

NOAA-GMD HIPPO data past and future: transport and chemistry in the troposphere. (HIPPO-NOAA-GMD Rack Data Set)

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PANTHER: (PAN and other Trace Hydrohalocarbon Experiment,) 200 lb., 6-channel GC (gas chromatograph).

- * 3 ECD (electron capture detectors), packed columns.
- * 1 ECD with a TE (thermal electric) cooled RTX-200 capillary column.
- * 2-channel MSD (mass selective detector). 2 independent samples concentrated onto TE cooled Haysep traps, two temp programmed RTX-624 capillary columns.
- * Tunable diode laser hygrometer (May Comm Inst.)

Measures: H₂O, N₂O, SF₆, CCl₂F₂ (CFC-12), CCl₃F (CFC-11), CBrClF₂ (halon-1211), H₂, CH₄, CO, PAN (peroxyl acetyl nitrate), methyl halides CH₃I, CH₃Br, CH₃Cl, the sulfur compounds COS, CS₂, hydrochlorofluorocarbons CHClF₂ (HCFC-22), C₂H₃Cl₂F (HCFC-141b), C₂H₃ClF₂ (HCFC-142b), and hydrofluorocarbon C₂H₂F₄ (HFC-134a)



UCATS: (Unmanned aircraft systems Chromatograph for Atmospheric Trace Species), 60 lb. GC, TDL and Photometer.

- * 2-Channel ECD GC, packed columns.
- * Tunable diode laser hygrometer (May Comm Inst.)
- * Dual-beam ozone photometer (2B Inst.)

Measures: N₂O, SF₆, H₂, CH₄, CO, O₃ and H₂O.



NWAS: (NOAA Whole Air Sampler) 20 lb. per 12 flask pkg., 2 to 4 NWAS pkg per flight, 6 in rack.

- * Total > 48 flask per flight, 6 flasks per profile. [2 to 4 NWAS pkg +2 AWAS-Elliot Atlas]
- * MSD (analysis by HATS/ESRL flask lab - Steve Montzka *et al.*)
- * ECD, NDIR, FID and RGA (analysis by CCGG/ESRL flask lab - Pat Lang *et al.*)
- * MSD (analysis by INSTARR/CU isotopes flask lab - James White *et al.*)

Measures: CO, CO₂, CH₄ and isotopes, H₂, SF₆, N₂O, tetrachloroethylene (C₂Cl₄), CCl₄, CFC-11, CFC-12, CFC-13, CFC-113, CFC-114, CFC-115, HCFC-22, HCFC-124, HCFC-141b, HCFC-142b, HCFC-227ea, HFC-23, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-365mfc, halon-1211, halon-1301, halon-2402, chloroform (CHCl₃), methyl chloroform (CH₃CCl₃), chloroethane (CH₃CH₂Cl), dichloromethane (CH₂Cl₂), methyl halides (CH₃Cl, CH₃I, CH₃Br), bromoform (CHBr₃), dibromomethane (CH₂Br₂), acetylene (C₂H₂), propane (C₃H₈), benzene (C₆H₆), perfluoropropane (PFC-218), iso-pentane (C₅H₁₂), n-butane (C₄H₁₀), n-pentane (C₅H₁₂), n-hexane (C₆H₁₄), carbonyl sulfide (OCS), and carbon disulfide (CS₂).



Overview

Classify the HIPPO data set:

Location of tracer gradient.

Stratosphere

Troposphere

Inter Hemispheric

Source of the tracer gradient.

Growth

Photolysis

OH and more...

Relate this to >> how the data set is and can be used.

Stratospheric Tracers: Long lived

	~ strat lifetime (years)	
CO ₂	> 500	} Growth >> <u>age</u> of stratospheric air and transport <u>time scales</u> .
SF ₆	> 500	
CFC-115	> 500	} Photolytic Loss >> distributed mass flux and chemistry
CFC-13	> 500	
N ₂ O	~ 120	
CFC-12	~ 100	
CFC-113	~ 85	
halon-1301	~ 65	
<u>CFC-11</u>	<u>~ 50</u>	
CCl ₄	~ 35	
halon-2402	~ 20	
halon-1211	~ 16	
O ₃ (stratospheric sources)		<u>CFC-11</u> and <u>O₃</u> best signal to noise stratospheric signature in trop

