Supplement for:

Chemical characterisation of atmospheric aerosols during a 2007 summer field campaign at Brasschaat, Belgium: sources and source processes of biogenic secondary organic aerosol

Y. Gómez-González[1], W. Wang[2], R. Vermeylen[1], X. Chi[2,*], J. Neirynck[3], I. A. Janssens[4], W. Maenhaut[2], and M. Claeys[1]

[1]Department of Pharmaceutical Sciences, University of Antwerp (Campus Drie Eiken), Antwerp, Belgium

[2]Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University, Gent, Belgium

[3]Research Institute for Nature and Forest (INBO), Geraardsbergen, Belgium

[4]Department of Biology, University of Antwerp (Campus Drie Eiken), Antwerp, Belgium

[*]present address: Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany

Correspondence to: M. Claeys (magda.claeys@ua.ac.be)

Implications of the Arrhenius temperature relationship

Rates of chemical reactions depend not only on substrate concentrations, but also on the activation energy (Ea) required for the reaction to occur. Temperature determines the fraction of molecules present with sufficient energy to react, i.e., above the Ea of that specific reaction. At a given temperature, the higher Ea, the fewer molecules will be present with sufficient energy to react. However, higher Ea's also imply a larger relative increase in reaction rates, and thus a higher temperature sensitivity (e.g., Box 1 in Davidson and Janssens, 2006). Higher temperatures will thus stimulate the rate of reactions with high Ea more than they will that of reactions with low Ea. However, in the case of intermediate compounds, changes in the concentration with temperature are less easily interpretable. Both the formation and destruction reactions are characterised by an Ea, such that the change in concentration of such a compound with

temperature depends on the temperature responses of both the formation and destruction reactions. In any case, the much lower Ea for *cis*-pinonic acid than for MBTCA should be interpreted as MBTCA concentrations exhibiting a much larger relative increase with temperature compared to concentrations of *cis*-pinonic acid.

Davidson, E.A. and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165−173, 2006.

