Georgia Tech | Earth and Atmospheric Sciences

Global Emissions of Hydrogen Chloride and Fine Particulate Chloride from Continental Sources

Bingqing Zhang, Huizhong Shen, Xiao Yun, Qirui Zhong, Barron Henderson, Xuan Wang, Liuhua Shi, Sachin S. Gunthe, L. Gregory Huey, Shu Tao, Armistead G. Russell, Pengfei Liu*

Jun 2022

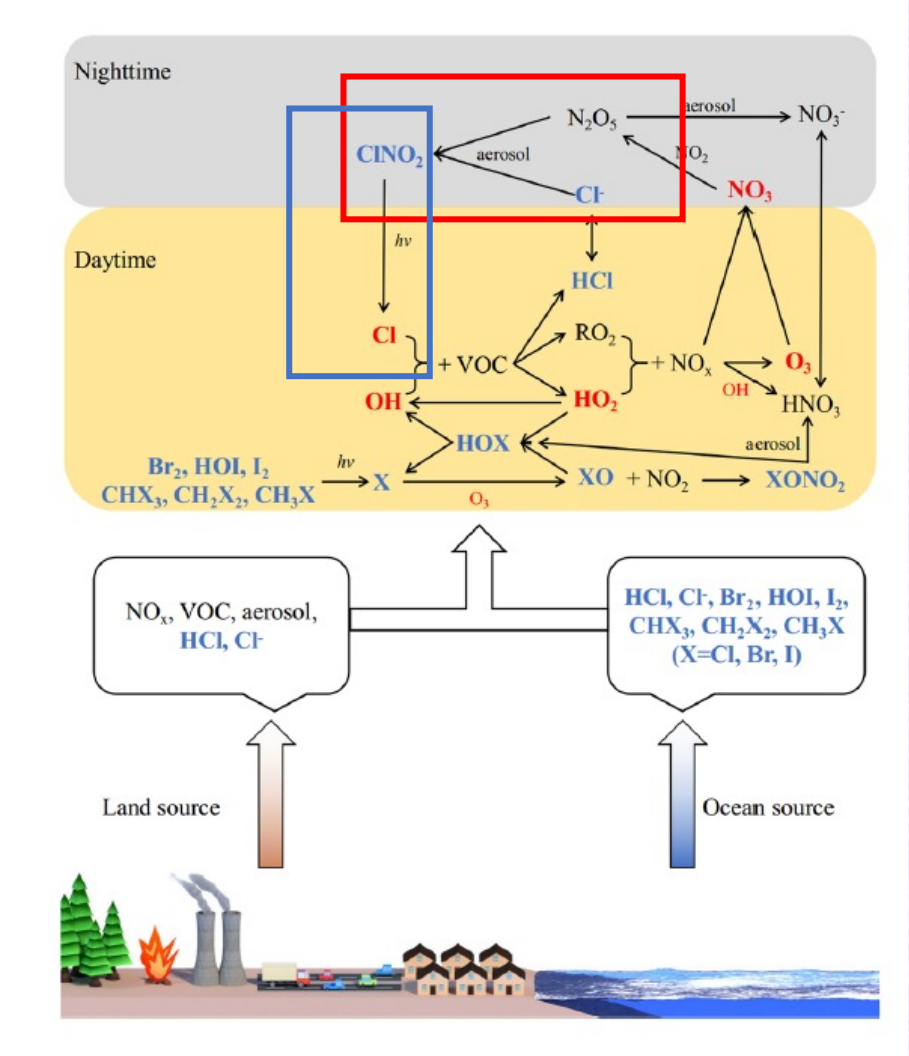
Zhang, B., Shen, H., Yun, X., Zhong, Q., Henderson, B. H., Wang, X., Shi, L., Gunthe, S. S., Huey, L. G., Tao, S., Russell, A. G., & Liu, P. (2022). Global Emissions of Hydrogen Chloride and Particulate Chloride from Continental Sources. *Environmental Science & Technology, 56(7), 3894-3904. https://doi.org/10.1021/acs.est.1c05634*

Introduction

Chlorine chemistry in the atmosphere

- Tropospheric chlorine radical can oxidize volatile organic compounds (VOC) to produce OH, HO_2; destroy ozone directly; change the partitioning between HO_2/OH and NO/NO_2

