Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Urban-scale analysis of the seasonal trend of stabilized-Criegee intermediates and their effect to sulfate formation in the Greater Tokyo Area

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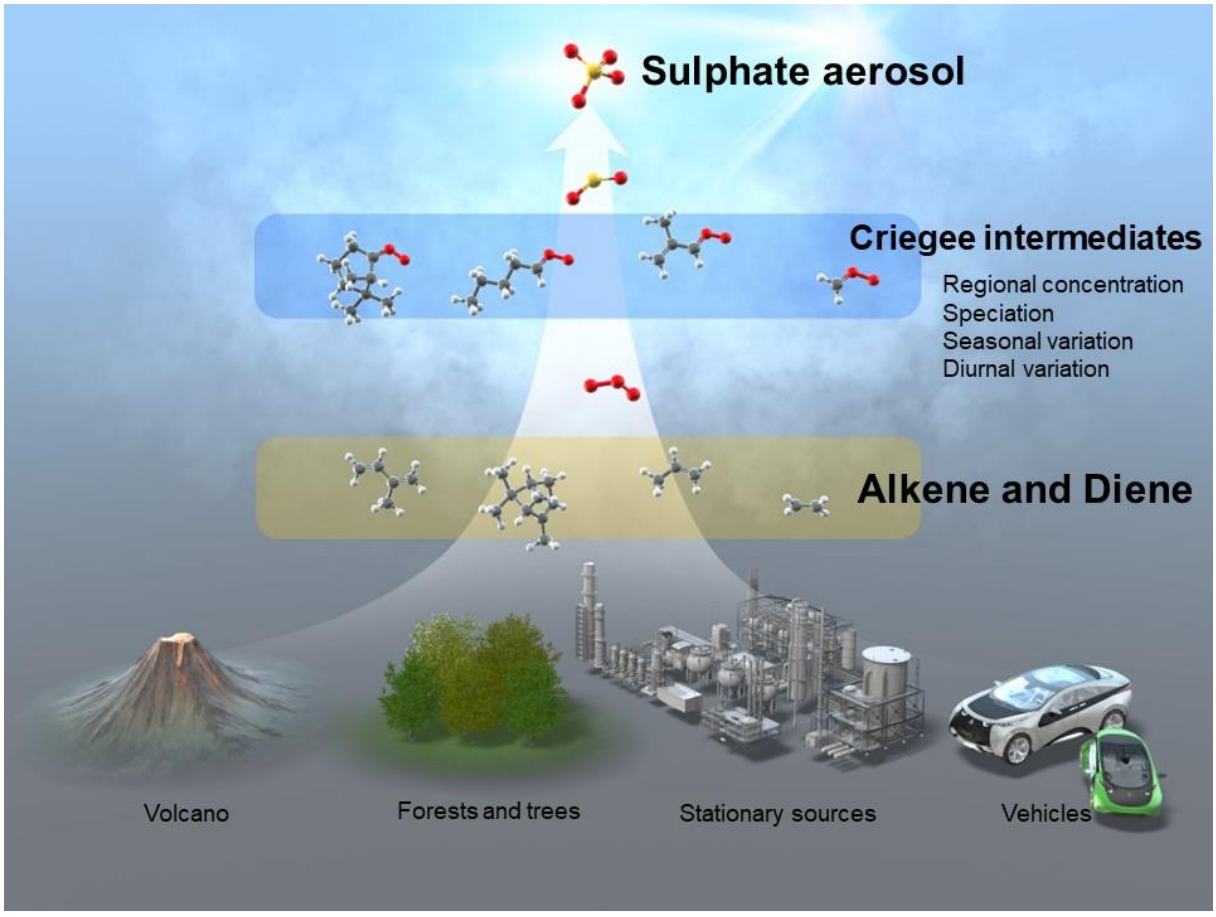

Table S1: Calculation setup for CMAQ.

Model	CMAQv5.2.1
Boundary condition (D1)	MOZART-4/GEOS5
Boundary condition (D2 and D3)	Nested from parent domain
Initial condition (D1)	CMAQ default (profile)
Initial condition (D2 and D3)	Nested from parent domain
Number of grids	207 × 157 (D1), 141 × 147 (D2), 51 × 57 (D3)
Gas chemistry	saprc07tc
Aerosol chemistry	aero6
Aqueous chemistry	cloud_acm_ae6
Photolysis	phot_inline
Horizontal advecion	yamo
Vertical advection	wrf
Horizontal diffusion	hdiff/multiscale
Vertical diffusion	vdiff/acm2
Dry deposition	m3dry

Table S2: sCI generation reactions incorporated into SAPRC-07.

alkenes	Products of alkene ozonolysis
ethene	HCHO + 0.37*SCI1 + 0.13*HO2 + 0.13*OH + 0.63*CO
propene	0.5*CCHO + 0.5*HCHO + 0.12*SCI1 + 0.06*ESCI2 + 0.06*ZSCI2 + 0.82*HO2 + 0.36*OH + 0.56*CO + 0.28*MEO2
13-butadiene	0.5*HCHO + 0.5*ACROLEIN + 0.12*SCI1 + 0.06*ESCI7 + 0.06*ZSCI7 + 0.42*HO2 + 0.08*OH + 0.59*CO + 0.17*ETHENE
isoprene	0.20*MVK + 0.30*MACR + 0.11*SCI1 + 0.022*ESCI8 + 0.022*ZSCI8 + 0.033*ESCI9 + 0.033*ZSCI9 + 0.271*HO2 + 0.27*OH + 0.522*CO + 0.7085*HCHO + 0.051*MEO2 + 0.027*RO2C + 0.027*RO2XC + 0.1275*PROPENE
α-pinene	0.10*ESCI10 + 0.10*ZSCI10 + 0.80*OH + 0.20*CO + 0.40*RO2C + 0.40*RO2XC
methyl vinyl ketone	0.60*HCHO + 0.12*SCI1 + 0.06*ESCI12 + 0.06*ZSCI12 + 0.78*HO2 + 0.36*OH + 1.06*CO + 0.78*MECO3 + 0.10*CCHO
methacrolein	0.5*HCHO + 0.09*SCI1 + 0.045*ESCI14 + 0.045*ZSCI14 + 0.91*HO2 + 0.82*OH + 1.32*CO + 0.91*MECO3

acrolein	1.1*HCHO + 0.12*SCI1 + 0.06*ESCI13 + 0.06*ZSCI13 + 0.56*HO2 + 0.36*OH + 1.34*CO
OLE1	0.12*SCI1 + 0.015*ESCI2 + 0.015*ZSCI2 + 0.015*ESCI6 + 0.015*ZSCI6 + 0.015*ESCI3 + 0.015*ZSCI3 + 0.015*ESCI5 + 0.015*ZSCI5 + 0.28*HO2 + 0.36*OH + 0.50*HCHO + 0.125*CCHO + 0.374*RCHO + 0.025*ALK1 + 0.025*ALK2 + 0.025*ALK4 + 0.07*MEO2 + 0.105*RO2C + 0.105*RO2XC
OLE2	0.045*ESCI2 + 0.045*ZSCI2 + 0.0225*ESCI3 + 0.0225*ZSCI3 + 0.0225*SCI1 + 0.0225*SCI4 + 0.19625*HO2 + 0.6325*OH + 0.6325*CO + 0.03125*ALK1 + 0.50*CCHO + 0.375*RCHO + 0.125*HCHO + 0.52125*MEO2 + 0.225*RO2C + 0.225*RO2XC
terpenes($C_{10}H_{16}$)	0.050*ESCI10 + 0.050*ZSCI10 + 0.576*OH + 0.226*CO + 0.35*RO2C + 0.35*RO2XC + 0.30*HCHO + 0.074*SCI1 + 0.028*ESCI11 + 0.028*ZSCI11 + 0.026*HO2 + 0.299*XC
sesquiterpenes($C_{15}H_{24}$)	0.050*ESCI10 + 0.050*ZSCI10 + 0.576*OH + 0.226*CO + 0.35*RO2C + 0.35*RO2XC + 0.30*HCHO + 0.074*SCI1 + 0.028*ESCI11 + 0.028*ZSCI11 + 0.026*HO2 + 0.299*XC

