Comprehensive multiphase chlorine chemistry in the box model CAABA/MECCA: Implications to atmospheric oxidative capacity

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1 Model inputs

Initial concentrations of CO, CH_4, NO_x, non-methane hydrocarbons (NMHCs), various VOCs and aerosol properties considered for simulations over both the locations are described in Table 1 S1. The levels of gas-phase chemical species in Delhi are based on a recent field campaign conducted at Indian Institute of Delhi (IITD) during winter season of 2018 [1]. In addition to listed species in table 3 for Delhi, additional chemical species are considered for simulations which include acetone (9 nmol/mol), methanol (12 nmol/mol), acetaldehyde (6.1 nmol/mol), acetonitrile (7.5 nmol/mol), methyl ethyl ketone (1.3 nmol/mol), styrene (1.4 nmol/mol), pinene (0.14 nmol/mol), formaldehyde (1.8 nmol/mol), ethanol (1.7 nmol/mol), acetic acid (6 nmol/mol), propanol (0.4 nmol/mol), methyl vinyl ketone (0.3 nmol/mol), NH_3 (25.1 nmol/mol) and SO_2 (2.1 nmol/mol) [1–4]. Measurements of aerosols (stated in Table 1) has been carried out in another field campaign during February 2018–January 2019 in Delhi [5]. The concentration of gaseous species in Leicester are from Sommariva et al., 2018 and 2021 [6, 7]. The aerosol properties are based on previously reported studies.

Table S1: Initial values of various gases (in nmol/mol) and aerosols opted for simulations over Delhi and Leicester.

Species	Delhi	Leicester
Ozone	26	20
Nitrogen oxides	154	19
Carbon monoxide	1340	140
Methane	2250	1900
Ethane	20	6.3
Ethene	14	0.67
Propane	29	2.30
Propene	4	0.19
i-Butane	11	0.59
n-butane	22	0.97
Acetylene	10	0.49
Toluene	5.13	0.19
Benzene	2.81	0.20
Isoprene	0.80	0.02
Xylene	3.13	0.16
Ethyl benzene	0.667	0.03
1,2,4-Trimethyl Benzene (TMB)	0.834	0.05
1,3,5- TMB	0.427	0.02
H_2O (mol/mol)	0.0146	0.0055
Monodisperse radius (μm)	0.11	0.15
Liquid water content (m^3/m^3)	22.77E-12	1.2E-10
NO_3^- (molec/cm^3)	3.59E10	1.2E10
SO_4^{2-} (molec/cm^3)	2.45E10	7.4E9
NH_4^+ (molec/cm^3)	1.62E11	5.0E10
Cl^- (molec/cm^3)	1.01E11	3.4E9

2 Results

2.1 Cl_2 budget

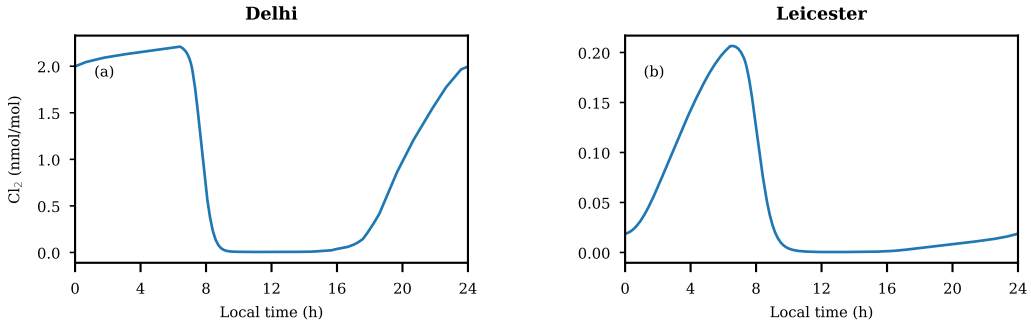

Figure S1: Diurnal variation in Cl_2 over (left panel) Delhi and (right panel) Leicester.

