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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

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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
<i>Inorganic chemistry</i>			
IN-1	OP + O2 + M	→ O3	$5.67\text{E-}34 \times M \times O2 \times (T/300)^{-2.8}$
IN-2	OD + M	→ 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	→ NO2	$ktr(\text{NO} + \text{OP})$
IN-4	OD + H2O	→ 2.0 OH	$2.2\text{E-}10 \times \text{H2O}$
IN-5	O3 + NO	→ NO2 + O2	$1.4\text{E-}12 \exp(-1310/T)$
IN-6	O3 + NO2	→ NO3 + O2	$1.4\text{E-}12 \exp(-2470/T)$
IN-7	O3 + OH	→ HO2 + O2	$1.7\text{E-}12 \exp(-940/T)$
IN-8	O3 + HO2	→ OH + 2 O2	$2.03\text{E-}16 \times (300/T)^{-4.57} \exp(693/T)$
IN-9	NO + NO3	→ NO2 + NO2	$1.8\text{E-}11 \exp(110/T)$
IN-10	NO + HO2	→ NO2 + OH	$3.6\text{E-}12 \exp(270/T)$
IN-11	NO3 + HO2	→ NO2 + OH + O2	$3.5\text{E-}12$
IN-12	NO2 + NO3	→ N2O5	$ktr(\text{NO2} + \text{NO3})$
IN-13	NO2 + OH + M	→ HNO3	$ktr(\text{NO2} + \text{OH})$
IN-14	N2O5	→ NO2 + NO3	$ktr(\text{N2O5})$
IN-15	OH + H2	→ HO2 + H2O	$7.7\text{E-}12 \exp(-2100/T)$
IN-16	OH + HO2	→ O2 + H2O	$4.8\text{E-}11 \exp(250/T)$
IN-17	OH + H2O2	→ HO2 + H2O	$2.9\text{E-}12 \exp(-160/T)$
IN-18	HO2 + HO2	→ H2O2	$FH2O \times 2.2\text{E-}13 \exp(600/T)$
IN-19	HO2 + HO2 + M	→ H2O2	$FH2O \times 1.9\text{E-}33 \exp(980/T)$

Table S1: Continued.

IN-20	OH + HNO ₃	→ NO ₃ + H ₂ O	$k(\text{OH} + \text{HNO}_3)$
IN-21	SO ₂ + OH	→ HO ₂ + H ₂ SO ₄	$ktr(\text{SO}_2 + \text{OH})$
IN-22	SO ₂ + CH ₃ O ₂	→ H ₂ SO ₄ + HCHO + HO ₂	4.0E-17
IN-23	OH + HONO	→ NO ₂	$2.5\text{E-}12 \exp(-260/T)$
IN-24	OH + NO	→ HONO	$ktr(\text{OH} + \text{NO})$
<i>Heterogeneous chemistry</i>			
HE-1	H ₂ SO ₄	→ aerosol sink	$5.0\text{E-}6 \times M / 2.55\text{E}19$
<i>Methane chemistry</i>			
MA-1	OH + CH ₄	→ CH ₃ O ₂	$1.85\text{E-}20 \times T^{2.8} \times \exp(-987/T)$
MA-2	CH ₃ O ₂ + NO	→ HCHO + HO ₂ + NO ₂	$2.3\text{E-}12 \exp(360/T)$
MA-3	CH ₃ O ₂ + NO ₃	→ HCHO + HO ₂ + NO ₂	1.3E-12
MA-4	OH + CH ₃ OH	→ HO ₂ + HCHO + H ₂ O	$6.38\text{E-}18 \exp(144/T) \times T^2$
MA-5	HO ₂ + CH ₃ O ₂	→ 0.9 CH ₃ O ₂ H + 0.1 HCHO	$3.8\text{E-}13 \exp(780/T)$
MA-6	CH ₃ O ₂ H + OH	→ HCHO + OH	$1.0\text{E-}12 \exp(190/T)$
MA-7	CH ₃ O ₂ H + OH	→ CH ₃ O ₂ + H ₂ O	$1.9\text{E-}12 \exp(190/T)$
MA-8	OH + HCHO	→ CO + HO ₂ + HO ₂	$1.25\text{E-}17 \times T^2 \times \exp(615/T)$
MA-9	NO ₃ + HCHO	→ HNO ₃ + CO + HO ₂	$2.0\text{E-}12 \exp(-2440/T)$
MA-10	OH + CO	→ HO ₂ + CO ₂	$1.44\text{E-}13 + 3.43\text{E-}33 \times M$
<i>Ethane and ethanol chemistry</i>			
EA-1	OH + C ₂ H ₆	→ C ₂ H ₅ O ₂ + H ₂ O	$6.9\text{E-}12 \exp(-1000/T)$
EA-2	C ₂ H ₅ O ₂ + NO	→ HO ₂ + CH ₃ CHO + NO ₂	$2.55\text{E-}12 \exp(380/T)$
EA-3	C ₂ H ₅ O ₂ + NO ₃	→ HO ₂ + CH ₃ CHO + NO ₂	2.3E-12

