Supplementary Materials

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

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Table S1: Atmospheric stability classes in the sub-grid model components.

Stability class	Name	Temperature difference ΔT between 10 m and 25 m	Mapping to P-G class	Line-source parameterization of ambient turbulence			
				a	b	c	d
1	Unstable	ΔT < -0.5°	A, B, C	110.62	0.932	18.333	1.8096
2	Neutral	-0.5° < ΔT < 0.0°	D	86.49	0.923	14.333	1.7706
3	Moderately stable	0.0° < ΔT < 0.5°	E	61.14	0.915	12.5	1.0857
4	Stable	ΔT > 0.5°	F	61.14	0.915	12.5	1.0857

Table S2: 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)

Table S2: Continued.

IN-9	NO + NO3	$\longrightarrow$	NO2 + NO2	1.8E-11 exp(110/T)
IN-10	NO + HO2	$\longrightarrow$	NO2 + OH	3.6E-12 exp(270/T)
IN-11	NO3 + HO2	$\longrightarrow$	NO2 + OH + O2	3.5E-12
IN-12	NO2 + NO3	$\longrightarrow$	N2O5	ktr(NO2 + NO3)
IN-13	NO2 + OH + M	$\longrightarrow$	HNO3	ktr(NO2 + OH)
IN-14	N2O5	$\longrightarrow$	NO2 + NO3	ktr(N2O5)
IN-15	OH + H2	$\longrightarrow$	HO2 + H2O	7.7E-12 exp(-2100/T)
IN-16	OH + HO2	$\longrightarrow$	O2 + H2O	4.8E-11 exp(250/T)
IN-17	OH + H2O2	$\longrightarrow$	HO2 + H2O	2.9E-12 exp(-160/T)
IN-18	HO2 + HO2	$\longrightarrow$	H2O2	$FH2O$ × 2.2E-13 exp(600/T)
IN-19	HO2 + HO2 + M	$\longrightarrow$	H2O2	$FH2O$ × 1.9E-33 exp(980/T)
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}

Table S2: Continued.

MA-5	HO2 + CH3O2	⟶	0.9 CH3O2H + 0.1 HCHO	3.8E-13 exp(780/T)
MA-6	CH3O2H + OH	⟶	HCHO + OH	1.0E-12 exp(190/T)
MA-7	CH3O2H + OH	⟶	CH3O2 + H2O	1.9E-12 exp(190/T)
MA-8	OH + HCHO	⟶	CO + HO2 + HO2	1.25E-17 × T^2 × exp(615/T)
MA-9	NO3 + HCHO	⟶	HNO3 + CO + HO2	2.0E-12 exp(-2440/T)
MA-10	OH + CO	⟶	HO2 + CO2	1.44E-13 + 3.43E-33 × M
Ethane and ethanol chemistry				
EA-1	OH + C2H6	⟶	C2H5O2 + H2O	6.9E-12 exp(-1000/T)
EA-2	C2H5O2 + NO	⟶	HO2 + CH3CHO + NO2	2.55E-12 exp(380/T)
EA-3	C2H5O2 + NO3	⟶	HO2 + CH3CHO + NO2	2.3E-12
EA-4	OH + CH3CHO	⟶	0.95 CH3COO2 + 0.05 CH3O2 + 0.05 CO	4.4E-12 exp(365/T)
EA-5	CH3COO2 + NO2 + M	⟶	PAN	ktr(CH3OO2 + NO2)
EA-6	PAN + M	⟶	CH3COO2 + NO2	ktr(PAN)
EA-7	CH3COO2 + NO	⟶	NO2 + CH3O2 + CO2	7.5E-12 exp(290/T)
EA-8	OH + C2H5OH	⟶	CH3CHO + HO2	6.7E-18 exp(511/T) × T^2
n-butane chemistry				
NB-1	OH + NC4H10	⟶	SECC4H9O2	2.03E-17 exp(78/T) × T^2
NB-2	NO + SECC4H9O2	⟶	NO2 + 0.65 HO2 + 0.65 CH3COC2H5 + 0.35 CH3CHO + 0.35 C2H5O2	2.54E-12 exp(360/T)
NB-3	OH + CH3COC2H5	⟶	CH3COCHO2CH3	2.53E-18 exp(503/T) × T^2
NB-4	CH3COCHO2CH3 + NO	⟶	NO2 + CH3COO2 + CH3CHO	2.54E-12 exp(360/T)

Table S2: Continued.

