

1           **Supplementary material for the Manuscript**

2           **Seasonal cycle and temperature dependence of**  
3 **pinene oxidation products, dicarboxylic acids and**  
4 **nitrophenols in fine and coarse air particulate**  
5 **matter**

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1 To analyze the observed temperature dependence (range 275-300 K) of the 3-methyl-  
2 1,2,3-butanetricarboxylic acid (3-MBTCA) concentration, we have compiled a simple  
3 conceptual model considering the temperature dependences during the following steps  
4 and processes in the production and loss of 3-MBTCA.

### 5 *Temperature dependence of emission and oxidation of pinene*

6 The mechanism of emission from plants is usually explained as emission from terpene  
7 pools within the plant needles or leaves (from resins stored in ducts, glands or trichomes)  
8 and the emission rate is typically reported to be only temperature dependent. The  
9 quantitative dependence has been described by several authors (Juuti et al., 1990; Lamb  
10 et al., 1985; Tingey et al., 1980). For the current simulation of pinene emission, we used  
11 the empiric temperature dependent emission model for Scots Pine (*pinus silvestris*) to  
12 estimate the temperature dependence (Komenda et al., 2003):

$$13 \quad C_{PE} = \Phi_{PE} EF$$

$$14 \quad C_{PE}^{P,S} = \Phi_{PE}^{P,S} EF$$

$$15 \quad \Phi_{PE} = \Phi_{PE}^{P,S} \exp \left[ \frac{C_{TP}}{R} \left( \frac{T - T_s}{T T_s} \right) \right]$$

$$16 \quad \ln \left( \frac{C_{PE}}{C_{PE}^{P,S}} \right) = - \frac{C_{TP}}{R} \left( \frac{1}{T} - \frac{1}{T_s} \right)$$

17  $C_{PE}$  is the concentration of emitted pinene;  $\Phi_{PE}$  is pinene emission rate (ng g(dry  
18 weight)<sup>-1</sup> h<sup>-1</sup>), and EF is the emission factor, which is to scale the linear fit of pinene  
19 emission and assumed as 1.5 g h m<sup>-3</sup>.  $\Phi_{PE}^{P,S}$  is the pinene acid emission rate from pool (ng

1 g(dry weight)<sup>-1</sup> h<sup>-1</sup>) at standard temperature T<sub>S</sub>, c<sub>TP</sub> is the empirical parameter describing  
2 the temperature dependence (J mol<sup>-1</sup>), and T<sub>S</sub> is the standard temperature. At 298 K,  $\Phi_{PE}^{P,S}$   
3 = (23±9.3) ng g(dw)<sup>-1</sup> h<sup>-1</sup>,  $\frac{c_{TP}}{R} = (9.1\pm0.4) 10^3$  K (Komenda et al., 2003) ; R is the gas  
4 constant (8.31J K<sup>-1</sup> mol<sup>-1</sup>). T is temperature (K, ranged from 275 to 300 K) and T<sub>S</sub> is  
5 standard temperature (300 K). The calculated natural logarithms of ratios C<sub>PE</sub> over  
6 C<sub>PE,300</sub> were plotted against inverse temperature (Fig. S2a). C<sub>PE</sub> was plotted against  
7 inverse temperature and fitted with an Arrhenius-type expression of the form C<sub>PE</sub> = A  
8 exp[-E<sub>A</sub>/(R T)] (Fig. S2b).

9 We assume as a first approximation this first step to be independent of environmental  
10 conditions (e.g. oxidant concentration) and to yield a constant amount of pinonic acid  
11 (PA) (linearly scaling with the precursor emission), which essential means that the  
12 lifetime of pinene is shorter than the average transport time of the emitted biogenic VOC  
13 to the sampling site. This assumption was supported by the fact that pinic acid has a  
14 similar temperature dependence value to that of pinene emission (see temperature  
15 dependence of pinic acid). As a result:

$$16 \quad C_{PE} = C_{PA(\text{produced})}.$$

### 17 ***Temperature dependence of gas-particle partitioning of pinonic acid***

18 The partitioning of a semi-volatile compound between the gas and particle phase is  
19 generally described by the ratio of the particle phase concentration and the concentration  
20 in the gas phase (FGP), normalized by the total concentration of organic material in the  
21 particle phase (FPP). The resulting partitioning coefficient K<sub>i</sub> (m<sup>3</sup>/μg) (Odum et al., 1996)  
22 or its inverse C<sub>i</sub>\* (μg/m<sup>3</sup>) (Donahue et al., 2006) of a compound i strongly depends on the

1 vapor pressure of *i*. Pinonic acid is a semi-volatile species with a C\* value between 900-  
 2 4000  $\mu\text{g}/\text{m}^3$  (Jimenez et al., 2009). Applying these values together with a typical ambient  
 3 organic aerosol mass loading (i.e. 5  $\mu\text{g}/\text{m}^3$ ) (Hock et al., 2008) to the temperature range  
 4 of interest shows that the relative amount of pinonic acid in the gas phase is always more  
 5 than 99 %, which means that even at lower ambient temperatures pinonic acid is  
 6 dominantly present in the gas phase.

$$7 \quad \text{FGP}_{\text{PA}} = 1 - \text{FPP}_{\text{PA}} = \frac{1}{1 + \frac{C_{\text{PA}}^*}{C_{\text{OA}}}} = \frac{C_{\text{PA}}^*}{C_{\text{PA}}^* + C_{\text{OA}}}$$

$$8 \quad \frac{\text{FGP}_{\text{PA}}}{\text{FGP}_{\text{PA}}^{\text{S}}} = \frac{C_{\text{PA}}^{*,\text{S}} + C_{\text{OA}}}{C_{\text{PA}}^{*,\text{S}} + C_{\text{OA}} \frac{C_{\text{PA}}^{*,\text{S}}}{C_{\text{PA}}^*}}$$

$$9 \quad C_{\text{PA}}^* = \frac{1}{K_{\text{PA}}}$$

$$10 \quad \frac{C_{\text{PA}}^{*,\text{S}}}{C_{\text{PA}}^*} = \frac{K_{\text{PA}}}{K_{\text{PA}}^{\text{S}}}$$

11 Since the vapor pressure is a function of temperature, following the Clausius Clapeyron  
 12 equation, also  $K_i$  or  $C_i^*$  vary with temperature (Chung and Seinfeld, 2002; Takekawa et  
 13 al., 2003).

$$14 \quad \frac{K_{\text{PA}}(T_2)}{K_{\text{PA}}(T_1)} = \frac{T_2}{T_1} \exp\left[\frac{\Delta H_{\text{PA}}^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$15 \quad \frac{K_{\text{PA}}}{K_{\text{PA}}^{\text{S}}} = \frac{T}{T_{\text{S}}} \exp\left[\frac{\Delta H_{\text{PA}}^0}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{S}}}\right)\right]$$

$$\ln\left(\frac{FGP_{PA}}{FGP_{PA}^S}\right) = \ln\left\{\frac{C_{PA}^{*,S} + C_{OA}}{C_{PA}^{*,S} + C_{OA} \frac{T}{T_S} \exp\left[\frac{\Delta H_{PA}^0}{R} \left(\frac{1}{T} - \frac{1}{T_S}\right)\right]}\right\}$$

2  $C_{OA}$  is organic aerosol concentration ( $5 \mu\text{g m}^{-3}$ ) (Hock et al., 2008).  $C_{PA}^{*,S}$  is the effective  
 3 saturation concentration at standard temperature ( $T_S = 300\text{K}$ ) ( $4000 \mu\text{g m}^{-3}$ ) (Jimenez et  
 4 al., 2009);  $\Delta H_{PA}^0$  is the enthalpy of pinonic acid vaporisation ( $5.90 \times 10^4 \text{J mol}^{-1}$ ) (Saathoff  
 5 et al., 2009).  $T$  is temperature (K, ranged from 275 to 300 K). The calculated natural  
 6 logarithms of ratios  $FGP_{PA}$  over  $FGP_{PA,S}$  were plotted against inverse temperature (Fig.  
 7 S3a), and good linear correlation was found ( $R^2 = 0.95$ ).  $E_a/R$  is opposite number of  
 8 linear fit slope (26 K), and  $\Delta E_a/R$  is the deviation of linear fit slope (1.4 K).  $FGP_{PA}$  was  
 9 plotted against inverse temperature and fitted with an Arrhenius-type expression of the  
 10 form  $FGP_{PA} = A \exp[-E_a/(R T)]$  (Fig. S3b).

