Distributions and correlations of organic trace gases measured during the Asian Summer Monsoon Chemical and Climate Impact Project (ACCLIP)

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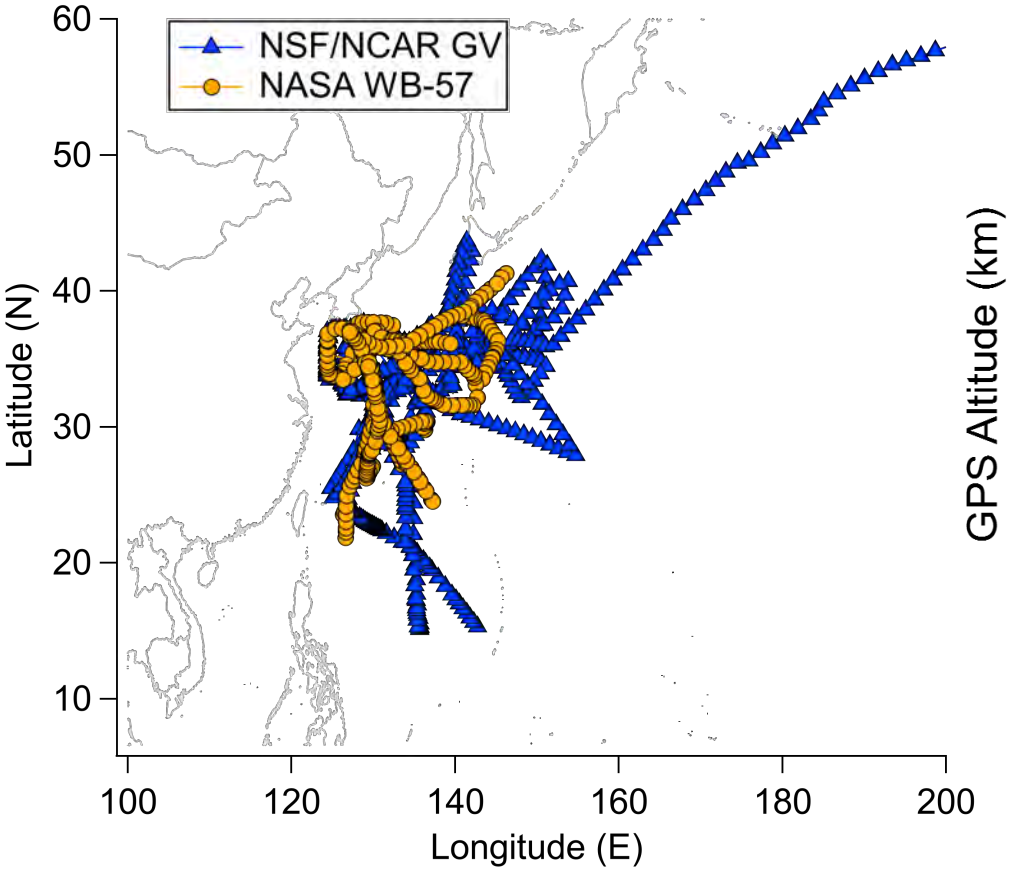
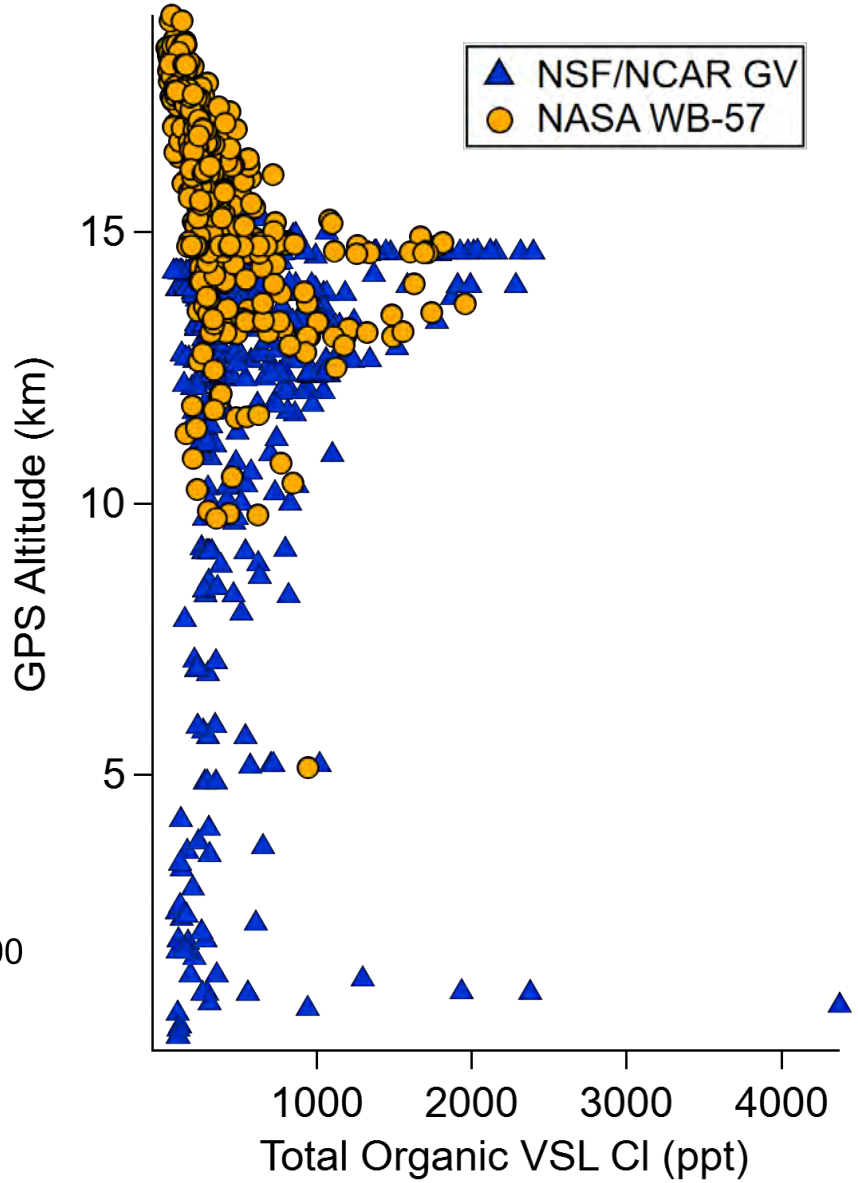
Outline

- Trace gas distributions and correlations
  - Influence of convective encounter, transport time, and regional emissions
  - Tracer correlation relationships and comparisons to regional surface measurements

- Vertical profiles of organic chlorine
  - Long-lived organic Cl (CFCs, CCl4, CH3Cl)
  - HCFCs (HCFC-22, HCFC-141b, HCFC-142b)
  - Very short lived chlorine (dichloromethane, chloroform, …)

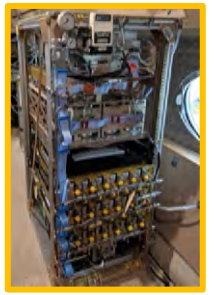
Whole Air Samples (WAS) Collected During ACCLIP





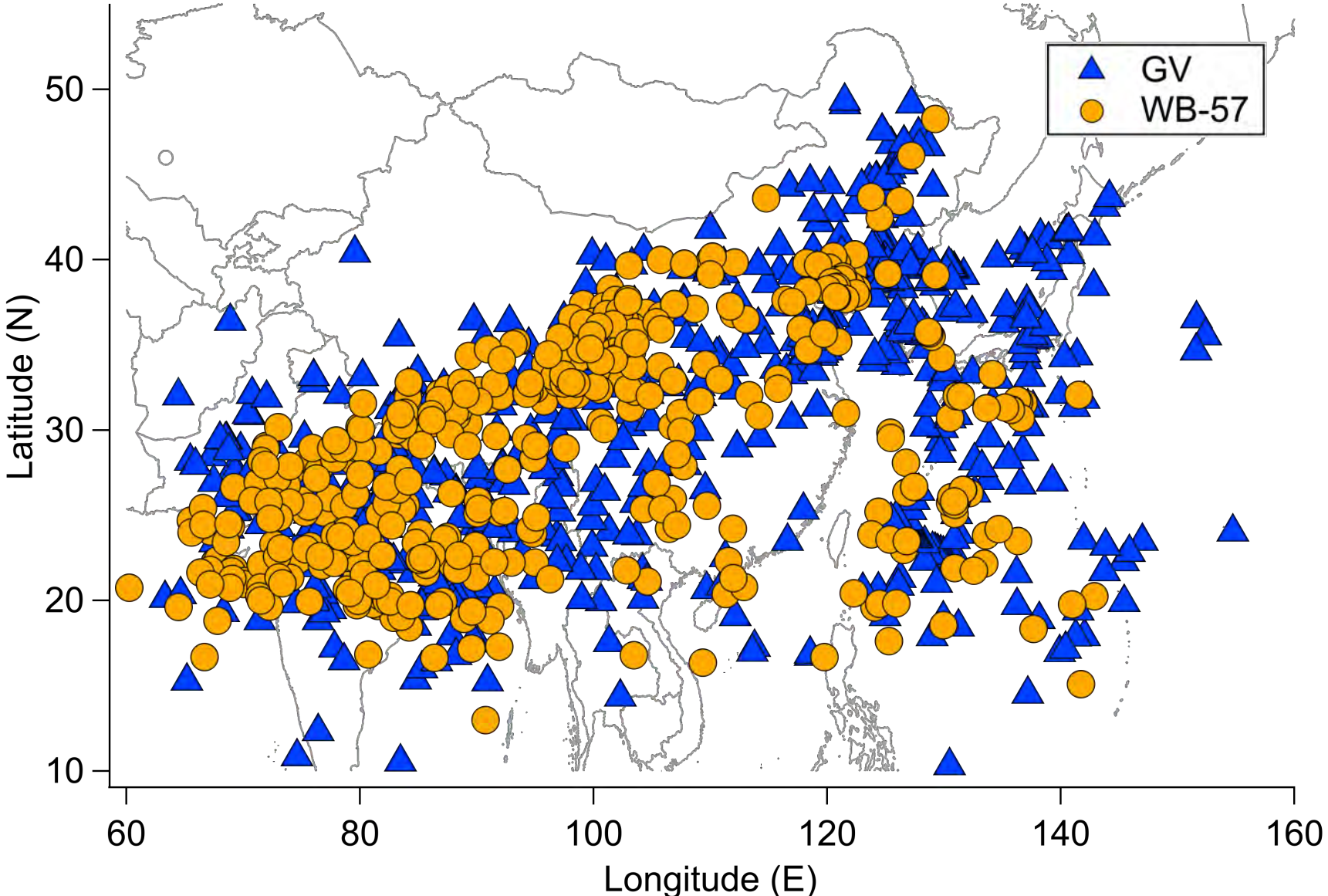
NASA WB-57
604 Whole Air Samples

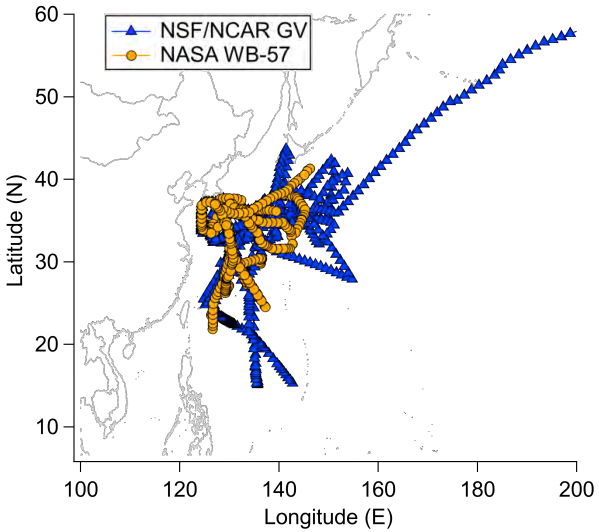
NSF/NCAR GV
739 Whole Air Samples



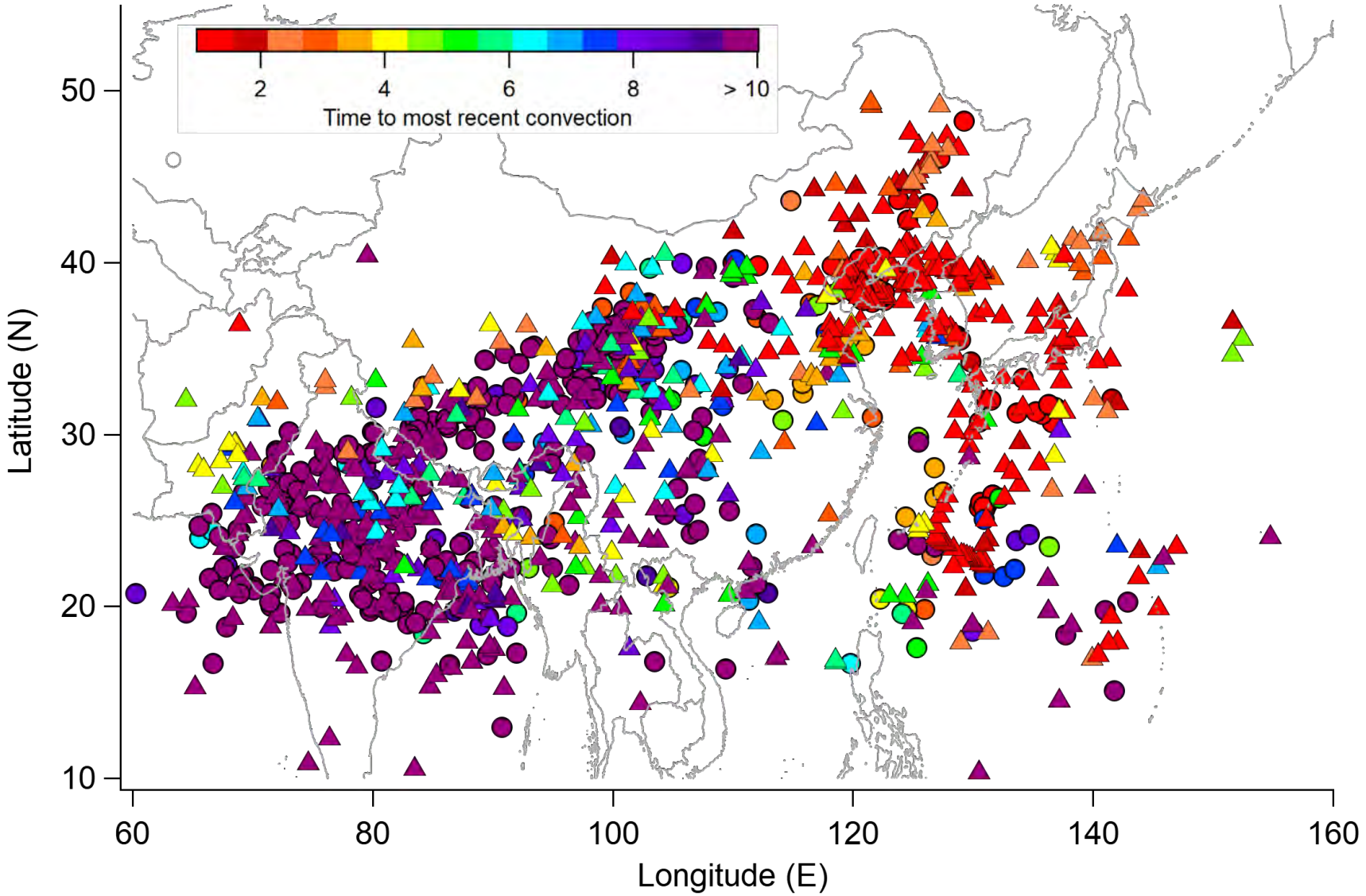
TOGA Photo Credit: Rebecca Hornbrook
GV Photo Credit: Tony Rice
WB-57 Credit: Henry Selkick