Ethene chemistry				
EE-1	C2H4 + OH +M	⟶	CH2O2CH2OH	*ktr*(OH + C2H4)
EE-2	CH2O2CH2OH + NO	⟶	NO2 + 2 HCHO + HO2	2.54E-12 exp(360/T)
EE-3	C2H4 + O3	⟶	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	⟶	CH3CHO2CH2OH	*ktr*(OH + C3H6)
PE-2	NO + CH3CHO2CH2OH	⟶	NO2 + CH3CHO + HCHO + HO2	2.54E-12 exp(360/T)
PE-3	O3 + C3H6	⟶	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)
o-xylene chemistry				
OX-1	OXYL + OH	⟶	OXYLOHO2	1.36E-11
OX-2	OXYLOHO2 + NO	⟶	NO2 + CH3COCHO + MEMALDIAL + HO2	2.54E-12 exp(360/T)
OX-3	MEMALDIAL + OH	⟶	MEMALO2	5.58E-11
OX-4	MEMALO2 + NO	⟶	NO2 + HO2 + CH3COCHO + HCOCHO	2.54E-12 exp(360/T)
OX-5	OH + CH3COCHO	⟶	CH3COO2 + CO	1.9E-12 exp(575/T)
OX-6	OH + HCOCHO	⟶	HO2 + 2 CO	6.6E-18 exp(820/T) × T^2
Isoprene chemistry				
IS-1	C5H8 + OH	⟶	ISOPO2	2.7E-11 exp(390/T)
IS-2	ISOPO2 + NO	⟶	0.776 MVK + 0.776 HCHO + 0.12 ISOPO2 + HO2 + NO2	2.54E-12 exp(360/T)
IS-3	MVK + OH	⟶	MVKO2	4.1E-12 exp(453/T)
IS-4	MVKO2 + NO	⟶	CH3COCHO + HCHO + HO2 + NO2	1.4E-12 exp(-180/T)

Table S2: Continued.

Reaction no.	Educts		Products	ε_1	ε_2	ε_3	ε_4
Photolysis reactions							
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:

$FH2O = 1 + 1.4\text{E-}21 \exp(2200/T) \times \text{H2O}$;
$k(\text{OH + HNO3}) = K_1 + (K_3 \times \text{M})/(1.0 + (K_3 \times \text{M}/K_4)$ 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 S3: Additional chemical reactions and photo-dissociation reactions of EmChem09-mod. The scheme includes all reactions of EmChem03-mod given in Table S2.

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)

Table S3: Continued.

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
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

Table S3: Continued.

Monoterpene chemistry				
MT-1	APINENE + OH	⟶	PRODAPINOH + MTO2	1.2E-11 exp(444/T)
MT-2	APINENE + NO3	⟶	PRODAPINNO3 + MTO2	1.2E-12 exp(490/T)
MT-3	APINENE + O3	⟶	0.8 PRODAPINO3 + 0.8 MTO2 + 0.2 BLOC + 0.46 OH	6.3E-16 exp(-580/T)
MT-4	LIMONENE + OH	⟶	PRODLIMOOH + MTO2	1.7E-10
MT-5	LIMONENE + NO3	⟶	PRODLIMONO3 + MTO2	1.3E-11
MT-6	LIMONENE + O3	⟶	PRODLIMOO3 + 0.67 OH + 0.19 HCHO + MTO2	2.0E-16
MT-7	MTO2 + NO	⟶	NO2 + HO2 + 0.78 MTKETONE	2.54E-12 exp(360/T)
MT-8	MTO2 + HO2	⟶	0.493 MTO2H	0.914 × 2.91E-13 exp(1300/T)
MT-9	MTO2 + CH3O2	⟶	MTO2H	2.91E-13 exp(1300/T)
MT-10	MTO2 + C2H5O2	⟶	MTO2H	2.91E-13 exp(1300/T)
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
Semi-volatile organic compounds				
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)

Table S3: Continued.

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

Photolysis reactions

				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 S4: 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 × 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-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-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 × T^2 × exp(615/T)
MA-10	OH + CO	⟶	HO2 + CO2	1.44E-13 + 3.43E-33 × 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 S5: Comparison of performance statistics of CMAQ (4-km res.), EPISODE-CityChem and TAPM for NO_2 based on hourly concentration values for a 14 days period in July 2012 at four urban background monitoring stations. Observed mean concentrations at 52NG, 51BF, 13ST and 27TA are 8.67, 11.96, 21.50, and 12.73 µg m^{-3}, respectively. Number of observations: $N = 336$.

Station code	Model	$\overline{M}$ [µg/m^{-3}]	Bias [µg/m^{-3}]	Corr [-]	RMSE [µg/m^{-3}]
52NG	CMAQ	9.43	0.76	0.55	8.27
	EPISODE-CC	4.32	-4.35	0.66	4.69
	TAPM	6.44	-2.23	0.73	5.57
51BF	CMAQ	7.44	-4.52	0.69	4.11
	EPISODE-CC	7.02	-4.94	0.48	4.65
	TAPM	10.00	-1.95	0.51	8.13
13ST	CMAQ	13.65	-7.85	0.61	7.77
	EPISODE-CC	21.98	0.47	0.58	10.19
	TAPM	20.54	-0.96	0.57	13.09
27TA	CMAQ	10.12	-2.61	0.45	5.38
	EPISODE-CC	8.37	-4.36	0.38	7.54
	TAPM	33.06	20.33	0.20	13.63

Table S6: 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 (STD; observed, modelled), overall bias (Bias), correlation (Corr), root mean squared error (RMSE), and index of agreement (IOA).