Table S1: Continued.

EA-4	OH + CH ₃ CHO	→ 0.95 CH ₃ COO ₂ + 0.05 CH ₃ O ₂ + 0.05 CO	4.4E-12 exp(365/ <i>T</i>)
EA-5	CH ₃ COO ₂ + NO ₂ + M	→ PAN	<i>ktr</i> (CH ₃ COO ₂ + NO ₂)
EA-6	PAN + M	→ CH ₃ COO ₂ + NO ₂	<i>ktr</i> (PAN)
EA-7	CH ₃ COO ₂ + NO	→ NO ₂ + CH ₃ O ₂ + CO ₂	7.5E-12 exp(290/ <i>T</i>)
EA-8	OH + C ₂ H ₅ OH	→ CH ₃ CHO + HO ₂	6.7E-18 exp(511/ <i>T</i>) × <i>T</i> ²
<i>n</i> -butane chemistry			
NB-1	OH + NC ₄ H ₁₀	→ SECC ₄ H ₉ O ₂	2.03E-17 exp(78/ <i>T</i>) × <i>T</i> ²
NB-2	NO + SECC ₄ H ₉ O ₂	→ NO ₂ + 0.65 HO ₂ + 0.65 CH ₃ COC ₂ H ₅ + 0.35 CH ₃ CHO + 0.35 C ₂ H ₅ O ₂	2.54E-12 exp(360/ <i>T</i>)
NB-3	OH + CH ₃ COC ₂ H ₅	→ CH ₃ COCHO ₂ CH ₃	2.53E-18 exp(503/ <i>T</i>) × <i>T</i> ²
NB-4	CH ₃ COCHO ₂ CH ₃ + NO	→ NO ₂ + CH ₃ COO ₂ + CH ₃ CHO	2.54E-12 exp(360/ <i>T</i>)
<i>Ethene chemistry</i>			
EE-1	C ₂ H ₄ + OH + M	→ CH ₂ O ₂ CH ₂ OH	<i>ktr</i> (OH + C ₂ H ₄)
EE-2	CH ₂ O ₂ CH ₂ OH + NO	→ NO ₂ + 2 HCHO + HO ₂	2.54E-12 exp(360/ <i>T</i>)
EE-3	C ₂ H ₄ + O ₃	→ 1.14 HCHO + 0.63 CO + 0.13 HO ₂ + 0.13 OH + 0.14 H ₂ O ₂	9.1E-15 exp(-2580/ <i>T</i>)
<i>Propene chemistry</i>			
PE-1	OH + C ₃ H ₆ + M	→ CH ₃ CHO ₂ CH ₂ OH	<i>ktr</i> (OH + C ₃ H ₆)
PE-2	NO + CH ₃ CHO ₂ CH ₂ OH	→ NO ₂ + CH ₃ CHO + HCHO + HO ₂	2.54E-12 exp(360/ <i>T</i>)
PE-3	O ₃ + C ₃ H ₆	→ 0.545 HCHO + 0.545 CH ₃ CHO + 0.56 CO + 0.36 OH + 0.28 HO ₂ + 0.09 H ₂ O ₂ + 0.1 CH ₄ + 0.28 CH ₃ O ₂	5.5E-15 exp(-1880/ <i>T</i>)

Table S1: Continued.