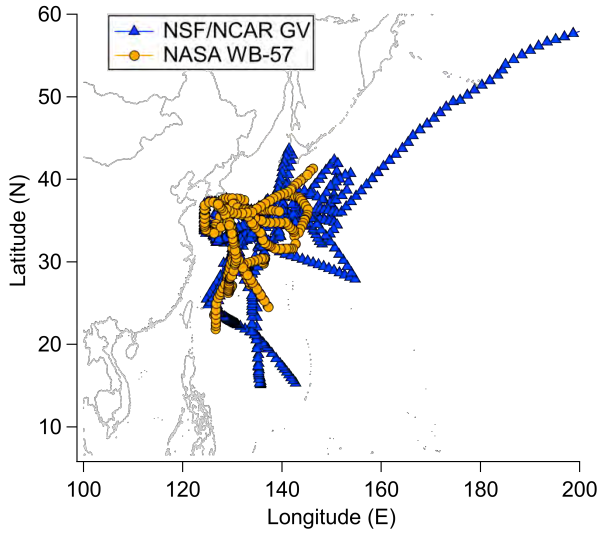
Locations of Most Recent Convective Encounter for WAS samples higher than 500 hPa (5.5 km)



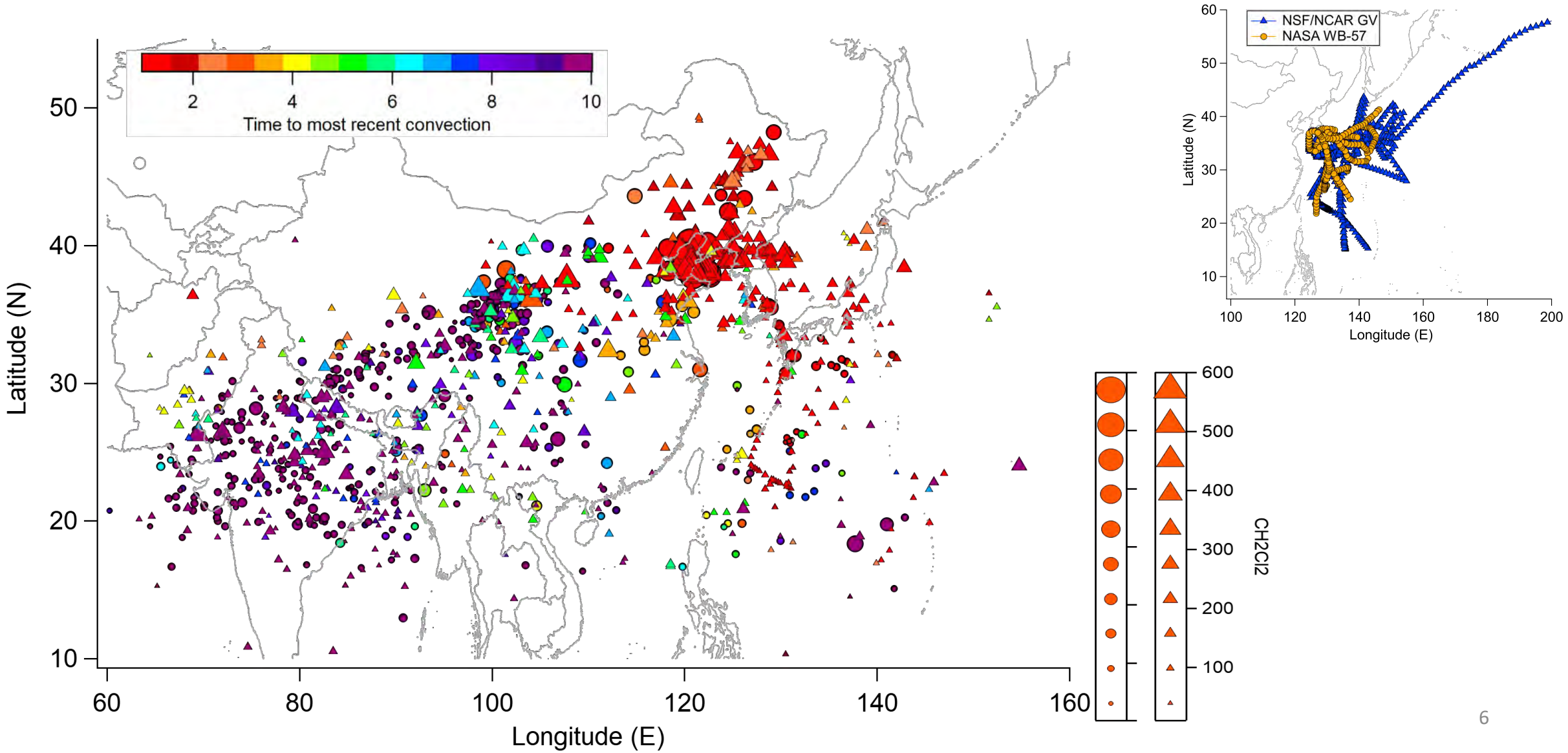


Time of Most Recent Convective Encounter for WAS samples higher than 500 hPa (5.5 km)

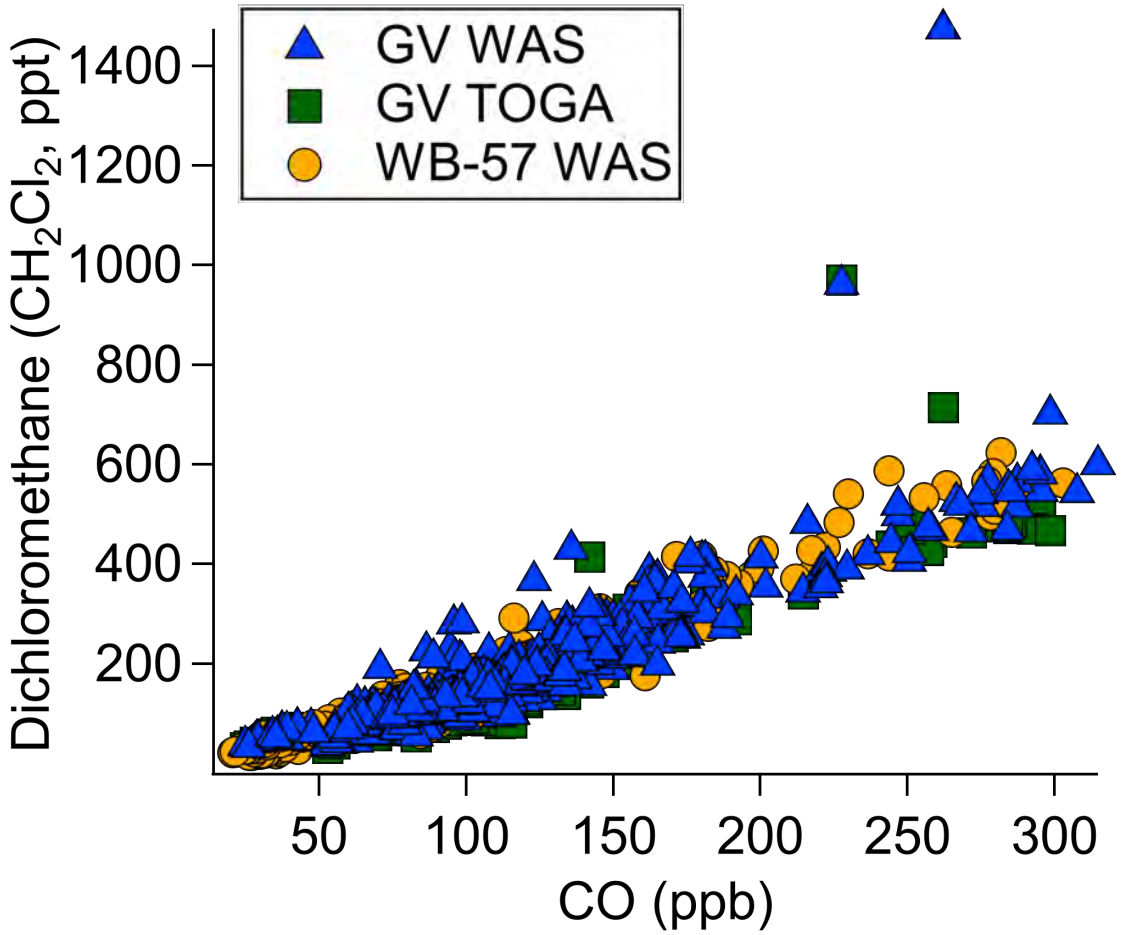


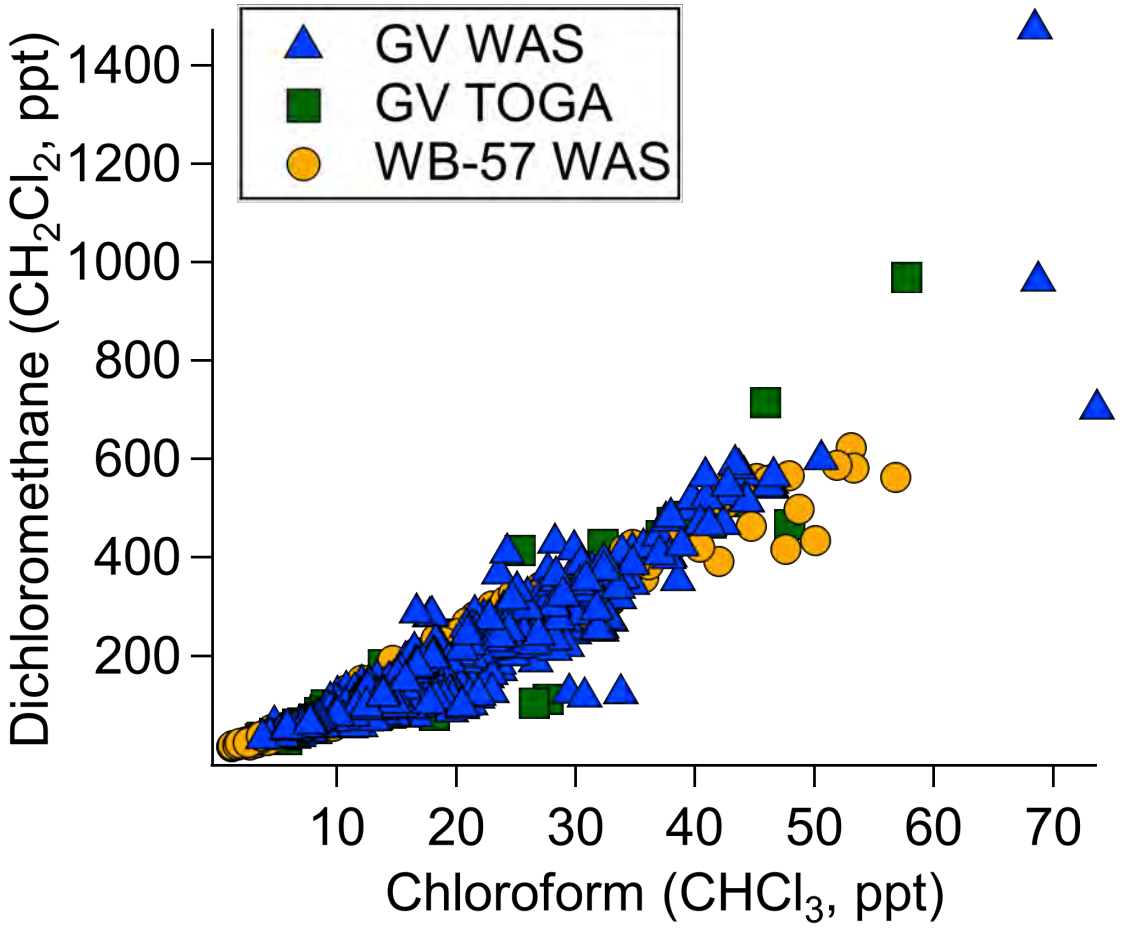


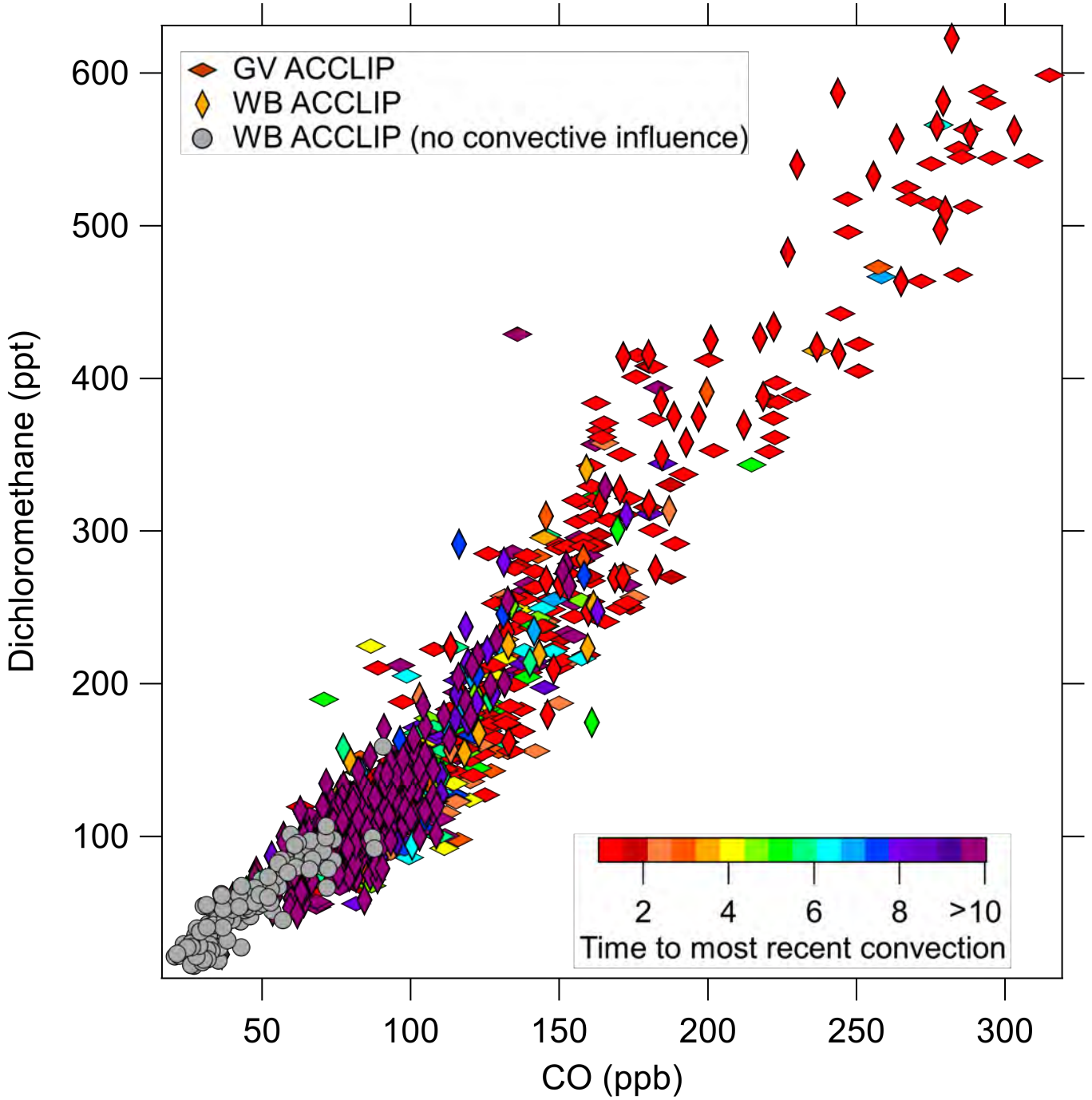
Time of Most Recent Convective Encounter for WAS samples higher than 500 hPa (5.5 km)



