Geoscientific
Model Development

Supplement of

The Eulerian urban dispersion model EPISODE – Part 2: Extensions to the source dispersion and photochemistry for EPISODE–CityChem v1.2 and its application to the city of Hamburg

Matthias Karl et al.

Correspondence to: Matthias Karl (matthias.karl@hzg.de)

Table S1: Chemical reactions and photo-dissociation reactions of the EmChem03-mod scheme. For notes on rate coefficient functions see end of table.

Reaction no.	Educts	Products	Rate coefficient
Inorganic chemistry			
IN-1	OP + O2 + M	⟶ O3	5.67E-34 × M × O2 × (T/300)$^{-2.8}$
IN-2	OD + M	⟶ OP	1.8E-11 exp(107/T) × N2 + 3.2E-11 exp(67/T) × O2
IN-3	OP + NO + M	⟶ NO2	ktr(NO + OP)
IN-4	OD + H2O	⟶ 2.0 OH	2.2E-10 × H2O
IN-5	O3 + NO	⟶ NO2 + O2	1.4E-12 exp(-1310/T)
IN-6	O3 + NO2	⟶ NO3 + O2	1.4E-12 exp(-2470/T)
IN-7	O3 + OH	⟶ HO2 + O2	1.7E-12 exp(-940/T)
IN-8	O3 + HO2	⟶ OH + 2 O2	2.03E-16 × (300/T)$^{-4.57}$ exp(693/T)
IN-9	NO + NO3	⟶ NO2 + NO2	1.8E-11 exp(110/T)
IN-10	NO + HO2	⟶ NO2 + OH	3.6E-12 exp(270/T)
IN-11	NO3 + HO2	⟶ NO2 + OH + O2	3.5E-12
IN-12	NO2 + NO3	⟶ N2O5	ktr(NO2 + NO3)
IN-13	NO2 + OH + M	⟶ HNO3	ktr(NO2 + OH)
IN-14	N2O5	⟶ NO2 + NO3	ktr(N2O5)
IN-15	OH + H2	⟶ HO2 + H2O	7.7E-12 exp(-2100/T)
IN-16	OH + HO2	⟶ O2 + H2O	4.8E-11 exp(250/T)
IN-17	OH + H2O2	⟶ HO2 + H2O	2.9E-12 exp(-160/T)
IN-18	HO2 + HO2	⟶ H2O2	*FH2O* × 2.2E-13 exp(600/T)
IN-19	HO2 + HO2 + M	⟶ H2O2	*FH2O* × 1.9E-33 exp(980/T)

Table S1: Continued.

IN-20	OH + HNO3	$\longrightarrow$ NO3 + H2O	k(OH + HNO3)
IN-21	SO2 + OH	$\longrightarrow$ HO2 + H2SO4	ktr(SO2 + OH)
IN-22	SO2 + CH3O2	$\longrightarrow$ H2SO4 + HCHO + HO2	4.0E-17
IN-23	OH + HONO	$\longrightarrow$ NO2	2.5E-12 exp(-260/T)
IN-24	OH + NO	$\longrightarrow$ HONO	ktr(OH + NO)
Heterogeneous chemistry			
HE-1	H2SO4	$\longrightarrow$ aerosol sink	5.0E-6 × M / 2.55E19
Methane chemistry			
MA-1	OH + CH4	$\longrightarrow$ CH3O2	1.85E-20 × $T^{2.8}$ × exp(-987/T)
MA-2	CH3O2 + NO	$\longrightarrow$ HCHO + HO2 + NO2	2.3E-12 exp(360/T)
MA-3	CH3O2 + NO3	$\longrightarrow$ HCHO + HO2 + NO2	1.3E-12
MA-4	OH + CH3OH	$\longrightarrow$ HO2 + HCHO + H2O	6.38E-18 exp(144/T) × T^2
MA-5	HO2 + CH3O2	$\longrightarrow$ 0.9 CH3O2H + 0.1 HCHO	3.8E-13 exp(780/T)
MA-6	CH3O2H + OH	$\longrightarrow$ HCHO + OH	1.0E-12 exp(190/T)
MA-7	CH3O2H + OH	$\longrightarrow$ CH3O2 + H2O	1.9E-12 exp(190/T)
MA-8	OH + HCHO	$\longrightarrow$ CO + HO2 + HO2	1.25E-17 × T^2 × exp(615/T)
MA-9	NO3 + HCHO	$\longrightarrow$ HNO3 + CO + HO2	2.0E-12 exp(-2440/T)
MA-10	OH + CO	$\longrightarrow$ HO2 + CO2	1.44E-13 + 3.43E-33 × M
Ethane and ethanol chemistry			
EA-1	OH + C2H6	$\longrightarrow$ C2H5O2 + H2O	6.9E-12 exp(-1000/T)
EA-2	C2H5O2 + NO	$\longrightarrow$ HO2 + CH3CHO + NO2	2.55E-12 exp(380/T)
EA-3	C2H5O2 + NO3	$\longrightarrow$ HO2 + CH3CHO + NO2	2.3E-12

Table S1: Continued.