11 With an opposite sign the same is true for the temperature dependent partitioning of 3-  
 12 MBTCA itself, since the very low vapor pressure of this compound always (i.e.  
 13 independent from temperature within the relevant temperature range) drives 3-MBTCA  
 14 into the condensed phase. In summary, the gas-particle-partitioning has no contribution to  
 15 the observed temperature dependence of the observed 3-MBTCA concentration (also  
 16 indicated by the almost horizontal line in Fig. 4).

### 17 ***Temperature dependence of OH oxidation of pinonic acid***

18 Pinonic acid is known to be an essential precursor of 3-MBTCA (Szmigielski et al.,  
 19 2007; Müller et al. 2010). During this process, we considered the temperature dependence  
 20 of reaction rate and OH concentration ( $C_{OH}$ ).

$$\ln\left(\frac{k_{OH(PA)}}{k_{OH(PA)}^S}\right) = \ln\left(\frac{A \exp\left(-\frac{E_a}{R T}\right)}{A \exp\left(-\frac{E_a}{R T_s}\right)}\right) = -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_s}\right)$$

2  $E_a$  is the enthalpy of reaction between pinonic acid and OH, which is not available.  
 3 Since the reaction between pinonic acid and OH takes place at the aldehyde group, we  
 4 took the empirical temperature dependence ( $E_a/R$ ) of propionaldehyde ( $410 \pm 250$  K)  
 5 (Atkinson et al. 2006) to estimate  $E_a$  of OH oxidation of pinonic acid.  $E_a$  is ( $-3.4 \pm 2.1$  kJ  
 6  $\text{mol}^{-1}$ ), and thus cause insignificant temperature dependence of overall OH oxidation of  
 7 pinonic acid.

8 The natural logarithms of ratios between OH concentration data and OH concentration  
 9 at highest temperature (300 K) were plotted against inverse averaged ambient  
 10 temperature (range 275-300 K) (Fig. S4a), and linear correlation was found ( $R^2 = 0.79$ ).  
 11 The OH data used were taken from simulations with the ECHAM/MESSy Atmospheric  
 12 Chemistry (EMAC) model (Jöckel et al., 2006).  $E_a/R$  is opposite number of linear fit  
 13 slope (13000 K), and  $\Delta E_a/R$  is the deviation of linear fit slope (910 K).  $C_{OH}$  was plotted  
 14 against inverse temperature and fitted with an Arrhenius-type expression of the form  $C_{OH}$   
 15  $= A \exp[-E_a/(R T)]$  (Fig. S4b).

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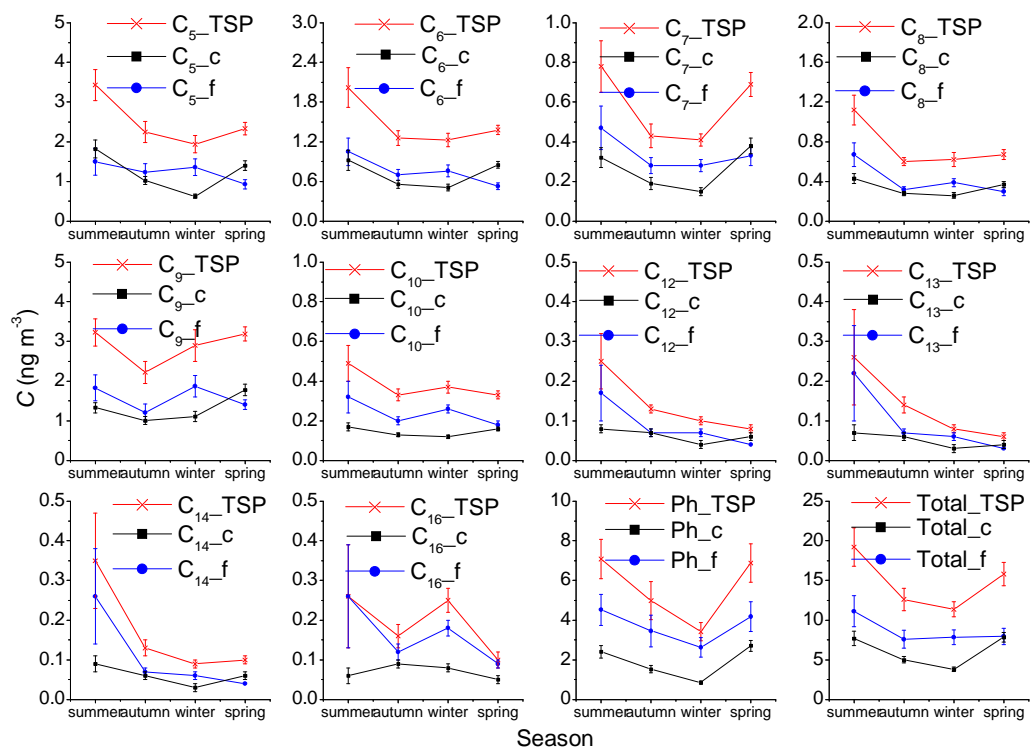
1 Figure caption:

2 Fig. S1 Seasonal variation of dicarboxylic acids mass concentrations in fine, coarse, and  
3 total particulate matter (TSP). The data points are mean values for different seasons  
4 (summer: JJA, autumn: SON, winter: DJF, spring: MAM). The error bars are standard  
5 errors of the mean, and the lines are to guide the eye.

6 Fig. S2 Normalized Arrhenius-type plot of the temperature dependence (275-300 K)  
7 modeled for the emission of pinene ( $C_{PE}$ ) (panel a) and  $C_{PE, 300}$  is concentration of emitted  
8 pinene at 300K. Line is linear fit. Arrhenius-type plot of the temperature dependence  
9 (275-300 K) modeled for the emission of pinene (panel b) assuming EF as  $1.5 \text{ g h m}^{-3}$ .  
10 Line is exponential fit with an Arrhenius-type expression  $C_{PE} = A \exp[-E_A/(R T)]$ .

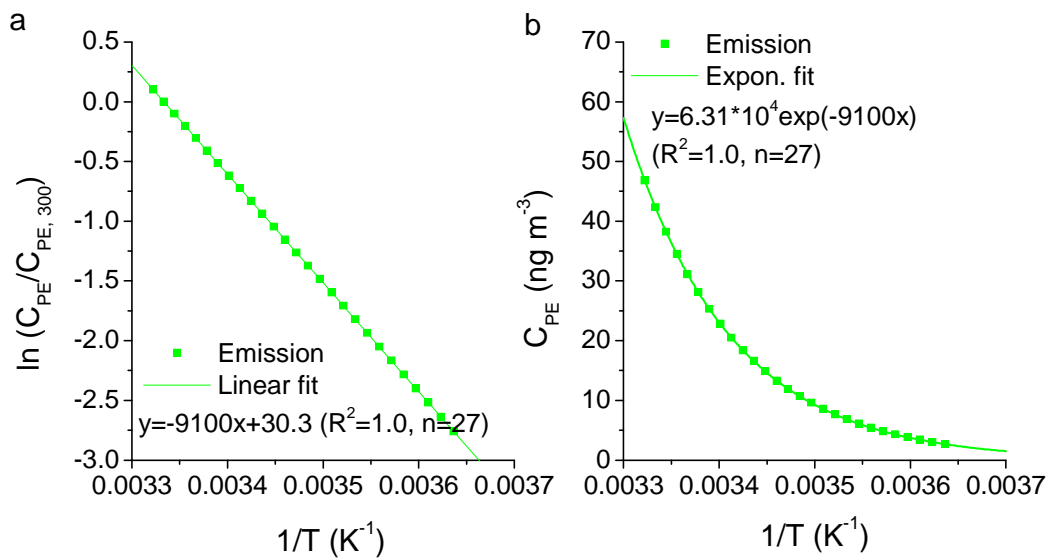
11 Fig. S3 Normalized Arrhenius-type plot of the temperature dependence (275-300 K)  
12 modeled for the gas-particle partitioning of pinonic acid ( $FGP_{PA}$ ) (panel a) and  $FGP_{PA, s}$  is  
13 value at 300 K. Line is linear fit. Arrhenius-type plot of the temperature dependence  
14 (275-300 K) modeled for the gas-particle partitioning of pinonic acid (panel b). Line is  
15 exponential fit with an Arrhenius-type expression  $FGP_{PA} = A \exp[-E_A/(R T)]$ .

16 Fig. S4 Normalized Arrhenius-type plot of the temperature dependence (275-300 K)  
17 modeled for the concentration of OH radicals ( $C_{OH}$ ) (panel a) and  $C_{OH, T_{max}}$  is value at  
18 highest temperature. Line is linear fit. Arrhenius-type plot of the temperature dependence  
19 (275-300 K) modeled for the gas-particle partitioning of pinonic acid (panel b). Line is  
20 exponential fit with an Arrhenius-type expression  $C_{OH} = A \exp[-E_A/(R T)]$ .