Campaign-wide high degrees of correlations in tracer relationships

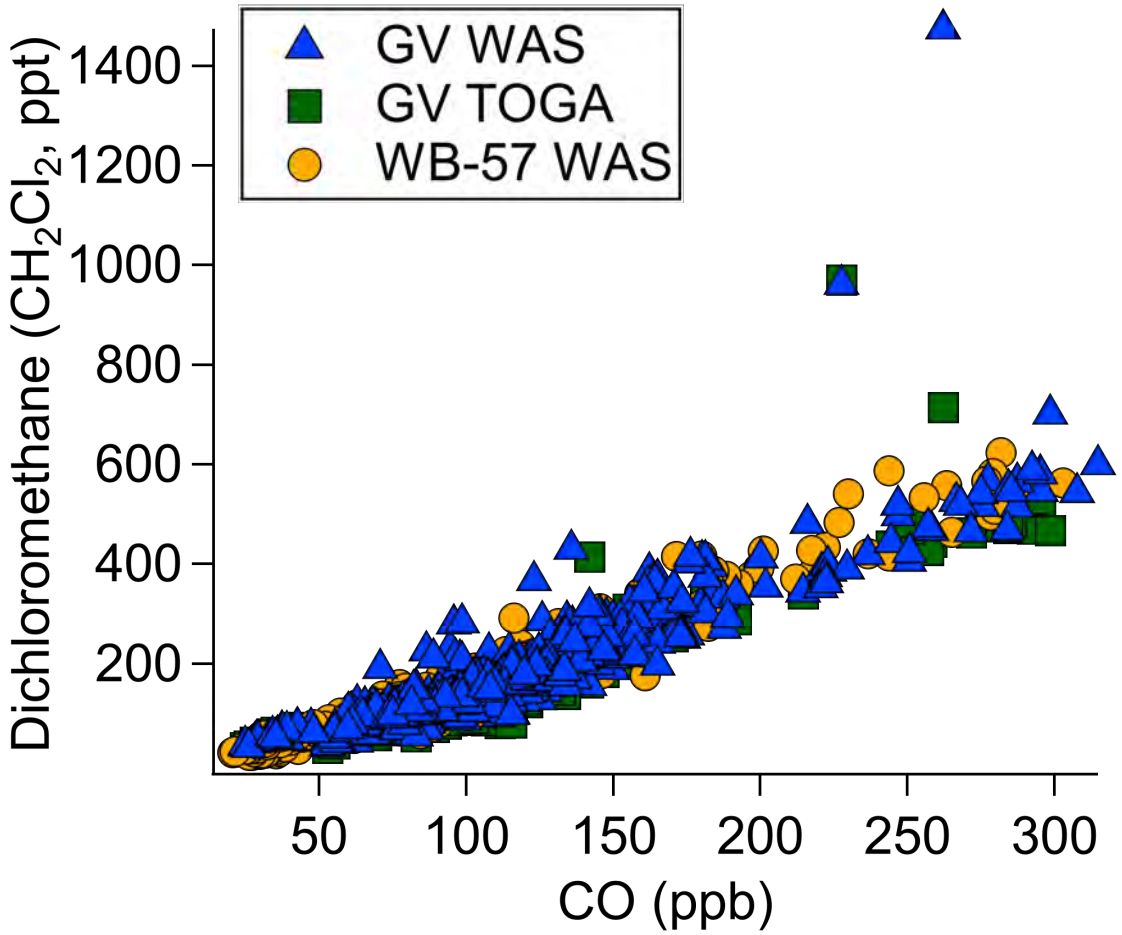


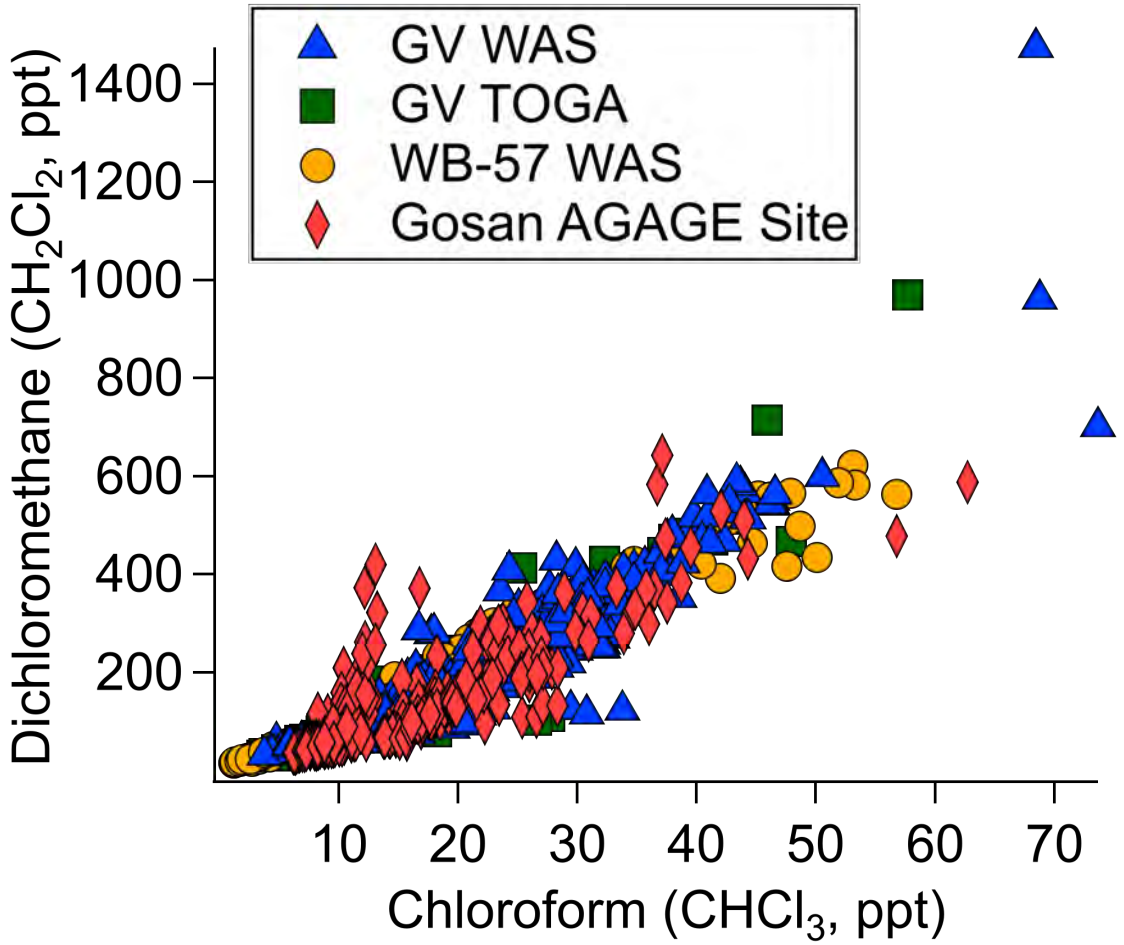




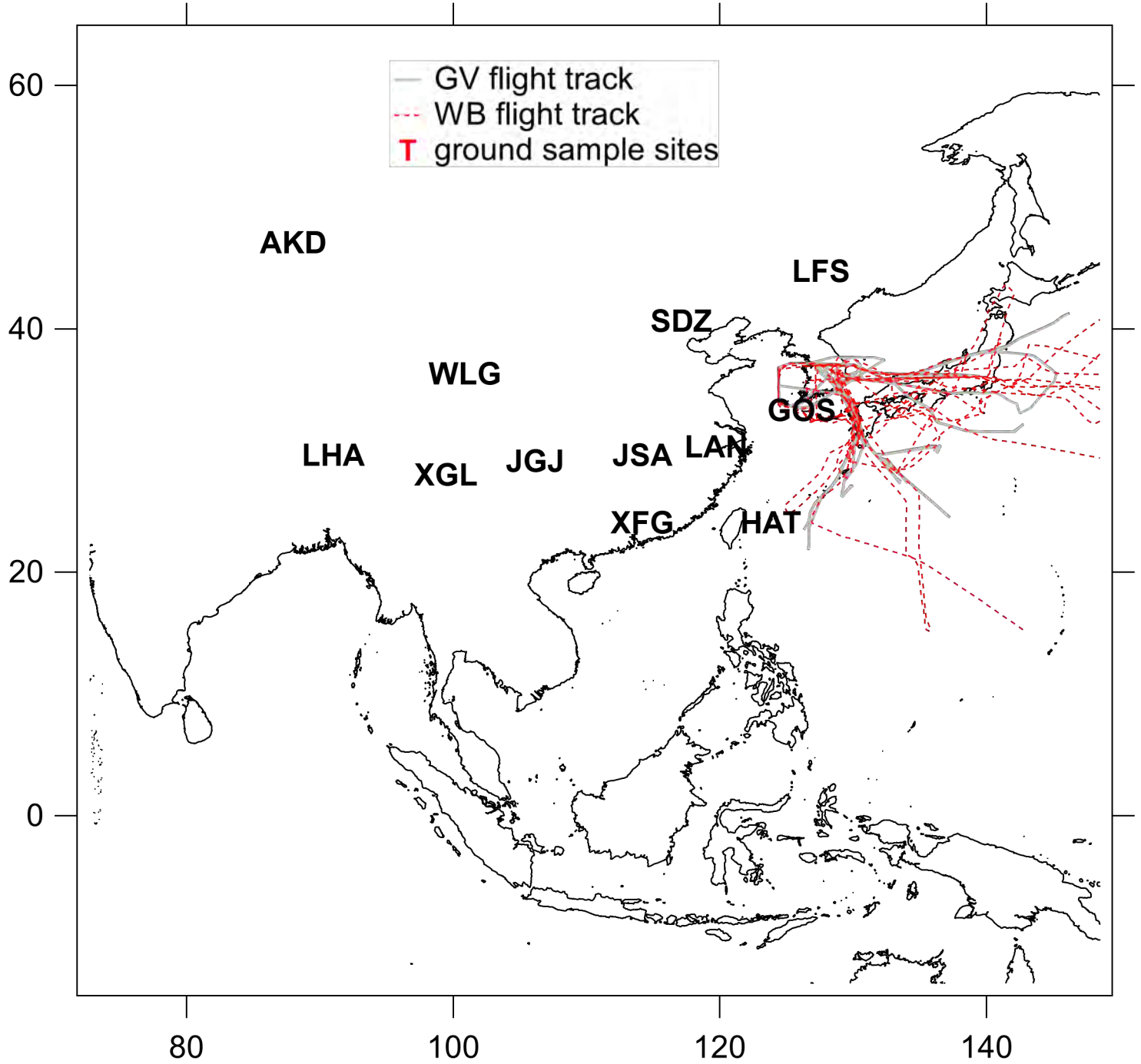
Recent convective influence (from E. China) dominates highest organic trace gas concentrations during ACCLIP

Campaign-wide high degrees of correlations in tracer relationships





Update! The GOSAN AGAGE site is ~100 km south of the Korean peninsula, 500 km northeast of Shanghai, China, and 250 km west of Kyushu, Japan.



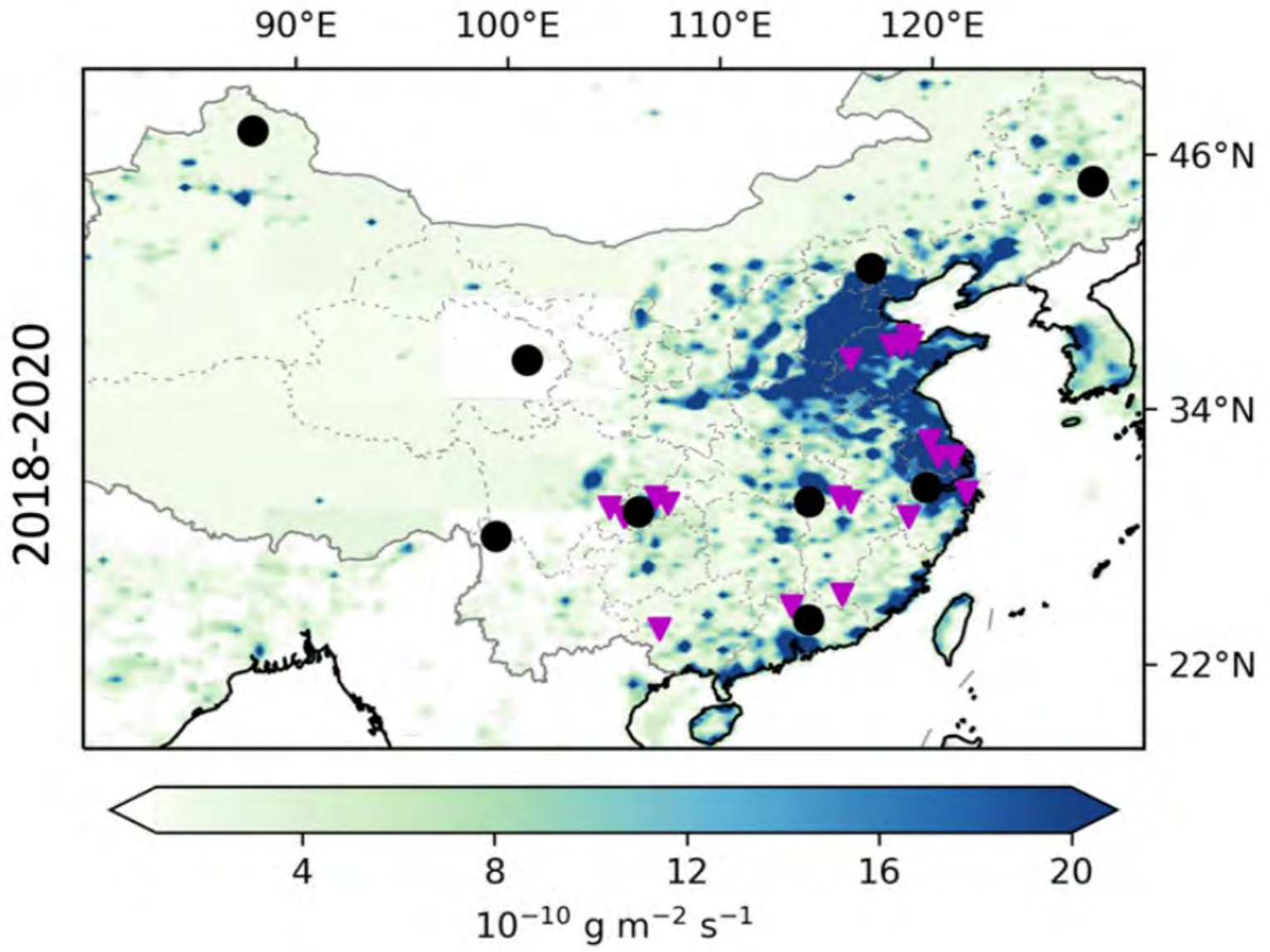
Ground Sites:

