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Key Points:

- We conduct the first global simulation of atmospheric perchlorate using a three-dimensional chemical transport model
- Gas-phase production of perchlorate in the stratosphere and its subsequent transport cannot explain observations at many surface sites
- Analysis of modeled and observed ^{17}O excess suggests that non-stratospheric sources are important for the occurrence of natural perchlorate

Supporting Information:

Supporting Information may be found in the online version of this article.

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





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Stratospheric Gas-Phase Production Alone Cannot Explain Observations of Atmospheric Perchlorate on Earth

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Abstract Perchlorate has been observed in many environments on Earth and Mars but its sources remain poorly quantified. In this study, we use a global three-dimensional chemical transport model to simulate perchlorate's gas-phase photochemical production, atmospheric transport, and deposition on Earth's surface. Model predictions are compared to newly compiled observations of atmospheric concentrations, deposition flux, and oxygen isotopic composition of perchlorate. We find that the modeled gas-phase production of perchlorate is consistent with reported stratospheric observations. Nevertheless, we show that this mechanism alone cannot explain the high levels of perchlorate observed at many near-surface sites (aerosol concentrations $>0.1 \text{ ng m}^{-3}$ and deposition fluxes $>10 \text{ g km}^{-2} \text{ yr}^{-1}$) or the low ^{17}O -excess observed in perchlorate sampled from pristine environments ($<+18.4\%$). We discuss four hypotheses to explain the model-observation discrepancies and recommend laboratory and field observations to address key uncertainties in atmospheric sources of perchlorate.

Plain Language Summary Perchlorate (ClO_4^-) pollution is an environmental issue because excessive exposure can affect the thyroid and disrupt hormonal balance, especially for infants. Perchlorate on Earth has both human and natural sources. Industrial perchlorate is used for explosives and rocket fuels. Perchlorate also occurs naturally and accumulates in many deserts on Earth and in the soil of Mars. Atmospheric chemistry has long been considered a source of natural perchlorate, but its contribution remains uncertain. In this study, we use a 3-D atmospheric model to estimate how much of the perchlorate occurrence on Earth can be explained by known and plausible reactions between gases containing chlorine and oxygen. We find that these reactions can explain the abundance of stratospheric perchlorate. However, they cannot explain many tropospheric observations of perchlorate, especially those in Antarctica and urban areas. Our analysis of oxygen isotopic anomalies also suggests that stratospheric chemistry alone cannot account for all the natural perchlorate found in deserts. We discuss four possible explanations for the differences between observations and model predictions. We recommend some future research that can reduce the uncertainties in the sources of atmospheric perchlorate and improve our understanding of the occurrence of natural perchlorate in planetary atmospheres.

1. Introduction

Perchlorate (ClO_4^-) contamination of drinking water, food, and air has been an emerging environmental concern because of its potentially adverse impacts on thyroid function and hormones, especially for infants and toddlers (Calderón et al., 2017; Niziński et al., 2021; Steinmaus, 2016; Wan et al., 2015). Synthetic perchlorate, which is manufactured for military purposes, aerospace applications, and other commercial products (e.g., fireworks and road flares), sometimes leaks to the environments, creating high perchlorate levels (Dasgupta et al., 2006; Urbansky, 2002).

In contrast, non-synthetic perchlorate has more enigmatic origins. High abundance of soil perchlorate has been observed in arid regions on Earth and Mars (Hecht et al., 2009; Jackson et al., 2015). Oxygen isotopes suggest

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that atmospheric ozone (O_3) is involved in the formation of perchlorate sampled from the Atacama desert of Chile and Death Valley in the US (Bao & Gu, 2004; Jackson et al., 2010). Laboratory experiments have studied various perchlorate-production mechanisms, such as aqueous reaction of oxychlorine (Cl_xO_y) in the presence of ozone and/or UV light (Dasgupta et al., 2005; Estrada et al., 2021; Kang et al., 2006, 2008, 2009), solid-gas interactions between chloride and ozone (Estrada et al., 2021; Jackson et al., 2018; Kang et al., 2008), photo-catalyzed electrochemistry (Carrier & Kounaves, 2015; D. Liu & Kounaves, 2019), and plasma chemistry during electric discharge (Dasgupta et al., 2005; Rao, Mohan, et al., 2012; Wu et al., 2018). However, the contribution of these mechanisms to the occurrence of non-synthetic perchlorate on Earth remains elusive.

Both synthetic and non-synthetic perchlorate might have contributed to trends in environmental perchlorate. Changes in US groundwater perchlorate were attributed to propellant production, rocket testing, fireworks disposal, and the use of Chilean fertilizers (Böhlke et al., 2009; Sturchio et al., 2012). Van Stempvoort et al. (2019) analyzed samples from the Great Lakes and inferred an increase in perchlorate inputs over the twentieth century. Ice-core observations show higher perchlorate deposition fluxes in the Arctic, Antarctica, and mid-latitude glaciers since the 1980s (e.g., Jiang et al., 2020). Nonetheless, it is still unclear to what extent atmospheric processes have driven these trends.

To date, three studies have investigated the atmospheric production of perchlorate using photochemical models. Jaeglé et al. (1996) used a box model to simulate perchlorate production via ClO (g) uptake on stratospheric aerosols and suggested that it might explain an unknown inorganic chlorine species observed in the stratosphere following Mt. Pinatubo's eruption in 1991. However, the assumed ClO uptake coefficient was later found to be two-orders-of-magnitude larger than the upper limit derived from laboratory measurements (Abbatt, 1996). Following perchlorate detection on Mars, Catling et al. (2010) and Smith et al. (2014) used 1-D models to simulate atmospheric production of perchlorate via gas-phase pathways. They showed that gas-phase chemistry can explain the observed perchlorate abundance in the soil of the Atacama desert but not on Mars. However, their modeling results were based on a relatively simple parameterization of halogen chemistry and did not quantitatively incorporate isotopic information.

