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The impact of sea spray aerosol on photochemical ozone formation over eastern China: heterogeneous reaction of chlorine particles and radiative effect

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Abstract. Eastern China has suffered from severe photochemical O_3 (ozone) pollution in recent years. In this coastal region, atmospheric environment can be influenced by sea spray aerosol (SSA) from marine emissions. However, the extent and mechanisms by which SSA affects O_3 formation remain incompletely understood. Here, using the WRF-CMAQ model, this study investigates the comprehensive effect of SSA on radical chemistry and O_3 formation in the lower troposphere across four seasons. SSA (over 50% are particulate chlorine) can reach further inland through an atmospheric "bridge" aloft, interacting with the nitrogen-containing gases from continental anthropogenic emissions to reduce NO_x levels and release Cl radicals. The NO_x reduction increases O_3 in VOCs-limited region while decreasing them in NO_x-limited zones. Elevated Cl radicals enhances VOCs degradation and O_3 formation during morning hours. Meanwhile, the scattering properties of SSA reduces daytime O_3 formation by diminishing photolysis rates. Due to the contrast effect of SSA via different mechanisms, the response of O_3 vary seasonally and geographically. In winter, SSA increases O_3 in eastern China due to the dominant effect of NO_x reduction in VOCs-limited regions. In spring and autumn, similar effects occur in North China Plain, whereas southern China sees a decrease due to the NO_x reduction in NO_x-limited region and reduced photolysis rates. In summer, O_3 increases are observed only around Bohai, with reductions elsewhere driven by NO_x reductions in NO_x-limited regions and decreased photolysis. This study highlights the important, varying, but previously unreported role of SSA in shaping tropospheric photochemistry over eastern China.

1 Introduction

In recent years, eastern China has grappled with severe photochemical O_3 (ozone) pollution, eliciting widespread concern from governmental and academic sectors (Wang et al., 2022; Lu et al., 2018; Wang et al., 2017). Elevated O_3 concentrations pose serious threats to public health and have detrimental effects on vegetation growth and crop yields (Fleming et al., 2018; Lefohn et al., 2018; Liu et al., 2018a; Feng et al., 2022). Traditionally perceived as a warm-season issue (Lu et al., 2020), O_3 pollution has recently been documented during winter and spring, driven by substantial reductions in NO_x emissions juxtaposed against relatively stable VOC (volatile organic compounds) emissions in China since 2013 (Li et al., 2021). The escalations of O_3 levels following the Clean Air Action in 2013 underscores the need for a nuanced understanding of its formation mechanisms throughout the year (Liu and Wang, 2020a, b; Wei et al., 2022).

Sea spray aerosol (SSA) is a major natural particulate source in the atmosphere (Weis and Ewing, 1999; Roth and Okada, 1998), generated from oceanic surfaces through wave-breaking and bubble-bursting processes (Lewis and Schwartz, 2004). According to IPCC reports, an estimated 3300 Tg of SSA annually enters the atmospheric boundary layer, driven by wind stress on ocean surfaces, contributing to complex atmospheric chemical interactions. The rapid economic growth in coastal areas, coupled with unique challenges of complex atmospheric pollutions, particularly in eastern China, has highlighted the role of SSA in atmospheric oxidation processes. While previous studies have indicated the potential impact of SSA on coastal O_3 levels (Dai et al., 2020; Knipping and Dabdub, 2003), a comprehensive and systematic investigations into the mechanisms of these effects is lacking.

SSA influences near-ground O_3 formation through multiple mechanisms. SSA can significantly scatter incoming solar radiation that reaches the ground, thereby diminishing the actinic flux within the troposphere (Lohmann and Feichter, 2005; Hatzianastassiou et al., 2007). This reduction in solar energy lowers the rate of photochemical reactions crucial for O_3 generation. Near-ground O_3 primarily forms through photochemical reactions between NO_x and VOCs under sunlight, with its production heavily dependent on the amount of solar radiation penetrating to the surface. As a prominent source of atmospheric aerosols, SSA can attenuate this solar radiation, leading to decreased photolysis rates of NO_2 and, consequently, reduced O_3 formation (Li et al., 2011; Xing et al., 2017). Currently, this mechanism—the impact of SSA on ground-level ozone through the modulation of photolysis rates—is often overlooked in previous studies on the influence of SSA on O_3 concentrations.

Besides, particulate chlorine in SSA engages in heterogeneous chemical reactions with nitrogen-containing gases, releasing Cl radicals that enhance atmospheric oxidation and affect photochemical O_3 formation. While the traditional pathway for urban O_3 formation involves the reaction of VOCs with hydroxyl radicals (OH), recent research underscores the significant role of

Cl radicals in similar processes (Faxon and Allen, 2013; Qiu et al., 2019; Young et al., 2014). Chlorine radicals react with VOCs more rapidly than OH radicals, despite their lower atmospheric concentrations, making their oxidations potential comparably significant (Aschmann and Atkinson, 1995; Nelson et al., 1990; Wingenter et al., 1999).

Particulate chlorine reacts with N_2O_5 to form nitroxyl chloride ($ClNO_2$), which releases chlorine radicals upon photolysis, contributing significantly to atmospheric Cl levels (Thornton et al., 2010; Bertram and Thornton, 2009; Roberts et al., 2009). These reactions are outlined in R1 and R2 (where g and cd represent the gas and condensed phases, respectively). Observations of $ClNO_2$ have shown high concentrations in eastern China, indicating active chlorine chemistry (Tham et al., 2016; Yun et al., 2018; Wang et al., 2016).

$$N_2O_5(g) + Cl^-(cd) \rightarrow ClNO_2(g) + NO_3^-(cd) \qquad (R1)$$

$$ClNO_2(g) + hv \rightarrow Cl \cdot (g) + NO_2(g) \qquad (R2)$$

Particulate chlorine can also react with NO_2 to produce nitrosyl chloride (ClNO), which, like $ClNO_2$, can release Cl radicals (R3 and R4) under photolysis (Finlayson-Pitts, 2003; Faxon and Allen, 2013).

$$2NO_2(g) + Cl^-(cd) \rightarrow ClNO(g) + NO_3^-(cd) \qquad (R3)$$

$$ClNO(g) + hv \rightarrow Cl \cdot (g) + NO(g) \qquad (R4)$$

Furthermore, particulate chlorine can also directly react with NO_3 to release Cl radicals (R5), which is a potentially important nighttime source of Cl radicals (Gershenzon et al., 1999; Seisel et al., 1999).

$$NO_3(g) + Cl^-(cd) \rightarrow Cl \cdot (g) + NO_3^-(cd) \qquad (R5)$$

The original CMAQ model only considered the reaction between particulate chlorine and N_2O_5, neglecting other significant chlorine-related heterogeneous chemical processes. To accurately assess the effect of SSA on O_3 concentration, it is essential to integrate recent findings on the heterogeneous chemistry of chlorine and update chemical models accordingly. This integration will provide a more comprehensive understanding of SSA's role in photochemical O_3 generation, addressing a critical gap in current atmospheric chemistry research.

Heterogeneous chemical reactions of SSA with NO_x can alter NO_x concentrations, thereby affecting O_3 production. As illustrated by reactions R1-R5, nitrogen oxides undergo heterogeneous chemical reactions with particulate chlorine at night,

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leading to reduced NO_x concentrations. By morning, the photolysis of ClNO and $ClNO_2$ results in the release and subsequent increase NO_x concentrations. The relationship between O_3 and its precursors is highly nonlinear and varies by region and time due to the differences in the O_3 formation regime. In VOC-limited urban and suburban areas, decreases in NO_x levels can paradoxically lead to increase in O_3 concentration. Conversely, in NO_x-limited rural areas, a reduction in NO_x levels typically leas to a decrease in O_3 production, highlighting the complex dynamics of atmospheric chemistry (Wang et al., 2017).

In terms of model-based studies, Knipping and Dabdub (2003) incorporated SSA emissions into their model, finding that O_3 concentration in the coastal areas of California in United States increased by 12 ppb in the morning and 4 ppb at the noon. Similarly, Sarwar and Bhave (2007) utilized the CMAQ model to explore the impact of SSA emissions on O_3 across the eastern United States, revealing that the associated chlorine chemical processes increased the oxidation of VOCs, thereby enhancing O_3 production. This resulted in increases of up to 12 ppb and 6 ppb in the maximum hourly O_3 concentrations in the Houston and New York-New Jersey regions, respectively, and daily maximum 8-hour average O_3 concentrations rose by 8 ppb and 4 ppb. Dai et al. (2020) investigated the impact of $ClNO_2$ from sea-salt chloride on O_3 in Pearl River Delta, China, and found an increase of up to 2.0 ppb over the inland areas during marine winds and up to 3.8 ppb and 6.5 ppb over the South China Sea. However, these studies did not fully account for the tripartite influence of SSA on O_3 concentration, nor did they integrate the complete heterogeneous chemistry of chlorine particulates, leading to potential uncertainties in assessing the impact of SSA.

In this study, we employed the WRF-CMAQ model to evaluate the impact of SSA on the tropospheric chemistry in eastern China during different seasons. The response of HO_2, OH radicals and O_3 caused by SSA were quantified. Section 2 demonstrate the modeling settings, SSA emission calculation, and experiment designs. Sections 3 discusses the impact of SSA on the tropospheric chemistry. We conclude with a summary of our findings and discussions in Section 4.