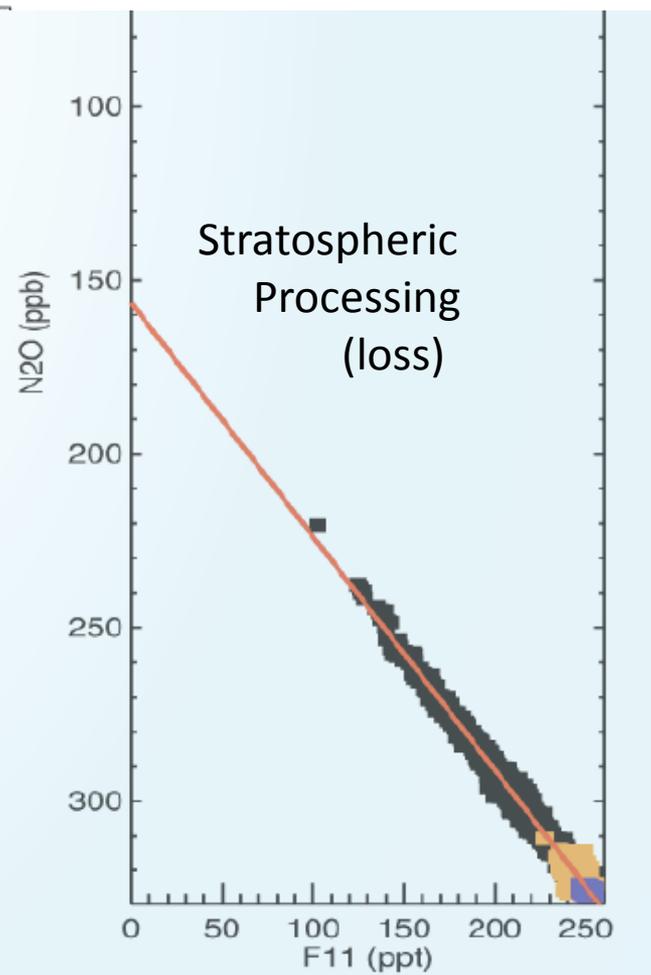
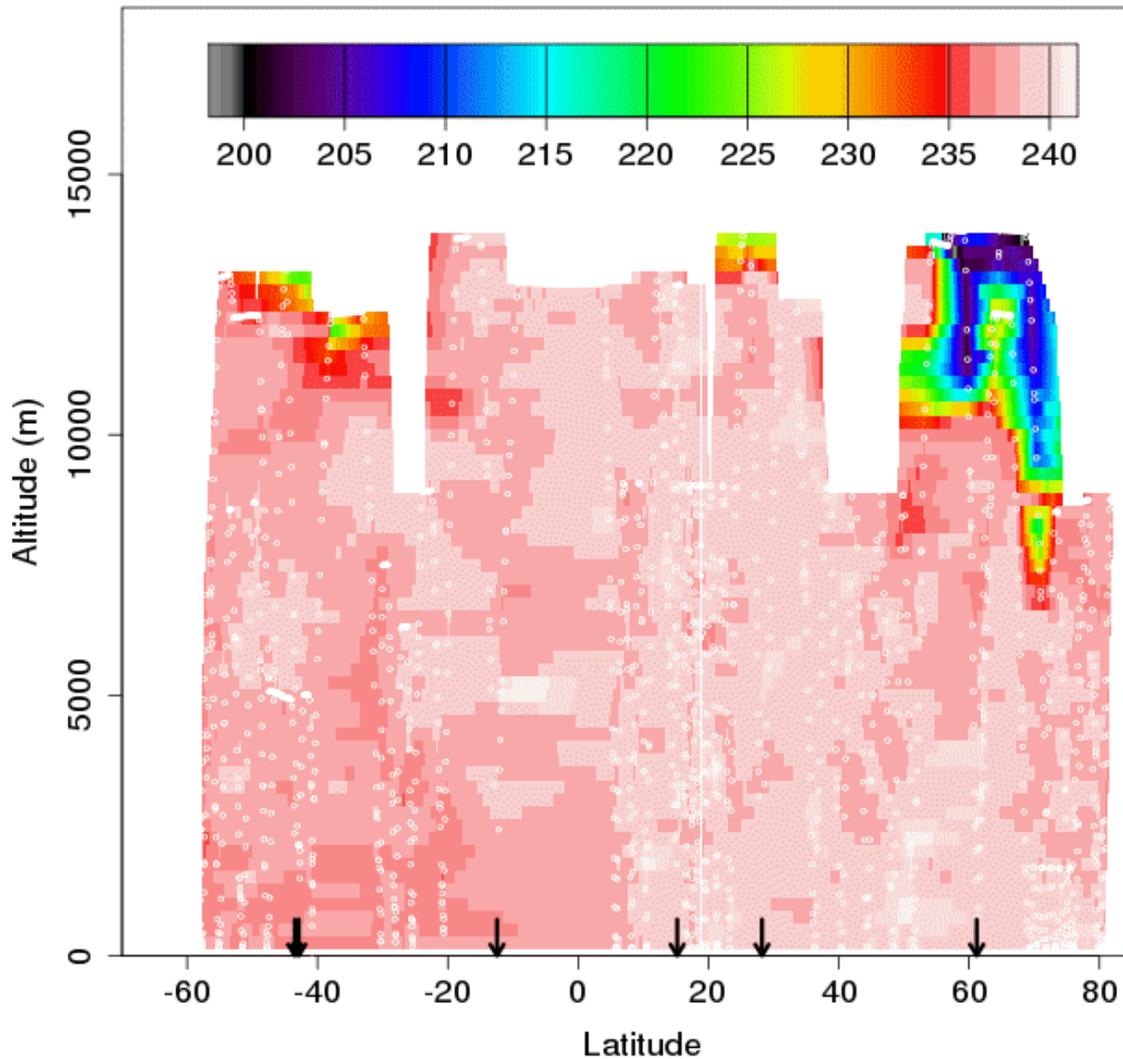
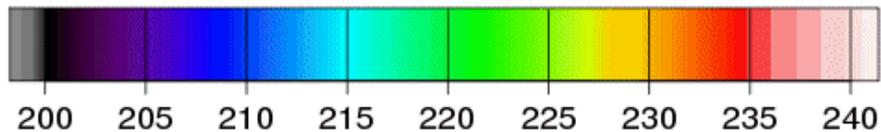
CFC-11 strat-signature in the troposphere will only mix back up to tropospheric value.