Station	Meteorological variable	N	$\bar{O}$	$\bar{M}$	STD_O	STD_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 S7: 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		

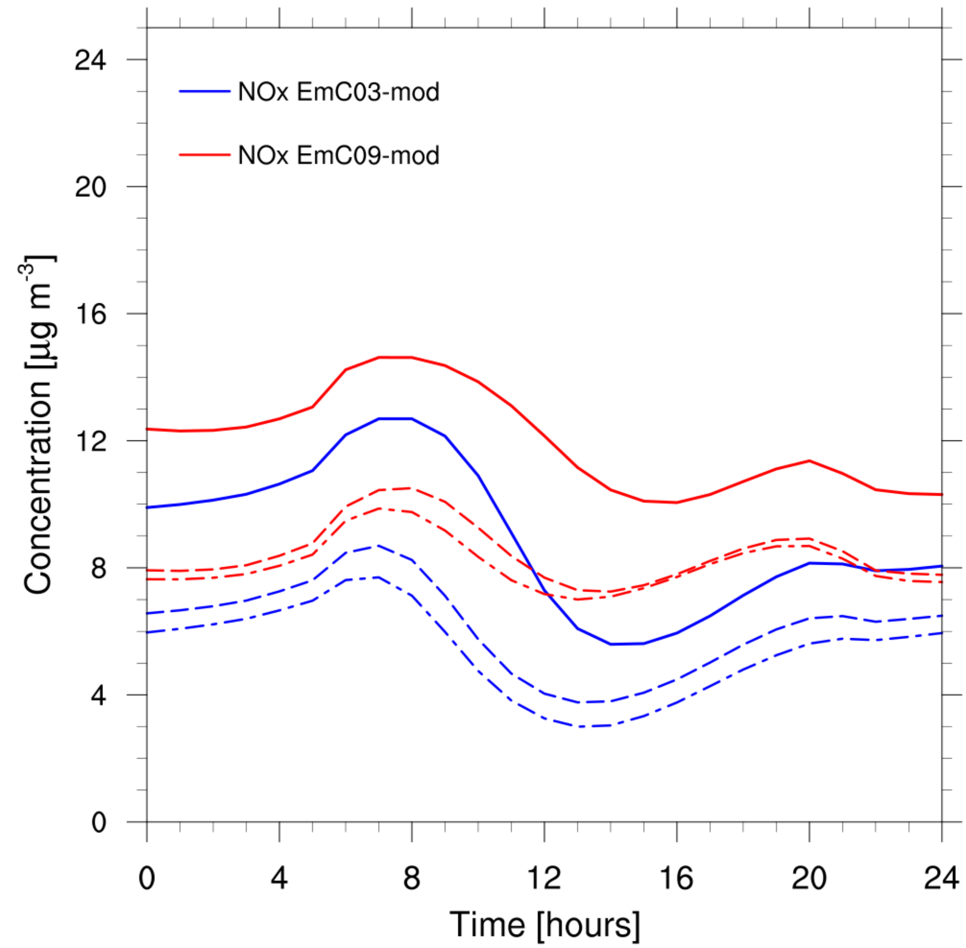
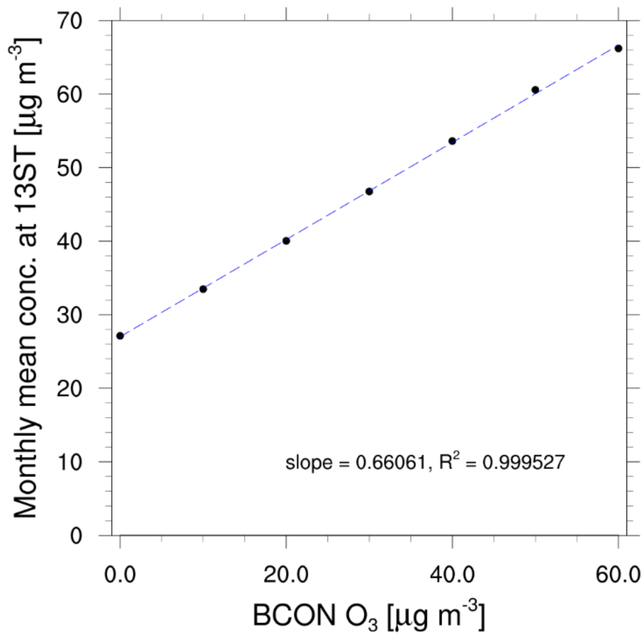


Figure S1: Comparison of the daily NO_X concentration (μg m^{-3}) cycle with EmChem09-mod (red lines) with EmChem03-mod (blue lines) for three different VOC/NO_X ratios. As average from a test run with NO_X emission of 4.3×10^{-8} g s^{-1} m^{-2} and NMVOC emissions corresponding to a VOC/NO_X ratio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

(a)



(b)

