Trifluoroacetic acid deposition from emissions of HFO-1234yf in India, China, and the Middle East

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Key points

1. The expected concentrations of trifluoroacetic acid (TFA) from the degradation of HFO-1234yf ($CF_3CF=CH_2$) emitted now and in the future by India, China, and the Middle East were calculated using GEOS-Chem and WRF-Chem models.
2. We conclude that, with the current knowledge of the effects of TFA on humans and ecosystems, the projected emissions through 2040 would not be detrimental.
3. We carried out various tests and conclude that the model results are robust.
4. The major uncertainty in the knowledge of the TFA concentrations and their spatial distributions is due to uncertainties in the future projected emissions.

Abstract

We have investigated trifluoroacetic acid (TFA) formation from emissions of HFO-1234yf, its dry and wet deposition, and rainwater concentration over India, China, and the Middle East with GEOS-Chem and WRF-Chem models. We estimated the TFA deposition and rainwater concentrations between 2020 and 2040 for four previously published HFO-1234yf emission scenarios to bound the possible levels of TFA. We evaluated the capability of GEOS-Chem to capture the wet deposition process by comparing calculated sulfate in rainwater with observations. Our calculated TFA amounts over the U.S., Europe, and China were comparable to those previously reported when normalized to the same emission. A significant proportion of TFA was found to be deposited outside the emission regions. The mean and the extremes of TFA rainwater concentrations calculated for the four emission scenarios from GEOS-Chem and WRF-Chem were orders of magnitude below the no observable effect concentration. The ecological and human health impacts now and continued use of HFO-1234yf in India, China, and the Middle East are estimated to be insignificant based on the current understanding, as summarized by Neale et al. (2021).

Keywords: HFO-1234yf, Trifluoroacetic acid, wet and dry deposition, India, China, the Middle East.

1.   Introduction

The use of olefinic hydrofluorocarbons (HFCs) as substitutes for HFC-134a (1,1,1,2-tetrafluoroethane, CF_3CFH_2) are increasing in both the developed and developing countries (Velders et al., 2009). HFC-134a is a replacement for chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which were phased out under the Montreal Protocol and its many amendments and adjustments (WMO/UNEP Quadrennial Ozone Layer Assessment, 2007). HFC-134a is a potent greenhouse gas with a 100-year global warming potential (GWP) of 1600 (Hodnebrog et al., 2020). HFO-1234yf (2,3,3,3-tetrafluoropropene, $CF_3CF=CH_2$) with a 100-year GWP of <1 (IPCC report (Myhre et al., 2013)) is a replacement for HFC-134a in automobile air conditioners (MAC) (Papadimitriou et al., 2008). The atmospheric degradation of HFO-1234yf leads to trifluoro acetyl fluoride ($CF_3C(O)F$) (Young and Mabury, 2010). $CF_3C(O)F$ hydrolyzes rapidly to yield trifluoroacetic acid (TFA, $CF_3-C(O)OH$), which is removed from the atmosphere by dry and wet deposition (George et al., 1994). The chemical lifetime of HFC-134a (~14 years) is such that it is reasonably well-mixed globally upon emission into the atmosphere. Therefore, its degradation and the TFA formed will occur across the globe. Only about 30% of the emitted HFC-134a leads to TFA (Kotamarthi et al., 1998). Later research (Wallington et al., 1996) shows that hot $CF_3C(O)H$ formed in the degradation scheme would reduce the TFA yield from HFC-134a. This reduction is not explicitly considered here, but we acknowledge that the noted TFA yields from HFC-134a can be viewed as upper limits. A large fraction of the formed TFA is deposited into the oceans. The fraction of HFC-134a degraded per year from one year's emission would be small, leading to small TFA in rainwater concentrations at a given location. However, as HFC-

71 134a accumulates in the atmosphere, more TFA would be produced. HFO-1234yf has a shorter
72 chemical lifetime of a few (~10) days (Myhre et al., 2013) and its degradation leads almost
73 exclusively (~100%) to $CF_3C(O)F$. Therefore, TFA deposition per year of emission will be higher,
74 depending on the year, and more localized spatially.

75   Previous studies have focused on TFA formation from emissions of either HFC-134a at
76 the current or previous levels (Kanakidou et al., 1995; Kotamarthi et al., 1998) or HFO-1234yf
77 substituted for current levels of HFC-134a usage (Luecken et al., 2010); then, they have mostly
78 scaled it for scenarios of HFO-1234yf emissions in the future over the continental U.S. and Europe
79 (Henne et al., 2012; Papasavva et al., 2009). Some works have distinguished between uses of HFC-
80 134a in MAC versus total usage, while others have evaluated maximum use scenarios. These
81 studies suggest that toxic levels of TFA in water bodies are not produced over Europe, North
82 America, and China if HFO-1234yf replaces all the current use of HFC-134a (Henne et al., 2012;
83 Kazil et al., 2014; Luecken et al., 2010; Wang et al., 2018). Russell et al. (2012) conducted a model
84 study to determine TFA concentration in terminal water bodies in the contiguous U.S., with TFA
85 deposition rates from Luecken et al. (2010). They found that after 50 years of continuous
86 emissions, aquatic concentrations of 1 to 15 $\mu g\ L^{-1}$ are projected, with extreme concentrations of
87 up to 50 to 200 $\mu g\ L^{-1}$ in the arid southwestern U.S.

88   Kazil et al. (2014) investigated, using the WRF-Chem model, the atmospheric turnover
89 time of HFO-1234yf, the dry and wet deposition of TFA, and the TFA rainwater concentration
90 over the contiguous U.S. between May and September 2006. They also examined where TFA
91 deposited emissions of three specific regions in the U.S. They concluded that the average TFA
92 rainwater concentration was 0.89 $\mu g\ L^{-1}$ for the contiguous U.S. Although Kazil et al. (2014) used
93 emissions twice as large as that used by Luecken et al. (2010), the TFA rainwater concentrations
94 were comparable. Kazil et al. (2014) used the measured HFC-134a to CO ratio from the Los
95 Angeles area to obtain potential HFO-1234yf emissions. They also showed that TFA rainwater
96 concentrations reached significantly higher values (7.8 $\mu g\ L^{-1}$) at locations with very low
97 precipitation on shorter time scales. A comparably low TFA wet deposition occurred in the dry
98 western U.S. The work of Wang et al. (2018) is similar to that of Henne et al. (2012) and used the
99 GEOS-Chem model and examined the rainwater content and deposited amounts of TFA over
100 Europe, the U.S, and China, with similar findings. Henne et al. (2012) is the only study that used
101 two different models (FLEXPART and STOCHEM) to study the TFA deposition and rainwater
102 concentration over Europe.

103   The above-noted studies focused on the U.S. and Europe, and most recently China. The
104 U.S. and Europe emissions of the sum of HFC-134a and HFO-1234yf are expected to increase
105 only in proportion to the population in the future since the per capita number of MAC, stationary
106 AC, and other cooling units are unlikely to increase rapidly. India, China, and the Middle East are
107 the regions with expected large increases in HFO-1234yf use. In these regions, the number of units
108 and associated usage will increase rapidly as the economies grow. Perhaps Latin America and parts
109 of Africa would also see similar increases. The above-noted studies from the U.S. and Europe do
110 not allow us to draw firm conclusions about TFA's formation from realistic future emissions from

111 Asia (China and the Indian subcontinent), where the markets are not saturated, and meteorology
112 is very different from North America and Europe. The rate of degradation of parent compounds
113 and precipitation will differ in the warmer tropical and subtropical regions from those seen for the
114 U.S. and Europe; the seasonality will also be different. The precipitation across Asia is associated
115 with the Asian monsoon, which is stronger in comparison to the monsoon in the southwest U.S. It
116 is also essential to look at the Middle East emissions since the studies of Kazil et al. (2014) and
117 Russell et al. (2012) showed that TFA rainwater concentrations are larger over drier areas of the
118 U.S., and there can be more accumulation in arid regions.

119 In 2019 the Kigali Amendment to the Montreal Protocol went into force. According to the
120 amendment the production and use of HFCs has to be phased down in the coming decades. This
121 should reduce the emissions of HFCs such as HFC-134a, but will likely increase emissions of
122 HFO-1234yf.

123 A description of the models used (GEOS-Chem and WRF-Chem), HFO-1234yf emission
124 scenarios, and the chemical scheme are given in section 2. In section 3, we compare the
125 precipitation in GEOS-Chem and WRF-Chem with observations. We evaluate the GEOS-Chem
126 model's ability to reproduce wet deposition by comparing sulfate rainwater concentrations with
127 observations. We performed simulations using both the models for the three domains individually
128 to calculate the TFA's dry and wet deposition and rainwater concentrations over India, China, and
129 the Middle East. We performed two-year runs in GEOS-Chem to check for interannual variability.
130 We compare our simulation results with other studies for the U.S., Europe, and China. The HFO-
131 1234yf emissions from all the regions together were also simulated to assess the interregional
132 effects. Major findings from this study are summarized in section 4.

133

2. Methods

2.1. Model description

136 ***GEOS-Chem***: We used the GEOS-Chem (v12.0.3, www.geos-chem.org) global three-
137 dimensional chemical transport model driven by GEOS-FP assimilated meteorological data.
138 GEOS-Chem has a fully coupled tropospheric NO_x-O_x-hydrocarbon-aerosol chemistry. The
139 simulations were made at $2°\times2.5°$ resolution and 47 vertical levels from the surface to ~80 km.
140 The wet deposition of aerosols and soluble gases by precipitation includes the scavenging in
141 convective updrafts, in-cloud rainout, and below-cloud washout (Amos et al., 2012; Liu et al.,
142 2001). The dry deposition was calculated using a resistance-in-series parameterization, which is
143 dependent on environmental variables and lookup table values (Wesely, 1989). The simulations
144 were conducted for 2015 and 2016 following a 2-month spin-up.

