*Supplemental Information*

Isoprene Peroxy Chemistry Operates Competitively in Areas of East China

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Table S1. List of all measured VOCs in Taizhou (rural site) and Shanghai (urban site).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Taizhou | |  |  | Shanghai |  |
| No. | Species | Average (ppb) | | No. | Species | Average (ppb) |
| 1 | Ethane | | 2.11 | 1 | Acetylene | 1.02 |
| 2 | Ethylene | | 1.1 | 2 | Ethylene | 1.02 |
| 3 | Propane | | 2.04 | 3 | Formaldehyde | 3.06 |
| 4 | Propene | | 0.16 | 4 | Ethane | 3.25 |
| 5 | Isobutane | | 0.4 | 5 | Acetonitrile | 0.27 |
| 6 | n-Butane | | 0.64 | 6 | Propylene | 0.28 |
| 7 | Acetylene | | 0.98 | 7 | Propane | 2.29 |
| 8 | trans-2-Butene | | 0 | 8 | Ethanol | 2.04 |
| 9 | 1-Butene | | 0.07 | 9 | Chloromethane | 0.47 |
| 10 | cis-2-Butene | | 0.05 | 10 | Acrylonitrile | 0.02 |
| 11 | cycloprntane | | 0 | 11 | 1,3-Butadiene | 0.01 |
| 12 | Isopentane | | 0.42 | 12 | Acrolein | 0.08 |
| 13 | n-Pentane | | 0.26 | 13 | Trans-2-butene | 0.03 |
| 14 | Chloromethane | | 0.41 | 14 | 1-Butene | 0.08 |
| 15 | Vinylchloride | | 0.02 | 15 | Cis-2-butene | 0.03 |
| 16 | 1,3-Butadiene | | 0.01 | 16 | Isobutene | 0.08 |
| 17 | Acetaldehyde | | 1.87 | 17 | Propanal | 0.15 |
| 18 | Bromomethane | | 0.01 | 18 | Acetone | 3.01 |
| 19 | Chloroethane | | 0.05 | 19 | Isobutane | 0.73 |
| 20 | Freon11 | | 0.32 | 20 | n-Butane | 0.9 |
| 21 | 1-Pentene | | 0 | 21 | Isopropyl alcohol | 0.11 |
| 22 | trans-2-Pentene | | 0 | 22 | 1-Propanol | 0.03 |
| 23 | Isoprene | | 0.17 | 23 | Vinyl chloride | 0.01 |
| 24 | Acrolein | | 0.09 | 24 | Chloroethane | 0.02 |
| 25 | cis-2-Pentene | | 0 | 25 | Isoprene | 0.02 |
| 26 | Propanal | | 0.32 | 26 | Methacrolein | 0.02 |
| 27 | 1,1-Dichloroethylene | | 0 | 27 | Methyl vinyl ketone | 0.03 |
| 28 | 2,2-dimethylbutane | | 0.02 | 28 | Crotonaldehyde | 0.5 |
| 29 | Acetone | | 3.74 | 29 | Cyclopentane | 0.06 |
| 30 | Acetonitrile | | 0.2 | 30 | 1-Pentene | 0.01 |
| 31 | Dichloromethane | | 0.95 | 31 | Trans-2-pentene | 0 |
| 32 | 2,3-Dimethylbutane | | 0.02 | 32 | Cis-2-pentene | 0 |
| 33 | 2-Methylpentane | | 0.11 | 33 | 2-Methyl-1-butene | 0.01 |
| 34 | 3-Methylpentane | | 0.08 | 34 | 2-Methyl-2-butene | 0 |
| 35 | MTBE | | 0.1 | 35 | 3-Methyl-1-butene | 0 |
| 36 | 1-Hexene | | 0.01 | 36 | n-Butanal | 0.07 |
| 37 | n-Hexane | | 0.15 | 37 | Methyl ethyl ketone | 0.56 |
| 38 | Methacrolein | | 0.1 | 38 | Tetrahydrofuran | 0.04 |
| 39 | 1,1-Dichloroethane | | 0.01 | 39 | Isopentane | 0.56 |
| 40 | 2,4-Dimethylpentane | | 0.02 | 40 | n-Pentane | 0.31 |
| 41 | Methyl Vinyl ketone | | 0.11 | 41 | 1-Butanol | 0.17 |
| 42 | Methylcyclopentane | | 0.04 | 42 | Carbon disulfide | 0.02 |
| 43 | cis-1,2-Dichloroethylene | | 0 | 43 | 1-Hexene | 0.01 |