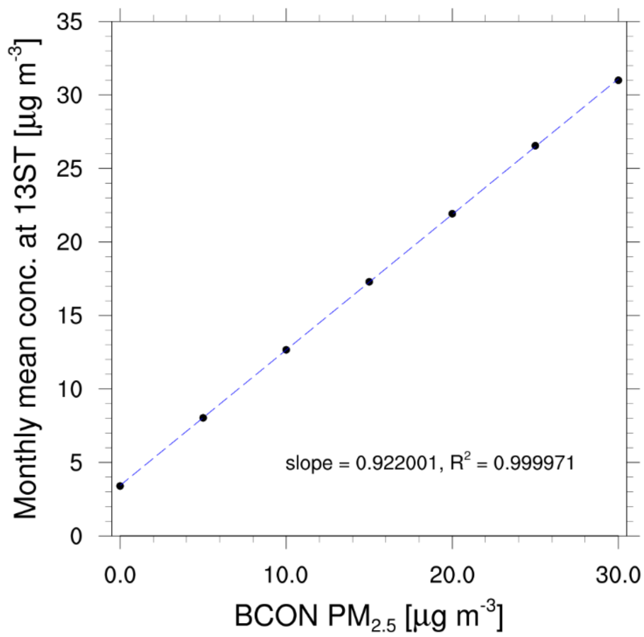


Figure S2: Test of the boundary conditions for the lateral entrainment into the model domain of Hamburg. Relationship between the monthly mean concentration (July 2012) in the grid cell where station 13ST is located and the BCON offset added to the CMAQ concentrations at the lateral boundaries: (a) for O_3 and (b) for $PM_{2.5}$. Zero BCON offset corresponds to the original boundary conditions from CMAQ.

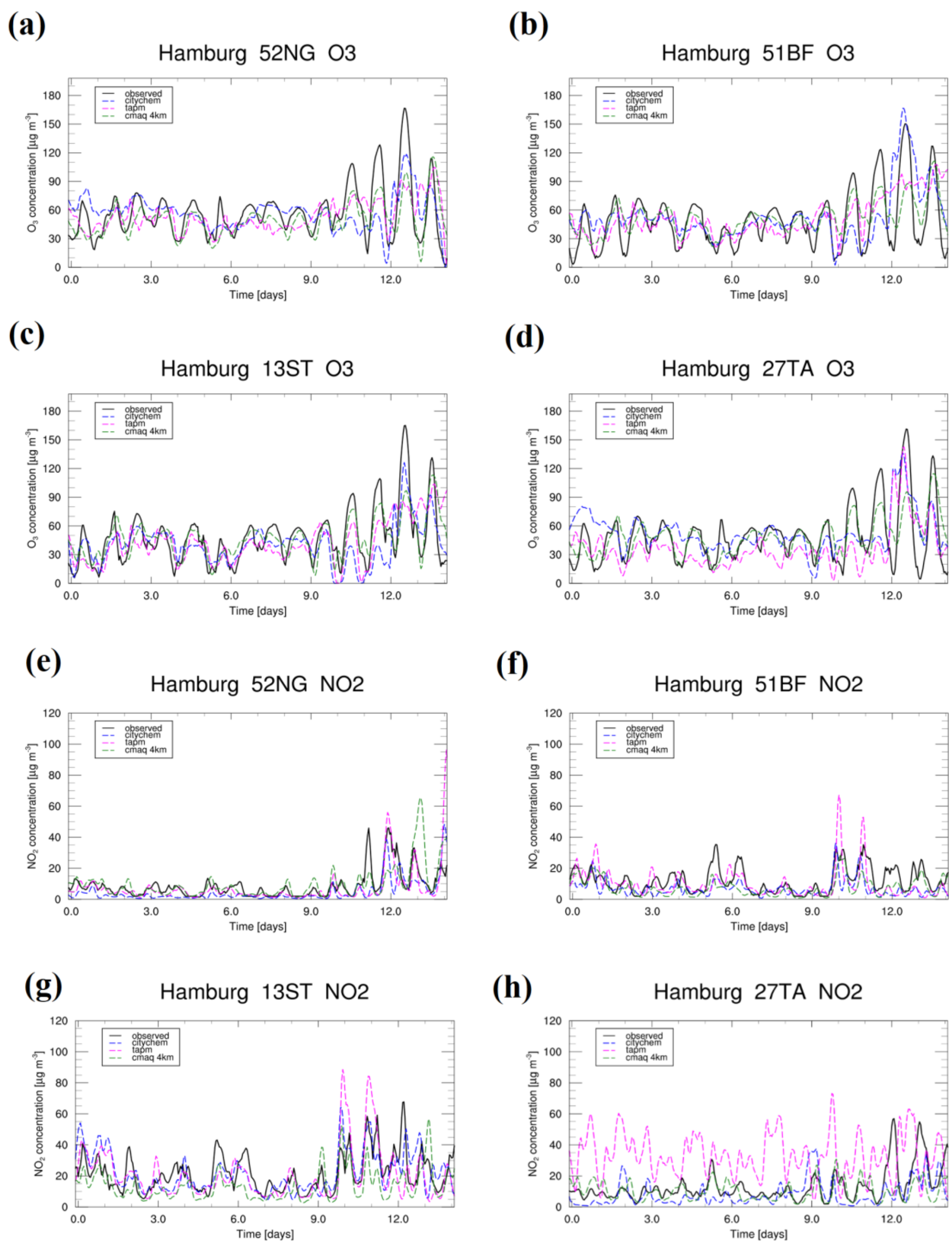
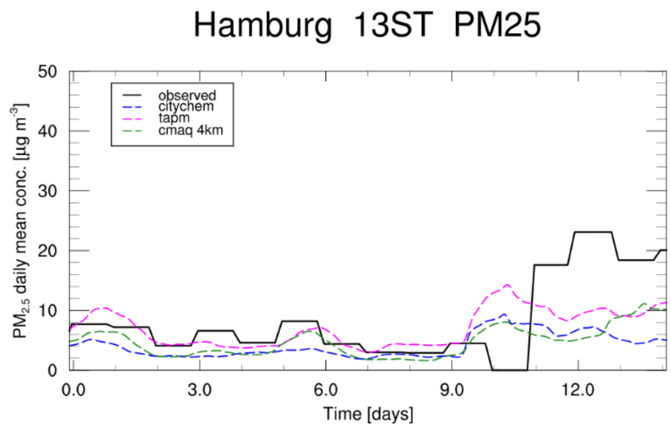