a. OLE1, OLE2, TERP, and SESQ represent the lamped species of alkenes (k_{OH} < 7 × 10^4 ppm^{-1} min^{-1}); alkenes (k_{OH} > 7 × 10^4 ppm^{-1} min^{-1}); terpenes, except for α-pinene; and sesquiterpenes, respectively, where k_{OH} is the rate constant of the alkenes and OH reaction. b. ESCI and ZSCI represent geometrical isomers of the *E* (*trans*-) and *Z* (*cis*-) forms of SCI. c. Other products explanation; MEO2, methyl peroxy radicals; MVK, methyl vinyl ketone; MACR, methacrolein; RO2C, peroxy radical operator representing NO to NO_2 and NO_3 to NO_2 conversions, and the effects of peroxy radical reactions on acyl peroxy and other peroxy radicals; RO2XC, peroxy radical operator representing NO consumption (used in conjunction with organic nitrate formation), and the effects of peroxy radical reactions on NO_3, acyl peroxy radicals, and other peroxy radicals; $MECO_3$, acetyl peroxy radicals; RCHO, Lumped C3+ Aldehydes. Mechanism based on propionaldehyde; ALK1, Alkanes and other non-aromatic compounds that react only with OH, and have kOH (OH radical rate constant) between 2 and 5 × 10^2 ppm^{-1} min^{-1}. (Primarily ethane); ALK2, Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 × 10^2 and 2.5 × 10^3 ppm^{-1} min^{-1}. (Primarily

propane); ALK4, Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5×10^3 and 1×10^4 ppm^{-1} min^{-1}; XC, Lost Carbon or carbon in unreactive products.

Table S3: List of unimolecular decomposition reactions of sCIs.

SCI	decomposition mechanism	Products	A (s^{-1})	B	Ea (kcal mol^{-1})
SCI1	13ring	HCOOH	1.345×10^{11}	4	8024
ESCI2	13ring	CCOOH	3.733×10^{12}	1.35	7445
ZSCI2	14Hmig	CO + 2*OH + HCHO	2.635×10^{-2}	25	-2685
	13ring	CCOOH	4.360×10^{11}	2.98	10755
ESCI3	13ring	RCOOH	5.589×10^{12}	1.03	7464
ZSCI3	14Hmig	xRCHO + OH	3.768×10^{-2}	24.3	-2571
	13ring	RCOOH	1.176×10^{12}	2.41	10584
SCI4	14Hmig	xACETONE + OH	2.204×10^{-1}	23.6	-2367
	13ring	MEK	3.816×10^{12}	1.21	10140
ESCI5	13ring	RCOOH	5.285×10^{12}	1.2	7380
ZSCI5	14Hmig	xRCHO + OH	4.178×10^{-2}	24.5	-2490
	13ring	RCOOH	7.032×10^{11}	2.6	10562
ESCI6	13ring	RCOOH	5.285×10^{12}	1.2	7380
ZSCI6	14Hmig	xRCHO + OH	4.178×10^{-2}	24.5	-2490
	13ring	RCOOH	7.032×10^{11}	2.6	10562
ESCI7	13ring	RCOOH	1.035×10^{13}	0.8	8139
ZSCI7	15ring	RCHO	8.715×10^{11}	0.66	5727
	13ring	RCOOH	5.026×10^{11}	2.34	9126
ESCI8	13ring	MEK	5.517×10^{12}	0.48	10385
	14Hmig	xMVK + OH	6.265×10^{-3}	25.9	-2737

ZSCI8	15ring	RCHO	1.198×10^{12}	0.65	5617
	13ring	MEK	2.076×10^{12}	1.12	8291
ESCI9	13ring	RCOOH	2.453×10^{12}	1.46	7832
ZSCI9	15ring	RCHO	1.956×10^{12}	0.44	6102
	13ring	RCOOH	8.008×10^{11}	1.68	8476
ESCI10	13ring	PRD2	4.036×10^{11}	2.43	6732
ZSCI10	14Hmig	xPROD2 + OH	6.373×10^{-1}	23	-2099
	13ring	PRD2	2.802×10^{11}	3.45	9906
ESCI11	13ring	PRD2	2.295×10^{12}	1.23	10358
	14Hmig	xPROD2 + OH	2.358×10^{-1}	23.27	-2251
ZSCI11	13ring	PRD2	3.744×10^{12}	1.33	8425
ESCI12	13ring	RCOOH	1.176×10^{12}	2.3	9127
ZSCI12	13ring	RCOOH	5.178×10^{11}	2.41	7141
ESCI13	13ring	RCOOH	1.011×10^{12}	2.72	9444
ZSCI13	13ring	RCOOH	7.424×10^{11}	2.21	6656
ESCI14	14Hmig	xRCHO + OH	2.375×10^{-5}	30.08	-3644
	13ring	RCHO	1.439×10^{12}	2.34	12328
ZSCI14	13ring	RCHO	2.361×10^{12}	0.78	5162

MEK, Ketones and other non-aldehyde oxygenated products that react with OH radicals faster than 5×10^{-13} but slower than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}; PRD2, Ketones and other non-aldehyde oxygenated products that react with OH radicals faster than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}. xRCHO, Formation of RCHO from alkoxy radicals formed in peroxy radical reactions with NO and NO_3 (100% yields) and RO_2 (50% yields); xACETONE, same as xRCHO, but for acetone; xPROD2 same as xRCHO, but for PRD2.

Table S4: Detailed information on sCI + water monomer (H_2O). Products were estimated from the products[1] of the SCI1 + H_2O reaction and represented in the expressions in SAPRC-07. Numbers of A, B, and Ea are the parameters of the modified Arrhenius equation ($k(T) = A\,(\frac{T}{300})^{B} \exp(-\frac{Ea}{RT})$) cited from quantum chemical calculation results[2].

SCI	Products	A (cm^3 $molec^{-1}$ s^{-1})	B	Ea (kcal mol^{-1})
SCI1	0.4*HCHO + 0.55*ROOH + 0.05*HCOOH	9.056×10^{-15}	1.23	698
ESCI2	0.4*CCHO + 0.55*ROOH + 0.05*CCOOH	6.045×10^{-15}	1.27	-405
ZSCI2	0.4*CCHO + 0.55*ROOH + 0.05*CCOOH	3.177×10^{-15}	1.68	2513
ESCI3	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	1.832×10^{-15}	0.92	-652
ZSCI3	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.413×10^{-15}	1.39	2300
SCI4	0.45*ACET + 0.55*ROOH	2.085×10^{-15}	1.91	1677
ESCI5	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	1.832×10^{-15}	0.92	-652
ZSCI5	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.413×10^{-15}	1.39	2300
ESCI6	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	1.832×10^{-15}	0.92	-652
ZSCI6	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.413×10^{-15}	1.39	2300
ESCI7	0.4*MACR + 0.55*ROOH + 0.05*RCOOH	3.470×10^{-15}	1.46	1073
ZSCI7	0.4*MACR + 0.55*ROOH + 0.05*RCOOH	2.354×10^{-15}	1.73	3059
ESCI8	0.45*MVK + 0.55*ROOH	2.924×10^{-15}	1.46	3132
ZSCI8	0.45*MVK + 0.55*ROOH	9.278×10^{-16}	2.27	1858
ESCI9	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	4.351×10^{-15}	1.74	929
ZSCI9	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.425×10^{-15}	1.52	2977
ESCI10	0.45*PROD2 + 0.55*R6OOH	1.295×10^{-14}	0.17	-71
ZSCI10	0.45*PROD2 + 0.55*R6OOH	5.283×10^{-17}	3.83	1023
ESCI11	0.45*PROD2 + 0.55*R6OOH	3.030×10^{-16}	2.37	1525
ZSCI11	0.45*PROD2 + 0.55*R6OOH	2.931×10^{-16}	2.64	-121
ESCI12	0.4*MGLY + 0.55*ROOH + 0.05*RCOOH	9.804×10^{-15}	1.53	2258
ZSCI12	0.4*MGLY + 0.55*ROOH + 0.05*RCOOH	2.435×10^{-15}	1.03	-131
ESCI13	0.4*GLY + 0.55*ROOH + 0.05*RCOOH	9.804×10^{-15}	1.53	2258
ZSCI13	0.4*GLY + 0.55*ROOH + 0.05*RCOOH	2.639×10^{-15}	1.59	370
ESCI14	0.45*GLY + 0.55*ROOH	4.674×10^{-15}	1.87	4177
ZSCI14	0.45*GLY + 0.55*ROOH	1.133×10^{-15}	1.68	-757

ROOH, Lumped organic hydroperoxides with 2-4 carbons; R6OOH, Lumped organic hydroperoxides with five or more carbons; ACET, Acetone; MACR, Methacrolein; MVK, Methyl vinyl ketone; PROD2, Ketones and other non-aldehyde oxygenated products that react

with OH radicals faster than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}; MGLY, Methyl Glyoxal; GLY, Glyoxal.