EA-4	OH + CH3CHO	$\longrightarrow$	0.95 CH3COO2 + 0.05 CH3O2 + 0.05 CO	4.4E-12 exp(365/T)
EA-5	CH3COO2 + NO2 + M	$\longrightarrow$ PAN	ktr(CH3OO2 + NO2)
EA-6	PAN + M	$\longrightarrow$ CH3COO2 + NO2	ktr(PAN)
EA-7	CH3COO2 + NO	$\longrightarrow$ NO2 + CH3O2 + CO2	7.5E-12 exp(290/T)
EA-8	OH + C2H5OH	$\longrightarrow$ CH3CHO + HO2	6.7E-18 exp(511/T) × T^2
n-butane chemistry			
NB-1	OH + NC4H10	$\longrightarrow$ SECC4H9O2	2.03E-17 exp(78/T) × T^2
NB-2	NO + SECC4H9O2	$\longrightarrow$ NO2 + 0.65 HO2 + 0.65 CH3COC2H5 + 0.35 CH3CHO + 0.35 C2H5O2	2.54E-12 exp(360/T)
NB-3	OH + CH3COC2H5	$\longrightarrow$ CH3COCHO2CH3	2.53E-18 exp(503/T) × T^2
NB-4	CH3COCHO2CH3 + NO	$\longrightarrow$ NO2 + CH3COO2 + CH3CHO	2.54E-12 exp(360/T)
Ethene chemistry			
EE-1	C2H4 + OH +M	$\longrightarrow$ CH2O2CH2OH	ktr(OH + C2H4)
EE-2	CH2O2CH2OH + NO	$\longrightarrow$ NO2 + 2 HCHO + HO2	2.54E-12 exp(360/T)
EE-3	C2H4 + O3	$\longrightarrow$ 1.14 HCHO + 0.63 CO + 0.13 HO2 + 0.13 OH + 0.14 H2O2	9.1E-15 exp(-2580/T)
Propene chemistry			
PE-1	OH + C3H6 + M	$\longrightarrow$ CH3CHO2CH2OH	ktr(OH + C3H6)
PE-2	NO + CH3CHO2CH2OH	$\longrightarrow$ NO2 + CH3CHO + HCHO + HO2	2.54E-12 exp(360/T)
PE-3	O3 + C3H6	$\longrightarrow$ 0.545 HCHO + 0.545 CH3CHO + 0.56 CO + 0.36 OH + 0.28 HO2 + 0.09 H2O2 + 0.1 CH4 + 0.28 CH3O2	5.5E-15 exp(-1880/T)

Table S1: Continued.

o-xylene chemistry				
OX-1	OXYL + OH	$\longrightarrow$	OXYLOHO2	1.36E-11
OX-2	OXYLOHO2 + NO	$\longrightarrow$	NO2 + CH3COCHO + MEMALDIAL + HO2	2.54E-12 exp(360/T)
OX-3	MEMALDIAL + OH	$\longrightarrow$	MEMALO2	5.58E-11
OX-4	MEMALO2 + NO	$\longrightarrow$	NO2 + HO2 + CH3COCHO + HCOCHO	2.54E-12 exp(360/T)
OX-5	OH + CH3COCHO	$\longrightarrow$	CH3COO2 + CO	1.9E-12 exp(575/T)
OX-6	OH + HCOCHO	$\longrightarrow$	HO2 + 2 CO	6.6E-18 exp(820/T) $\times T^2$
Isoprene chemistry				
IS-1	C5H8 + OH	$\longrightarrow$	ISOPO2	2.7E-11 exp(390/T)
IS-2	ISOPO2 + NO	$\longrightarrow$	0.776 MVK + 0.776 HCHO + 0.12 ISOPO2 + HO2 + NO2	2.54E-12 exp(360/T)
IS-3	MVK + OH	$\longrightarrow$	MVKO2	4.1E-12 exp(453/T)
IS-4	MVKO2 + NO	$\longrightarrow$	CH3COCHO + HCHO + HO2 + NO2	1.4E-12 exp(-180/T)

Table S1: Continued.

Reaction no.	Educts		Products	ε_1	ε_2	ε_3	ε_4
Photolysis reactions							
PH-1	O3	$\longrightarrow$	OD	2.00E-04	1.400	0.86	0.33
PH-2	O3	$\longrightarrow$	OP	1.23E-03	0.600	0.92	0.41
PH-3	NO2	$\longrightarrow$	OP + NO	1.45E-02	0.400	0.91	0.38
PH-4	H2O2	$\longrightarrow$	2 OH	2.20E-05	0.750	0.88	0.35
PH-5	HNO3	$\longrightarrow$	NO2 + OH	3.00E-06	1.250	0.87	0.33
PH-6	HCHO	$\longrightarrow$	CO + 2 HO2	5.40E-05	0.790	0.88	0.34
PH-7	HCHO	$\longrightarrow$	CO + H2	6.65E-05	0.600	0.89	0.35
PH-8	CH3CHO	$\longrightarrow$	CH3O2 + HO2 + CO	1.35E-05	0.940	0.87	0.33
PH-9	CH3COC2H5	$\longrightarrow$	CH3COO2 + C2H5O2	2.43E-05	0.877	0.92	0.41
PH-10	CH3COCHO	$\longrightarrow$	CH3COO2 + CO + HO2	9.72E-05	0.877	0.92	0.41
PH-11	HCOCHO	$\longrightarrow$	1.9 CO + 0.1 HCHO + 0.5 HO2	5.40E-04	0.790	0.92	0.41
PH-12	NO3	$\longrightarrow$	NO + O2	3.53E-02	0.081	0.92	0.42
PH-13	NO3	$\longrightarrow$	NO2 + OP	8.94E-02	0.059	0.92	0.42
PH-14	N2O5	$\longrightarrow$	NO2 + NO3	3.32E-05	0.567	0.88	0.35
PH-15	CH3O2H	$\longrightarrow$	HCHO + OH + HO2	2.27E-05	0.620	0.88	0.35
PH-16	HONO	$\longrightarrow$	OH + NO	3.22E-03	0.400	0.91	0.38