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

Table S1: Continued.

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

Notes:

Special rate constants and reaction parameters:

$$FH2O = 1 + 1.4E-21 \exp(2200/T) \times H2O;$$

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

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:

$ktr(\text{NO}+\text{OP}): k_0/M = 1.0\text{E-}31 (300/T)^{1.6}$, $k_\infty = 3.0\text{E-}11 (300/T)^{-0.3}$, $F_c = 0.85$;
 $ktr(\text{NO}_2+\text{NO}_3): k_0/M = 3.6\text{E-}30 (300/T)^{4.1}$, $k_\infty = 9.7\text{E-}12 (300/T)^{-0.2}$, $F_c = 0.35$;
 $ktr(\text{NO}_2+\text{OH}): k_0/M = 3.3\text{E-}30 (300/T)^{3.0}$, $k_\infty = 4.1\text{E-}11$, $F_c = 0.40$;
 $ktr(\text{N}_2\text{O}_5): k_0/M = 1.3\text{E-}3 (300/T)^{3.5} \exp(-11000/T)$, $k_\infty = 9.7\text{E}14 (300/T)^{-0.1} \exp(-11080/T)$;
 $ktr(\text{OH}+\text{NO}): k_0/M = 7.4\text{E-}31 (300/T)^{2.4}$, $k_\infty = 3.3\text{E-}11 (300/T)^{0.3}$, $F_c = \exp(-T/1420)$;
 $ktr(\text{CH}_3\text{OO}_2 + \text{NO}_2): k_0/M = 2.7\text{E-}28 (300/T)^{7.1}$, $k_\infty = 1.2\text{-}11 (300/T)^{0.9}$, $F_c = 0.3$;
 $ktr(\text{PAN}): k_0/M = 4.9\text{E-}3 (300/T)^{-12100}$, $k_\infty = 5.4\text{E}16 \exp(-13830/T)$, $F_c = 0.3$;
 $ktr(\text{OH}+\text{C}_2\text{H}_4): k_0/M = 8.6\text{E-}29 (300/T)^{3.1}$, $k_\infty = 9.0\text{E-}12 (300/T)^{0.85}$, $F_c = 0.48$;
 $ktr(\text{OH}+\text{C}_3\text{H}_6): k_0/M = 8.0\text{E-}27 (300/T)^{3.5}$, $k_\infty = 3.0\text{E-}11 (300/T)$, $F_c = 0.5$;
 $ktr(\text{SO}_2+\text{OH}): k_0/M = 4.0\text{E-}31 (300/T)^{-3.3}$, $k_\infty = 2.0\text{E-}12$, $F = 0.45^{1/(1 + \log_{10}(k_0/k_\infty)^2)}$