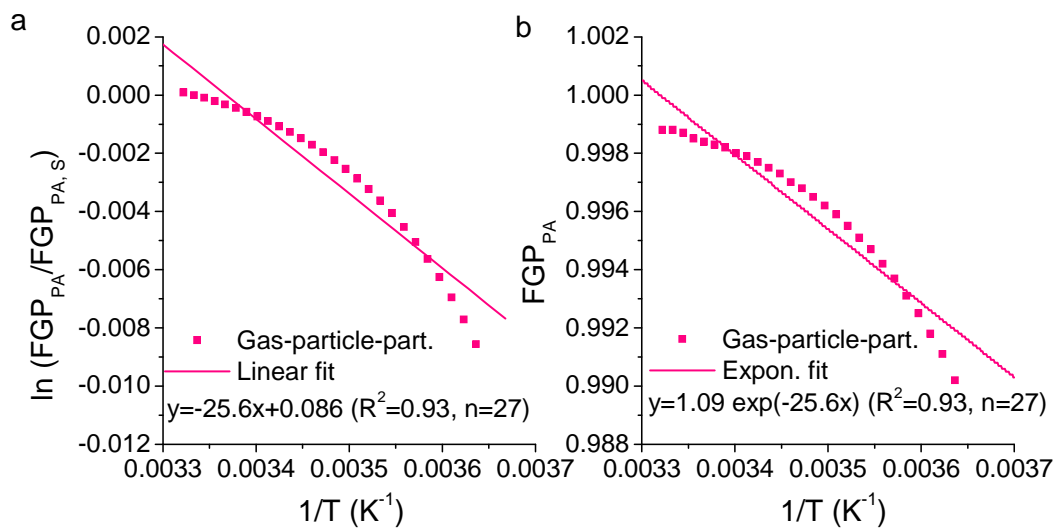
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Fig. S1



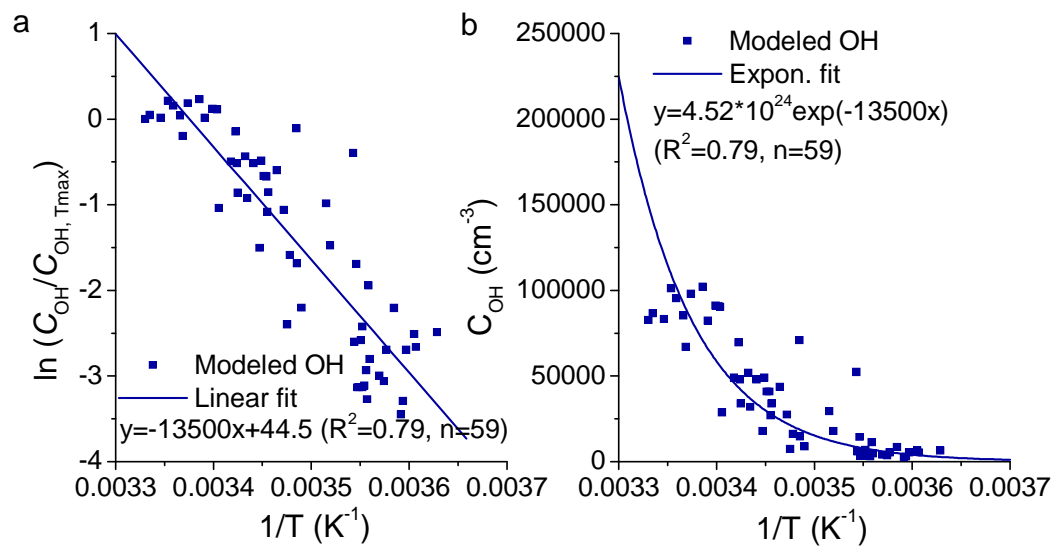
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Fig. S2



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Fig. S3



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Fig. S4

1 Table S1. Overview of air samples in coarse mode. Sample ID (running number); sampling period and time; sampled air volume;  
 2 concentrations of dicarboxylic acids (a), nitrophenols and pinene oxidation products (b). Abbreviations are the same as Table 1.

3  
 4  
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a. Dicarboxylic acid concentrations in coarse particulate matter

Sample ID	Sampling Period	Sampling time d	Sampled air volume m <sup>3</sup>	T K	Ph ng m <sup>-3</sup>	C <sub>5</sub> ng m <sup>3</sup>	C <sub>6</sub> ng m <sup>3</sup>	C <sub>7</sub> ng m <sup>3</sup>	C <sub>8</sub> ng m <sup>3</sup>	C <sub>9</sub> ng m <sup>3</sup>	C <sub>10</sub> ng m <sup>3</sup>	C <sub>12</sub> ng m <sup>3</sup>	C <sub>13</sub> ng m <sup>3</sup>	C <sub>14</sub> ng m <sup>3</sup>	C <sub>16</sub> ng m <sup>3</sup>
MZ31a	01.06.06-06.06.06	4.95	2199	282.3	1.64	1.66	0.78	0.14	0.40	1.55	0.11	0.06	0.06	0.05	BDL <sup>a</sup>
MZ32a	06.06.06-08.06.06	1.99	876	287.0	2.53	1.98	1.05	BDL	0.47	1.65	0.20	0.10	0.05	0.08	0.01
MZ33a	08.06.06-13.06.06	4.99	2186	293.8	2.73	1.77	0.60	0.29	0.34	1.43	0.17	0.06	0.04	0.06	0.03
MZ34a	13.06.06-14.06.06	1.03	445	298.9	5.02	3.61	2.81	0.70	0.64	1.35	0.25	0.08	0.04	0.08	0.03
MZ35a	14.06.06-21.06.06	6.97	2999	294.9	1.35	1.55	0.58	0.23	0.36	1.31	0.14	0.06	0.03	0.06	0.03
MZ36a	21.06.06-22.06.06	0.97	422	294.2	1.57	1.36	1.14	0.30	0.42	0.69	0.09	0.04	BDL	BDL	0.03
MZ39a	22.06.06-27.06.06	4.97	2170	293.9	1.78	1.69	0.59	0.24	0.35	1.40	0.12	0.05	0.04	0.03	0.02
MZ40a	27.06.06-04.07.06	6.96	3045	295.4	1.31	1.48	0.39	0.15	0.35	0.88	0.22	0.19	0.18	0.22	0.24
MZ41a	04.07.06-11.07.06	6.96	3019	297.1	3.82	0.53	0.49	0.17	0.26	0.96	0.14	0.05	0.02	BDL	BDL
MZ42a	11.07.06-14.07.06	3.03	1326	298.2	2.99	2.15	0.84	0.36	0.46	1.29	0.15	0.07	0.04	0.07	0.03
MZ43a	14.07.06-17.07.06	2.97	1310	296.4	2.17	1.89	0.60	0.28	0.45	0.78	0.15	0.10	0.08	0.17	0.13
MZ44a	17.07.06-19.07.06	1.99	873	297.7	4.95	3.56	1.86	0.66	1.03	2.20	0.39	0.25	0.35	0.37	0.24
MZ45a	19.07.06-21.07.06	1.98	872	299.9	4.19	3.25	1.26	0.54	0.60	2.07	0.29	0.12	0.06	0.14	0.05
MZ46a	21.07.06-26.07.06	5.00	2151	300.3	3.26	3.11	1.61	0.83	0.78	1.84	0.25	0.12	0.25	0.22	0.10
MZ47a	26.07.06-02.08.06	6.97	3025	296.9	1.81	1.81	0.68	0.31	0.40	1.98	0.17	0.06	0.04	0.09	0.04
MZ51a	09.08.06-16.08.06	7.01	3044	289.5	0.91	0.86	0.38	0.17	0.28	1.14	0.07	0.03	BDL	0.03	0.01
MZ52a	16.08.06-23.08.06	6.95	3081	291.3	2.31	1.76	1.33	0.56	0.35	1.80	0.15	0.07	0.03	BDL	0.09
MZ53a	23.08.06-30.08.06	6.96	3104	289.3	1.48	0.59	0.46	0.10	0.18	0.92	0.09	0.04	0.02	0.05	BDL
MZ54a	30.08.06-06.09.06	7.04	3132	292.1	2.27	1.55	0.42	0.14	0.48	1.42	0.23	0.13	0.12	0.06	0.15
MZ55a	06.09.06-11.09.06	5.00	2232	292.0	1.44	0.90	0.47	0.16	0.22	0.79	0.07	0.03	0.02	0.03	0.02
MZ59a	11.09.06-18.09.06	6.86	2999	293.6	1.94	1.75	0.52	0.24	0.31	1.08	0.19	0.12	0.12	0.15	0.15
MZ60a	18.09.06-25.09.06	7.02	3033	291.2	1.28	1.25	0.45	0.17	0.33	1.19	0.15	0.08	0.06	0.10	0.08
MZ61a	25.09.06-02.10.06	6.97	3038	290.1	0.69	0.78	0.77	0.12	0.19	0.73	0.09	0.05	0.07	0.06	0.06
MZ62a	02.10.06-09.10.06	6.99	3057	286.9	0.56	0.58	0.23	BDL	0.17	0.49	0.09	0.08	0.08	0.09	0.11
MZ63a	09.10.06-16.10.06	6.98	3088	287.5	3.37	1.55	0.52	0.40	0.29	1.20	0.14	0.05	BDL	BDL	0.05
MZ66a	16.10.06-23.10.06	6.96	3054	286.5	2.23	1.05	0.80	0.35	0.39	1.83	0.15	0.08	BDL	BDL	0.08
MZ67a	23.10.06-30.10.06	6.97	3051	287.8	1.17	0.78	0.75	0.15	0.33	0.89	0.12	0.09	0.16	0.14	0.15
MZ68a	30.10.06-02.11.06	3.02	1332	281.6	0.94	0.68	1.14	0.20	0.33	0.80	0.17	0.12	0.11	0.12	0.13