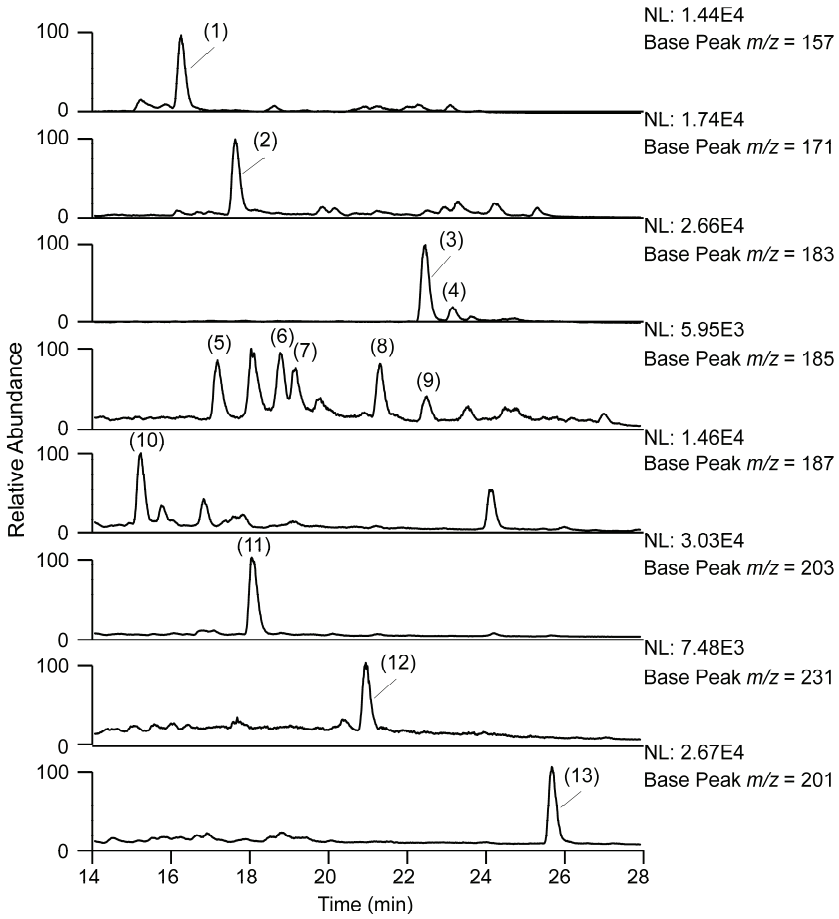

Figure S1. Extracted ion chromatograms (EICs) of selected terpenoic acids [(1) terebic acid, (2) terpenylic acid, (3) *cis*-pinonic acid, (4) caronic acid, (5) ketolimononic acid, (6) limonic acid, (7) homoterpenylic acid, (8) *cis*-pinic acid, (9) caric acid, (10) unknown MW 188, (11) MBTCA, (12) diaterpenylic acid acetate], and sebacic acid, used as internal recovery standard, for a day-time sample collected on 11 June 2007. Abbreviation: NL, normalisation level.

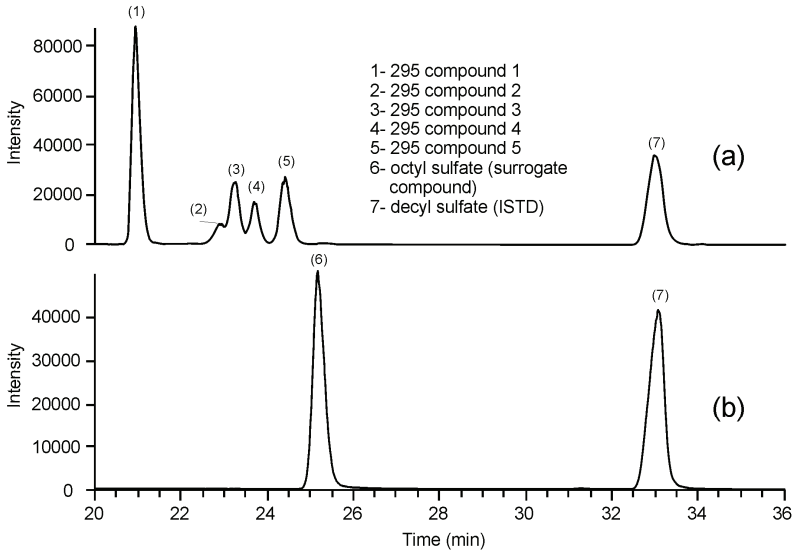

Figure S2. Extracted ion chromatograms (EICs) of (a) α-pinane-related MW 295 nitrooxy organosulfates (*m/z* 294) and decyl sulfate (used as internal recovery standard; *m/z* 237) for a night-time sample collected on 29 June 2007; and (b) a calibration mixture containing octyl sulfate (0.3 ng/μL); surrogate compound; *m/z* 209) and decyl sulfate (2.1 ng/μL; internal recovery standard).

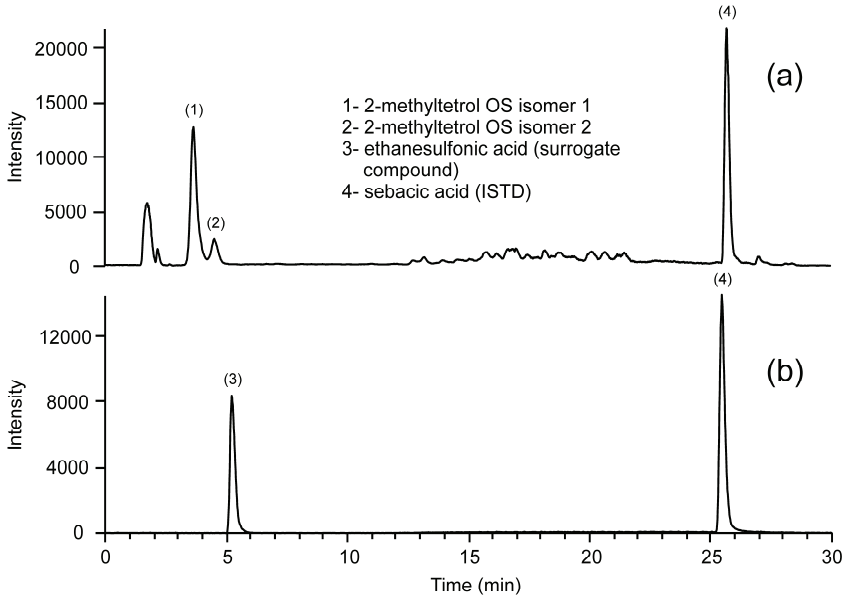

Figure S3. Extracted ion chromatograms (EICs) of (a) 2-methyltetrol OSs (MW 216; *m/z* 215) and sebacic acid [used as internal recovery standard (ISTD); *m/z* 201] for a day-time sample collected on 25 June 2007; and (b) a calibration mixture containing ethanesulfonic acid (4.2 ng/μL; surrogate compound; *m/z* 109) and sebacic acid (1.1 ng/μL; internal recovery standard).