Notes:
Special rate constants and reaction parameters:

$FH2O = 1 + 1.4\text{E-}21 \exp(2200/T) \times \text{H2O}$;
$k(\text{OH} + \text{HNO3}) = K_1 + (K_3 \times \text{M})/(1.0 + (K_3 \times \text{M}/K_4))$ with $K_1 = 2.4\text{E-}14 \exp(460/T)$, $K_3 = 6.5\text{E-}34 \exp(1335/T)$, $K_4 = 2.7\text{E-}17 \exp(2199/T)$;

Rate coefficients for three-body reactions using the Troe expression (e.g. Atkinson et al., 2006), where the reaction rates are calculated as: $ktr = \frac{k_0 k_\infty}{k_0 + k_\infty} F$, with the broadening factor F calculated using the approximate expression: $log_{10} F \cong \frac{log_{10} F_c}{1 + [log_{10}(k_0/k_\infty)/N]^2}$, where $N = [0.75 - 1.27 log_{10} F_c]$, are given as follows:

ktr (NO+OP): k_0/M = 1.0E-31 $(300/T)^{1.6}$, k_∞ = 3.0E-11 $(300/T)^{-0.3}$, F_c = 0.85;
ktr (NO2+NO3): k_0/M = 3.6E-30 $(300/T)^{4.1}$, k_∞ = 9.7E-12 $(300/T)^{-0.2}$, F_c = 0.35;
ktr (NO2+OH): k_0/M = 3.3E-30 $(300/T)^{3.0}$, k_∞ = 4.1E-11, F_c = 0.40;
ktr (N2O5): k_0/M = 1.3E-3 $(300/T)^{3.5}$ exp(-11000/T), k_∞ = 9.7E14 $(300/T)^{-0.1}$ exp(-11080/T);
ktr (OH+NO): k_0/M = 7.4E-31 $(300/T)^{2.4}$, k_∞ = 3.3E-11 $(300/T)^{0.3}$, F_c = exp(-T/1420);
ktr (CH3OO2 + NO2): k_0/M = 2.7E-28 $(300/T)^{7.1}$, k_∞ = 1.2-11 $(300/T)^{0.9}$, F_c = 0.3;
ktr (PAN): k_0/M = 4.9E-3 $(300/T)^{-12100}$, k_∞ = 5.4E16 exp(-13830/T), F_c = 0.3;
ktr (OH+C2H4): k_0/M = 8.6E-29 $(300/T)^{3.1}$, k_∞ = 9.0E-12 $(300/T)^{0.85}$, F_c = 0.48;
ktr (OH+C3H6): k_0/M = 8.0E-27 $(300/T)^{3.5}$, k_∞ = 3.0E-11 $(300/T)$, F_c = 0.5;
ktr (SO2+OH): k_0/M = 4.0E-31 $(300/T)^{-3.3}$, k_∞ = 2.0E-12, $F = 0.45^{1/(1 + log_{10}(k_0/k_\infty)^2)}$

Table S2: Additional chemical reactions and photo-dissociation reactions of EmChem09-mod. The scheme includes all reactions of EmChem03-mod given in Table S1.

Reaction no.	Educts	Products	Rate coefficient
MA-11	CH3O2 + CH3O2	$\longrightarrow$ 2. HCHO + 2. HO2	7.4E-13 exp(-520/T)
MA-12	CH3O2 + CH3O2	$\longrightarrow$ CH3OH + HCHO	1.03E-13 exp(365/T) – 7.4E-13 exp(-520/T)
EA-9	C2H5O2 + HO2	$\longrightarrow$ C2H5OOH	3.8E-13 exp(900/T)
EA-10	C2H5OOH + OH	$\longrightarrow$ CH3CHO + OH	8.01E-12
EA-11	C2H5OOH + OH	$\longrightarrow$ C2H5O2	1.9E-12 exp(190/T)
EA-12	CH3COO2 + HO2	$\longrightarrow$ 0.41 CH3COO2H + 0.15 O3 + 0.44 OH + 0.44 CH3O2 + 0.15 CH3COOH	5.2E-13 exp(980/T)
EA-13	CH3COO2H + OH	$\longrightarrow$ CH3COO2	1.9E-12 exp(190/T)
EA-14	CH3O2 + CH3COO2	$\longrightarrow$ 0.9 HO2 + HCHO + 0.9 CH3O2 + 0.1 CH3COOH	2.0E-12 exp(500/T)
EA-15	CH3COO2 + CH3COO2	$\longrightarrow$ CH3O2 + CH3O2	2.9E-12 exp(500/T)
NB-5	SECC4H9O2 + HO2	$\longrightarrow$ 0.95 BURO2H	0.625 × 2.91E-13 exp(1300/T)
NB-6	CH3COCHO2CH3 + HO2	$\longrightarrow$ MEKO2H	0.625 × 2.91E-13 exp(1300/T)
NB-7	MEKO2H + OH	$\longrightarrow$ CH3COCHO2CH3	1.9E-12 exp(190/T)
NB-8	BURO2H + OH	$\longrightarrow$ SECC4H9O2	1.9E-12 exp(190/T)
NB-9	BURO2H + OH	$\longrightarrow$ OH + CH3COC2H5	2.15E-11
EE-4	CH2O2CH2OH + HO2	$\longrightarrow$ ETRO2H	1.2E-11
EE-5	ETRO2H + OH	$\longrightarrow$ CH3CHO + OH	1.38E-11
EE-6	ETRO2H + OH	$\longrightarrow$ CH2O2CH2OH	1.9E-12 exp(190/T)
PE-4	CH3CHO2CH2OH + HO2	$\longrightarrow$ 0.795 PRRO2H	0.52 × 2.91E-13 exp(1300/T)
PE-5	PRRO2H + OH	$\longrightarrow$ CH3COCH2OH + OH	2.44E-11