MZ69a	02.11.06-06.11.06	7.00	3034	280.9	1.71	1.06	0.44	0.26	0.17	0.71	0.11	0.04	BDL	BDL	0.07
MZ70a	06.11.06-16.11.06	6.98	3055	281.1	1.22	0.73	0.31	0.09	0.24	0.64	0.09	0.03	BDL	0.05	0.06
MZ71a	16.11.06-23.11.06	6.98	3063	281.8	1.53	0.87	0.60	0.24	0.26	0.99	0.14	0.05	BDL	0.01	BDL
MZ74a	23.11.06-30.11.06	6.95	2808	282.2	1.09	0.75	0.42	0.09	0.25	1.42	0.14	0.07	0.06	0.08	0.09
MZ75a	30.11.06-07.12.06	6.95	3023	281.4	0.73	0.64	0.61	0.21	0.52	1.93	0.19	0.08	BDL	BDL	0.12
MZ76a	07.12.06-14.12.06	7.00	3058	279.8	0.86	0.79	0.77	0.24	0.32	0.56	0.09	0.04	BDL	BDL	0.05
MZ77a	14.12.06-21.12.06	6.98	3011	277.4	0.87	0.58	0.44	0.14	0.29	1.03	0.15	0.06	BDL	0.02	0.12
MZ80a	21.12.06-28.12.06	6.91	3048	275.6	0.90	0.82	0.37	0.10	0.23	1.42	0.13	0.05	0.03	0.05	BDL
MZ81a	28.12.06-04.01.07	7.03	3005	278.3	0.79	0.87	0.53	0.10	0.33	1.30	0.17	0.07	0.05	BDL	0.19
MZ82a	04.01.07-11.01.07	6.99	3056	281.9	0.55	0.34	0.23	BDL	0.17	0.40	0.08	0.06	0.06	0.06	0.07
MZ83a	11.01.07-18.01.07	6.96	3050	281.2	0.79	0.62	0.38	0.08	0.21	1.08	0.12	0.04	0.03	0.06	0.08
MZ84a	18.01.07-25.01.07	7.01	3100	278.4	0.59	0.27	0.32	0.09	0.10	0.42	0.04	0.02	BDL	0.02	0.04
MZ87a	25.01.07-01.02.07	6.94	3030	277.3	0.79	0.54	0.53	0.21	0.18	1.14	0.11	BDL	0.04	0.03	0.06
MZ88a	01.02.07-08.02.07	6.99	3056	278.0	0.76	0.57	0.57	0.11	0.16	0.83	0.09	BDL	0.02	0.02	0.06
MZ89a	08.02.07-15.02.07	6.96	3040	280.2	1.41	0.62	0.63	0.25	0.23	1.60	0.11	0.04	0.04	0.06	0.06
MZ93a	22.02.07-01.03.07	6.93	3023	281.5	1.27	0.95	0.74	0.23	0.33	1.63	0.13	0.05	0.04	0.05	0.06
MZ94a	01.03.07-08.03.07	7.00	3110	281.5	1.62	0.82	0.71	0.17	0.21	1.11	0.10	0.05	BDL	0.05	0.05
MZ95a	08.03.07-15.03.07	7.00	3025	281.0	1.75	0.94	1.03	0.25	0.25	1.24	0.16	0.06	0.04	0.06	0.11
MZ96a	15.03.07-22.03.07	6.97	3091	279.6	1.03	0.78	0.47	0.17	0.19	1.05	0.13	BDL	0.03	0.05	0.09
MZ97a	22.03.07-29.03.07	6.97	3025	282.0	3.97	1.32	0.75	0.36	0.34	2.23	0.20	0.07	0.05	0.06	0.06
MZ100a	29.03.07-05.04.07	6.94	3038	284.2	4.01	1.44	0.81	0.38	0.38	2.28	0.15	0.05	0.03	0.04	0.05
MZ101a	05.04.07-12.04.07	7.01	3061	284.5	1.99	1.09	0.70	0.32	0.31	1.35	0.17	0.07	0.05	0.07	0.07
MZ102a	12.04.07-19.04.07	6.97	3085	289.7	3.89	1.97	1.10	0.54	0.47	1.67	0.17	0.07	0.04	0.08	0.03
MZ103a	19.04.07-26.04.07	7.05	3078	288.6	3.19	1.64	1.06	0.51	0.39	1.63	0.15	0.07	0.04	0.05	0.03
MZ104a	26.04.07-03.05.07	6.97	3047	290.0	3.74	2.17	1.15	0.65	0.56	2.73	0.26	0.12	0.08	0.11	0.08
MZ107a	03.05.07-10.05.07	7.00	3078	289.4	2.99	1.51	0.81	0.41	0.41	1.77	0.14	0.04	0.04	0.06	0.03
MZ108a	10.05.07-17.05.07	6.93	3075	288.0	1.68	1.24	0.79	0.35	0.38	2.09	0.11	0.05	0.04	0.06	0.03
MZ109a	17.05.07-24.05.07	7.09	3094	292.2	2.60	1.93	0.99	0.49	0.52	2.27	0.16	0.07	0.06	0.06	0.05
MZ112a	24.05.07-31.05.07	6.90	3011	290.6	2.75	1.39	0.67	0.40	0.41	1.75	0.13	BDL	BDL	0.04	0.02