O₃ strat-signature can chemically equilibrate back to troposphere values < 20 days.

HIPPO4 Northbound CFC_11

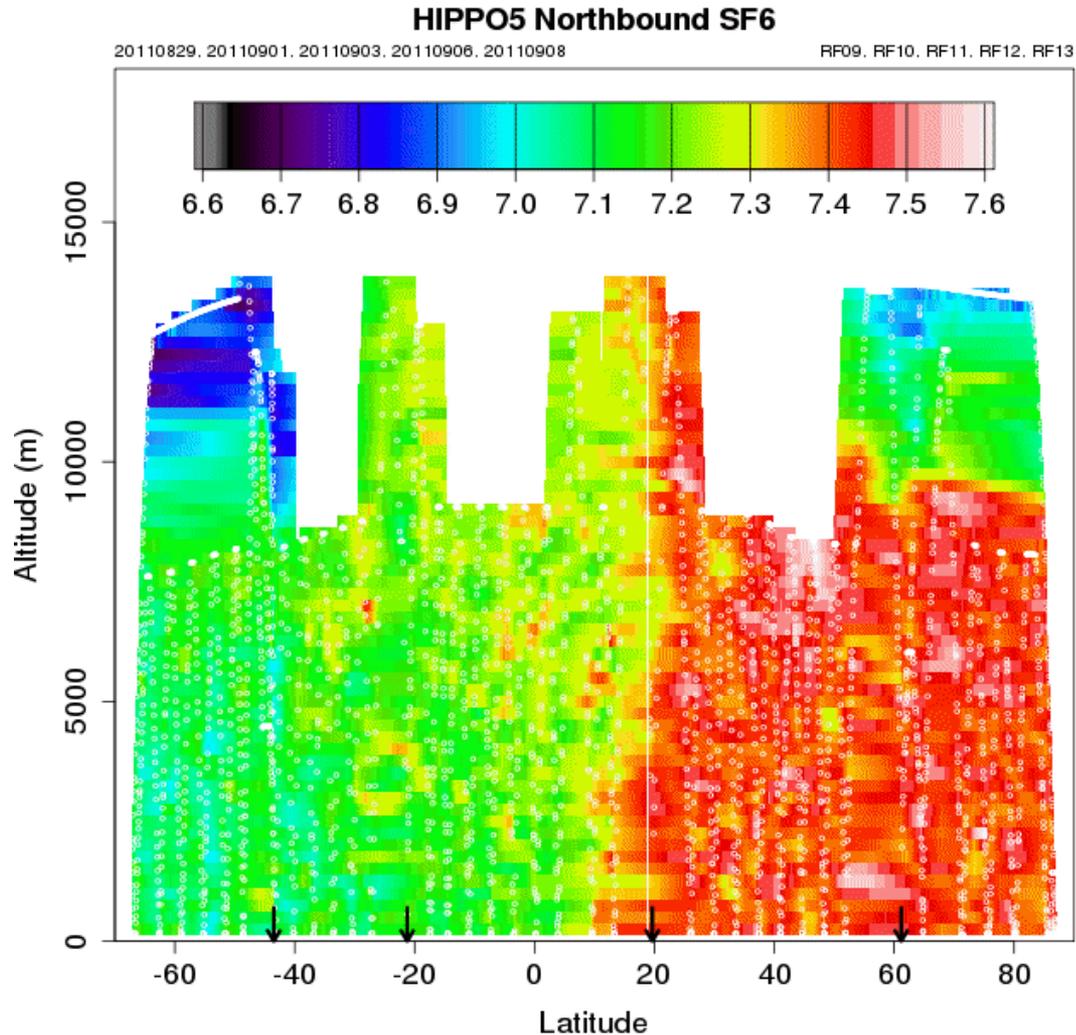
20110628, 20110630, 20110704, 20110706, 20110707, 20110710

RF06, RF07, RF08, RF09, RF10, RF11



Troposphere tracers: In rapid growth,
Strong and variable surface source and sinks
Short lived due to OH, photolysis, etc..