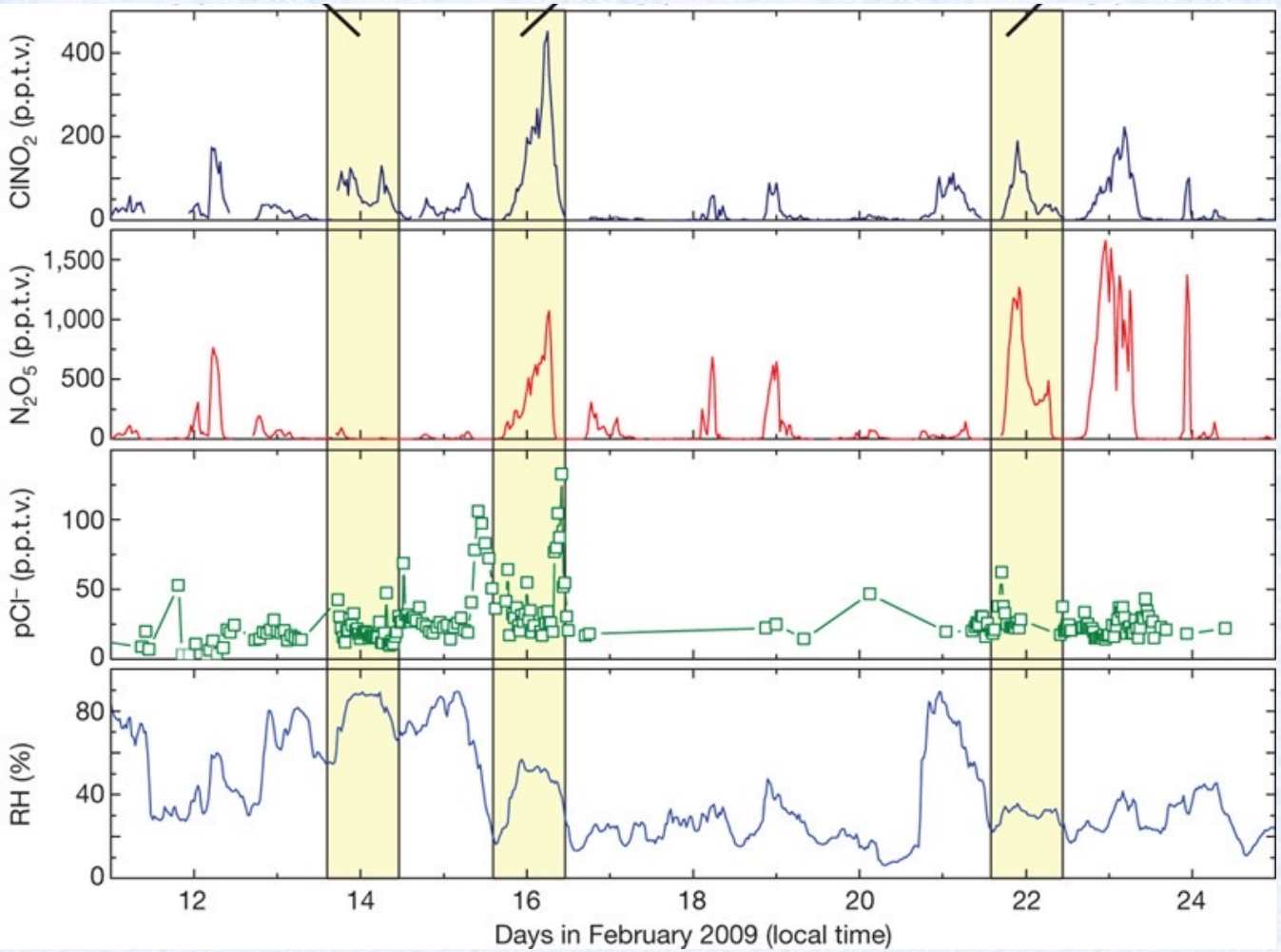
- Heterogenous reaction of particulate Cl and N_2O_5 produce $ClNO_2$, a reservoir of Cl radical which will form at night and photolysis in the daytime to release Cl radical (Wang et al, 2019)

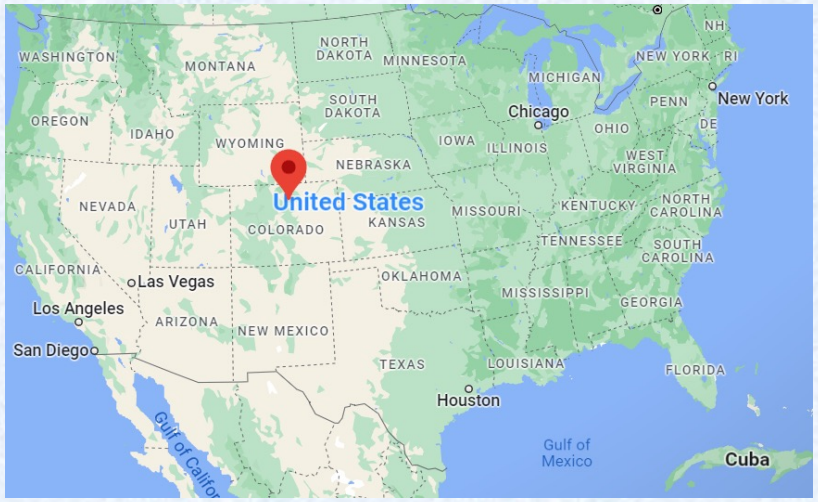


Li, Q., et al. (2020). "Potential Effect of Halogens on Atmospheric Oxidation and Air Quality in China." Journal of Geophysical Research: Atmospheres **125(9): e2019JD032058.**