2 Methodology

2.1 Model settings

The CMAQ model (version 5.1) driven by the Weather Research and Forecasting (WRF) model were utilized to perform simulations in this study. The configuration and emission inputs were consistent with those used in Hong et al. (2020). Specifically, the simulation environment was structured into two nested domains within the WRF and CMAQ models, featuring horizontal resolutions of 81 km and 27km, respectively (Fig. S1). These domains included 23 vertical layers extending up to 50 hPa. The inner domain focused on eastern China, where the detailed analysis was conducted, while the outer domain encompassed a broader area, including the land regions of East Asia and the Western Pacific. This broader scope allowed for a comprehensive consideration of SSA emission transport into the region of interest. Meteorological initial and boundary conditions for the WRF model were derived from the NCEP/NCAR final (FNL) reanalysis gridded data, which have a horizontal resolution of 1°×1°. Chemical boundary conditions for the CMAQ model were sourced from the Model for Ozone and Related Chemical Tracers, version 4 (MOZART-4) results. Although CMAQ is an offline chemical transport model that does not inherently account for the feedback effects of pollutants on meteorological variables, it implements an in-line method (Binkowski et al., 2007) to compute solar radiation and photolysis rates using predicted concentrations of aerosol and O_3. This approach enables the model to assess the effect of aerosols (e.g., SSA) on photochemical processes by adjusting photolysis rates accordingly.

In the CMAQ simulation, we utilized the SAPRC07TIC (Carter, 2010; Hutzell et al., 2012; Xie et al., 2013) and AERO6i (Lin et al., 2013; Pye et al., 2015) mechanisms to represent gas-phase chemical and aerosol processes, respectively. Initially, the CMAQ model was configured to only account for the heterogeneous reaction of particulate chlorine with N_2O_5 (R1) (Sarwar et al., 2012; Sarwar et al., 2014). To provide a more comprehensive evaluation of SSA's impact on photochemistry, we expanded the model's capability to include heterogeneous reactions of particulate chlorine with NO_2 (R3) and NO_3 (R5). We developed a linear segmentation function to parametrize the uptake coefficients of NO_2 and NO_3 on aerosol surfaces, reflecting their strong positive correlation with relative humidity (Dentener et al., 1996; Stutz et al., 2004). The selection of maximum and minimum uptake coefficients for NO_2 and NO_3 was based on laboratory findings, aligning with methodologies from previous modeling studies by Wang et al. (2012) and Zheng et al. (2015). A detailed exposition of these modifications and their implications for the model's chemistry of heterogeneous reactions is documented in Hong et al. (2020).

Both anthropogenic and natural emissions were incorporated in the simulation to ensure comprehensive atmospheric modeling. Anthropogenic sources included routine pollutant emissions from the MIX emission inventory (http://www.meicmodel.org/) (Li et al., 2017), international shipping emissions from HTAP (Hemispheric Transport Atmospheric Pollution) emissions version 2.0 dataset (Janssens-Maenhout et al., 2015), and chlorine emissions (HCl and Cl_2) from the 2014 ACEIC (Anthropogenic Chlorine Emission Inventory for China) (Hong et al., 2020; Liu et al., 2018b). For natural sources, biogenic emissions were calculated using the Model of Emissions of Gas and Aerosols from Nature (MEGAN) (Guenther et al., 2012), which utilized meteorological inputs from the WRF simulation. SSA emissions were calculated inline in the CMAQ model (see Section 2.2).

We utilized the process analysis module within the CMAQ model to quantify the production and loss of model species. This diagnostic tool employs both integrated process rate (IPR) and integrated reaction rate (IRR) methods. The IPR method assesses the contributions of various physical and chemical processes to pollutant concentrations, while the IRR method determines the contributions from specific chemical reactions. Process analysis has been extensively used in prior research to elucidate the chemical mechanism underlying O_3 formation (Wang et al., 2015; Chen et al., 2018; Liu et al., 2021).

2.2 SSA emission calculation

The SSA emission was calculated on line in the CMAQ model, utilizing a source function developed by Gantt et al. (2015), which builds upon the foundational source function established by Gong (2003). Gantt et al. (2015) introduced two main modifications to enhance the model's accuracy. Firstly, a sea surface temperature (SST) correction function was incorporated, based on the findings of Ovadnevaite et al. (2014), to account for the substantial impact of SST on SSA fluxes. This correction function linearly adjusts to SST variations, reflecting its influence on emission rates (e.g., Barthel et al., 2019; Liu et al., 2021). Secondly, the shape factor of the source function was adjusted to increase the emission of submicron SSA particles, altering the flux distribution to better reflect observed atmospheric conditions (see Fig. S1 in Gantt et al. (2015)). Additionally, surf-enhanced emissions were reduced by narrowing the defined surf zone from 50 m to 25 m from the coast, aligning with the modifications in Gantt et al. (2015). The composition of dry SSA remains consistent with that of seawater, containing Cl^- (55.4%), Na^+ (30.8%), SO_4^{2-} (7.7%), Mg^{2+} (3.8%), Ca^{2+} (1.2%), and K^+ (1.1%).

2.3 Experiment setting

We conducted simulations for January, April, July, and October of 2015 to represent the typical atmospheric conditions for each season in eastern China. A 10-day spin-up period preceded the actual modeling to stabilized initial conditions. The simulations incorporating all emissions were designated as the baseline scenario (BASE). Additionally, a sensitivity experiment (NOSA), which excluded SSA emissions, was performed to discern the specific contributions of SSA to surface O_3 levels. The seasonal impacts of SSA emissions were assessed by comparing the differences in simulated pollutant concentrations between the BASE and NOSA experiments.

Model validation was rigorously carried out against observational data from eastern China for the corresponding periods (Hong et al., 2020). The validation confirmed that the WRF-CMAQ model capably simulated key meteorological factors (temperature, relative humidity, and wind speed) and routine pollutant concentrations (O_3, NO_2, CO, $PM_{2.5}$, PM_{10}, and SO_2), along with particulate chlorine concentrations. This validation provides a solid foundation for our confidence in further exploring the impact of SSA on tropospheric photochemistry using these modeling results. Detailed validation results were described in Hong et al. (2020).

3 Result and discussion

3.1 SSA transport

We used particulate Na^+ as a proxy for SSA, due to its major presence and relatively inactive in the atmosphere (Neumann et al., 2016). Our analysis distinguished regions significantly affected by SSA by comparing Na^+ concentrations from BASE and NOSA experiments (Fig. 1). Near the ocean, areas exhibiting elevated Na^+ align with high SSA emissions zones (Fig. S2). In eastern China, increased Na^+ concentrations are notably due to SSA transport from the ocean, diminishing progressively with distance from the coast. Cities such as Shanghai and Guangzhou, located along the coastline of eastern China, displayed significant Na^+ increases (>1 μg/m^3), indicating marked influence of SSA. Smaller yet notable increases (>0.1 μg/m^3) extend into broader inland areas spanning several provinces including Liaoning, Tianjin, and down to Guangxi. More than 80% of the inland region's Na^+ within ~100 km of the coast (e.g., Shanghai, Zhejiang, Fujian, Guangdong, and Guangxi) is attributable to SSA, decreasing to 10%-60% towards central regions like Hubei. The terrain influences regional SSA impacts distinctly. In northern China, the Taihang Mountains impede westward SSA transport, confining its influence to the North China Plain. Conversely, lower terrain elevations in southern China facilitate broader inland SSA dispersal. Seasonally, the inland reach of SSA is most extensive in July, propelled further by the southerly summer monsoon.

SSA transport also occurs via an "aloft bridge" over the planetary boundary layer, enhancing its penetration inland. Figures 1c, 1d, and 1e illustrates vertical-diurnal variations of SSA-induced Na^+ concentration in Beijing, Shanghai, and Guangzhou, pinpointed in Fig. 1a. These profiles reveal that while coastal cities like Shanghai show higher surface-level concentrations, more inland cities such as Guangzhou and Beijing exhibit elevated concentrations aloft, especially in October. This pattern suggests that SSA is not only transported horizontally near the surface but also vertically mixed upward from the coast before descending inland, influenced by varying thermodynamic properties and boundary layer structures between continental and marine areas. Similar transport features were observed in northwestern Europe, where SSA influences extend approximately 400 km inland (Chen et al., 2016).

Additionally, the impact of SSA on particulate Cl^- concentrations is shown in Fig S3 and S4. The spatial distributions of SSA-induced Cl^- near the surface mirrors that of Na^+ (Fig. 1). However, due to SSA's higher Cl^- emissions relative to Na^+, regions experiencing >80% change in Cl^- are more extensive, underlining its substantial impact. Notably, in cities like Beijing and Guangzhou, Cl^- concentrations are higher aloft than at the surface, a distinction more pronounced than for Na^+. This is likely due to greater Cl^- depletion through reactions with HNO_3 and H_2SO_4 (Liu et al., 2015), and heterogenous reactions with nitrogen-containing gases prevalent in polluted lower atmospheric layers.

3.2 Heterogeneous reactions of particulate Cl^- with nitrogen-containing gases

Particulate Cl^-, a chemically active and abundant component of SSA, undergoes heterogeneous reactions with NO_2, NO_3, and N_2O_5, releasing Cl radicals in the process. Figure 2 shows the influence of these reactions on particulate Cl^- concentrations, revealing significant negative impacts along coastal regions. This suggests that SSA from ocean mixes with nitrogen-containing gases from continental sources, leading to enhanced chlorine depletion in these areas. Seasonally, the greatest depletion occurs in January, followed by October, April, and July, likely due to variations in NO_2 levels. In January, a notable depletion along the eastern Chinese coastline is observed, with significant reductions in Bohai Bay, the Yangtze River Delta region, and the Pearl River Delta region during April and October. In July, pronounced depletion is evident in Bohai Bay and YRD, while the PRD shows less impact. Depletion diminishes progressively inland, with coastal areas experiencing the most significant effects.