Table S2: Continued.

PE-6	CH3COCH2OH + OH	$\longrightarrow$ CH3COCHO + HO2	1.6E-12 exp(305/T)
PE-7	PRRO2H + OH	$\longrightarrow$ CH3CHO2CH2OH	1.9E-12 exp(190/T)
OX-7	OXYLOHO2 + HO2	$\longrightarrow$ 0.227 OXYO2H	0.859 × 2.91E-13 exp(1300/T)
OX-8	OXYO2H + OH	$\longrightarrow$ OXYLOHO2	4.2E-11
OX-9	MEMALDIAL + HO2	$\longrightarrow$ MEMALO2H	0.706 × 2.91E-13 exp(1300/T)
OX-10	MEMALO2H + OH	$\longrightarrow$ MEMALO2	1.9E-12 exp(190/T)
IS-5	ISOPO2 + HO2	$\longrightarrow$ 0.857 ISRO2H	1.4E-12 exp(-180/T)
IS-6	ISRO2H + OH	$\longrightarrow$ OH + ISOPO2	7.5E-11
IS-7	MVKO2 + HO2	$\longrightarrow$ MVKO2H	0.625 × 2.91E-13 exp(1300/T)
IS-8	MVKO2H + OH	$\longrightarrow$ MVKO2	2.2E-11
Monoterpene chemistry			
MT-1	APINENE + OH	$\longrightarrow$ PRODAPINOH + MTO2	1.2E-11 exp(444/T)
MT-2	APINENE + NO3	$\longrightarrow$ PRODAPINNO3 + MTO2	1.2E-12 exp(490/T)
MT-3	APINENE + O3	$\longrightarrow$ 0.8 PRODAPINO3 + 0.8 MTO2 + 0.2 BLOC + 0.46 OH	6.3E-16 exp(-580/T)
MT-4	LIMONENE + OH	$\longrightarrow$ PRODLIMOOH + MTO2	1.7E-10
MT-5	LIMONENE + NO3	$\longrightarrow$ PRODLIMONO3 + MTO2	1.3E-11
MT-6	LIMONENE + O3	$\longrightarrow$ PRODLIMOO3 + 0.67 OH + 0.19 HCHO + MTO2	2.0E-16
MT-7	MTO2 + NO	$\longrightarrow$ NO2 + HO2 + 0.78 MTKETONE	2.54E-12 exp(360/T)
MT-8	MTO2 + HO2	$\longrightarrow$ 0.493 MTO2H	0.914 × 2.91E-13 exp(1300/T)
MT-9	MTO2 + CH3O2	$\longrightarrow$ MTO2H	2.91E-13 exp(1300/T)
MT-10	MTO2 + C2H5O2	$\longrightarrow$ MTO2H	2.91E-13 exp(1300/T)

Table S2: Continued.

MT-11	PRODAPINOH + OH	$\longrightarrow$ MTO2		1.0E-30
MT-12	PRODAPINNO3 + OH	$\longrightarrow$ MTO2		1.0E-30
MT-13	PRODAPINO3 + OH	$\longrightarrow$ MTO2		1.0E-30
MT-14	PRODLIMOOH + OH	$\longrightarrow$ MTO2		1.0E-30
MT-15	PRODLIMONO3 + OH	$\longrightarrow$ MTO2		1.0E-30
MT-16	PRODLIMOO3 + OH	$\longrightarrow$ MTO2		1.0E-30
MT-17	MTKETONE + OH	$\longrightarrow$ MTO2		1.0E-30
MT-18	MTO2H + OH	$\longrightarrow$ MTO2		1.0E-30
Semi-volatile organic compounds				
SV-1	ISOPO2 + NO	$\longrightarrow$ 0.003 BLOC + 0.101 BSOC		2.54E-12 exp(360/T)
SV-2	ISOPO2 + HO2	$\longrightarrow$ 0.024 BLOC + 0.119 BSOC		0.706 × 2.91E-13 exp(1300/T)
SV-3	MTO2 + NO	$\longrightarrow$ 0.052 BLOC + 0.184 BSOC		2.54E-12 exp(360/T)
SV-4	MTO2 + HO2	$\longrightarrow$ 0.327 BLOC + 0.180 BSOC		2.91E-13 exp(1300/T)
SV-5	BSOC + OH	$\longrightarrow$ BLOC		4.0E-11
SV-6	OXYLOHO2 + NO	$\longrightarrow$ 0.063 ALOC		2.54E-12 exp(360/T)
SV-7	OXYLOHO2 + HO2	$\longrightarrow$ 0.710 ALOC		2.91E-13 exp(1300/T)
SV-8	CH3CHO2CH2OH + HO2	$\longrightarrow$ 0.205 ALOC		0.52 × 2.91E-13 exp(1300/T)
SV-9	SECC4H9O2 + HO2	$\longrightarrow$ 0.050 ALOC		0.625 × 2.91E-13 exp(1300/T)
SV-10	BLOC + OH	$\longrightarrow$ MTO2		1.0E-30
SV-11	ALOC + OH	$\longrightarrow$ OXYLOHO2		1.0E-30