Introduction

High ClNO2 concentrations are observed in regions far from the ocean



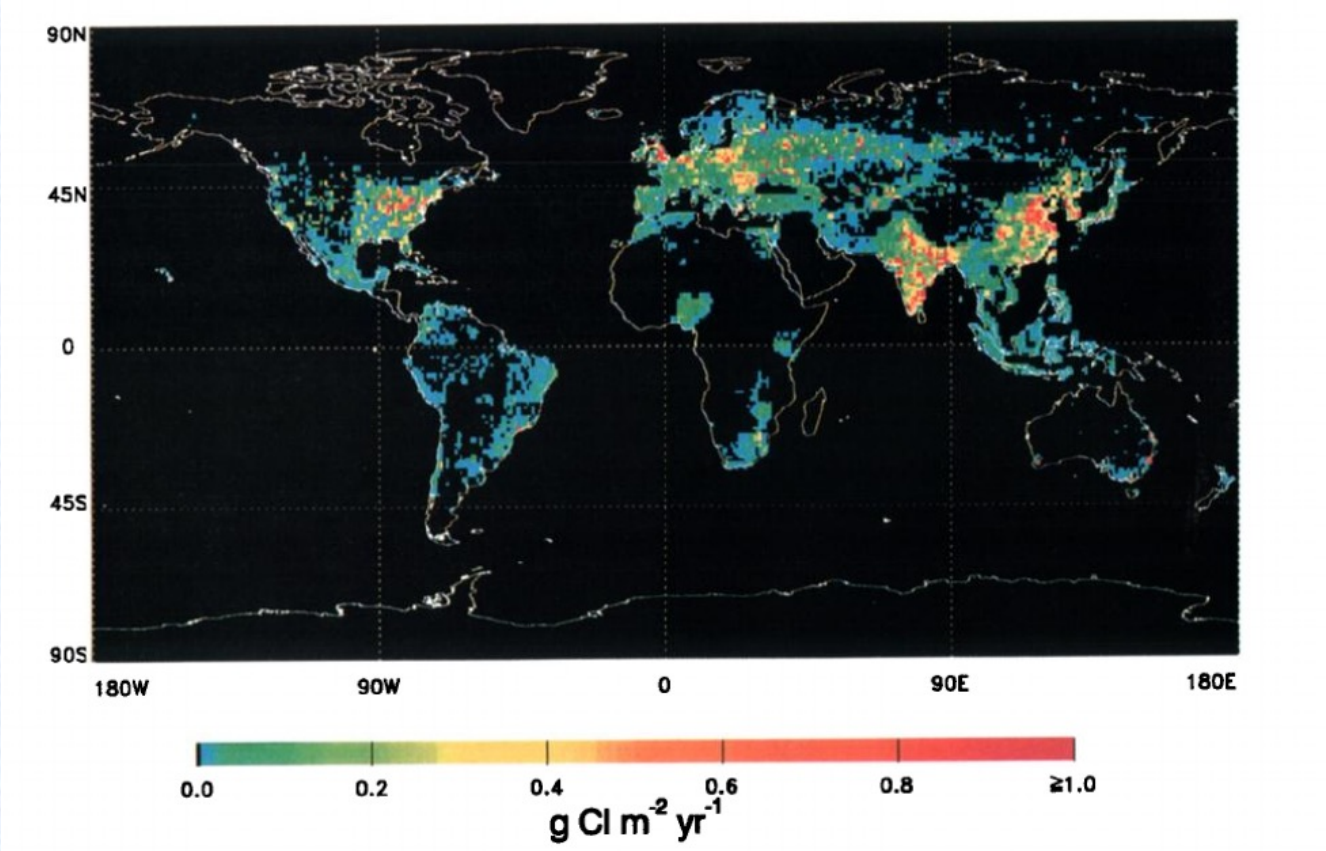


Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., & Brown, S. S. (2010). A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. Nature, 464(7286), 271-274. https://doi.org/10.1038/nature08905

Introduction

Current chlorine emission estimates studies

- 1990 Reactive Chlorine Emission Inventory (RECI)
- Spatial resolution: 1°× 1°
- The HCl emitted in 1990 is 4.6Tg from fossil fuel and 2Tg from waste burning

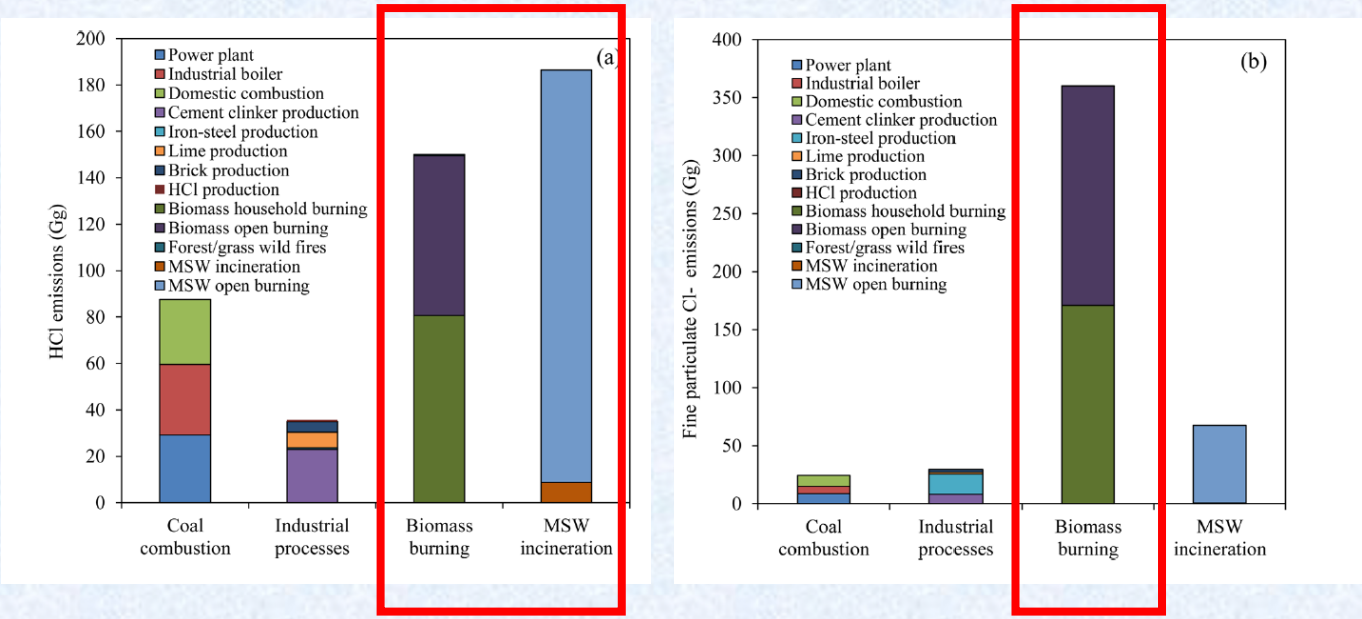


McCulloch, A., et al. (1999). "Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory." Journal of Geophysical Research: Atmospheres **104(D7): 8391-8403.**