| 44 | Methyl Ethyl ketone | | 0.6 | 44 | Methylcyclopentane | 0.05 |
| 45 | Chloroform | | 0.12 | 45 | Cyclohexane | 0.07 |
| 46 | 1,1,1-Trichloroethane | | 0 | 46 | 4-Methyl-1-pentene | 0 |
| 47 | 2-Methylhexane | | 0.03 | 47 | 2-Methyl-1-pentene | 0.01 |
| 48 | Cyclohexane | | 0.04 | 48 | 2-Methyl-2-pentene | 0 |
| 49 | 2,3-Dimethylpentane | | 0.01 | 49 | Dichloromethane | 0.98 |
| 50 | 3-Methylhexane | | 0.05 | 50 | 2-Pentanone | 0.03 |
| 51 | Tetrachloromethane | | 0.1 | 51 | n-Pentanal | 0.03 |
| 52 | Benzene | | 0.42 | 52 | 3-Pentanone | 0.01 |
| 53 | 2,2,4-Trimethylpentane | | 0.01 | 53 | 2,2-Dimethylbutane | 0.02 |
| 54 | 1,2-Dichloroethane | | 0.64 | 54 | 2,3-Dimethylbutane | 0.02 |
| 55 | n-Heptane | | 0.06 | 55 | 2-Methylpentane | 0.12 |
| 56 | Trichloroethylene | | 0.05 | 56 | 3-Methylpentane | 0.11 |
| 57 | Methylcyclohexane | | 0.03 | 57 | n-Hexane | 0.29 |
| 58 | 2-Pentanone | | 0.02 | 58 | Chlorodifluoromethane | 0.11 |
| 59 | 1,2-Dichloropropane | | 0.21 | 59 | Methyl tert-butyl ether | 0.11 |
| 60 | n-Pentanal | | 0.08 | 60 | Toluene | 0.62 |
| 61 | 3-Pentanone | | 0.02 | 61 | Bromomethane | 0.01 |
| 62 | Bromodichloromethane | | 0 | 62 | 1,1-Dichloroethene | 0 |
| 63 | 2,3,4-Trimethylpentane | | 0.01 | 63 | Cis-1,2-dichloroethene | 0 |
| 64 | 2-Methylheptane | | 0.01 | 64 | Trans-1,2-dichloroethene | 0 |
| 65 | 3-Methylheptane | | 0.02 | 65 | Cyclohexanone | 0.05 |
| 66 | trans-1,3-Dichloropropene | | 0 | 66 | Methylcyclohexane | 0.04 |
| 67 | Toluene | | 0.56 | 67 | 1,1-Dichloroethane | 0.01 |
| 68 | n-Octane | | 0.04 | 68 | 1,2-Dichloroethane | 0.54 |
| 69 | cis-1,3-Dichloropropene | | 0 | 69 | n-Hexanal | 0.09 |
| 70 | 1,1,2-Trichloroethane | | 0.02 | 70 | Methyl isobutyl ketone | 0.02 |
| 71 | Tetrachloroethylene | | 0.04 | 71 | Methyl butyl ketone | 0.02 |
| 72 | n-Hexanal | | 0.22 | 72 | 2,4-Dimethylpentane | 0.01 |
| 73 | 1,2-Dibromoethane | | 0 | 73 | 2-Methylhexane | 0.03 |
| 74 | Chlorobenzene | | 0.03 | 74 | 2,3-Dimethylpentane | 0.02 |
| 75 | Ethylbenzene | | 0.16 | 75 | 3-Methylhexane | 0.04 |
| 76 | n-Nonane | | 0.02 | 76 | n-Heptane | 0.06 |
| 77 | m/p-Xylene | | 0.11 | 77 | Styrene | 0.06 |
| 78 | o-Xylene | | 0.1 | 78 | Ethylbenzene | 0.23 |
| 79 | Styrene | | 0.02 | 79 | m/p-Xylene | 0.44 |
| 80 | i-Propylbenzene | | 0.01 | 80 | o-Xylene | 0.17 |
| 81 | n-Propylbenzene | | 0.02 | 81 | Trans-1,3-dichloropropene | 0 |
| 82 | m-Ethyltoluene | | 0.02 | 82 | Cis-1,3-dichloropropene | 0 |
| 83 | p-Ethyltoluene | | 0.02 | 83 | Chlorobenzene | 0.02 |
| 84 | n-Decane | | 0.02 | 84 | 1,2-Dichloropropane | 0.04 |
| 85 | 1,3,5-Trimethylbenzene | | 0.02 | 85 | 2,2,4-Trimethylpentane | 0.02 |
| 86 | o-Ethyltoluene | | 0.05 | 86 | 2,3,4-Trimethylpentane | 0.02 |
| 87 | 1,2,4-Trimethylbenzene | | 0.02 | 87 | 2-Methylheptane | 0.02 |
| 88 | 1,3-Dichlorobenzene | | 0.01 | 88 | 3-Methylheptane | 0.03 |