Table S1. Terpenoic acids, organosulfates and nitrooxy organosulfates measured; surrogate and internal recovery standards.

Organic species (MW)	Formula	RT (min)[a]	BVOC precursor
Terpenoic acids			
diaterpenylic acid acetate (232)	$C_8H_{16}O_6$	20.64	α-/β-pinene 1,8-cineole
MBTCA (204)	$C_8H_{11}O_6$	18.06	α-/β-pinene
cis-pinonic acid (184)	$C_{10}H_{16}O_3$	22.48	α-/β-pinene
cis-pinic acid (186)	$C_9H_{14}O_4$	21.29	α-/β-pinene
terebic acid (158)	$C_7H_{10}O_4$	16.21	α-/β-pinene Δ^3-carene
terpenylic acid (172)	$C_8H_{12}O_4$	17.24	α-/β-pinene
unknown (188)	$C_8H_{12}O_5$	15.18	α-/β-pinene
caronic acid (184)	$C_{10}H_{16}O_3$	23.19	Δ^3-carene
caric acid (186)	$C_8H_{14}O_4$	22.52	Δ^3-carene
ketolimononic acid (186)	$C_9H_{14}O_4$	17.10	limonene
limonic acid (186)	$C_9H_{14}O_4$	18.77	limonene
homoterpenylic acid (186)	$C_9H_{14}O_4$	19.15	β-pinene
Organosulfates and nitrooxy organosulfates			
2-methyltetrols (216)	$C_6H_{10}O_7S$	3.60; 4.37	isoprene
2-methyltetrols mono-nitrates (261)[b]	$C_5H_{11}O_9SN$	12.2; 12.7; 14.0	isoprene
2-methyltetrols di-nitrates (306)[b]	$C_5H_{10}O_{11}SN_2$	19.30; 20.50; 22.4; 23.90	isoprene
2- and 3-hydroxyglutaric acid (228)	$C_5H_{12}O_7S$	6.06	α-pinene
unknown (212)	$C_5H_8O_7S$	4.88; 6.92	unknown
unknown (226)	$C_5H_8O_8S$	11.00	unknown
pinanediol mono-nitrates (295)	$C_{10}H_{17}O_7SN$	20.93; 22.82; 23.16; 23.58; 24.27	α-pinene
Surrogate and internal recovery standards			
ethanesulfonic acid	$C_2H_6O_3S$	5.49	–
sodium octanesulfate	$C_8H_{17}O_9NaSO_4$	24.73	–
sebacic acid	$HO_2C(CH_2)_8CO_2H$	25.70	–
decyl sodium sulfate	$C_{10}H_{19}Na.H_2SO_4$	32.43	–

[a]RTs are given for the T3 C18 column, except for the α-pinane-related MW 295 nitrooxy organosulfates, octane sulfate and decyl sodium sulfate which were analysed using the Hypersyl Gold C18 column;
[b]show several resolved and unresolved peaks; only the resolved ones with a S/N>10 were included.

Table S2. Quantitative aspects for the determination of terpenoic acids and organosulfates. The analytes mentioned in the same box were quantified using the calibration curve obtained for the analyte in bold letters of the first row.

