

Development of iron-mediated molecular chlorine chemistry in GEOS-Chem: model description, evaluation and global atmospheric implication

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Abstract. Molecular chlorine (Cl_2) plays a significant role in shaping atmospheric oxidative capacity (AOC), yet the GEOS-Chem global model tends to underestimate Cl_2 concentrations due to incomplete representations of its formation pathways. Here, we adapt an iron (Fe)-mediated Cl_2 formation mechanism into the GEOS-Chem model, explicitly representing the dynamic solubility of iron and Cl_2 production. This implementation enables the GEOS-Chem model to better reproduce observed Cl_2 concentrations, increasing correlation coefficient from 0.55 to 0.88 relative to the Base simulation (without Fe-Cl mechanism). Global surface mean Cl_2 concentration increases about fivefold (from 0.4 to 2.2 pptv) which strengthens radical propagation, causing approximately threefold and fourfold rise in global Cl and ClO radicals, respectively. These radical perturbations further result in pronounced spatial heterogeneity in AOC. While global mean OH decreases by 5.7% due to Cl-driven O_3 removal and conversion of HOx to ClOx, eastern China experiences concurrent increases in O_3 and OH (up to 14%), as enhanced RO_2 formation from Cl-accelerated VOCs oxidation elevates both OH and O_3 under high- NO_x conditions. Consequently, the strengthened AOC intensifies regional secondary aerosol formation with wintertime $\text{PM}_{2.5}$ in eastern China surges by up to 6%, driven primarily by accelerated nitrate production. Conversely, a discernible decline in $\text{PM}_{2.5}$ occurs in the downwind regions with enhanced AOC and also remote marine regions. These findings underscore the importance to consider iron-chlorine coupling chemistry in the GEOS-Chem global model for accurately representing atmospheric oxidation processes and enhancing its reliability of air quality assessments.

1 Introduction

Chlorine chemistry has been recognized as an important factor in regulating atmospheric oxidative capacity (AOC), air quality and global climate (Saiz-Lopez and Von Glasow, 2012; Simpson et al., 2015; Hossaini et al., 2016; Li et al., 2022; Li et al., 2023b; Saiz-Lopez et al., 2023; Saiz-Lopez et al., 2025). Chlorine radicals (Cl), which react more rapidly with many volatile organic compounds (VOCs) than hydroxyl radical (OH) (Faxon and Allen, 2013; Sun et al., 2025), can alter the abundance and cycling of key atmospheric radicals and oxidants (such as OH, HO_2 , RO_2 and O_3) through coupled reaction pathways (Faxon et al., 2015; Chen et al., 2025a; Chen et al., 2025b; Saiz-Lopez and Von Glasow, 2012).

Molecular chlorine (Cl_2) is a key chlorine-containing species and can serve as an efficient source of Cl radicals through fast photolysis (Dai et al., 2025; Liu et al., 2017; Priestley et al., 2018). Cl_2 is generally thought to be formed through several pathways, including autocatalytic gas-phase reactions (e.g., $\text{ClO} + \text{ClO}$, $\text{ClOO} + \text{Cl}$, $\text{ClNO}_3 + \text{Cl}$), heterogeneous uptake reactions of OH, ClNO_2 , ClNO_3 , and HOCl on acidic chloride-containing aerosol (Simpson et al., 2015; Wang et al., 2019), and O_3 uptake by aerosol (Li et al., 2023a). Beyond these pathways, photo-driven chloride activation has also been increasingly recognized as a potential source of Cl_2 production, with relevant processes involving iron (Fe), TiO_2 , particulate nitrate and NH_4Cl (Li et al., 2020; Peng et al., 2022; Li et al., 2026). In particular, laboratory (Wittmer et al., 2015a; Wittmer et al., 2015b; Wittmer and Zetzsch, 2017) and field studies (Chen et al., 2024; Chen et al., 2025b; Röckmann et al., 2024) both suggest that

40 aerosols containing soluble iron and chloride may generate Cl_2 through Fe(III)-mediated photochemical processes, serving as a considerable additional source of Cl radicals. This mechanism has inspired recent studies on whether enhanced Cl_2 production could promote Cl-initiated atmospheric CH_4 removal (Li et al., 2023b; Gorham et al., 2024; Meidan et al., 2024; Van Herpen et al., 2025). Besides, it also provides a basis for understanding missing daytime Cl_2 and its subsequent impacts on AOC and regional air quality (Van Herpen et al., 2023; Chen et al., 2024; Chen et al., 2025b).

45 A realistic treatment of soluble Fe aerosols is important for simulating Fe(III)-mediated Cl_2 production. Earlier simulations about iron–chlorine chemistry treat aerosol iron solubility with fixed assumptions (e.g., a constant photoreactive Fe fraction of 1.8% (Van Herpen et al., 2023), or prescribed soluble Fe fractions of 4% for dust and 40% for non-dust sources (Chen et al., 2024)). These simplified treatments neglect the dynamic changes in Fe solubility that occur during atmospheric transport, which are driven by aerosol acidification and complexation with organic ligands (Chen and Grassian, 2013). Observations

50 have shown increased Fe solubility from locations near dust sources to downwind regions during atmospheric transport processes (Zhi et al., 2025; Rodríguez et al., 2021; Srinivas et al., 2014; Takahashi et al., 2011). In addition, Fe aerosols from different sources exhibit distinct dissolution behaviors. For example, Fe in coal-combustion particles dissolves much more rapidly than that in mineral dust because of the higher acidity and the presence of reactive organic and inorganic coatings in coal-combustion particles (Baldo et al., 2022). Fe emitted from biomass burning also tends to exhibit higher initial solubility

55 than mineral dust (Wang et al., 2021b; Paris et al., 2010), making its soluble Fe emissions broadly comparable to those from dust sources (Zhang and Zheng, 2024). Therefore, a source-dependent, dynamic and process-based parameterization of Fe solubility is needed to improve the accuracy and reliability of model representations of Fe(III)-mediated Cl_2 photochemical production. Recently, Meidan et al. (2024) has conducted the first global-scale attempt to link iron and Cl_2 production using an asynchronous modelling framework with a more physically based treatment of iron dissolution. However, in their

60 configuration, the online feedbacks between iron dissolution, chlorine activation, atmospheric oxidants, and secondary aerosol formation remain incompletely represented.

Herein, we updated the chemical mechanism in the GEOS-Chem global atmospheric chemistry model to include Fe(III)-mediated Cl_2 formation pathway together with a more explicit treatment of Fe dissolution. Model performance was evaluated against observations of aerosol Fe concentrations, Fe solubility, and Cl_2 concentrations. The influences of Cl_2

65 photolysis on the distribution of Cl radicals and other reactive chlorine species, AOC, and the associated feedbacks on air quality were then examined. Our results contribute to a better understanding of Fe-driven chlorine chemistry in the atmospheric halogen cycles and suggest that incorporating dynamic Fe solubility and iron-halogen interactions can enhance the representation of chlorine chemistry in the GEOS-Chem global model.

2 Methods

70 2.1 Model description

Global chemical transport model GEOS-Chem (version 14.2.3, <https://doi.org/10.5281/zenodo.10246546>) was employed to assess the influence of reactive chlorine chemistry on atmospheric processes. The standard chemical mechanism comprises 293 species and 921 reactions, providing a comprehensive representation of the chemical cycling of nitrogen oxides (NO_x), oxidants (OH , NO_3 and O_3), volatile organic compounds (VOCs), aerosols, and halogens (Cl, Br, and I) in the troposphere and

75 stratosphere. Within the GEOS-Chem standard framework, the formation of Cl_2 is primarily driven by the heterogeneous uptake of HOCl , ClNO_2 , ClNO_3 , and OH onto chloride-containing aerosols (e.g. sea salt aerosols). These processes are dynamically modulated by aerosol acidity (pH), liquid water content (LWC), and specific surface area. Although gas-phase reactions (e.g., ClO self-reaction, $\text{ClOO} + \text{Cl}$ and $\text{ClNO}_3 + \text{Cl}$) are explicitly represented as well, they contribute marginally to the total Cl_2 budget compared to heterogeneous pathways. The chemical sinks for Cl_2 are photolysis and gas-phase oxidation

80 by OH , with photolysis serving as the dominant sink which generates Cl atoms.