Alongside the depletion of Cl^-, NO_x concentration decrease due to the heterogeneous reaction between Cl^- and NO_2, NO_3, and N_2O_5 across eastern China. Figure 3 presents the seasonal changes in NO_x mixing ratios caused by SSA, showing a substantial reduction, particularly in the coastal regions of eastern China, with the most significant decreases occurring in January and the least in July. The incorporation of SSA into the model results in a decrease in NO_x mixing ratios by up to 3-5 ppbv (5-10%) across different months. Given the critical role of NO_x as an O_3 precursor, these reductions could significantly influence O_3 level, a topic that we will explore in detail in Section 3.5.

The reactions of particulate Cl^- with NO_2 and N_2O_5 result in the production of $ClNO$ and $ClNO_2$, respectively, which are crucial precursors to Cl radicals. Figures 4a and 4b display the spatial variations in their mixing ratios induced by SSA, specifically analysed at 5:00 LST due to the nocturnal accumulation of these compounds. The figures demonstrate that SSA significantly increases $ClNO$ and $ClNO_2$ levels across eastern China, particularly in coastal regions. The spatial and seasonal patterns of these increases align closely with reductions in Cl^- (Fig. 2) and NO_x (Fig. 3), highlighting the important impact of SSA on these heterogeneous reactions. The most substantial effects of SSA are observed in January, followed by October, April, and July. In January, pronounced increases in $ClNO$ and $ClNO_2$ levels are noted in southeastern coastal regions of eastern China. In April and October, significant increases are localized to Bohai Bay, YRD, and PRD. In July, increases remain high in Bohai Bay and YRD. The transport of SSA inland results in diminishing increases of $ClNO$ and $ClNO_2$ from the coastline inward. Quantitatively, $ClNO$ mixing ratios increase by up to 1.0, 1.1, 1.1, 1.3 ppbv in January, April, July, and October, respectively. Over 80% of the $ClNO$ in coastal areas is sourced from SSA emissions, with some areas nearing 100% contribution (Fig. S5a). For $ClNO_2$, the maximum increases are 1.0, 0.8, 0.5, 0.8 ppbv in respective months, with a broader regional impact compared to $ClNO$ (Fig. S5b). Southern China experiences a more pronounced impact from SSA compared to the norther part, with the influence markedly tapering off towards inland regions like Hubei, Chongqing, and Guizhou where contributions decrease to around 10%.

The heterogeneous reactions between SSA and nitrogen-containing gases release Cl radicals as a result. Figure 4c show the spatial distribution of SSA-induced Cl radical concentrations in different seasons. The increases in precursor compounds ClNO and $ClNO_2$ during nighttime enhance their photolysis after sunrise, which significantly boosts Cl radical concentrations. High increases are evident in January in the Taiwan Strait, reaching up to 2.9×10^4 molecule cm^{-3}. The concentrations peak in April and July in the Bohai Sea, the Yellow Sea and the Taiwan Strait, with the highest increase of 4.0×10^4 and $8.1.0\times10^4$ molecule cm^{-3}, respectively. October also shows substantial increases in the Taiwan Strait and Bohai Bay. The coastal regions see Cl radical concentrations boosted by $0.2\text{-}2\times10^4$ molecule cm^{-3}, indicating a strong link between coastal SSA emissions and increased Cl radicals. These regions experiencing elevated Cl radical levels correspond with areas showing increases in ClNO and $ClNO_2$ mixing ratios (Figs. 4a and 4b). Notably, nearly 100% of the Cl radicals in oceanic regions stem from SSA emissions, with over 40% in eastern China attributed to the same source (Fig. S5c). The IRR process analysis module helps trace the main pathways driving this increase (Figure S6), including ClNO photolysis, $ClNO_2$ photolysis, reaction of ClO and NO, heterogeneous reaction of particulate Cl^- with NO_3, and other processes (including Cl_2 photolysis, reaction of HCl and OH, and etc.). Daytime increases in Cl radicals are predominantly due to the photolysis of ClNO and $ClNO_2$ following sunrise.

Furthe es the vertical-diurnal variations in SSA-induced Cl radical concentrations in Beijing, Shanghai, and Guangzhou. This analysis shows that SSA emissions significantly elevate Cl radical concentrations after sunrise, especially during the morning hours. These increases are more pronounced at higher altitudes shortly after sunrise, reflecting the vertical mixing and transport processes that distribute Cl radicals throughout the atmospheric column.

3.3 Radiative effect of SSA

SSA plays a significant role in modulating incoming solar radiation through scattering, which influences the photolysis rates of various photochemical species. As O_3 formation is closely linked to the photolysis of NO_2 ($J(NO_2)$), examining the impact of SSA on this process is crucial. Figure 6 highlights that the $J(NO_2)$ decreases by up to 15.1%, 5.7%, 6.0%, and 11.8% in January, April, July, and October, respectively, particularly in oceanic and coastal areas. This reduction in $J(NO_2)$ correlates well with the spatial distributions of SSA emission (Fig. S2) and SSA-induced Na^+ concentration, underscoring the significant radiative effect of SSA. Despite relatively modest reductions in coastal regions (1-5%), such changes are significant enough to influence O_3 formation considerably. According to a study by Fan and Li (2022), similar decreases in photolysis rate (1-4%) caused by SSA led to reductions in O_3 mixing ratios by up to 1-2% in eastern China during July.

Additionally, the photolysis rates of photochemical gases generally increase with altitude due to the rising actinic flux (Gao et al., 2020). Figure 6 also presents the vertical-diurnal variations in J(NO_2) changes caused by SSA in Beijing, Shanghai, and Guangzhou. The influence of SSA on J(NO_2) is notably lesser in Beijing compared to the other two cities. A significant reduction in J(NO_2) is observed around noon (12:00 LST), coinciding with the daily peak in actinic flux. This reduction extends into the upper troposphere, serval kilometers above the surface, where the decrease in J(NO_2) can surpass that observed at lower altitudes.

The reduction in radiation due to SSA not only impacts J(NO_2) but also affects the photolysis rate of other photochemical species, including J(O_3) (Fig. S7 and S8), which are crucial for OH radical production in the atmosphere. The spatial and seasonal distribution patterns of J(O_3) reductions mirror those of J(NO_2), highlighting a consistent influence across photochemical species. These changes are poised to affect the photochemical formation of OH and O_3, implications of which will be explored in subsequent sections.

3.4 Impacts of SSA on HO_x radical

The Cl radicals released from SSA contribute to atmospheric oxidation similarly to OH radicals, catalyzing the conversion of VOCs into HO_2 radicals. Figures 7a and 7b illustrates the spatial distribution of the SSA-induced increases in HO_2 radicals near the ground across eastern China and adjacent oceanic areas, corresponding with the significant rise in Cl radicals. This increase is primarily due to the enhanced VOC degradation by Cl radicals. In more remote oceanic regions, a decrease in HO_2 can be observed, likely due to lower VOC concentrations and diminished photochemical reactions, which are consequences of the potent radiative effects of SSA.

Figures 7c, 7d, and 7e present the vertical-diurnal variations of SSA-induced HO_2 concentrations in different months. Notably, HO_2 concentrations significantly increase after sunrise, driven by Cl radicals generated from the photolysis of ClNO and $ClNO_2$. However, a reduction in HO_2 is observed around noon, particularly at altitudes above the PBL, attributed to the pronounced radiative effect of SSA. In October, unlike other months, there is an increase in HO_2 concentration over the boundary layer in Beijing, suggesting a reduced radiative effect of SSA during this period in northern inland regions. Moreover, a more substantial chemical contribution from Cl radicals in October leads to a sustained increase in HO_2 levels over the boundary layer.

In the present of NO, HO_2 converts into OH radicals, forming a critical HO_x chemical cycle. Figures 8a and 8b shows the spatial distribution of SSA-induced OH radicals near the ground, showing similar spatial and seasonal patterns to those of HO_2, especially prominent in the North China Plain, Bohai Bay, and the YRD. However, in southern China, the area showing a decrease in OH is more extensive than that for HO_2, stretching from oceanic regions to inland areas.

Figure 8 also shows the vertical-diurnal variations of SSA-induced OH concentrations in different months. The radiation effect distinctly influences OH concentrations, particularly in southern coastal cities. For instance, in July, the increase in OH concentration during early morning is significantly offset by a noon-time decrease due to the radiation effect of SSA, resulting in an overall reduction in OH levels.

We employed the IRR process analysis module to elucidate the primary mechanisms driving the increase in OH radicals caused by SSA (Fig. 9). OH production is facilitated by several processes, including HO_2 conversion, O_3 photolysis, HONO photolysis, ozonolysis of some VOCs, and others such as H_2O_2 photolysis. Among these, HO_2 conversion accounts for over 70% of total OH generation, followed by O_3 and HONO photolysis. In Guangzhou, a southern coastal city, the contribution from O_3 photolysis to OH production is notably higher than that in other regions, likely due to the lower latitude with higher radiation levels. During the morning, the increase in OH is driven by enhanced HO_2 conversion caused by SSA. While in Guangzhou, the afternoon sees a decrease in HO_2 conversions, which can be attributed to the decreased HO_2 concentrations (Fig. 7e). Additionally, the reduced O_3 photolysis, exacerbated by SSA's enhanced radiative effects and overall reduction in O_3 concentrations due to decreased NO_x levels in a NO_x-limited regime (see section 3.5), further decreases OH production.

