ACIDIC REACTION PRODUCTS OF MONO- AND SESQUITERPENES IN ATMOSPHERIC FINE PARTICLES IN BOREAL FOREST IN HYYTIÄLÄ, FINLAND

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A large amount of biogenic VOCs (monoterpenes and sesquiterpenes) is emitted to the atmosphere by vegetation, especially in the densely forested boreal regions (Hakola et al., 2006). In the atmosphere, these compounds are oxidized producing reaction products, which may take part in the formation and growth of new particles (Tunved et al., 2006). Even though organic compounds account for 20-90 % of the total fine particle mass concentration in a wide variety of atmospheric environments (Kanakidou et al., 2005), only little is known about their detailed composition.

For many sesquiterpenes atmospheric lifetimes are so short that their concentrations in the air cannot even be measured. Therefore knowledge about real atmospheric concentrations of the reaction products of terpenes is essential for different kind of aerosol studies. In this study, acidic reaction products of biogenic VOCs, which affect the formation and growth of fine particles, were analyzed from PM 2.5 aerosol samples taken at Hyytiälä, Finland.

Highest concentrations for all studied compounds were measured in summer, except pinonic acid in 2010. (Table 1). Concentrations peaking in summer are most clear for caryophyllic acid. It is known to be emitted from typical boreal trees only in July and August (Hakola et al. 2006). Limonic acid concentrations increased already in spring. Pinonic acid is showing relatively high concentrations also in winter. Pinonic acid is more volatile compared to other acids measured here so that cold winter temperatures may have more effect on it's gas-particle distribution. In summer 2010 concentrations of pinonic and pinic acids were clearly lower than in 2011.

Concentrations of pinonic and pinic acids had relatively good correlation during summer months. This was expected since they have same precursors i.e. they are both reaction products of a- and b-pinene. Average concentrations for pinonic acid were 40% higher than for pinic acid. Ambient monoterpenes pinic and caric acids show clearly the highest concentrations during summer months concomitant with their precursors (Hakola et al., 2012). β-caryophyllinic acid also has highest concentrations in summer, but it's precursor β-caryophyllene cannot be found in ambient air due to it's high reactivity. Limonic acid concentrations increase already in spring even though limonene concentrations are still low.

Table 1. Average concentrations of bio acids during different seasons (summer 2010 - summer 2011).

		Average concentrations (ng m^{-3})					
Bio acid	Precursor	Sum 10	Aut 10	Win 10/11	Spr 11	Sum 11	Aut 11
Pinonic acid	α-pinene	5.7	7.4	9.5	5.8	14.8	8.8
Pinic acid	α-pinene	2.6	4.4	1.5	0.8	10.1	2.0
Caric acid	3-carene	7.0	2.1	2.5	3.5	7.3	4.0
Limonic acid	limonene	1.0	0.9	0.5	1.8	1.7	1.2
β-caryophyllinic acid	β-caryophyllene	3.3	0.8	0.5	0.6	2.8	1.2

Bioacids and their precurosors show a similar trend, α-pinene and its reaction products (pinic acid+pinonic acid) having the highest concentrations and limonene and its reaction product limonic acid the lowest.

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