GOS: Gosan
(preliminary data from S. Park)

HAT: Hateruma Island
(prelim. data from T. Saito, S. Andrews)

China stations:
An et al. (2021, 2023)
Nat. Commun. 2021, 12 (1), 7279.
Environ. Sci. Technol. 2023, 57, 37, 13925–13936

Estimated chloroform emission in China (2018-2020)

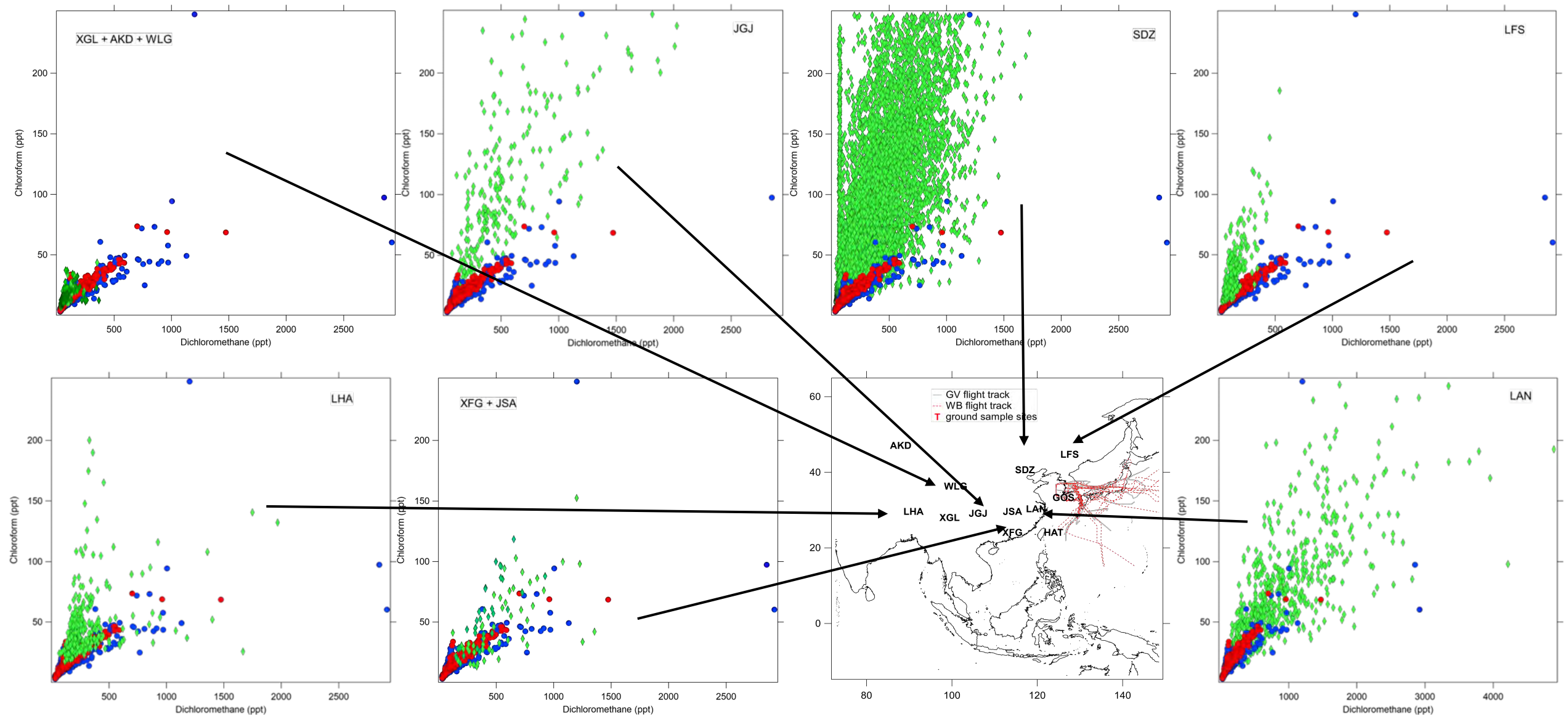


● = measurement site

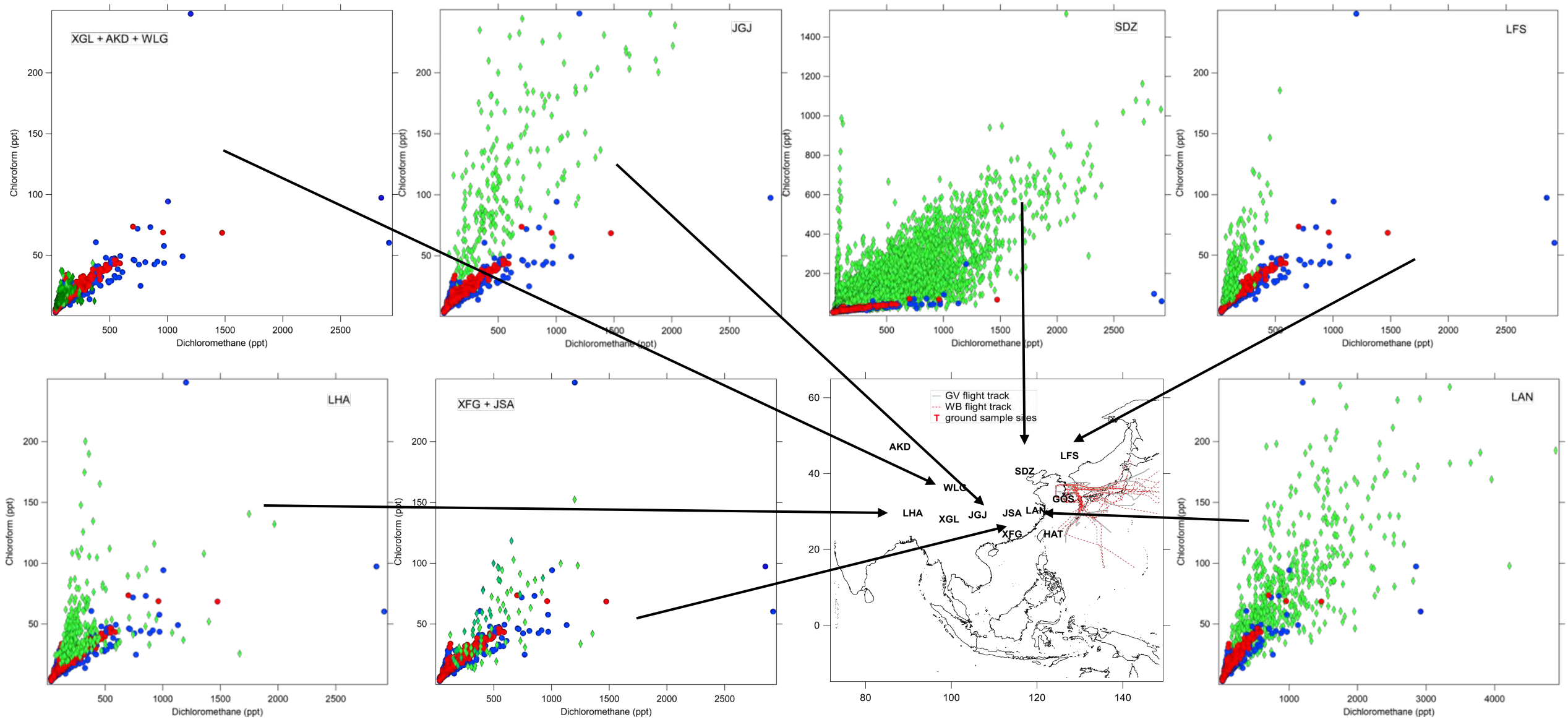
▼ = industrial source

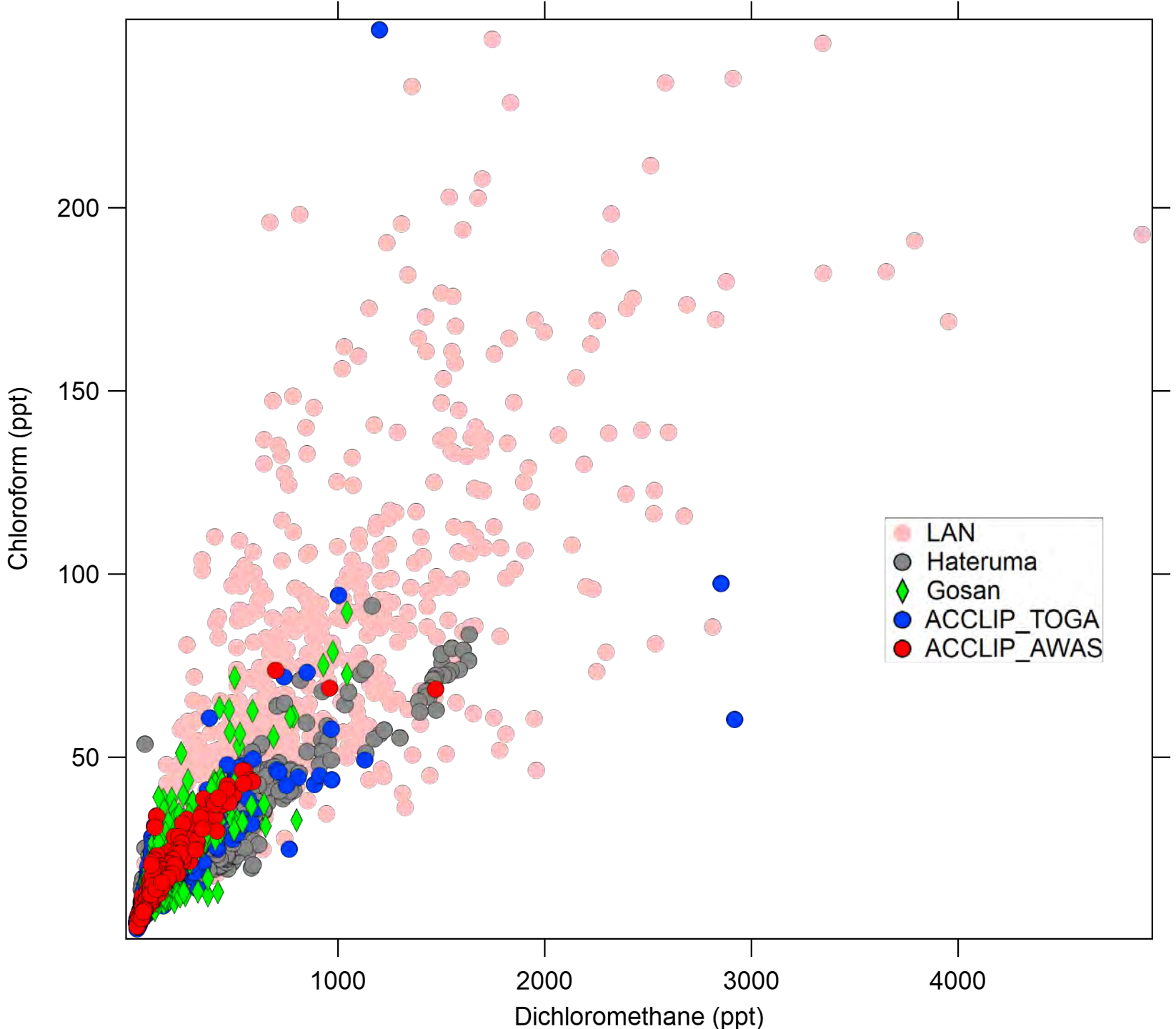
From An et al., 2023

$CHCl_3$:CH_2Cl_2 correlations: Surface and airborne



$CHCl_3$:CH_2Cl_2 correlations: Surface and airborne



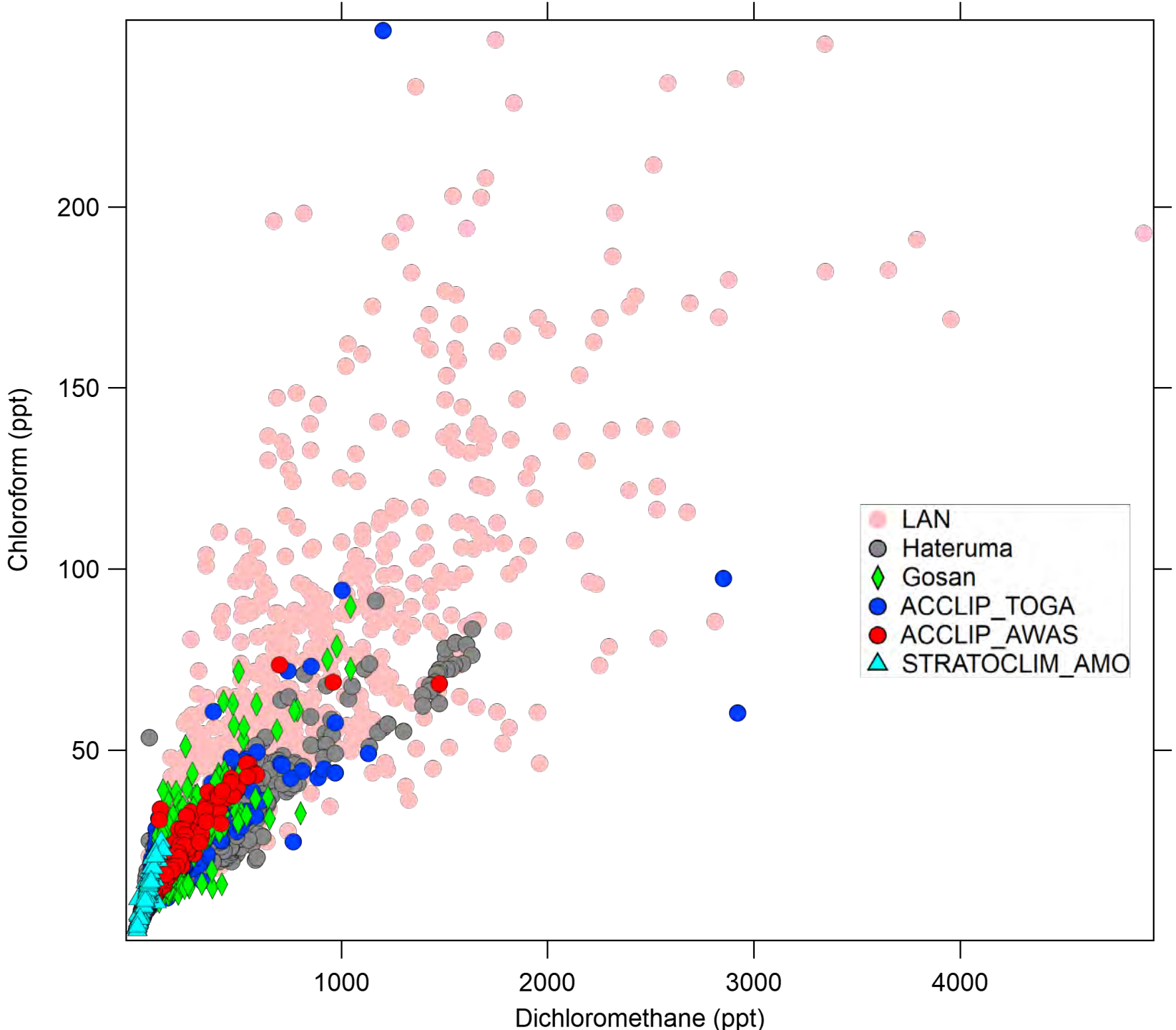


Similar tracer correlation of chloroform and dichloromethane observed in ACCLIP airborne measurements and at surface sites in E. China and offshore E. Asia.