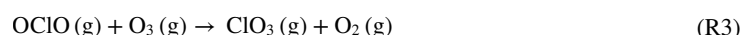
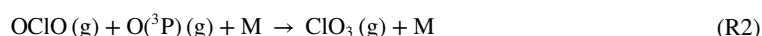
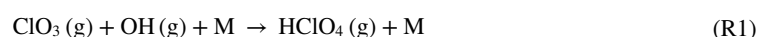
In this study, we revisit the importance of atmospheric production of perchlorate using a state-of-the-art 3-D chemical transport model that includes a detailed representation of halogen chemistry in the Earth's atmosphere. We use the model to interpret perchlorate observations in atmospheric aerosols and deposition samples, as well as the observed isotopic composition of perchlorate in pristine arid environments.

2. Methods: Models and Observations

2.1. Global Model of Atmospheric Perchlorate

We use the GEOS-Chem global 3-D chemical transport model (version 13.3.2) to simulate the production, transport, and deposition of perchlorate on Earth. GEOS-Chem has a detailed representation of oxidant-aerosol-radiation interactions in the troposphere and stratosphere (Eastham et al., 2014, 2022; X. Wang et al., 2021). Recent studies evaluated the model's performance in simulating stratospheric composition (Eastham et al., 2022; Knowland et al., 2022) and tropospheric halogen chemistry (X. Wang et al., 2021). We use Modern-Era Retrospective analysis for Research and Applications Version 2 meteorological dataset (Gelaro et al., 2017) with a spatial resolution of 4° latitude \times 5° longitude \times 72 vertical levels to drive the model and perform simulations from 2016 to 2018.

To model the photochemical production of atmospheric perchlorate, we add three species (ClO_3 (g), Cl_2O_4 (g), and perchlorate) and nine gas-phase reactions (Table S1 in the Supporting Information S1) to the GEOS-Chem chemistry scheme. These reactions include:



For perchloric acid ($HClO_4$ (g)) formation via ClO_3 (g) + OH (g) (R1), we use the rate constant estimated from ab initio studies (R. S. Zhu & Lin, 2001, 2003). ClO_3 (g) has been observed in the laboratory (Grothe &

Willner, 1994; Kopitzky et al., 2002) and can be produced via $\text{OCIO}(\text{g}) + \text{O}(^3\text{P})(\text{g})$ (R2) and $\text{OCIO}(\text{g}) + \text{O}_3(\text{g})$ (R3) (Green et al., 2004; Wayne et al., 1995). We do not include the photolysis of $\text{ClO}_3(\text{g})$ or the thermal decomposition of $\text{ClO}_3(\text{g})$ and $\text{Cl}_2\text{O}_4(\text{g})$ because of the current lack of reliable constraints on the kinetics. Our modeled $\text{HClO}_4(\text{g})$ production rate via R1 is thus likely an overestimate (the effects of adding $\text{ClO}_3(\text{g})$ photolysis are discussed in Section 4.1).

Once HClO_4 forms in the modeled atmosphere, we assume it quickly condenses onto aerosols, stays in the particulate phase as a perchlorate ion ($\text{ClO}_4^-(\text{p})$), and is chemically inert—similar to the fate of atmospheric H_2SO_4 . In our simulation, the only loss of $\text{ClO}_4^-(\text{p})$ in the stratosphere is via advection to the troposphere and gravitational settling of stratospheric aerosols. In the troposphere, we assume $\text{ClO}_4^-(\text{p})$ undergoes wet and dry deposition to the surface and use deposition parameterizations described in Emerson et al. (2020), H. Liu et al. (2001), and Q. Wang et al. (2014). Text S1 in the Supporting Information S1 provides details on the model configuration.

2.2. Observations of Atmospheric Perchlorate

Not many studies have reported observations of atmospheric perchlorate because perchlorate occurs at much lower concentration than other major inorganic species (e.g., nitrate and sulfate) and is challenging to measure. Murphy and Thomson (2000) reported the first detection of $\text{ClO}_4^-(\text{p})$ in the lower stratosphere from the mass spectra of aerosols. Surface observations of $\text{ClO}_4^-(\text{p})$ are mostly from urban and rural sites in East Asia (Shi et al., 2011; Shirahata, 2012; Takeuchi et al., 2012; C. Wang et al., 2017; Yamada et al., 2009, 2012; Yao et al., 2015; Zheng et al., 2022; H. Zhu et al., 2021). Observations in more remote locations were reported in Handa et al. (2010) (Okinawa, Japan) and Jiang et al. (2021) (from a cruise between Shanghai, China and Antarctica). Measurements of perchlorate in deposition samples are available in North America (Andraski et al., 2014; Munster et al., 2009; Rajagopalan et al., 2009; Van Stempvoort et al., 2020) and East Asia (Lin et al., 2019; Yamada et al., 2009, 2012). Perchlorate concentration in ice-core and snow-pit samples has also been used for inferring deposition fluxes (Cole-Dai et al., 2018; Crawford et al., 2017; Du et al., 2019; Furdui et al., 2018; Furdui & Tomassini, 2010; Jiang et al., 2016, 2020; Rao, Wake, et al., 2012).

We compile observations of perchlorate in tropospheric aerosols and surface deposition samples from 24 published studies (see Tables S2 and S3 in the Supporting Information S1 for summary and Figure S1 in the Supporting Information S1 for observation locations). To focus on the background conditions, we exclude observations obtained during and shortly after fireworks displays, which can release synthetic perchlorate into the atmosphere (e.g., Munster et al., 2009; Shi et al., 2011).