Building on this framework, we integrated a Fe(III)-mediated pathway for Cl₂ formation in GEOS-Chem, with the goal of exploring the potential feedback between the iron cycle and reactive chlorine chemistry as well as global AOC.

2.2 Development of the Fe(III)-mediated Cl₂ formation (IMC) mechanism

2.2.1 Emissions of chlorine

85 In this study, emissions of chlorine from both natural and anthropogenic sources are considered. Natural chlorine emissions are dominated by sea-salt aerosols (SSA), which are calculated based on the spatiotemporal variations in environmental factors, including wind speed, sea surface temperature (SST) and sea-ice fraction. SSA is categorized into fine-mode particles (with diameter of 0.2~1 μm) and coarse-mode particles (with diameter of 1~8 μm), accounting for 16% and 84% of total SSA emissions, respectively. Correspondingly, sea-salt chloride (pCl) is present at a fixed mass fraction of 55.04% of SSA in each mode(Wang et al., 2019). Anthropogenic chlorine emissions (HCl + fine-mode pCl) primarily originate from waste incineration, biomass burning, and industrial processes (Fu et al., 2018; Yin et al., 2022; Chang et al., 2024). Following Fu et al. (2018), a global anthropogenic chlorine emission inventory is constructed and updated to 2023 using the latest activity data and relevant emission factors. The partitioning between HCl and pCl is dynamically determined by the ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes, 2007) in GEOS-Chem following Wang et al. (2020).

95 2.2.2 Emissions of iron

Iron (Fe) emissions include both dust-bound Fe and non-dust Fe. Dust-bound Fe emissions are determined by the corresponding dust emissions and the Fe content of the mineral components. Natural dust emissions are based on a semi-empirical function which combines the topographic source function used in Goddard Chemistry Aerosol Radiation and Transport (GOCART) scheme (Ginoux et al., 2004) with the dust entrainment and deposition (DEAD) mobilization scheme (Zender et al., 2003) by Duncan Fairlie et al. (2007). Anthropogenic dust includes fine particulate matter (PM_{2.5}) emissions from anthropogenic fugitive, combustion and industrial processes (AFCID) (Philip et al., 2017). In the model, dust emissions are represented in four distinct size bins with diameters of 0.2~2.0 μm (DST1), 2.0~3.6 μm (DST2), 3.6~6.0 μm (DST3), and 6.0~12.0 μm (DST4). Natural mineral dust is distributed across all four size bins, and originates mainly from the Sahara Desert in North Africa, the Arabian Desert, the deserts of Central and East Asia, and the Australian deserts. In contrast, anthropogenic dust is exclusively assigned to the finest bin (DST1) and primarily concentrated in regions with intensive human activity, including northern China, India, and parts of Europe.

In the standard GEOS-Chem mechanism, dust-bound Fe is simplified by assuming a uniform Fe mass fraction (3.5%) of dust emissions. However, incorporating explicit soil mineralogy is essential for capturing spatial variability and Fe solubility (Gonçalves Ageitos et al., 2023; Nickovic et al., 2012; Scanza et al., 2015; M. S. Johnson and Meskhidze, 2013). In this study, we adopt the soil mineralogical map updated by Nickovic et al. (2012) which is based on the earlier dataset of Claquin et al. (1999). Claquin et al. (1999) identified eight key minerals, including illite (4% as Fe), smectite (11% as Fe), hematite (57.5% as Fe), kaolinite (0.24% as Fe), feldspars (0.34% as Fe), quartz (0% as Fe), calcite (0% as Fe), and gypsum (0% as Fe). Building upon this, Nickovic et al. (2012) introduced a more realistic particle-size distribution by incorporating higher-resolution soil texture data, and redistributed iron oxides across both clay (< 2 μm) and silt size, thereby establishing a more physically consistent mineralogical structure. To reduce computational cost while capturing essential chemical processes, only illite, smectite, and hematite are explicitly represented because kaolinite and feldspar collectively accounting for less than 6% of total mineral Fe (as shown in Fig. S1).

Non-dust iron emissions primarily comprise biomass burning (including wildfires) and other anthropogenic sources. Biomass-burning (BB) Fe emissions are scaled from the Quick Fire Emissions Dataset (QFED) since previous studies have demonstrated that QFED offers superior performance in capturing the spatial and temporal variability of fire activities compared to other inventories (Wu et al., 2025). Following the methodology of Hamilton et al. (2019), Fe emissions from BB

are parameterized based on a mass ratio to black carbon (Fe:BC = 0.06), with 25% and 75% of BB Fe treated with BC-like and dust-like physical properties, respectively, to approximate their different transport and removal behaviors. Anthropogenic non-BB Fe originates mainly from shipping, aviation, and other human activities. In this study, anthropogenic non-BB Fe emissions are scaled to anthropogenic primary sulfate emissions from the Community Emissions Data System (CEDS) emission inventory which extends to 2023 and updates shipping fuel sulfur content by incorporating IMO sulfur-content agreements, assuming a fixed mass ratio of 1:30 following previous studies (Chen et al., 2024; Alexander et al., 2009).

2.2.3 New iron-bearing species

Since the Fe(III)-mediated chlorine chemistry is primarily constrained to fine particles (Chen et al., 2024), eight new iron-bearing tracers associated with the IMC mechanism are introduced into the model. These tracers can be grouped into two major groups based on their source characteristics: dust-bound Fe (Dust Fe) and non-dust Fe (Non-Dust Fe). Dust Fe includes soluble and insoluble fractions of three representative iron-bearing minerals (hematite, illite, and smectite), while non-dust Fe encompasses contributions from biomass burning and other anthropogenic sources. Since the initial solubility of Fe is strongly influenced by its source and mineralogical structure, differentiated solubility values are assigned to each tracer (as shown in Table 1). In details, dust-bound Fe is initialized with solubilities ranging from 0% to 5%, depending on the chemical stability of the corresponding mineral (Hamilton et al., 2019; Scanza et al., 2018). For biomass-burning Fe, whose reported solubility spans from 2.19% to 46%(Zhang and Zheng, 2024), a representative value of 20% is adopted. For other anthropogenic Fe sources (primarily combustion-derived Fe), a solubility of 4% is applied following previous studies (Luo et al., 2008; Hamilton et al., 2019; Scanza et al., 2018). In addition, each tracer is assigned specific physical proxy properties to represent its atmospheric behaviors. Specifically, fine dust Fe follows the physical characteristics of fine-mode dust (DST1), including its prescribed density and deposition parameters. For non-dust Fe, we adopt the physical characteristics of black carbon, as these iron species are typically co-emitted and internally mixed with carbonaceous aerosols. Soluble and insoluble non-dust Fe is further mapped to hydrophilic and hydrophobic host species, respectively. This treatment ensures that the simulated Fe tracers undergo more physically reasonable atmospheric transport and scavenging processes.

Table 1. Summary of implemented iron-bearing tracers and associated species properties.

Group	Type	Initial solubility	New tracers	Properties proxy
Dust Fe	hematite Fe	0%	hema_sol, hema_insol	DST1
	illite Fe	2.75%	illi_sol, illi_insol	DST1
	smectite Fe	5%	smec_sol, smec_insol	DST1
Non-Dust Fe	biomass burning Fe	20%	anFe_sol, anFe_insol	Black carbon
	other anthropogenic Fe	4%		Black carbon

2.2.4 Parameterization of iron dissolution kinetics

Once released, insoluble Fe undergoes complex chemical processing that facilitates its transformation into soluble forms during atmospheric transport. The conversion is collectively driven by three primary mechanisms: proton-promoted dissolution, ligand-mediated dissolution, and photochemical reductive dissolution. To capture these processes, a multi-stage parameterization scheme is implemented to describe the dynamic dissolution kinetics. Distinct dissolution rates are assigned according to the source of each Fe tracer. Specially, dust-bound Fe generally exhibits chemically stable mineral structures and is treated using the slow kinetics scheme. In contrast, non-dust Fe, characterized by a more amorphous structure and greater specific surface area, follows medium kinetics pathways. The specific dissolution processes and parameterization details are described below, with *i* denoting the corresponding dissolution regime (slow or medium) in each equation.