Introduction

Current chlorine emission estimates studies

- HCl and particulate Cl emission from China in 2014
- Spatial resolution: 0.1°× 0.1°
- The HCl emitted in 2014 is 458Gg and particulate Cl emitted is 486Gg



Fu, X., et al. (2018). "Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China." Environmental Science & Technology **52(3): 1644-1654.**

Aims of this study

Georgia Tech Earth and Atmospheric Sciences

Develop an up-to-date and high-resolution global emission inventory

- **Species**: HCl, particulate Cl
- **Spatial resolution**: 0.1°× 0.1°
- **Time range**: monthly emission available from 1960 to 2014
- **Method:** Bottom-up method (the following equation) to calculate the country-level emissions and using proxies (such as population, powerplants and industry locations) for spatial gridding.

$$E = \sum_i E_i = \sum_i A_i \times EF_i$$

- **Source categories**: including 36 sources categorized in 6 source sectors (i.e., energy, industrial, residential, open waste burning, open biomass burning, and agricultural sectors).

List of sectors and emission factors

Georgia Tech | Earth and Atmospheric Sciences

List of sectors and emission factors

sector	subsector	fuel	emission factor (g/kg) HCl	refs.	pCl	refs.
energy production	coal combustion	anthracite	calculated based on chlorine content and removal efficiency			
		coke				
		bituminous coal				
		lignite				
		peat				
	waste combustion	municipal waste	3.20	US EPA, 2014	1.74	US EPA, 2014; Reff. 2009
		industrial waste	3.20	US EPA, 2014	1.74	US EPA, 2014; Reff. 2009
	biomass combustion	solid biomass	0.06	Andreae, 2019	0.05	Andreae, 2019
industrial processes	coal combustion	anthracite	calculated based on chlorine content and removal efficiency			
		coke				
		bituminous coal excluding coke and brick production				
		lignite	calculated based on uncontrolled EF for PM, HCl and pCl weight percentage, chlorine content in different countries and removal efficiency			
		peat				
	coke production	bituminous coal used in coke production	calculated based on chlorine content, assuming no pollution control			
	brick production	bituminous coal used in brick production				
	waste combustion	municipal waste	3.20	US EPA, 2014	1.74	US EPA, 2014; Reff. 2009
		industrial waste	3.20	US EPA, 2014	1.74	US EPA, 2014; Reff. 2009
	biomass combustion	solid biomass	0.06	Andreae, 2019	0.05	Andreae, 2019

List of sectors and emission factors

Georgia Tech | Earth and Atmospheric Sciences

Sector	Subsector	Fuel	Emission factor (g/kg) HCl	Refs.	pCl	Refs.
Residential processes	Coal combustion	Anthracite	Calculated based on chlorine content			
		Coke				
		Bituminous Coal				
		Lignite				
		Peat				
	Indoor biofuel combustion	Charcoal	0.06	Andreae, 2019	0.05	Andreae, 2019
		Firewood	0.06		0.05	
		Brushwood	0.06		0.05	
		Straw	0.18		0.57	
		Dung	0.038		0.35	
		Corn cob	0.18		0.57	
Open waste burning			calculate based on country-level waste composition (from World Bank) and chlorine content in different types of waste, assuming HCl-to-pCl ratio is10.3 from measurement.			
Open biomass burning	Biomass burning	Savannah and grassland	0.13	Andreae, 2019	0.30	Andreae, 2019
		Temperate forest	0.04		0.27	
		Boreal forest	0.13		0.22	
		Deforestation	0.13		0.17	
		Peat	0.01		0.11	
Agricultural processes	Biomass burning	Agricultural residue	0.18		0.30b	

Results and discussion

Georgia Tech Earth and Atmospheric Sciences

HCl and pCl emissions by sectors and regions in 2014

- The magnitudes of global HCl and pCl emissions are comparable, although the major sources are different.
- Emissions of pCl are mainly from uncontrolled combustion processes, including indoor biofuel burning and open biomass burning.
- Emissions of HCl and pCl mainly from African and Asian countries.