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	→ 2. HCHO + 2. HO2	7.4E-13 exp(-520/T)
MA-12	CH3O2 + CH3O2	→ CH3OH + HCHO	1.03E-13 exp(365/T) – 7.4E-13 exp(-520/T)
EA-9	C2H5O2 + HO2	→ C2H5OOH	3.8E-13 exp(900/T)
EA-10	C2H5OOH + OH	→ CH3CHO + OH	8.01E-12
EA-11	C2H5OOH + OH	→ C2H5O2	1.9E-12 exp(190/T)
EA-12	CH3COO2 + HO2	→ 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	→ CH3COO2	1.9E-12 exp(190/T)
EA-14	CH3O2 + CH3COO2	→ 0.9 HO2 + HCHO + 0.9 CH3O2 + 0.1 CH3COOH	2.0E-12 exp(500/T)
EA-15	CH3COO2 + CH3COO2	→ CH3O2 + CH3O2	2.9E-12 exp(500/T)
NB-5	SECC4H9O2 + HO2	→ 0.95 BURO2H	0.625 × 2.91E-13 exp(1300/T)
NB-6	CH3COCHO2CH3 + HO2	→ MEKO2H	0.625 × 2.91E-13 exp(1300/T)
NB-7	MEKO2H + OH	→ CH3COCHO2CH3	1.9E-12 exp(190/T)
NB-8	BURO2H + OH	→ SECC4H9O2	1.9E-12 exp(190/T)
NB-9	BURO2H + OH	→ OH + CH3COC2H5	2.15E-11
EE-4	CH2O2CH2OH + HO2	→ ETRO2H	1.2E-11
EE-5	ETRO2H + OH	→ CH3CHO + OH	1.38E-11
EE-6	ETRO2H + OH	→ CH2O2CH2OH	1.9E-12 exp(190/T)
PE-4	CH3CHO2CH2OH + HO2	→ 0.795 PRRO2H	0.52 × 2.91E-13 exp(1300/T)
PE-5	PRRO2H + OH	→ CH3COCH2OH + OH	2.44E-11

Table S2: Continued.

PE-6	CH ₃ COCH ₂ OH + OH	→ CH ₃ COCHO + HO ₂	1.6E-12 exp(305/ <i>T</i>)
PE-7	PRRO ₂ H + OH	→ CH ₃ CHO ₂ CH ₂ OH	1.9E-12 exp(190/ <i>T</i>)
OX-7	OXYLOHO ₂ + HO ₂	→ 0.227 OXYO ₂ H	0.859 × 2.91E-13 exp(1300/ <i>T</i>)
OX-8	OXYO ₂ H + OH	→ OXYLOHO ₂	4.2E-11
OX-9	MEMALDIAL + HO ₂	→ MEMALO ₂ H	0.706 × 2.91E-13 exp(1300/ <i>T</i>)
OX-10	MEMALO ₂ H + OH	→ MEMALO ₂	1.9E-12 exp(190/ <i>T</i>)
IS-5	ISOPO ₂ + HO ₂	→ 0.857 ISRO ₂ H	1.4E-12 exp(-180/ <i>T</i>)
IS-6	ISRO ₂ H + OH	→ OH + ISOPO ₂	7.5E-11
IS-7	MVKO ₂ + HO ₂	→ MVKO ₂ H	0.625 × 2.91E-13 exp(1300/ <i>T</i>)
IS-8	MVKO ₂ H + OH	→ MVKO ₂	2.2E-11
<i>Monoterpene chemistry</i>			
MT-1	APINENE + OH	→ PRODAPINOH + MTO ₂	1.2E-11 exp(444/ <i>T</i>)
MT-2	APINENE + NO ₃	→ PRODAPINNO ₃ + MTO ₂	1.2E-12 exp(490/ <i>T</i>)
MT-3	APINENE + O ₃	→ 0.8 PRODAPINO ₃ + 0.8 MTO ₂ + 0.2 BLOC + 0.46 OH	6.3E-16 exp(-580/ <i>T</i>)
MT-4	LIMONENE + OH	→ PRODLIMO ₂ OH + MTO ₂	1.7E-10
MT-5	LIMONENE + NO ₃	→ PRODLIMONO ₃ + MTO ₂	1.3E-11
MT-6	LIMONENE + O ₃	→ PRODLIMO ₂ O ₃ + 0.67 OH + 0.19 HCHO + MTO ₂	2.0E-16
MT-7	MTO ₂ + NO	→ NO ₂ + HO ₂ + 0.78 MTKETONE	2.54E-12 exp(360/ <i>T</i>)
MT-8	MTO ₂ + HO ₂	→ 0.493 MTO ₂ H	0.914 × 2.91E-13 exp(1300/ <i>T</i>)
MT-9	MTO ₂ + CH ₃ O ₂	→ MTO ₂ H	2.91E-13 exp(1300/ <i>T</i>)
MT-10	MTO ₂ + C ₂ H ₅ O ₂	→ MTO ₂ H	2.91E-13 exp(1300/ <i>T</i>)

Table S2: Continued.

