

**Carbonyl compounds
in boreal coniferous
forest air**

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Carbonyl compounds in boreal coniferous forest air in Hyytiälä, Southern Finland

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Abstract

A variety of C₁-C₁₂ carbonyl compounds were measured in the air of a boreal coniferous forest located in Hyytiälä, Southern Finland. 24-h samples were collected during March and April in 2003 using DNPH (2,4-dinitrophenyl hydrazine) coated C₁₈-cartridges and analyzed by liquid chromatography-mass spectrometry (LC-MS).

Altogether 22 carbonyl compounds were quantified. The most abundant carbonyls were acetone (24-h average 1340 ng/m³), formaldehyde (480 ng/m³) and acetaldehyde (360 ng/m³). In contrast, scaling of concentrations against reactivity with the hydroxyl (OH) radical significantly increased the contribution of larger aldehydes and ketones (e.g. decanal, octanal and 6-methyl-5-hepten-2-one). Concentrations of monoterpene reaction products nopinone (9 ng/m³) and limona ketone (5 ng/m³) were low compared to the most abundant low molecular weight carbonyls. The total concentration of carbonyl compounds in Hyytiälä in April/March 2003 was much higher than the concentration of aromatic hydrocarbons and monoterpenes in April 2002.

Lifetimes of the measured carbonyls with respect to reactions with OH radicals, ozone (O₃), and nitrate (NO₃) radicals as well as photolysis were estimated. The main sinks for most of the carbonyl compounds in Hyytiälä in springtime are expected to be reactions with the OH radical and photolysis. For 6-methyl-5-hepten-2-one and limona ketone also reactions with ozone are important. The sources of carbonyl compounds are presently highly uncertain. Due to the relatively short lifetimes of aldehydes and ketones, secondary biogenic and anthropogenic sources, that is oxidation of volatile organic compounds, and primary biogenic sources are expected to dominate in Hyytiälä.

1. Introduction

Carbonyl compounds (aldehydes and ketones) are a class of organic compounds that have both primary and secondary anthropogenic and biogenic sources. These sources are not well known, but anthropogenic sources include at least car exhaust emissions,

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wood combustion and solvent evaporation (Friedrich and Obermeier, 1999). Some coniferous trees (“*Pinus sylvestris*” and “*Picea abies*”) have been shown to emit significant amounts of acetone and acetaldehyde (Janson et al., 2001) and agricultural species (Arey et al., 1991; Köning et al., 1995) as well as stressed plants (Hakola et al., 2001) have been found to emit C₆ carbonyl compounds. Also other carbonyl compounds can be emitted from plants, but these emission rates are poorly known (Fall, 1999). In addition to the direct emissions, carbonyls are formed in the atmosphere from the oxidation of other volatile organic compounds.

Carbonyls can comprise a substantial proportion of total volatile organic compounds in the atmosphere (Fehsenfeld et al., 1992) and they play an important role in photochemical reactions. Aldehydes and ketones undergo photolysis and react with hydroxyl (OH) radicals and nitrate (NO₃) radicals (Atkinson, 2000). Carbonyls and their reaction products participate in formation of ozone and peroxyacetyl nitrate (PAN). Some of the higher molecular weight carbonyls are semivolatile and their contribution to new particle formation may be substantial (Matsunaga et al., 2004). Since some carbonyls (e.g. formaldehyde) are water soluble, significant concentrations have been measured in fogs and clouds (Grosjean and Wright, 1983). In aerosol particles carbonyls may also act as surfactants (Finlayson-Pitts and Pitts, 2000) hence changing their surface properties. Long-chained carbonyls (≥C₅) may form surface films on droplets by lining up with the polar ends in the water and nonpolar, hydrophobic ends projecting into air. Photolysis of aldehydes can be a major source of hydroxyl radicals during the day (Possanzini et al., 2002). Some of the carbonyls are also known to have toxic and carcinogenic properties.