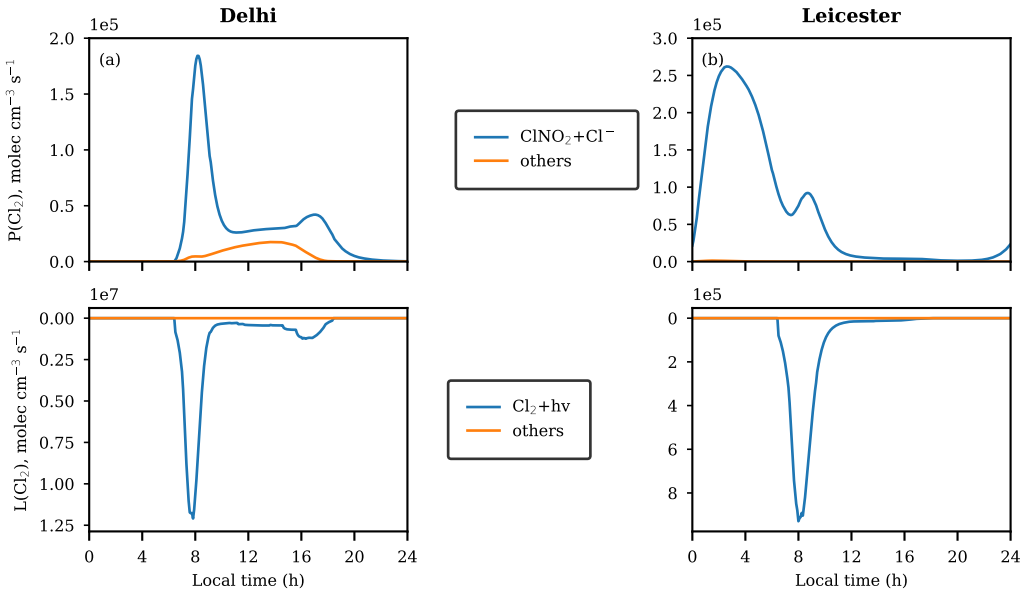

Figure S2: Production and loss of Cl_2 over (left panel) Delhi and (right panel) Leicester.

2.2 $ClNO_2$ yield

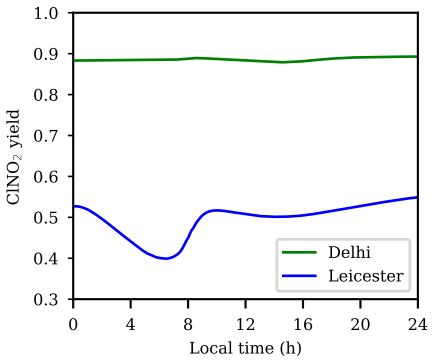

Figure S3: Model simulated $ClNO_2$ yield in Delhi and Leicester.

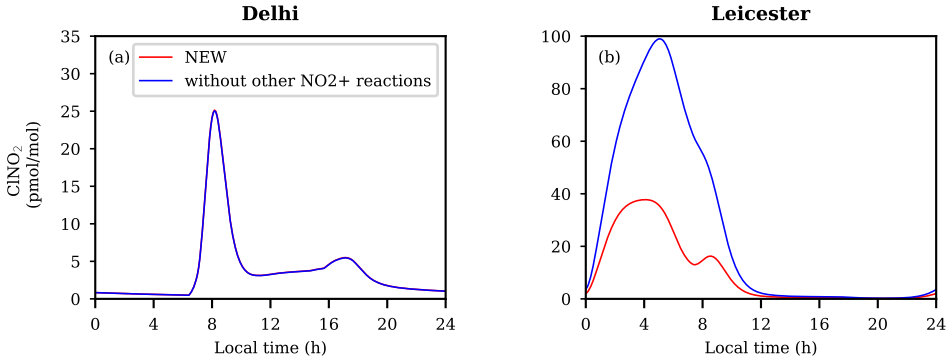

Figure S4: Diurnal variation in $ClNO_2$ over (a) Delhi and (b) Leicester.