Figure S3. Comparison of EPISODE-CityChem (blue) with TAPM (magenta) and CMAQ (dark green) for (a) - (d) O_3 hourly concentrations (in µg m^{-3}) and (e) - (h) NO_2 hourly concentrations (in µg m^{-3}) at urban background stations (52NG, 51BF, 13ST, 27TA) during a 14-days period (12 - 25 July 2012). Observations are shown as black lines.

(a)



(b)

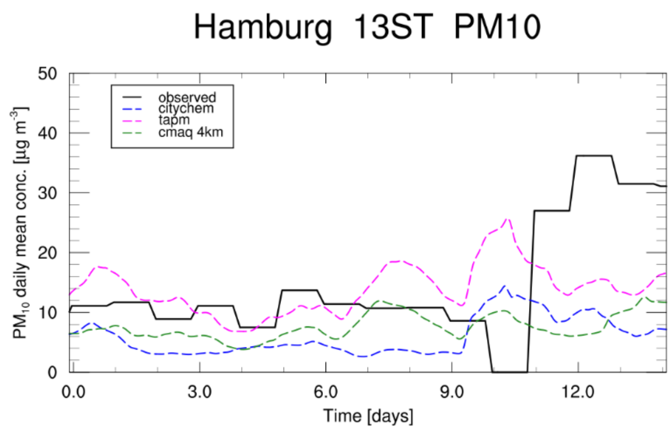


Figure S4: Comparison of EPISODE-CityChem (blue) with TAPM (magenta) and CMAQ (dark green) for (a) $PM_{2.5}$ daily mean concentrations (µg m^{-3}) and (b) PM_{10} daily mean concentrations (µg m^{-3}) at urban background station 13ST during a 14-days period (12 - 25 July 2012). Observations are shown as black lines.