Proton-promoted dissolution. Proton-promoted dissolution occurs as acidic species (e.g., H₂SO₄, HNO₃) release H⁺ ions that attack the crystal lattice of iron oxides, mobilizing iron into the aerosol phase. This process is supported by numerous field observations which demonstrate a significant positive correlation between iron solubility and acidic ions (Zhang et al., 2021;

Zhang et al., 2023; Zhu et al., 2020). Following Meskhidze et al. (2005), the acid-promoted dissolution rate constant, $k(\text{Fe}_{\text{sol}})_{\text{proton}}$, is parameterized as Eq (1):

$$k(\text{Fe}_{\text{sol}})_{\text{proton}} = K_i(T) \times \alpha(\text{H}^+)^{m_i} \times f(\nabla G_r) \times A_i \times MW \quad \text{Eq(1)}$$

where $K_i(T)$ ($\text{mol m}^{-2} \text{s}^{-1}$) is the temperature-dependent rate constant, m_i (unitless) is the empirical reaction order and A_i ($\text{m}^2 \text{g}^{-1}$) is the specific surface area of the particle, with distinct formulations or values adopted for slow and medium dissolution regimes following Hamilton et al. (2019). $f(\nabla G_r)$ is the thermodynamic response function, which accounts for the system's deviation from chemical equilibrium. Based on Luo et al. (2008), this value is simplified to 1. MW is the molecular weight of the species with unit of g mol^{-1} . $\alpha(\text{H}^+)$ represents the proton activity, which can be calculated as Eq(2):

$$\alpha(\text{H}^+) = 10^{-\text{pH}} \quad \text{Eq(2)}$$

For simplify, aerosol pH is determined by the concentration of major acidic species (sulfate) and the alkaline buffering capacity of mineral dust (calcite). Following Luo et al. (2008), we assume 6% of mineral dust is soluble calcite.

Ligand-mediated dissolution. Ligand-mediated dissolution involves the formation of stable complexes between organic ligands (e.g., dicarboxylic acids, oxalate) and dissolved Fe(III), which effectively inhibits the hydrolysis and subsequent precipitation of iron thus increasing its solubility. Extensive studies have highlighted that organic ligands significantly enhance iron solubility and bioavailability, particularly in organic-rich environments. As oxalate is the most abundant dicarboxylic acid in the atmosphere, field observations have consistently identified a strong positive correlation between oxalate concentrations and soluble iron (Li et al., 2024; Zhang et al., 2021; Zhang et al., 2024). Consequently, this study adopts a ligand-enhanced dissolution parameterization following Hamilton et al. (2019), with the reaction rate expressed as:

$$k(\text{Fe}_{\text{sol}})_{\text{ligand}} = a_i \times [\text{C}_2\text{O}_4^{2-}] + b_i \quad \text{Eq(3)}$$

where a_i and b_i represent the source-specific rate coefficients, consistent with the values in Hamilton et al. (2019).

Since explicitly resolving full photochemical formation mechanism of oxalate would impose substantial computational cost, oxalate concentrations are diagnosed using a proxy approach. Following Hamilton et al. (2019), secondary organic aerosol (SOA) is adopted as the proxy, as its formation pathways are closely associated with the photochemical oxidation of organic precursors that also lead to oxalate production. Finally, concentration of oxalate ($[\text{C}_2\text{O}_4^{2-}]$ ($\mu\text{mol L}^{-1}$)) is calculated from simulated SOA concentrations as Eq (4):

$$[\text{C}_2\text{O}_4^{2-}] = 15 \times \frac{[\text{SOA}]}{\text{Max}[\text{SOA}]} \quad \text{Eq(4)}$$

The scaling factor of 15 is adopted from multi sensitivity simulations, which has been shown to reasonably capture the spatial characteristics of global oxalate distributions (Scanza et al., 2018). $\text{Max}[\text{SOA}]$ denotes the global maximum SOA concentration diagnosed from the standard simulation.

Photochemical reductive dissolution. Photochemical reductive dissolution involves the reduction of Fe(III) to the more soluble Fe(II) via ligand-to-metal charge transfer (LMCT) activated by solar radiation absorbing. However, since redox cycling equilibrates much faster than aerosol transport, no additional valence-specific tracers are introduced. Instead, the instantaneous Fe(III)/Fe(II) ratio is diagnosed under a quasi-steady-state assumption during the calculation of Cl_2 production (Section 2.2.5), determined by the local photochemical radiation flux.

2.2.5 Parameterization of IMC mechanism

In this study, the total dissolved iron ($\text{totFe}_{\text{sol}}$, unit: mol m^{-3}) is defined as the sum of soluble Fe originating from both mineral dust and non-dust (anthropogenic and biomass burning) sources:

$$\text{totFe}_{\text{sol}} = \text{hema}_{\text{sol}} + \text{illi}_{\text{sol}} + \text{smec}_{\text{sol}} + \text{anFe}_{\text{sol}} \quad \text{Eq(5)}$$

where hema_{sol} , illi_{sol} , smec_{sol} represent soluble iron from hematite, illite, and smectite, respectively, and anFe_{sol} denotes soluble Fe from biomass burning and other anthropogenic emissions.

Since the formation of Cl_2 depends strongly on the solar-radiation-driven Fe redox cycle, the fraction of Fe(II) is diagnosed

following the empirical formulation of Van Herpen et al. (2023) as Eq(6):

$$f(\text{FeII}) = k_2 \times \frac{I}{I_0} \times \left(k_1 + k_2 \times \frac{I}{I_0} \right)^{-1} \quad \text{Eq(6)}$$

where I is the instantaneous solar irradiance (W m^{-2}) and I_0 is the reference irradiance (600 W m^{-2}). The rate constants k_1 (0.19 min^{-1}) and k_2 (1.9 min^{-1}), representing the oxidation rate of Fe(II) to Fe(III) and photoreduction rate of Fe(III) to Fe(II), respectively, following the values specified in Van Herpen et al. (2023).

Laboratory studies have shown that IMC mechanism can be suppressed under specific chemical conditions. Specifically, when the molar ratio of $\text{Cl}^-/\text{Fe(III)}$ reaches approximately 955, the formation of photosensitive iron-chloride complexes is substantially inhibited due to the extremely low concentration of total Fe(III), leading to negligible Cl_2 production (Wittmer et al., 2015b). To avoid overestimating the contribution of this pathway in “high-chloride, low-iron” environments, this critical threshold is incorporated into the parameterization. Consequently, the final expression for the Cl_2 production rate (P_{Cl_2} , $\text{mol m}^{-3} \text{ min}^{-1}$) is as Eq(7):

$$P_{\text{Cl}_2} = \text{totFe}_{\text{sol}} \times k_1 \times f(\text{FeII}) \times \frac{1}{2} \quad \left(\text{for } \frac{[\text{Cl}^-]}{[\text{Fe(III)}]} < 955 \right) \quad \text{Eq(7)}$$

2.3 Model simulation scenarios

To evaluate the atmospheric impacts of IMC mechanism, we conduct three sensitivity simulations. The three scenarios differ in their treatment of Cl_2 formation and iron solubility (Table 2). The “Base” simulation excludes both the IMC mechanism and iron solubility effects. The “FixFeS” simulation includes the IMC mechanism with a uniform fraction of 1.8 % for photoactive soluble iron, following the ratio treatment of photoactive Fe in Van Herpen et al. (2023). The “VarFeS” simulation incorporates both the IMC mechanism and a dynamic representation of iron solubility modulated by proton processing, organic complexation, and mineralogical variability. Since the fraction of dissolved Fe that is photochemically active is not well constrained, we use dissolved Fe as a proxy for the Fe pool available for IMC-driven Cl_2 production. This configuration enables us to separately evaluate the impact of the IMC mechanism and the role of iron solubility on Cl_2 formation.

Table 2. Summary of sensitivity scenarios.