145 The global anthropogenic emissions were from Emissions Database for Global
146 Atmospheric Research (version 4.3). The global emissions are superseded by regional emission
147 inventories for India (Speciated Multi-pOllutants Generator (SMOG) and MIX) (Li et al., 2017;
148 Pandey et al., 2014; Sadavarte and Venkataraman, 2014), China (MIX), Europe (EMEP), U.S.
149 (National Emissions Inventory (NEI) 2011) (NEI2011, http://ww.epa.gov/air-emissions-
150 inventories), Canada (Criteria Air Contaminants (CAC), http://www.ec.gc.ca/), and Mexico

(BRAVO) (Kuhns et al., 2005). We used the biomass burning from Global Fire Emissions Database (GFED) version 4 (Giglio et al., 2013). The biogenic VOC emissions were from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 inventory of Guenther et al (2012). The details on other emissions are described in David et al. (2018, 2019).

WRF-Chem: The Weather Research and Forecast with Chemistry (WRF-Chem) model (Fast et al., 2006; Grell et al., 2005) version 4.1.3, was used to simulate meteorology and chemistry over India, China, and the Middle East individually. The WRF-Chem simulations were integrated for 14 months, beginning 1 November 2014 and ending 31 December 2015, with the first two months of the simulation was used to spin up the model chemistry. The three model domains, shown in Figure 1, have a horizontal grid spacing of 30 km and 40 vertical levels reaching a model top of 50 hPa. The vertical levels stretch in size with a fine resolution near the surface and a coarser resolution in the upper troposphere. The model meteorology was initialized with Global Forecast System (GFS) archived at 0.5° and a temporal resolution of 6 hours. Observational nudging is applied for temperature, moisture, and winds to keep large-scale features in line with the observed meteorology. The model physics and chemistry options that were used are summarized in Table S1 in the supplementary information. The Model for Ozone and Related chemical Tracers (MOZART) gas-phase chemical mechanism and the Global Ozone Chemistry Aerosol Radiation and Transport (GOCART) scheme for aerosols (MOZCART) (Pfister et al., 2011) were used to simulate ozone and aerosol chemistry. TFA chemistry was added to this chemical option. Six-hourly results from the Community Atmosphere Model with Chemistry (CAM-Chem), which has a similar chemistry mechanism as the WRF-Chem model configuration, were used (Tilmes et al., 2015) to initialize trace gas and aerosol mixing ratios as well as to provide lateral boundary conditions. HFO-1234yf and TFA were initialized with the GEOS-Chem results described above. The Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.04; Guenther, 2007) was used to represent the net biogenic emissions for both gases and aerosols. Anthropogenic emissions were from the Emissions Database for Global Atmospheric Research – Hemispheric Transport of Air Pollution (EDGAR-HTAP) emission inventory (Janssens-Maenhout et al., 2015). The Fire Inventory from NCAR version 1 (FINNv1.6; Wiedinmyer et al., 2011) was implemented to provide daily varying emissions of trace species from biomass burning.

The wet removal scheme in WRF-Chem for MOZART chemistry, based on Neu and Prather (2012), was used to compute the dissolution of soluble trace gases into precipitation and their release into the gas phase upon evaporation of hydrometeors. Neu and Prather (2012) estimate trace gas removal by multiplying the effective Henry's law equilibrium aqueous concentration by the net precipitation formation (conversion of cloud water to precipitation, minus evaporation of precipitation). Dry deposition of trace gases was described with the Wesely (1989) parameterization. Diagnostic information on the wet and dry deposition of TFA was determined every time step and accumulated values were included in the output files.

2.2.   Emissions

190   HFO-1234yf is just now entering the market driven by regional (e.g., the European Union's
191   MAC Directive 2006/40/EC), national (e.g., Japan and U.S.) F-gas regulations, and the Kigali
192   Amendment to the Montreal Protocol. HFC-134a is currently the primary working fluid of MAC
193   and other applications (refrigerant, insulating foams, and aerosol propellants). Therefore, we have
194   to estimate the future emission levels from the three regions of interest. Unlike the developed
195   countries, India, China, and the Middle East are growing rapidly and the use of air conditioning
196   and refrigeration (and other uses of HFCs and HFOs) are expected to increase rapidly. Therefore,
197   one has to consider the likely economic growth and other factors in estimating emissions levels.
198   Here, we explore a few different potential scenarios for emissions of HFO-1234yf.

199   TFA production from HFO-1234yf increases linearly with the rise in HFO-1234yf
200   emissions, i.e., there is no feedback on this process since the primary drivers for the degradation
201   of this chemical, the OH radical, will not be altered by their relatively small emissions. In addition,
202   the changes in the abundance of OH in the troposphere in the next few decades are unlikely to be
203   different (say <13%) than the current levels based on the changes seen over the past few decades
204   (Rigby et al., 2017). Therefore, we can estimate the extent of TFA formation from a set of
205   modeling calculations that employed a fixed total amount of HFO-1234yf from each region. After
206   that, we can calculate the extent of TFA formation for various possible emission scenarios.

207   We used four future HFO-1234yf emissions scenarios for the 2020 to 2040 period: (1)
208   estimate of the upper range scenario HFO-1234yf emissions based on Velders et al. (2015)
209   estimate; (2) lower range scenario of HFO-1234yf based on Velders et al. (2015) estimate; (3) the
210   Greenhouse Gas Air Pollution Interactions and Synergies (GAINS) model (Amann et al., 2011)
211   with maximum technically feasible reduction (MTFR) estimates of HFO-1234yf; and (4) the
212   GAINS 'maximum HFO' (max HFO) scenario. Given the relatively short lifetime of HFO-1234yf,
213   the TFA production per year is dependent only on the emissions in that year. Figure 2 shows the
214   HFO-1234yf emission projection from India, China, and the Middle East for the four scenarios
215   between 2020 and 2040. The scenario based on Kumar et al. (2018) is similar to the fourth scenario
216   we considered. Therefore, we have not specifically included this possibility.

217   The emission estimates of HFO-1234yf in the GAINS model depends on when countries
218   will comply with the Kigali Amendment, current and future emissions based on country-level
219   activity data, uncontrolled emission factors, the removal efficiency of emission control measures,
220   and the extent to which such measures are applied (Purohit and Höglund-Isaksson, 2017). The
221   GAINS model uses the fuel input for the transport sector that is provided by the exogenous
222   projections (e.g., International Energy Agency's World Energy Outlook 2017). First, using the
223   annual mileage per vehicle (veh-km) and specific fuel consumption (SFC), GAINS estimates the
224   number of vehicles (by type, fuel). Second, using the penetration rate of a MAC, the number of
225   vehicles with MAC is calculated. Next, using the specific refrigerant charge (different for MAC
226   used in vehicle types), the HFO-1234yf consumption in mobile air conditioners is calculated. Note
227   that the HFO-1234yf is assumed to be substituted for HFC-134a, one-to-one, in all vehicles. For
228   HFO-1234yf use in MAC, HFO-1234yf emissions are estimated separately for "banked"
229   emissions, i.e., leakage from equipment in use, and for "scrapping" emissions, i.e., emissions

230 released at the end-of-life of the equipment. The leakage rate in the GAINS model assumes a
231 percentage of the charge per year. For example, if the refrigerant charge in MAC is 0.5 kg then the
232 emissions from the bank will be 0.05 kg (= 0.5 kg×0.1) per year, where the leakage rate is 10%
233 per year. This leakage rate is a steady refrigerant loss through seals, hoses, connections, valves,
234 etc. from every MAC over the entire use-phase (annually). At the end-of-life, the scrapped
235 equipment is assumed to be fully loaded with refrigerant, which needs recovery, recycling, or
236 destruction. At the same time, if there are regulations in place (e.g., MAC Directive 2006/40/EC
237 in European Union) - a package of measures including leak prevention during use and refill,
238 maintenance, and end of life recovery, and recollection of refrigerants, GAINS consider these good
239 practices as a control option with a removal efficiency of 50% for *in-use* and 80% for *end-of-life* -
240 based on secondary sources (Purohit et al., 2020). However, no such measures are assumed for
241 India, China, and the Middle East. Thus, these emissions can be considered the maximum likely
242 emissions. The MTFR version of the GAINS scenario assumes that the maximum technically
243 feasible reductions are applied across the sectors in India, China, and the Middle East. The Velders
244 et al. (2015) emissions also follow the Kigali amendment. The 'Shared Socioeconomic Pathways'
245 (SSPs) SSP3 and SSP5 are the lower and upper range scenarios, respectively, used in Velders et
246 al. (2015) calculated for 11 geographic regions and 13 use categories. Kumar et al. (2018) highlight
247 that many applications in India will likely transition to something other than HFOs. These trends
248 are not unique to India and will likely be replicated in China and the Middle East. Therefore, the
249 four HFO-1234yf emission scenarios for the 2020 to 2040 period represent emissions that are
250 higher than should be expected and, therefore, are upper limit estimates of the potential impact of
251 TFA in these regions.