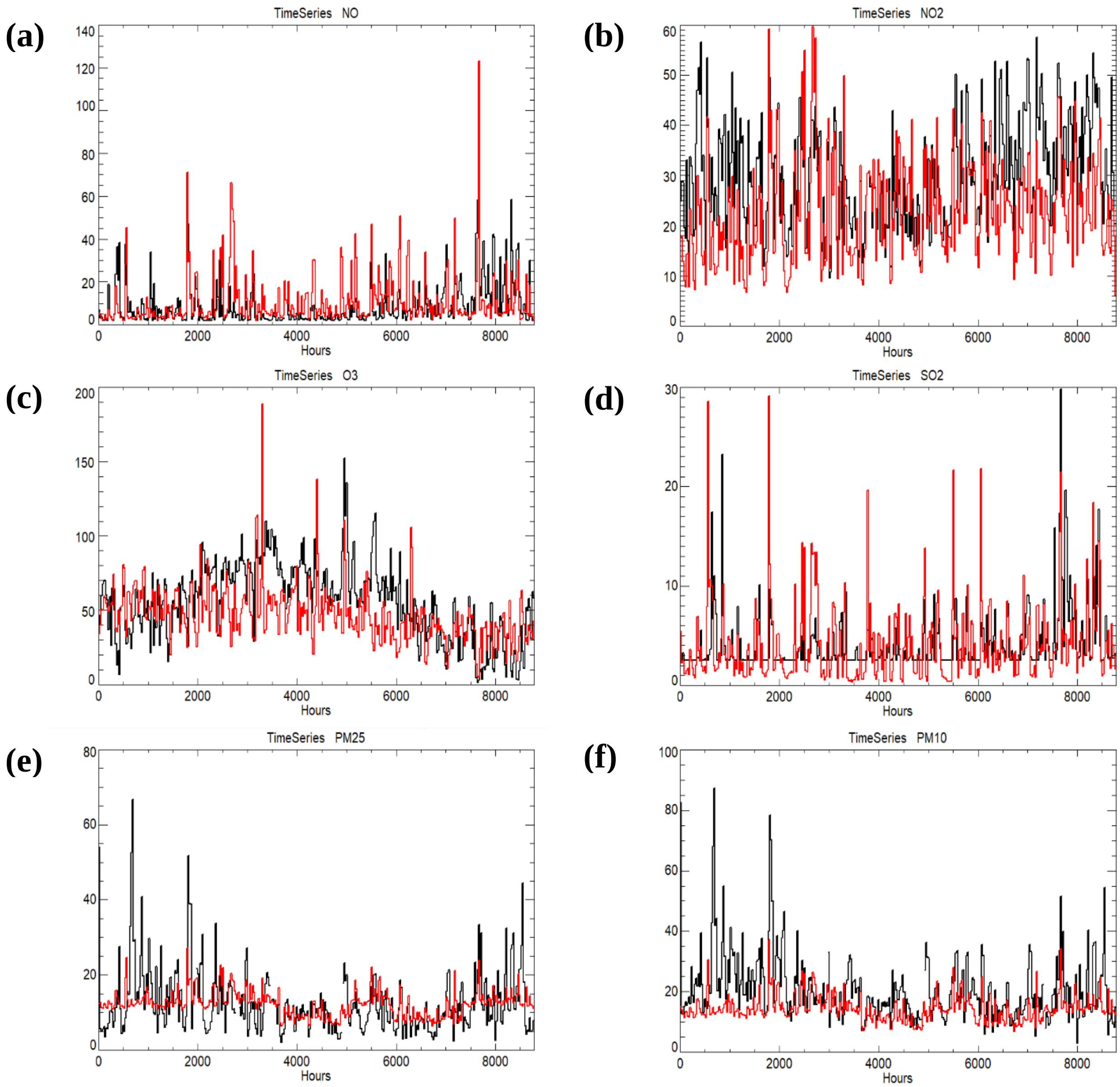


Figure S5: Time series comparing modelled and observed concentrations (in µg m^{-3}) at Sternschanze (station 13ST): (a) NO (daily mean), (b) NO_2 (daily mean), (c) O_3 (maximum of daily 8-h running mean), (d) SO_2 (daily mean), (e) $PM_{2.5}$ (daily mean), and (f) PM_{10} (daily mean). Observed values 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).