Experiment (Scenario)	IMC mechanism	Iron solubility treatment
Exp1(Base)	No	Not included
Exp2(FixFeS)	Yes	Fixed at 1.8%
Exp3(VarFeS)	Yes	Process-based variable solubility

Each simulation is performed at 4° latitude $\times$ 5° longitude horizontal resolution with 47 vertical levels (extending from the surface to 0.01 hpa), driven by MERRA-2 meteorological fields. All runs are initialized from identical concentration fields representative of realistic atmospheric conditions and span a 1.5-year period from 1 June 2022 to 31 December 2023. The first six months serves as a spin-up to minimize the influence of initialization, and all analyses are based on output from the year of 2023. Aside from the updated chlorine and iron emissions described above (section 2.2.1 and 2.2.2), the simulations use the standard suite of GEOS-Chem emission inventories. In details, anthropogenic and ship emissions of CO , NO_x , NH_3 , SO_2 , VOCs, BC and OC are taken from the Community Emissions Data System (CEDS) version 2 (Hoesly et al., 2018). Biomass burning emissions follow QFED version 2.5r1 (Darmenov and Da Silva, 2015) while biogenic VOC emissions are calculated online by Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 (Guenther et al., 2012), as implemented by Hu et al. (2015). Aircraft emissions of CO , NO_x , SO_2 , VOCs, BC and OC are taken from AEIC (Stettler et al., 2011). All emission inputs correspond to the simulation year 2023 except for AEIC aircraft emissions and AFCID, which are based on 2019 and 2015 due to data availability.

2.4 Observations for model evaluation

To assess model performance for iron dissolution processes and IMC mechanism, simulation results are evaluated against compiled observational datasets of solubility of iron and concentration of iron as well as Cl_2 . Global datasets provided by Myriokefalitakis et al. (2018) and Mahowald et al. (2009) are expanded with additional new observations records for both Fe concentration and solubility (as shown in Table S1). These additional data points primarily cover Asian regions, which are sparsely represented in previous datasets but are characterized by high pCl emissions. In total, the final synthesized dataset comprises 1399 and 1089 observational points for total Fe concentration and Fe solubility, respectively.

In contrast to iron, observational data for Cl_2 are far more limited. Reported Cl_2 concentrations range from a few ppt to approximately 1 ppb, indicating a wide dynamic range driven by regional emission characteristics and rapid atmospheric reactions. Currently available Cl_2 observations are characterized by limited spatial coverage, predominantly distributed across the coastal regions of China, North America, Europe, and Canada (as shown in Fig. S2). For this study, a total of 25 observational points of Cl_2 are compiled. Since several sites report only peak values or nighttime averages, measurements are subsequently normalized for comparison with the model results. Detailed information for the observational dataset of Cl_2 is provided in Table S2.

3 Results and discussions

3.1 Model evaluation

3.1.1 Evaluation of total Fe concentrations and solubility against observations

Since three simulation scenarios share identical total iron emissions and transport processes, they yield effectively the same total aerosol Fe concentrations. Moreover, while the “Base” and “FixFeS” scenarios employ either no or uniform iron solubility, only the “VarFeS” scenario incorporates a physically based, dynamic representation of iron solubility. Therefore, the comparison of total Fe concentrations and solubility with observations in this section focuses on simulation results from the “VarFeS” scenario.

As illustrated in Fig. 1, global distribution of total aerosol Fe concentration is broadly consistent between the model simulations and the available observations. Elevated Fe concentrations (typically exceeding $2 \mu\text{g m}^{-3}$) are concentrated over major arid and semi-arid regions, including the North Africa, the Middle East and Central Asia, reflecting the dominance of intense mineral dust emissions in these areas (Wu et al., 2021; Shao et al., 2011). A localized enhancement is also simulated over southern South America, mainly reflecting the contribution of dust-derived Fe from the Patagonian dust source region (Fig. S3), which has been identified as an important dust source in the Southern Hemisphere (Demasy et al., 2024; Gassó and Stein, 2007; Paparazzo et al., 2018). Similarly, enhanced Fe loadings are also simulated in regions characterized by extensive anthropogenic activities, such as the North China Plain, Indian and Europe. In contrast, over remote oceanic regions far from dust sources and in areas with limited anthropogenic (like central Pacific and Southern Ocean), both simulations and observations exhibit low Fe loadings, consistent with progressive deposition during long-range transport. In addition, the model also effectively captures the primary intercontinental transport pathways, such as atmospheric outflow of North African dust toward North Atlantic and South America, and the transport of Central Asian dust to the North Pacific (Zan et al., 2025), as evidenced by the gradually decreasing Fe concentration along these routes.

The comparison between simulated and observed Fe solubility reveals more pronounced regional heterogeneity, reflecting the combined effects of iron speciation, source characteristics, and atmospheric processing. Modelled surface mean value of total Fe solubility at all the observational sites globally is 3.4%, which is in good agreement with the observational value of 3.2%. Generally, the model simulates low solubility (typically $< 2\%$) over major dust source regions such as the Sahara Desert, the Gobi Desert, and inland Australia Desert, consistent with the dominance of poorly soluble iron oxides in freshly emitted

mineral dust in these areas. A similar feature is found over southern South America, where the enhanced Fe is mainly associated with freshly emitted Patagonian dust. The low solubility in this region is therefore consistent with the dominance of relatively insoluble mineral Fe phases and the limited atmospheric aging near the dust source. In contrast, remote oceanic regions exhibit substantially higher solubility, in line with previous observational evidences that Fe solubility increases during long-range transport (Takahashi et al., 2011; Srinivas et al., 2014; Rodríguez et al., 2021). In addition to atmospheric processing, regional differences in Fe source composition also contribute to the spatial variability of Fe solubility. Although both mid-to-high-latitude North America and East Asia experience frequent open biomass burning, they exhibit distinct Fe solubility patterns. As shown in Fig. S3, the relatively high solubility over northern North America is mainly associated with the stronger contribution of boreal biomass-burning Fe, which is represented with relatively high initial solubility in the model. In East Asia, however, aerosol Fe is mainly from mineral dust transported from the Taklimakan and Gobi deserts, as well as anthropogenic fugitive, combustion, and industrial Fe sources (Philip et al., 2017; Zhu et al., 2025; Bunnell et al., 2025; Sakata et al., 2025), which generally correspond to lower Fe solubility. Therefore, the biomass-burning Fe signal is largely diluted by these larger Fe inputs, leading to lower bulk Fe solubility over East Asia despite the occurrence of biomass burning. Notably, the observational datasets display substantial inherent spatial variability, with solubility values differing by orders of magnitude even between nearby sites. This strong spatial heterogeneity highlights the sensitivity of Fe solubility to local environmental conditions, including acidic gases concentrations, organic ligands availability, the diversity of aerosol origins, and even sample storage and analytical protocols. Overall, the model reproduces the large-scale gradients in Fe solubility, but local discrepancies persist, underscoring the regional diversity of solubilization mechanisms and the remaining uncertainties in their parameterization within the model.