Table S5: Detailed information on sCI + water dimer ($(H_2O)_2$). Products were estimated from the products[1] of the SCI1 + H_2O reaction and represented in the expressions in SAPRC-07 (therefore, the products are same as that of SCI + water monomer). Numbers of A, B, and Ea are the parameters of the modified Arrhenius equation ($k(T) = A\,(\frac{T}{300})^B \exp(-\frac{Ea}{RT})$). According to this table, Ea is 0 in all SCIs because there was no solution in the curve approximation when Ea was not 0. Therefore, Ea was set to 0.

SCI	Products	A (cm^3 $molec^{-1}$ s^{-1})	B	Ea (kcal mol^{-1})
SCI1	0.4*HCHO + 0.55*ROOH + 0.05*HCOOH	2.900×10^{-33}	-11.096	0
ESCI2	0.4*CCHO + 0.55*ROOH + 0.05*CCOOH	4.964×10^{-32}	-14.742	0
ZSCI2	0.4*CCHO + 0.55*ROOH + 0.05*CCOOH	4.209×10^{-36}	-4.8155	0
ESCI3	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.251×10^{-32}	-15.967	0
ZSCI3	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	8.888×10^{-36}	-5.7662	0
SCI4	0.45*ACET + 0.55*ROOH	3.628×10^{-35}	-7.2807	0
ESCI5	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.251×10^{-32}	-15.967	0
ZSCI5	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	8.888×10^{-36}	-5.7662	0
ESCI6	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	3.251×10^{-32}	-15.967	0
ZSCI6	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	8.888×10^{-36}	-5.7662	0
ESCI7	0.4*MACR + 0.55*ROOH + 0.05*RCOOH	3.786×10^{-34}	-9.6829	0
ZSCI7	0.4*MACR + 0.55*ROOH + 0.05*RCOOH	6.243×10^{-37}	-3.0628	0
ESCI8	0.45*MVK + 0.55*ROOH	6.525×10^{-37}	-3.0979	0
ZSCI8	0.45*MVK + 0.55*ROOH	9.914×10^{-36}	-6.3786	0
ESCI9	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	6.927×10^{-34}	-9.8761	0
ZSCI9	0.4*RCHO + 0.55*ROOH + 0.05*RCOOH	1.172×10^{-36}	-3.5087	0
ESCI10	0.45*PROD2 + 0.55*R6OOH	3.308×10^{-32}	-14.535	0
ZSCI10	0.45*PROD2 + 0.55*R6OOH	7.396×10^{-36}	-7.5476	0
ESCI11	0.45*PROD2 + 0.55*R6OOH	7.385×10^{-36}	-7.2284	0
ZSCI11	0.45*PROD2 + 0.55*R6OOH	1.145×10^{-33}	-12.473	0
ESCI12	0.4*MGLY + 0.55*ROOH + 0.05*RCOOH	2.718×10^{-35}	-5.7373	0
ZSCI12	0.4*MGLY + 0.55*ROOH + 0.05*RCOOH	8.339×10^{-33}	-14.011	0
ESCI13	0.4*GLY + 0.55*ROOH + 0.05*RCOOH	2.718×10^{-35}	-5.7373	0
ZSCI13	0.4*GLY + 0.55*ROOH + 0.05*RCOOH	2.161×10^{-33}	-11.809	0
ESCI14	0.45*GLY + 0.55*ROOH	4.273×10^{-38}	0.5796	0
ZSCI14	0.45*GLY + 0.55*ROOH	2.702×10^{-32}	-15.508	0

Table S6: Detailed information on sCI + sulfur dioxide (SO_2). Products were represented in the expressions in SAPRC-07. Rate constants are suggested values in the previous study.[2]

SCI	Products	Rate Constant (cm^3 $molec^{-1}$ s^{-1})
SCI1	HCHO + SULF + SULRXN	3.7×10^{-11}
ESCI2	CCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI2	CCHO + SULF + SULRXN	2.7×10^{-11}
ESCI3	RCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI3	RCHO + SULF + SULRXN	2.7×10^{-11}
SCI4	ACET + SULF + SULRXN	1.6×10^{-10}
ESCI5	RCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI5	RCHO + SULF + SULRXN	2.7×10^{-11}
ESCI6	RCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI6	RCHO + SULF + SULRXN	2.7×10^{-11}
ESCI7	RCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI7	RCHO + SULF + SULRXN	2.7×10^{-11}
ESCI8	MVK + SULF + SULRXN	1.4×10^{-10}
ZSCI8	MVK + SULF + SULRXN	2.7×10^{-11}
ESCI9	RCHO + SULF + SULRXN	1.4×10^{-10}
ZSCI9	RCHO + SULF + SULRXN	2.7×10^{-11}
ESCI10	PRD2 + SULF + SULRXN	1.4×10^{-10}
ZSCI10	PRD2 + SULF + SULRXN	2.7×10^{-11}
ESCI11	PRD2 + SULF + SULRXN	1.4×10^{-10}
ZSCI11	PRD2 + SULF + SULRXN	4.0×10^{-11}
ESCI12	MGLY + SULF + SULRXN	1.4×10^{-10}
ZSCI12	MGLY + SULF + SULRXN	2.7×10^{-11}
ESCI13	GLY + SULF + SULRXN	1.4×10^{-10}
ZSCI13	GLY + SULF + SULRXN	2.7×10^{-11}
ESCI14	MGLY + SULF + SULRXN	1.4×10^{-10}
ZSCI14	MGLY + SULF + SULRXN	2.7×10^{-11}

SULF, sulfates; SULRXN, precursor of aerosol sulfate.

Table S7: Detailed information on sCI + nitrogen dioxide (NO_2). Products were represented in the expressions in SAPRC-07. Rate constants are suggested values in the previous study[2].

SCI	Products	Rate Constant (cm^3 $molec^{-1}$ s^{-1})
SCI1	HCHO + NO3	4.0×10^{-12}
ESCI2	CCHO + NO3	4.0×10^{-12}
ZSCI2	CCHO + NO3	4.0×10^{-12}
ESCI3	RCHO + NO3	4.0×10^{-12}
ZSCI3	RCHO + NO3	4.0×10^{-12}
SCI4	ACET + NO3	4.0×10^{-12}
ESCI5	RCHO + NO3	4.0×10^{-12}
ZSCI5	RCHO + NO3	4.0×10^{-12}
ESCI6	RCHO + NO3	4.0×10^{-12}
ZSCI6	RCHO + NO3	4.0×10^{-12}
ESCI7	RCHO + NO3	4.0×10^{-12}
ZSCI7	RCHO + NO3	4.0×10^{-12}
ESCI8	MVK + NO3	4.0×10^{-12}
ZSCI8	MVK + NO3	4.0×10^{-12}
ESCI9	RCHO + NO3	4.0×10^{-12}
ZSCI9	RCHO + NO3	4.0×10^{-12}
ESCI10	PRD2 + NO3	4.0×10^{-12}
ZSCI10	PRD2 + NO3	4.0×10^{-12}
ESCI11	PRD2 + NO3	4.0×10^{-12}
ZSCI11	PRD2 + NO3	4.0×10^{-12}
ESCI12	MGLY + NO3	4.0×10^{-12}
ZSCI12	MGLY + NO3	4.0×10^{-12}
ESCI13	GLY + NO3	4.0×10^{-12}
ZSCI13	GLY + NO3	4.0×10^{-12}
ESCI14	MGLY + NO3	4.0×10^{-12}
ZSCI14	MGLY + NO3	4.0×10^{-12}

Table S8: Detailed information on sCI + nitric acid (HNO_3). Products were estimated from products[3] of SCI1 + HNO_3 and represented in the expressions in SAPRC-07. Rate constants are suggested values in the previous study[4].