2.3. Analysis of ^{17}O Excess of Perchlorate Originating From Photochemistry

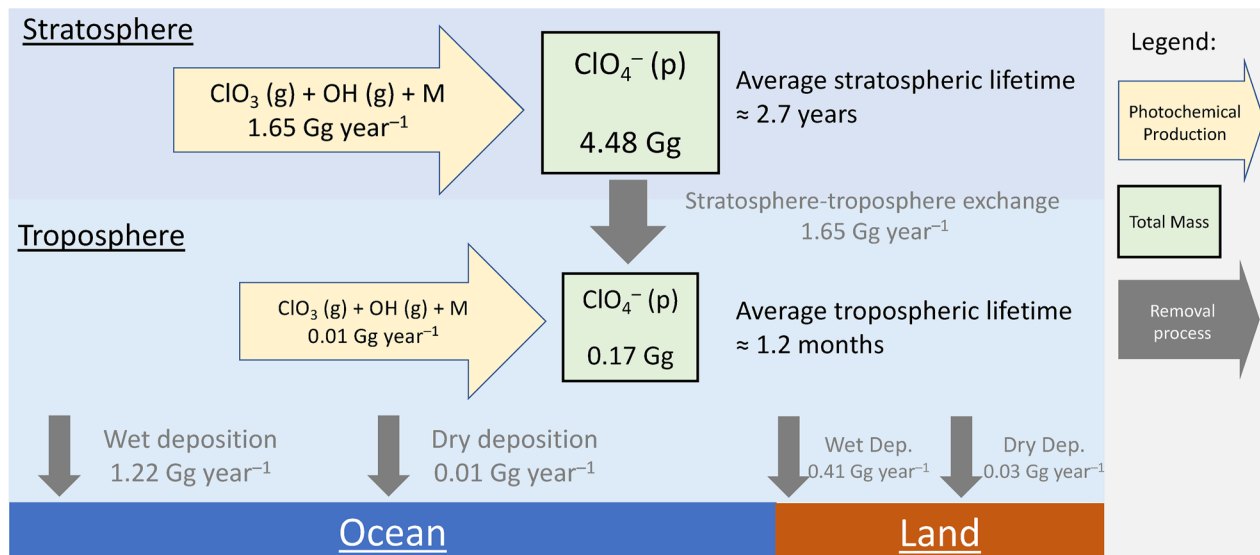
Measurements and models of ^{17}O excess ($\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) are powerful tools for investigating atmospheric oxidation processes (Thiemens, 2006), and here we use them for understanding the origins of environmental perchlorate. In Earth's atmosphere, a large positive $\Delta^{17}\text{O}$ originated from mass-independent fractionation during ozone formation and can transfer from ozone to other species via oxidation (Thiemens, 2006). For species that have multiple formation pathways (e.g., nitrate and sulfate), $\Delta^{17}\text{O}$ provides quantitative information on the contribution of ozone-related pathways relative to those involving other oxidants (Alexander et al., 2020; Chan et al., 2021; Chen et al., 2016). Environmental observations of high $\Delta^{17}\text{O}(\text{ClO}_4^-)$ (up to +18.4‰) have been interpreted as evidence of an atmospheric origin of natural perchlorate (e.g., Bao & Gu, 2004; Jackson et al., 2010), but process-based modeling of $\Delta^{17}\text{O}(\text{ClO}_4^-)$ has not been attempted. We conduct a bottom-up estimate of the $\Delta^{17}\text{O}$ of the perchlorate formed via photochemistry using simulated reaction rates and assumptions about $\Delta^{17}\text{O}$ in oxidants and intermediate species (Text S2 in the Supporting Information S1).

3. Results

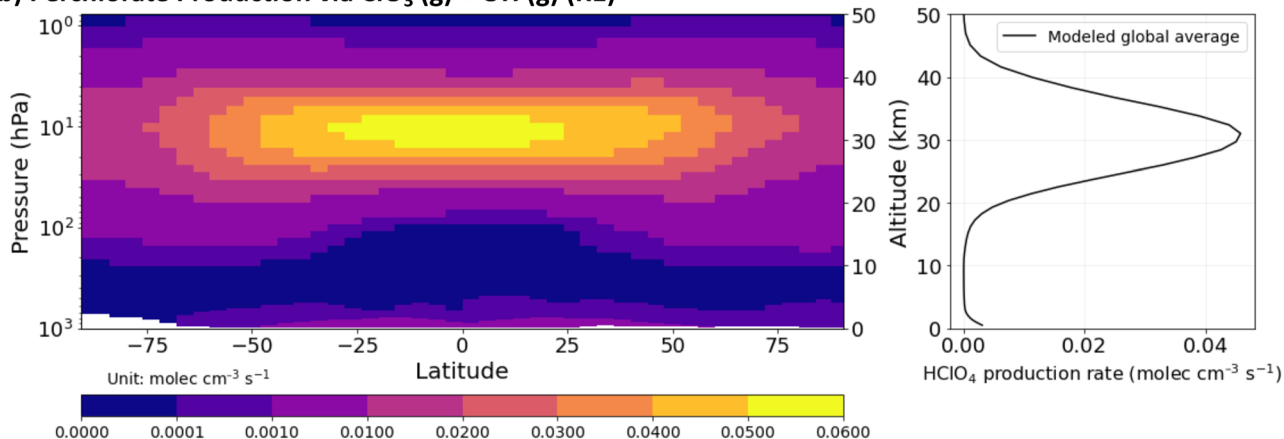
3.1. Modeled Global Budget and Spatial Distribution of Perchlorate

Figure 1a shows the modeled budget of atmospheric perchlorate for 2016–2018. The model predicts that the stratosphere dominates perchlorate photochemical production ($1.65 \text{ Gg ClO}_4^- \text{ yr}^{-1}$) compared to the troposphere ($0.01 \text{ Gg ClO}_4^- \text{ yr}^{-1}$) (Figure 1a). Perchlorate production is largest in the stratosphere due to higher concentrations of reactive chlorine species (originating from the photolysis of chlorofluorocarbons and CH_3Cl) and