Table S2: Continued.

				ε1	ε2	ε3	ε4
Photolysis reactions							
PH-17	C2H5OOH	$\longrightarrow$	HO2 + CH3CHO + OH	2.27E-05	0.620	0.88	0.35
PH-18	ETRO2H	$\longrightarrow$	HO2 + OH + 1.56 HCHO + 0.22 CH3CHO	2.27E-05	0.620	0.88	0.35
PH-19	BURO2H	$\longrightarrow$	OH + 0.65 HO2 + 0.65 CH3CO2H5 + 0.25 CH3CHO + 0.25 C2H5O2	2.27E-05	0.620	0.88	0.35
PH-20	PRRO2H	$\longrightarrow$	CH3CHO + HCHO + HO2	2.27E-05	0.620	0.88	0.35
PH-21	MEKO2H	$\longrightarrow$	CH3CHO + CH3COO2 + OH	2.27E-05	0.620	0.88	0.35
PH-22	CH3COO2H	$\longrightarrow$	CH3O2 + OH	2.27E-05	0.620	0.88	0.35
PH-23	OXYO2H	$\longrightarrow$	OH + CH3COCHO + MEMALDIAL + HO2	2.27E-05	0.620	0.88	0.35
PH-24	MEMALO2H	$\longrightarrow$	OH + HO2 + HCOCHO + CH3COCHO	2.27E-05	0.620	0.88	0.35

Table S3: Chemical reactions and photo-dissociation reactions of the EP10-Plume scheme.

Reaction no.	Educts	Products	Rate coefficient			
IN-1	OP + O2 + M	$\longrightarrow$ O3	$5.67\text{E-}34 \times M \times O2 \times (T/300)^{-2.8}$			
IN-2	OD + M	$\longrightarrow$ OP	$1.8\text{E-}11\ \exp(107/T) \times N2 + 3.2\text{E-}11\ \exp(67/T) \times O2$			
IN-3	OP + NO + M	$\longrightarrow$ NO2	$ktr\,(NO + OP)$			
IN-4	OD + H2O	$\longrightarrow$ 2.0 OH	$2.2\text{E-}10 \times H2O$			
IN-5	O3 + NO	$\longrightarrow$ NO2 + O2	$1.4\text{E-}12\ \exp(-1310/T)$			
IN-7	O3 + OH	$\longrightarrow$ HO2 + O2	$1.7\text{E-}12\ \exp(-940/T)$			
IN-8	O3 + HO2	$\longrightarrow$ OH + 2 O2	$2.03\text{E-}16 \times (300/T)^{-4.57}\ \exp(693/T)$			
IN-10	NO + HO2	$\longrightarrow$ NO2 + OH	$3.6\text{E-}12\ \exp(270/T)$			
IN-13	NO2 + OH + M	$\longrightarrow$ HNO3	$ktr\,(NO2 + OH)$			
MA-8	OH + HCHO	$\longrightarrow$ CO + HO2 + HO2	$1.25\text{E-}17 \times T^2 \times \exp(615/T)$			
MA-10	OH + CO	$\longrightarrow$ HO2 + CO2	$1.44\text{E-}13 + 3.43\text{E-}33 \times M$			
			ε_1	ε_2	ε_3	ε_4
PH-1	O3	$\longrightarrow$ OD	2.00E-04	1.400	0.86	0.33
PH-2	O3	$\longrightarrow$ OP	1.23E-03	0.600	0.92	0.41
PH-3	NO2	$\longrightarrow$ OP + NO	1.45E-02	0.400	0.91	0.38
PH-5	HNO3	$\longrightarrow$ NO2 + OH	3.00E-06	1.250	0.87	0.33
PH-6	HCHO	$\longrightarrow$ CO + 2 HO2	5.40E-05	0.790	0.88	0.34
PH-7	HCHO	$\longrightarrow$ CO + H2	6.65E-05	0.600	0.89	0.35

Table S4: Statistical comparison of meteorological variables modelled with TAPM and observations for 2012 based on hourly values. Statistical parameters: number of observations (N), mean (observed, modelled), standard deviation (SD; observed, modelled), overall bias (Bias), correlation (Corr), root mean squared error (RMSE), and index of agreement (IOA).