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

Table S2: Continued.

<i>Photolysis reactions</i>							
				ϵ_1	ϵ_2	ϵ_3	ϵ_4
PH-17	C2H5OOH	→	HO2 + CH3CHO + OH	2.27E-05	0.620	0.88	0.35
PH-18	ETRO2H	→	HO2 + OH + 1.56 HCHO + 0.22 CH3CHO	2.27E-05	0.620	0.88	0.35
PH-19	BURO2H	→	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	→	CH3CHO + HCHO + HO2	2.27E-05	0.620	0.88	0.35
PH-21	MEKO2H	→	CH3CHO + CH3COO2 + OH	2.27E-05	0.620	0.88	0.35
PH-22	CH3COO2H	→	CH3O2 + OH	2.27E-05	0.620	0.88	0.35
PH-23	OXYO2H	→	OH + CH3COCHO + MEMALDIAL + HO2	2.27E-05	0.620	0.88	0.35
PH-24	MEMALO2H	→	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	→ O3	$5.67E-34 \times M \times O2 \times (T/300)^{-2.8}$			
IN-2	OD + M	→ OP	$1.8E-11 \exp(107/T) \times N2 + 3.2E-11 \exp(67/T) \times O2$			
IN-3	OP + NO + M	→ NO2	$ktr(NO + OP)$			
IN-4	OD + H2O	→ 2.0 OH	$2.2E-10 \times H2O$			
IN-5	O3 + NO	→ NO2 + O2	$1.4E-12 \exp(-1310/T)$			
IN-7	O3 + OH	→ HO2 + O2	$1.7E-12 \exp(-940/T)$			
IN-8	O3 + HO2	→ OH + 2 O2	$2.03E-16 \times (300/T)^{-4.57} \exp(693/T)$			
IN-10	NO + HO2	→ NO2 + OH	$3.6E-12 \exp(270/T)$			
IN-13	NO2 + OH + M	→ HNO3	$ktr(NO2 + OH)$			
MA-8	OH + HCHO	→ CO + HO2 + HO2	$1.25E-17 \times T^2 \times \exp(615/T)$			
MA-10	OH + CO	→ HO2 + CO2	$1.44E-13 + 3.43E-33 \times M$			
			ϵ_1	ϵ_2	ϵ_3	ϵ_4
PH-1	O3	→ OD	2.00E-04	1.400	0.86	0.33
PH-2	O3	→ OP	1.23E-03	0.600	0.92	0.41
PH-3	NO2	→ OP + NO	1.45E-02	0.400	0.91	0.38
PH-5	HNO3	→ NO2 + OH	3.00E-06	1.250	0.87	0.33
PH-6	HCHO	→ CO + 2 HO2	5.40E-05	0.790	0.88	0.34
PH-7	HCHO	→ 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		