SF₆ > In rapid NH growth (surface source.)



Latitudinal surface information

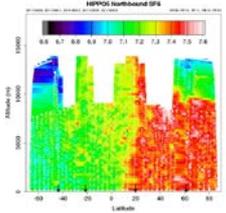
Dominant feature :
Inter Hemispheric
Exchange

Troposphere tracers: In rapid growth,
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 Short lived due to OH, photolysis, etc..

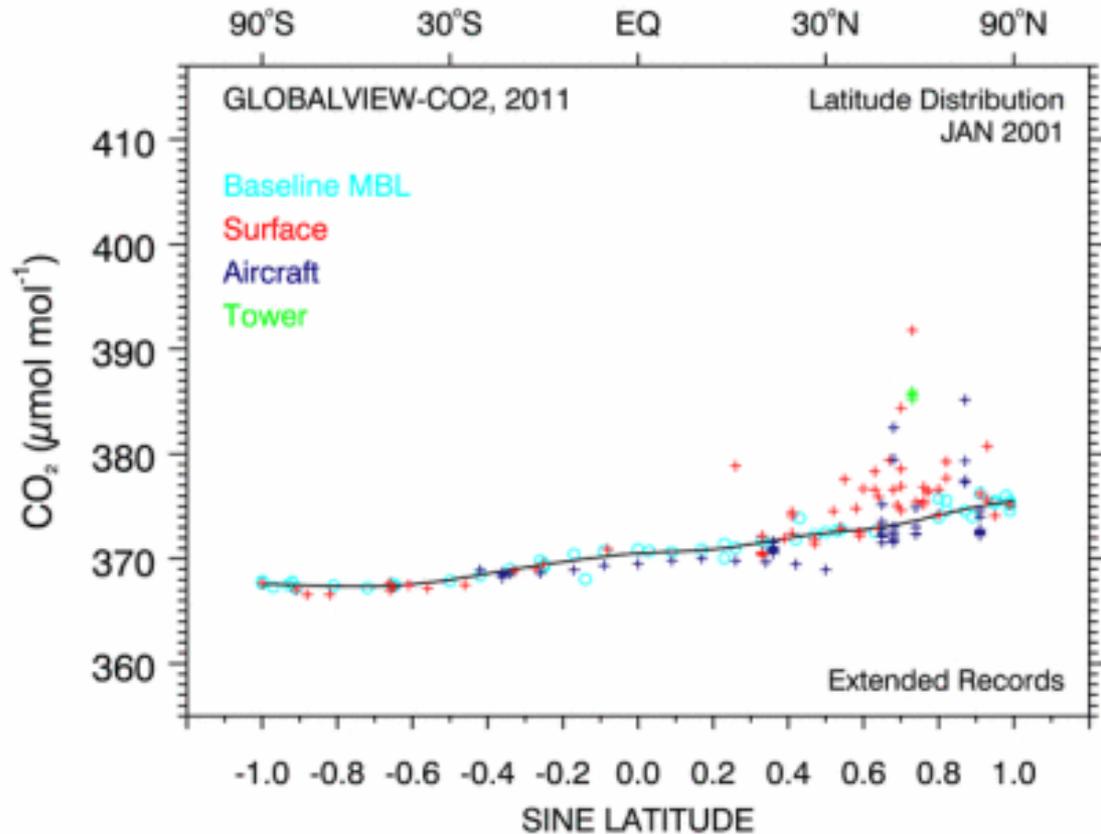
SF_6 > In rapid NH growth (surface source.)