| 89 | 1,4-Dichlorobenzene | | 0.01 | 89 | n-Octane | 0.07 |
| 90 | 1,2,3-trimethylbenzene | | 0.02 | 90 | Chloroform | 0.09 |
| 91 | Benzylchloride | | 0 | 91 | iso-Propylbenzene | 0.03 |
| 92 | m-Diethylbenzene | | 0.01 | 92 | n-Propylbenzene | 0.03 |
| 93 | p-Diethylbenzene | | 0.02 | 93 | m-Ethyltoluene | 0.04 |
| 94 | 1,2-Dichlorobenzene | | 0.01 | 94 | p-Ethyltoluene | 0.03 |
| 95 | n-Undecane | | 0.02 | 95 | 1,3,5-Trimethylbenzene | 0.02 |
| 96 | Formaldehyde | | 4.32 | 96 | o-Ethyltoluene | 0.03 |
| 97 | Acetonitrile | | 0.18 | 97 | 1,2,4-Trimethylbenzene | 0.04 |
| 98 | Propylene | | 0.3 | 98 | 1,2,3-Trimethylbenzene | 0.02 |
| 99 | Acetaldehyde | | 1.43 | 99 | Freon-12 | 0.45 |
| 100 | Formic acid | | 0.55 | 100 | PAN | 0.69 |
| 101 | Acrolein | | 0.15 | 101 | Benzyl chloride | 0.01 |
| 102 | Acetic acid | | 3.19 | 102 | n-Noe | 0.05 |
| 103 | Pyrrole | | 0 | 103 | Trichloroethylene | 0.02 |
| 104 | Furan | | 0.04 | 104 | 1,1,1-Trichloroethane | 0 |
| 105 | Isoprene | | 0.39 | 105 | 1,1,2-Trichloroethane | 0.02 |
| 106 | Dihydropyrrole | | 0.01 | 106 | m-Diethylbenzene | 0.02 |
| 107 | Acrylic acid | | 0.65 | 107 | p-Diethylbenzene | 0.02 |
| 108 | Propionic acid | | 1.39 | 108 | alpha-Pinene | 0 |
| 109 | Benzene | | 0.34 | 109 | beta-Pinene | 0 |
| 110 | Methyl furan | | 0.04 | 110 | Cinene | 0 |
| 111 | Furanone | | 0.03 | 111 | Freon-11 | 0.19 |
| 112 | Dihydromethylfuran | | 0.09 | 112 | n-Decane | 0.04 |
| 113 | Butyric acid | | 0.7 | 113 | 1,3-Dichlorobenzene | 0.01 |
| 114 | Toluene | | 0.41 | 114 | 1,4-Dichlorobenzene | 0.18 |
| 115 | Phenol | | 0.03 | 115 | 1,2-Dichlorobenzene | 0.01 |
| 116 | Furan aldehyde | | 0.04 | 116 | Carbon tetrachloride | 0.08 |
| 117 | Dimethylfuran | | 0.02 | 117 | n-Undecane | 0.03 |
| 118 | Maleic anhydride | | 0.14 | 118 | Bromodichloromethane | 0 |
| 119 | Furfuryl alcohol | | 0.09 | 119 | Tetrachloroethylene | 0.04 |
| 120 | Hydroxy furanone | | 0.04 | 120 | 1,1,2,2-Tetrachloroethane | 0.01 |
| 121 | Styrene | | 0.02 | 121 | Freon-114 | 0.01 |
| 122 | Benzaldehyde | | 0.09 | 122 | 1,2,4-Trichlorobenzene | 0.08 |
| 123 | C8 aromatics | | 0.29 | 123 | Freon-113 | 0.06 |
| 124 | Cresol | | 0.02 | 124 | 1,2-Dibromoethane | 0 |
| 125 | Chlorobenzene | | 0.03 | 125 | Dibromochloromethane | 0 |
| 126 | Acetylacrylic acid | | 0.07 | 126 | Bromoform | 0 |
| 127 | C9 aromatics | | 0.03 | 127 | Hexachloro-1,3-butadiene | 0.03 |
| 128 | Naphthalene | | 0.02 |  |  |  |
| 129 | Trimethylphenol | | 0.01 |  |  |  |
| 130 | Terpene | | 0.27 |  |  |  |
| 131 | Tyrosol | | 0.01 |  |  |  |
| 132 | Nopinone | | 0.01 |  |  |  |
| 133 | Trihydroxytoluene | | 0.01 |  |  |  |
| 134 | Methylnaphthalene | | 0.01 |  |  |  |
| 135 | Naphthalenol | | 0 |  |  |  |
| 136 | Phthalic anhydride | | 0.03 |  |  |  |
| 137 | Syringol | | 0.01 |  |  |  |