SCI	Products	Rate Constant (cm^3 $molec^{-1}$ s^{-1})
SCI1	RNO3 + 0.21OH	5.4×10^{-10}
ESCI2	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI2	RNO3 + 0.21OH	5.4×10^{-10}
ESCI3	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI3	RNO3 + 0.21OH	5.4×10^{-10}
SCI4	RNO3 + 0.21OH	5.4×10^{-10}
ESCI5	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI5	RNO3 + 0.21OH	5.4×10^{-10}
ESCI6	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI6	RNO3 + 0.21OH	5.4×10^{-10}
ESCI7	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI7	RNO3 + 0.21OH	5.4×10^{-10}
ESCI8	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI8	RNO3 + 0.21OH	5.4×10^{-10}
ESCI9	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI9	RNO3 + 0.21OH	5.4×10^{-10}
ESCI10	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI10	RNO3 + 0.21OH	5.4×10^{-10}
ESCI11	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI11	RNO3 + 0.21OH	5.4×10^{-10}
ESCI12	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI12	RNO3 + 0.21OH	5.4×10^{-10}
ESCI13	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI13	RNO3 + 0.21OH	5.4×10^{-10}
ESCI14	RNO3 + 0.21OH	5.4×10^{-10}
ZSCI14	RNO3 + 0.21OH	5.4×10^{-10}

RNO3, Lumped Organic Nitrates.

Table S9: Detailed information on sCI + organic acid. Three organic acids, i.e., formic acid (HCOOH), acetic acid (CCOOH), and higher organic acid (RCOOH), were considered. A previous study[5] suggested HCOOH acts as a catalyst to decompose SCI. Products were estimated from SCI unimolecular decomposition and represented in the expressions in SAPRC-07. Rate constants are suggested values in the previous study[4].

SCI	Products			Rate Constant (cm^3 $molec^{-1}$ s^{-1})
	+ HCOOH	+ CCOOH	+ RCOOH	
SCI1	ROOH	ROOH	ROOH	1.2×10^{-10}
ESCI2	ROOH	ROOH	R6OOH	3.8×10^{-10}
ZSCI2	CO + 2*OH + HCHO + HCOOH	xCCHO + OH +CCOOH	xCCHO + OH + RCOOH	2.1×10^{-10}
ESCI3	ROOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI3	xRCHO + OH + HCOOH	xRCHO + OH + CCOOH	xRCHO + OH + RCOOH	2.1×10^{-10}
SCI4	xACETONE + OH + HCOOH	xACETONE + OH + CCOOH	xACETONE + OH + RCOOH	5.0×10^{-10}
ESCI5	R6OOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI5	xRCHO + OH + HCOOH	xRCHO + OH + CCOOH	xRCHO + OH + RCOOH	2.1×10^{-10}
ESCI6	R6OOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI6	xRCHO + OH + HCOOH	xRCHO + OH + CCOOH	xRCHO + OH + RCOOH	2.1×10^{-10}
ESCI7	ROOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI7	ROOH	R6OOH	R6OOH	2.1×10^{-10}
ESCI8	xMVK + OH + HCOOH	xMVK + OH + CCOOH	xMVK + OH + RCOOH	3.8×10^{-10}
ZSCI8	R6OOH	R6OOH	R6OOH	2.1×10^{-10}
ESCI9	R6OOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI9	R6OOH	R6OOH	R6OOH	2.1×10^{-10}
ESCI10	PRD2 + HCOOH	PRD2 + CCOOH	PRD2 + RCOOH	3.8×10^{-10}
ZSCI10	xPROD2 + OH + HCOOH	xPROD2 + OH + CCOOH	xPROD2 + OH + RCOOH	2.1×10^{-10}
ESCI11	xPROD2 + OH + HCOOH	xPROD2 + OH + CCOOH	xPROD2 + OH + RCOOH	3.8×10^{-10}
ZSCI11	PRD2	PRD2 + CCOOH	PRD2 + RCOOH	2.1×10^{-10}
ESCI12	ROOH	R6OOH	R6OOH	3.8×10^{-10}
ZSCI12	ROOH	R6OOH	R6OOH	2.1×10^{-10}
ESCI13	ROOH	ROOH	R6OOH	3.8×10^{-10}
ZSCI13	ROOH	ROOH	R6OOH	2.1×10^{-10}
ESCI14	RCHO	RCHO + CCOOH	RCHO + RCOOH	3.8×10^{-10}
ZSCI14	ROOH	R6OOH	R6OOH	3.8×10^{-10}

ROOH, Lumped organic hydroperoxides with 2–4 carbons; R6OOH, Lumped organic hydroperoxides with 5 or more carbons; PRD2, Ketones and other non-aldehyde oxygenated products that react with OH radicals faster than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}.

xRCHO, Formation of RCHO from alkoxy radicals formed in peroxy radical reactions with NO and NO_3 (100% yields) and RO_2 (50% yields); xACETONE, same as xRCHO, but for

acetone; xMVK, same as xRCHO, but for MVK (methyl vinyl ketone); xPROD2 same as xRCHO, but for PRD2.