3.5 Impacts of SSA on O_3

Figure 10 illustrates the spatial distribution of changes in the maximum daily average 8-hour (MDA8) O_3 mixing ratio near the ground after incorporating SSA emissions into the model. In January, there is a notable increase in O_3 mixing ratios across eastern China and surrounding oceanic areas, peaking at 6.3 ppbv. In April, the North China Plain, Bohai Bay, the Yellow Sea see increases up to 3.6 ppbv, while decreases up to 2.2 ppbv in southern China, South China Sea and East China Sea. By July, increased O_3 levels are confined to smaller areas like Bohai Bay and the Yellow Sea, with a maximum rise of 3.6 ppbv, whereas decreases up to 1.8 ppbv are observed in the eastern coastal and oceanic regions of China. The variations of O_3 mixing ratios in October range from decreases of 2.8 ppbv to increases of 3.7 ppbv, showing similar patterns to April. We hypothesize that the regional and seasonal variations in O_3 largely depend on O_3 formation regime.

To determine the O_3 formation regime, we analyzed the ratio of production rates between hydrogen peroxide (H_2O_2) and HNO_3

(P_{H2O2}/P_{HNO3}) (Fig. 10c), using thresholds established in previous studies (Tonnesen and Dennis, 2000; Gaubert et al., 2021; Liu et al., 2021). A P_{H2O2}/P_{HNO3} ratio below 0.06 indicates a VOC-limited region; ratios of 0.06 to less than 0.2 signify a transition zone; and ratios of 0.2 or higher indicate a NO_x-limited region. Our results indicate that areas exhibiting increased MDA8 O_3 are primarily within VOC-limited regions, while decreases predominantly occur in NO_x-limited regions. In high NO_x environments, the reaction between particulate Cl^- from SSA and NO_x leads to the formation of more Cl radicals, which can either reduce NO titration to O_3 or enhance O_3 production through interactions with VOCs. In contrast, in low NO_x conditions, the reactions between particulate Cl^- and NO_x consume NO_x, resulting in lower O_3 levels. However, deviations from these patterns occurs. For example, significant decreases in O_3 are observed in the PRD region during April, July, and October, and most of regions in continental eastern China during summer, which are typically characterized as VOCs-limited. This phenomenon is likely due to SSA-induced reductions in NO_2 photolysis rates overshadowing potential increase in O_3 levels.

Figure 11 shows the vertical-diurnal variations in SSA-induced O_3 concentrations in Beijing, Shanghai, and Guangzhou. Morning increases within the planetary boundary layer across these cities are attributed to enhanced VOCs oxidation by SSA-induced Cl radicals, promoting the formation of RO_2 and HO_2 radicals that react with NO to generate NO_2, thereby increasing O_3 production. Moreover, the variations in other timeframes largely reflect the interplay between heterogeneous reactions and radiative effects. In January, the prevailing reduction in NO_x within VOCs-limited areas elevates OH and O_3 levels in all three cities. April and October show similar patterns in Beijing and Shanghai, while Guangzhou exhibits declines due to the NO_x reduction in NO_x-limited environment coupled with decreased photolysis rates. In July, only in Beijing do O_3 levels rise during the morning hours, with reductions noted elsewhere, driven by NO_x decreases in NO_x-limited conditions and reduced photolysis.

We also find significant decreases in SSA-induced O_3 concentrations in the free troposphere and over oceanic regions. This decline is largely driven by enhanced O_3 depletion by Cl radicals in areas with scant VOCs, where SSA-induced Cl radicals preferentially react with O_3 to form ClO, as depicted in Fig. S9 and S10. This behavior mirrors stratospheric conditions where Cl radicals are pivotal in consuming O_3.

Our analysis indicates that while SSA can suppress daytime O_3 and HO_x levels through reduced photolysis rates, it also contributes to their morning production via the release of Cl radicals through heterogeneous reactions. Additionally, the interactions of SSA with nitrogen-containing species modulate NO_x levels, affecting O_3 variations according to the prevailing formation regime, leading to regional and seasonal discrepancies in O_3 responses. The findings of this study contrast with previous modeling studies (Knipping and Dabdub, 2003; Dai et al., 2020; Sarwar and Bhave, 2007), which primarily reported increases in O_3 attributable to SSA, highlighting the complex and variable impacts of SSA on coastal atmospheric chemistry.

4 Conclusions and implications

In this study, we utilized the WRF-CMAQ model to comprehensively investigate the complex interactions between SSA and continental anthropogenic emissions affecting O_3 formation in Eastern China. Figure 12 illustrate the mechanisms by which SSA influences radicals and O_3 formation in coastal areas. The process begins with the emission of SSA over oceanic areas. In addition to its horizontal transport from the ocean to inland areas near surfaces, SSA is also transported extensively over continental regions through a long-range transport above the planetary boundary layer. Once inland, SSA interacts with pollutants from both continental anthropogenic and natural sources. Three primary pathways are identified by which SSA impact radicals and O_3 formations: (1) SSA scatters solar radiation, reducing the photolysis rates of atmospheric chemicals and suppressing daytime formation of O_3 and subsequently OH radicals. (2) Heterogeneous reactions between particulate Cl^- in SSA and nitrogen-containing species (NO_2 and N_2O_5) produces ClNO and $ClNO_2$, which are key precursors of Cl radicals. These SSA-induced Cl radicals oxidize VOCs and produce more OH, enhancing atmospheric oxidation capacity and O_3 production during morning hours. (3) These reactions also reduce NO_x concentrations, an essential O_3 precursors. The resultant O_3 changes depend on its formation regime, subsequently influencing OH variations.

In summary, the influence of SSA on photochemical O_3 formation via the combination of these three pathways is both complex and variable, changing with regions and seasons. In winter, SSA notably increases OH and O_3 levels in eastern China due to significant NO_x reductions in VOCs-limited areas. In contrast, in spring and autumn, while similar increases are found in the North China Plain, southern China experiences decreases due to NO_x reductions in NO_x-limited areas and reduced photolysis rates. In summer, O_3 increases are confined to areas around Bohai, with reductions noted in other regions driven by NO_x reductions in NO_x-limited areas and decreased photolysis.

This study suggests that as global efforts intensify to control anthropogenic emissions, the natural contributions from sources like SSA are likely to play an increasingly significant role in regional air quality and climate dynamics. This underscores the necessity for atmospheric chemistry models to integrate the diverse and seasonally varying impacts of natural aerosols like SSA to improve predictions of air quality and to devise more effective environmental management strategies. This integration is crucial for accurately assessing future air quality trends and making informed policy decisions in the face of changing global emissions patterns.

Author contributions

Q.F., and Y.M.L. initiated the research. Y.M.L. and Y.Y.H. designed the research framework. Y.M.L. conducted model simulations and drew the figures. Y.M.L. and Y.Y.H. analyzed the results and wrote the paper with input from all authors. All authors contributed to the discussion and improvement of the paper.

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Competing interests

The authors declare that they have no conflict of interest.

Code/Data availability

The code or data used in this study are available upon request from Yiming Liu (liuym88@mail.sysu.edu.cn) and Yingying Hong (yyhong0809@foxmail.com).

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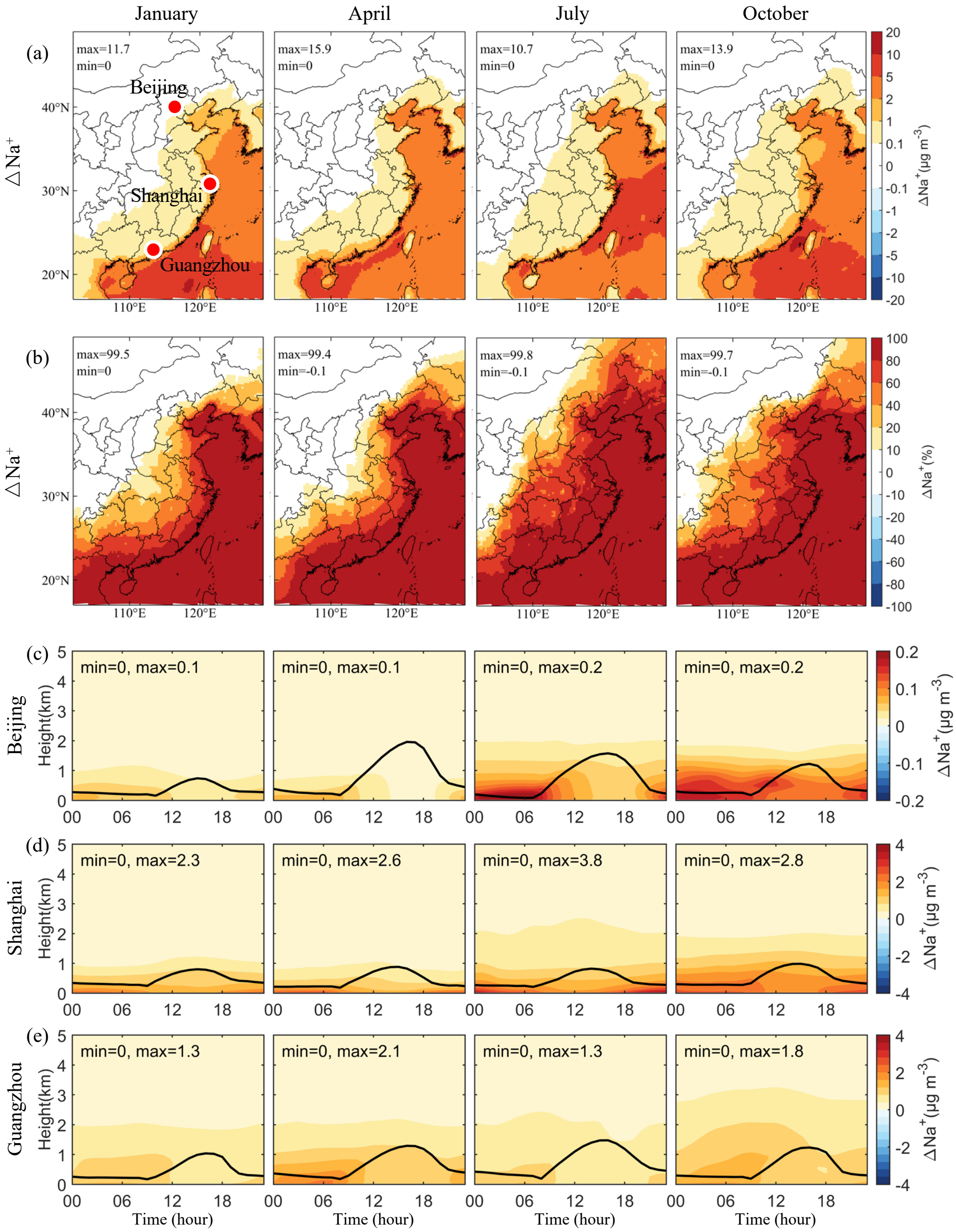