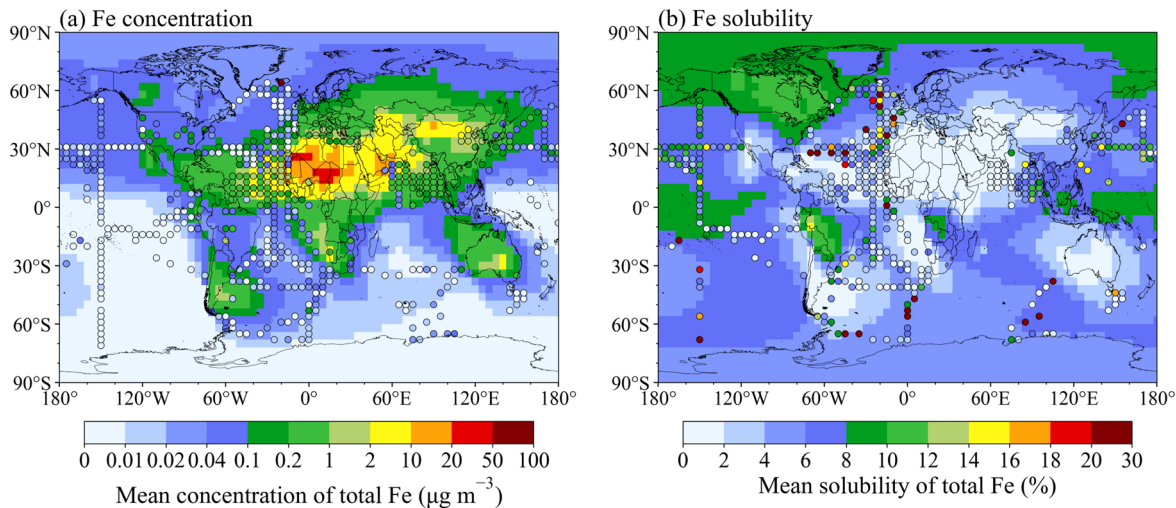
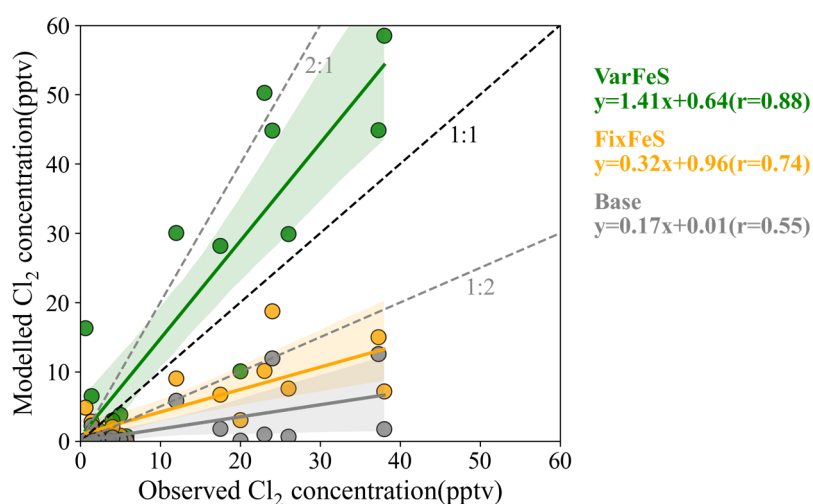


Figure 1. Comparison of modelled annual mean surface results with observational records for (a) total aerosol Fe concentration and (b) Fe solubility. Observations (circles) have been averaged to the resolution of the model grid.

3.1.2 Evaluation of Cl_2 concentrations against observations

Incorporating alternative dissolution pathways and IMC mechanism markedly improves the model’s ability to reproduce observed Cl_2 , with the correlation coefficient increasing from 0.55 (“Base”) to 0.88 (“VarFeS”) and reducing the normalized mean bias (NMB) from -82.5% to 45.9% . Specifically, for lower Cl_2 concentrations (below 10 pptv), the improvement is even more pronounced, with the NMB shifting from -86.3% to 18.0% . As shown in Fig. 2, the absence of IMC mechanism in the “Base” scenario leads to a systematic underestimation of Cl_2 , with simulated concentrations up to 83 % lower than observations. In the “FixFeS” scenario, a fixed 1.8 % fraction of photoactive Fe also results in a lower correlation with observations ($r = 0.74$) compared with “VarFeS” scenario. This discrepancy reflects the inability of a constant fraction to represent the realistic spatial variability of soluble Fe abundances. This is supported by the fact that Fe solubility itself exhibits significant regional heterogeneity. For instance, observed soluble Fe fractions can reach as high as 32% in the North Atlantic due to anthropogenic

305 pollutants from North America and Europe (Chen and Siefert, 2004). In contrast, by incorporating source-dependent variable Fe dissolution mechanism, the Cl₂ concentrations in the “VarFeS” scenario match observations better across most sites, even though an overall overestimation exists. In comparison with the previous nested GEOS-Chem study over North China by Chen et al. (2024), both studies consistently show that traditional gas-phase and heterogeneous Cl₂ formation mechanisms substantially underestimate observed Cl₂, while IMC mechanism markedly improves model performance. At the Wangdu site, 310 Chen et al. (2024) reported observed mean Cl₂ mixing ratios of 48 ± 51 pptv during the daytime and 28 ± 35 pptv at night, while their ‘RUNFe’ simulation reproduced approximately one-third of the observed daytime mean and one-half of the nighttime mean. In this study, the monthly mean Cl₂ mixing ratio at the Wangdu site is 58.5 pptv, broadly consistent with the observed daytime magnitude but higher than the nighttime mean. This overestimation may result from the inherent limitations of the IMC parameterization. Since the rate constants k_1 and k_2 adopted in this study are derived from field measurements 315 conducted in the North Atlantic (Van Herpen et al., 2023), so extending these regional constrained empirical parameters to a global scale may introduce inherent uncertainties, as the chemical composition and aging of aerosols vary geographically. The use of soluble Fe as a surrogate for photoactive Fe may also contribute to this positive bias, as only a fraction of dissolved Fe may effectively participate in photochemical Fe cycling. In addition, the current IMC parameterization also implicitly assumes a 100% conversion efficiency, where every two Fe(III)/Fe(II) photoactivate cycle yield one Cl₂ molecule production (as 320 reflected in the stoichiometric factor). However, photo-induced electrons or intermediate species (e.g., Cl radicals) may undergo competitive quenching or side reactions with other reducing constituents such as organic matter or reduced sulfur species. Furthermore, the simplified treatment of organic ligands also introduces uncertainty which neglects the potential competitive complexation between oxalate and chloride for Fe(III). Thus, actual Cl₂ yield may be overestimated under certain environmental conditions. Other potential uncertainties are discussed in Text S2 in the supplementary materials.



325 **Figure 2.** Comparison of modelled and normalized observed Cl₂ concentrations under different scenarios.

3.2 Effects on reactive chlorine species

Cl₂

As illustrated in Fig. 3, the inclusion of the IMC mechanism induces a profound shift in global mean surface Cl₂ concentrations, which increases from 0.4 (with a range of 0-11) pptv in the “Base” scenario to 2.2 (with a range of 0.01-57) pptv in the “VarFeS” 330 scenario. In the “Base” case, elevated concentrations of Cl₂ are confined mainly to coastal China, driven by heterogeneous uptake of ClNO₂ onto the surface of particulate chloride. In the “VarFeS” scenario for 2023, however, pronounced regional and seasonal heterogeneities exist in global Cl₂ distribution. Prominent Cl₂ hotspots are identified in the western Canada (WC: 8.2 ± 5.5 pptv), the eastern China (EC: 24.9 ± 16.3 pptv), the southern Asia (SA: 10.2 ± 7.6 pptv), the northern Eurasia (NE: 5.5 ± 2.3 pptv), and the tropical Atlantic (TA: 4.9 ± 1.8 pptv) (see Fig. S4 for regional definitions). Furthermore, distinct 335

seasonal patterns are observed in these regions (Fig. S5). In WC, the Cl_2 enhancement is predominantly triggered by extreme wildfire events in 2023 in summer. Wildfires simultaneously release large amounts of soluble Fe and pCl aerosols from biomass burning within a short period (Tang et al., 2021; Zhang et al., 2022) (the corresponding distribution of soluble Fe concentration is shown in Fig. S6), thereby eliminating precursor limitations on Cl_2 formation processes. During summer, when solar radiation is stronger, the concentration of Cl_2 reaches 11.4 ± 10.3 pptv, which is 2.4 times higher than it in winter in Canada. Consistently, the source-specific attribution analysis indicates that biomass-burning Fe provides a regionally important contribution to Cl_2 production over WC (Fig. S7). By contrast, Cl_2 enhancements in EC (mainly in North China Plain, NCP) and SA (mainly in India) are significantly amplified during winter. In boreal winter, elevated anthropogenic and dust-derived Fe from heating-related activities (coal and biomass combustion) and enhanced dust resuspension, together with high pCl emissions from coal burning and biomass burning, strongly favor Cl_2 production. Combined with wintertime meteorological synergies, such as shallow planetary boundary layer heights and frequent stagnant conditions that suppress vertical dispersion, these factors collectively lead to the persistent accumulation of Cl_2 in the surface layer. Consequently, the NCP and the northern India exhibit the strongest Cl_2 enhancement during winter, with mixing ratios reaching 40~60 pptv in December. Similarly, meteorological conditions and remarkable anthropogenic dust Fe emissions lead to noticeable Cl_2 production in NE during wintertime as well. In contrast to these regions, Cl_2 maxima over the TA are governed by the long-term background input of natural mineral dust Fe (Fig. S7). Although dust-bound Fe possesses lower solubility, the massive total flux ensures that soluble Fe concentrations ($43.5 \pm 19.0 \text{ ng m}^{-3}$) far above the global mean ($7.1 \pm 14.8 \text{ ng m}^{-3}$) (Fig. S6), coupled with abundant sea-salt chloride emissions, maintains a stable Cl_2 background in TA.