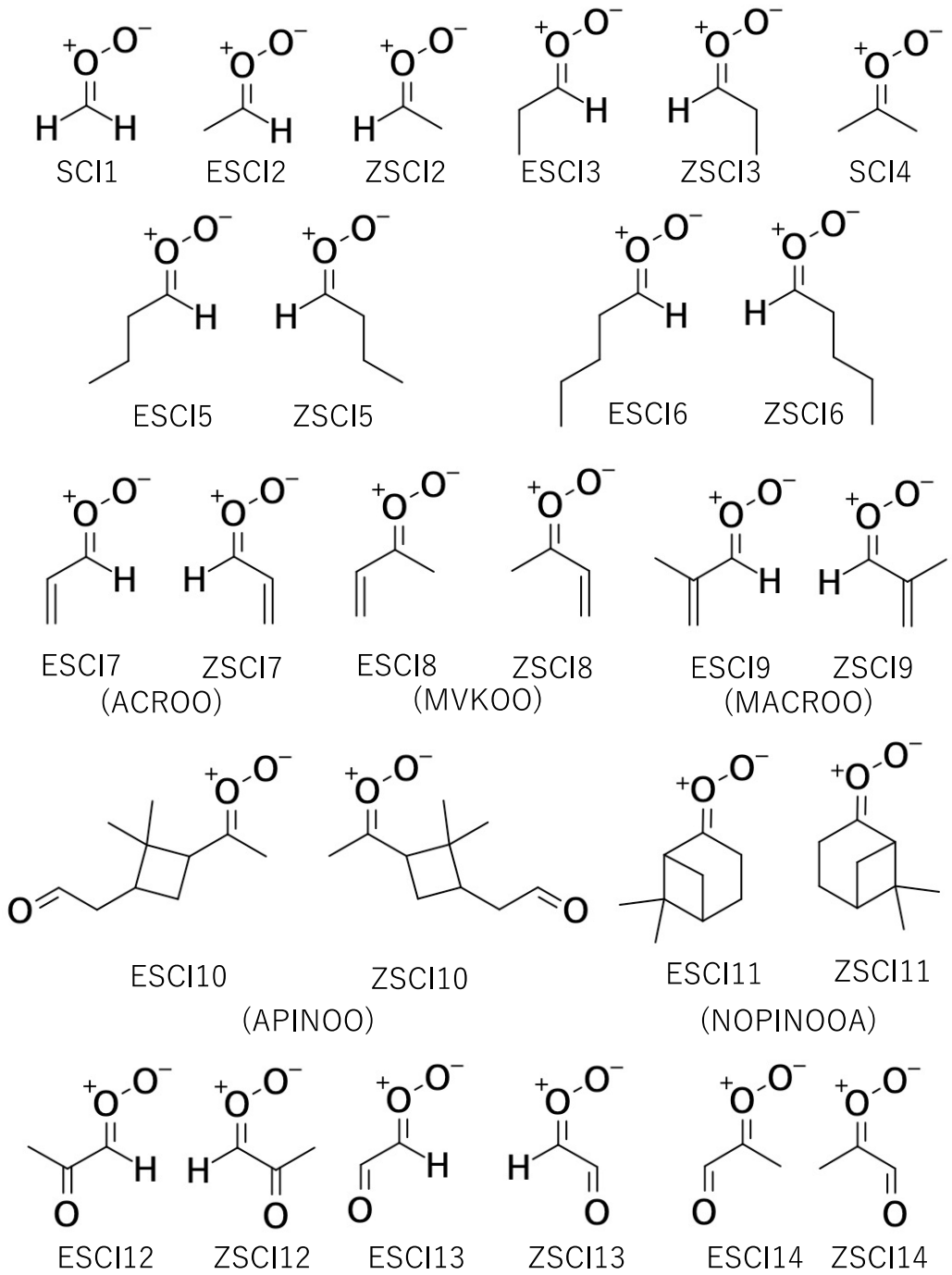

Figure S1: Chemical structures of sCIs applied in this study. Stereoisomers were depicted explicitly. Words inside parentheses are common names of SCIs. The structure was depicted by Marvin Sketch (https://chemaxon.com/marvin).

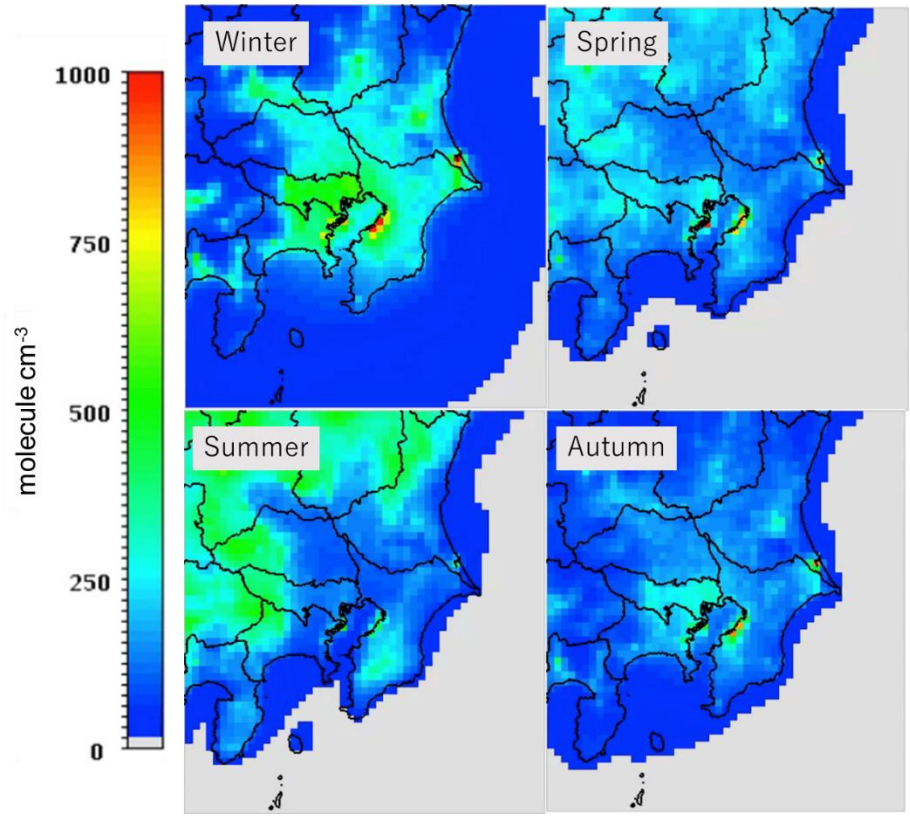

Figure S2: Seasonal change in episode average sCI concentration distributions.

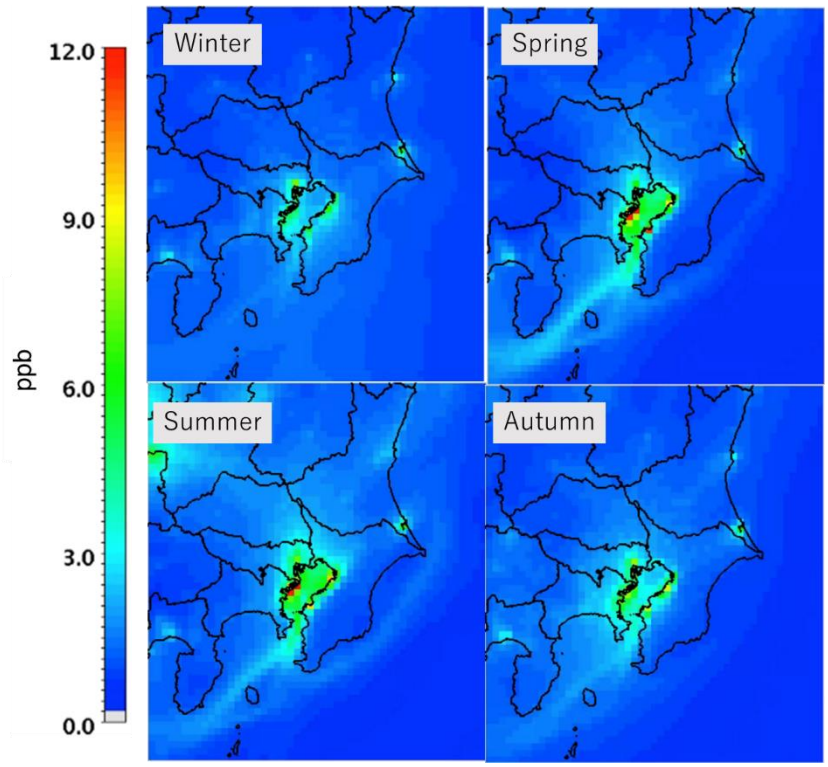

Figure S3: Seasonal change in episode average SO_2 concentration distributions.

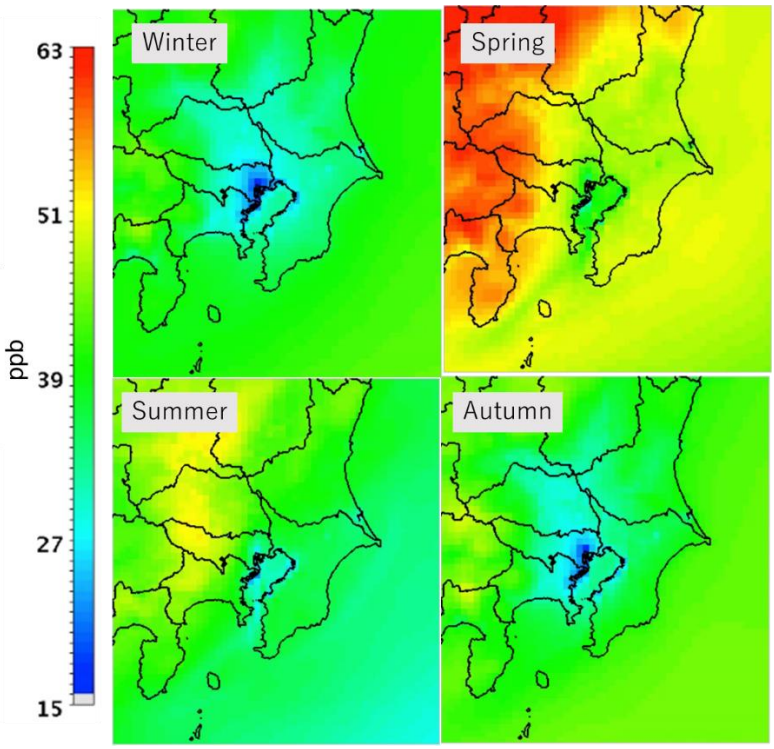

Figure S4: Seasonal change in episode average O_3 concentration distributions.