(a) Global Mass Budget of Perchlorate



(b) Perchlorate Production via $\text{ClO}_3 \text{ (g)} + \text{OH (g)}$ (R1)



(c) Perchlorate Concentration

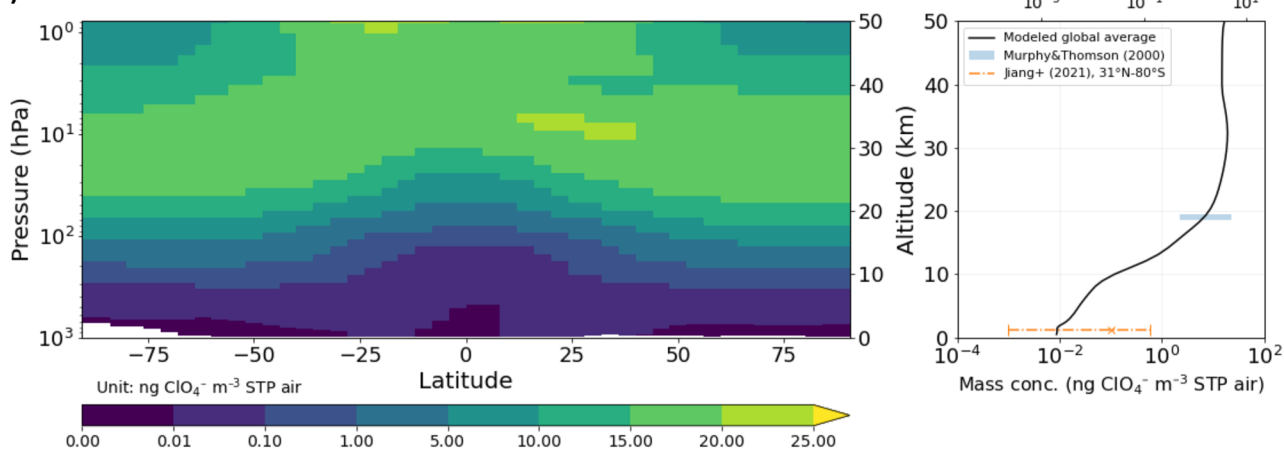


Figure 1. Average (a) global perchlorate mass budget, (b) perchlorate production via reaction between ClO_3 and OH (R1), and (c) perchlorate concentration in the modeled stratosphere and troposphere from the model simulation for 2016–2018. The blue-shaded region and the orange bar in the right panel of (c) indicate observations by Jiang et al. (2021) and Murphy and Thomson (2000) (X marker: median, range: maximum and minimum), respectively. Standard Temperature and Pressure (STP) condition is defined as $T = 273 \text{ K}$ and $P = 1,013 \text{ hPa}$.

oxidants (OH , O_3 , and $\text{O}(^3\text{P})$). The average atmospheric lifetime of stratospheric perchlorate (2.7 yr against stratosphere-troposphere exchange) is longer than that of tropospheric perchlorate (1.2 months against deposition). About 96% of the total mass of the modeled atmospheric perchlorate resides in the stratosphere (4.48 Gg). Modeled perchlorate accounts for 0.17% of total inorganic chlorine in the stratosphere. Modeled ClO_3 and Cl_2O_4 account for 0.01% of chlorine in stratospheric gas-phase Cl_xO_y species. The newly added ClO_3 - Cl_2O_4 - ClO_4^- chemistry's impacts on the concentrations of major stratospheric chlorine species in the model are negligible (Text S3 in the Supporting Information S1). About 97% of the modeled perchlorate is removed from the atmosphere via wet deposition (1.62 Gg yr^{-1}).

Figures 1b and 1c show the zonal average of modeled perchlorate production rate and concentration. Photochemical production of perchlorate maximizes in the tropical stratosphere at 30 km altitude as a result of the balance between increasing $[\text{ClO}_3 \text{ (g)}]$ and decreasing rate constants (R1 are pressure-dependent) at higher altitudes (Figure 1b). We find that $\text{OCIO} + \text{O}$ (R2) accounts for 97% of ClO_3 production in the stratosphere and that most of its production via R2 occurs during the day. The diurnal cycles of OCIO and O oppose each other, with OCIO maximizing at night and O during the day, yet there is still enough OCIO during the day to react with O (Text S4 in the Supporting Information S1). Our simulation predicts that $[\text{ClO}_4^- \text{ (p)}]$ maximize at 32 km ($19 \text{ ng ClO}_4^- \text{ m}^{-3}$ air at standard conditions $\approx 4.3 \text{ pmol ClO}_4^- \text{ mol}^{-1}$ air) (Figure 1c). Our results are consistent with $[\text{ClO}_4^- \text{ (p)}]$ observations by Murphy and Thomson (2000), who reported $0.5\text{--}5 \text{ pmol mol}^{-1}$ at 19 km altitude, where the modeled global average is $1.6 \text{ pmol mol}^{-1}$ (Figure 1c). After photochemical production in the tropical stratosphere, perchlorate is advected poleward by the Brewer–Dobson circulation and eventually crosses the tropopause. Once in the troposphere, modeled $[\text{ClO}_4^- \text{ (p)}]$ decreases by an order of magnitude owing to stronger vertical mixing and the loss via deposition. In the marine boundary layer, perchlorate production increases slightly due to the gas-phase chlorine species released from sea-salt aerosols (X. Wang et al., 2021).

3.2. Comparison to Observed Surface Concentrations and Deposition Fluxes

Figure 2a compares modeled and observed near-surface $[\text{ClO}_4^- \text{ (p)}]$ as a function of latitude. Modeled values are generally lower and have a narrower range ($10^{-3}\text{--}10^{-1} \text{ ng m}^{-3}$) compared to observations ($10^{-3}\text{--}10^2 \text{ ng m}^{-3}$). Our modeled average $[\text{ClO}_4^- \text{ (p)}]$ ($0.002 \text{ pmol mol}^{-1}$) is an order of magnitude lower than observations reported by Jiang et al. (2021) at more remote locations (median: $0.023 \text{ pmol mol}^{-1}$). We conducted Mann-Whitney U tests (details in Text S5 in the Supporting Information S1) and found that the observations from all published studies are statistically distinct from model predictions at the 95% significance level, except for the rural sites in Yuzhong County in China (Shi et al., 2011) and Lake Toya in Japan (Shirahata, 2012).