Table S2. Chemical reactions leading to the formation and MACR and MVK in the MOZART-TS1 mechanism.

| Reaction |  | Products | Rate |
| --- | --- | --- | --- |
| ISOP + OH |  | 0.6\*ISOPAO2 + 0.4\*ISOPBO2 | 2.54e-11 exp(410/T) |
| ISOPAO2 + CH3CO3 |  | CH3O2 + HO2 + CH2O + 0.39\*MACR + 0.61\*MVK + CO2 | 1.4e-11 |
| ISOPAO2 + CH3O2 |  | 0.25\*CH3OH + HO2 + 1.5\*CH2O + 0.31\*MACR + 0.44\*MVK | 5e-13 exp(400/T) |
| ISOPAO2 + HO2 |  | ISOPOOH | 8e-13 exp(700/T) |
| ISOPAO2 + NO |  | 0.08\*ISOPNITA + 0.92\*NO2 + 0.36\*MACR + 0.56\*MVK + 0.92\*CH2O + 0.92\*HO2 | 4.4e-12 exp(180/T) |
| ISOPAO2 + NO3 |  | NO2 + 0.4\*MACR + 0.6\*MVK + CH2O + HO2 | 2.4e-12 |
| ISOPBO2 + CH3CO3 |  | HYDRALD + CH3O2 + HO2 | 1.4e-11 |
| ISOPBO2 + CH3O2 |  | 0.25\*CH3OH + HO2 + 0.75\*CH2O + 0.75\*HYDRALD | 5e-13 exp(400/T) |
| ISOPBO2 + HO2 |  | ISOPOOH | 8e-13 exp(700/T) |
| ISOPBO2 |  | HPALD + HO2 | 1.6e+09 exp(-8300/T) |
| ISOPBO2 + NO |  | 0.87\*HYDRALD + 0.08\*ISOPNITB + 0.92\*NO2 + 0.92\*HO2 + 0.05\*GLYOXAL + 0.05\*GLYALD + 0.05\*CH3COCHO + 0.05\*HYAC | 4.4e-12 exp(180/T) |
| ISOPBO2 + NO3 |  | NO2 + 0.95\*HYDRALD + HO2 + 0.05\*GLYOXAL + 0.05\*GLYALD + 0.05\*CH3COCHO + 0.05\*HYAC | 2.4e-12 |