While some light carbonyls, such as formaldehyde, acetone and acetaldehyde, have been studied quite intensively, there are only a few studies on larger aldehydes and ketones. In this paper we report atmospheric concentrations for 22 different C₁-C₁₂ carbonyl compounds measured in a boreal coniferous forest located in Hyytiälä, Finland. Measurements were conducted in March and April 2003 during QUEST II (Quantification of Aerosol Nucleation in the European Boundary Layer) campaign.

2. Experimental

2.1. Site description

Measurements took place at the SMEAR (Station For Measuring Forest Ecosystem-Atmosphere Relations, 61°51' N, 24°17' E, 181 m a.s.l.) II station located in Hyytiälä, Central Finland. The forest around the station is dominated by conifers (mainly Scots pine but also Norway spruce) with some deciduous trees, such as aspen and birch. Fifteen minute averages of the temperature varied between -11.1 and 8.6°C during the measurement period. The site is described in more detail by Vesala et al. (1998).

2.2. Sampling and analysis

Sampling equipment was placed inside the forest with sampling inlet height at one meter above ground level. Samples were collected by drawing air through C₁₈-cartridges (Sep-Pak, Waters) coated with DNPH (2,4-dinitrophenyl hydrazine). An ozone scrubber (copper tubing coated with potassium iodide) was placed in front of the sampling cartridges. Flow rate was 976 ml/min and the sampling time was about 24 h.

Between 19 March and 13 April, 25 diurnal samples were collected. The carbonyl compounds were derivatized in cartridges to (2,4-dinitrophenyl)hydrazones during sampling. In the laboratory, the cartridges were eluted with 3 ml of acetonitrile and the eluants were analysed using a liquid chromatograph equipped with a XDB C-8 column (length 150 mm, i.d. 4.6 mm) and a mass spectrometer with negative atmospheric pressure chemical ionization (Agilent 1100 Series LC/MSD trap). Water buffered with 1 M ammonium acetate (1 ml/1 L H₂O) and acetonitrile were used in gradient elution. The analysis method was adapted from Grosjean et al. (1999).

DNPH-derivates of undecanal, heptanal, nonanal, trans-2-hexenal, lauraldehyde, decanal, 6-methyl-5-hepten-2-one (6-MHO), nopinone, octanal and limona ketone were prepared according to instructions from the manual for sampling and analysis of the co-operative programme for monitoring and evaluation of the long-range transmis-

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sions of air pollutants in Europe (EMEP, 1996). For hexanal, formaldehyde, methyl ethyl ketone (MEK), butanal, pentanal, propanal, acetaldehyde, acetone, acrolein, benzaldehyde, 2-butenal, m-tolualdehyde and methacrolein commercial liquid DNPH-carbonyl standard in acetonitrile (Carb Method 1004 DNPH Mix 2, Supelco) was used. Detection limits of the compounds varied from 1 ng/m³ to 135 ng/m³.

3. Results and discussion

3.1. Ambient concentrations of carbonyl compounds

Acetone, formaldehyde and acetaldehyde were the most abundant carbonyls in Hyytiälä in March/April 2003 contributing to 75% of all measured carbonyls (Fig. 1). Average 24-h concentrations of acetone, formaldehyde and acetaldehyde were 1340, 480 and 360 ng/m³, respectively (Fig. 2). However, also many other aldehydes and ketones were found. Average concentrations of nopinone and limona ketone, reaction products of monoterpenes β -pinene and limonene, were low (9 ng/m³ and 5 ng/m³) compared to the most abundant light carbonyl compounds. This is expected since also the monoterpene concentrations are low during early spring (Hakola et al., 2003). α -pinene is the most common monoterpene in ambient air in Hyytiälä, but no standard for the main α -pinene oxidation product, pinonaldehyde, was available and therefore pinonaldehyde was not measured. The concentrations of acrolein, 2-butenal, trans-2-hexenal, methacrolein, undecanal, m-tolualdehyde, nonanal and heptanal remained mostly below detection limit during the measurement period.