1

## 1 b. Pinene oxidation products and nitrophenols concentrations in coarse particulate matter

2

Sample ID	Sampling Period	Sampling time d	Sampled air volume m <sup>3</sup>	T K	3-MBTCA ng m <sup>-3</sup>	Pinic acid ng m <sup>3</sup>	Pinonic acid ng m <sup>3</sup>	4-Nitrocatechol ng m <sup>3</sup>	2-Nitrophenol ng m <sup>3</sup>	4-Nitrophenol ng m <sup>3</sup>
MZ31a	01.06.06-06.06.06	4.95	2199	282.3	0.50	1.10	0.27	0.20	0.44	0.67
MZ32a	06.06.06-08.06.06	1.99	876	287.0	0.95	0.17	BDL	0.56	2.32	2.38
MZ33a	08.06.06-13.06.06	4.99	2186	293.8	2.00	1.33	1.90	0.84	0.24	1.44
MZ34a	13.06.06-14.06.06	1.03	445	298.9	2.34	2.05	1.29	2.42	BDL	3.83
MZ35a	14.06.06-21.06.06	6.97	2999	294.9	1.25	1.13	0.20	0.23	BDL	0.35
MZ36a	21.06.06-22.06.06	0.97	422	294.2	0.76	0.45	0.28	1.43	BDL	0.81
MZ39a	22.06.06-27.06.06	4.97	2170	293.9	1.11	0.97	0.55	0.25	BDL	0.64
MZ40a	27.06.06-04.07.06	6.96	3045	295.4	1.76	2.14	BDL	0.06	BDL	0.27
MZ41a	04.07.06-11.07.06	6.96	3019	297.1	11.16	1.65	0.43	12.74	BDL	1.14
MZ42a	11.07.06-14.07.06	3.03	1326	298.2	2.60	1.63	0.89	0.78	BDL	1.24
MZ43a	14.07.06-17.07.06	2.97	1310	296.4	1.61	1.46	1.56	BDL	BDL	0.07
MZ44a	17.07.06-19.07.06	1.99	873	297.7	3.72	3.56	4.51	BDL	BDL	0.15
MZ45a	19.07.06-21.07.06	1.98	872	299.9	2.29	1.74	2.86	0.96	BDL	2.92
MZ46a	21.07.06-26.07.06	5.00	2151	300.3	2.51	2.62	1.40	BDL	BDL	BDL
MZ47a	26.07.06-02.08.06	6.97	3025	296.9	1.59	1.43	BDL	0.01	BDL	0.94
MZ51a	09.08.06-16.08.06	7.01	3044	289.5	0.45	0.45	0.27	0.13	BDL	0.60
MZ52a	16.08.06-23.08.06	6.95	3081	291.3	1.89	0.92	0.20	0.06	BDL	0.56
MZ53a	23.08.06-30.08.06	6.96	3104	289.3	1.88	0.64	0.91	0.78	0.82	0.27
MZ54a	30.08.06-06.09.06	7.04	3132	292.1	0.99	0.35	0.73	BDL	BDL	0.25
MZ55a	06.09.06-11.09.06	5.00	2232	292.0	1.16	0.84	0.35	0.20	BDL	1.78
MZ59a	11.09.06-18.09.06	6.86	2999	293.6	2.67	2.77	BDL	0.10	0.49	0.53
MZ60a	18.09.06-25.09.06	7.02	3033	291.2	2.04	2.32	BDL	BDL	0.43	0.56
MZ61a	25.09.06-02.10.06	6.97	3038	290.1	0.77	1.37	BDL	BDL	0.23	0.35
MZ62a	02.10.06-09.10.06	6.99	3057	286.9	0.22	0.55	BDL	BDL	BDL	0.54
MZ63a	09.10.06-16.10.06	6.98	3088	287.5	2.70	0.90	0.30	0.10	1.47	1.50
MZ66a	16.10.06-23.10.06	6.96	3054	286.5	1.07	0.75	0.26	BDL	0.52	1.54
MZ67a	23.10.06-30.10.06	6.97	3051	287.8	0.39	0.76	0.22	BDL	BDL	0.58
MZ68a	30.10.06-02.11.06	3.02	1332	281.6	0.15	0.44	BDL	BDL	BDL	0.72
MZ69a	02.11.06-09.11.06	7.00	3034	280.9	0.31	0.29	BDL	BDL	0.89	1.10
MZ70a	09.11.06-16.11.06	6.98	3055	281.1	0.15	0.34	0.80	BDL	BDL	BDL
MZ71a	16.11.06-23.11.06	6.98	3063	281.8	0.21	0.15	BDL	BDL	1.13	2.67
MZ74a	23.11.06-30.11.06	6.95	2808	282.2	0.17	0.28	0.54	BDL	0.41	1.20

MZ75a	30.11.06-07.12.06	6.95	3023	281.4	0.18	0.15	BDL	BDL	0.63	1.74
MZ76a	07.12.06-14.12.06	7.00	3058	279.8	BDL	0.30	0.78	BDL	BDL	0.05
MZ77a	14.12.06-21.12.06	6.98	3011	277.4	0.07	0.18	BDL	0.09	0.79	2.94
MZ80a	21.12.06-28.12.06	6.91	3048	275.6	0.06	0.49	BDL	0.55	1.50	6.97
MZ81a	28.12.06-04.01.07	7.03	3005	278.3	0.16	0.06	BDL	0.09	0.77	2.30
MZ82a	04.01.07-11.01.07	6.99	3056	281.9	BDL	0.03	BDL	BDL	BDL	0.50
MZ83a	11.01.07-18.01.07	6.96	3050	281.2	0.14	0.10	BDL	BDL	BDL	0.82
MZ84a	18.01.07-25.01.07	7.01	3100	278.4	BDL	0.02	BDL	BDL	BDL	1.12
MZ87a	25.01.07-01.02.07	6.94	3030	277.3	BDL	0.10	BDL	BDL	BDL	1.39
MZ88a	01.02.07-08.02.07	6.99	3056	278.0	0.04	0.15	BDL	BDL	BDL	1.18
MZ89a	08.02.07-15.02.07	6.96	3040	280.2	BDL	0.17	BDL	BDL	BDL	1.28
MZ93a	22.02.07-01.03.07	6.93	3023	281.5	0.23	0.31	0.30	BDL	BDL	1.31
MZ94a	01.03.07-08.03.07	7.00	3110	281.5	0.16	0.28	0.54	BDL	BDL	1.74
MZ95a	08.03.07-15.03.07	7.00	3025	281.0	0.51	0.29	BDL	BDL	BDL	2.35
MZ96a	15.03.07-22.03.07	6.97	3091	279.6	0.22	0.10	BDL	BDL	BDL	1.55
MZ97a	22.03.07-29.03.07	6.97	3025	282.0	0.69	0.38	1.24	BDL	BDL	2.43
MZ100a	29.03.07-05.04.07	6.94	3038	284.2	0.87	0.31	1.24	BDL	BDL	1.81
MZ101a	05.04.07-12.04.07	7.01	3061	284.5	0.45	0.25	0.53	BDL	BDL	1.89
MZ102a	12.04.07-19.04.07	6.97	3085	289.7	2.54	0.92	3.97	BDL	BDL	3.20
MZ103a	19.04.07-26.04.07	7.05	3078	288.6	1.79	1.03	1.75	BDL	0.20	1.60
MZ104a	26.04.07-03.05.07	6.97	3047	290.0	2.87	1.01	2.28	BDL	BDL	3.07
MZ107a	03.05.07-10.05.07	7.00	3078	289.4	1.04	0.92	1.73	BDL	BDL	0.78
MZ108a	10.05.07-17.05.07	6.93	3075	288.0	0.68	0.54	0.16	BDL	BDL	0.49
MZ109a	17.05.07-24.05.07	7.09	3094	292.2	2.45	0.59	0.22	BDL	0.15	0.58
MZ112a	24.05.07-31.05.07	6.90	3011	290.6	6.05	0.58	0.44	BDL	0.21	0.91

1 <sup>a</sup> BDL denotes below detection limit (limit of quantification listed in Table 1).

2

1 Table S2. Overview of air samples in fine mode. Sample ID (running number); sampling period and time; sampled air volume;  
 2 concentrations of dicarboxylic acids (a), nitrophenols and pinene oxidation products (b). Abbreviations are the same as Table 1.

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a. Dicarboxylic acid concentrations in fine particulate matter