252 To minimize numerical errors (in using small emissions) and compare them with previous
253 studies, we used HFO-1234yf emissions of ~40 Gg yr^{-1} from each of these regions. This value
254 corresponds to 2025 projected emissions from the GAINS model over India and the Middle East
255 if all the applications were to use HFO-1234yf in place of HFC-134a for China, the emission values
256 are for 2016 from Wang et al. (2018). Figure S1 in the supplementary information shows the annual
257 spatial distribution of HFO-1234yf over India, China, and the Middle East as simulated in: (i)
258 GEOS-Chem; and (ii) WRF-Chem models. We distributed this total emission across the
259 country/region of interest by scaling the emission to known anthropogenic CO emissions used in
260 the model. The anthropogenic CO is a good tracer for HFO-1234yf emissions since they originate
261 from similar applications (especially the transport sector) and in proportion to the distribution of
262 economic activities in the region/country of interest. We show the total emissions in each of the
263 three regions in both the models in the figure. The distribution varies to a small extent with the
264 season (shown in Figure S2 in the supplementary information), and the monthly variation in
265 emission is similar in both models. We also simulated GEOS-Chem over the US and Europe using
266 the total HFO-1234yf emissions from Wang et al. (2018) and Henne et al. (2012), respectively.
267
268 **2.3. Chemical scheme**

The chemical degradation of HFO-1234yf and the production of TFA were added to both the GEOS-Chem NO_x-O_x-hydrocarbon-aerosol chemistry scheme and the WRF-Chem MOZCART chemistry scheme. The detailed chemical scheme for the formation of TFA from HFO-1234yf is shown in Burkholder et al. (2015) and, therefore, not repeated here. The simplified representation of TFA production follows that of Kazil et al. (2014):

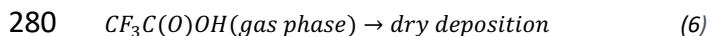
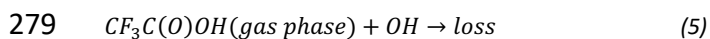
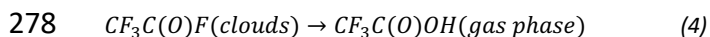
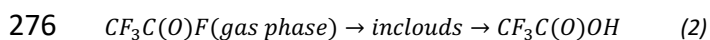
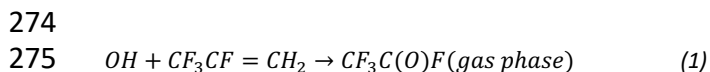
$$OH + CF_3CF = CH_2 \rightarrow CF_3C(O)F (gas\ phase) \qquad (1)$$

$$CF_3C(O)F (gas\ phase) \rightarrow inclouds \rightarrow CF_3C(O)OH \qquad (2)$$

$$CF_3C(O)F (clouds) \rightarrow Wet\ depostion \qquad (3)$$

$$CF_3C(O)F (clouds) \rightarrow CF_3C(O)OH (gas\ phase) \qquad (4)$$

$$CF_3C(O)OH (gas\ phase) + OH \rightarrow loss \qquad (5)$$

$$CF_3C(O)OH (gas\ phase) \rightarrow dry\ deposition \qquad (6)$$

The conversion of HFO-1234yf to TFA includes OH-initiated reaction of $CF_3CF=CH_2$ (Equation 1) with a temperature-dependent rate coefficient of 1.26×10^{-12} exp(-35/T) cm^3 molecule^{-1} s^{-1} to produce gas-phase $CF_3C(O)F$ (note that the initial OH reaction is the rate-limiting step in the conversion). The gas-phase removal of $CF_3C(O)F$ is not rapid but hydrolyzes to TFA in water (George et al., 1994) (Equation 2). The hydrolysis process is added to the heterogeneous chemistry with a hydrolysis rate of 150 s^{-1}, and Henry's Law solubility constant of 3 M atm^{-1}. TFA is highly soluble in cloud water. Upon cloud evaporation, the dissolved TFA is released into the gas phase (Equation 4). The gas-phase TFA is expected to be deposited either via dry (Equation 6) or wet deposition using Henry's Law solubility constant of 9×10^3 M atm^{-1} at a standard temperature of 298.15 K, $\Delta H/R = 9000$ K, dissociation coefficient of 0.65 mol L^{-1} at 298.15 K, and $\Delta E/R = -1562$ K. Thus, at cloud temperatures (generally <290 K) the effective Henry's Law of TFA is high, characterizing TFA as a highly soluble gas. The dry deposition rate for TFA is assumed to be the same as that for nitric acid (Henne et al., 2012; Kazil et al., 2014; Luecken et al., 2010). We also included the potential loss of gas-phase TFA by its reaction with OH radicals (Equation 5) with a rate coefficient of 9.35×10^{-14} cm^3 molecule^{-1} s^{-1}. Other potential losses of HFO-1234yf via reaction with Cl, O_3, and NO_3 are very small and all yield the same set of products. Therefore, we have not included them in the model. We also examined the possible removal of gas phase TFA by its reaction with Criegee intermediate (CI). We used the Bristol group's calculated concentrations of the Criegee intermediates (Chhantyal-Pun et al., 2017; Khan et al., 2018).

3. Results and Discussion
3.1. Sulfate concentration in rainwater

Wet deposition is one of the primary removal processes for TFA. This deposition depends on precipitation amounts and how well our model captures the wet deposition process, making it crucial to evaluate the models used here to capture these two factors.

First, we compared the annual total precipitation amounts calculated by GEOS-Chem and WRF-Chem with the observed daily total accumulated precipitation from the Tropical Rainfall Monitoring Mission (TRMM_3B42_daily product) in the three regions (Figure S3a in the supplementary information). The TRMM product is at a 0.25º×0.25º resolution. The spatial distribution of seasonal total precipitation in the three domains from the two models and TRMM is shown in Figure S4 in the supplementary information. Both the models captured the seasonal precipitation patterns. As seen in Figure S3a, the total precipitation amounts were a factor of 1.5-2 higher in GEOS-Chem compared to WRF and TRMM. (The ratio of total precipitation between GEOS-Chem and WRF-Chem(TRMM) were 2.6 (1.5), 2.2 (1.5), and 2.2 (1.4) for India, China, and the Middle East, respectively). WRF-Chem underestimated the precipitation amounts compared to TRMM in the three regions. Kumar et al. (2012; 2018) have addressed the precipitation biases in WRF-Chem compared to TRMM over South Asia. We attribute the higher precipitation in GEOS-Chem to: (a) the different model physics used; (b) the effects of a meteorology-driven chemistry transport model (GEOS-Chem) versus an "online" chemistry transport model (WRF-Chem) where chemistry is solved at the same time step as the meteorology; (c) and to the different grid spacings used by the two models, noting that the coarse GEOS-Chem grid cells contain several convective storms compared to that in WRF-Chem. The monthly variation in total precipitation is shown in Figure S3b (supplementary information), and both models have similar trends as that observed by TRMM.

To evaluate the accuracy of the TFA wet deposition, it is useful to compare sulfate wet deposition amounts produced by the oxidation of SO_2. The emissions of SO_2 are comparable in both the models (shown in Figure S5 in the supplementary information). We have measurements of sulfate rainwater concentrations in some of the regions. Further, the lifetime of SO_2 in the troposphere is comparable to that of HFO-1234yf. We hasten to add that while the HFO-1234yf degradation is controlled by gas phase OH reactions, that of SO_2 includes both gas and condensed phase processes. However, the removal of both sulfate and TFA are due to condensed phase reactions. The WRF-Chem model has been shown to capture the sulfate rainwater concentration over the continental U.S. by Kazil et al. (2014); we expect it to do well over this study's regions. However, GEOS-Chem has not been evaluated previously. There are no networks for measuring sulfate rainwater concentration in India and the Middle East. Yet, there are some observations of rainwater sulfate in the published articles in all three domains. The available data are sparse, and the observations for 2015 (the modeled year) are even fewer to make a comparison with WRF-Chem simulations. However, GEOS-Chem simulations were available from our previous work for 2000-2015. We used those results to compare with observations during that period. The observation locations (over land only) in the three domains are shown in Figure S6 in the supplementary information. Figure 3 shows the scatter plot of simulated and observed sulfate rainwater concentration in the three domains. Table 1 lists the statistics of the comparison between GEOS-Chem and the observations. Rainwater sulfate amounts calculated by GEOS-Chem correlate well (R>0.80) with observations. We see a bias of -13, -13, and -3% in India, China, and the Middle East domains, respectively. The negative bias in GEOS-Chem sulfate rainwater

concentration could be because the model integrates over a large area while the observations are point locations. It could also be, as noted earlier, because GEOS-Chem yields higher amounts of precipitation and thus could lead to smaller rainwater concentrations. We suggest that these values are good to at least a factor of two. In summary, the GEOS-Chem model shows considerable skill in reproducing mean sulfate rainwater concentrations and spatial variability of sulfate rainwater concentrations; therefore, it can be utilized to calculate TFA wet deposition.

3.2. Comparison of calculated TFA with previous studies

Before presenting the results of the calculations for India, China, and the Middle East from the present study, we note that our models agree with the previous studies over the U.S. (Kazil et al., 2014; Luecken et al., 2010), China (Wang et al., 2018), and Europe (Henne et al., 2012). Figure 4 shows the comparison of annual mean (a) TFA deposition (dry and wet combined), and (b) TFA rainwater concentration over the U.S., China, and Europe. We have normalized the emissions to match those of the previous studies for meaningful comparisons. (The emissions used to compare TFA from the U.S., China, and Europe are 24.5, 42.7, and 19.2 Gg yr^{-1}, respectively.) We note that average deposition rates differ in the model because of the differences in calculations' domain sizes. Given that the models vary in their versions, meteorology, physics, and the expected model variabilities, the observed agreement is reasonable. The TFA rainwater concentration in GEOS-Chem than in WRF-Chem simulations because the total precipitation amounts were factors of 1.5-2 higher in GEOS-Chem compared to WRF and TRMM as mentioned in section 3.1. We also show the comparison with our calculations over the U.S. for the summer months with previous studies (Kazil et al., 2014; Luecken et al., 2010; Wang et al., 2018) (Figure S7 in the supplementary information).