2.3 Sensitivity of air composition to chlorine chemistry

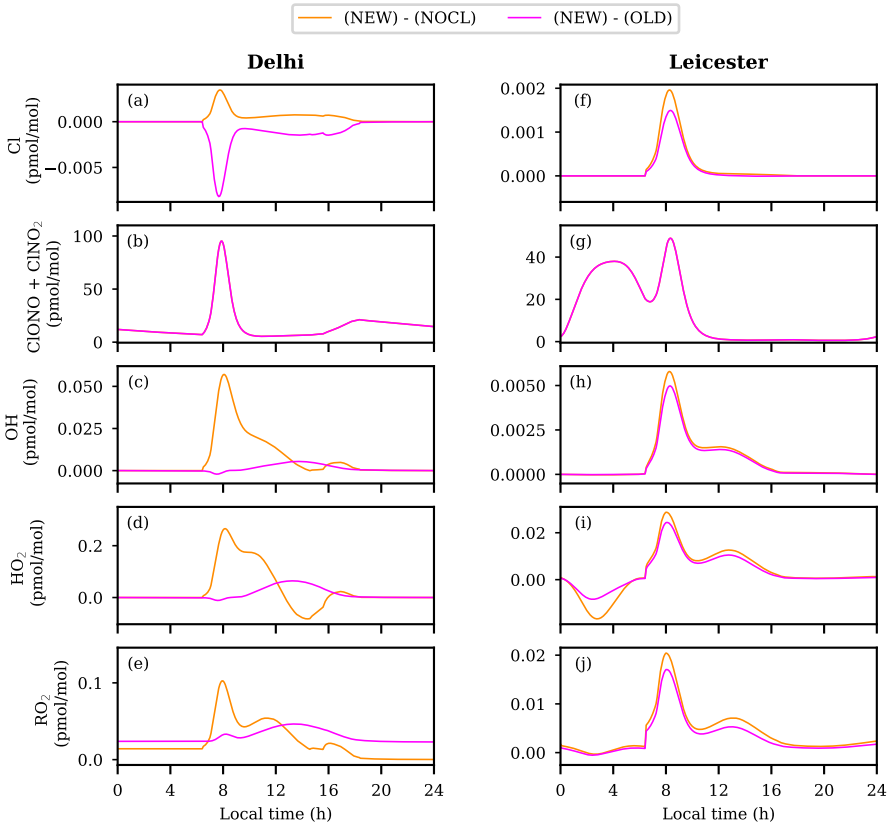

Figure S5: Differences in diurnal variation of Cl, $ClNO_2$ + ClONO, OH, HO_2, and RO_2 in model simulations over (left panel) Delhi and (right panel) Leicester.

In addition to the gas-phase composition, Cl chemistry also alters the levels of inorganic aerosol species at both locations, including the nitronium ion (NO_2^+), nitrate (NO_3^-), and oxalic acid (Fig.S6). The diurnal pattern of NO_2^+ is similar to that of N_2O_5 because dissociation of N_2O_5 is the major source of NO_2^+ production (A1). Chlorine chemistry (NEW simulation) reduces the modeled concentration of NO_2^+ by up to a factor of ≈8 and ≈2 in Delhi and Leicester, respectively, compared to without Cl chem simulation. Simulated NO_3^- is higher by upto 1.2 times over Delhi due to Cl chemistry. The measured mean NO_3^- over Delhi during high chloride period in winter-time is 5.3±3.2 ug/m^{-3} [5]. Simulated NO_3^- is higher by upto 1.4 times with the added Cl chemistry (NEW simulation) as compared to OLD simulation over Leicester. Simulated oxalic acid seems to be significantly higher due to Cl chemistry over Delhi and Leicester.