Table S3. Chemical reactions for the dynamics of ISOPOO radicals and formation of MACR and MVK in CIM.

| **Reaction** |  | **Products** | **Rate** |
| --- | --- | --- | --- |
| ISOP + OH |  | 0.315\*ISOPC1T + 0.315\*ISOPC1C + 0.111\*ISOPC4T + 0.259\*ISOPC4C | 2.54e-11 exp(410/T) |
| ISOPC1C + O2 |  | ISOPB1O2 | 6.0e-13 |
| ISOPC1C + O2 |  | ISOPZD1O2 | 7.0e-13 |
| ISOPC1T + O2 |  | ISOPB1O2 | 6.0e-13 |
| ISOPC1T + O2 |  | ISOPED1O2 | 4.0e-13 |
| ISOPC4C + O2 |  | ISOPB4O2 | 6.5e-13 |
| ISOPC4C + O2 |  | ISOPZD4O2 | 2.1e-13 |
| ISOPC4T + O2 |  | ISOPB4O2 | 6.5e-13 |
| ISOPC4T + O2 |  | ISOPED4O2 | 4.9e-13 |
| ISOPB1O2 |  | ISOPC1C + O2 | 2.24e+15 exp(-10865/T) |
| ISOPB1O2 |  | ISOPC1T + O2 | 2.22e+15 exp(-10355/T) |
| ISOPB4O2 |  | ISOPC4C + O2 | 2.49e+15 exp(-11112/T) |
| ISOPB4O2 |  | ISOPC4T + O2 | 2.49e+15 exp(-10890/T) |
| ISOPED1O2 |  | ISOPC1T + O2 | 1.83e+14 exp(-8930/T) |
| ISOPED4O2 |  | ISOPC4T + O2 | 2.08e+14 exp(-9400/T) |
| ISOPZD1O2 |  | ISOPC1C + O2 | 1.07e+14 exp(-8830/T) |
| ISOPZD4O2 |  | ISOPC4C + O2 | 1.75e+14 exp(-9054/T) |
| ISOPB1O2 + CH3CO3 |  | MVK + CH2O + HO2 + CO2 + CH3O2 | 1.4e-11 |
| ISOPB4O2 + CH3CO3 |  | MACR + CH2O + HO2 + CO2 + CH3O2 | 1.4e-11 |

Table S4. Statistical evaluation indexes for the performance of CIM and MOZART-TS1 in predicting the ambient concentrations of MACR and MVK.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Index | Formula | MACR | | MVK | |
| CIM | MOZART | CIM | MOZART |
| Mean Bias (MB) | A black and white math symbol  Description automatically generated | -0.20 | -3.68 | 3.23 | -5.16 |
| Mean Normalized Bias (MNB) | A mathematical equation with numbers and symbols  Description automatically generated | 0.03 | -0.19 | 0.19 | -0.21 |
| Normalized Mean Bias (NMB) | A black text on a white background  Description automatically generated | -1.24% | -22.50% | 13.45% | -21.48% |
| Mean Normalized Error (MNE) | A mathematical equation with numbers and symbols  Description automatically generated | 0.28 | 0.30 | 0.36 | 0.47 |
| Normalized Mean Error (NME) | A black and white math equation  Description automatically generated | 30.90% | 32.04% | 32.53% | 44.94% |

A graph with blue dots

Description automatically generated

Figure S1. Prevailing wind directions during the observation period in Shanghai.