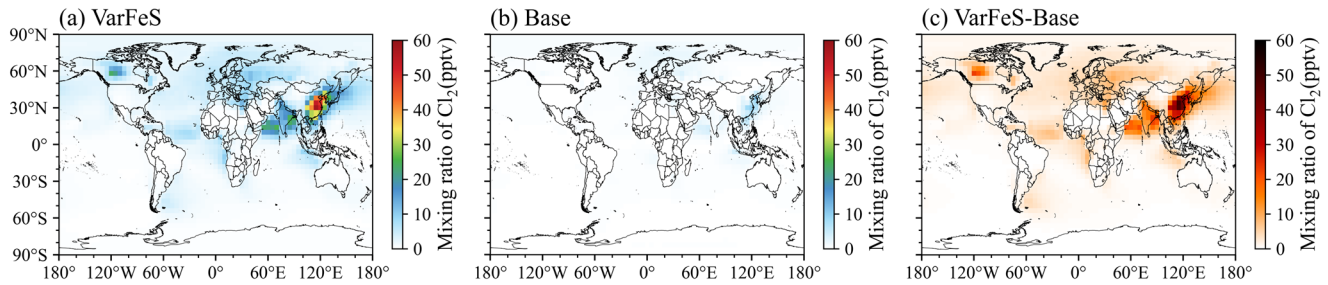


Figure 3. Spatial distributions of global surface Cl_2 mixing ratios under different simulation scenarios (a, b) and their corresponding absolute differences (c).

Other reactive chlorine species

Changes in Cl_2 concentrations exert substantial downstream impacts on the broader reactive chlorine species, as depicted in Fig. 4. The spatial distribution of elevated Cl radicals (Fig. 4a) closely tracks Cl_2 hotspots, reflecting the rapid photolysis of Cl_2 . This efficient conversion of Cl_2 to Cl enlarges atmospheric Cl radical reservoir within these source regions and extends its influence into downwind environments, yielding a maximum Cl radical increase of $2.14 \times 10^4 \text{ atoms cm}^{-3}$ compared to the “Base” scenario. The amplified Cl radical pool further intensifies the cycle involving Cl, O_3 , and ClO (ClOx cycling), driving a global rise in ClO concentrations by an average factor of 3.5, with peak enhancements reaching 84-fold (Fig. 4b). Strengthened ClOx cycling subsequently deepens its interaction with HOx and NOx chemical families, where rising ClO levels drive a 2.6-fold average increase in HOCl via the ClO and HO_2 reaction (Fig. 4c). This modelled response aligns closely with recent field observations which indicated that photochemical processing of aerosol iron is a key driver of daytime Cl_2 production and the subsequent formation of HOCl (Chen et al., 2025c).

Beyond the major Cl_2 production hotspots over Canada, northern China and India, the Tibetan Plateau (TP) also exhibits pronounced changes in Cl, ClO, and HOCl, likely driven by long-range transport from Southern Asia. Previous studies have shown that pre-monsoon biomass-burning emissions from western India can contribute over 60% of $\text{PM}_{2.5}$ concentrations on the TP via westerly transport (Yang et al., 2022). Besides, mineral dust from the Thar Desert (Wang et al., 2021a) and anthropogenic pollution from the Indo-Gangetic Plain (Xia et al., 2011) can be transported to the Himalayas by the combined

effects of the “Himalayan pump” and the prevailing pre-monsoon circulation. Thus, it is plausible that biomass-burning aerosols enriched in pCl and Fe, together with Fe-bearing mineral dust, facilitate the production of Cl₂. Then, under the TP’s intense ultraviolet radiation, Cl₂ is rapidly photolyzed, ultimately driving the pronounced enhancements in other reactive chlorine species observed in this region.

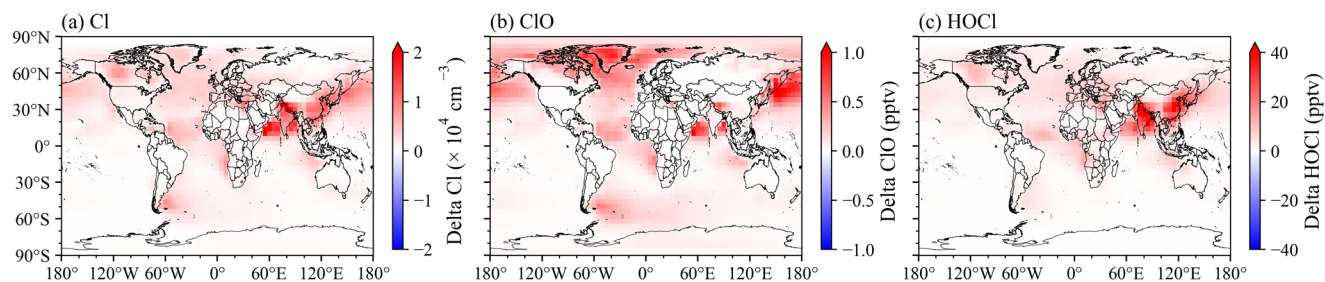


Figure 4. Corresponding absolute differences between the “VarFeS” and “Base” simulations for different reactive chlorine species.

3.3 Effects on atmospheric oxidative capacity (AOC)

RO₂

Inclusion of the IMC mechanism in “VarFeS” scenario significantly alters the concentration of RO₂, with global annual mean RO₂ concentration increasing by approximately 0.1 pptv and peak enhancement reaching 2 pptv. The spatial distribution of RO₂ enhancement closely follows the major Cl₂ hotspots which are driven by the role of Cl radicals. Since reaction rate constants for Cl radicals with most typical VOCs (such as methane, ethane, isoprene and α -pinene) exceed those for OH radicals by 1~2 orders of magnitude (Faxon and Allen, 2013; Sun et al., 2025), the Fe(III)-mediated Cl source greatly accelerates the production of R radicals, thereby driving rapid increases in RO₂. As a result, RO₂ increases by up to 30% (2.3% on global average), with the largest enhancements occurring in open biomass burning regions across the mid-to-high latitudes of the Northern Hemisphere. These results indicate that in regions with abundant VOC precursors (e.g., intense wildfire emissions), the contribution of Cl radicals generated via IMC mechanism can be strongly amplified. Besides, despite extremely low background pollutant levels, the relative enhancement of RO₂ remains high over Antarctica. This can be attributed to long-range transport of iron-containing aerosols from South American wildfires to the Southern Ocean, where Fe(III)-mediated photochemistry makes Cl radicals a major oxidant in these areas. Given the very low baseline RO₂ concentrations, even a slight increase leads to a disproportionately large relative change. It should be noted that the simulated RO₂ enhancement does not necessarily imply a uniform enhancement of AOC, as the subsequent oxidant response is strongly dependent on local NO_x and O₃ conditions (Pennacchio et al., 2025).