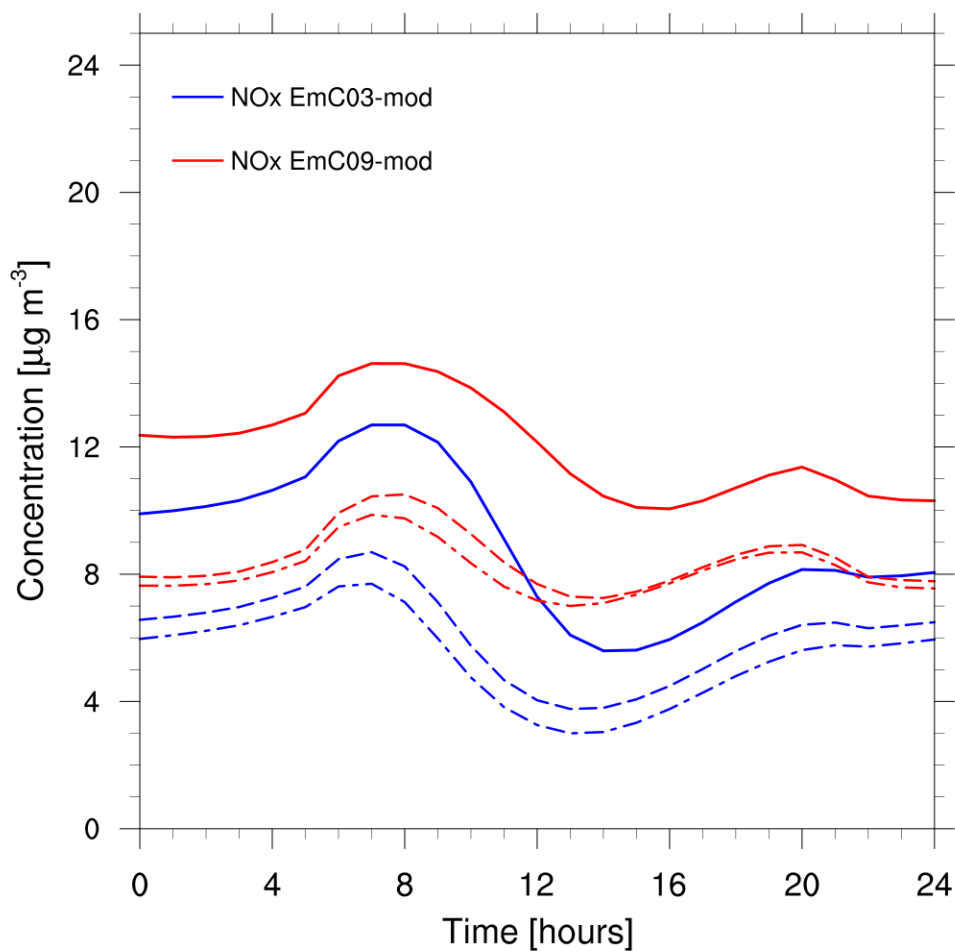


Figure S1: Comparison of the daily NO_x concentration (µg m⁻³) cycle with EmChem09-mod (red lines) with EmChem03-mod (blue lines) for three different VOC/NO_x ratios. As average from a test run with NO_x emission of $4.3 \times 10^{-8} \text{ g s}^{-1} \text{ m}^{-2}$ and NMVOC emissions corresponding to a VOC/NO_x ratio of 4:1 (solid lines), 8:1 (dashed lines) and 15:1 (dash-dotted lines), respectively.