Although the concentrations of the heavier C₅-C₁₂ aldehydes were lower than the light aldehydes, their contribution to local photochemistry is important due to faster reactions with the hydroxyl radical. Figures 1 and 2 show the OH reactivity-scaled concentrations of carbonyl compounds. Based on OH-reactivity, concentrations were

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scaled to formaldehyde equivalents according to Eq. (1).

$$C_{\text{eqv}} = \frac{\text{Conc.} \cdot k_{\text{OH}}}{k_{\text{OH}}(\text{HCHO})}. \quad (1)$$

The contribution of the C₅-C₁₂ aldehydes to the total carbonyl reactivity was 34%. Also 6-methyl-2-hepten-3-one (6-MHO) is important comprising 12% of the total OH-reactivity.

Daily variation of the sum of the 24-h averages of carbonyl concentrations and temperature is shown in Fig. 3. Average 24-h concentration of all measured carbonyls is 2850 ng/m³. Variation between days is quite high from 1760 to 4710 ng/m³.

Concentrations of carbonyl compounds in March/April 2003 were significantly higher than aromatic hydrocarbon and monoterpene concentrations measured in Hyytiälä in April 2002 (Fig. 4). In a rural site in Colorado carbonyl concentrations were three times higher than monoterpenes and aromatics (Fehsenfeld et al., 1992). However, in a rural site in Alabama monoterpene concentration was over two times higher than carbonyl concentration.

3.2. Calculation of reaction/photolysis rates

Average lifetimes of the measured carbonyls with respect to reactions with OH, O₃ and NO₃ were calculated based on oxidant concentration estimations in Hyytiälä by Hakola et al. (2003). Rate constants were obtained mainly from the National Institute for Standards and Technology Chemical Kinetics Database (NIST, 2003). Rate constants for reactions of OH-radical with octanal, decanal, undecanal, lauraldehyde and m-tolualdehyde were not found in literature and therefore the reaction rates were estimated using the structure-reactivity relationship described by Kwok and Atkinson (1995).

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Photolysis rates were calculated using Eq. (2) (Finlayson-Pitts and Pitts, 2000).

$$k_p(s^{-1}) = \sum_{\lambda=290\text{ nm}}^{\lambda_i} \Phi_{av}(\lambda)\sigma_{av}(\lambda)F_{av}(\lambda), \quad (2)$$

where k_p is the photolysis rate, Φ_{av} is the primary quantum yield and represents the fraction of excited molecules that undergo photochemistry averaged over the wavelength interval $\Delta\lambda$, centered at λ , $\sigma_{av}(\lambda)$ is the absorption cross section in base e, averaged over the wavelength interval $\Delta\lambda$, centered at λ , and $F_{av}(\lambda)$ is the actinic flux in photons summed over the wavelength interval $\Delta\lambda$, centered at λ , at a solar zenith angle θ corrected for season by correction factor of Earth-Sun distance D . Solar zenith angle was calculated using the method given in Finlayson-Pitts and Pitts (2000). The calculated midday solar zenith angle was 58° at Hyytiälä for 1 April. Actinic fluxes used in the calculations were for clear sky conditions and zenith angle 60° (Finlayson-Pitts and Pitts, 2000). These actinic fluxes are calculated for surface albedo (α) of 0.05. In a snow-covered coniferous forest like Hyytiälä, the surface albedo (α) is higher ($\alpha=0.26$ in Betts, 2000) and this leads to higher actinic fluxes and hence enhanced photochemistry. If calculated using the actinic fluxes for surface albedo 0.8, photolysis rates were 2.5 times higher.

Absorption cross sections and quantum yields were obtained from literature given in Table 1. For MEK quantum yields (Φ) were not found from literature and therefore values $\Phi=1$ and $\Phi=0.1$ were used in the estimations. The quantum yield value 1 represents maximum rate of photolysis, but the true rate constant may be much smaller, even zero. The uncertainty in estimating quantum yields is demonstrated by the variation in Φ values found in literature. For acetaldehyde quantum yields varied between 0.02 and 0.52 at wavelengths 290–330 nm and for acetone between 0.01 and 0.11 at wavelengths 302–335 nm (Finlayson-Pitts and Pitts, 2000). Correction factor ($D=1.001$) for Earth-Sun distance in April was obtained from Finlayson-Pitts and Pitts (2000).