Analyte (internal recovery standard)	**Conc.[a] range (ng/µL)**	**Conc.[a] levels**	**LOQ[a] [ng/µL (x pg)[a]]**	**R^2**
MBTCA (SA)[a]	0.11 – 2.70	8	0.11 (440)	0.9996
***cis*-pinic acid (SA)** limonic acid (SA) caric acid (SA)	0.04 – 1.00	8	0.04 (160)	0.9996
***cis*-pinonic acid (SA)** caronic acid (SA) ketolimononic acid (SA)	0.12 – 1.50	8	0.12 (480)	0.9994
terpenylic acid (SA) terebic acid (SA) homoterpenylic acid (SA) unknown MW 188 (SA)	0.14 – 1.60	6	0.14 (560)	0.9966
diaterpenylic acid acetate (SA)	0.15 – 13.3	10	0.15 (600)	0.9996
ethanesulfonic acid (SA) unknown MW 212 OS (∑2 isomers)[b] 2-methyltetrol OS (∑2 isomers)[b] unknown MW 226 OS 2-and 3-hydroxyglutaric acid OS 2-methyltetrol mono-nitrate OS (∑2 isomers)[b] 2-methyltetrol di-nitrate OS (∑4 isomers)[b]	0.12 – 36.7	10	0.12 (480)	0.9992
octanesulfate (DS)[a] pinanediol mono-nitrates (5 isomers)[c]	0.01 – 1.80	6	0.01 (40)	0.9993

[a]Abbreviations: SA (sebacic acid); Conc. (concentration); LOQ (limit of quantitation); DS (decyl sulfate); x (amount injected on column);
[b]The quantitation was performed using the summed peak areas of the isomers;
[c]The quantitation was performed for the five individual isomers.

Table S3 (part 1): Correlations obtained between OC, WSOC, the LC/MS organic species, temperature (T), ozone, and CO_2, and the D_N parameter (correlation coefficients >0.7 are in bold, those between 0.5 and 0.7 are in bold italic).

	OC	WSOC	MBTCA	*cis*-pinic	*cis*-pinonic	OS 295 sum	terebic
OC	1						
WSOC	**0.95**	1					
MBTCA	**0.81**	**0.91**	1				
cis-pinic	0.39	0.44	0.39	1			
cis-pinonic	0.16	0.19	0.21	**0.78**	1		
OS 295 sum	0.24	0.23	0.13	0.47	0.29	1	
terebic	**0.81**	**0.90**	**0.93**	***0.60***	0.42	0.18	1
terpenylic	**0.70**	**0.79**	**0.85**	***0.68***	***0.56***	0.25	**0.91**
unknown 188	**0.85**	**0.93**	**0.96**	0.34	0.05	0.20	**0.87**
diaterpenylic acid acetate	**0.78**	**0.89**	**0.99**	0.38	0.21	0.12	**0.93**
caronic	0.13	0.15	0.21	**0.73**	**0.95**	0.18	0.40
ketolimononic	***0.56***	***0.65***	***0.67***	***0.61***	***0.61***	0.23	**0.74**
limonic	***0.61***	***0.57***	0.43	***0.60***	0.36	**0.75**	0.46
homoterpenylic	**0.74**	**0.80**	**0.79**	**0.77**	***0.51***	0.43	**0.87**
caric	0.35	0.39	0.29	**0.81**	0.46	***0.69***	0.45
OS 226	**0.90**	**0.92**	**0.90**	0.38	0.12	0.27	**0.82**
OS 228	**0.84**	**0.92**	**0.84**	0.35	0.07	0.23	**0.83**
OS 212 sum	**0.89**	**0.95**	**0.93**	0.39	0.11	0.27	**0.88**
OS 261 sum	**0.80**	**0.85**	**0.90**	0.46	0.24	0.36	**0.83**
OS 216 sum	**0.84**	**0.88**	**0.91**	0.35	0.11	0.21	**0.84**
OS 306 sum	**0.83**	**0.84**	**0.79**	0.40	0.35	0.17	**0.77**
T_40m	***0.60***	***0.66***	**0.70**	0.41	0.42	0.03	**0.74**
O_3	0.37	0.49	***0.54***	0.25	0.26	-0.08	***0.62***
CO_2	0.46	0.46	0.15	0.45	0.15	0.47	0.28
D_N	0.02	0.08	0.21	-0.10	0.13	-0.39	0.17

Table S3 (part 2): Correlations obtained between OC, WSOC, the LC/MS organic species, temperature (T), ozone, and CO_2, and the D_N parameter (correlation coefficients >0.7 are in bold, those between 0.5 and 0.7 are in bold italic).