Figure 1: Changes in simulated monthly mean concentrations of particulate Na^+ induced by SSA during January, April, July and October 2015. Panels (a) and (b) present the spatial distribution of changes and percentage changes, respectively. Panels (c-e) display the vertical-diurnal variations of changes in Beijing, Shanghai and Guangzhou, respectively. The black line in Panels (c-e) is the simulated planetary boundary layer height.

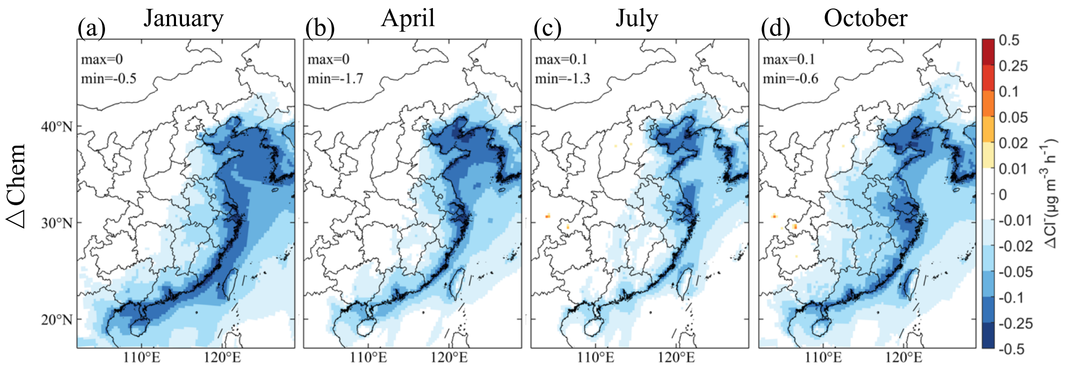
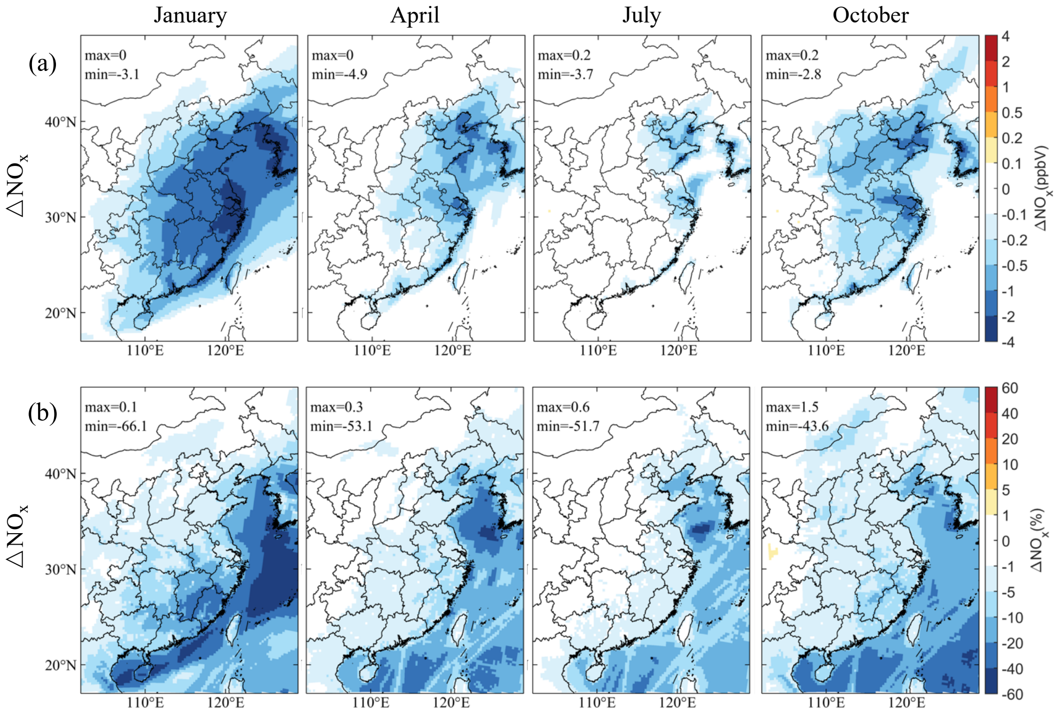


Figure 2: Changes in the contributions of heterogeneous reactions to the simulated monthly mean concentrations of particulate Cl^- near surface caused by SSA during (a) January, (b) April, (c) July and (d) October 2015. Heterogeneous reactions include reactions of particulate Cl^- with NO_2, NO_3, and N_2O_5.



620 **Figure 3: Changes in simulated monthly mean NO_x concentrations near surface caused by SSA during January, April, July and October 2015. Panels (a) and (b) present the spatial distribution of changes and percentage changes, respectively.**

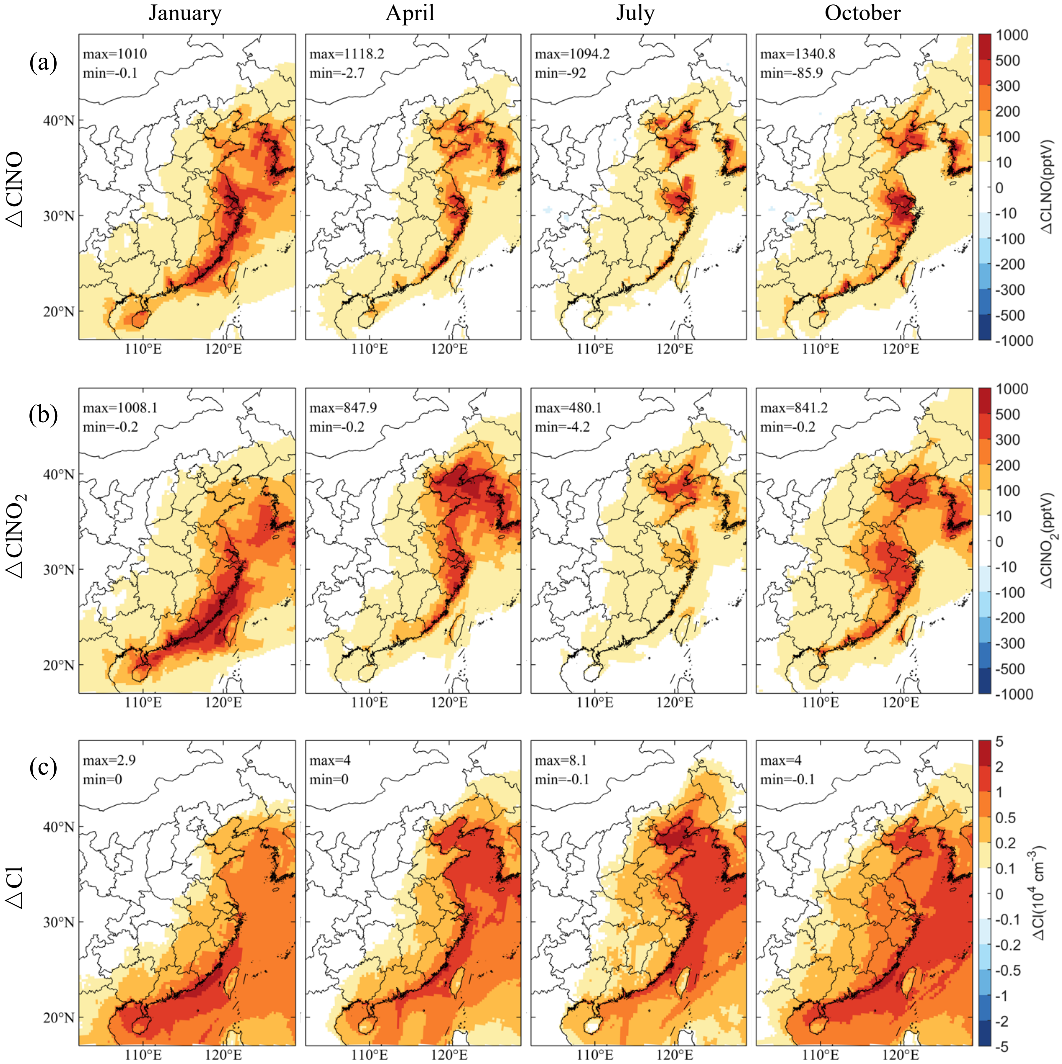


Figure 4: Spatial distribution of changes in simulated monthly mean concentrations of (a) ClNO and (b) ClNO$_2$ at 5:00 LST, and (c) daily mean Cl radicals near surface caused by SSA during January, April, July and October 2015.

