稳态假设视角下的OH自由基浓度反演

Steady-state-based imputation for OH

Different ESMs use different submodules (i.e. atmosphere, land, sea, and sea-ice) to realise coupled simulation. However, in terms of ambient O3 modelling, differences in the atmospheric settings contribute most to the cross-model divergences. BCC-ESM1 simulates 63 gas-phase chemical species, 33 photolytic reactions, and 135 chemical reactions. CESM2-WACCM is the model with the most sophisticated O3 chemistry, involving 231 gas-phase species, 150 pho-tolytic reactions, 403 kinetic chemistry reactions, and 30 heterogeneous reactions. GFDL-ESM4 considers 43 photolysis reactions, 190 gas-phase kinetic reactions, and 15 heterogeneous reactions. MRI-ESM2-0 includes 90 gas-phase species, 59 photolytic reactions, 184 kinetic chemistry reactions, and 16 heterogeneous reactions. UKESM1-0-LL considers 84 gas-phase species, 59 photolytic reactions, 224 kinetic reactions (199 bimolecular, 25 uni-molecular and termolecular), and 5 heterogeneous reactions. GISS-E2-1 is the model with the most simplified chemistry, as it uses the lumped VOC collections. It simulates 47 gas-phase chemical species, 28 photolysis reactions, 118 kinetic reactions. Detailed illustrations of chemistry configurations (i.e. involved chemical species and reactions) for each ESM have been documented in the relevant literature.

In its present conﬁguration, the model considers the fundamental chemical cycle of O x -NO x -HO x -CH 4 -CO with oxidation of VOCs and halogen chemistry calculating concentrations of 92 chemical species with 262 chemical reactions (58 photolytic, 183 kinetic, and 21 heterogeneous reactions). For VOCs, the model includes oxidation of ethane (C 2 H 6 ), ethene (C 2 H 4 ), propane (C 3 H 8 ), propene (C 3 H 6 ), butane (C 4 H 10 ), acetone, methanol, isoprene, and terpenes.

[OH]的浓度在CMIP6库中大多是已提供的，所以我们可以借助已知的[OH]，在稳态假设下反推[O(1D)]的浓度。

OH自由基的生成包括：

O(1D) + H2O → 2OH **(R1)**, *k*1 = 2.14×10-10 cm3 molecule-1 s-1

O3 + HO2 → 2O2 + OH **(R2)**, , preferred value as 2.0×10–15 cm3 molecule-1 s-1 at 298 K

NO + HO2 → NO2 + OH **(R3)**, , preferred value as 8.5×10–12 cm3 molecule-1 s-1 at 298 K.

OH自由基的消去反应包括：

**CO + OH + O2 → HO2 + CO2 (R4) (**lossco**)**

O3 + OH → O2 + HO2 (R5), , preferred value as 7.3×10–14 cm3 molecule-1 s-1 at 298 K.

OH + NO2 + M → HNO3 + M (R6), *k*6 preferred value as 3.0×10–11 cm3 molecule-1 s-1 at 298 K

**HO + HO** → **H2O + O** **(R7),** *k*7 = 6.2×10–14×(T/298)2.6×*e*(945/T), preferred value as 1.48×10–12 cm3 molecule-1 s-1 at 298 K.

**HO + HO + M** → **H2O2 + M** **(R8),** *k*8 = 3.9×10–11×(T/300)-0.47

**HO + HO2** → **H2O + O2** **(R9),** *k*9 = 4.8×10–11×exp(250/T), preferred value as 1.1×10–10 cm3 molecule-1 s-1 at 298 K.

**HO + NO + M** → **HONO + M** **(R10),** *k*10 = 3.3×10–11×(T/300)-0.3

所以OH自由基的稳态为：

2*k*1[O(1D)][H2O]+ *k*2[O3][HO2]+ *k*3[NO][HO2] = L(CO)+ *k*5[O3][OH]+ *k*6[OH][NO2]+2(*k*7+ *k*8)[OH]2+ *k*9[OH][HO2]+ *k*10[OH][NO]

我们可以求解[O(1D)]，以一元一次方程的形式。

2*k*1[O(1D)][H2O] = L(CO)+ *k*5[O3][OH]+ *k*6[OH][NO2]+2(*k*7+ *k*8)[OH]2+ *k*9[OH][HO2]+ *k*10[OH][NO] – *k*2[O3][HO2] – *k*3[NO][HO2]