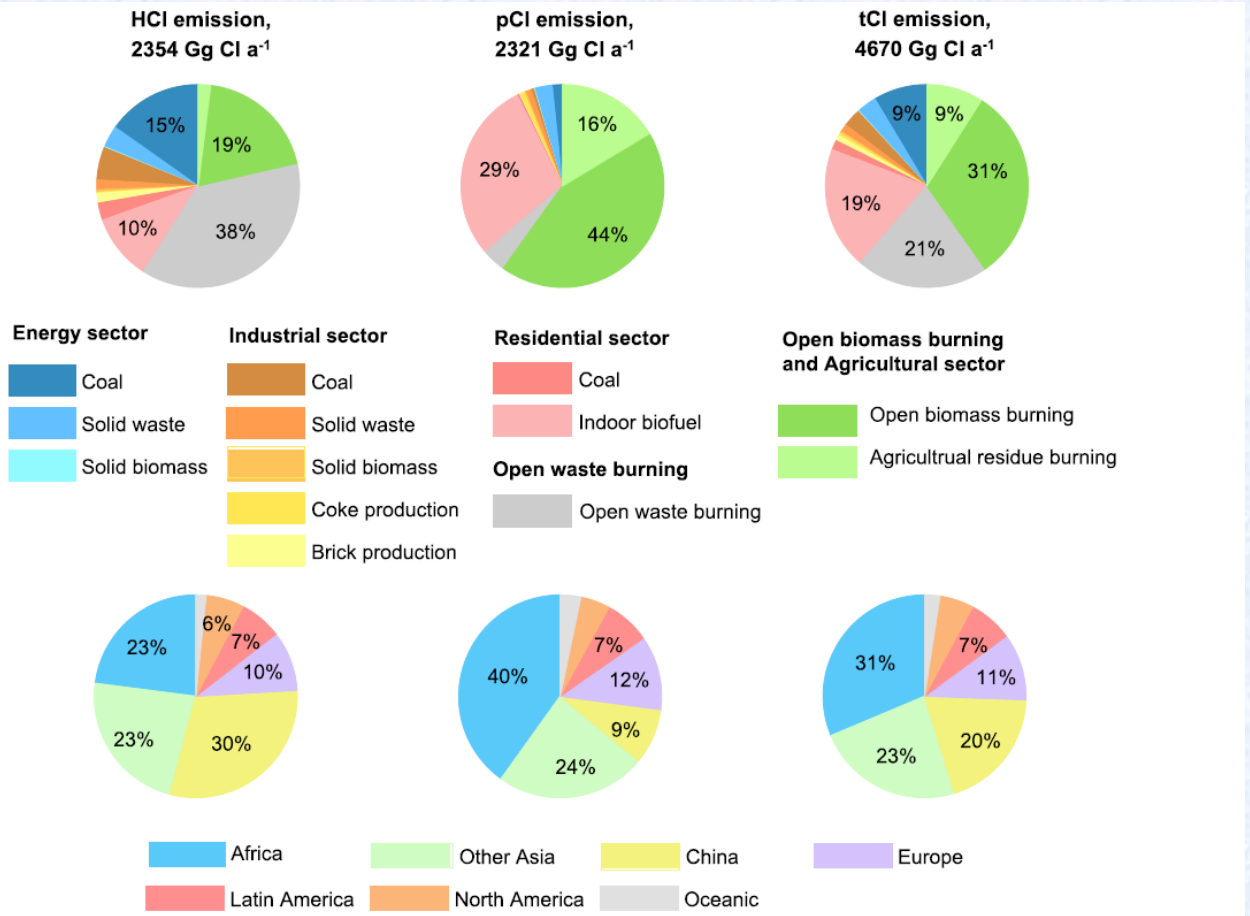
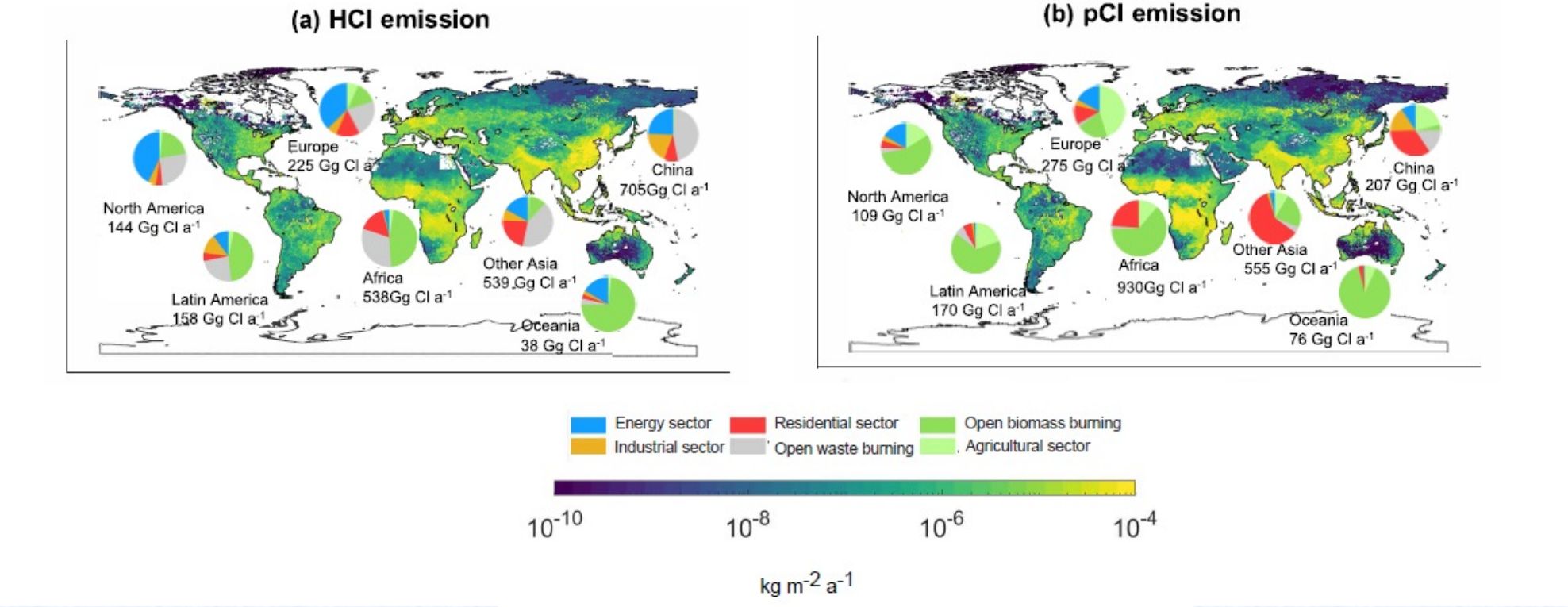


Figure 1. Pie charts show fractions of HCl, pCl, and tCl (HCl + pCl) annual emissions in 2014 by source sectors (a–c) and by emission regions (d–f). Percentage of emission by each major contributor (i.e., contribute more than 5%) is marked on the pie chart. Total emissions of HCl, pCl, and tCl are also marked.