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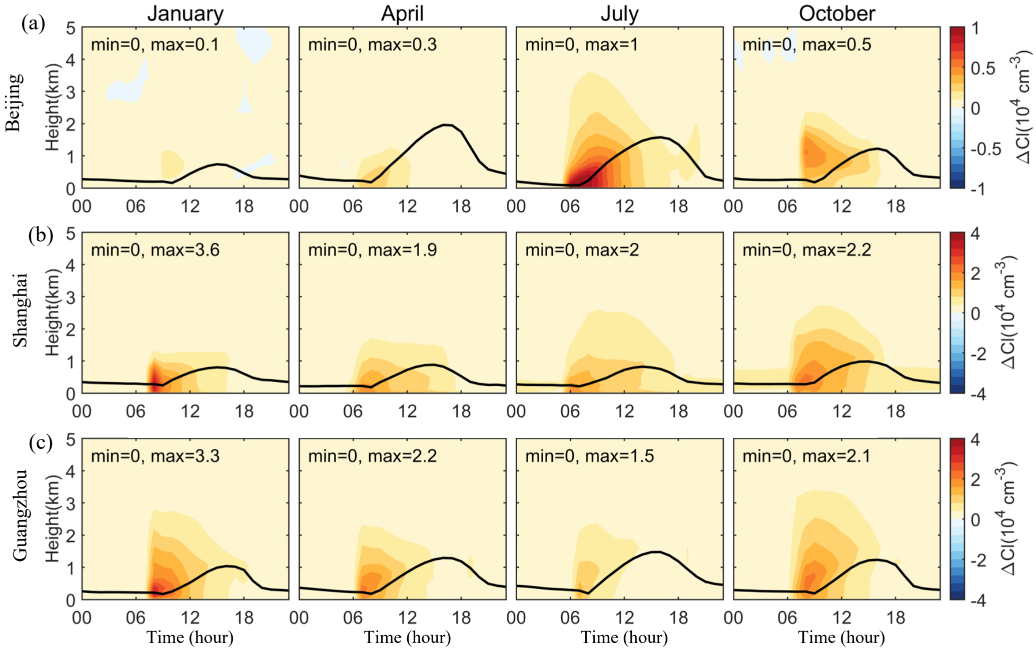

630 **Figure 5: Vertical-diurnal variations of changes in simulated monthly mean concentrations of Cl radicals caused by SSA in (a) Beijing, (b) Shanghai and (c) Guangzhou during January, April, July and October 2015. The black line is the simulated planetary boundary layer height.**

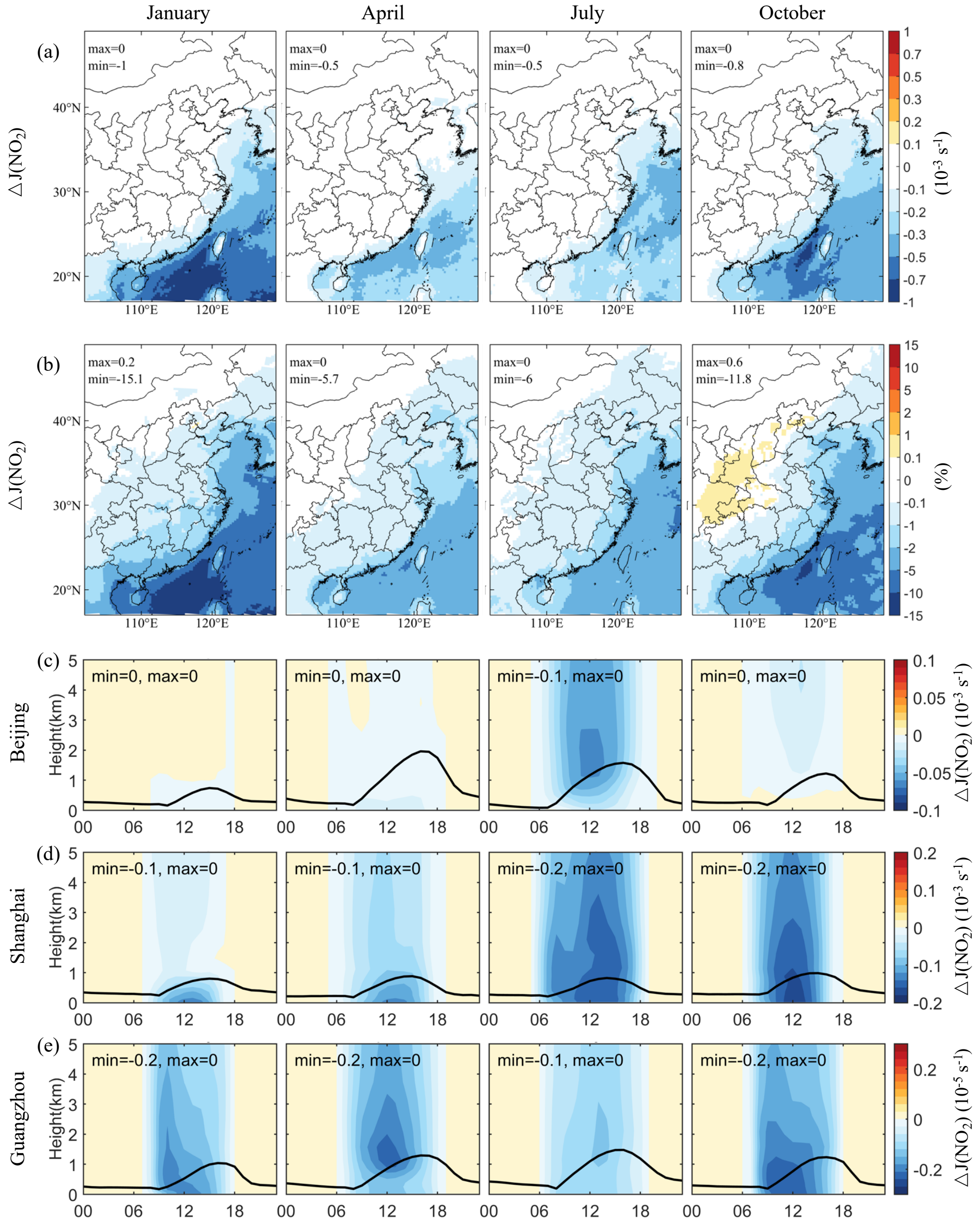

Figure 6: Changes in simulated monthly mean photolysis rate of NO_2 ($J(NO_2)$) induced by SSA during January, April, July and October 2015. Panels (a) and (b) present the spatial distribution of changes and percentage changes at 12:00 LST, respectively. Panels (c-e) display the vertical-diurnal variations of changes in Beijing, Shanghai and Guangzhou, respectively. The black line in Panels (c-e) is the simulated planetary boundary layer height.

