluster ions did not correlate with the measured amine concentrations. However, during the summer, peaks in positive cluster ions occurred simultaneously with peaks in EA+DMA and DEA. During the autumn, negative cluster ions peaked with EA+DMA.

Autumnal monoterpene emissions from the forest floor coincide with the elevated or peaked EA+DMA and PA+TMA concentrations, indicating that the sources of these amines may be similar as those of the monoterpenes which have been associated with litterfall and decomposition processes in the soil. Concentration development of DEA, β-pinene and α-pinene were very similar during the measurement period. DEA and β-pinene concentrations were high throughout the summer months, and after August decreased towards the end of the measurement period.

Our measurements covered a uniquely long time series during which amines showed pronounced seasonal variability; DEA had a summer maximum, whereas EA+DMA and TMA+PA had maxima during autumn. Similar to monoterpene emissions from the forest floor, amine concentrations seem to be linked with soil activity and litterfall, and not to trace gases in the atmosphere.