OH and HO₂

On a global scale, the spatial distribution of surface OH and HO₂ exhibit substantial changes driven primarily by chlorine-initiated cycling. With the inclusion of IMC mechanism, the global annual mean surface OH concentrations decreased by 2.5×10^4 atoms cm⁻³, which corresponds to a 5.7% relative reduction compared to the “Base” scenario. This decline is particularly evident in NO_x-limited oceanic and remote regions, driven by two synergistic pathways: first, Cl-initiated chemistry may suppress HO_x recycling as conversion of HO₂ and OH to Cl/ClO leads to a synchronized decline in OH levels (Simpson et al., 2015; Chen et al., 2024); secondly, since O₃ photolysis represents the primary source of OH radicals in most environments (Lelieveld et al., 2016), the widespread reduction of O₃ abundances by Cl radicals in these regions further curtails OH production. A similar mechanism was highlighted by Pennacchio et al. (2025), who demonstrated that Cl₂-driven chemistry can suppress OH production by reducing O₃ and NO₂ under low-to-moderate NO_x conditions, despite enhanced chlorine radical production. However, the variation characteristics are different regionally depending on the HO_x recycling efficiency. The oxidation of VOCs by Cl radicals generates additional RO₂, which subsequently enhances HO₂ production (Dai et al.,

2025). In NO_x-rich regions, elevated NO levels substantially accelerate the conversion of HO₂ to OH, thereby strengthening HO_x recycling and increasing OH abundances. This enhancement is also partly contributed by nighttime ClNO₂ chemistry, as nocturnal ClNO₂ formation followed by morning photolysis provides an additional Cl radical source, further promoting HO₂ production and subsequent OH regeneration (Liu et al., 2017; Riedel et al., 2014). The effect is particularly pronounced over the NCP, where enhanced RO₂ formation and efficient HO₂-to-OH conversion lead to a localized OH increase of up to 14%. Similarly, parts of the United States and Europe show rising OH concentrations, as strengthened HO_x cycling in these regions effectively boosts OH levels. In contrast, although a substantial rise in HO₂ is also predicted for India, the resulting change in OH remains minimal. This suggests that relatively abundant VOCs in India (Pakkattil and Ghude, 2025) already drive HO_x recycling toward high efficiency and near-saturation. Consequently, further regeneration becomes primarily constrained by the limited availability of NO_x, thus making OH production less sensitive to additional chlorine-driven HO₂ inputs. Furthermore, as noted by Pennacchio et al. (2025), the impact of Cl₂ is non-linearly dependent on its production intensity as well. In the NCP, which represents the highest Cl₂ production rate hotspot in our study (as shown in Fig. S8), chlorine-mediated radical chemistry may provide additional pathways (e.g., through the Cl + CH₃OOH reaction) for OH formation beyond the conventional NO-driven HO₂-to-OH conversion. This intensity-dependent response further helps explain the sharp contrast in OH variations between the NCP and other regions.

O₃

Including the IMC mechanism improves the model representation of surface O₃ relative to the Base scenario (Text S1 in the supplementary Materials), this provides further context for interpreting the simulated O₃ responses. As depicted in Fig. 5, O₃ shows two distinct responses due to differences in both regional variations in photochemical sensitivity to NO_x and local intensity of Cl₂ productions. Across most global regions with low NO_x levels, the concentration of O₃ declines as elevated Cl radicals tend to accelerate O₃ loss through direct reaction (forming ClO). This decline is further exacerbated by the formation of ClONO₂ (as shown in Fig. S9) via the reaction of ClO with NO₂ and its subsequent hydrolysis which acts as an efficient sink of NO_x thereby substantially suppresses O₃ photochemical production (Pennacchio et al., 2025). Consistent with the widespread decreases in surface O₃ outside high-NO_x source regions, the tropospheric O₃ burden declines from 367.9 Tg in the Base scenario to 357.3 Tg in the VarFeS scenario, corresponding to a 2.9% reduction. Conversely, the North China Plain (NCP) stands out as one of the few regions worldwide where O₃ increases markedly, which is attributed to its photochemical environment dominated by high NO_x levels and strong “VOCs limitation regime” (Liu et al., 2025; Yao et al., 2024). Under NO_x-excess conditions, the particularly high local Cl₂ production rate over the NCP likely further amplifies this positive O₃ response (Fig. S8). Acceleration of VOCs oxidation by Cl radicals substantially increases RO₂ concentrations and thereby promotes photochemical O₃ production, overcompensating for any NO_x loss via ClONO₂ pathways. By contrast, although India experiences comparable NO_x levels and elevated Cl₂ concentrations to those in NCP, a slight decrease in O₃ concentration is observed due to its distinct O₃ photochemical regime. Recent satellite evidence confirms that the majority of India predominantly resides within a “NO_x limited regime” with respect to ozone formation (Pakkattil and Ghude, 2025; Rawat and Naja, 2022). Consequently, the combination of chlorine-driven NO_x depletion together with the direct consumption of O₃ by Cl leads to decreased O₃ levels over India.

Overall, incorporating the IMC mechanism exerts regionally differentiated impacts on the global AOC. Over the NCP, atmospheric AOC is markedly enhanced, driven by accelerated radical chain reactions and elevated oxidant levels. In other regions, however, the influence of Cl chemistry is jointly modulated by the local photochemical environment, the NO_x-VOCs sensitivity regime, and background oxidant levels, resulting in a complex pattern in which enhancements and suppressions coexist.

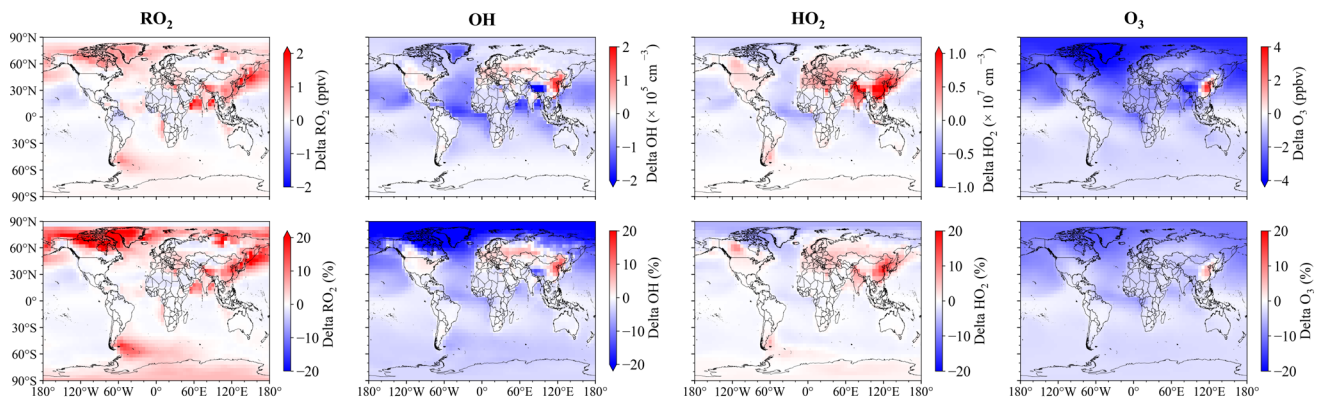


Figure 5. Comparison of absolute changes (top panel: VarFeS-Base) and relative changes (bottom panel: (VarFeS-Base)/Base) in annual mean surface concentration of RO₂, OH, HO₂ and O₃.

3.4 Effects on fine particle matters

Including the IMC mechanism significantly reshapes the global AOC by modulating radical cycling, which subsequently exerts a distinct influence on the formation and spatial distribution of fine particulate matter (PM_{2.5}) pollution, as shown in Fig. 6.

Spatially, PM_{2.5} enhancements are primarily concentrated in the mid-to-high latitude land areas of the Northern Hemisphere. While slight increases of roughly 0.5% are found in western Europe, northern America, Canada, and parts of the Arctic Ocean, the most pronounced response appears over the NCP, where PM_{2.5} rises by up to 2.5% (+2.2 μg m⁻³). From the perspective of chemical composition (Fig. S10), the PM_{2.5} enhancement is predominantly driven by nitrate formation. Over the NCP, nitrate rises by 1.9 μg m⁻³, accompanied by a smaller increase in ammonium (+0.4 μg m⁻³). This nitrate-dominated response is closely linked to elevated Cl₂ concentrations. Photolysis of Cl₂ generates highly reactive Cl radicals that substantially increase OH levels over the NCP. Since OH radicals are the critical daytime oxidants driving the conversion of nitrogen oxides into nitrate (Liu et al., 2020; Wang et al., 2026), the strengthened oxidizing environment accelerates nitrate formation and thereby increases PM_{2.5} mass concentration. This is consistent with previous studies reporting that increasing AOC significantly contributes to enhanced nitrate and PM_{2.5} concentrations (Feng et al., 2021; Fu et al., 2020; Zang et al., 2022). Importantly, this mechanism is further amplified under wintertime conditions, when stagnant meteorology and elevated precursor emissions coexist. In winter over the NCP, PM_{2.5} increases can reach up to 6.2% (Fig. S11). High NO_x levels, frequent stagnation, shallow boundary layers, and low-temperature conditions favorable for particulate nitrate stability collectively promote the partitioning of HNO₃ into the particle phase. As a result, nitrate formation is substantially enhanced, leading to a pronounced increase in PM_{2.5} in this region.