Results and discussion

Georgia Tech Earth and Atmospheric Sciences

Spatial distribution mappings in 2014

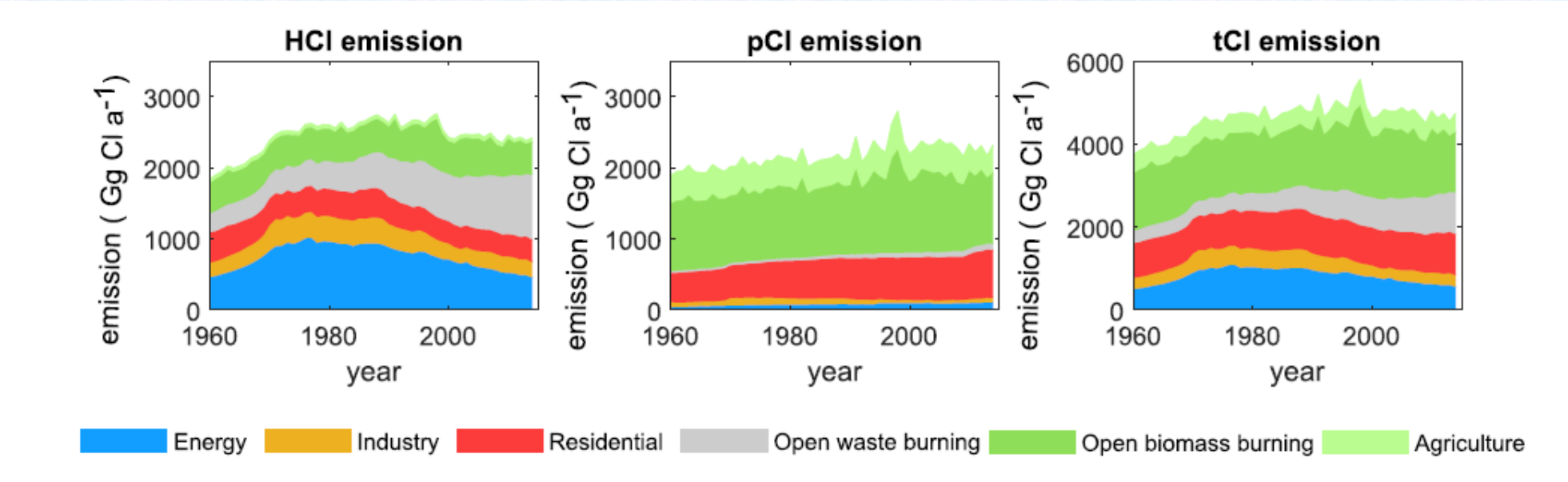


- High emissions of HCl and pCl collocate with high emissions of other major air pollutants such as $PM_{2.5}$, SO_2, and NO_x in populated regions.
- The major sources vary among different regions.

Results and discussion

Georgia Tech Earth and Atmospheric Sciences

Temporal variation and the driving factors



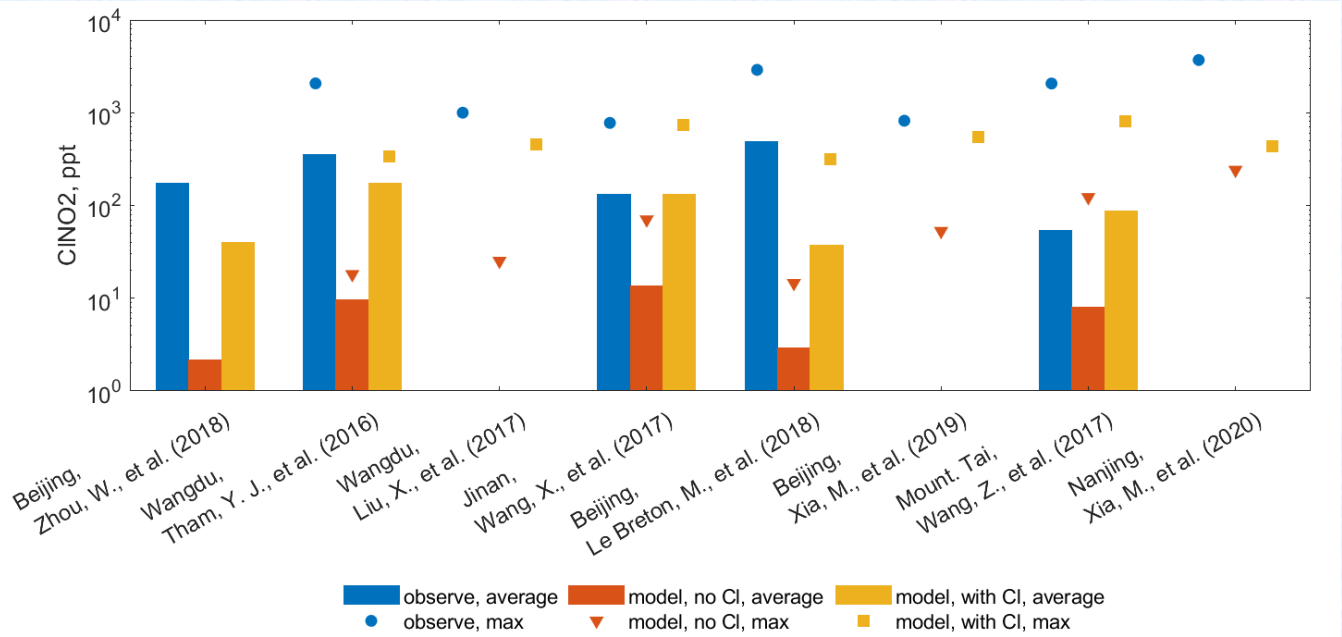
- The emission trends are mainly driven by sources related to anthropogenic sources, while emissions from wildfires fluctuate around a relative constant level.
- Emission of total Cl increase in early years, caused by the increasing of economy and population growth; and decrease after, driving by the wider use of air pollution control device.
- Further reduction might be challenging because a large fraction is from open biomass burning and residential sector without pollution control.