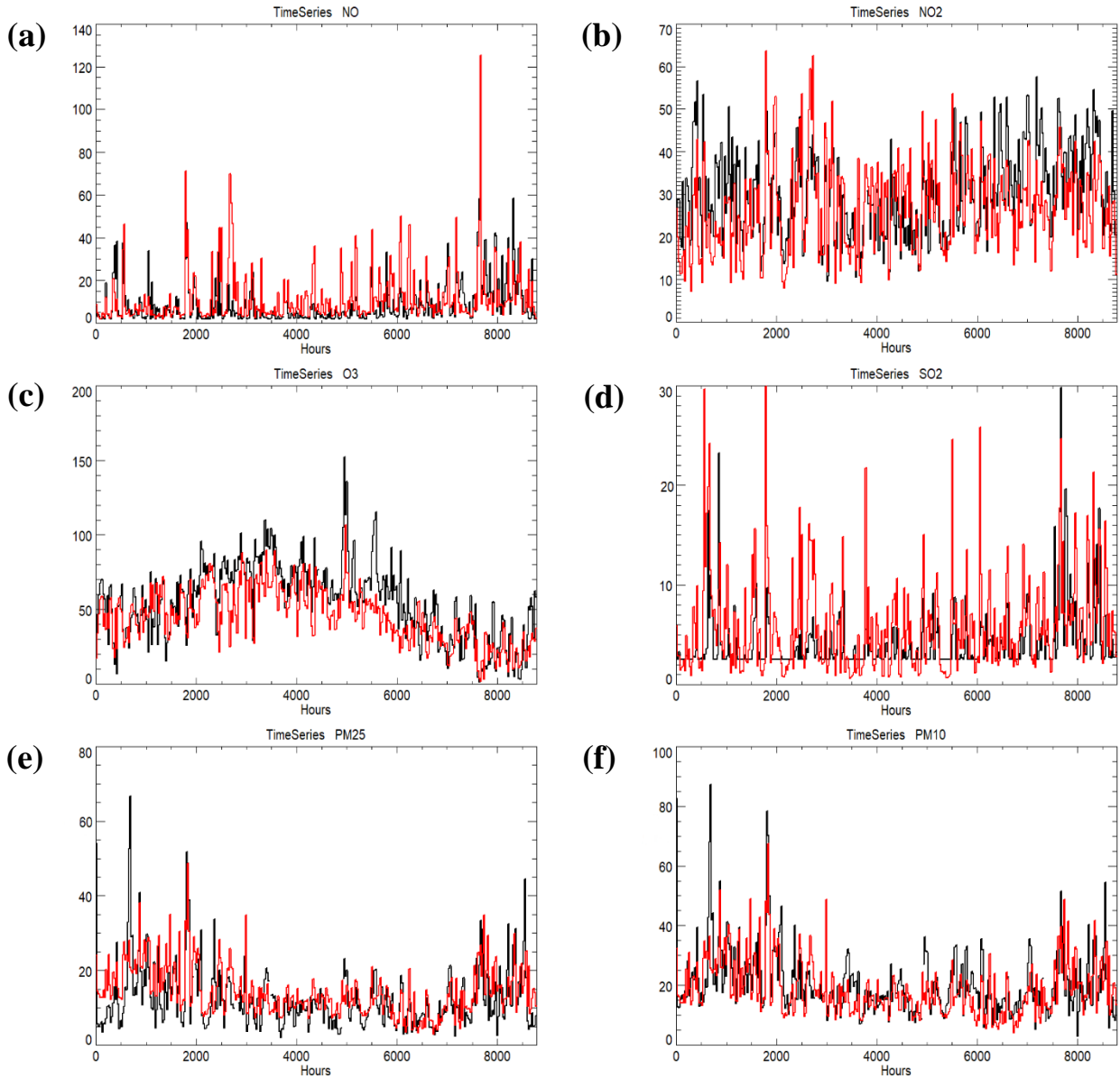


Figure S2: Time series comparing modelled and observed concentrations (in $\mu\text{g m}^{-3}$) at Sternschanze (station 13ST): (a) NO (daily mean), (b) NO₂ (daily mean), (c) O₃ (maximum of daily 8-h running mean), (d) SO₂ (daily mean), (e) PM_{2.5} (daily mean), and (f) PM₁₀ (daily mean). Observed values black lines, modelled values indicated as red lines. Lowest value of SO₂ observation data is 2.5 $\mu\text{g m}^{-3}$ (detection limit of the method).