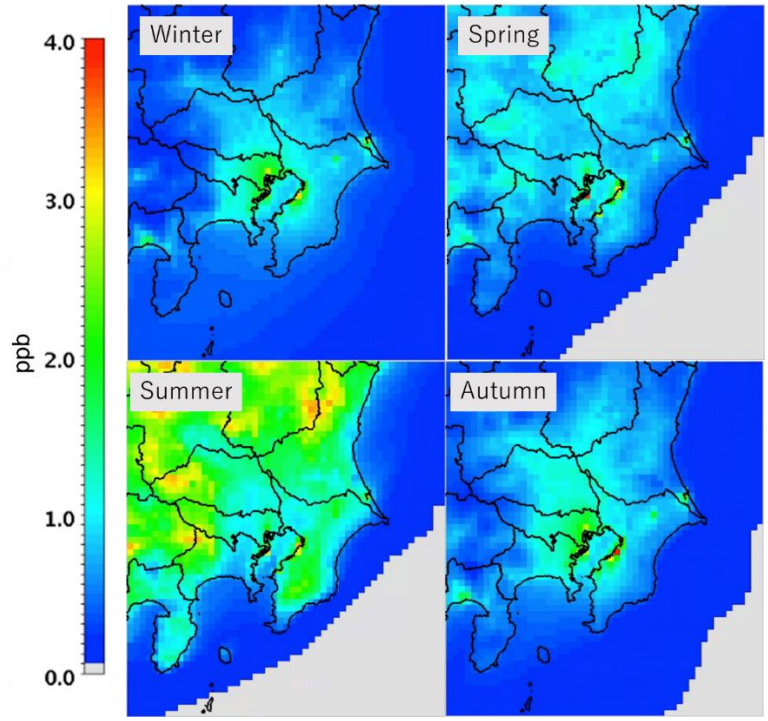

Figure S5: Seasonal change in episode average concentration distribution of VOCs, which generate sCIs.

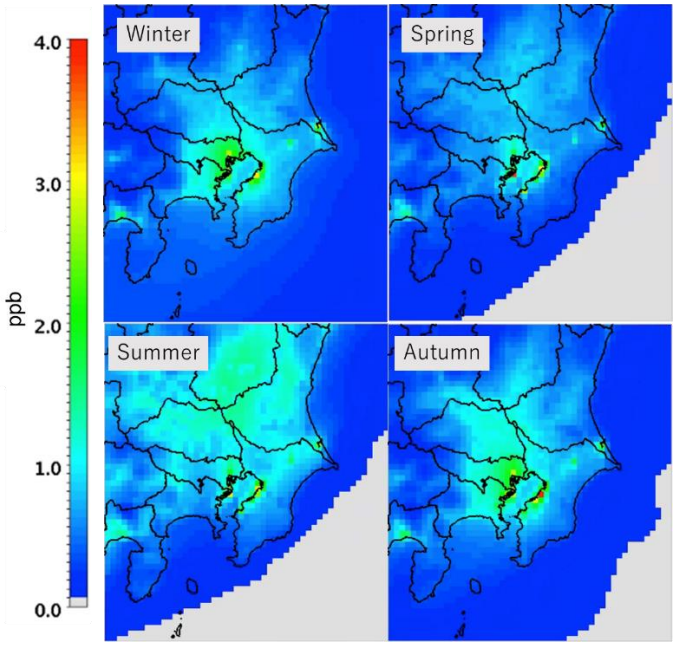

Figure S6: Seasonal change in episode average concentration distribution of AVOCs: ethene, propene, 1,3-butadiene, terminal alkene (OLE1), and internal alkene (OLE2).

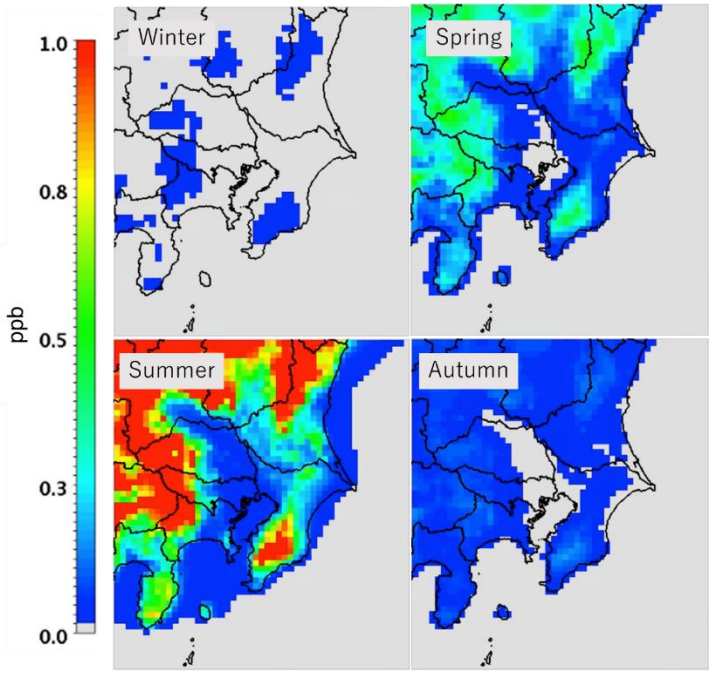

Figure S7: Seasonal change in episode average concentration distribution of BVOCs: isoprene, α -pinene, terpenes, and sesquiterpenes.

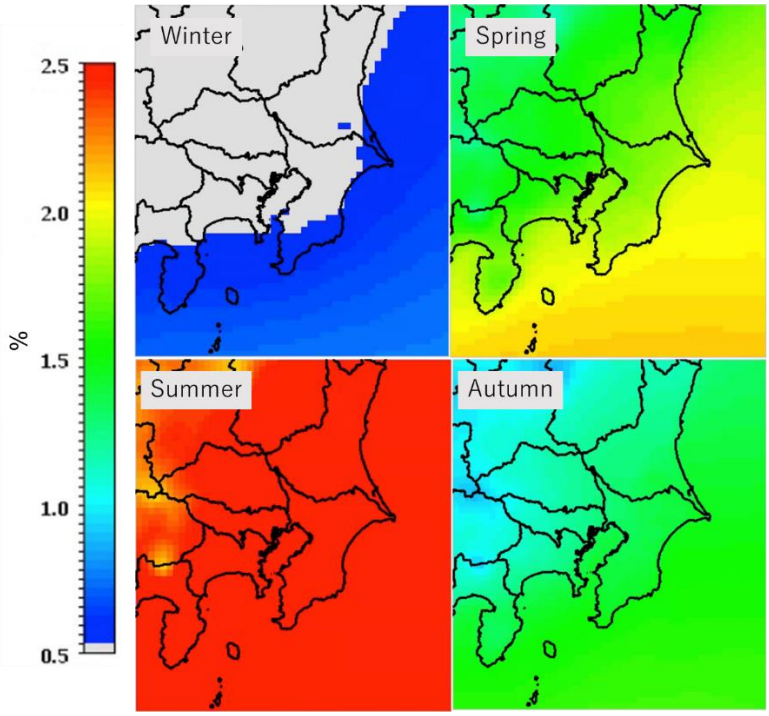

Figure S8: Seasonal change in episode average concentration distribution of water vapor.