Station	Meteorological variable	N	$\bar{O}$	$\bar{M}$	SD_O	SD_M	Bias	Corr	RMSE	IOA
Hamburg weather mast (10 m)	Temperature [°C]	8510	9.10	9.55	7.17	6.93	1.00	0.98	1.85	0.98
	Wind speed [m s^{-1}]	8604	3.00	2.95	1.55	1.32	-0.08	0.87	0.76	0.93
	Wind direction [°]	8604	180.6	202.8	89.5	83.0	16.94	0.79	57.54	0.89
	Tot. solar radiation [W m^{-2}]	8690	116.2	138.7	193.0	212.9	26.56	0.86	110.51	0.92
Hamburg weather mast (50 m)	Temperature [°C]	8441	9.43	9.38	7.04	6.95	0.60	0.98	1.54	0.99
	Wind speed [m s^{-1}]	8744	4.86	4.92	2.32	2.12	-0.02	0.85	1.24	0.92
	Wind direction [°]	8744	191.8	204.8	89.84	82.67	6.20	0.82	52.24	0.90
DWD Hamburg Airport (10 m)	Temperature [°C]	8784	9.36	9.31	7.26	6.90	-0.05	0.97	1.70	0.99
	Relative humidity [fraction]	8784	0.806	0.798	0.149	0.149	-0.08	0.74	0.11	0.86

Table S5: Stations of the Hamburg air quality monitoring network included in the comparison. Available pollutant measurements for 2012 are indicated by X. Station types: traffic (tra), industrial (ind), urban background (ubg).

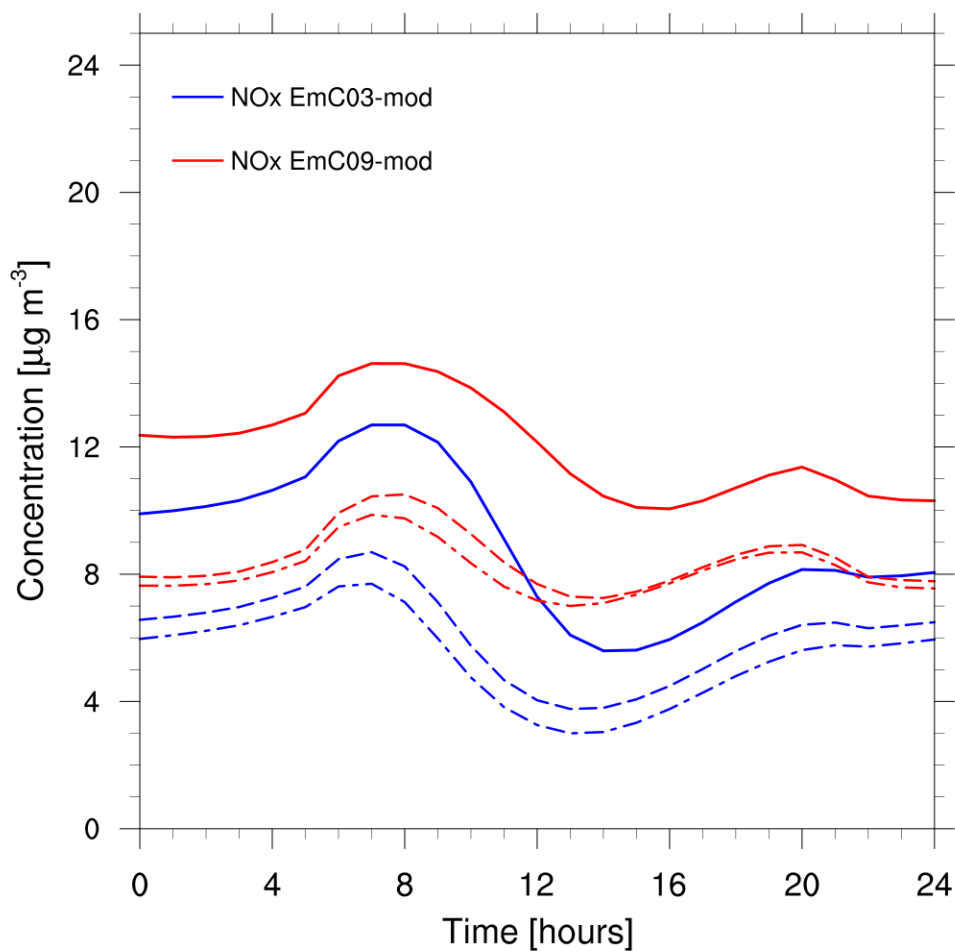| Station code	Station name	Coordinates (UTM 32N); height (a.s.l.)	Station type	O_3	SO_2	NO	NO_2	$PM_{2.5}$	PM_{10}
80KT	Altona-Elbhang	562611 E; 5933342 N; 25 m	ubg		X	X	X		X
21BI	Billbrook	571730 E; 5931713 N; 5 m	ind		X	X	X		X
51BF	Bramfeld	573434 E; 5943029 N; 31 m	ubg	X		X	X		
72FI	Finkenwerder West	555949 E; 5932255 N; 0 m	ind			X	X		X
68HB	Habichtstrasse	569743 E; 5938684 N; 12 m	tra			X	X	X	X
64KS	Kieler Strasse	562563 E; 5935470 N; 16 m	tra			X	X	X	
70MB	Max-Brauer Allee	562473 E; 5934507 N; 25 m	tra			X	X		X
17SM	Stresemannstrasse	563414 E; 5935091 N; 20 m	tra			X	X		X
52NG	Neugraben	556885 E; 5926120 N; 3 m	ubg	X		X	X		
13ST	Sternschanze	564134 E; 5935504 N; 15 m	ubg	X	X	X	X	X	X
20VE	Veddel	567752 E; 5930928 N; 5 m	ind		X	X	X	X	X
61WB	Wilhelmsburg	565692 E; 5929231 N; 3 m	ubg		X	X	X	X	X
54BL	Blankenese	552066 E; 5935753 N; 75 m	ubg	X		X	X		
27TA	Tatenberg	571900 E; 5927121 N; 2 m	ubg	X		X	X		
74BT	Billstedt	573088 E; 5932744 N; 18 m	ubg			X	X		