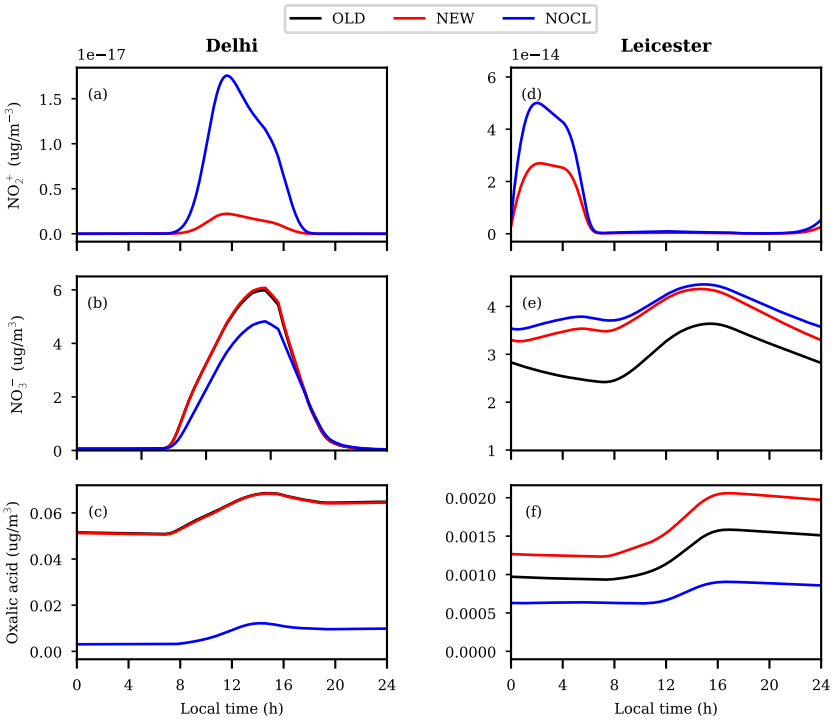

Figure S6: Impact of Cl chemistry on aerosols over (left panel) Delhi and (right panel) Leicester.