3.3. Atmospheric mixing ratios

Figure 5 shows the annual mean mixing ratios of HFO-1234yf over India, China, and the Middle East as simulated by GEOS-Chem and WRF-Chem. We present here only results with emissions in GEOS-Chem(WRF-Chem) of 41.3(41.9), 40.6(39.9), and 37.8(38.1) Gg yr^{-1} from India, China, and the Middle East, respectively. Expected TFA for other emissions can be simply scaled to the emissions of interest. The annual mean mixing ratio of HFO-1234yf in India, China, and the Middle East as simulated by GEOS-Chem(WRF-Chem) were 2.87(3.94) ppt, 2.49(3.70) ppt, and 1.82(2.49) ppt, respectively, and below 1 ppt (as seen in GEOS-Chem) outside of the three regions. The annual mean mixing ratio in the China domain was comparable to Wang et al. (2018). The highest (>40 ppt) simulated annual mean HFO-1234yf mixing ratio for India was in the Indo-Gangetic Plain (IGP), for China in the northeast region, and for the Middle East in northern Iran. The emission hotspots (Figure S1 in the supplementary information) in the three regions led to the largest annual mean HFO-1234yf mixing ratios in those regions. The WRF-Chem simulated higher annual mean HFO-1234yf mixing ratios compared to GEOS-Chem. Differences in annual mean HFO-1234yf mixing ratios between models for the same amount of emissions have been reported also by Henne et al. (2012). However, the overall spatial patterns are comparable between GEOS-

387   Chem and WRF-Chem. It should be noted that the change of HFO-1234yf emissions in any of the
388   three regions would change the HFO-1234yf mixing ratio within that region and will have minimal
389   effect on other regions.
390

3.4.   TFA deposition

392   GEOS-Chem simulated mean total deposition rates (dry and wet deposition combined) to
393   be 0.874, 0.501, and 0.477 kg km^{-2} yr^{-1}, respectively, in India, China, and the Middle East domains
394   for emissions of 41.3, 40.6, and 37.8 Gg yr^{-1}, respectively. WRF-Chem simulated mean deposition
395   rates (dry and wet) were 0.802, 0.342, and 0.284 kg km^{-2} yr^{-1} in India, China, and the Middle East
396   domains, respectively (Figure S8 in the supplementary information). Figure 6 shows the annual
397   total dry and wet TFA deposition rates in the three domains. The total annual dry deposition in
398   GEOS-Chem and WRF-Chem over the India domain was largest in eastern India and Bangladesh,
399   reaching up to 2 kg km^{-2} yr^{-1}. The wet deposition in the India domain mostly occurred in the
400   Himalayas' foothills, eastern IGP, parts of central India, and southwest India and was >3.5 kg km^2
401   yr^{-1}. In the China domain, the total dry and wet deposition rates in GEOS-Chem and WRF-Chem
402   were highest in southeast China. The total dry deposition rate in the Middle East domain was
403   highest in northern Iran. The wet deposition rate was the largest in parts of Iran, with differences
404   between the models. The wet deposition dominated the total TFA deposition. The combined annual
405   total deposition pattern was similar to that of wet deposition in the three domains (Figures 6 and
406   S8 in the supplementary information). The seasonal total deposition rates of TFA from dry and
407   wet depositions in the three domains are shown in Figure S9 in the supplementary information.
408   The seasonal deposition rates were highest for June-September, June-August, and April-October
409   in India, China, and the Middle East domains, respectively.
410   Figure 7 shows the percentage contribution of dry and wet deposition to total TFA
411   deposition between GEOS-Chem and WRF-Chem in the three domains. It should be noted that the
412   sum of the two (dry and wet) percent contributions do not add up to exactly 100% because of
413   transport in and/or out of the domains. For the total amount of HFO-1234yf emissions mentioned
414   in Figure S1(supplementary information) and discussed in section 2.2, the total TFA deposition
415   (dry and wet combined) in India, China, and the Middle East domains from GEOS-Chem were
416   23.4, 20.5, and 18.7 Gg yr^{-1}, respectively. The total annual dry(wet) deposition amounts account
417   for 21(36)%, 20(31)%, and 20(29)% of the annual emissions of HFO-1234yf in GEOS-Chem. In
418   WRF-Chem, the annual total TFA deposition was 19.4, 12.1, and 9.9 Gg yr^{-1}, respectively, in India,
419   China, and the Middle East domains. The dry(wet) TFA deposition was 10(37)%, 3(23)%, and
420   4(26)% of the emissions in India, China, and the Middle East domains, respectively. Table S2
421   (Supplementary Information) shows the seasonal TFA deposition (dry and wet) calculated from
422   GEOS-Chem and WRF-Chem models in the three domains. The lower TFA deposition in WRF-
423   Chem compared to GEOS-Chem is due to the venting of surface emissions into the free
424   troposphere (Grell et al., 2004; Kazil et al., 2014) that leads to lower dry deposition in WRF-Chem
425   (Figure 7a). The differences in deposition between models can also be attributed to differences in
426   model resolutions, model transport, meteorological conditions (e.g., precipitation), and cloud

427 treatment. These differences highlight the need for multi-model simulations to estimate the likely
428 variation in these parameters.

429   Figure 8 shows the total TFA deposition (dry and wet combined) for the four emission
430 scenarios (Figure 2) calculated from GEOS-Chem and WRF-Chem. Our results show that the
431 differences in the calculated extent of TFA formed and deposited are about a factor of two between
432 the models. In all cases, the computed TFA dry and wet deposition varies linearly with the
433 emissions. Therefore, we can calculate the amounts of TFA formed and deposited for any
434 envisioned emission of HFO-1234yf.

435

436 **3.5.   Rainwater concentrations**

437   Figure 9 shows the monthly variation in mean TFA rainwater concentration in the three
438 domains calculated from GEOS-Chem and WRF-Chem. The TFA rainwater concentration also
439 varies linearly with the emissions. Figure 9 shows the following: (a) higher concentrations are to
440 be expected when there is little rain/precipitation (Figure S10 in the supplementary information)
441 to remove TFA. This point has been noted in previous studies (Kazil et al., 2014; Russell et al.,
442 2012; Wang et al., 2018). So, if all the TFA were concentrated into a small amount of rain, the
443 concentrations have to be larger. Such events are infrequent. They are, relative to the rainier
444 regions, more frequent in the Middle East. The large rainwater concentration does not mean that
445 the amount of deposited TFA is larger; (b) The rainwater concentrations varied inversely with the
446 precipitation amount, as seen by comparing the rainwater TFA levels with the total precipitation
447 (Figure S10 in the supplementary information). A clear signal for the rainfall variation was seen
448 over India, where the monsoon season (June, July, August, and a part of September) bring large
449 and almost constant precipitation. This large precipitation makes the TFA rainwater concentrations
450 extremely small. In other words, this is simply a dilution effect; (c) When the rainfall is small,
451 there are considerable variations as one would expect. Lesser total precipitation arises because of
452 fewer showers and often in spatially and temporally sporadic events. So, the concentrations can
453 vary a great deal. This was also evident over China during dry seasons; and (d) the calculated TFA
454 rainwater concentrations were comparable to previous calculations for China (scaled to emissions,
455 Figure 4b). The variation of rainfall amounts and their geographical distribution as climate changes
456 are uncertain, but there are some estimates. For example, Terink et al., (2013) suggest that there
457 could be a ~20% decrease in precipitation over the Middle East region over the next 20 years. A
458 20% decrease in precipitation will correspond to TFA rainwater concentration less than 40 μg/L
459 (95th percentile). The annual mean precipitation over China is likely to increase; for example,
460 estimates are roughly increases of 0.078 mm/d in the 2020s and 0.218 mm/d in 2050s, with larger
461 changes in the summer months (rainy season) (Guo et al., 2017). The projected rainfall changes
462 across the Indian monsoon region could increase by 6% (RCP4.5) and 8% (RCP8.5) in the mid-
463 21st century (Krishnan et al., 2020).

464   It is important to know the regions of high TFA rainwater concentrations. Therefore, we
465 plotted the spatial pattern of annual mean TFA rainwater concentration in the three domains from
466 both models (Figure S11 in the supplementary information). It is noticeable that most of the regions

467   in all three domains did not have high TFA rainwater concentrations. There were some grids with
468   TFA rainwater concentrations that exceeded 50 μg L^{-1} for emissions of ~40 Gg yr^{-1}. The high TFA
469   rainwater concentration seen in the western part of India and China domains is because of input at
470   the lateral boundaries from a global model. As mentioned in section 3.1, the precipitation in GEOS-
471   Chem was higher, resulting in lower TFA rainwater concentration. Focusing on the highest
472   possible rainwater concentrations is misleading since that does not tell us the amount of wet TFA
473   deposition, which is shown in Figure 6. However, it is clear that if the emissions of HFO-1234yf
474   reach the large numbers noted by the IIASA/GAINS model (max HFO, Figure 2d) for 2040, there
475   will be significant areas with larger TFA rainwater concentrations. The wet deposition does not
476   tell the whole story either since a substantial fraction of the rainwater ends up in the oceans every
477   year. The estimation of the TFA retained on land will be critical for further estimating the long-
478   term impact. Such a hydrology study is warranted but beyond the scope of this work.

3.5.1. Comparison of expected TFA rainwater levels with No Observable Effects Concentrations

481   The primary reason for carrying out these calculations was to estimate the potential impact
482   of HFO-1234yf usage in the three regions of the study for the current and future emissions. The
483   effects of interest here are TFA formation from HFO-1234yf and its consequences to human and
484   ecosystem health. Figure 10 shows the mean TFA rainwater concentration for the four emission
485   scenarios calculated from GEOS-Chem and WRF-Chem. In all the scenarios, the annual mean
486   TFA rainwater concentration was well below the no observed effect concentration (NOEC) for
487   aquatic species, which is >10,000 μg L^{-1} (Solomon et al., 2016), with an outlier for the most
488   sensitive alga as 120 μg L^{-1} (Boutonnet et al., 2011). The negligible impact of TFA formation
489   during the atmospheric oxidation of HFCs, HCFCs, and HFOs has been established for some time.
490   The WMO/UNEP Quadrennial Ozone Assessment (2007) concluded that TFA from the
491   degradation of HCFCs and HFCs would not result in environmental concentrations capable of
492   significant ecosystem damage. Hurley et al., (2008) concluded in their study that the products of
493   the atmospheric oxidation of $CF_3CF=CH_2$ will have a negligible environmental impact. Solomon
494   et al., (2016) also concluded in their study that the concentrations of TFA and its salts in the
495   environment that result from degradation of HCFCs, HFCs, and HFOs in the atmosphere do not
496   present a risk to humans and the environment.