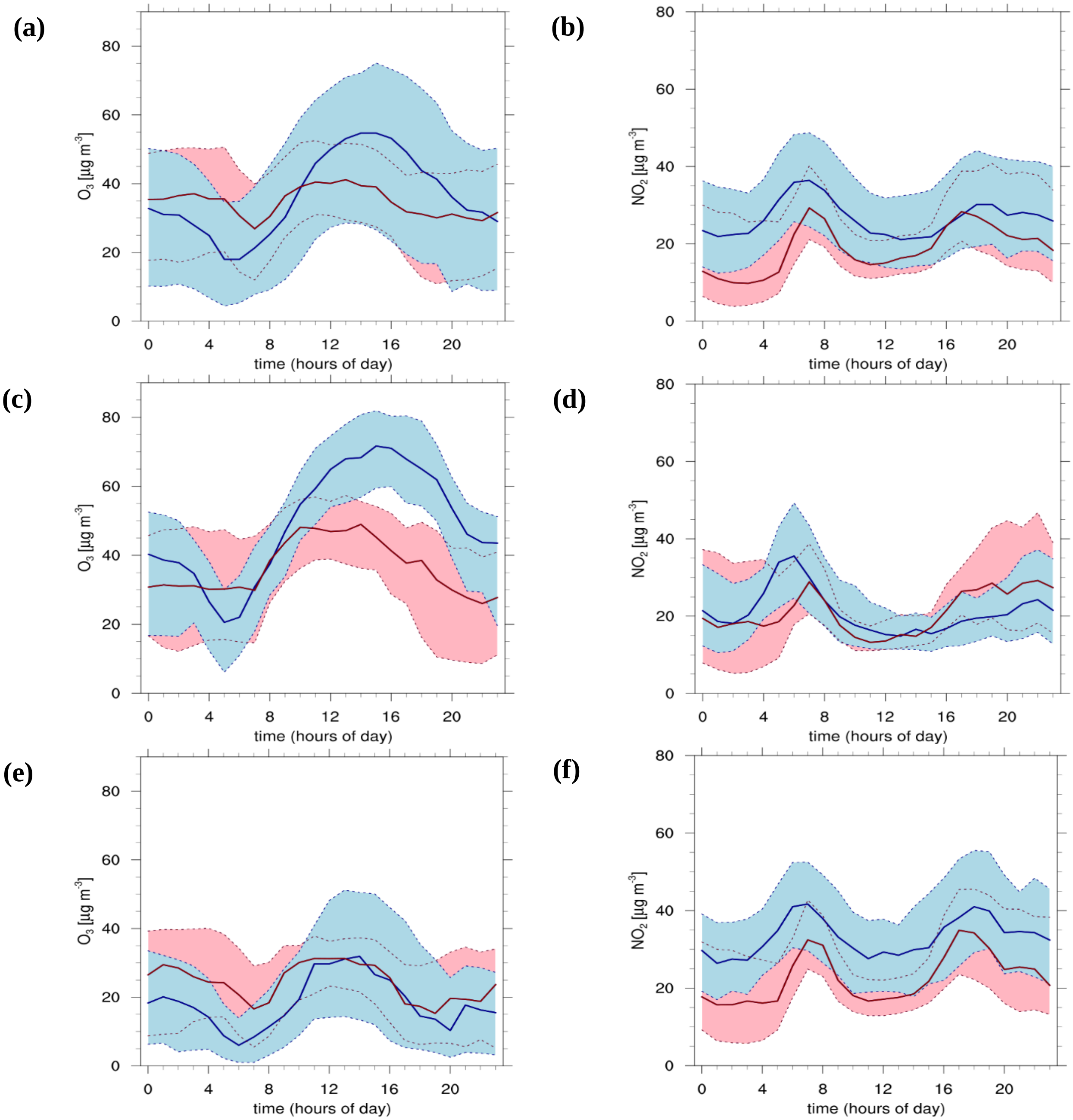


Figure S6: Diurnal cycle of O_3 and NO_2 concentrations (in µg m^{-3}) at Sternschanze (station 13ST) based on the hourly modelled and observed values: (a) yearly O_3, (b) yearly NO_2, (c) summer O_3, (d) summer NO_2, (e) autumn O_3, and (f) autumn NO_2. Modelled median shown as red line and observed median as blue line. Shaded area reflects the band width between the 25th percentile and the 75th percentile (model red-shaded; observation blue-shaded). Summer is defined as June−August (JJA), autumn is defined as September−November (SON).