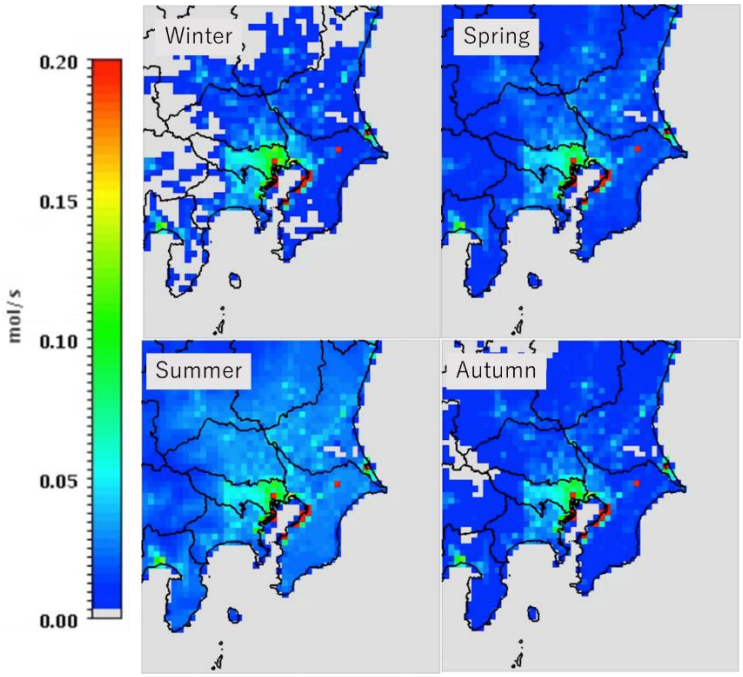

Figure S9: Seasonal change in episode average emissions distribution of AVOCs.

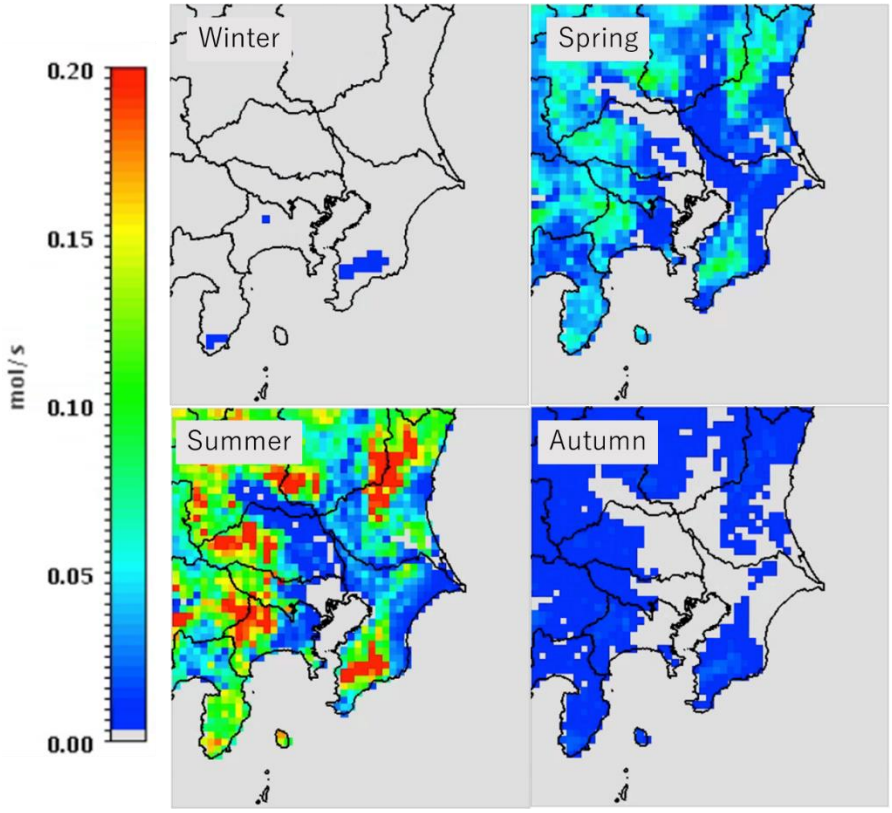

Figure S10: Seasonal change in episode average emissions distribution of BVOCs.

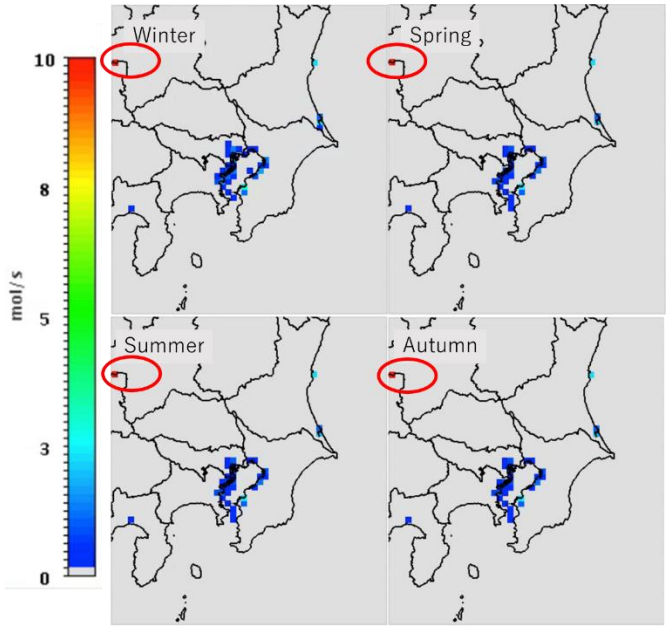

Figure S11: Seasonal change in episode average emissions distribution of SO_2. The spot shown with a red circle is the emissions from a volcano (Mt. Asama), which reached 52, 69, 235, and 214 mol/s in winter, spring, summer, and autumn, respectively.

Table S10: Contribution of three sCIs-loss processes in the standard atmospheric condition, which are determined dependent on calculated results. The unit is s^{-1} and major sCIs in the targeted region of this study are highlighted in green.

sCIs	Unimolecular Decomposition	Water	Other Reactions	Total Loss
SCI1	0.3	575.0	16.7	592.0
ESCI2	53.0	14,200.0	23.7	14,276.7
ZSCI2	136.0	0.5	16.9	153.4
ESCI3	74.0	9,800.0	23.7	9,897.7
ZSCI3	205.0	1.2	16.9	223.0
SCI4	478.0	5.6	25.6	509.1
ESCI5	92.0	9,650.0	23.7	9,765.7
ZSCI5	127.0	1.2	16.9	145.1
ESCI6	92.0	9,650.0	23.7	9,765.7
ZSCI6	127.0	1.2	16.9	145.1
ESCI7	14.0	66.5	23.7	104.2
ZSCI7	4,000.0	0.1	16.9	4,017.0
ESCI8	50.0	0.1	23.7	73.8
ZSCI8	7,701.6	1.4	16.9	7,719.8
ESCI9	10.0	131.0	23.7	164.7
ZSCI9	2,500.4	0.1	16.9	2,517.3
ESCI10	62.0	9,700.0	23.7	9,785.7
ZSCI10	634.0	1.0	16.9	651.9
ESCI11	375.0	1.2	23.7	399.9
ZSCI11	2.0	270.0	17.5	289.5
ESCI12	0.1	3.9	23.7	27.6
ZSCI12	19.0	2,288.0	16.9	2,323.9
ESCI13	0.0	3.9	23.7	27.6
ZSCI13	140.0	495.0	16.9	651.9
ESCI14	3.8	0.0	23.7	27.5
ZSCI14	71,000.0	8,500.0	18.1	79,518.1