The modeled wet deposition flux ranges from about 0.1 to $10 \text{ g km}^{-2} \text{ yr}^{-1}$, with decreasing values toward high latitudes (Figure 2b). Catling et al. (2010) estimated a long-term average perchlorate deposition flux of $1.9 \times 10^5 \text{ molecules cm}^{-2} \text{ s}^{-1}$ over the Atacama desert, where our model predicts a deposition flux of $6.3 \times 10^4 \text{ molecules cm}^{-2} \text{ s}^{-1}$. At the US sites studied by Rajagopalan et al. (2009) and the ice-cores/snow-pits sites in the northern hemisphere, model predictions are within the same order of magnitude as the observations. At other locations, however, observed deposition fluxes ($10^{-1}\text{--}10^4 \text{ g km}^{-2} \text{ yr}^{-1}$) are much larger than the model, especially near urban areas and over Antarctica (Figure 2b and Table S4 in the Supporting Information S1). Overall, the model significantly underestimates observed near-surface $[\text{ClO}_4^- \text{ (p)}]$ (observed median/model median ≈ 42) and perchlorate deposition flux (observed median/model median ≈ 2).

3.3. Modeled $\Delta^{17}\text{O}$ of Perchlorate Compared to Observations in Pristine Arid Environments

Figure 3 shows observations of $\Delta^{17}\text{O}(\text{ClO}_4^-)$ in relatively pristine environments where atmospheric deposition is likely an important source of perchlorate and other soil salts (e.g., nitrate) (Arenas-Díaz et al., 2022; Jackson et al., 2010, 2016; Michalski et al., 2004, 2005). These environments have been arid for $10^4\text{--}10^7 \text{ yr}$ (Catling et al., 2010; Jackson et al., 2016; Li et al., 1996), so soluble species can accumulate near the surface. Measured $\Delta^{17}\text{O}(\text{ClO}_4^-)$ of these samples have a median of $+9.2\text{‰}$ and values up to $+18.4\text{‰}$ (Table S5 in the Supporting Information S1). These measurements cannot be explained solely by synthetic perchlorate, which has $\Delta^{17}\text{O} \approx 0\text{‰}$ because all its oxygen atoms originate from water molecules (Bao & Gu, 2004). The high $\Delta^{17}\text{O}(\text{ClO}_4^-)$ in these environments has been interpreted as evidence of an atmospheric origin (Bao & Gu, 2004; Jackson et al., 2010), because oxygen atoms originating from ozone and most stratospheric oxidants have large positive $\Delta^{17}\text{O}$ (Brinjkji & Lyons, 2021).