497   Neale et al. (2021) have summarized the impact of TFA on human and ecosystem health.
498   Their conclusion suggests that the NOEC on aquatic systems is >10,000 μg L^{-1}. As shown in
499   Figures 9, 10, and S11 (supplementary information), the expected rainwater concentrations are at
500   least two orders of magnitude lower than the NOEC. Also, the rainwater concentrations of TFA,
501   even for the 2040 emissions, are roughly comparable to those currently observed in China (Chen
502   et al., 2019) and about ten times greater than those presently observed over Germany (Freeling et
503   al., 2020). They also note that large TFA concentrations have been observed in people's blood in
504   China with no ill effects on the endpoints measured in that work (Duan et al., 2020).

505   TFA quantities deposited via dry deposition to land and vegetation would be much smaller
506   than those noted in Neale et al. (2021) to have any significant detrimental health effect. Indeed,

507   they note that there are other sources of TFA that are much higher than those expected from HFO-
508   1234yf degradation. Neale et al. (2021) also point out that the TFA deposited to snow in the Arctic
509   would not significantly contribute to marine water bodies even if it all melted down since the
510   volume of the melt would be much smaller than those of the receiving water bodies.

511   Lastly, since TFA can accumulate over land and water bodies, we can estimate the
512   influence of accumulation on the potential future impacts. The total TFA amount in rainfall would
513   not change. However, the amounts in water bodies could increase. For the 20 years modeled here,
514   the total TFA in water bodies would be larger than those observed for 2020 if TFA merely
515   accumulates. It is hard to calculate precisely where the water bodies would accumulate TFA
516   without a hydrological model. However, these values would still be orders of magnitude smaller
517   than the NOEC of >10,000 μg L^{-1}. For example, if all the TFA produced in these regions were to
518   end up in the top 15 meters of the world's oceans, we expect the TFA levels to increase by about
519   0.015 μg L^{-1} by 2040.

520   Based on these observations, and assuming that the NOEC concentration holds, it appears
521   that the TFA from the expected emissions of HFO-1234yf in these three regions would not
522   constitute a health threat to plants or humans (even if we assume that there is no water treatment
523   to remove TFA in drinking water).

524

525 **3.6.   Interannual variability**
526   The model results discussed in the previous sections are for one year, 2015. To assess the
527   influence of interannual variability in meteorology, we simulated the TFA deposition and
528   rainwater concentration for 2016 with the GEOS-Chem model for the total HFO-1234yf emissions
529   described in section 2.2. Figure 11 shows the fraction of TFA in the three domains for 2015 and
530   2016 that is: (a) dry deposited; (b) wet deposited; and (c) the annual mean TFA rainwater
531   concentrations. The total precipitation in both years was comparable (shown in Figure S12 in the
532   supplementary information). The results of our two-year simulations lead us to conclude that the
533   interannual differences are small. Therefore, we suggest that the results of 2015 are applicable
534   going forward to 2040.

535

536 **3.7.   Simultaneous emissions from multiple regions**
537   It is important to note that most TFA is deposited outside of the domains, even though the
538   estimated lifetime of HFO-1234yf is about ten days. Therefore, TFA is dispersed significantly
539   from the source region. Figure 12a shows that roughly 25-50% of the HFO-1234yf emitted from
540   a given region was converted and deposited (via dry and wet deposition) as TFA within the domain
541   (see Figure 1 for domain boundaries). Figure 12b shows the percentage of TFA deposition (dry
542   and wet combined) calculated from GEOS-Chem and WRF-Chem within the three domains over
543   land. The remaining TFA was transported outside the domain. It is difficult to quantify the exact
544   locations of these depositions outside the domain since the concentrations get very small even
545   though in the aggregate that accounts for somewhere between 30% and 45%. The fraction that was
546   deposited within the region of emission was even smaller and ranged between 7% and 27%.

547   Therefore, it can be concluded that a significant fraction ended up in the oceans. This is especially
548   true for India and the Middle East emissions. Interestingly, a substantial amount of the TFA from
549   the Middle East emissions are deposited in the Arabian Sea. Therefore, we conclude that even
550   though HFO-1234yf is short-lived, it is still sufficiently long-lived to travel thousands of
551   kilometers. Such an expectation is in accord with the calculated distances traveled by an airmass
552   for even about 2 m s[1].

553   The deposition outside of the region and domains also means that the emitting regions are
554   not the only area affected by their emission of HFO-1234yf. This is in spite of the relatively short
555   turnover time of HFO-1234yf. (Note: We call this the turnover time because of the way we
556   calculate it in the model.) Since the three countries/regions studied here are adjacent to each other
557   and their domains overlap (Figure 1), it is possible to estimate the impact of the neighbors'
558   emissions on each other. We consider the emissions over the rest of the world (excluding India,
559   China, the Middle East, the US, and Europe) from Fortems-Cheiney et al. (2015) assuming HFC-
560   134a is substituted with HFO-1234yf on a mole-per-mole basis (the maximum likely emissions
561   scenario). Figure S13 in the supplementary information shows the annual spatial distribution of
562   HFO-1234yf emissions from all the regions as simulated in GEOS-Chem. The percentage
563   deposition of TFA (dry and wet combined) from global and regional (individual regions) emissions
564   of HFO-1234yf is shown in Figure 13. The TFA deposition increased by 7-18% in the three
565   domains because of the emissions from its neighbors. Figure 13 suggests that if the entire world
566   switches to HFO-1234yf, the impact of TFA from the near and far neighbors would be noticeable,
567   but still be at most a factor of 2 or 3 larger. Figure S14 in the supplementary information shows
568   the spatial pattern of the annual total TFA via (a) dry and (b) wet deposition rates from global
569   emissions of HFO-1234yf. The dominant TFA deposition regions were most parts of India,
570   southeast China, parts of Iran, and the southern Arabian Sea. We discussed in section 3.5.1 the
571   potential impacts of such a global switch.

572

573   **3.8.   Reaction of TFA with Criegee intermediates**
574   We examined the influence of CI's potential reactions with TFA on its tropospheric levels.
575   We used the CI concentrations in the boundary layer (0-2 km) from Chhantyal-Pun et al. (2017)
576   in GEOS-Chem and simulated the model for seven months (January to July) using 2015
577   meteorology. Figure S15 in the supplementary information shows the mean surface CI
578   concentration for those seven months calculated at 2° x 2.5° spatial resolution. The CI
579   concentrations in the three regions of our study were less than 2500 molecules cm^{-3}. We calculated
580   the percentage decrease in total TFA deposition within the three domains by including the CI
581   chemistry. We assumed at all the CI reactions with TFA have the rate coefficient measured for
582   that of CH_2OO with TFA, i.e., $5 \times 10^{-18}T^2e^{1620/T}$ cm^3 molecules^{-1} s^{-1}. Figure 14 shows the
583   spatial pattern of decrease in total TFA deposition (dry and wet combined) for seven months by
584   including CI reaction with gas phase TFA for emissions of HFO-1234yf by (a) India, (b) China,
585   and (c) the Middle East. In most of the locations within the three domains, the decrease in total
586   TFA deposition was <2.5%. At a few places in southeast Asia (Figure 14a), western China (Figure

14b), and northern Africa (Figure 14c), the TFA deposition decreased by 7-25%. The decrease in TFA deposition due to CI was 0.03, 0.32, and 0.08 Gg (total for seven months) for India, China, and the Middle East domains, respectively. Figure S16 shows the percentage decrease in mean surface TFA mixing ratio by including the reaction of CI with TFA following the emissions of HFO-1234yf emissions from (a) India, (b) China, and (c) the Middle East. The decrease in the mean surface TFA mixing ratio is less than 2% (0.01 ppt). Overall, the impact of CI on TFA deposition/mixing ratio was small in the regions of study.

4.   Summary

We have investigated TFA formation from emissions of HFO-1234yf, its dry and wet deposition, and rainwater concentration over India, China, and the Middle East with GEOS-Chem and WRF-Chem models. We estimated the TFA deposition and rainwater concentrations between 2020 and 2040 for four HFO-1234yf emission scenarios. The models were simulated for a year (2015), with additional 2016 simulations to understand the interannual variability. We also simulated the model using global emissions to assess interregional effects on TFA deposition. The main results of the study are summarized below:

- Using two models at different spatial resolutions helped us assess the variation in model transport, precipitation, and cloud treatment. These variations yield slightly different calculated TFA levels from the emission of HFO-1234yf. Even though there are discernable differences, the overall conclusions are the same and point to this study's robustness.
- The accuracy of the GEOS-Chem model's ability to calculate wet deposition over the regions of interest was tested by comparing calculated sulfate rainwater concentration with observations. The model reproduces well the multiyear sulfate rainwater concentration (-3% to -13% bias) and its spatial variability (R>0.80) in the three domains.
- Our calculated TFA amounts over the U.S., Europe, and China were comparable to those previously reported when normalized to the same emissions.
- The controlling factor for the amount of TFA from HFO-1234yf is its emissions. The uncertainties in the models and chemistry are secondary to the extent of emissions.
- The TFA deposition was largest over eastern India, southeast China, northern Iran, and the southern Arabian Sea. The TFA wet deposition was comparable between the two models.
- There are large variations in TFA rainwater concentrations associated with rainfall extent. The mean TFA rainwater concentration calculated for the four emission scenarios from GEOS-Chem and WRF-Chem was below the no observable effect concentration (NOEC), suggesting the ecological and human health impacts to be not significant.
- With a chemical turnover time of HFO-1234yf of 10 days, its impact is not local and extends well beyond the region of emissions. This study highlights the enhanced TFA formation by the simultaneous use of HFO-1234yf by neighboring regions. If all the Northern Hemisphere countries were to use HFO-1234yf, the impact would be higher by a factor of 2 or 3. However, these amounts are still much lower than the NOEC noted above.