Figure S1: Comparison of the daily NO_X concentration ($\mu g\ m^{-3}$) cycle with EmChem09-mod (red lines) with EmChem03-mod (blue lines) for three different VOC/NO_X ratios. As average from a test run with NO_X emission of $4.3 \times 10^{-8}\ g\ s^{-1}\ m^{-2}$ and NMVOC emissions corresponding to a VOC/NO_X ratio of 4:1 (solid lines), 8:1 (dashed lines) and 15:1 (dash-dotted lines), respectively.
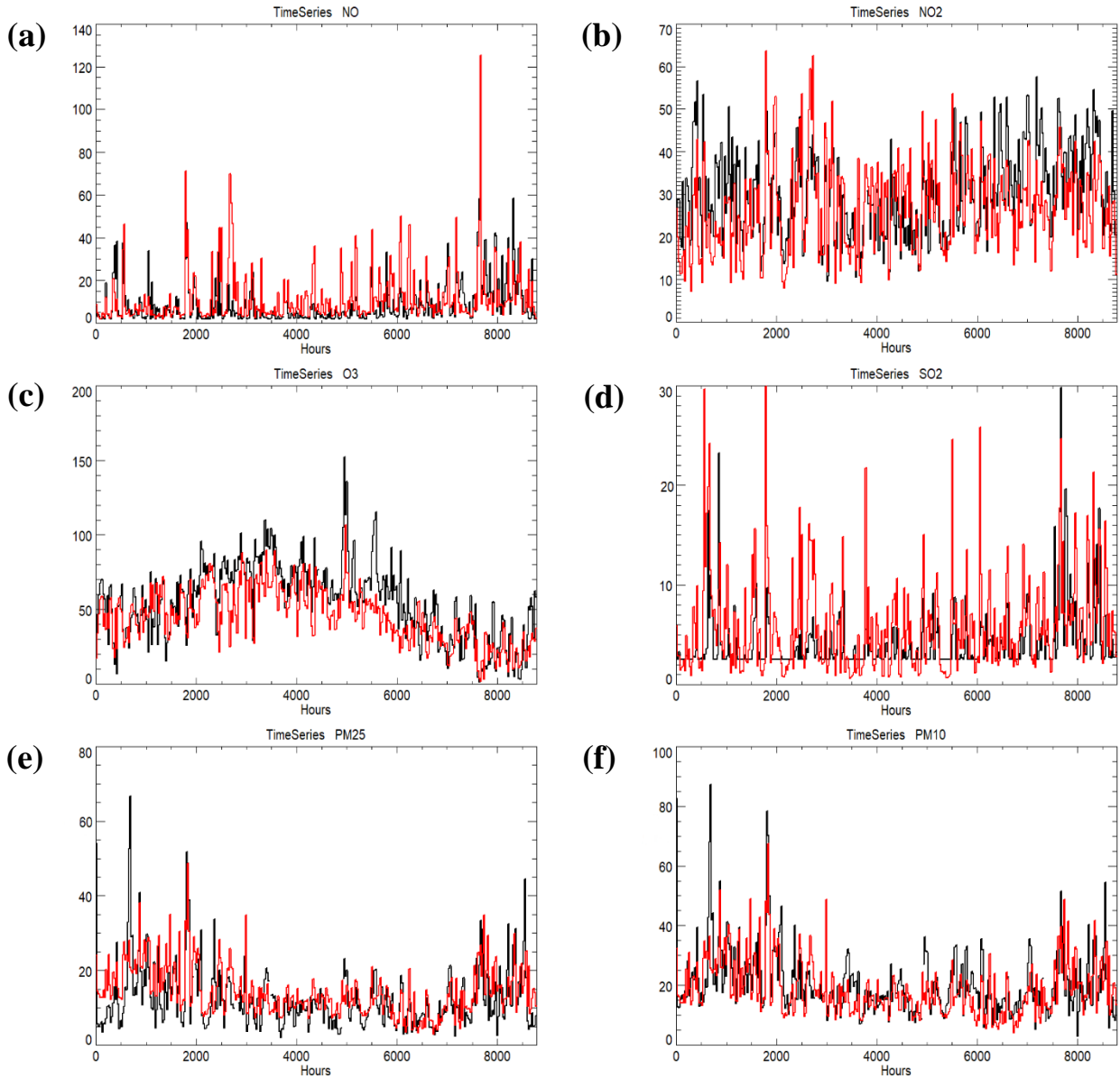
Figure S2: Time series comparing modelled and observed concentrations (in µg m^{-3}) at Sternschanze (station 13ST): (a) NO (daily mean), (b) NO$_2$ (daily mean), (c) O$_3$ (maximum of daily 8-h running mean), (d) SO$_2$ (daily mean), (e) PM$_{2.5}$ (daily mean), and (f) PM$_{10}$ (daily mean). Observed values black lines, modelled values indicated as red lines. Lowest value of SO$_2$ observation data is 2.5 µg m^{-3} (detection limit of the method).