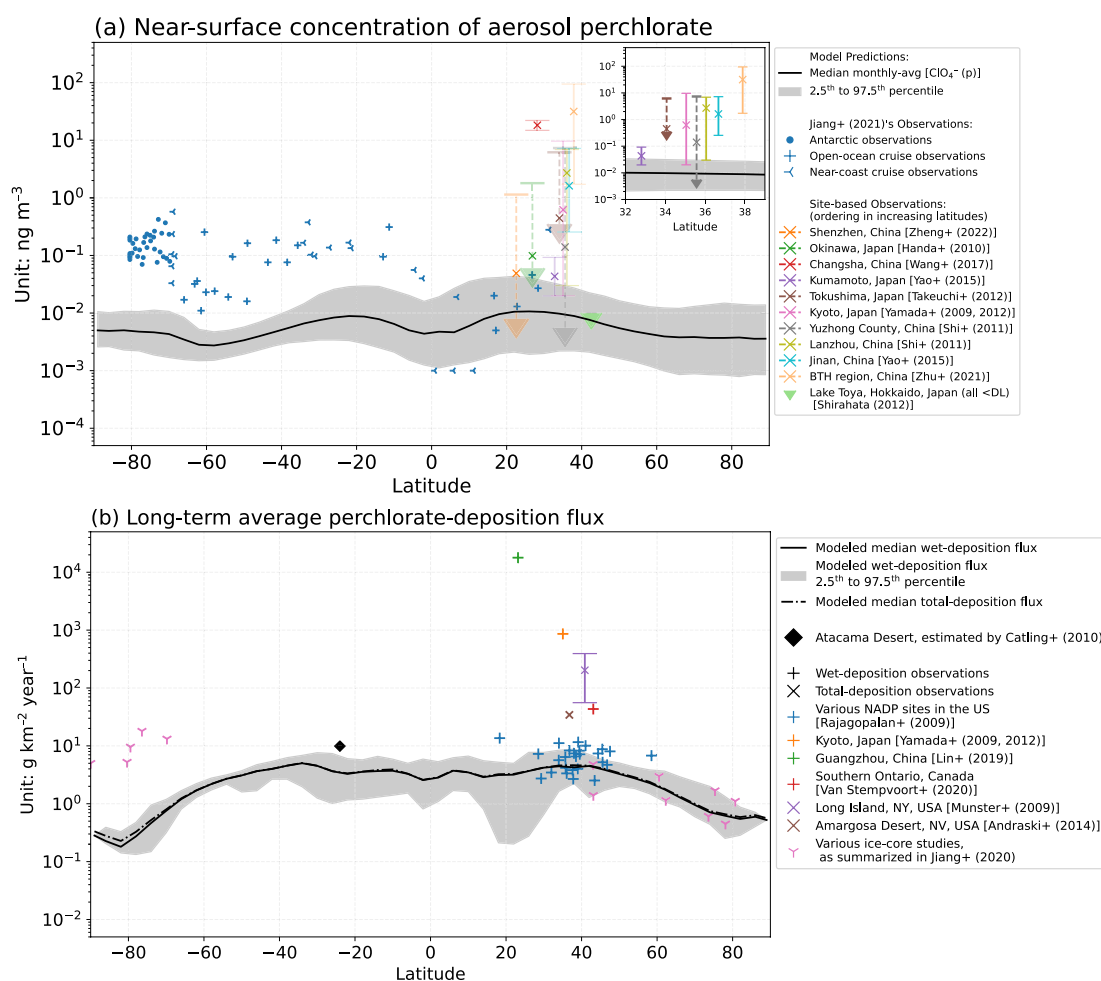


Figure 2. Modeled and observed (a) near-surface concentration of aerosol perchlorate and (b) perchlorate deposition flux as a function of latitude. Concentrations at sites where all observations are above the detection limit are shown as mean (X marker), with the error bar indicating the minimum and maximum. For sites with observations below the detection limit, the X marker indicates the median while the inverted-triangle marker's upper side indicates the detection limit. The Jiang et al. (2021) cruise observations that are ≥ 200 km away from the coast are classified as “open-ocean.” For ice-core/snow-pit sites, we show the estimated post-1980 deposition flux summarized by Jiang et al. (2020). The gray area in (a) shows the modeled spatial and temporal variability, while in (b) it shows the spatial variability only.

Our modeled bottom-up estimates of $\Delta^{17}\text{O}(\text{ClO}_4^-)$ are significantly higher (average = $+28.5\%$; 2.5th percentile = $+25.2\%$; 97.5th percentile = $+29.5\%$) than observed values (Figure 3). The high modeled $\Delta^{17}\text{O}(\text{ClO}_4^-)$ originates from OCIO (g) (average modeled $\Delta^{17}\text{O} = +45.5\%$), which leads to high $\Delta^{17}\text{O}$ in ClO_3 (g) and thus perchlorate (R1–R3). Virtually all OCIO (g) forms via the reactions between ClO , BrO , and IO , which dominantly obtain their oxygen from ozone. Indeed, modeled $\Delta^{17}\text{O}(\text{ClO}_4^-)$ is similar to the measured $\Delta^{17}\text{O}$ of the perchlorate produced by ozone oxidation of chloride in laboratory experiments ($+29.5$ to $+32.5\%$) (Estrada et al., 2021). However, this high $\Delta^{17}\text{O}(\text{ClO}_4^-)$ resulting from photochemistry is distinct from published observations (Figure 3).

A possible interpretation of this discrepancy between modeled and observed $\Delta^{17}\text{O}$ is that atmospheric perchlorate production includes additional low- $\Delta^{17}\text{O}$ pathways. These pathways could involve low- $\Delta^{17}\text{O}$ oxygen atoms from O_2 (g), tropospheric OH , HO_2 , H_2O_2 , and/or water to form perchlorate. For instance, if we assume that a perchlorate molecule gets two oxygen atoms from tropospheric OCIO (g) (average modeled $\Delta^{17}\text{O} = +39.5\%$) and another two oxygen atoms from other tropospheric oxidants with $\Delta^{17}\text{O} = 0\%$, the resulting $\Delta^{17}\text{O}(\text{ClO}_4^-)$ would be $+19.8\%$, which is close to the highest observed $\Delta^{17}\text{O}(\text{ClO}_4^-)$.

The second interpretation is that the $\Delta^{17}\text{O}(\text{ClO}_4^-)$ observed in these pristine arid environments is the result of mixing high- $\Delta^{17}\text{O}$ perchlorate from photochemistry and a low- $\Delta^{17}\text{O}$ perchlorate from non-atmospheric-chemistry sources. To explain the observed difference between $\Delta^{17}\text{O}(\text{NO}_3^-)$ in aerosols and desert soils, Michalski