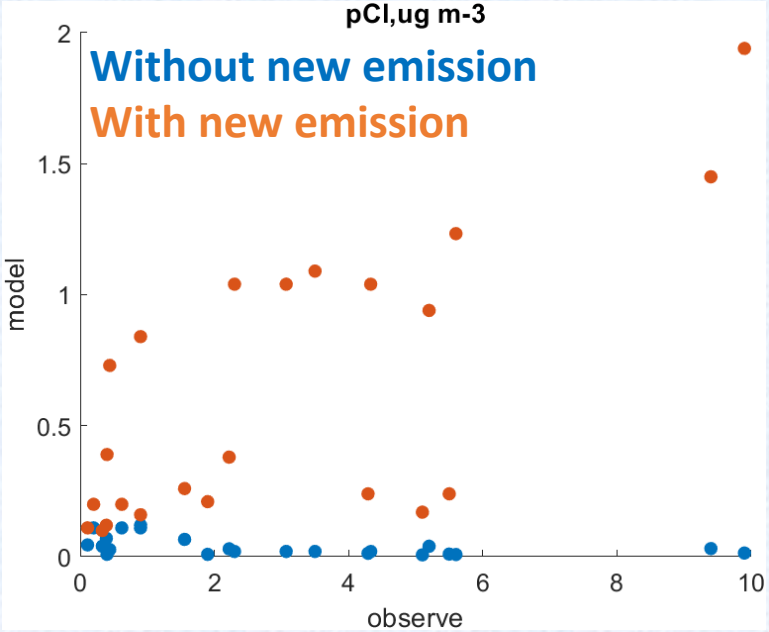
Ongoing works

Georgia Tech Earth and Atmospheric Sciences

The long time period and fine resolution emission inventory provided by this study can be used to study tropospheric chlorine chemistry in chemical transport model.

- This emission inventory can be validated by comparing model simulations with observations (from planeflight measurements and ground-level observations, including HCl, pCl, $ClNO_2$)
  - E.g. Comparison of ClNO2 (left) and pCl (right) with observations in China





- Our current research focus on the effects of chlorine emission to **ClNO2 and Cl radical**.

$$\boldsymbol{Cl^-}(\boldsymbol{s}) + N_2O_5(g) \rightarrow ClNO_2 \text{ (night)}$$

$$ClNO_2 \xrightarrow{hv} Cl\cdot + NO_2 \ (day)$$

Summary

Georgia Tech Earth and Atmospheric Sciences

- We derived a global emission of HCl and pCl emissions from continental sources (anthropogenic processes + biomass burning) with a fine spatial resolution and long time period (1960-2014).The emission files can be added in HEMCO without any modification.
  - The magnitude of HCl and pCl emissions are comparable, although the major sources are different
  - Future reduction of Cl emissions from non-sea salt aerosol sources might be challenging since a large portion is contributed by processes without pollution control
  - Our result is mostly consistent with other existing studies
  - Adding our emissions can fill some of the gap between observations and simulations.
- We will update the emission to more recent years
- We are considering to estimate chlorine emissions from other non-combustion sources such as disinfectant from wastewater treatment plants and road salt for deicing purposes