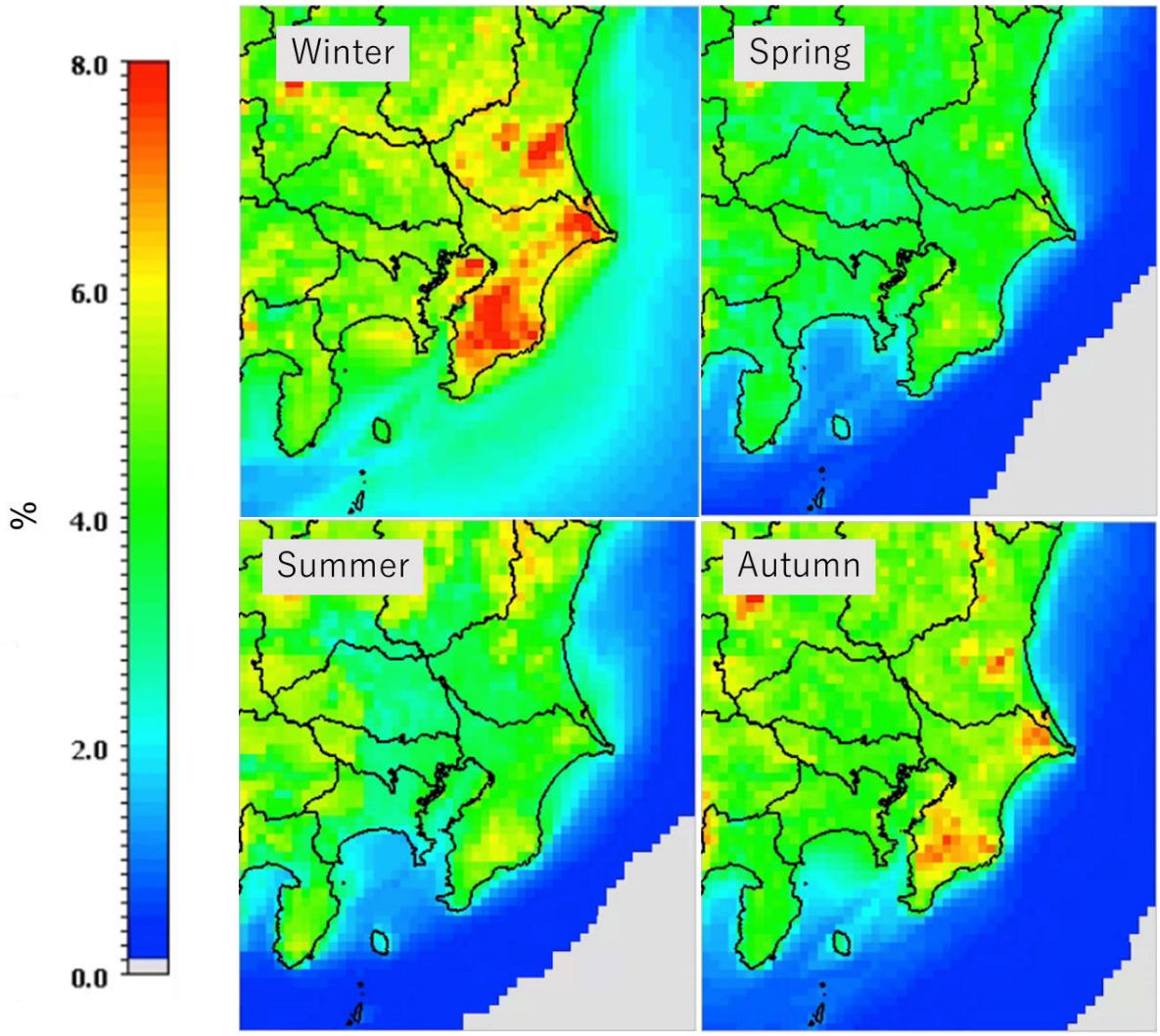

Figure S12: Seasonal changes in the average episode distribution of the increased OH.

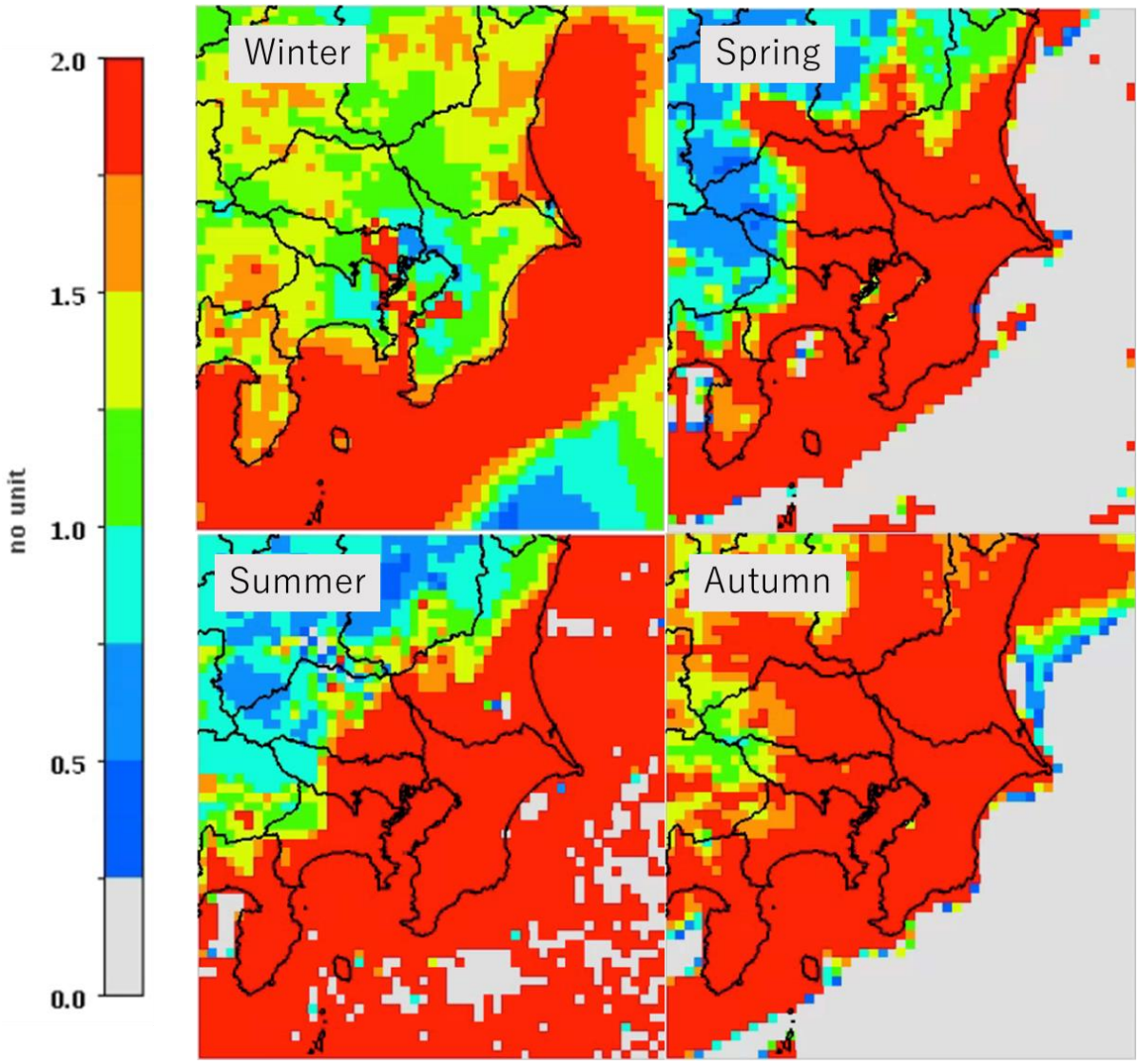

Figure S13: Seasonal average distribution of the ratio of $k_{OH}\Delta[OH]$ / $k_{CI}\Delta[CI]$ where k_{OH} is the rate constant of the reaction of SO_2 + OH at 298 K (1.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and k_{CI} is that of SO_2 + sCIs. Δ[OH] and Δ[CI] are the changes on the concentration of OH and sCIs before and after the incorporation of sCIs chemistry to the chemical mechanism of SAPRC-07, respectively.

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