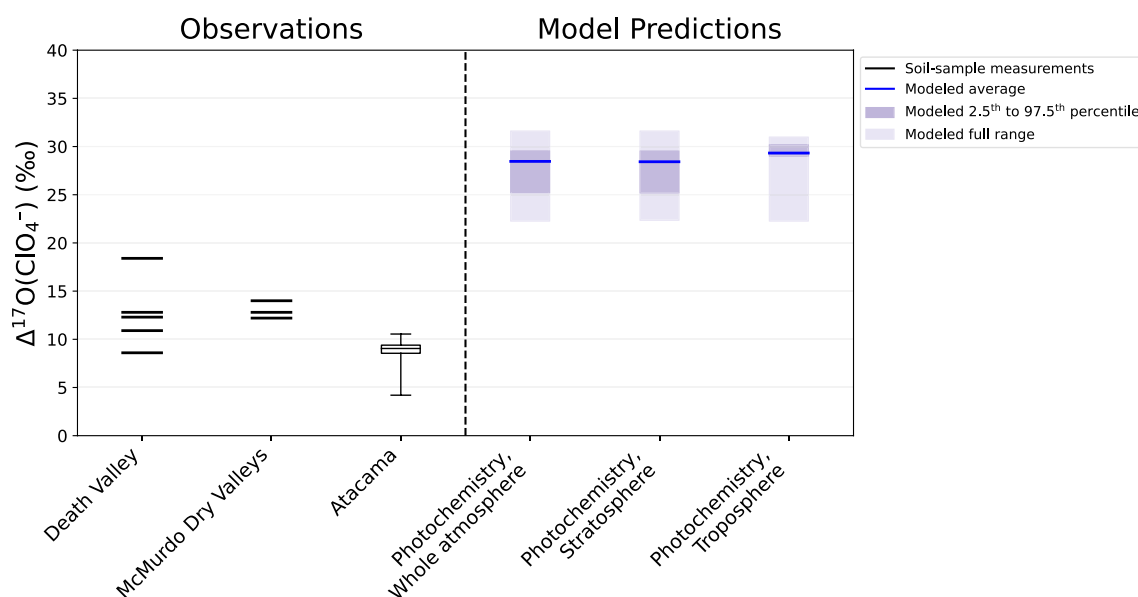


Figure 3. Comparison of $\Delta^{17}\text{O}(\text{ClO}_4^-)$ observed in pristine arid environments samples (left) and model predictions (right). Observed $\Delta^{17}\text{O}(\text{ClO}_4^-)$ values in Death Valley and McMurdo Dry Valleys are shown as individual measurements (horizontal bars), because of small sample sizes. The larger set of published values for the Atacama Desert ($n = 22$) are shown as a box and whisker plot, with whiskers indicating minimum and maximum. The references can be found in Table S5 in the Supporting Information S1. For model predictions (Text S2 in the Supporting Information S1), the line indicates the average $\Delta^{17}\text{O}(\text{ClO}_4^-)$ weighted by the modeled perchlorate production rate.

et al. (2004) suggests that desert nitrate is a mixture of high- $\Delta^{17}\text{O}$ atmospheric nitrate and low- $\Delta^{17}\text{O}$ biogenic nitrate. Jackson et al. (2010) discussed similar concepts while interpreting the observed correlation between $\Delta^{17}\text{O}(\text{ClO}_4^-)$ and $\delta^{18}\text{O}(\text{ClO}_4^-)$ in desert samples. Estrada et al. (2021) demonstrated that low- $\Delta^{17}\text{O}$ perchlorate can be produced via UV-activated aqueous oxidation of Cl_xO_y species in the laboratory. Assuming our estimated $\Delta^{17}\text{O}$ for perchlorate produced from photochemistry is correct and pristine arid environments are influenced by a source of perchlorate with $\Delta^{17}\text{O} = 0\text{‰}$, the $\Delta^{17}\text{O}(\text{ClO}_4^-) = +18.4\text{‰}$ observation in Death Valley would indicate that this non-atmospheric-chemistry source accounts for about 35% of perchlorate mass there.

4. Hypotheses for Explaining Discrepancies Between Observations and Model

Our global model prediction of atmospheric perchlorate is consistent with early measurements of stratospheric perchlorate (Figure 1c), observed perchlorate deposition fluxes at US sites studied by Rajagopalan et al. (2009), and cryospheric sites in the northern hemisphere (Figure 2b). However, our model simulations significantly underestimates observations of near-surface $[\text{ClO}_4^- (\text{p})]$ and perchlorate deposition flux at many other locations, especially those near and downwind of metropolitan areas and Antarctica (Figure 2). In addition, our model predicts $\Delta^{17}\text{O}(\text{ClO}_4^-)$ values that are higher than the highest $\Delta^{17}\text{O}(\text{ClO}_4^-)$ observed in soils (Figure 3), suggesting missing atmospheric pathways for perchlorate formation in our model and/or emissions of non-synthetic perchlorate. We explore four hypotheses to explain these discrepancies between model and observations.

4.1. Hypothesis I: Gas-Phase Reaction Rates Are Uncertain

Many rate constants in our current $\text{ClO}_3\text{-Cl}_2\text{O}_4\text{-ClO}_4^-$ chemistry scheme are based on theoretical ab initio studies for combustion conditions (in particular R1, $T = 300\text{--}3,000\text{ K}$), and have not been experimentally validated. Our modeling results are thus inherently uncertain. In addition, we have not included ClO_3 photolysis in our main simulation due to lack of consensus on its absorption cross-sections. Sensitivity simulations including ClO_3 photolysis result in factors of 3–61 decrease in the production of perchlorate (Text S6 in the Supporting Information S1), further exacerbating the model underestimate of observed near-surface $[\text{ClO}_4^- (\text{p})]$ and perchlorate deposition flux. Increasing the rate constant of R1 could offset this decrease in perchlorate. However, this would not resolve the current model-observation discrepancy in $\Delta^{17}\text{O}(\text{ClO}_4^-)$.

4.2. Hypothesis II: Multi-Phase Atmospheric Production of Perchlorate Is Important

Laboratory experiments demonstrated that perchlorate production is possible via aqueous-phase oxidation of Cl_xO_y species or gas-solid-plasma interactions (Carrier & Kounaves, 2015; Dasgupta et al., 2005; Estrada et al., 2021; Jackson et al., 2018; Kang et al., 2006, 2008, 2009; D. Liu & Kounaves, 2019; Rao, Mohan, et al., 2012; Wu et al., 2018). Some of these reactions could potentially occur on aerosols, in clouds, and/or land surfaces. However, these mechanisms require high-UV conditions and are thus unlikely to be important in the lower troposphere. In the stratosphere, the higher UV flux and the surfaces provided by stratospheric aerosols and polar stratospheric clouds may promote condensed-phase production of perchlorate (Jaeglé et al., 1996; Roberts, 2009). However, perchlorate-production chemistry in highly acidic mediums is currently under-studied. More observational constraints from laboratory experiments and field measurements are required to understand these possible multi-phase pathways for perchlorate production.

4.3. Hypothesis III: Non-Synthetic Perchlorate Emitted From Human Activities and Wildfires Is Important

Observations at urban and rural sites often show higher $[\text{ClO}_4^- (\text{p})]$ and perchlorate deposition flux than background sites (Figure 2). Dasgupta et al. (2006) estimated that the average annual US synthetic perchlorate production is about 10.6 Gg yr^{-1} , which is about 10 times the modeled atmospheric production. The leakage of synthetic perchlorate into groundwater systems has been reported (Cao et al., 2020; Urbansky, 2002). The direct release of synthetic perchlorate into the lower troposphere is also possible, for example, via fireworks and road flares (Munster et al., 2009; Munster & Hanson, 2009). However, given the dominantly military applications of synthetic perchlorate (Dasgupta et al., 2006), we expect the stockpiles to be stored securely. Even in the case of leakage, the short lifetime of perchlorate in the lower troposphere limits the spatial extent of synthetic perchlorate's influence on $[\text{ClO}_4^- (\text{p})]$ and perchlorate deposition flux. The non-synthetic perchlorate that formed as a byproduct during the industrial production of Cl_xO_y disinfection chemicals is likely minor (Dasgupta et al., 2006; Stanford et al., 2013) and cannot explain atmospheric observations.