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3.3. Lifetimes of carbonyl compounds in Hyytiälä

Calculated lifetimes and reaction rates are presented in Table 1. For most of the compounds the main sinks in Hyytiälä in spring are expected to be reactions with the OH radical and photolysis. For 6-MHO and limona ketone also reactions with ozone are important. However, more quantum yield and absorption cross section measurements are required to verify these conclusions. Some additional estimates of the photolytic lifetimes of carbonyl compounds can be found in the literature. In the study of Moortgat (2001) estimated photolytic lifetimes of nopinone and limona ketone are longer than the lifetime of acetaldehyde. Hence, for these compounds photolysis is not expected to be as important loss process as reactions with OH radicals and ozone. Photolytic lifetimes of nonanal and 2-butenal were close to the lifetimes of pentanal and butanal (Moortgat, 2001).

The most important reaction for formaldehyde in Hyytiälä in spring is photolysis (photolytic lifetime 8 h). Overall lifetimes for 6-MHO and limona ketone due to OH-radical and ozone are very short, 35 min and 1.3 h, respectively. For larger aldehydes (C_4 - C_{12}) main reaction is with OH radicals (average lifetime about 18 h), but also photolysis is important (average lifetime for C_4 - C_9 aldehydes about 1.5 d).

Other possible sinks are scavenging by aqueous droplets and dry deposition. Grosjean and Wright (1983) identified up to ten C_1 - C_6 carbonyls in fog, ice fog, mist, cloud water or rainwater samples and also several unidentified carbonyls were present. Kawamura et al. (2001) studied wet deposition of carbonyls in Los Angeles. They found that wet scavenging is an important loss process for formaldehyde. For the other C_1 - C_4 aldehydes wet deposition was less significant. Formaldehyde was more efficiently scavenged than acetaldehyde and propanal by a factor of 10 and 30, respectively. The air/rain molar ratios increased with an increase in carbon number of aldehydes. This is in accordance with Henry's Law constants (Zhou and Mopper, 1990). Satsumabayashi et al. (2001) found significant concentrations of pinonaldehyde (0.16–13 $\mu\text{g/l}$) in rain and snow in central Japan.

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Based on model simulations by Zhang et al. (2002), dry deposition is likely to be an important loss process for C_1 - C_8 carbonyls in evergreen-needleleaf forests at temperatures above the temperature at which stomata starts opening. However, there are no measurements available to support this.

5 3.4. Sources of carbonyl compounds

Main source of formaldehyde in this rural forested site is expected to be oxidation of hydrocarbons and other volatile organic compounds. Formaldehyde has also primary sources such as biomass burning and automobile exhaust, but because the lifetime of formaldehyde is relatively short (in the order of hours, see Table 1), it is not transported far from the emission sources during daytime. In global estimates of formaldehyde emissions biomass burning and automobile exhausts are much less important than hydrocarbon oxidation (Singh et al., 2000). Emissions from automobile exhaust and biomass burning comprise 5% of the formaldehyde produced from methane oxidation.

In our dataset formaldehyde shows highest positive linear correlation with propanal ($R^2=0.64$), acetaldehyde ($R^2=0.63$) and butanal ($R^2=0.55$). The main source of these light carbonyls in Hyytiälä is probably the oxidation of higher hydrocarbons. Acetaldehyde, propanal and butanal have all been detected in automobile exhausts and in wood combustion emissions (Schauer et al., 2002; McDonald et al., 2000). In a global emission estimate by Singh et al. (2004), main sources of acetaldehyde and propanal are oceanic. Transport of marine air is not expected to be an important source in Hyytiälä. In addition to oceanic sources, oxidation of hydrocarbons and primary biogenic emissions are globally more significant than primary anthropogenic sources. However, very little is known about the sources of butanal, propanal and acetaldehyde and the estimation by Singh et al. (2004) is a first highly uncertain estimate.