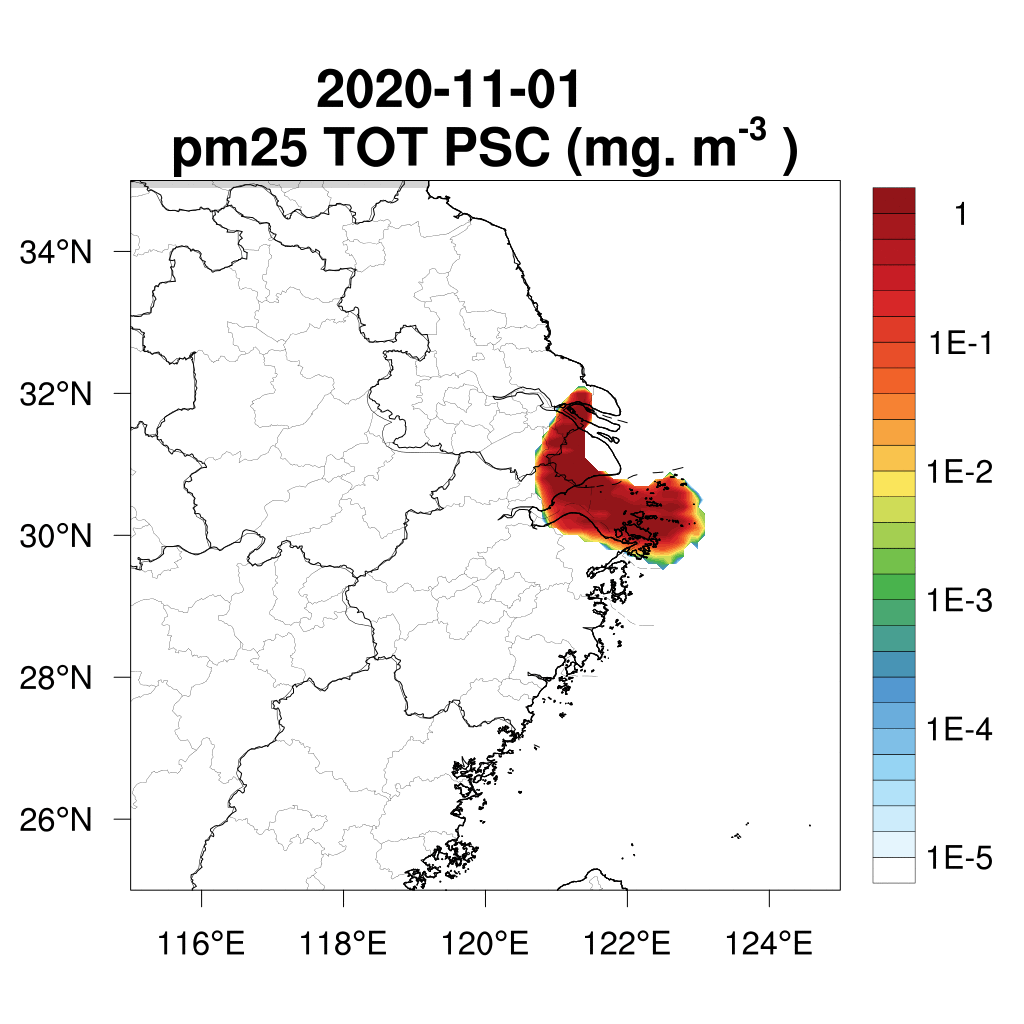


Figure S2. PM2.5 source appointment during the observation period in Shanghai.