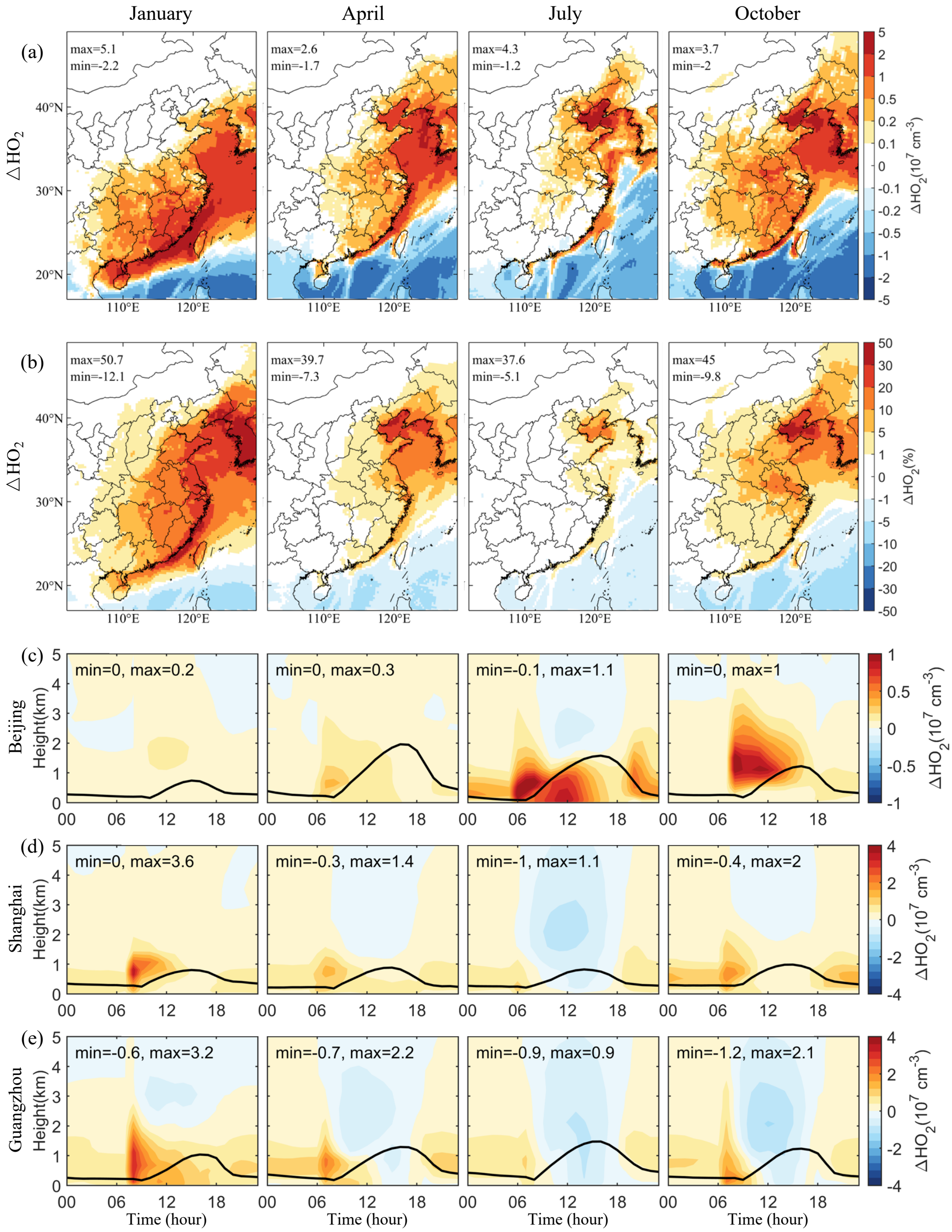

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Figure 7: The same as Fig. 1 but for simulated monthly mean HO$_2$ radical concentrations.

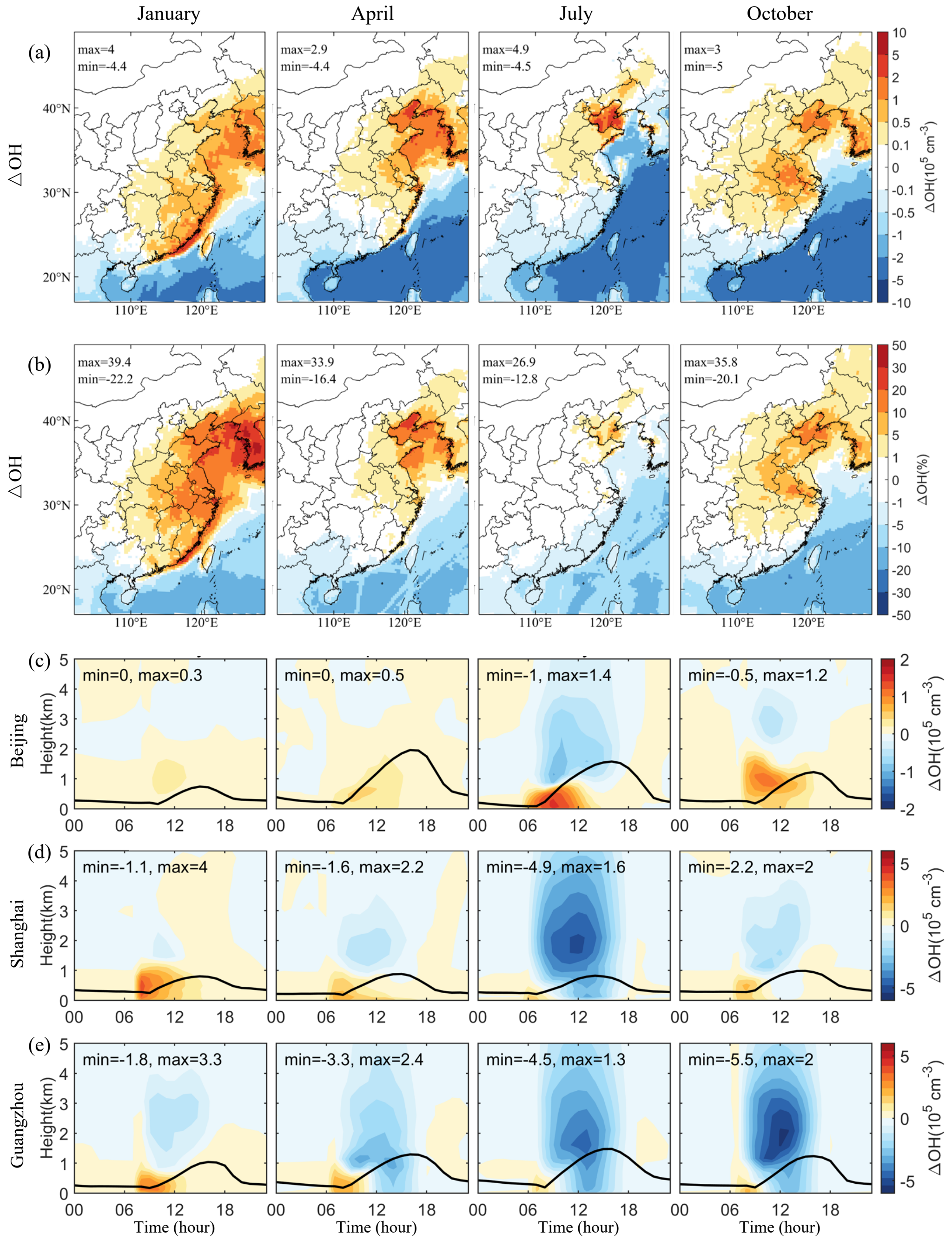

Figure 8: The same as Fig. 1 but for simulated monthly mean OH radical concentrations.

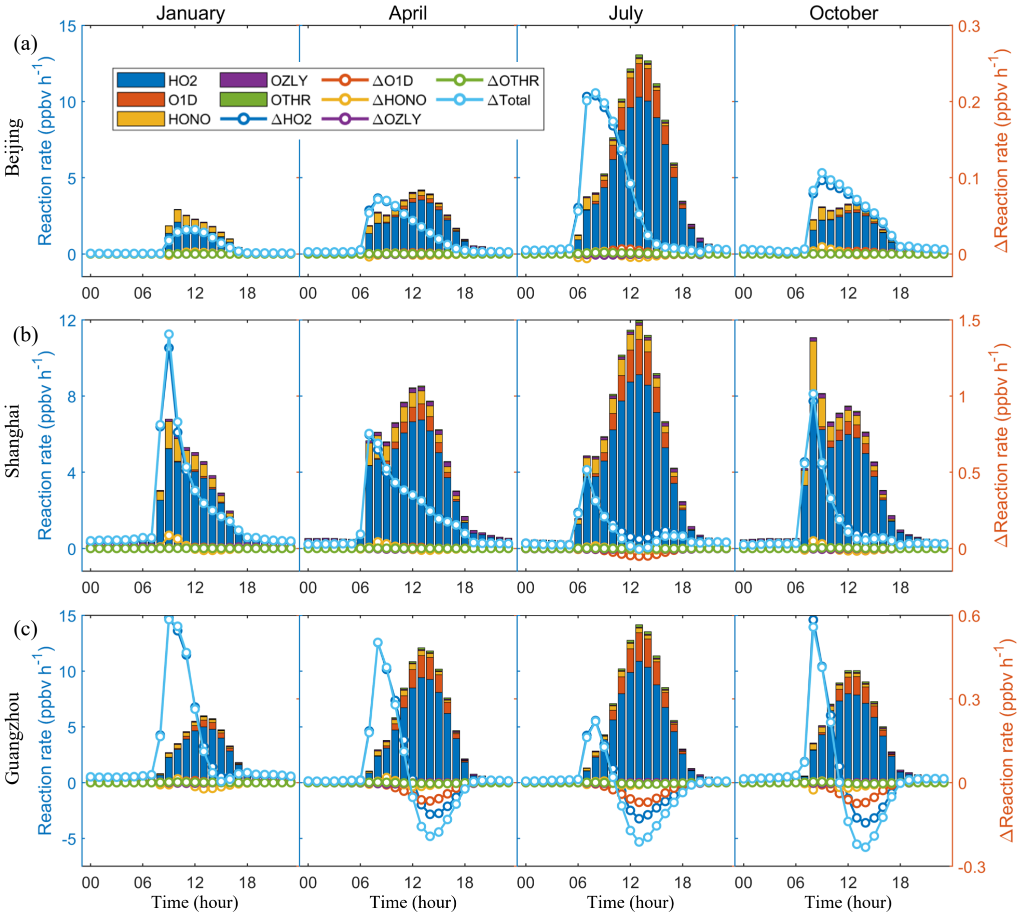

Figure 9: Contribution of different pathways to the OH production near surface and its changes caused by SSA in (a) Beijing, (b) Shanghai, and (c) Guangzhou during January, April, July and October 2015. These pathways include HO_2 conversion (HO_2), O_3 photolysis (O1D), HONO photolysis (HONO), ozonolysis of some VOCs (OZLY), and others (OTHR, including H_2O_2 photolysis, and etc.).