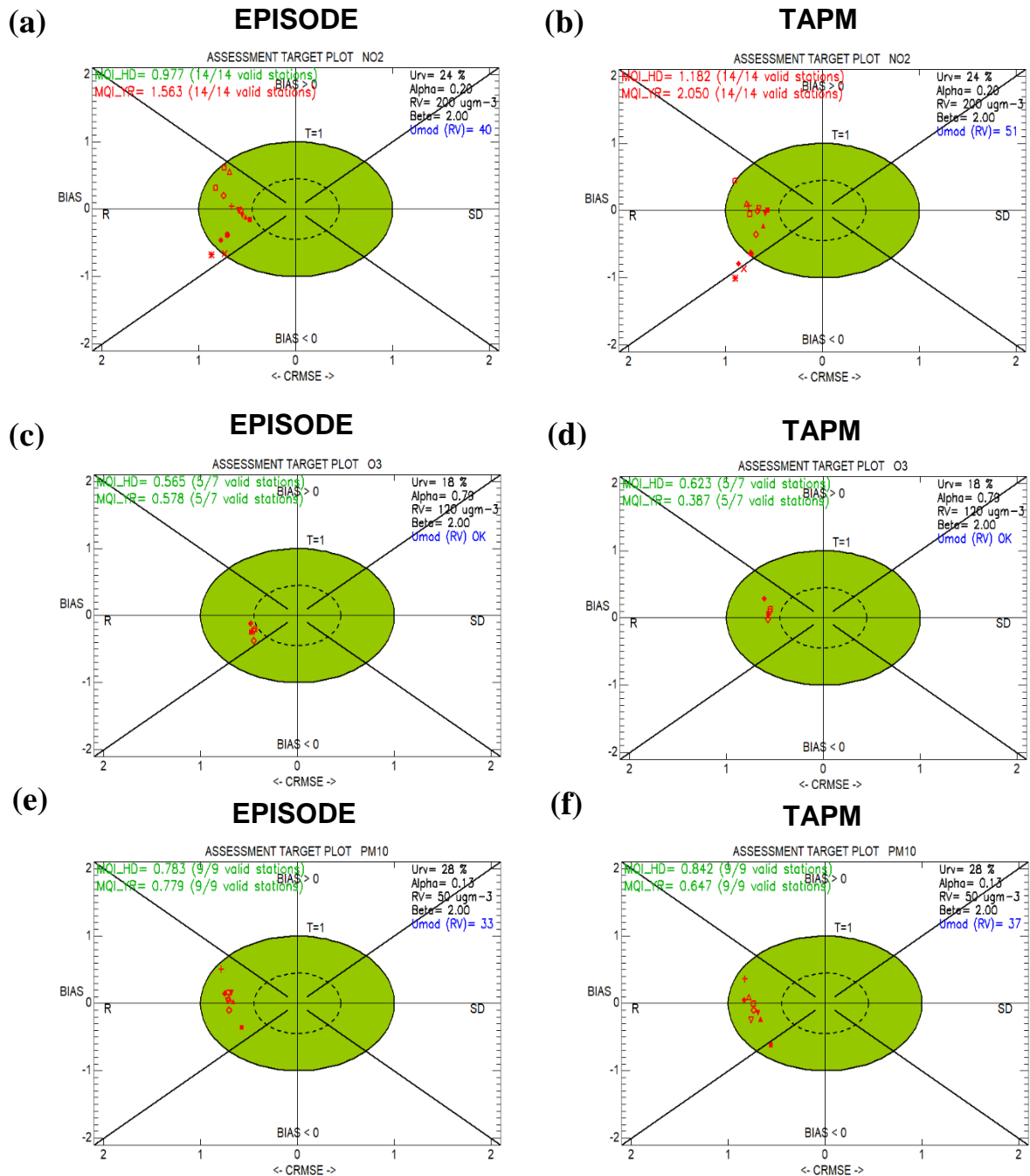


Figure S3: Target diagram obtained from the FAIRMODE DELTA Tool for (a) NO₂ (hourly mean) by EPISODE, (b) NO₂ (hourly mean) by TAPM, (c) O₃ (maximum of daily 8-h running mean) by EPISODE, (d) O₃ (maximum of daily 8-h running mean) by TAPM, (e) PM₁₀ (daily mean) by EPISODE, and (f) PM₁₀ (daily mean) by TAPM.

References

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