Here, we consider a potential source of perchlorate from combustion by analogy with the well-known source of atmospheric sulfate from fuel combustion. Elemental or organic sulfur in fossil fuels and biomass reacts with $\text{O}_2 (\text{g})$ at high temperatures to produce $\text{SO}_2 (\text{g})$, some of which is further oxidized to sulfate aerosols during combustion (Sarbasov et al., 2018). Pyrogenic sulfate has a characteristic $\Delta^{17}\text{O} \approx 0\text{‰}$ because all of its oxygen atoms originate from $\text{O}_2 (\text{g})$ and tropospheric water (Dominguez et al., 2008; Lee et al., 2002). Similar to sulfur, chlorine is emitted by the combustion of coal, biofuel, solid waste and biomass, mostly in the form of $\text{HCl} (\text{g})$ and particulate chloride (Lobert et al., 1999; McCulloch et al., 1999). The inventory of Zhang et al. (2022) reports a global emission of $4,675 \text{ Gg Cl yr}^{-1}$ from continental sources, most of which are related to combustion. If only 0.1% of emitted chlorine was in the form of perchlorate, the resulting source ($4.6 \text{ Gg Cl yr}^{-1}$) would exceed our modeled photochemical production ($0.59 \text{ Gg Cl yr}^{-1}$). In comparison, global emission inventories suggest that a few percent of anthropogenic sulfur is emitted as sulfate (Chin et al., 2000; Dominguez et al., 2008). Pyrogenic perchlorate, which should have $\Delta^{17}\text{O} \approx 0\text{‰}$, could mix with photochemically produced perchlorate and explain the lower $\Delta^{17}\text{O}(\text{ClO}_4^-)$ observed near some urban and/or vegetated regions.

4.4. Hypothesis IV: Perchlorate Is Re-Emitted From Land and Ocean After Deposition

The land and ocean could act as perchlorate reservoirs if atmospheric production of perchlorate and subsequent deposition occurs over geologic timescales on Earth. Perchlorate is known to accumulate in arid regions (Jackson et al., 2015) and has been detected in oceans, albeit at trace levels of up to $1.2 \mu\text{g/L}$ (Her et al., 2011; Martinelango et al., 2006; Qin et al., 2014). Human activities can also introduce synthetic perchlorate into soil and ocean (e.g., via unintended contamination) and alter the geographic distribution of environmental perchlorate (Dasgupta et al., 2006; Urbansky, 2002).

We hypothesize that perchlorate in soils and surface ocean could be re-emitted to the atmosphere via dust and sea-spray particles. Although re-emission is not a net source of perchlorate in the Earth system, this redistribution between troposphere, land, and ocean reservoirs may still be important for atmospheric perchlorate. Re-emissions can increase near-surface $[\text{ClO}_4^- (\text{p})]$ and deposition flux downwind of deserts and regions with perchlorate-contaminated soil. For example, Andraski et al. (2014) suggested that eolian dust fluxes might have caused the higher perchlorate deposition flux observed at their desert site.

Re-emission processes do not involve new perchlorate formation and thus will not directly alter $\Delta^{17}\text{O}(\text{ClO}_4^-)$. Nevertheless, post-emission atmospheric transport can mix perchlorate originating from different sources and may still affect the final $\Delta^{17}\text{O}(\text{ClO}_4^-)$ observed in environments.

5. Conclusion and Implications

We implement a $\text{ClO}_3\text{-Cl}_2\text{O}_4\text{-ClO}_4^-$ chemistry scheme assuming gas-phase production of perchlorate into the GEOS-Chem model. While our simulation can explain reported observations of $[\text{ClO}_4^-(\text{p})]$ in the stratosphere, it significantly underestimates observed $[\text{ClO}_4^-(\text{p})]$ and perchlorate deposition fluxes at many surface sites. Our predicted $\Delta^{17}\text{O}$ of perchlorate produced from photochemistry is higher than all of the observations of environmental $\Delta^{17}\text{O}(\text{ClO}_4^-)$ to date, suggesting that missing atmospheric production pathways and/or emission sources with a low- $\Delta^{17}\text{O}$, that is, not involving ozone in perchlorate production.

To address the discrepancies between observations and model predictions, we discuss four hypotheses: (a) uncertainty in assumed gas-phase kinetics, (b) multiphase chemical production of perchlorate, (c) combustion sources of non-synthetic perchlorate, and (d) perchlorate re-emission from Earth's surface. A combination of several of these hypotheses may be required to explain perchlorate observations.

New laboratory measurements and field observations are needed to test these hypotheses. These include: (a) laboratory measurements of gas-phase perchlorate formation via Cl_xO_y chemistry under atmospheric conditions; (b) laboratory measurements of multiphase reactions of Cl_xO_y for acidic aerosols; (c) atmospheric observations of $[\text{ClO}_4^-(\text{p})]$ in wildfire plumes and urban outflow to constrain a potential combustion source; (d) observations of $[\text{ClO}_4^-(\text{p})]$ above the open ocean and deserts to assess the importance of perchlorate re-emissions; and (e) direct measurement of $\Delta^{17}\text{O}(\text{ClO}_4^-)$ in aerosols.

Data Availability Statement

Model code, simulation outputs, digitized observation-summary tables, and Python scripts for reproducing the analysis results/figures are available on <https://doi.org/10.5281/zenodo.7754444>.

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