2.4 Sensitivity to $ClNO_2$ + Cl^- reaction

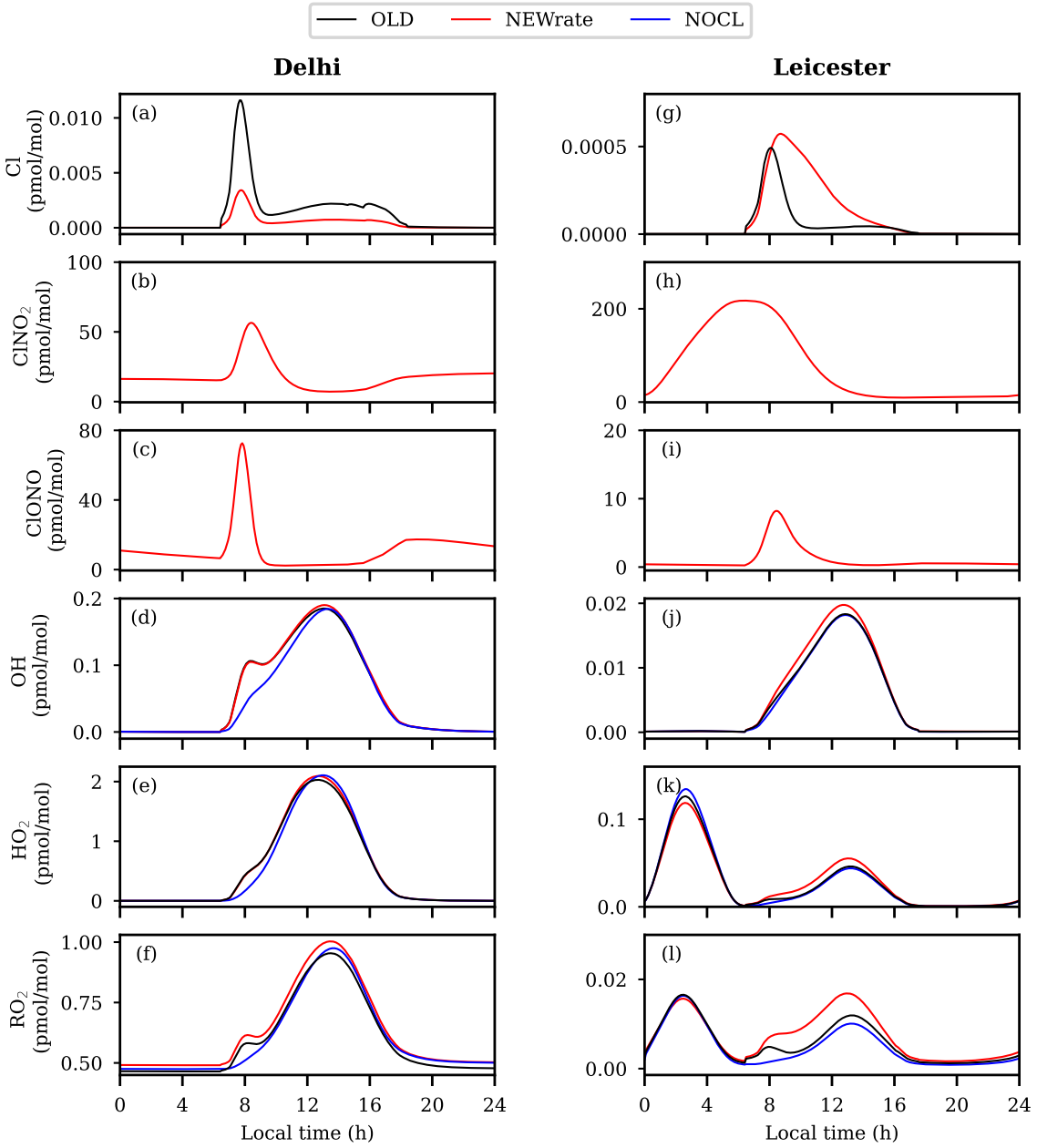

Figure S7: Model simulated diurnal variations in Cl, $ClNO_2$, ClONO, OH, HO_2, and RO_2 in Delhi (left panel) and Leicester (right panel).