Similar to formaldehyde, acetone shows highest positive correlation with propanal ($R^2=0.66$) and acetaldehyde ($R^2=0.56$). According to emission inventories, the main sources of acetone are primary biogenic emissions and oxidation of anthropogenic and biogenic VOCs (Singh et al., 2000). Other important sources are decaying plant matter,

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biomass burning and direct anthropogenic sources. Trees can be an important source of acetone in Hyytiälä. Janson and Serves (2001) found high concentrations of acetone in branch emission measurements of Scots pine and Norway spruce conducted in Hyytiälä in March/April in 1999. Oxidation of monoterpenes is an important secondary source of acetone. High acetone yields were measured in reactions of monoterpenes with OH radicals and O₃ (Reissell et al., 1999). In spite of the cold season, emissions of monoterpenes have been detected in enclosure measurement of Scots pine and Norway spruce during March and April (Hakola et al., 2003; Janson and Serves, 2001). However, due to the long lifetime, acetone can be transported long distances.

Nopinone shows positive linear correlation with decanal ($R^2=0.56$). Nopinone is a reaction product of the biogenic hydrocarbon β -pinene (Hakola et al., 1994). Ozonolysis of plant lipids, either on leaf surfaces or on atmospheric particulate matter, can be an important source of long-chain aldehydes in forest environments (Bowman et al., 2003). A source for nonanal can be ozonolysis of oleic acid, which is biologically produced and ubiquitously present in the biosphere (Yokouchi et al., 1990). However, in our study nonanal remained below the detection limit (131 ng/m³). It is possible that some of decanal and octanal in the air of Hyytiälä is emitted directly from the trees. Small emissions of decanal, octanal and other heavier C₆-C₁₂ aldehydes have been detected in enclosure measurements of orange leaves (Possanzini et al., 2000) and oaks (König et al., 1995). Automobile exhausts and wood combustion are known anthropogenic sources of these high molecular weight aldehydes (Schauer et al., 2002; McDonald et al., 2000). Lifetimes of C₆-C₁₂ aldehydes are short (in the order of hours, see Table 1) and they are most probably not transported far from source areas. Also hexanal and heptanal are mentioned in a study by Bowman et al. (2003), where it is suggested that long-chain aldehydes are produced from ozonolysis of plant lipids, and in enclosure measurements of various plants by Possazzini et al. (2000) and König et al. (1995). In this study hexanal and heptanal do not correlate with other long-chain aldehydes. Hexanal shows highest linear relationship with butanal ($R^2=0.53$), which is more connected to formaldehyde and other small carbonyls. Heptanal concentrations

remained below the detection limit (28 ng/m³) during most of the days.

The lifetime of methyl ethyl ketone (MEK) is longer than the lifetime of other carbonyls, excluding acetone (Table 1). MEK does not show positive correlation with most of the compounds. Highest correlation is with acetone ($R^2=0.38$). Because of the longer lifetime (several days), MEK can be transported much longer distances than the other measured carbonyls. Known anthropogenic sources of MEK are automobile exhaust and wood combustion (Schauer et al., 2002; McDonald et al., 2000). MEK is also used as solvent (Friedrich and Obermeier, 1999). In the emission inventory by Singh et al. (2004) it is concluded that primary anthropogenic emissions are insignificant as a global source of MEK compared to primary biogenic sources, biomass burning and oxidation of anthropogenic hydrocarbons, but data for quantitative estimations of the magnitude of these emissions are not available.

6-methyl-5-hepten-2-one (6-MHO) did not show positive correlation with any other carbonyls ($R^2<0.10$). Ozonolysis of linalool can lead to formation of 6-MHO (Shu et al., 1997) but this does not explain the relatively high concentrations of 6-MHO observed in Hyytiälä. Linalool has not been detected in ambient air or in the emissions of Scots pine at Hyytiälä in the early spring (Tarvainen et al., submitted, 2004¹). Fruekilde et al. (1998) have found that the ozonolysis of epicuticular wax from leaves of deciduous trees is a possible source for 6-MHO in ambient air. A series of non-volatile and volatile terpenes common in vegetation contain the structural element necessary for the formation of 6-MHO by ozonolysis of C=C double bond.

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4. Conclusions

A variety of carbonyl compounds were quantified in air inside a boreal coniferous forest. The most abundant carbonyls were acetone, formaldehyde and acetaldehyde. When concentrations were scaled against reactivity with the OH-radical, contribution from higher molecular weight aldehydes and ketones increased significantly. Because of low monoterpene concentrations in early spring, concentrations of reaction products nopinone and limona ketone were also low compared to the most abundant carbonyls.