CO_2 > Strong and variable surface source and sink.

CH_4 > “ plus weak OH chemistry.



GLOBALVIEW



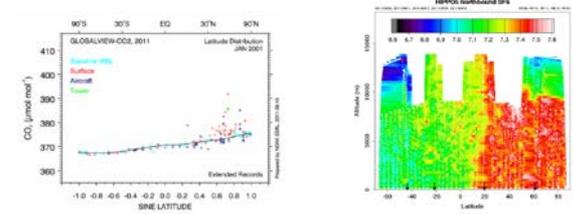
Prepared by NOAA ESRL, 2011-09-16

Add

temporal and MBL/land surface information .

Troposphere tracers: In rapid growth,
 Strong and variable surface source and sinks
 Short lived due to OH, photolysis, etc..

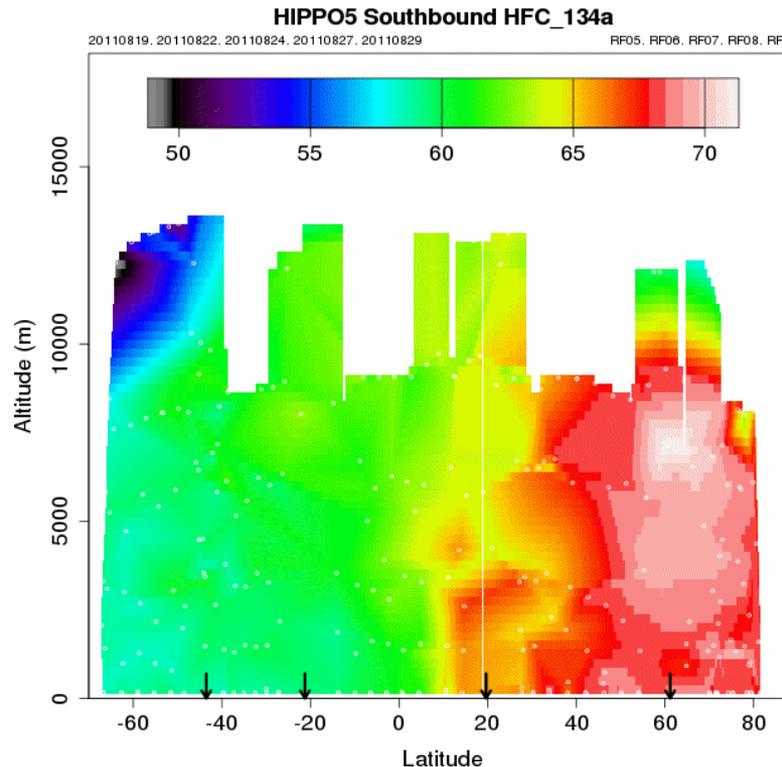
- SF₆ > In rapid NH growth (surface source.)
- CO₂ > Strong and variable surface source and sink.
- CH₄ > “ plus weak OH chemistry.