Sample ID	Sampling Period	Sampling time d	Sampled air volume m <sup>3</sup>	T K	Ph ng m <sup>-3</sup>	C <sub>5</sub> ng m <sup>3</sup>	C <sub>6</sub> ng m <sup>3</sup>	C <sub>7</sub> ng m <sup>3</sup>	C <sub>8</sub> ng m <sup>3</sup>	C <sub>9</sub> ng m <sup>3</sup>	C <sub>10</sub> ng m <sup>3</sup>	C <sub>12</sub> ng m <sup>3</sup>	C <sub>13</sub> ng m <sup>3</sup>	C <sub>14</sub> ng m <sup>3</sup>	C <sub>16</sub> ng m <sup>3</sup>
MZ31b	01.06.06-06.06.06	4.95	2012	282.3	1.45	0.93	0.71	0.16	0.36	1.76	0.17	0.08	0.05	0.06	0.01
MZ32b	06.06.06-08.06.06	1.99	801	287.0	6.95	2.30	2.19	0.53	0.92	4.64	0.52	0.20	0.12	0.39	0.02
MZ33b	08.06.06-13.06.06	4.99	1996	293.8	3.53	0.47	0.34	0.24	0.26	1.15	0.16	0.03	0.02	0.04	BDL <sup>a</sup>
MZ34b	13.06.06-14.06.06	1.03	406	298.9	13.38	1.94	1.88	0.73	1.65	3.68	0.61	0.21	0.09	0.20	0.07
MZ35b	14.06.06-21.06.06	6.97	2736	294.9	1.83	0.42	0.22	0.12	0.14	0.58	0.06	0.02	BDL	BDL	BDL
MZ36b	21.06.06-22.06.06	0.97	385	294.2	9.40	6.15	2.71	0.88	0.85	2.56	0.24	0.17	0.06	0.19	0.04
MZ39b	22.06.06-27.06.06	4.97	1984	293.9	2.11	0.54	0.34	0.05	0.25	0.63	0.07	0.03	0.01	0.01	0.01
MZ40b	27.06.06-04.07.06	6.96	2782	295.4	2.42	0.16	0.24	0.10	0.38	0.52	0.08	0.02	0.01	0.02	BDL
MZ41b	04.07.06-11.07.06	6.96	2756	297.1	3.88	3.34	1.19	0.48	0.87	3.57	0.29	0.14	0.09	0.17	0.07
MZ42b	11.07.06-14.07.06	3.03	1211	298.2	4.67	0.65	0.55	0.23	0.52	0.78	0.14	0.04	0.03	0.05	0.02
MZ43b	14.07.06-17.07.06	2.97	1196	296.4	6.72	2.02	2.53	1.77	1.87	3.47	1.31	1.24	2.04	2.05	2.05
MZ44b	17.07.06-19.07.06	1.99	796	297.7	8.15	2.38	2.53	1.34	1.41	3.82	0.88	0.40	0.50	0.69	0.82
MZ45b	19.07.06-21.07.06	1.98	798	299.9	6.35	0.85	0.77	0.41	1.00	2.00	0.52	0.09	0.07	0.03	0.05
MZ46b	21.07.06-26.07.06	5.00	1960	300.3	3.54	1.23	0.80	0.26	0.42	0.75	0.22	0.08	BDL	0.09	0.13
MZ47b	26.07.06-02.08.06	6.97	2761	296.9	2.90	1.41	0.54	0.47	0.45	0.34	0.26	0.16	0.18	0.16	0.09
MZ51b	09.08.06-16.08.06	7.01	2790	289.5	1.36	0.57	0.20	0.09	0.17	0.62	0.06	0.02	0.02	0.02	0.02
MZ52b	16.08.06-23.08.06	6.95	2776	291.3	1.61	0.45	0.29	BDL	0.11	0.38	0.06	0.02	BDL	BDL	BDL
MZ53b	23.08.06-30.08.06	6.96	2806	289.3	1.32	1.27	0.86	0.12	0.37	1.64	0.10	0.05	0.03	0.05	BDL
MZ54b	30.08.06-06.09.06	7.04	2838	292.1	2.89	0.44	0.59	BDL	0.37	1.05	0.21	0.09	0.08	0.12	0.12
MZ55b	06.09.06-11.09.06	5.00	2030	292.0	1.62	0.30	0.17	0.12	0.16	0.69	0.08	0.02	0.01	0.01	0.01
MZ59b	11.09.06-18.09.06	6.86	2717	293.6	7.46	2.04	1.17	0.26	0.26	0.73	0.09	0.03	0.01	0.03	BDL
MZ60b	18.09.06-25.09.06	7.02	2740	291.2	3.22	0.63	0.33	0.32	0.24	1.21	0.19	0.04	0.03	0.04	BDL
MZ61b	25.09.06-02.10.06	6.97	2737	290.1	2.13	1.28	0.82	0.17	0.19	0.73	0.10	BDL	0.03	0.03	0.02
MZ62b	02.10.06-09.10.06	6.99	2767	286.9	1.19	0.83	0.41	0.15	0.29	0.18	0.12	0.10	0.11	0.10	0.20
MZ63b	09.10.06-16.10.06	6.98	2798	287.5	12.46	3.46	0.90	0.58	0.34	1.36	0.17	0.03	BDL	0.06	BDL
MZ66b	16.10.06-23.10.06	6.96	2767	286.5	2.92	0.65	0.64	0.22	0.26	1.28	0.16	0.03	BDL	0.02	BDL
MZ67b	23.10.06-30.10.06	6.97	2762	287.8	1.78	0.83	0.63	0.26	0.34	0.22	0.23	0.12	0.15	0.09	0.17
MZ68b	30.10.06-02.11.06	3.02	1209	281.6	1.42	1.14	0.81	BDL	0.38	1.65	0.27	BDL	0.07	0.14	0.16



MZ69b	02.11.06-09.11.06	7.00	2745	280.9	3.80	1.63	0.84	0.29	0.31	1.15	0.21	0.05	0.04	0.02	BDL
MZ70b	09.11.06-16.11.06	6.98	2765	281.1	1.67	0.93	0.51	0.17	0.42	1.42	0.27	0.14	0.19	0.20	0.16
MZ71b	16.11.06-23.11.06	6.98	2764	281.8	1.65	0.91	1.19	0.25	0.29	1.66	0.30	0.06	0.03	0.03	0.14
MZ74b	23.11.06-30.11.06	6.95	2478	282.2	4.07	2.12	0.79	0.58	0.56	3.63	0.39	0.09	0.08	0.10	0.11
MZ75b	30.11.06-07.12.06	6.95	2735	281.4	1.94	1.18	0.77	0.23	0.44	2.54	0.37	0.05	0.03	0.04	0.15
MZ76b	07.12.06-14.12.06	7.00	2771	279.8	2.08	1.25	0.83	BDL	0.34	1.15	0.20	0.07	0.12	0.10	0.17
MZ77b	14.12.06-21.12.06	6.98	2712	277.4	2.88	1.51	1.12	0.39	0.53	2.76	0.33	0.08	0.06	0.06	0.16
MZ80b	21.12.06-28.12.06	6.91	2762	275.6	3.86	2.72	0.65	0.31	0.53	3.06	0.28	0.09	0.07	0.10	0.02
MZ81b	28.12.06-04.01.07	7.03	2707	278.3	3.06	2.01	1.48	0.42	0.78	3.61	0.43	0.10	0.07	0.04	0.24
MZ82b	04.01.07-11.01.07	6.99	2767	281.9	0.69	0.55	0.53	BDL	0.27	0.12	0.13	0.09	0.11	0.09	0.21
MZ83b	11.01.07-18.01.07	6.96	2757	281.2	2.45	1.16	0.57	0.25	0.31	1.87	0.23	0.06	0.03	0.07	0.31
MZ84b	18.01.07-25.01.07	7.01	2809	278.4	1.40	0.83	0.50	0.16	0.22	1.50	0.17	0.07	0.05	0.05	0.15
MZ87b	25.01.07-01.02.07	6.94	2749	277.3	1.99	0.99	0.58	0.13	0.30	1.96	0.23	0.03	0.03	0.05	0.23
MZ88b	01.02.07-08.02.07	6.99	2769	278.0	3.60	1.49	0.82	0.38	0.32	2.06	0.30	BDL	0.04	0.06	0.30
MZ89b	08.02.07-15.02.07	6.96	2757	280.2	0.82	0.35	0.33	0.15	0.22	1.08	0.13	BDL	0.02	0.04	0.12
MZ90b	15.02.07-22.02.07	7.02	2702	279.0	7.65	2.79	1.18	0.45	0.47	0.65	0.31	0.07	0.06	0.06	0.12
MZ93b	22.02.07-01.03.07	6.93	2744	281.5	1.71	0.80	0.46	0.24	0.32	2.00	0.25	0.07	0.04	0.08	0.20
MZ94b	01.03.07-08.03.07	7.00	2823	281.5	1.64	0.84	0.45	0.26	0.28	1.81	0.18	0.06	0.03	0.05	0.14
MZ95b	08.03.07-15.03.07	7.00	2722	281.0	3.97	1.12	0.79	0.31	0.46	1.87	0.21	0.05	0.04	0.04	0.11
MZ96b	15.03.07-22.03.07	6.97	2810	279.6	0.98	0.64	0.40	0.20	0.21	1.01	0.14	0.02	0.03	0.03	0.15
MZ97b	22.03.07-29.03.07	6.97	2734	282.0	10.57	2.12	0.90	0.87	0.69	1.81	0.28	0.08	0.05	0.06	0.10
MZ100b	29.03.07-05.04.07	6.94	2748	284.2	7.21	1.49	0.80	0.48	0.37	1.37	0.20	0.04	0.02	0.05	0.07
MZ101b	05.04.07-12.04.07	7.01	2776	284.5	2.86	0.79	0.51	0.30	0.31	1.56	0.21	BDL	0.03	0.04	0.07
MZ102b	12.04.07-19.04.07	6.97	2799	289.7	4.40	0.74	0.57	0.30	0.39	1.66	0.23	BDL	0.03	0.06	BDL
MZ103b	19.04.07-26.04.07	7.05	2793	288.6	4.18	0.84	0.38	0.21	0.20	1.39	0.17	BDL	BDL	0.03	BDL
MZ104b	26.04.07-03.05.07	6.97	2761	290.0	5.62	0.95	0.45	0.33	0.24	2.07	0.21	0.04	0.02	0.03	BDL
MZ107b	03.05.07-10.05.07	7.00	2796	289.4	2.08	0.52	0.39	0.20	0.17	0.79	0.09	0.03	0.02	BDL	BDL
MZ108b	10.05.07-17.05.07	6.93	2793	288.0	1.21	0.71	0.45	0.20	0.16	0.83	0.09	0.03	BDL	0.03	0.02
MZ109b	17.05.07-24.05.07	7.09	2808	292.2	6.74	0.57	0.29	BDL	0.18	0.93	0.13	BDL	BDL	BDL	BDL
MZ112b	24.05.07-31.05.07	6.90	2732	290.6	2.83	0.76	0.50	0.28	0.20	1.24	0.14	0.03	BDL	0.04	BDL