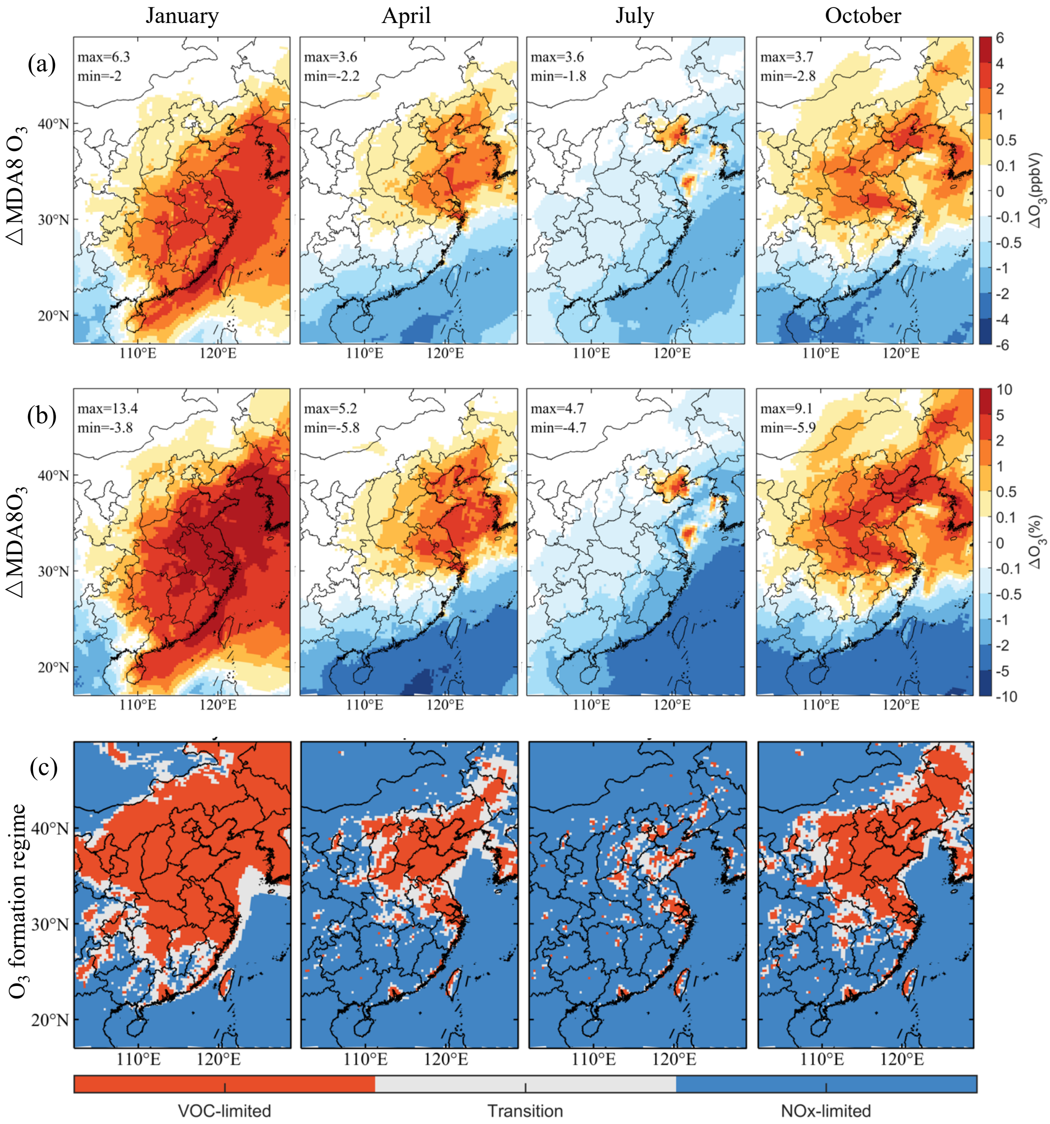

Figure 10: Changes in the simulated monthly mean mixing ratio of MDA8 O_3 induced by SSA and daytime O_3 formation regime during January, April, July and October 2015. Panels (a) and (b) present the spatial distribution of changes and percentage changes, respectively. Panels (c) display the spatial distribution of daytime (8:00 – 20:00 LST) O_3 formation regime. The regime is estimated by the ratio of the production rates of H_2O_2 to HNO_3 (P_{H2O2}/P_{HNO3}). VOC-limited region: $P_{H2O2}/P_{HNO3} < 0.06$; NOx-limited region: $P_{H2O2}/P_{HNO3} \geq 0.2$, Transition zone: $0.06 \leq P_{H2O2}/P_{HNO3} < 0.2$. The production rates of H_2O_2 and HNO_3 are calculated using the integrated reaction rate (IRR) diagnose tool in the CMAQ model.

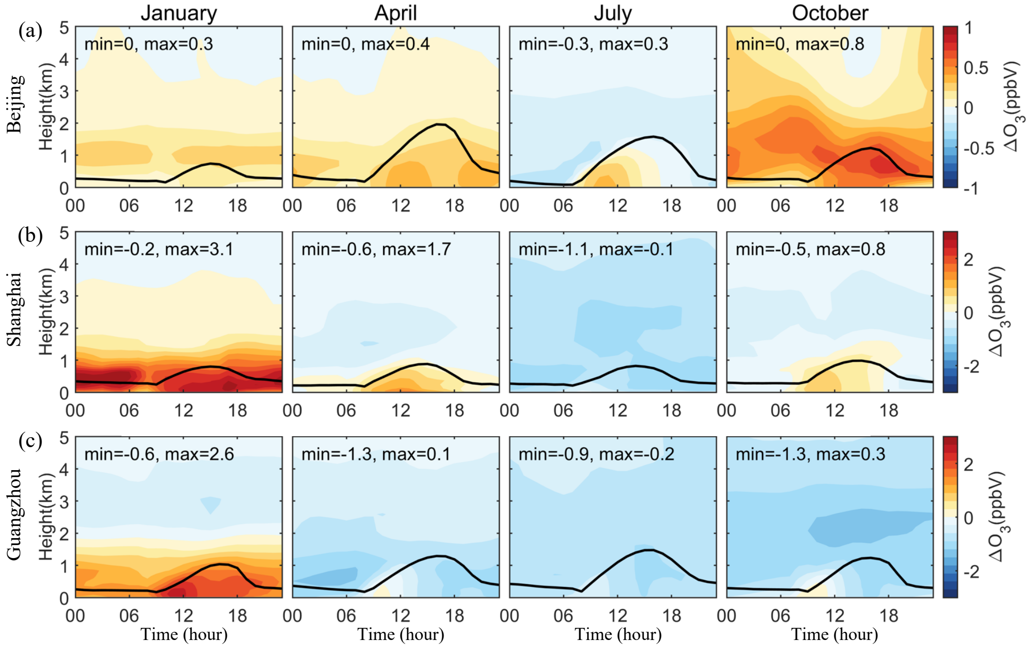

Figure 11: Vertical-diurnal variations of changes in simulated monthly mean O_3 mixing ratios caused by SSA in (a) Beijing, (b) Shanghai and (c) Guangzhou during January, April, July and October 2015. The black line is the simulated planetary boundary layer height.

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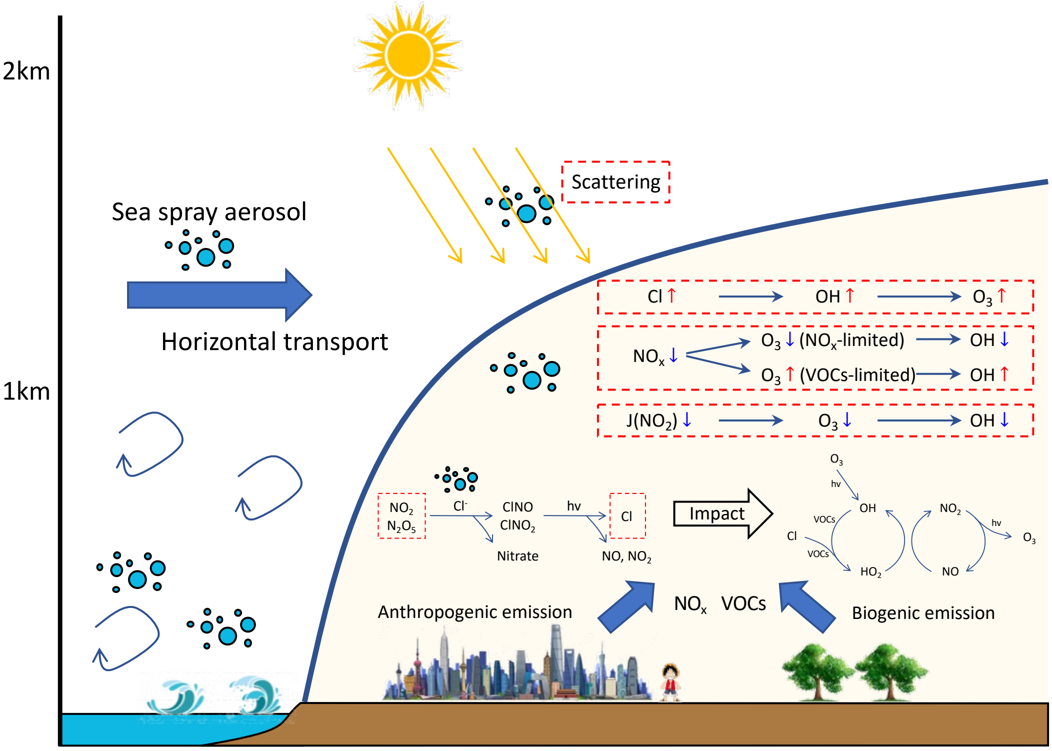

Figure 12: Schematic map showing the impact of SSA on the radicals and O_3 formation in coastal areas.