In contrast, regions located downwind of the enhanced Cl₂ production zones, as well as adjacent marine areas, exhibit a general decrease in PM_{2.5} concentrations. This reduction is likely attributable to the accelerated oxidation of NO_x and other precursors near the source regions under strengthened AOC. As NO_x is more rapidly converted to HNO₃ and subsequently to particulate nitrate, these species undergo earlier deposition and removal, thereby diminishing the reservoir of precursors available for long-range transport and secondary aerosol formation. Consequently, the downwind regions experience lower PM_{2.5} levels. In addition, this decreasing pattern is also consistent with the spatial distribution of sulfate reductions (Fig. S10). Under conditions of enhanced HO_x cycling, nitrate and sulfate do not respond uniformly to the IMC mechanism. While nitrate formation is primarily driven by increased OH oxidation (Liu et al., 2020; Wang et al., 2026), sulfate production is governed not only by gas-phase OH oxidation of SO₂ but also by aqueous, heterogeneous, and transition-metal-catalyzed oxidation pathways (Guo et al., 2024; Gao et al., 2024; He et al., 2025). Besides, hydroxymethanesulfonate (HMS) formed through the reaction between dissolved SO₂ and HCHO can subsequently be oxidized by aqueous OH radicals to sulfate (Song et al., 2019; Dovrou et al., 2022; Ma et al., 2020). Though elevated regional OH levels promote HCHO production which further increases the concentration of HMS (Fig.S12), HMS formation may temporarily sequester precursor SO₂, and its subsequent oxidation is

likely insufficient to offset the suppression of sulfate formation via direct SO₂ oxidation. Therefore, sulfate concentrations slightly decrease over the NCP despite the enhanced OH levels.

It should be noted, however, that the GEOS-Chem model employs a simplified SOA scheme, which likely leads to an underestimation of the impact of chlorine chemistry on SOA formation and, consequently, on total PM_{2.5} concentrations. Overall, the IMC mechanism enhances regional AOC, thereby promoting the formation and accumulation of PM_{2.5} near source regions and redistributing particulate matter on a regional scale. Therefore, future regional air-quality management strategies need to consider the roles of iron cycling and halogen chemistry jointly.

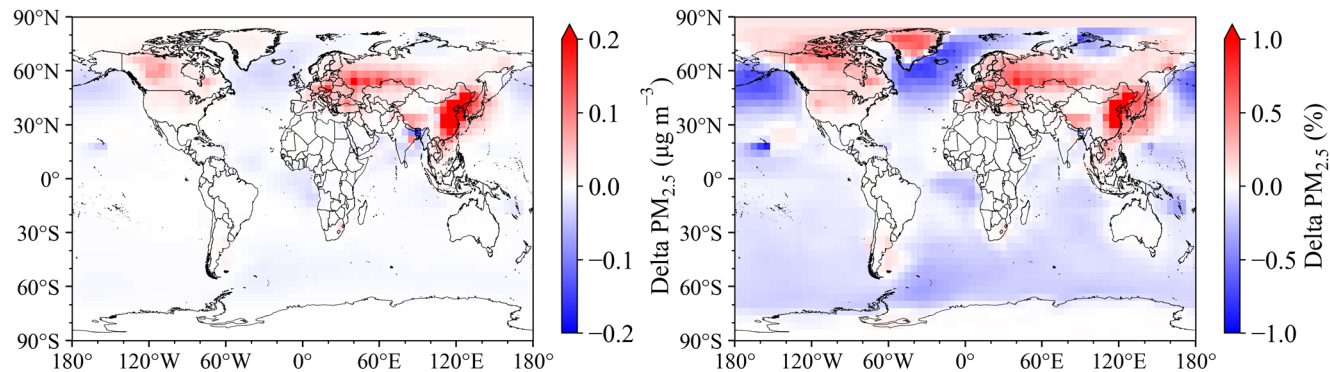


Figure 6. Comparison of absolute changes (left: VarFeS-Base) and relative changes (right: (VarFeS-Base)/Base) in annual mean surface concentration of PM_{2.5}.

4 Conclusions

We incorporated an Fe(III)-mediated Cl₂ production mechanism into the GEOS-Chem global atmospheric chemistry model to quantify its impacts on global atmospheric oxidative capacity, ozone chemistry, and secondary aerosol formation. Incorporating this pathway enhances GEOS-Chem’s ability to represent observed Cl₂ concentrations, increasing the correlation coefficient from 0.55 to 0.88 relative to “Base” scenario.

Substantial changes in global reactive chlorine species and atmospheric oxidative capacity emerge following the model update. Global mean tropospheric Cl₂ increases from 0.4 to 2.2 pptv, with hotspots exceeding 40 pptv over the eastern China and India. Rapid photolysis of Cl₂ expands the Cl radical reservoir and strengthens VOCs oxidation, leading to a 2.3 % increase in global RO₂ (peaking at 30 % in wildfire-influenced regions). Enhanced Cl-driven oxidation perturbs HOx recycling by O₃ depletion and converting OH and HO₂ into Cl and ClO in the remote marine regions, leading to a synchronized decline in OH and ultimately a 5.7% reduction in the global mean OH levels. In contrast, the eastern China exhibits concurrent increases in both O₃ and OH (up to +14 %), as Cl-accelerated VOCs oxidation under its strongly VOC-limited chemical regime. Such perturbations significantly impact regional air quality. Specifically, Fe-Cl chemistry elevates PM_{2.5} mass concentrations across the mid-to-high latitude Northern Hemisphere. The most pronounced response occurs in eastern China, where PM_{2.5} increases by up to 2.5 %, primarily driven by accelerated NO_x oxidation under elevated daytime OH. This effect is further intensified during stagnant winter episodes, with localized PM_{2.5} surges reaching 6 %, while PM_{2.5} is reduced downstream.

In summary, model results demonstrate that Fe(III)-mediated Cl₂ production can exert substantial impacts on global radical budget and regional AOC. By promoting near-source aerosol formation while diminishing downwind concentrations, this mechanism reshapes the spatial pattern of secondary pollution. Considering this pathway is therefore essential for accurately representing atmospheric oxidation processes and enhancing the reliability of air quality assessments.

Data availability

For model evaluation, the observational datasets used to evaluate simulated total aerosol Fe concentrations and Fe solubility

were mainly compiled from the global datasets of Myriokefalitakis et al. (2018) and Mahowald et al. (2009), with additional observational records summarized in Table S1. The Cl₂ observational dataset used to evaluate the performance of the implemented Fe(III)-mediated Cl₂ formation mechanism is presented in Table S2. Surface O₃ observations used for model evaluation were obtained from publicly available air-quality monitoring datasets, including OpenAQ (<https://openaq.org>), the China National Environmental Monitoring Centre (<http://www.cnemc.cn>), the U.S. Environmental Protection Agency (<https://www.epa.gov>), and the European Environment Agency (<https://www.eea.europa.eu/en>). For model development, the standard GEOS-Chem model version 14.2.3 used in this study is publicly available at (<https://doi.org/10.5281/zenodo.10246546>), the soil mineralogical data used to represent dust Fe were taken from Nickovic et al. (2012), the modified GEOS-Chem source-code files associated with Fe dissolution processes and Cl₂ formation mechanisms implemented in this study are available on Zenodo (<https://doi.org/10.5281/zenodo.20529218>).

Author contributions

JC: conceptualization, methodology, formal analysis, software, visualization, writing (original draft preparation), writing (review and editing). XS: methodology. CQ: methodology. JL: methodology. QC: methodology, funding acquisition, writing (review and editing). XF: conceptualization, methodology, resources, funding acquisition, supervision, writing (review and editing).

Competing interests

The authors declare that they have no conflict of interest.

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