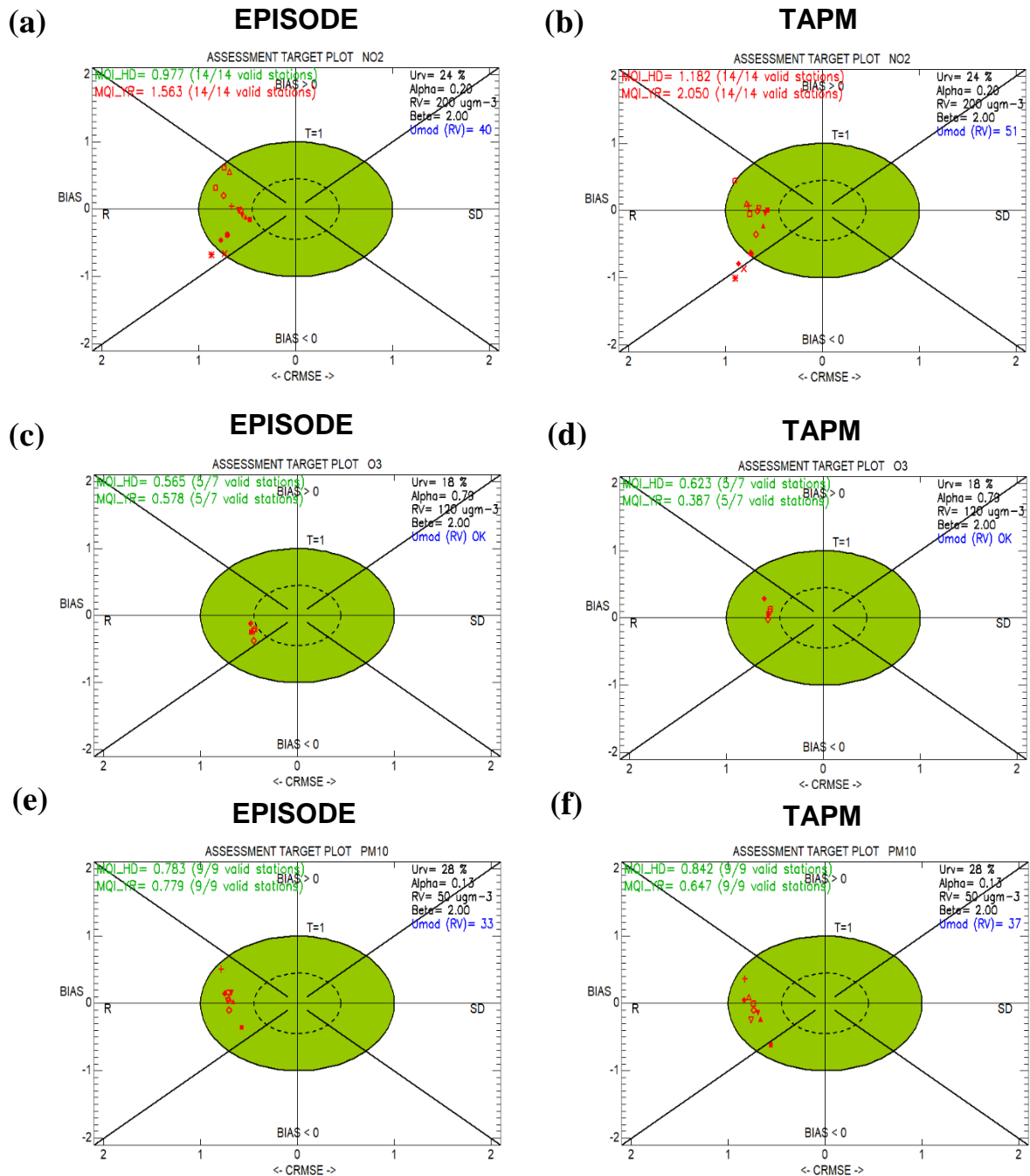**Figure S3:** Target diagram obtained from the FAIRMODE DELTA Tool for (a) NO_2 (hourly mean) by EPISODE, (b) NO_2 (hourly mean) by TAPM, (c) O_3 (maximum of daily 8-h running mean) by EPISODE, (d) O_3 (maximum of daily 8-h running mean) by TAPM, (e) PM_{10} (daily mean) by EPISODE, and (f) PM_{10} (daily mean) by TAPM.

References

Atkinson, R., Baulch, D. L., Cox, R.A., Crowley, J.N., Hampson, R. F., Hynes, R.G., Jenkin, M.

E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for

atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem.

Physics, 6, 3625–4055, https://doi.org/10.5194/acp-6-3625-2006, 2006.