	terpe-nylic	un-known 188	diaterpe-nylic acid acetate	caronic	keto-limono-nic	limonic	homo-terpeny-lic	caric
OC								
WSOC								
MBTCA								
cis-pinic								
cis-pinonic								
OS 295 sum								
terebic								
terpenylic	1							
unknown 188	**0.79**	1						
diaterpenylic acid acetate	**0.86**	**0.95**	1					
caronic	***0.53***	0.03	0.20	1				
ketolimononic	**0.89**	***0.59***	***0.69***	***0.55***	1			
limonic	***0.57***	0.49	0.41	0.29	0.50	1		
homoterpenylic	**0.93**	**0.78**	**0.80**	0.45	**0.83**	**0.73**	1	
caric	***0.53***	0.33	0.27	0.42	0.47	**0.75**	**0.70**	1
OS 226	**0.78**	**0.95**	**0.88**	0.11	***0.59***	***0.61***	**0.78**	0.34
OS 228	**0.71**	**0.90**	**0.83**	0.05	***0.56***	0.45	***0.70***	0.36
OS 212 sum	**0.80**	**0.98**	**0.91**	0.10	***0.61***	***0.56***	**0.79**	0.39
OS 261 sum	**0.85**	**0.91**	**0.89**	0.23	0.70	***0.66***	**0.84**	0.45
OS 216 sum	**0.75**	**0.94**	**0.88**	0.12	***0.54***	***0.50***	**0.74**	0.29
OS 306 sum	**0.72**	**0.77**	**0.76**	0.30	***0.61***	***0.60***	**0.76**	0.37
T_40m	***0.69***	***0.59***	**0.70**	0.42	**0.70**	0.27	***0.62***	0.18
O_3	0.47	***0.56***	0.26	0.44	-0.06	0.35	***0.56***	0.02
CO_2	0.28	***0.52***	0.11	0.11	0.08	**0.73**	***0.57***	**0.72**
D_N	0.24	0.11	0.25	0.14	0.38	-0.26	0.04	-0.33

Table S3 (part 3): Correlations obtained between OC, WSOC, the LC/MS organic species, temperature (T), ozone and CO_2, and the D_N parameter (correlation coefficients >0.7 are in bold, those between 0.5 and 0.7 are in bold italic).

	OS 226	OS 228	OS 212 sum	OS 261 sum	OS 216 sum	OS 306 sum	T_40m	O_3	CO_2	D_N
OC										
WSOC										
MBTCA										
cis-pinic										
cis-pinonic										
OS 295 sum										
terebic										
terpenylic										
unknown 188										
diaterpenylic acid acetate										
caronic										
ketolimononic										
limonic										
homoterpenylic										
caric										
OS 226	1									
OS 228	**0.85**	1								
OS 212 sum	**0.96**	**0.94**	1							
OS 261 sum	**0.93**	**0.77**	**0.92**	1						
OS 216 sum	**0.94**	**0.81**	**0.95**	**0.92**	1					
OS 306 sum	**0.84**	***0.62***	**0.80**	**0.88**	**0.78**	1				
T_40m	***0.60***	***0.51***	***0.61***	***0.67***	***0.63***	***0.63***	1			
O_3	0.39	***0.58***	0.49	0.39	0.40	0.33	***0.56***	1		
CO_2	0.37	***0.50***	0.43	0.29	0.14	0.29	-0.19	-0.48	1	
D_N	0.10	0.01	0.08	0.15	0.09	0.13	0.49	0.36	***-0.69***	1

Table S4 (part 1): Principal component loadings for the 8-component solution of the PCA on the fine front filter data and the data for several meteorological parameters and inorganic trace gases (loadings >0.7 are in bold, those between 0.5 and 0.7 are in bold italic).