1

1 b. Pinene oxidation products and nitrophenols concentrations in fine particulate matter

2

Sample ID	Sampling Period	Sampling time d	Sampled air volume m <sup>3</sup>	T K	3-MBTCA ng m <sup>-3</sup>	Pinic acid ng m <sup>3</sup>	Pinonic acid ng m <sup>3</sup>	4-Nitrocatechol ng m <sup>3</sup>	2-Nitrophenol ng m <sup>3</sup>	4-Nitrophenol ng m <sup>3</sup>
MZ31b	01.06.06-06.06.06	4.95	2012	282.3	2.68	0.48	0.82	5.02	1.24	0.93
MZ32b	06.06.06-08.06.06	1.99	801	287.0	8.98	7.20	3.98	16.81	5.22	2.76
MZ33b	08.06.06-13.06.06	4.99	1996	293.8	11.94	1.81	0.53	10.99	1.47	1.57
MZ34b	13.06.06-14.06.06	1.03	406	298.9	22.27	7.28	1.62	26.30	8.51	5.23
MZ35b	14.06.06-21.06.06	6.97	2736	294.9	4.97	0.83	0.21	3.49	1.00	0.68
MZ36b	21.06.06-22.06.06	0.97	385	294.2	6.07	2.62	3.65	2.14	2.26	2.35
MZ39b	22.06.06-27.06.06	4.97	1984	293.9	7.01	0.59	0.59	4.35	0.81	0.85
MZ40b	27.06.06-04.07.06	6.96	2782	295.4	10.17	1.02	0.72	4.64	BDL	0.44
MZ41b	04.07.06-11.07.06	6.96	2756	297.1	3.38	2.45	0.52	1.17	1.54	2.49
MZ42b	11.07.06-14.07.06	3.03	1211	298.2	14.05	1.07	1.03	8.82	1.34	1.74
MZ43b	14.07.06-17.07.06	2.97	1196	296.4	16.85	8.25	1.65	BDL	BDL	BDL
MZ44b	17.07.06-19.07.06	1.99	796	297.7	26.00	8.61	0.88	BDL	BDL	BDL
MZ45b	19.07.06-21.07.06	1.98	798	299.9	15.36	1.47	0.36	17.81	3.21	2.82
MZ46b	21.07.06-26.07.06	5.00	1960	300.3	15.16	5.11	BDL	1.03	BDL	BDL
MZ47b	26.07.06-02.08.06	6.97	2761	296.9	9.17	9.05	1.33	1.73	0.76	1.08
MZ51b	09.08.06-16.08.06	7.01	2790	289.5	2.31	0.61	BDL	5.36	0.57	0.95
MZ52b	16.08.06-23.08.06	6.95	2776	291.3	4.59	0.04	BDL	0.21	1.06	0.76
MZ53b	23.08.06-30.08.06	6.96	2806	289.3	0.55	1.33	0.83	0.17	0.77	0.71
MZ54b	30.08.06-06.09.06	7.04	2838	292.1	7.57	1.49	BDL	0.45	1.37	0.65
MZ55b	06.09.06-11.09.06	5.00	2030	292.0	5.17	1.21	BDL	11.33	1.03	2.28
MZ59b	11.09.06-18.09.06	6.86	2717	293.6	14.38	0.27	0.22	1.66	2.08	1.34
MZ60b	18.09.06-25.09.06	7.02	2740	291.2	12.00	3.01	1.25	2.04	1.78	1.97
MZ61b	25.09.06-02.10.06	6.97	2737	290.1	4.75	2.31	BDL	1.14	0.85	0.93
MZ62b	02.10.06-09.10.06	6.99	2767	286.9	1.32	1.79	BDL	1.30	1.29	1.64
MZ63b	09.10.06-16.10.06	6.98	2798	287.5	12.42	0.07	1.23	3.36	4.36	4.50
MZ66b	16.10.06-23.10.06	6.96	2767	286.5	5.31	BDL	0.38	1.84	2.83	2.59
MZ67b	23.10.06-30.10.06	6.97	2762	287.8	1.70	1.82	0.58	1.17	1.26	1.63
MZ68b	30.10.06-02.11.06	3.02	1209	281.6	0.66	1.40	BDL	2.08	1.30	2.54
MZ69b	02.11.06-09.11.06	7.00	2745	280.9	1.67	0.46	0.38	2.59	2.38	2.34
MZ70b	09.11.06-16.11.06	6.98	2765	281.1	0.98	1.13	0.16	1.98	BDL	0.04
MZ71b	16.11.06-23.11.06	6.98	2764	281.8	0.62	0.35	BDL	3.07	3.10	7.94
MZ74b	23.11.06-30.11.06	6.95	2478	282.2	1.12	2.60	0.89	2.71	1.34	2.31

MZ75b	30.11.06-07.12.06	6.95	2735	281.4	1.16	0.40	0.49	2.15	2.20	4.82
MZ76b	07.12.06-14.12.06	7.00	2771	279.8	0.24	0.56	0.76	3.17	0.75	0.47
MZ77b	14.12.06-21.12.06	6.98	2712	277.4	0.46	0.05	0.17	8.09	2.73	6.76
MZ80b	21.12.06-28.12.06	6.91	2762	275.6	0.31	0.20	-	-	0.72	2.15
MZ81b	28.12.06-04.01.07	7.03	2707	278.3	0.87	BDL	BDL	8.08	4.56	10.22
MZ82b	04.01.07-11.01.07	6.99	2767	281.9	0.21	0.69	0.58	0.61	0.43	1.12
MZ83b	11.01.07-18.01.07	6.96	2757	281.2	0.78	0.37	0.21	2.79	0.80	1.58
MZ84b	18.01.07-25.01.07	7.01	2809	278.4	0.34	0.23	0.27	2.53	0.79	3.43
MZ87b	25.01.07-01.02.07	6.94	2749	277.3	0.15	0.15	BDL	3.62	0.63	3.10
MZ88b	01.02.07-08.02.07	6.99	2769	278.0	0.25	0.36	0.26	9.47	1.19	5.73
MZ89b	08.02.07-15.02.07	6.96	2757	280.2	0.13	0.16	0.21	1.36	0.48	1.78
MZ90b	15.02.07-22.02.07	7.02	2702	279.0	1.30	0.43	0.16	4.15	2.08	6.33
MZ93b	22.02.07-01.03.07	6.93	2744	281.5	0.77	0.41	BDL	1.82	0.66	2.46
MZ94b	01.03.07-08.03.07	7.00	2823	281.5	1.01	0.37	BDL	2.85	0.86	2.61
MZ95b	08.03.07-15.03.07	7.00	2722	281.0	3.30	1.44	0.19	12.29	2.17	5.26
MZ96b	15.03.07-22.03.07	6.97	2810	279.6	0.60	0.17	BDL	0.88	0.39	3.02
MZ97b	22.03.07-29.03.07	6.97	2734	282.0	5.02	0.54	0.21	6.31	2.91	6.70
MZ100b	29.03.07-05.04.07	6.94	2748	284.2	5.39	0.60	0.29	4.76	2.30	4.57
MZ101b	05.04.07-12.04.07	7.01	2776	284.5	3.17	0.80	BDL	5.47	1.44	2.62
MZ102b	12.04.07-19.04.07	6.97	2799	289.7	10.57	0.48	BDL	2.29	1.35	3.09
MZ103b	19.04.07-26.04.07	7.05	2793	288.6	9.75	0.31	BDL	1.95	1.64	2.03
MZ104b	26.04.07-03.05.07	6.97	2761	290.0	14.34	0.49	BDL	4.27	2.13	2.12
MZ107b	03.05.07-10.05.07	7.00	2796	289.4	5.12	0.02	BDL	BDL	0.64	0.55
MZ108b	10.05.07-17.05.07	6.93	2793	288.0	1.89	0.14	BDL	BDL	0.56	0.85
MZ109b	17.05.07-24.05.07	7.09	2808	292.2	16.87	0.41	0.18	2.09	1.39	1.12
MZ112b	24.05.07-31.05.07	6.90	2732	290.6	6.48	0.08	BDL	0.22	0.59	1.01

1 <sup>a</sup> BDL denotes below detection limit (limit of quantification listed in Table 1).

2

1 Table S3. Correlation coefficient ( $R^2$ ) between investigated compounds in samples of coarse particulate matter (n=20-57).