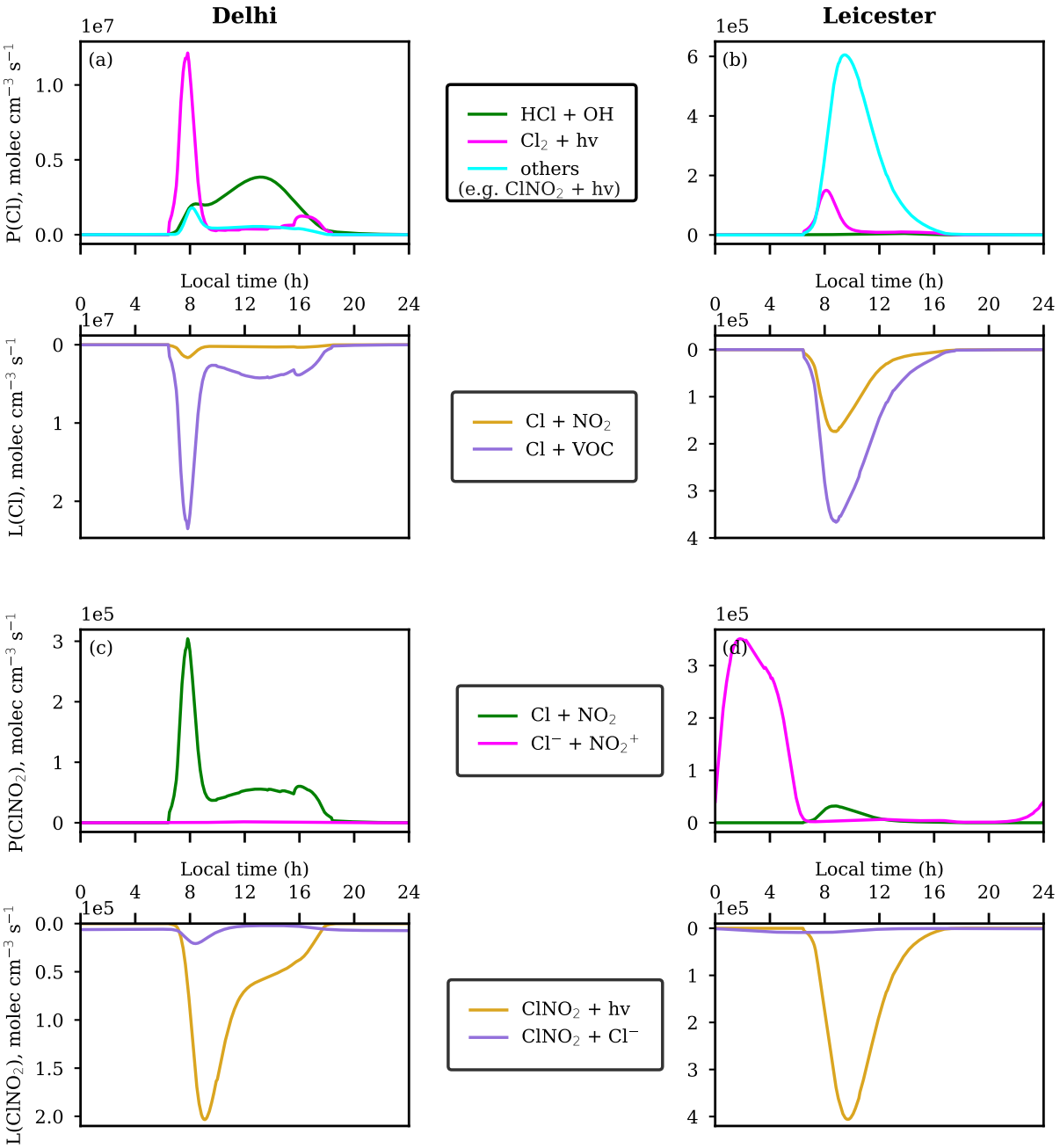

Figure S8: Production and loss of (a, b) Cl and (c, d) $ClNO_2$ in Delhi (left panel) and Leicester (right panel) in NEWrate simulation.

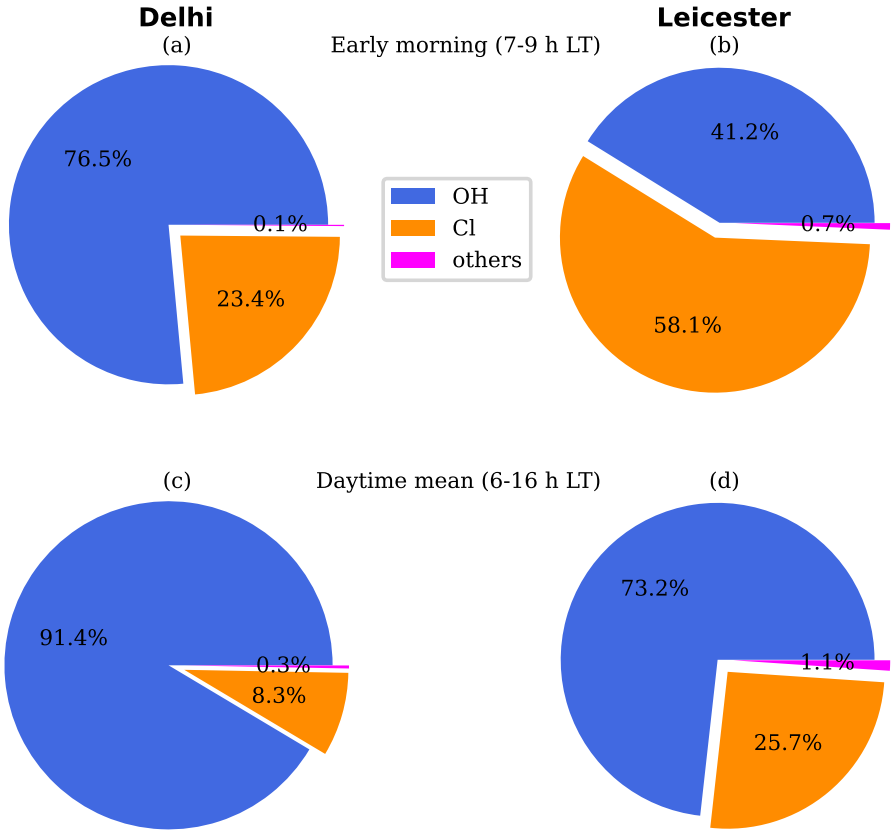

Figure S9: Atmospheric oxidative capacity (AOC) of radicals during (a, b) early morning time (7-9 h LT) and (c, d) daytime mean (6-16 h LT) in Delhi (left panel) and Leicester (right panel) as depicted in NEWrate simulation.

References

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