Hateruma data: 2022 preliminary data, T. Saito.

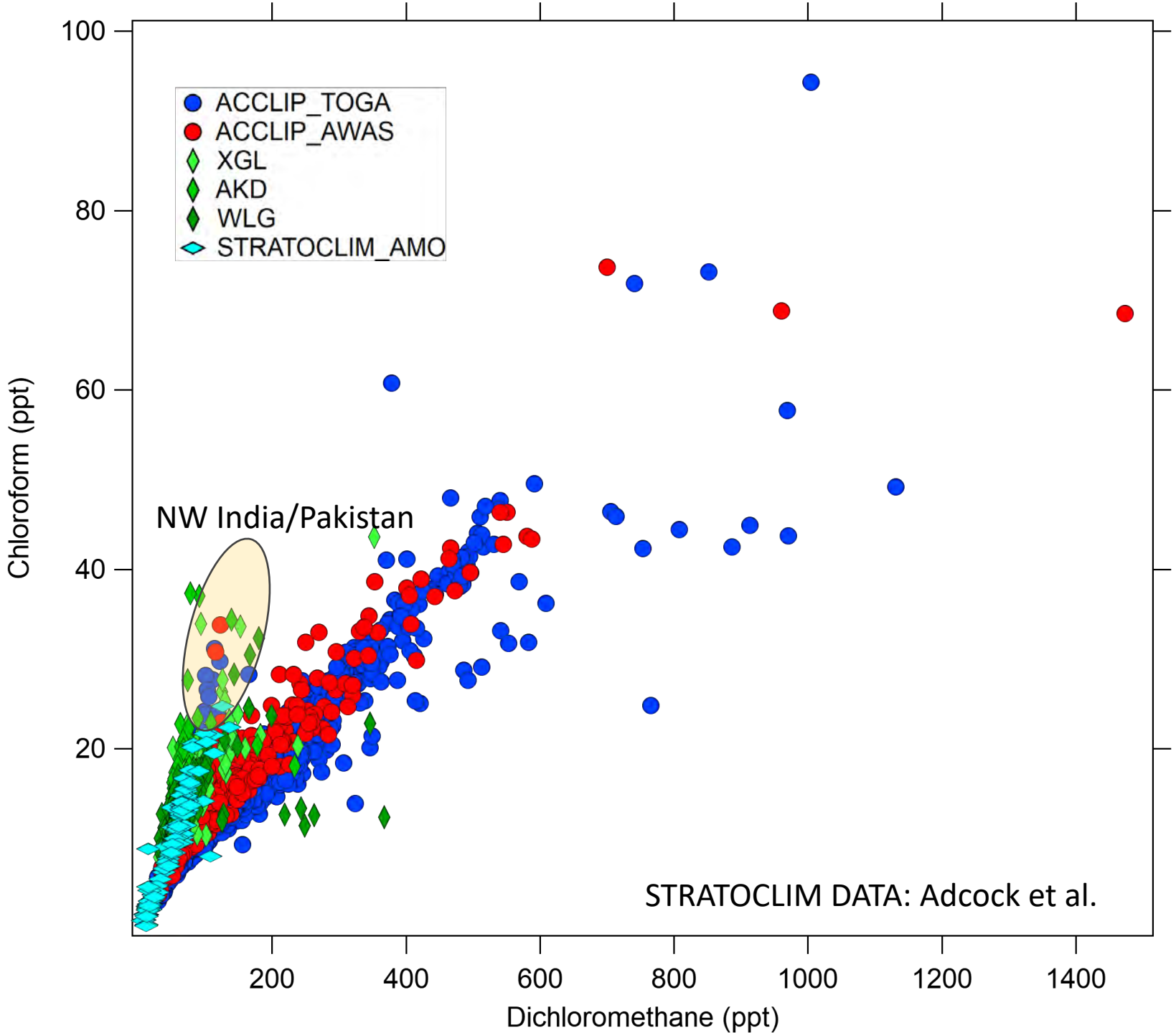
Gosan data: May-Sept., 2022, from S. Park and G. Lee

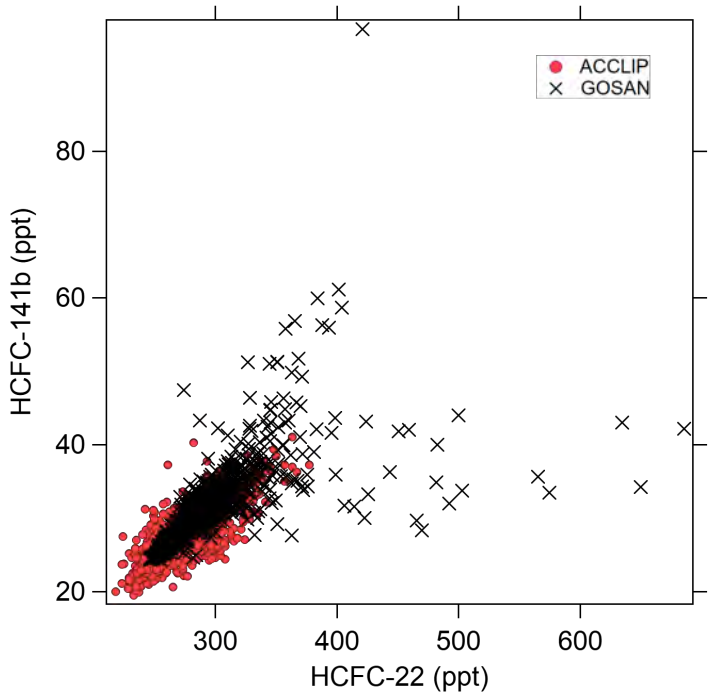
LAN data: An et al., 2021, 2023

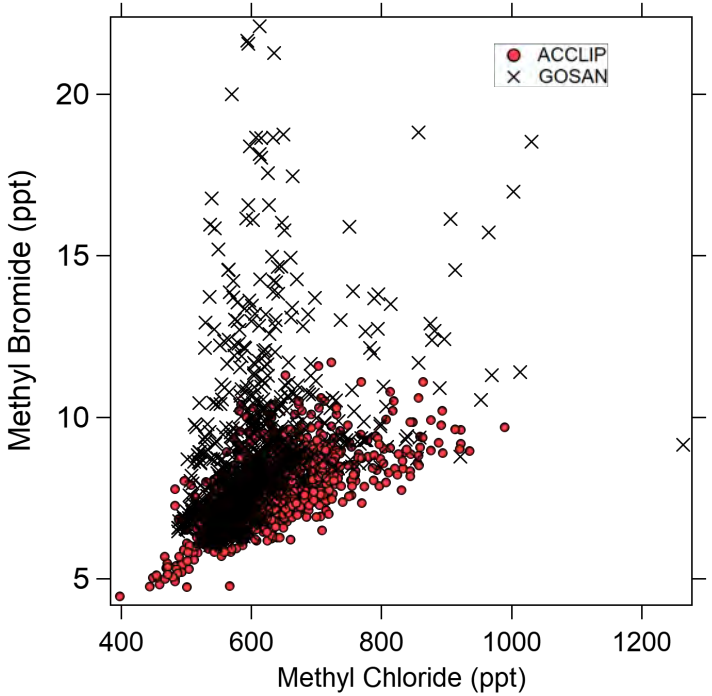


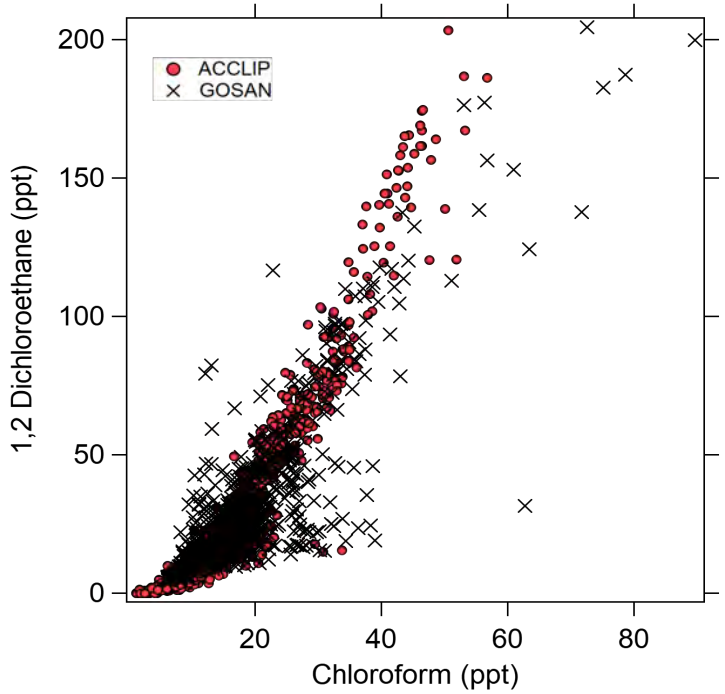
Similar tracer correlation of chloroform and dichloromethane observed in ACCLIP airborne measurements and at surface sites in E. China and offshore E. Asia.

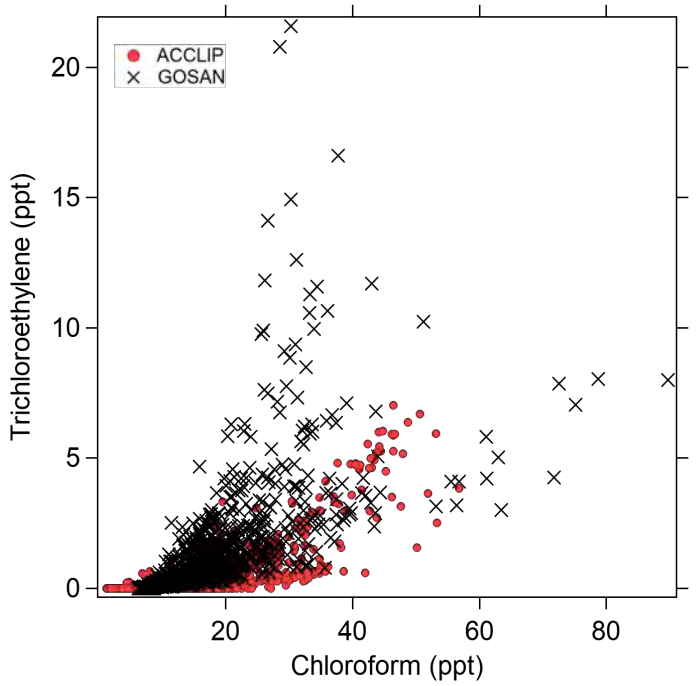
StratoClim data (2017) has reduced range and tracer correlation slope with higher $CHCl_3$:CH_2Cl_2.


ACCLIP_TOGA
ACCLIP_AWAS
XGL
AKD
WLG
STRATOCLIM_AMO
NW India/Pakistan
STRATOCLIM DATA: Adcock et al.
Chloroform (ppt)
Dichloromethane (ppt)
100
80
60
40
20
200
400
600
800
1000
1200
1400



