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Diel cycles of isoprenoids in the emissions of Norway spruce, different Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010

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Cuvette based emission rates of monoterpenes and sesquiterpenes from four chemotypes of Scots pine (Pinus sylvestris) and one chemotype of Norway spruce (Picea abies) as well as the ambient mixing ratios of monoterpenes were determined during HUMPPA-COPEC 2010 summer campaign. Differences in chemical composition as well as in emission strength were observed between the different chemotypes. The chemotypes of Scots pine can be classified according to species with high, no and intermediate content of Δ3-carene. The "no- Δ3-carene" chemotype was found to be the strongest emitter of monoterpenes. From this chemotype, ß-myrcene, a very reactive organic gas, was the dominant species accounting for more than 35 % of the total emission rates of isoprenoids followed by ß-phellandrene ($\sim$34%). Myrcene emission rates ranged from 0.8 up to 24 μg/g (dw)/h. α-farnesene was the dominant sesquiterpene species, with measured average emission rates of 318 ng/g (dw)/h. In the high Δ3-carene chemotype, which is the most studied in Hyytiälä, Δ3-carene was more than 48 % of the total monoterpene emission. The mean Δ3-carene emission rate, circa 609 ng/g (dw)/h reported here is consistent with the previously reported value during the same season. The terpene emission from spruce was dominated by limonene (35%), ß-phellandrene (15%), α-pinene (14 %) and eucalyptol (9%). Total spruce monoterpene emissions ranged from 0.549 up to 12.2 μg/g (dw)/h. Overall the total terpene flux (monoterpenes + sesquiterpenes) from all studied plant species varied from 230 ng/g (dw)/h up to 66 μg/g (dw)/h.
The total ambient monoterpenes (including α-pinene, Δ3-carene, ß-pinene and ß-myrcene) measured during the campaign varied in mixing ratio from a few ppt to over one ppb. The most abundant biogenic VOCs measured above the canopy were α-pinene and Δ3-carene and these two compounds together contributed more than 50% of the total monoterpenes. The diel cycles of isoprenoid mixing ratios showed high levels during the night-time which is consistent with continued low nocturnal emission and a low and stable boundary layer. The chirality of [U+F061]-pinene was dominated by (+)-enantiomers both in the direct emission and in the atmosphere. The effect of herbivore attack on the plant shoot was studied and found to significantly influence the enantiomeric signature of monoterpenes in similar manner as has been observed from mechanical damage. The exceptionally hot temperatures recorded in the summer of 2010 were reflected by strong emission of terpenes and consequently high ambient mixing ratios.