	Component							
	1	2	3	4	5	6	7	8
TC	**0.81**	0.12	0.24	0.03	-0.05	0.26	0.43	0.05
OC	**0.82**	0.11	0.26	0.05	0.03	0.10	0.43	0.15
EC	0.26	0.08	-0.01	-0.04	-0.29	**0.71**	0.15	-0.33
WSOC	**0.90**	0.14	0.29	0.00	-0.02	0.03	0.21	0.06
NH4	***0.55***	0.00	**0.77**	0.11	-0.05	-0.07	-0.11	0.15
SO4	***0.54***	0.03	**0.76**	-0.03	0.03	-0.05	-0.22	0.13
NO3	0.48	-0.04	***0.64***	0.31	0.04	-0.11	0.23	0.18
Cl	-0.01	-0.03	0.14	0.25	**0.87**	0.05	-0.08	-0.05
Na	-0.08	-0.04	-0.16	-0.02	**0.96**	-0.06	0.04	0.00
Mg	0.15	-0.05	0.01	-0.03	**0.88**	0.01	0.25	-0.02
K	0.14	0.04	***0.64***	-0.02	0.09	-0.01	0.37	-0.08
Ca	0.42	-0.12	0.23	0.08	0.14	-0.08	**0.75**	0.02
MSA	0.25	-0.13	0.09	0.07	**0.77**	-0.20	-0.11	0.18
oxalate	***0.69***	0.01	***0.66***	0.08	-0.03	-0.16	0.12	0.12
malonate	**0.85**	-0.06	0.24	-0.01	0.17	0.04	-0.13	0.14
succinate	**0.80**	-0.02	***0.55***	0.01	-0.05	-0.14	0.10	0.05
glutarate	***0.55***	-0.03	-0.18	0.10	0.06	-0.06	***0.65***	0.21
MBTCA	**0.93**	0.14	0.12	-0.19	-0.02	-0.04	0.08	-0.06
cis-pinic	0.33	**0.86**	0.04	0.16	-0.06	0.01	-0.03	-0.03
cis-pinonic	0.04	**0.94**	0.01	-0.17	-0.05	0.01	0.05	0.02
terebic	**0.83**	0.37	0.27	-0.16	-0.06	-0.06	0.11	-0.04
terpenylic	**0.79**	***0.52***	0.12	-0.15	0.00	0.08	-0.06	-0.05
188 unknown	**0.97**	0.01	0.14	-0.02	0.03	-0.01	0.06	-0.02
diaterpenylic_acid_acetate	**0.92**	0.14	0.14	-0.22	-0.01	-0.03	0.03	-0.07

Table S4 (part 2): Principal component loadings for the 8-component solution of the PCA on the fine front filter data and the data for several meteorological parameters and inorganic trace gases (loadings >0.7 are in bold, those between 0.5 and 0.7 are in bold italic).

	Component							
	1	2	3	4	5	6	7	8
caronic	0.03	**0.90**	-0.04	-0.21	-0.10	-0.03	0.04	0.03
caric	0.34	***0.66***	0.03	***0.52***	-0.09	0.10	-0.07	-0.04
ketolimononic	***0.62***	***0.57***	0.16	-0.26	-0.11	0.08	-0.11	-0.02
limonic	***0.56***	0.45	-0.15	0.46	0.04	0.22	0.16	0.12
homoterpenylic	**0.78**	***0.55***	0.09	0.08	-0.01	0.10	0.03	-0.09
212_OS sum	**0.95**	0.08	0.20	0.03	0.05	-0.02	0.11	0.04
216_OS sum	**0.91**	0.06	0.01	-0.06	0.11	-0.02	0.21	0.05
226_OS	**0.95**	0.08	0.05	0.00	0.11	0.02	0.16	0.10
228_OS	**0.85**	0.04	0.48	0.09	0.04	-0.09	0.03	0.08
261_OS sum	**0.93**	0.23	-0.06	-0.03	0.05	0.02	0.10	0.00
295_OS sum	0.24	0.46	-0.11	***0.56***	0.15	0.00	-0.02	0.22
306_OS sum	***0.54***	0.28	0.16	-0.14	-0.17	0.11	***0.55***	-0.23
RH	-0.07	-0.24	0.25	**0.71**	-0.10	0.04	-0.23	-0.22
T_40m	***0.59***	0.36	0.09	-0.47	-0.13	-0.13	0.23	0.03
Sunshine	0.27	0.13	-0.05	**-0.89**	-0.09	0.03	-0.10	0.03
WS_40m	-0.05	-0.36	-0.32	-0.32	0.43	-0.28	0.15	-0.18
Precipitation	-0.14	-0.01	-0.15	0.04	0.00	-0.09	-0.07	**-0.74**
SO2	-0.11	0.06	0.13	-0.11	***0.53***	0.48	-0.15	***0.51***
O3	0.38	0.20	0.50	-0.41	-0.04	***-0.53***	-0.04	0.03
NO	0.02	-0.02	-0.14	-0.26	-0.11	**0.73**	-0.04	0.19
NO2	-0.05	0.08	-0.06	0.28	0.08	**0.84**	-0.07	0.13
D_N	0.14	-0.01	-0.02	**-0.86**	-0.07	0.03	-0.14	-0.02