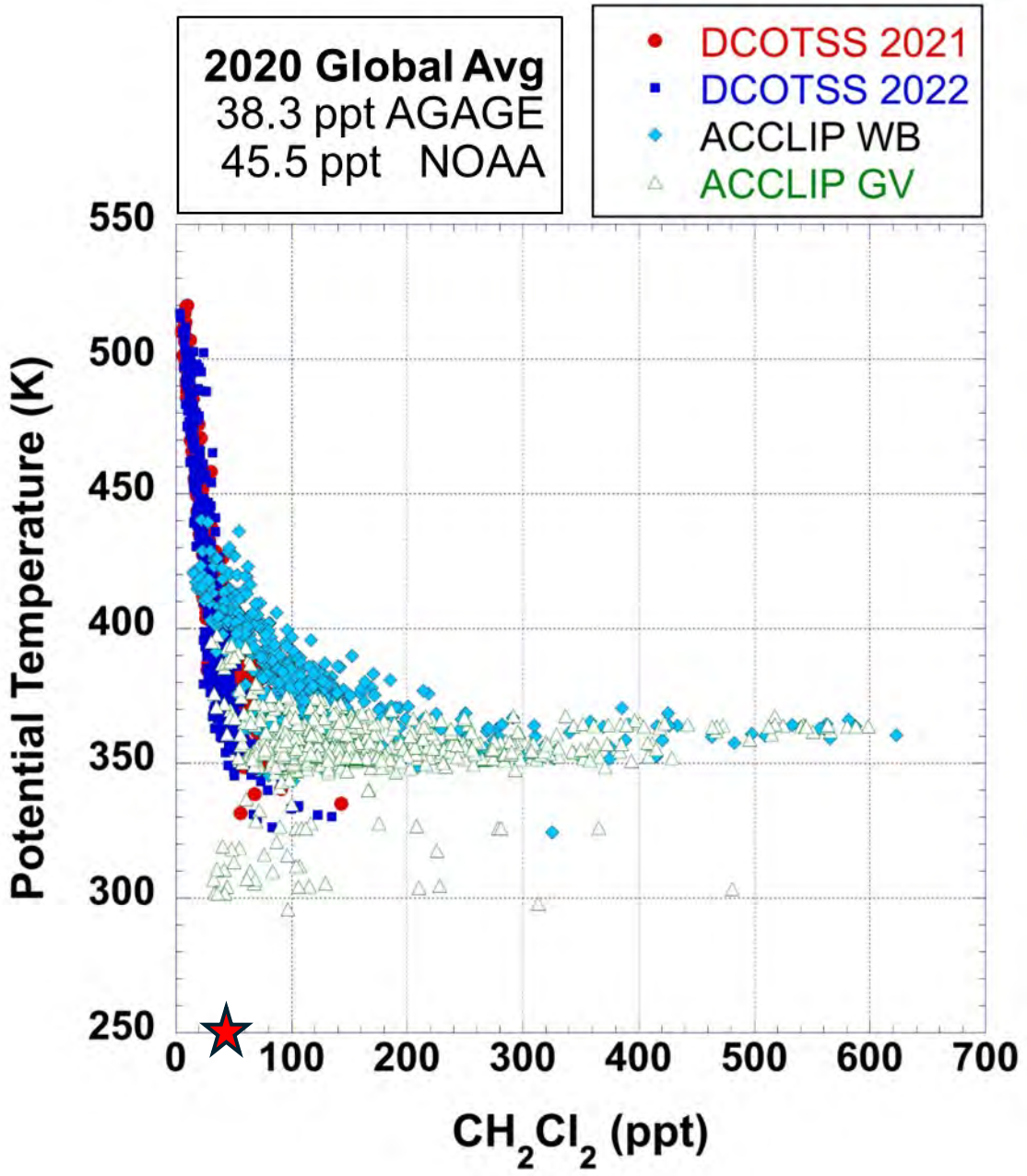


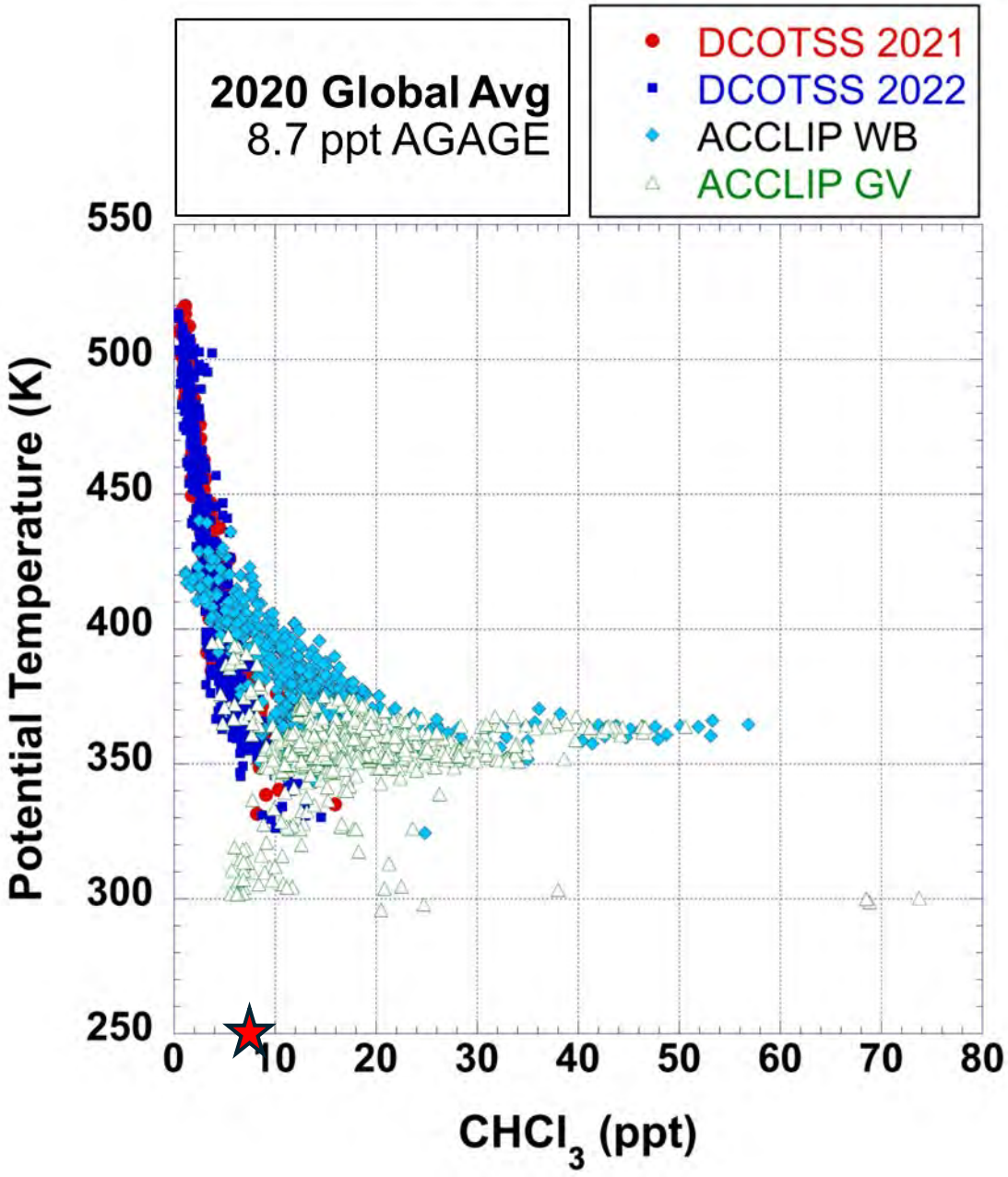


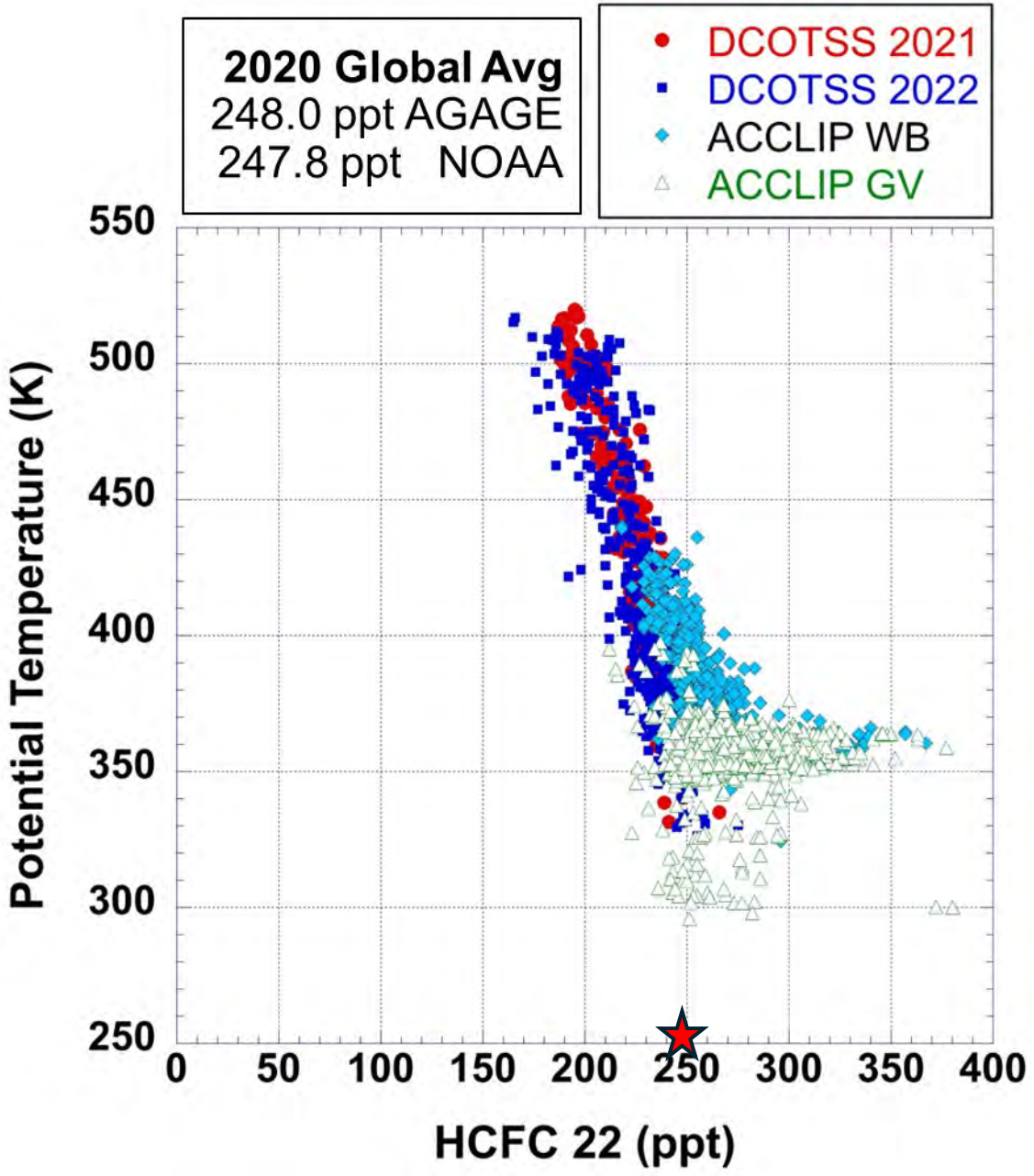


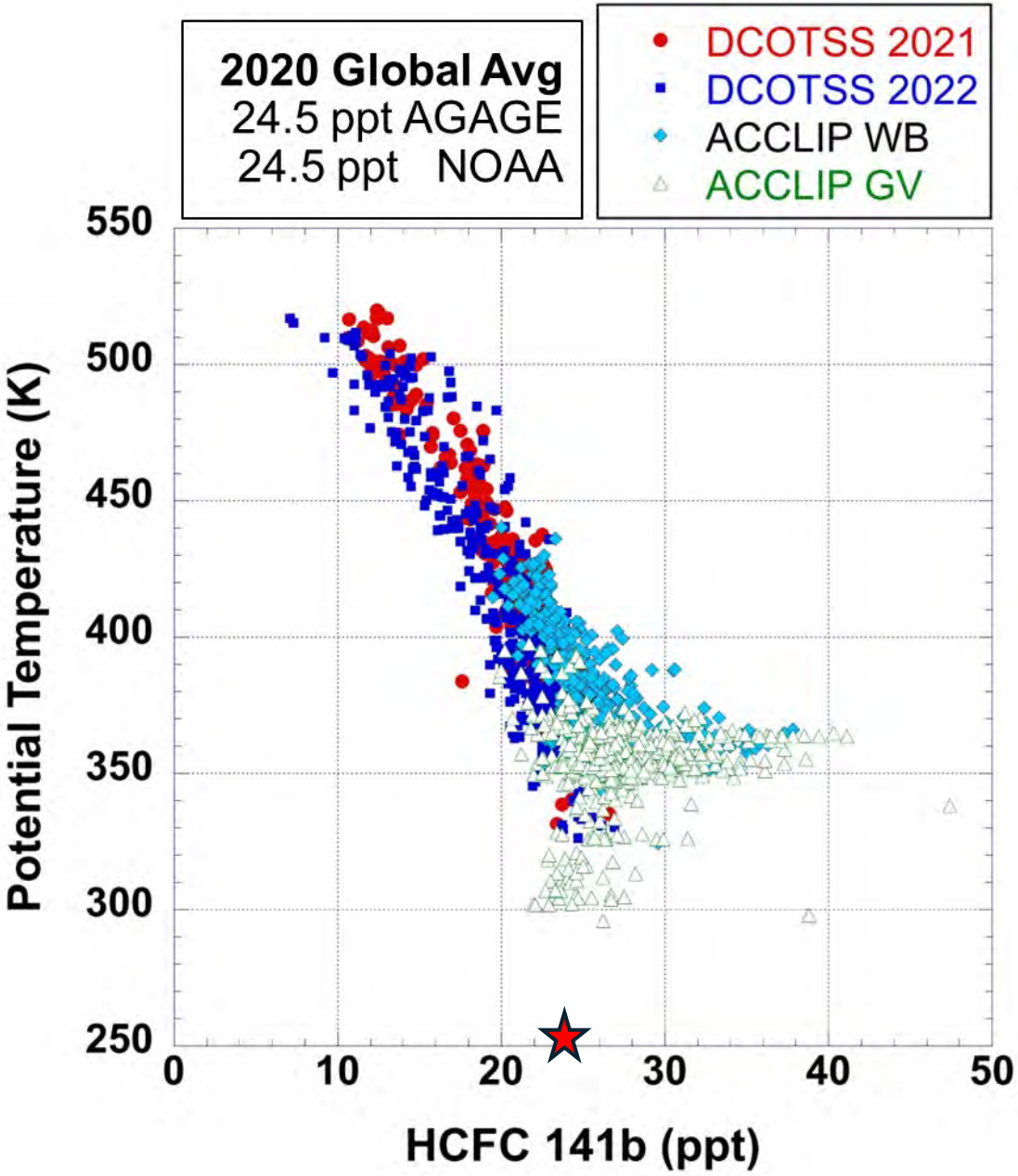
Comparison of trace gas correlations measured during ACCLIP (GV+WB) and at Gosan Island (May – Sept., 2022)*

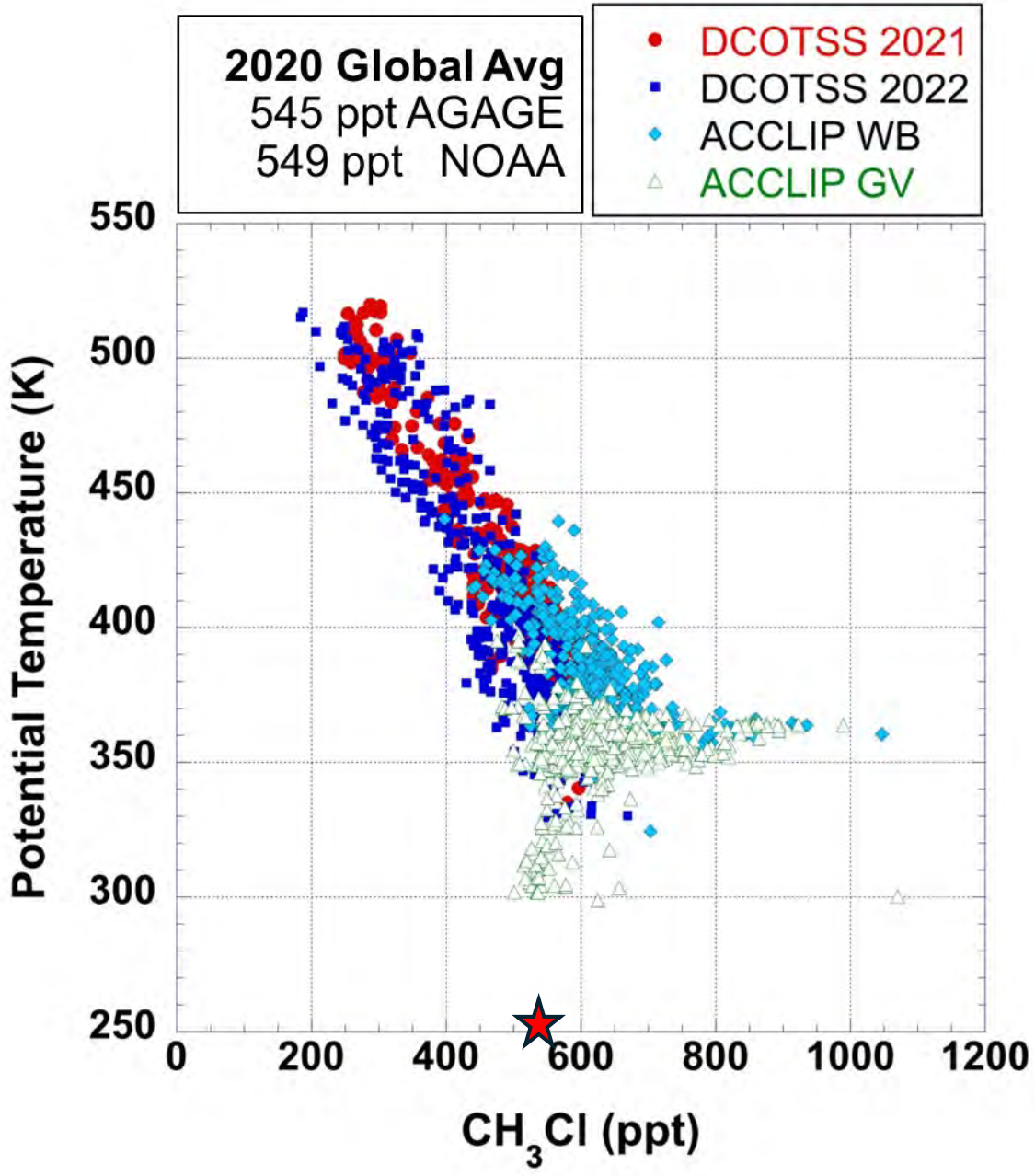
Gosan: **Preliminary** Data courtesy of S. Park and G. Lee