- We estimate that continued use of HFO-1234yf in India, China, and the Middle East are unlikely to lead to detrimental human health effects based on the current understanding of the effects of TFA in water bodies, as summarized by Neale et al. (2021). (Note we do not assume the water is treated specifically to remove TFA before consumption.)
- We note that a hydrology model of the water flow and TFA concentrations in them would be beneficial to quantify the extent of TFA accumulation in pools and flow out to large water bodies.

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861

862 **Tables**

863 **Table 1.** The slope, correlation coefficient (R), intercept (c), mean bias (MB), and the number of
864 points (N) of simulated (GEOS-Chem) and observed sulfate rainwater concentration over the three
865 domains.

Region	Slope	R	c	MB	N
India	0.771	0.816	0.210	-0.255±0.778	54
China	0.799	0.911	0.655	-1.07±2.700	89
Middle East	1.42	0.880	-2.81	-0.187±2.71	5

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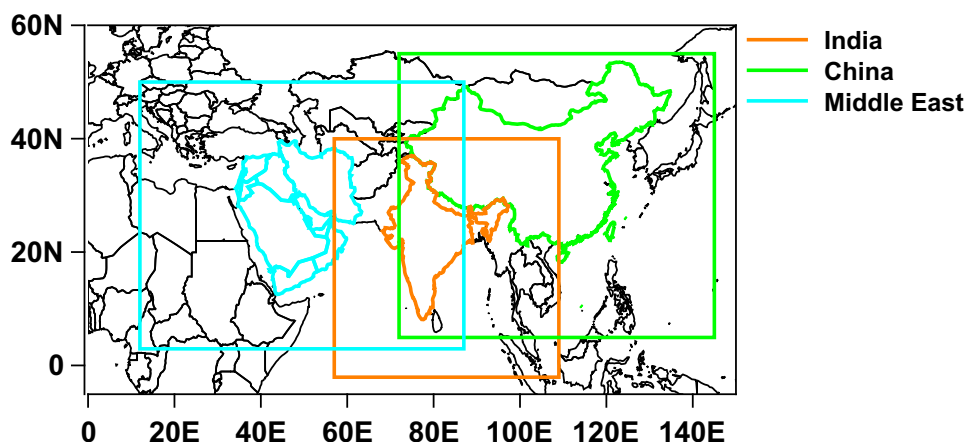
 Figures

868
869 **Figure 1.** The model domains for India, China, and the Middle East used in the present study and
870 also for WRF-Chem simulations. The land regions for the emissions are shown in color.
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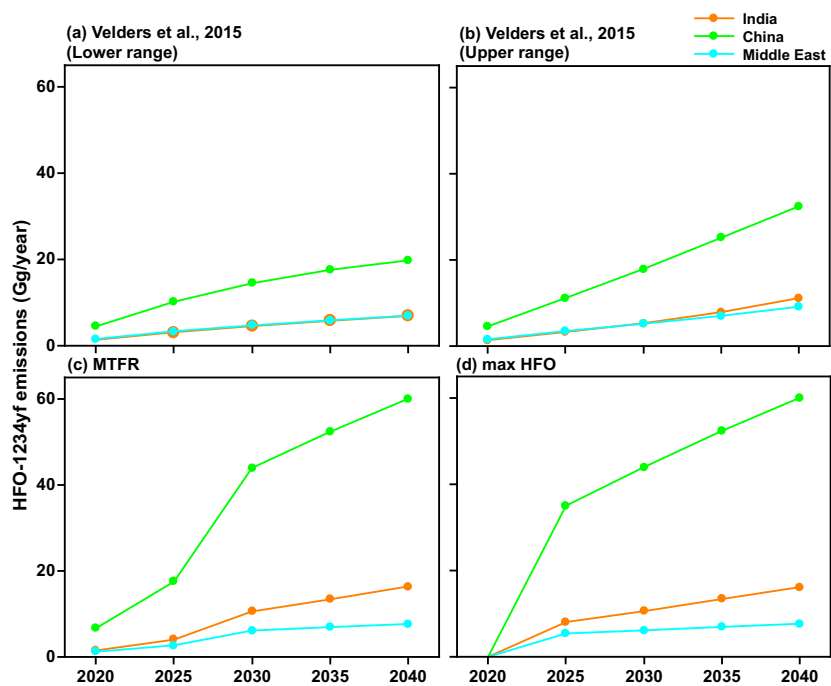
872

873
874 **Figure 2.** The projected HFO-1234yf emissions scenarios between 2020 and 2040 from Velders
875 et al. (2015) (a) lower and (b) upper ranges, IIASA GAINS model for (c) Maximum Technically
876 Feasible Reduction (MTFR) and (d) max HFO in India, China, and the Middle East.
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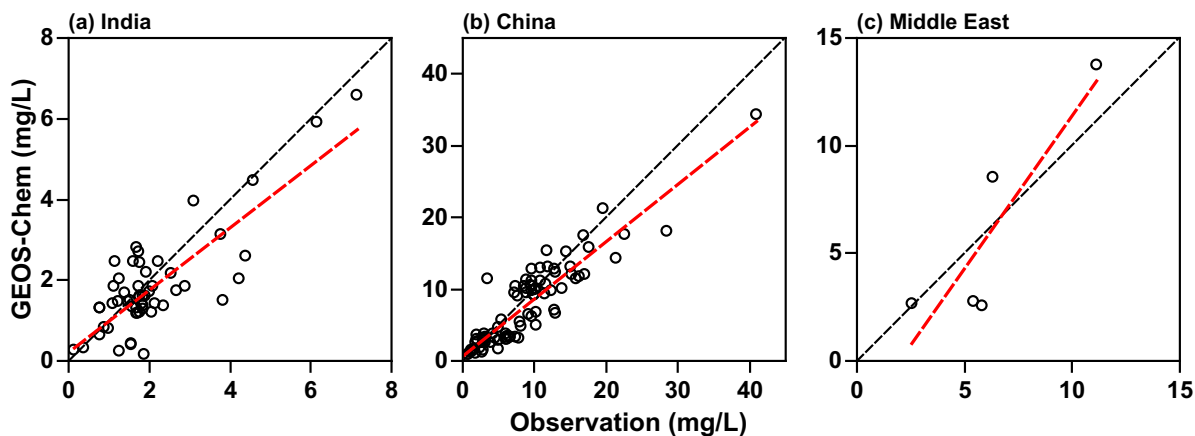
878
879 **Figure 3.** Scatter plot of simulated and observed sulfate rainwater concentration in (a) India, (b)
880 China, and (c) the Middle East for 2000-2015. The linear regression line is shown in red. The black
881 dashed line corresponds to slope = 1. The data for the Middle East is very limited.
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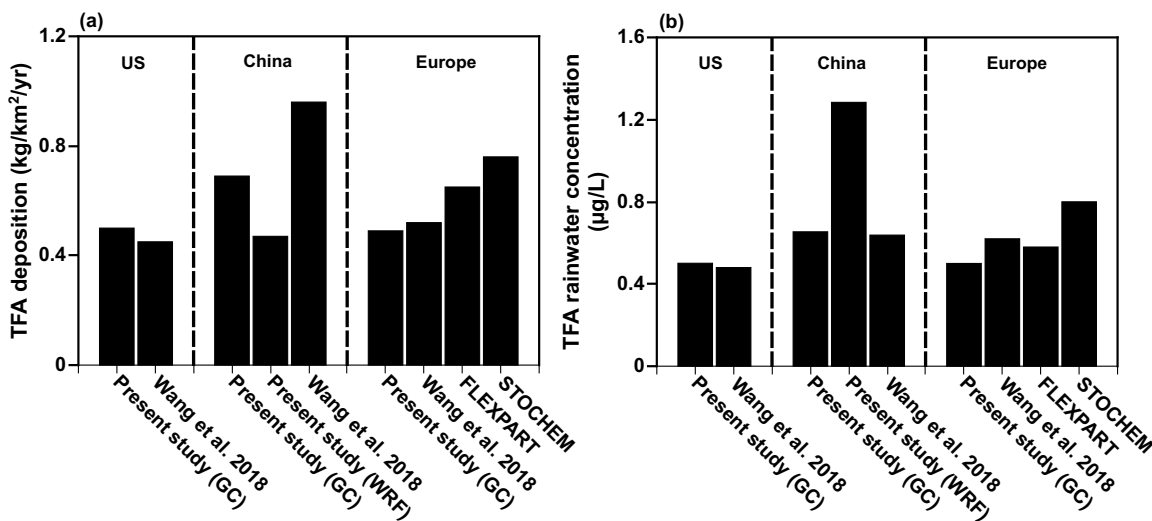
884
885 **Figure 4.** Comparison of the present study with other studies over the U.S., China, and Europe for
886 (a) TFA deposition, and (b) TFA rainwater concentration. Note the emissions are 24.53 Gg yr^{-1},
887 42.65 Gg yr^{-1}, and 19.16 Gg yr^{-1} for the U.S., China, and Europe, respectively.
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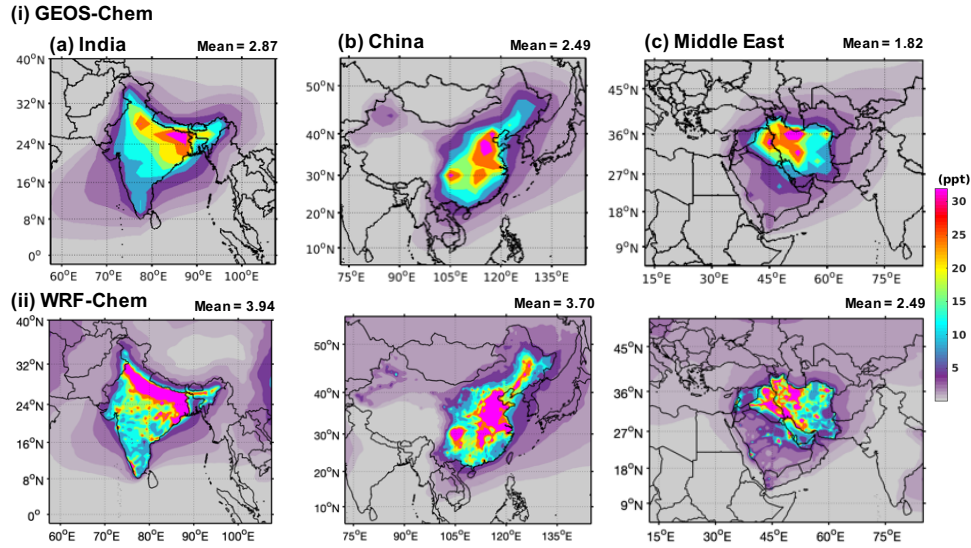