Concentration of carbonyl compounds in Hyytiälä in March/April 2003 was much higher than the concentration of aromatic hydrocarbons and monoterpenes in April 2002 and therefore the contribution of the carbonyls to the total amount of volatile organic compounds is significant at this rural forested site.

Main sinks for most of the carbonyl compounds in Hyytiälä in springtime are expected to be reactions with the OH radical and photolysis. For 6-MHO and limona ketone also reactions with ozone are important.

The sources of carbonyl compounds are presently highly uncertain. Because of the relatively short lifetimes of aldehydes and ketones, secondary production from the oxidation of other organic compounds and primary biogenic sources are expected to dominate in Hyytiälä. However, some small local anthropogenic sources (wood combustion or traffic) may also exist.

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Table 1. Rate constants and calculated lifetimes of the carbonyl compounds measured in this study.

	Photolysis rate	Rate constants (cm ³ /molec/s)			Lifetime ^a due to			
	K _p *10 ⁵ (s ⁻¹)	k(OH)	K(O ₃)	k(NO ₃)	Photolysis ^b	OH ^c	O ₃ ^d	NO ₃ ^e
Formaldehyde	3.563 ^v	9.38E-12 ^a	2.09E-24 ^b	5.60E-16 ^a	8 h	2.6 d	15000 a	317 d
Acetaldehyde	0.142 ^w	6.15E-12 ^a	5.99E-21 ^c	2.72E-15 ^a	8.1 d	3.6 d	5.4 a	65 d
Propanal	0.484 ^{v,w,x}	9.98E-12 ^a		6.50E-15 ^a	2.4 d	2.2 d		27 d
Butanal	0.723 ^{v,w,y}	2.38E-11 ^d		1.11E-14 ^a	1.6 d	22 h		16 d
Pentanal	0.746 ^{v,y}	2.76E-11 ^o		1.81E-14 ^f	1.5 d	19 h		9.8 d
Hexanal	0.884 ^{v,y,z}	2.86E-11 ^d		2.37E-14 ^f	1.3 d	18 h		7.5 d
Heptanal		2.96E-11 ^g		2.43E-14 ^f		18 h		7.3 d
Octanal		2.86E-11				19 h		
Nonanal		3.60E-11 ^h			~1.6 d	15 h		
Decanal		3.14E-11				17 h		
Undecanal		3.28E-11				16 h		
Laurinaldehyde		3.42E-11				15 h		
MEK	0.397/0.0397 ^{F,v,w}	1.20E-12 ^a			2.9/29 d			
Acetone	0.021 ^{v,w}	2.19E-13 ⁱ		3.00E-17 ^a	56 d	100 d		16 a
Nopinone		1.43E-11 ^j			>8 d	1.5 d		
trans-2-hexenal		4.40E-11 ^k	1.28E-18 ^f	1.21E-14 ^k		12 h	9.1 d	15 d
Limona ketone		1.29E-10 ^j	1.50E-16 ^f	1.05E-11 ^l	>8 d	4 h	2 h	24 min
6-MHO		1.60E-10 ^m	3.94E-16 ^f			3.3 h	42 min	
Methacrolein	0.094 ^{v,y,z}	2.76E-11 ⁿ	1.30E-18 ^g	3.30E-15 ^p	12 d	19 h	8.9 d	54 d
Benzaldehyde		7.09E-12 ^q		2.01E-15 ^r		3.1 d		88 d
2-butenal		2.81E-11 ^s	1.74E-18 ^f	5.11E-15 ^u	~1.6 d	19 h	6.7 d	35 d

^aAn atmospheric lifetime is defined as the time required for the compound concentration value to degrade to a value of 1/e of its initial concentration.

^b Photolysis rates are calculated for midday clear sky conditions at Hyttiälä, 1 April.

^cFor 12-hour daytime average OH radical concentration of 5.3*10⁵ molecule cm⁻³.