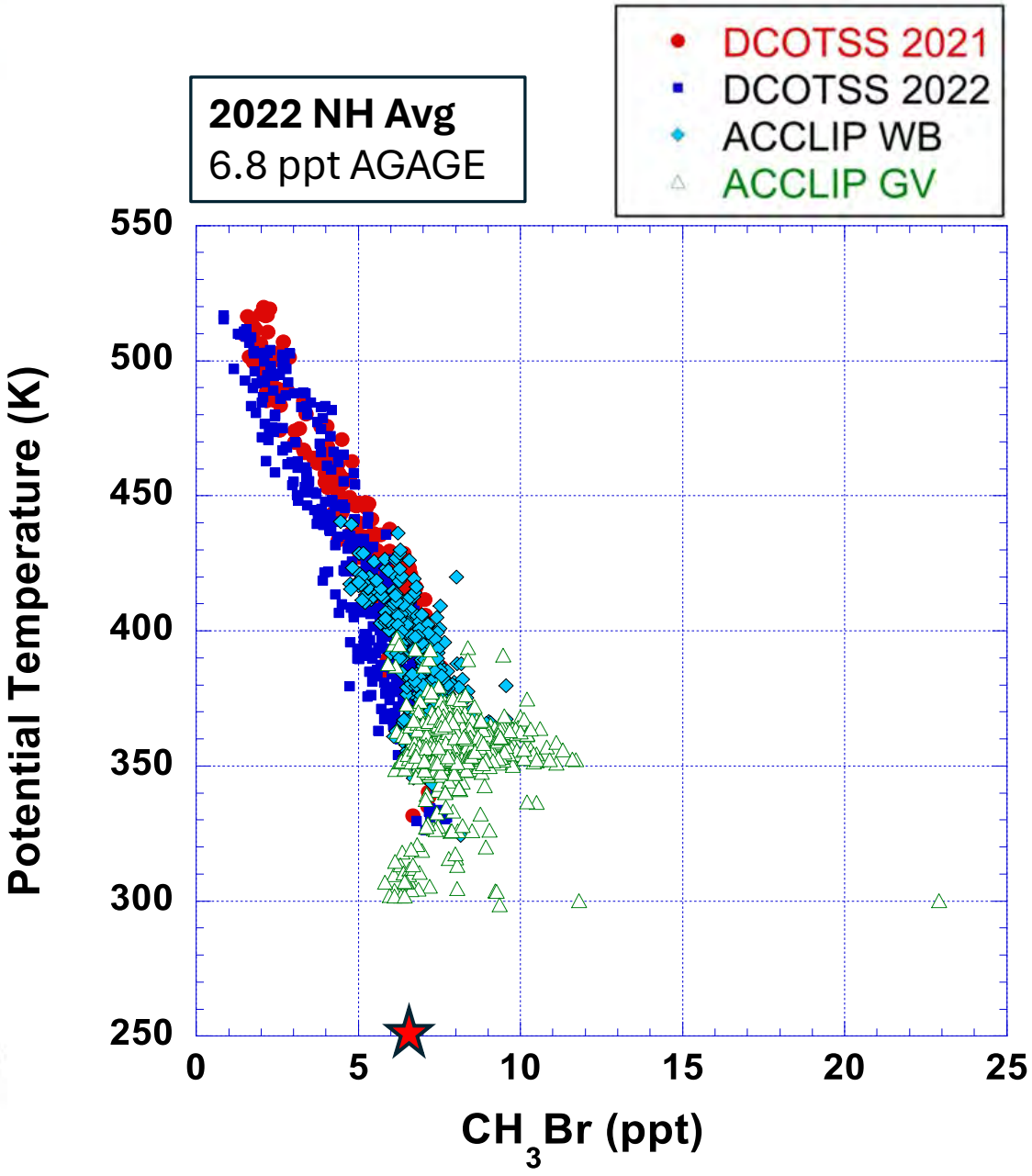

2020 Global Avg
38.3 ppt AGAGE
45.5 ppt NOAA
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
100
200
300
400
500
600
700
CH2Cl2 (ppt)


2020 Global Avg
8.7 ppt AGAGE
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
10
20
30
40
50
60
70
80
CHCl3 (ppt)

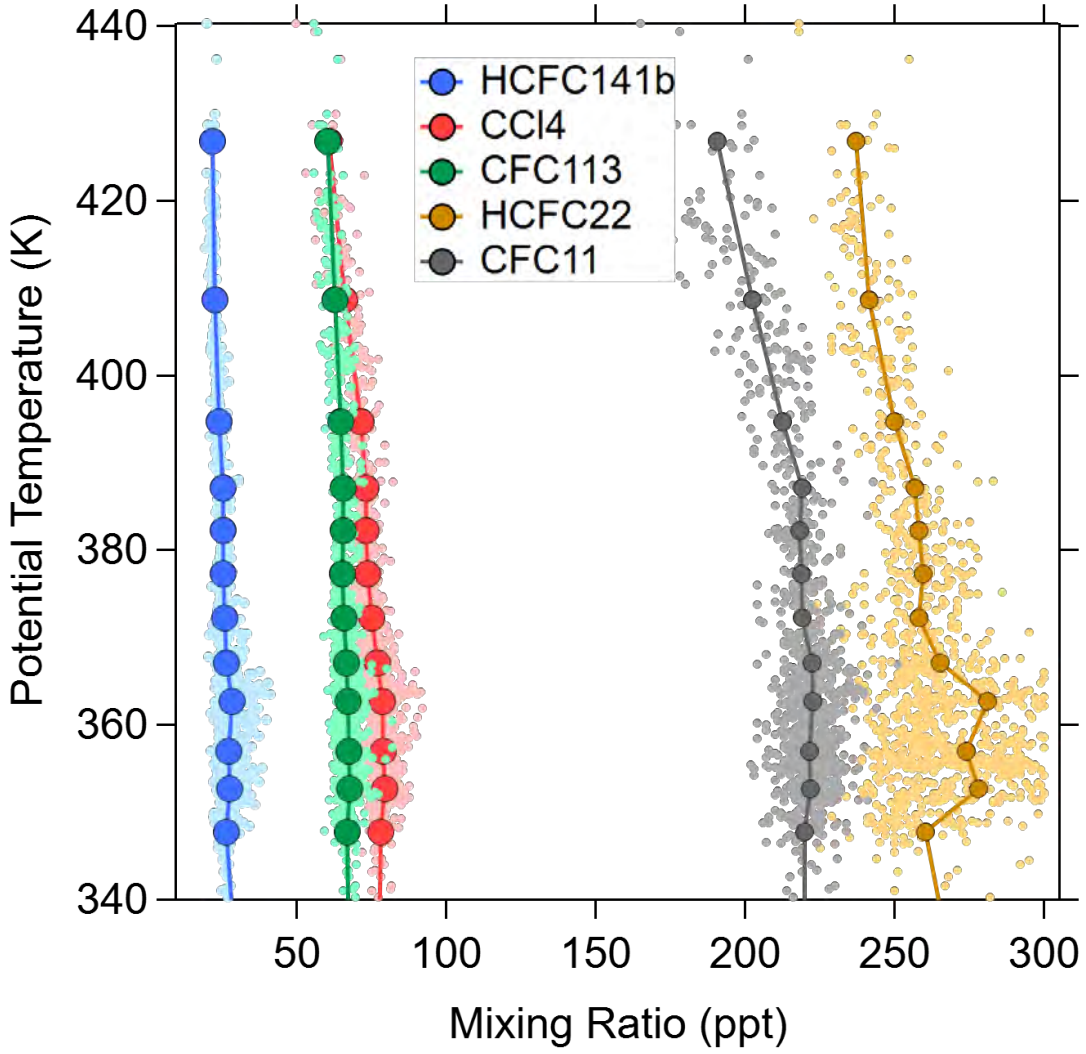

2020 Global Avg
248.0 ppt AGAGE
247.8 ppt NOAA
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
50
100
150
200
250
300
350
400
HCFC 22 (ppt)

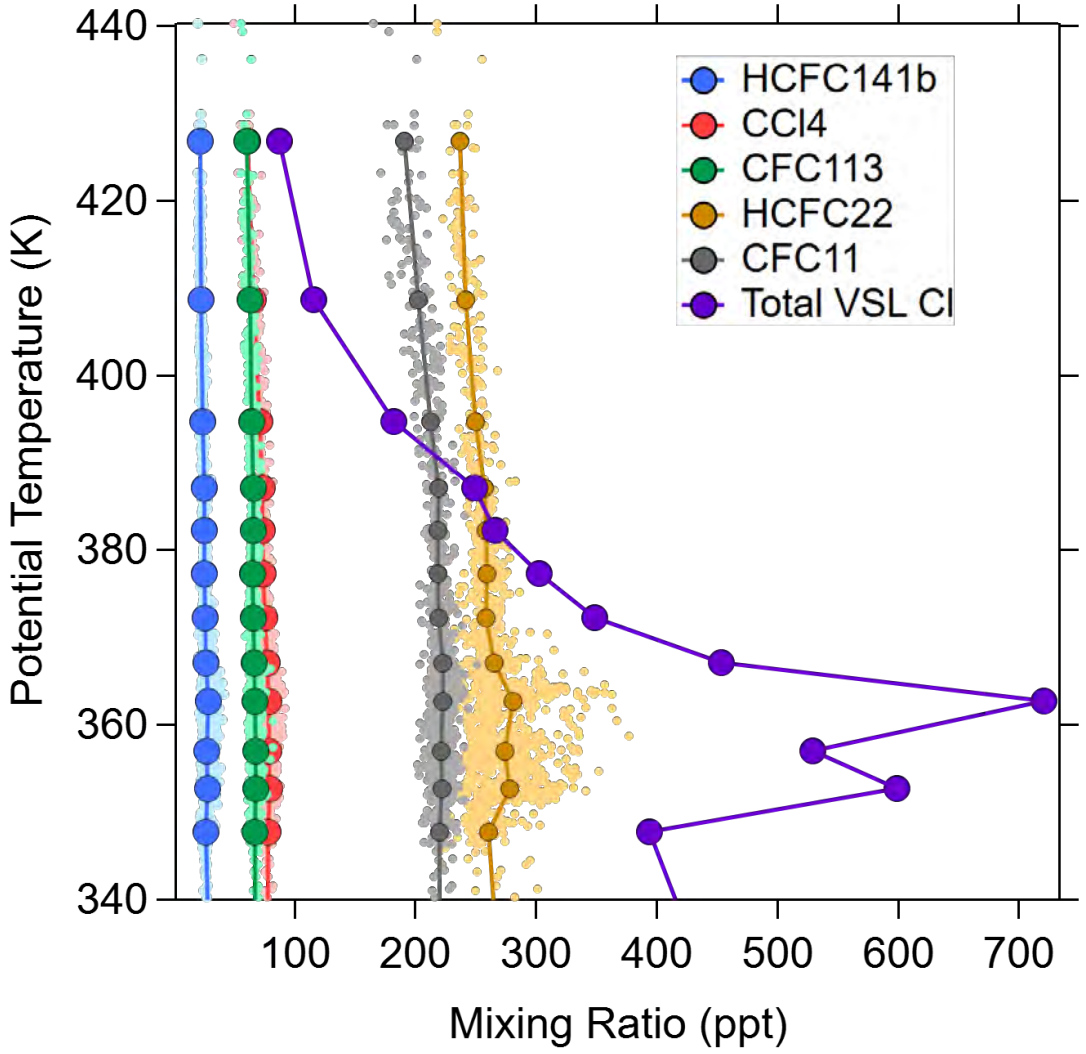

2020 Global Avg
24.5 ppt AGAGE
24.5 ppt NOAA
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
10
20
30
40
50
HCFC 141b (ppt)


2020 Global Avg
545 ppt AGAGE
549 ppt NOAA
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
200
400
600
800
1000
1200
CH3Cl (ppt)

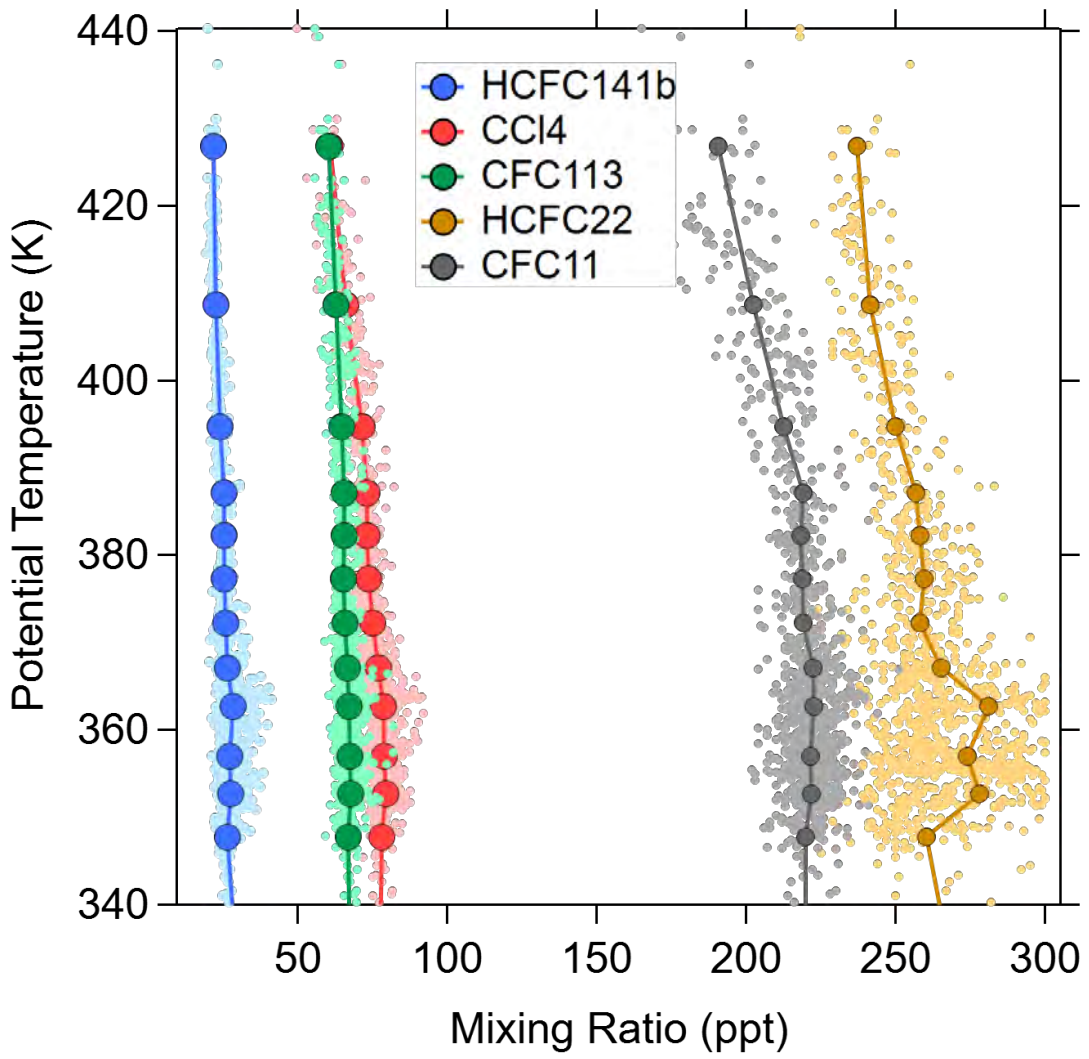

2022 NH Avg
6.8 ppt AGAGE
DCOTSS 2021
DCOTSS 2022
ACCLIP WB
ACCLIP GV
Potential Temperature (K)
550
500
450
400
350
300
250
0
5
10
15
20
25
CH3Br (ppt)