Supplementary Information

Georgia Tech Earth and Atmospheric Sciences

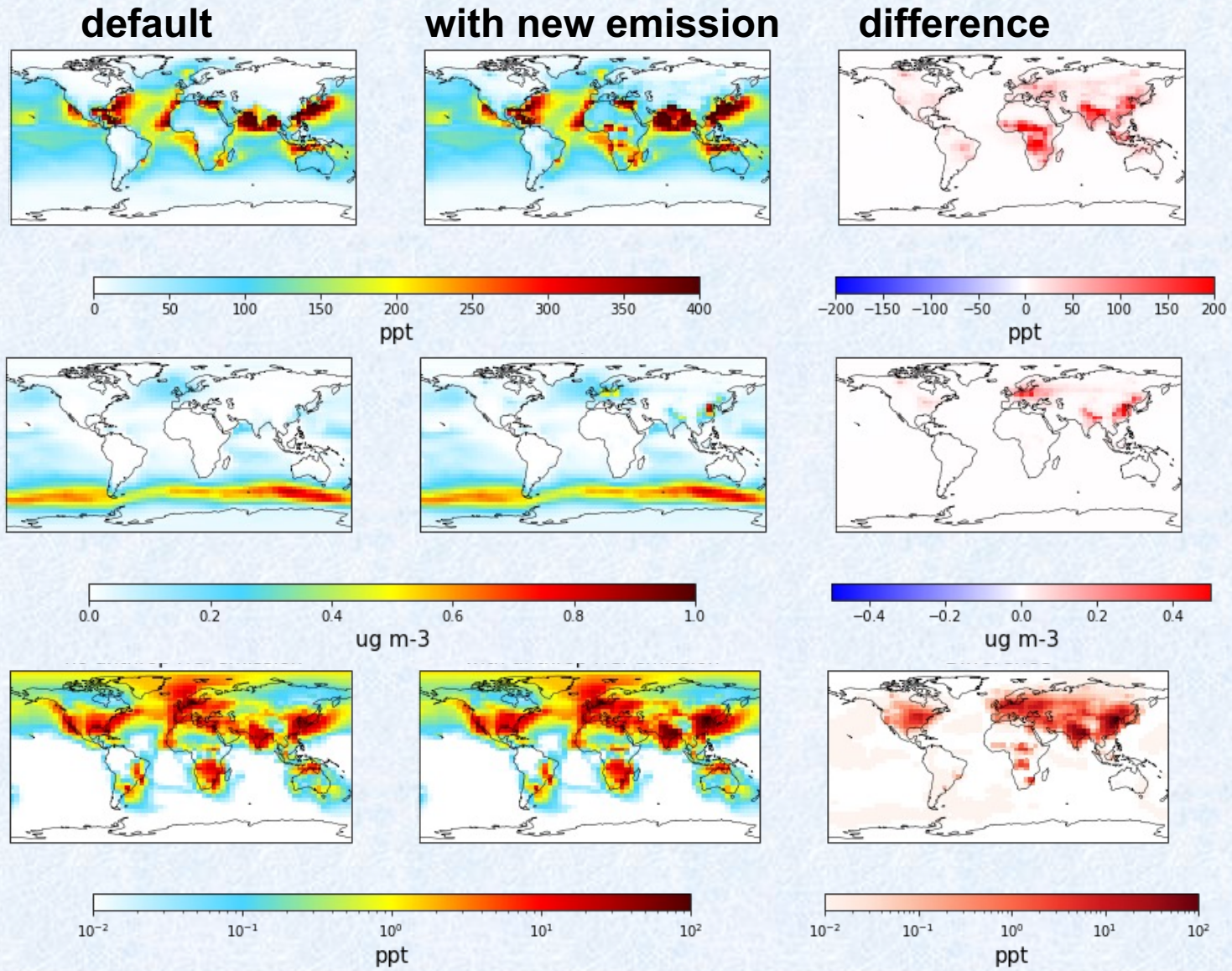
Comparison with other studies

Species	Sector	Year	Country/Region	This study (Unit: Gg)	Data Reported (Unit: Gg)
HCl	Coal combustion	1990	World	1291 (786 - 1519)	6600 (400 - 12800)
HCl	Waste burning	1990	World	702 (589 - 987)	4600 (300 - 8900)
HCl	Total	2014	China	727 (546 - 1638)	458 (307 - 838)
pCl	Total	2014	China	207 (89 - 307)	486 (292 - 885)
HCl	Total	2008	U.S.	158 (82 - 276)	137
HCl	Total	2014	U.S.	94 (62 - 238)	75
HCl	Open waste burning	2015	India	66 (32 - 96)	120 (40 - 220)
HCl	Coal combustion	2012	China	327 (255 - 851)	233
HCl	Waste incineration	2012	China	37 (21 - 50)	3
HCl	Waste incineration	2003	China	6 (2 - 8)	0.5
HCl	Waste incineration	2010	China	27 (14 - 32)	3.6 (1.9 - 5.8)

Supplementary information

Georgia Tech Earth and Atmospheric Sciences

- **Geos-Chem simulation (4 °× 5°)**
- Annual average HCl
- Annual average pCl (SALACL)
- Annual average nighttime ClNO2

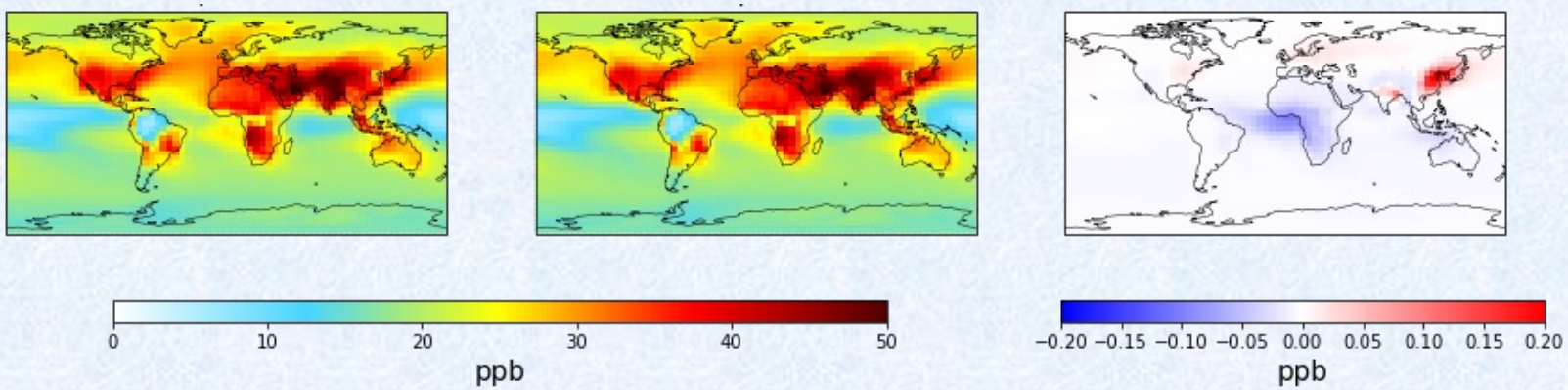


Supplementary information

Georgia Tech Earth and Atmospheric Sciences

- **Geos-Chem simulation (4 °× 5°)** **default** **with new emission** **difference**

- Annual average ozone



- Annual average PM2.5