^dFor a monthly average O₃ concentration of 9.96*10¹¹ molecule cm⁻³ (41ppbv).

^eFor a 12-hour nighttime average NO₃ concentration of 6.51*10⁷ molecule cm⁻³.

All rate constants are at 298 ± 5 K. F=calculated using quantum yields F =1/F=0.1 as estimates)

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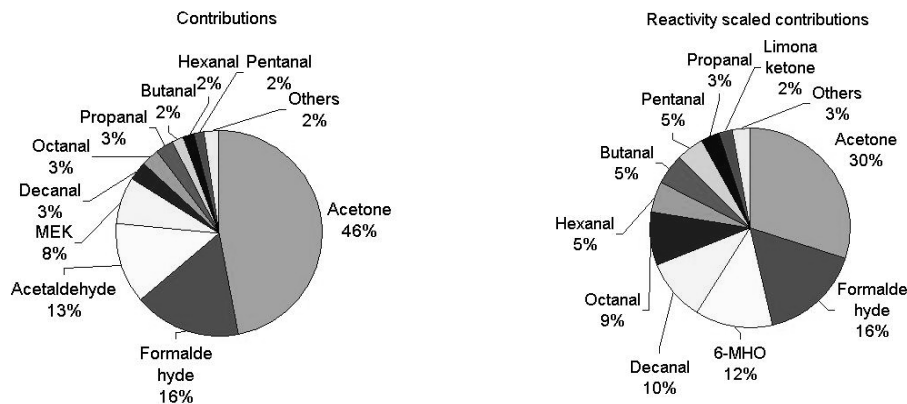


Fig. 1. Contributions of the individual carbonyl compounds to the total average concentration and to the reactivity scaled concentration.

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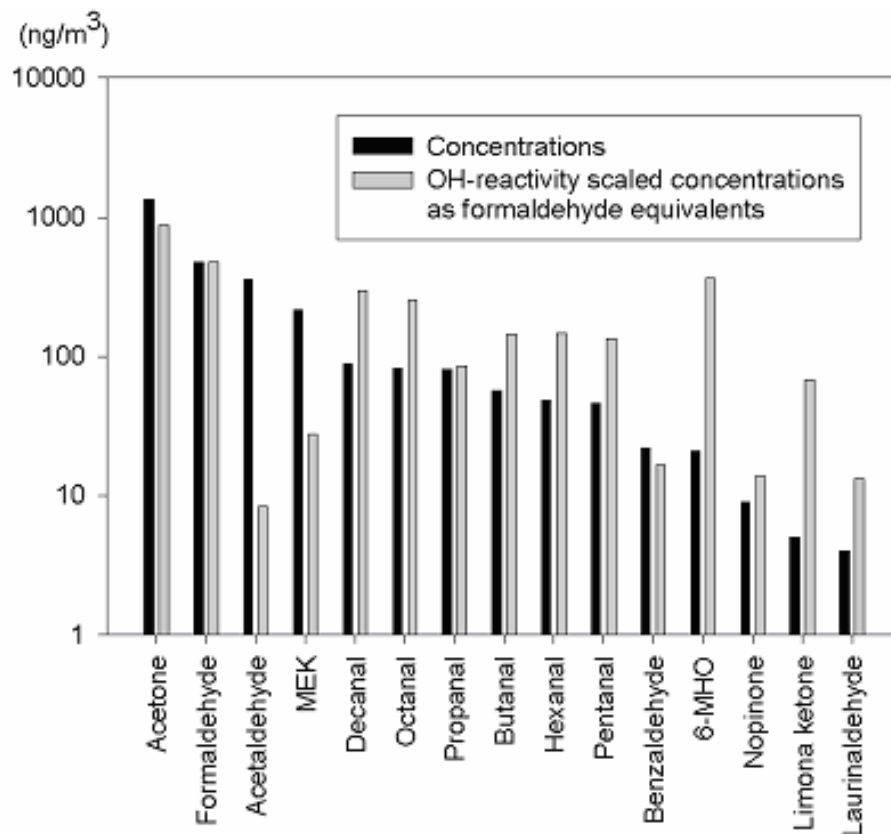


Fig. 2. Average 24-h concentrations of carbonyl compounds and OH-reactivity scaled concentrations (C_{eqv} , as formaldehyde equivalents) in ambient air at Hyttälä, 19 March–13 April 2003.