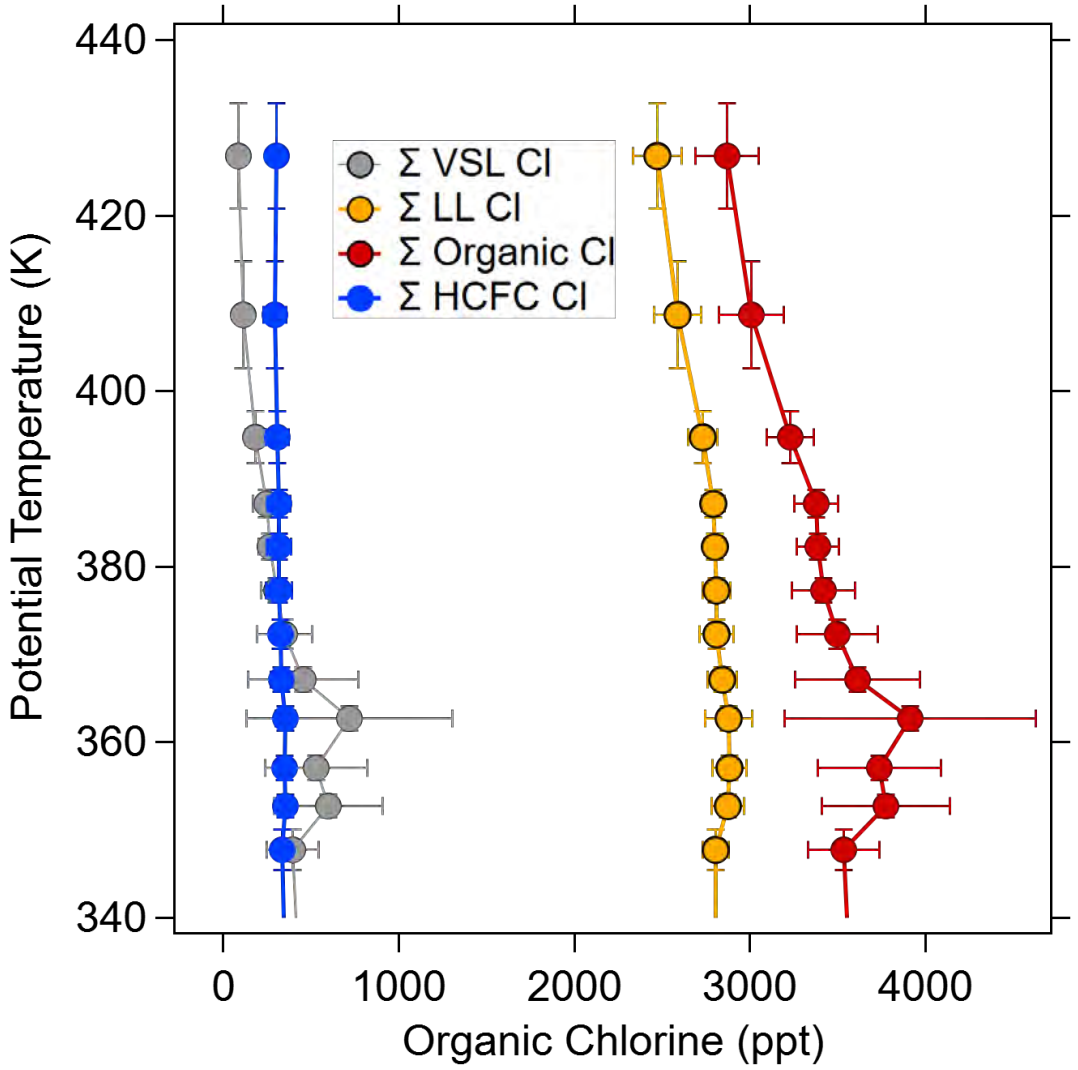
Selected halocarbon profiles vs potential temperature



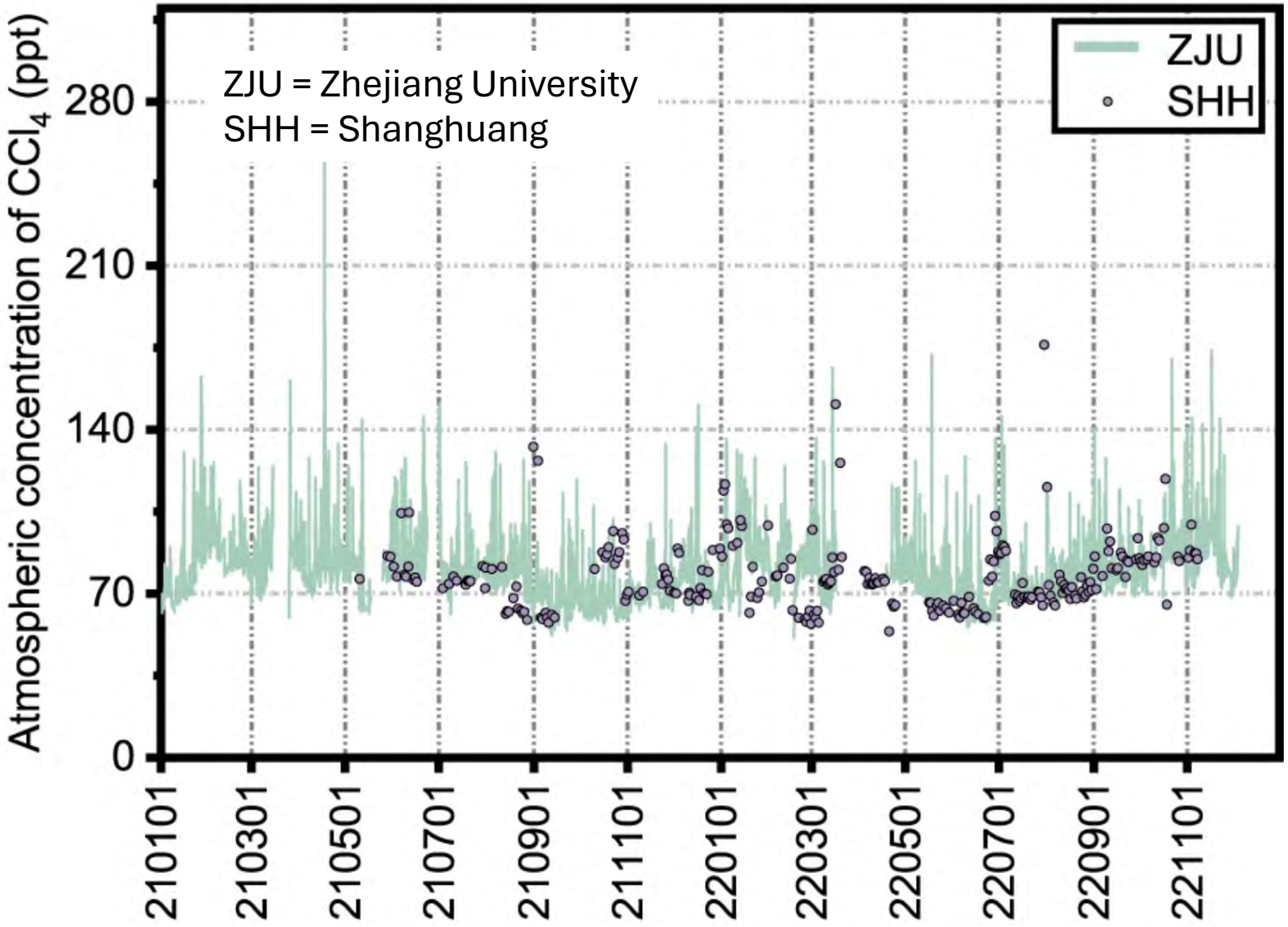


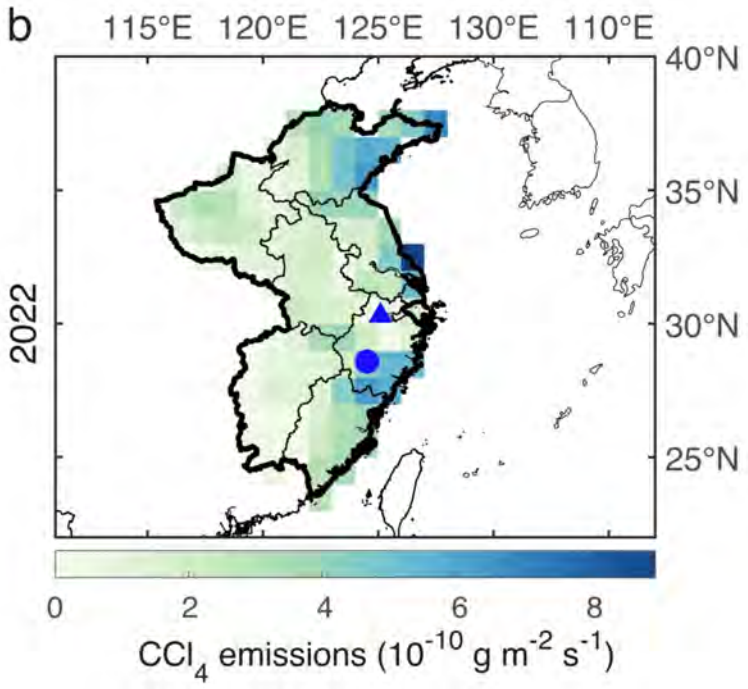
Selected and total organic chlorine profiles vs potential temperature





CCl_4 emissions in Eastern China





CCl_4 in 2022

ZJU = 80.0 -+14.6 ppt

SHH = 77.9 -+14.6 ppt

Li, B., Huang, J., Hu, X. et al. CCl4 emissions in eastern China during 2021–2022 and exploration of potential new sources. Nat. Commun. 15, 1725 (2024).

Binned averages of selected organic chlorine: comparison to NH background

Theta range	CFC11	CFC12	CFC113	CFC114	CH3CCl3	CCl4	CH3Cl	HCFC22	HCFC141b	HCFC142b
350-360	221.7	496.5	67.6	15.9	1.17	79.1	645.0	276.2	27.4	22.0
360-370	222.5	493.6	66.9	15.9	1.14	77.9	651.7	273.2	27.5	22.1
370-380	219.0	490.8	65.6	15.6	1.10	74.4	614.7	258.8	25.7	21.8
380-390	218.8	490.6	65.6	15.5	1.08	73.3	628.0	257.6	25.3	21.8
390-400	212.5	484.7	64.7	15.4	1.06	71.5	599.4	250.0	24.1	21.8
360-380	**220.8**	**492.2**	**66.3**	**15.7**	**1.12**	**76.1**	**633.2**	**266.0**	**26.6**	**21.9**
380-400	**216.7**	**488.6**	**65.3**	**15.5**	**1.08**	**72.7**	**618.5**	**255.1**	**24.9**	**21.8**
Background	*219.3*	*488.7*	*67.6*	*16.4**	*1.07*	*75.0*	*540.0*	*254.5*	*24.9*	*21.3*

Theta range	CFC11	CFC12	CFC113	CFC114	CH3CCl3	CCl4	CH3Cl	HCFC22	HCFC141b	HCFC142b
350-360	101%	102%	100%	97%	109%	105%	119%	109%	110%	103%
360-370	101%	101%	99%	97%	107%	104%	121%	107%	110%	104%
370-380	100%	100%	97%	95%	103%	99%	114%	102%	103%	102%
380-390	100%	100%	97%	94%	101%	98%	116%	101%	102%	102%
390-400	97%	99%	96%	94%	99%	95%	111%	98%	97%	102%
360-380	**101%**	**101%**	**98%**	**96%**	**105%**	**102%**	**117%**	**105%**	**107%**	**103%**
380-400	**99%**	**100%**	**97%**	**94%**	**100%**	**97%**	**115%**	**100%**	**100%**	**102%**

Binned averages of organic halogen groups: comparison to NH background

Theta range	LL_Cl	HCFC_Cl	VSL_Cl	TOT_Cl		CH3Br	Halon_Br	VSL_Br	TOT_Br
350-360	2877	351	564	3756		8.13	7.36	4.29	19.6
360-370	2862	342	587	3762		7.79	7.16	3.47	18.2
370-380	2809	321	326	3460		7.42	7.13	1.94	16.4
380-390	2796	318	258	3380		7.24	6.94	1.33	15.5
390-400	2730	307	182	3229		6.88	6.73	0.96	14.6
360-380	**2835**	**332**	**456**	**3611**		**7.61**	**7.14**	**2.71**	**17.3**
380-400	**2774**	**314**	**232**	**3330**		**7.12**	**6.87**	**1.21**	**15.2**
Background	2735	321	118	3240		6.80	7.30	5.00	18.9

Theta range	LL_Cl	HCFC_Cl	VSL_Cl	TOT_Cl		CH3Br	TOT_Halons	VSL_Br	TOT_Br
350-360	105%	109%	478%	116%		120%	101%	86%	104%
360-370	105%	107%	498%	116%		115%	98%	69%	96%
370-380	103%	100%	276%	107%		109%	98%	39%	87%
380-390	102%	99%	218%	104%		106%	95%	27%	82%
390-400	100%	96%	154%	100%		101%	92%	19%	77%
360-380	**104%**	**103%**	**387%**	**111%**		**112%**	**98%**	**54%**	**92%**
380-400	**101%**	**98%**	**197%**	**103%**		**105%**	**94%**	**24%**	**81%**

Summary

- Many organic trace gases measured during ACCLIP show strong correlations.
  - Slope determined by relative emissions and loss/mixing processes
  - Time to convective influence a major factor for land based convection
  - For $CHCl_3$:CH_2Cl_2, ACCLIP correlation slope and range similar to ground sites at Gosan and Hateruma, but different from sites in NE and W. China (Lhasa exception?)
- VSL-Cl observations are a major perturbation to Cl budget
  - HCFCs and methyl halides also show effect of recent convection
  - On average, methyl chloride enhancements add about 90 ppt Cl to total organic chlorine budget in the UT