2 Abbreviations are the same as Table 1.

3

	Ph	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>5-7</sub>	C <sub>8-10</sub>	C <sub>12-16</sub>	Di_Total <sup>a</sup>
Ph	1.00														
C <sub>5</sub>	0.63	1.00													
C <sub>6</sub>	0.45	0.60	1.00												
C <sub>7</sub>	0.62	0.62	0.60	1.00											
C <sub>8</sub>	0.49	0.75	0.54	0.56	1.00										
C <sub>9</sub>	0.38	0.31	0.19	0.41	0.40	1.00									
C <sub>10</sub>	0.48	0.61	0.39	0.39	0.71	0.36	1.00								
C <sub>12</sub>	0.16	0.35	0.16	0.12	0.49	0.09	0.67	1.00							
C <sub>13</sub>	0.08	0.26	0.13	0.11	0.39	0.04	0.45	0.68	1.00						
C <sub>14</sub>	0.12	0.34	0.14	0.12	0.40	0.05	0.47	0.66	0.83	1.00					
C <sub>16</sub>	0.01	0.01	0.00	0.00	0.07	0.00	0.23	0.46	0.44	0.33	1.00				
C <sub>5-7</sub>	0.65				0.75	0.32	0.58	0.29	0.22	0.28	0.00	1.00			
C <sub>8-10</sub>	0.49	0.49	0.31	0.53				0.22	0.13	0.14	0.01	0.55	1.00		
C <sub>12-16</sub>	0.07	0.24	0.11	0.09	0.38	0.04	0.53					0.23	0.17	1.00	
Di_Total	0.66											0.93	0.78	0.31	1.00
3-MBTCA	0.53	0.64	0.26	0.51	0.44	0.17	0.36	0.30	0.21	0.28	0.01	0.55	0.28	0.20	0.55
Pinic acid	0.28	0.51	0.21	0.26	0.39	0.04	0.37	0.42	0.44	0.53	0.08	0.43	0.13	0.43	0.40
Pinonic acid	0.55	0.44	0.26	0.42	0.45	0.20	0.39	0.21	0.18	0.27	0.01	0.43	0.31	0.18	0.46
Sum	0.57	0.72	0.34	0.52	0.58	0.19	0.52	0.42	0.35	0.47	0.04	0.65	0.35	0.37	0.64
4-Nitrocatechol	0.20	0.03	0.00	0.00	0.00	0.05	0.00	0.02	0.02	0.05	0.05	0.00	0.03	0.05	0.02
2-Nitrophenol	0.00	0.00	0.01	0.22	0.01	0.02	0.01	0.02	0.07	0.04	0.05	0.01	0.01	0.05	0.02
4-Nitrophenol	0.05	0.01	0.05	0.03	0.00	0.06	0.04	0.01	0.06	0.03	0.06	0.03	0.05	0.04	0.03
Nitrophenols	0.02	0.00	0.01	0.00	0.00	0.04	0.02	0.00	0.08	0.06	0.06	0.01	0.05	0.03	0.02

4 To be continued

1 Continued

	3-MBTCA	Pinic acid	Pinonic acid	Sum <sup>b</sup>	4-Nitrocatechol	2-Nitrophenol	4-Nitrophenol	Nitrophenols
Ph								
C <sub>5</sub>								
C <sub>6</sub>								
C <sub>7</sub>								
C <sub>8</sub>								
C <sub>9</sub>								
C <sub>10</sub>								
C <sub>12</sub>								
C <sub>13</sub>								
C <sub>14</sub>								
C <sub>16</sub>								
C <sub>5-7</sub>								
C <sub>8-10</sub>								
C <sub>12-16</sub>								
Di_Total								
3-MBTCA	1.00							
Pinic acid	0.62	1.00						
Pinonic acid	0.38	0.23	1.00					
Sum				1.00				
4-Nitrocatechol	0.06	0.05	0.01	0.00	1.00			
2-Nitrophenol	0.02	0.10	0.14	0.09	0.01	1.00		
4-Nitrophenol	0.01	0.03	0.02	0.00	0.00	0.27	1.00	
Nitrophenols	0.02	0.04	0.00	0.00	0.00			1.00

2 <sup>a</sup> the total of aliphatic dicarboxylic acids and phthalic acids;

3 <sup>b</sup> the sum of pinene oxidation products (3-MBTCA, pinic acid and pinonic acid).

1 Table S4. Correlation coefficient ( $R^2$ ) between investigated compounds in samples of coarse particulate matter (n=46-58).

2 Abbreviations are the same as Table 1.

3

	Ph	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>5-7</sub>	C <sub>8-10</sub>	C <sub>12-16</sub>	Di_Total <sup>a</sup>
Ph	1.00														
C <sub>5</sub>	0.40	1.00													
C <sub>6</sub>	0.35	0.56	1.00												
C <sub>7</sub>	0.41	0.35	0.63	1.00											
C <sub>8</sub>	0.36	0.25	0.68	0.70	1.00										
C <sub>9</sub>	0.17	0.28	0.49	0.37	0.52	1.00									
C <sub>10</sub>	0.19	0.13	0.57	0.72	0.82	0.49	1.00								
C <sub>12</sub>	0.08	0.08	0.41	0.64	0.59	0.19	0.75	1.00							
C <sub>13</sub>	0.03	0.03	0.27	0.52	0.44	0.11	0.66	0.95	1.00						
C <sub>14</sub>	0.06	0.06	0.38	0.60	0.53	0.18	0.73	0.97	0.97	1.00					
C <sub>16</sub>	0.01	0.02	0.27	0.51	0.41	0.12	0.68	0.86	0.91	0.89	1.00				
C <sub>5-7</sub>	0.47				0.52	0.43	0.38	0.27	0.16	0.24	0.15	1.00			
C <sub>8-10</sub>	0.24	0.29	0.62	0.55				0.37	0.24	0.34	0.26	0.52	1.00		
C <sub>12-16</sub>	0.04	0.04	0.33	0.57	0.49	0.15	0.72					0.20	0.30	1.00	
Di_Total	0.34											0.81	0.83	0.51	1.00
3-MBTCA	0.41	0.01	0.12	0.22	0.26	0.03	0.18	0.13	0.09	0.13	0.05	0.07	0.09	0.10	0.11
Pinic acid	0.13	0.08	0.37	0.41	0.51	0.16	0.45	0.41	0.30	0.39	0.24	0.23	0.29	0.33	0.38
Pinonic acid	0.12	0.33	0.22	0.12	0.17	0.22	0.09	0.08	0.03	0.07	0.01	0.31	0.22	0.04	0.26
Sum	0.41	0.05	0.25	0.35	0.42	0.09	0.31	0.24	0.17	0.24	0.10	0.18	0.21	0.18	0.26
4-Nitrocatechol	0.02	0.04	0.01	0.02	0.06	0.11	0.06	0.03	0.01	0.02	0.01	0.03	0.11	0.00	0.07
2-Nitrophenol	0.52	0.14	0.44	0.36	0.59	0.32	0.51	0.28	0.02	0.17	0.01	0.27	0.43	0.09	0.41
4-Nitrophenol	0.13	0.10	0.20	0.27	0.16	0.22	0.32	0.02	0.00	0.00	0.15	0.17	0.25	0.04	0.24
Nitrophenols	0.22	0.11	0.11	0.04	0.07	0.19	0.04	0.01	0.04	0.03	0.02	0.13	0.17	0.02	0.09

4 To be continued

1 Continued

	3-MBTCA	Pinic acid	Pinonic acid	Sum <sup>b</sup>	4-Nitrocatechol	2-Nitrophenol	4-Nitrophenol	Nitrophenols
Ph								
C <sub>5</sub>								
C <sub>6</sub>								
C <sub>7</sub>								
C <sub>8</sub>								
C <sub>9</sub>								
C <sub>10</sub>								
C <sub>12</sub>								
C <sub>13</sub>								
C <sub>14</sub>								
C <sub>16</sub>								
C <sub>5-7</sub>								
C <sub>8-10</sub>								
C <sub>12-16</sub>								
Di_Total								
3-MBTCA	1.00							
Pinic acid	0.34	1.00						
Pinonic acid	0.02	0.14	1.00					
Sum				1.00				
4-Nitrocatechol	0.00	0.00	0.51	0.01	1.00			
2-Nitrophenol	0.24	0.18	0.06	0.31	0.01	1.00		
4-Nitrophenol	0.01	0.00	0.00	0.02	0.00	0.33	1.00	
Nitrophenols	0.00	0.01	0.00	0.00	0.01			1.00

2 <sup>a</sup> the total of aliphatic dicarboxylic acids and phthalic acids;

3 <sup>b</sup> the sum of pinene oxidation products (3-MBTCA, pinic acid and pinonic acid).