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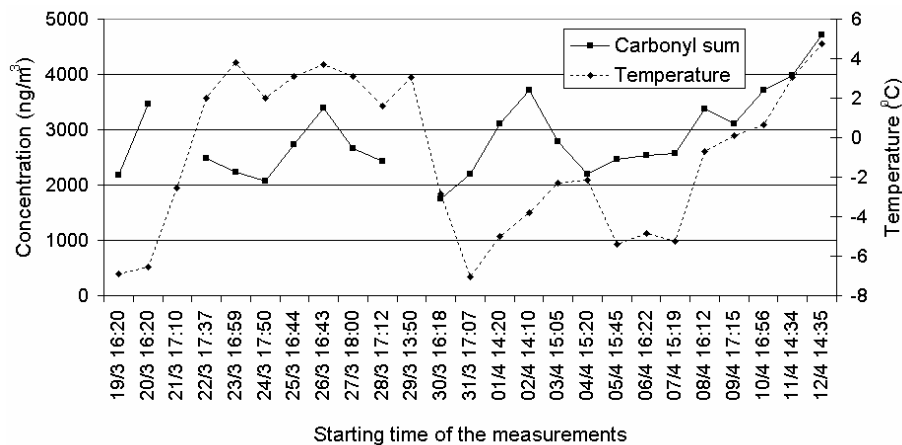


Fig. 3. Daily variation of carbonyl compounds in ambient air at Hyytilä, 19 March–13 April 2003, based on 24-h samples.

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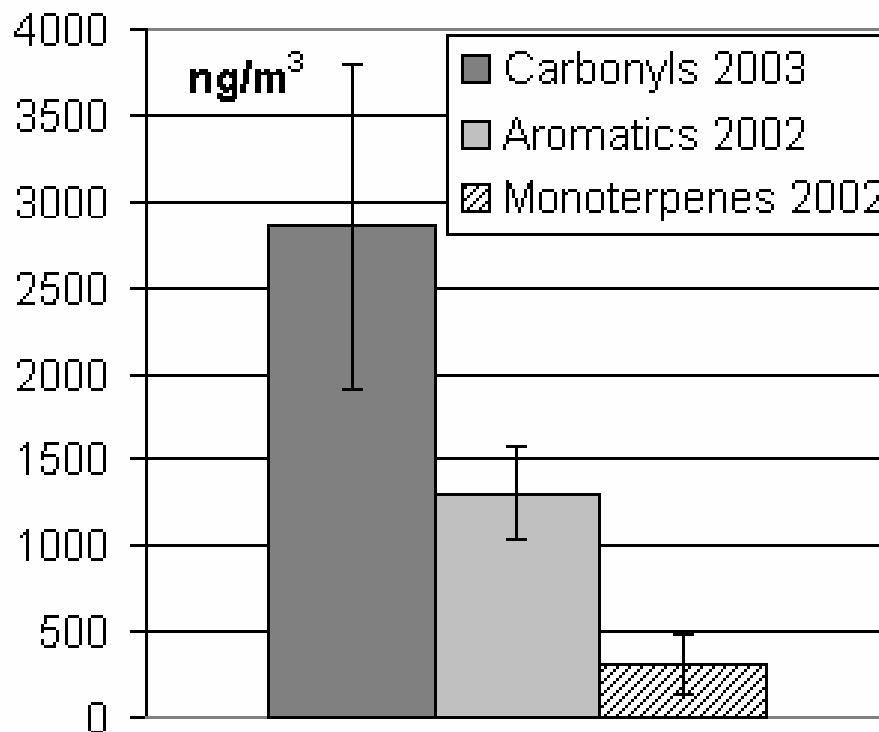


Fig. 4. Average and standard deviation of carbonyl concentrations (24-h samples) measured in March/April 2003 and aromatic hydrocarbon and monoterpene concentrations measured in April 2002 (3-h continuous sampling, 15–29 April).

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