Figure 5. Annual mean surface mixing ratios of HFO-1234yf simulated in (i) GEOS-Chem and (ii) WRF-Chem over (a) India, (b) China, and (c) the Middle East. The number at the top of each panel gives the mean HFO-1234yf mixing ratios within the domains.

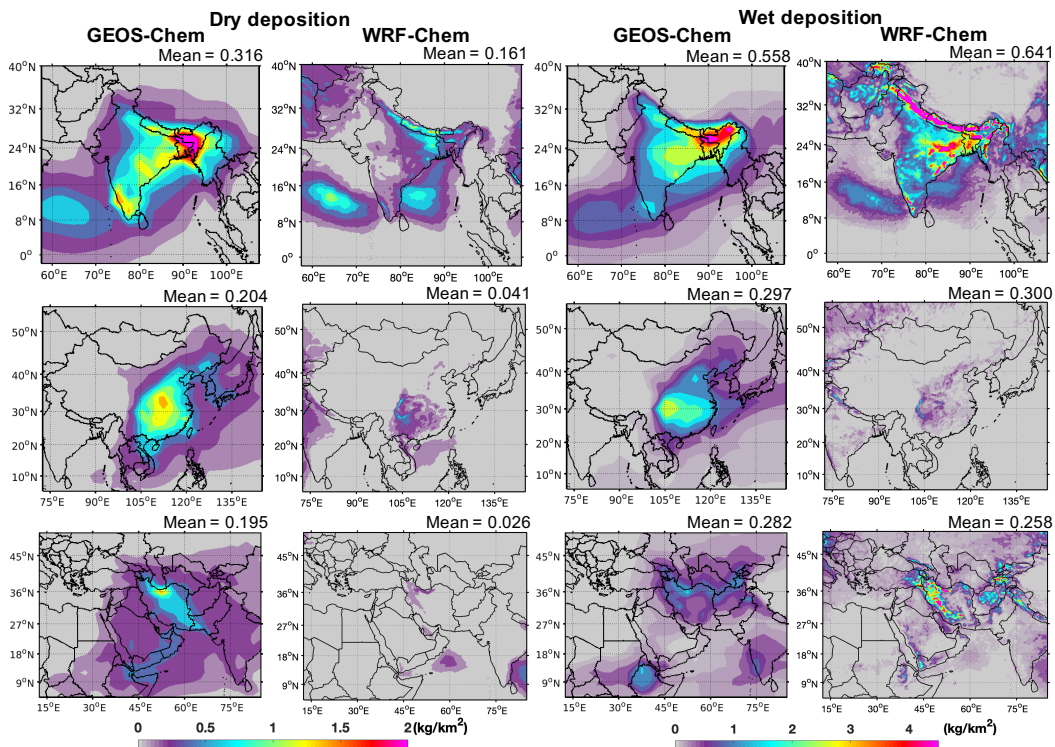
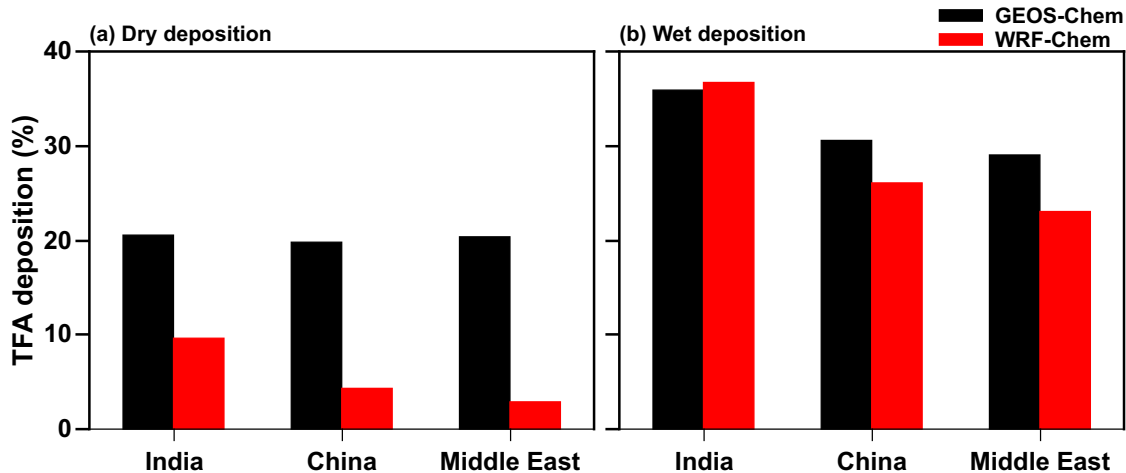



Figure 6. GEOS-Chem and WRF-Chem simulated annual total deposition rates of TFA (kg km^{-2} yr^{-1}) from (a) dry and (b) wet deposition in India, China, and the Middle East domains. The number at the top of each panel gives the mean dry and wet deposition rates within the domains.

900

901 **Figure 7.** Percentage contribution of (a) dry and (b) wet deposition to total annual TFA deposition

902 simulated in GEOS-Chem and WRF-Chem in the three domains.

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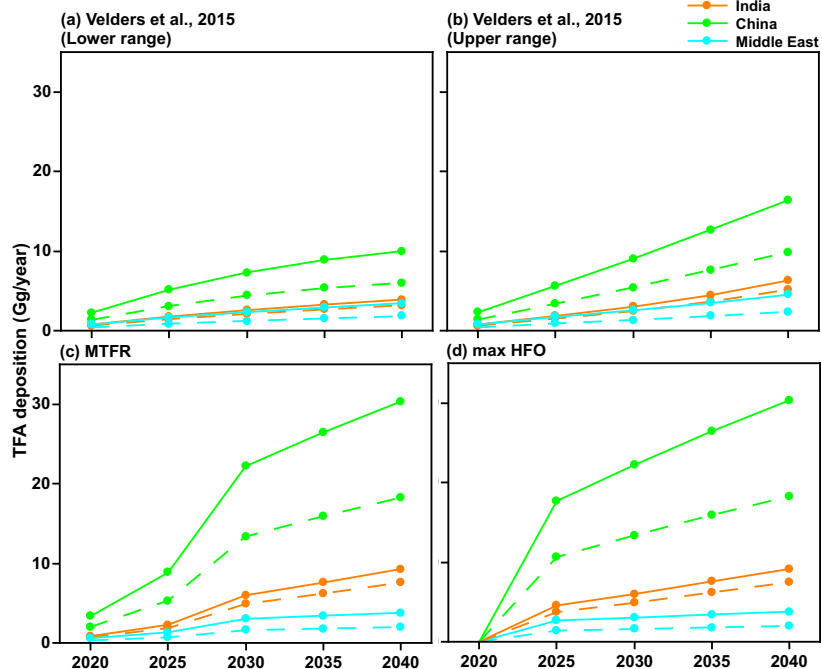
904

905 **Figure 8.** Total TFA deposited (dry and wet combined) in four emission scenarios for 2020 to

906 2040 within India, China, and the Middle East domains calculated using GEOS-Chem (solid lines)

907 and WRF-Chem (dashed lines). The values from the two models are reasonably close for India

908 and the Middle East, while they differ by almost a factor two for China.