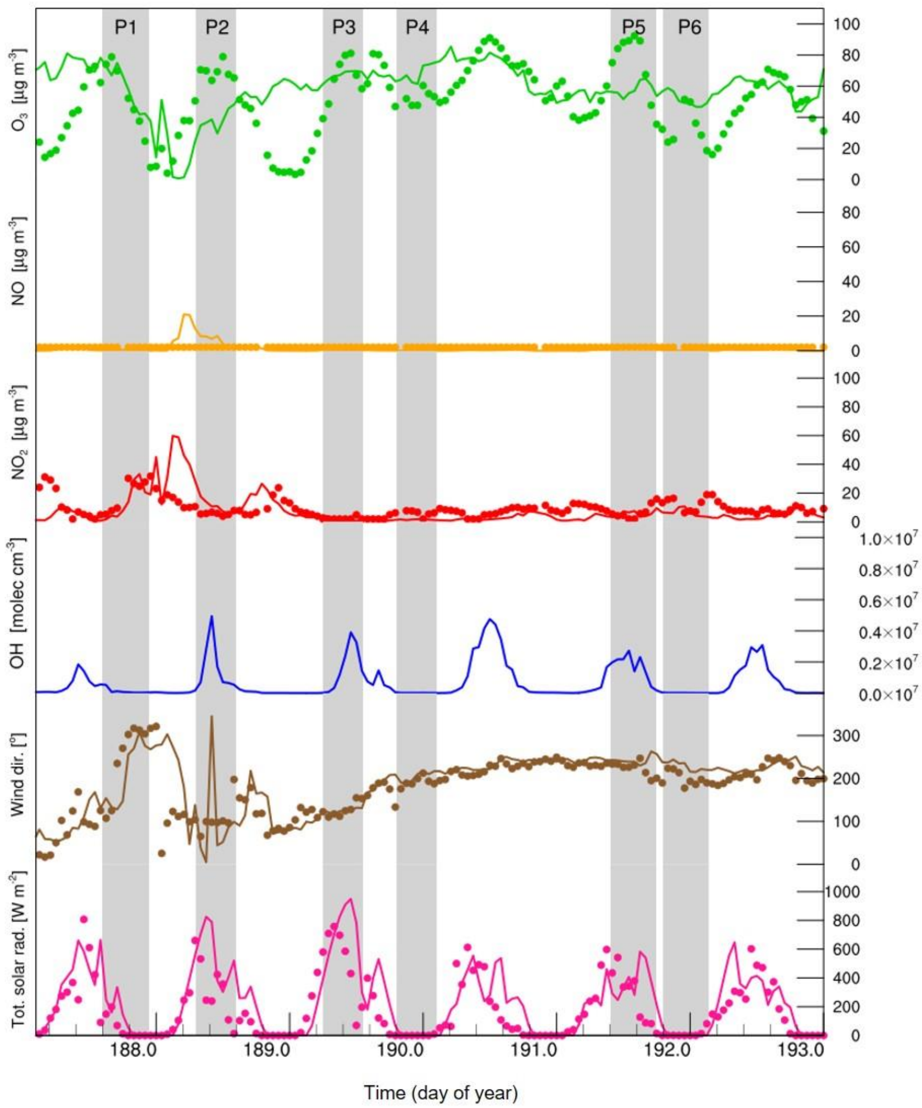


Figure S7: Ozone variation in a summer 6-day episode (5–10 July, 2012): hourly concentrations of O_3 (μg m^{-3}), NO (μg m^{-3}), NO_2 (μg m^{-3}), OH radical (molecule cm^{-3}), wind direction (degrees) and hourly total solar radiation (W m^{-2}) at station Tatenberg (27TA) in the south east of Hamburg. Observations indicated by filled circles and model results by solid lines. Six short periods with ozone under predicted by the model at 13ST shown as grey shaded area, labelled with P1−P6.

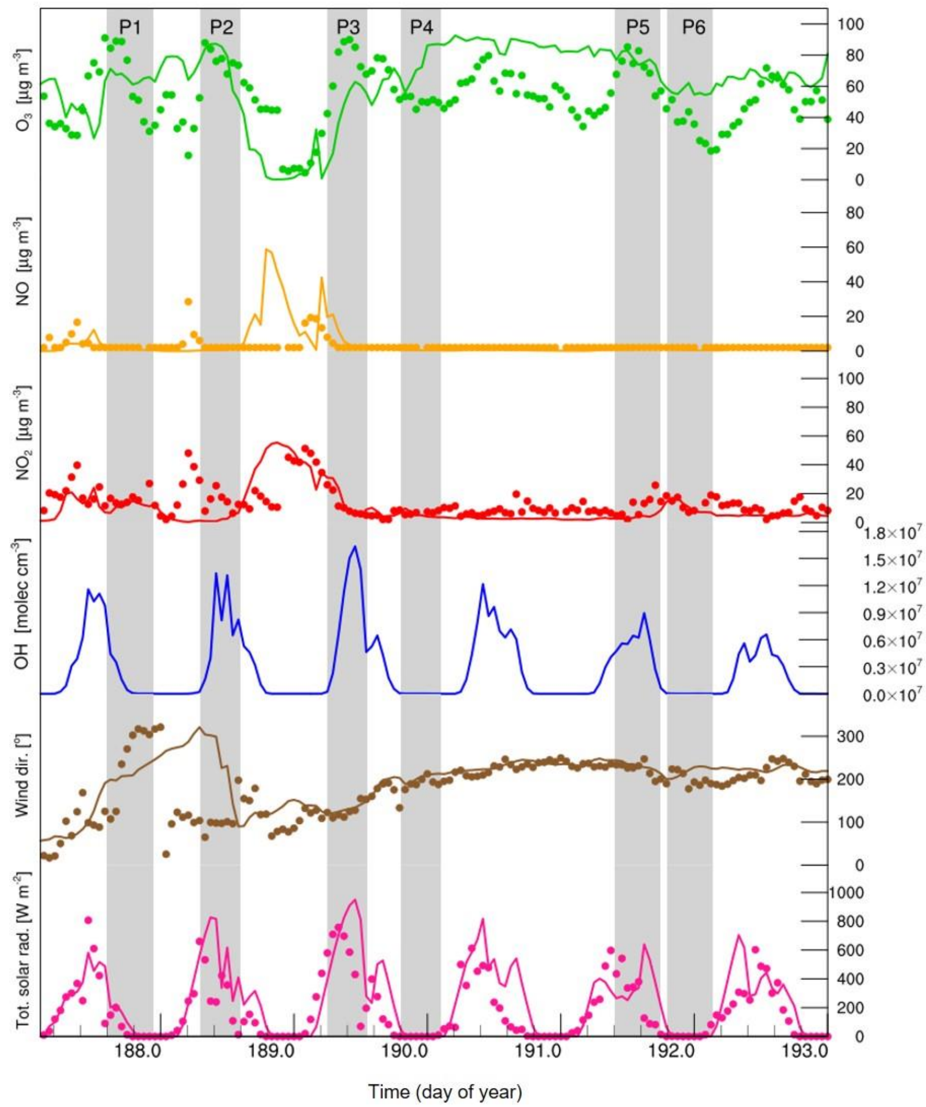


Figure S8: Ozone variation in a summer 6-day episode (5–10 July, 2012): hourly concentrations of O_3 (µg m^{-3}), NO (µg m^{-3}), NO_2 (µg m^{-3}), OH radical (molecule cm^{-3}), wind direction (degrees) and hourly total solar radiation (W m^{-2}) at station Blankenese (54BL) at the western border of the domain. Observations indicated by filled circles and model results by solid lines. Six short periods with ozone under predicted by the model at 13ST shown as grey shaded area, labelled with P1−P6.

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.