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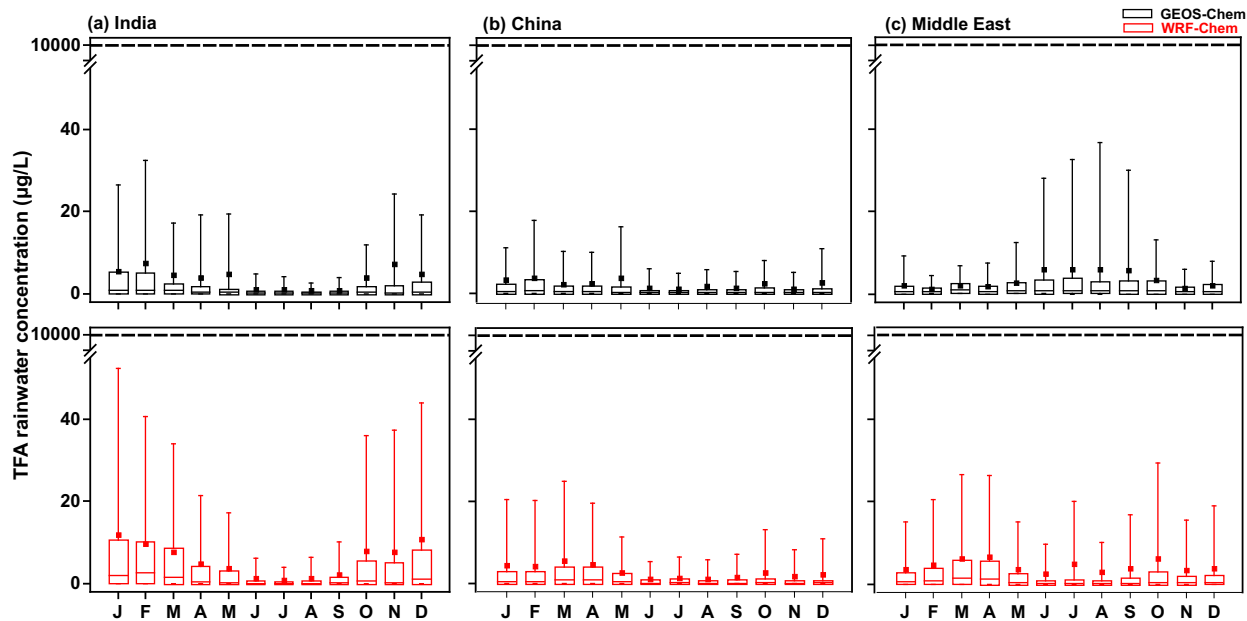
Figure 9. Box and whisker plot of TFA rainwater concentration calculated from GEOS-Chem and WRF-Chem in the three domains. In the box plot, the inside line and square are the median and mean, respectively. Box boundaries are 25th and 75th percentiles, and whiskers indicate the 5th and 95th percentiles. The dashed horizontal line is the No Observable Effect Concentration (NOEC) level. It is important to note that these values, including the 95th percentile values are at least 100 times lower than the NOEC for harming aquatic bodies even when normalized for higher projected emissions in 2040.
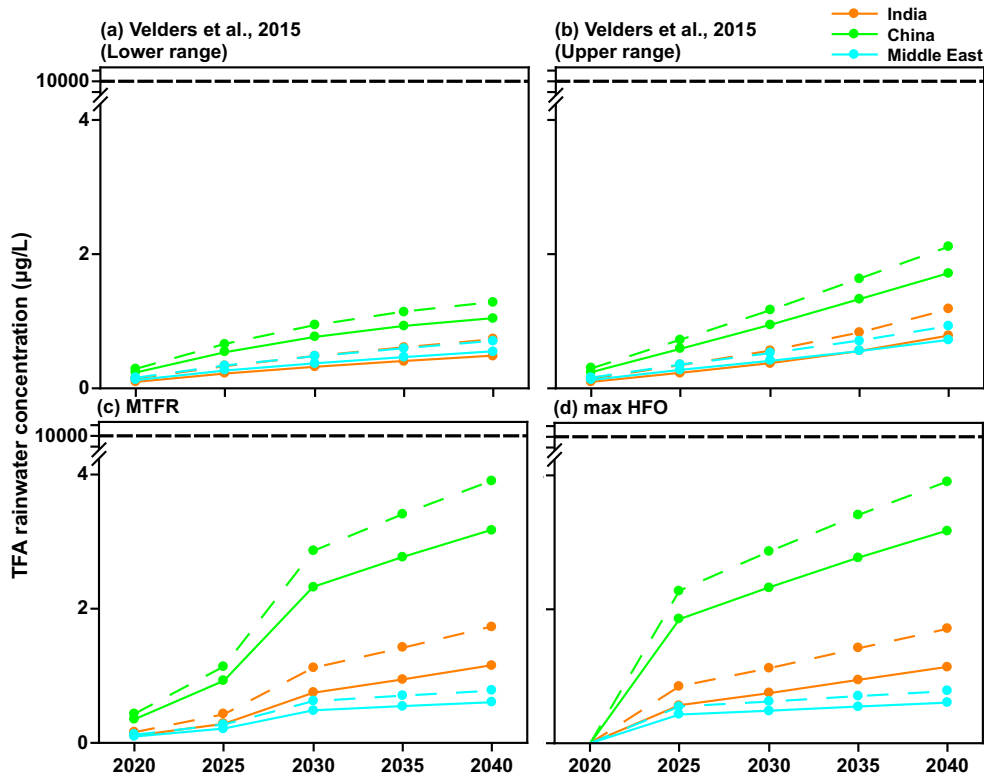
Figure 10. Mean TFA rainwater concentration in four scenarios for 2020 to 2040 for India, China, and the Middle East domains calculated using GEOS-Chem (solid lines) and WRF-Chem (dashed lines). The NOEC is denoted above, and it is two orders of magnitude larger than calculated TFA concentrations for any of the scenarios.
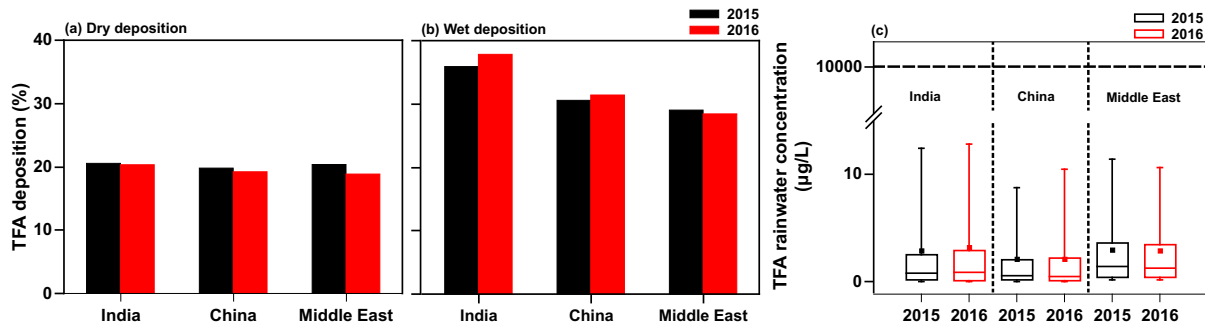
Figure 11. Annual percentage of total TFA (a) dry and (b) wet deposition, and (c) annual mean TFA rainwater concentrations in India, China, and the Middle East domains from GEOS-Chem for 2015 and 2016. The dashed horizontal line is the NOEC level.

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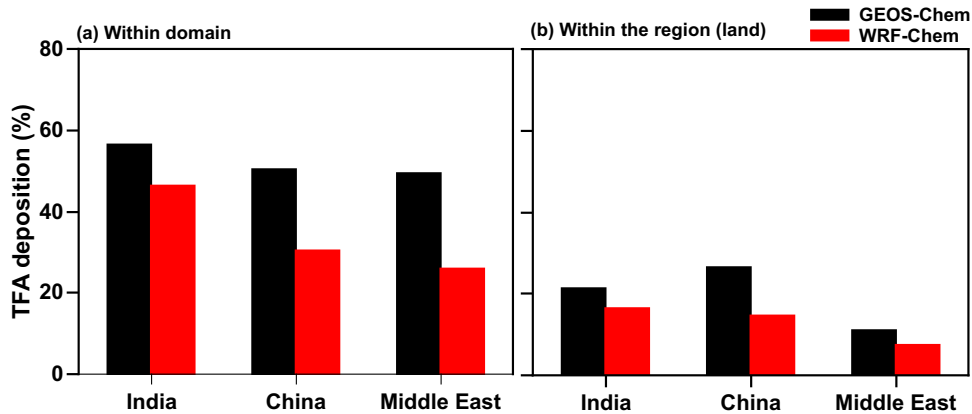
Figure 12. Annual percentage of total TFA deposition (dry and wet combined) calculated from
GEOS-Chem and WRF-Chem within the three (a) domains and (b) regions (land).

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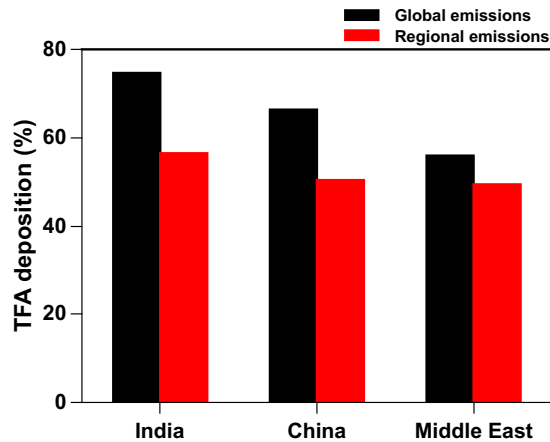
Figure 13. Annual percentage of total TFA deposition (dry and wet combined) in India, China,
and the Middle East from global and regional (individual regions) emissions.

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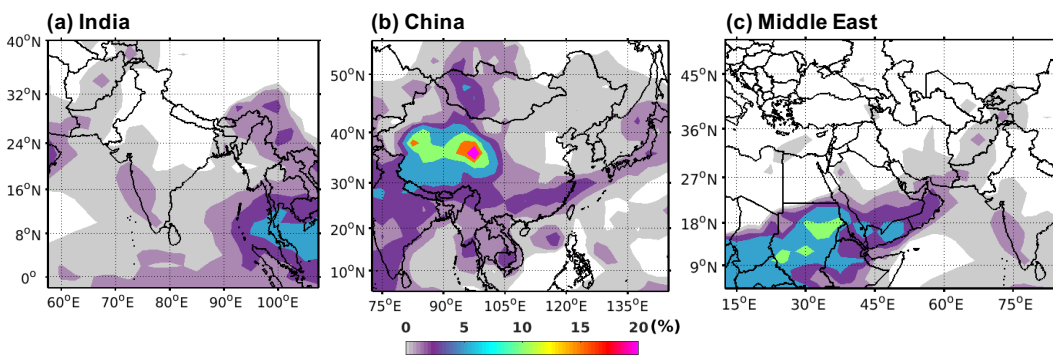
Figure 14. Percentage decrease in TFA deposition (dry and wet combined) by adding Criegee
intermediate chemistry to HFO-1234yf emissions over (a) India, (b) China, and (c) the Middle
East domains.

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