~ total lifetime
(years)

HCFC-143a	47. (OH)
HFC-125	28
HCFC-142b	17
HFC-134a	13
HCFC-22	12
HCFC-141b	9.2
HFC-152a	1.5

Replacement: typically in rapid NH growth but ...
 molecules substantial OH loss in troposphere.
 long stratospheric lifetimes > 50 years.



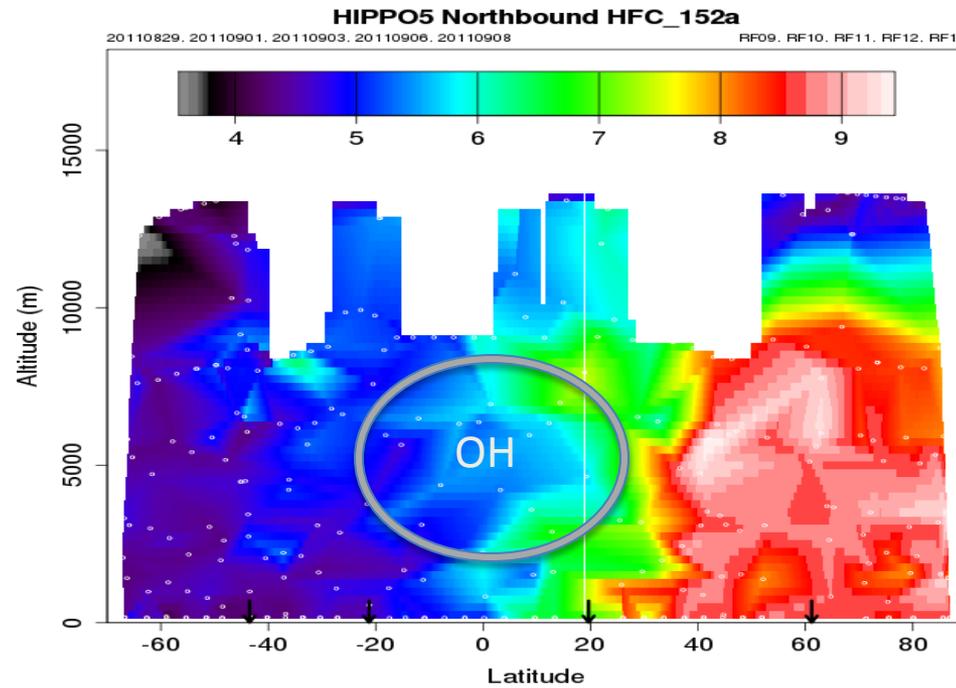
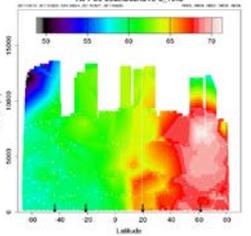
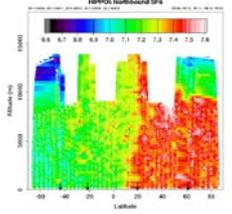
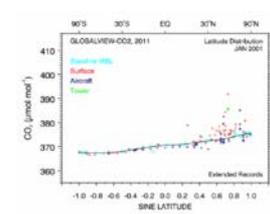
Gradients
similar to
SF₆

Troposphere tracers: In rapid growth,
Strong and variable surface source and sinks
Short lived due to OH, photolysis, etc..

- SF₆ > In rapid NH growth (surface source.)
- CO₂ > Strong and variable surface source and sink.
- CH₄ > “ plus weak OH chemistry.

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(years)

HCFC-143a	47. (OH)
HFC-125	28
HCFC-142b	17
HFC-134a	13
HCFC-22	12
HCFC-141b	9.2
CH ₃ CCl ₃	5.0
<u>HFC-152a</u>	<u>1.5</u>
Exchange time	1.3
CH ₃ Cl	1.0
CH ₃ Br	0.8
CHCl ₃	0.4
CH ₂ Cl ₂	0.4
CH ₂ Br ₂	0.34
C ₂ Cl ₄	0.25



Gradients
contain
free trop
chemistry.

Free troposphere OH, photolysis loss rates equivalent to...
large scale bulk troposphere transport time scales.

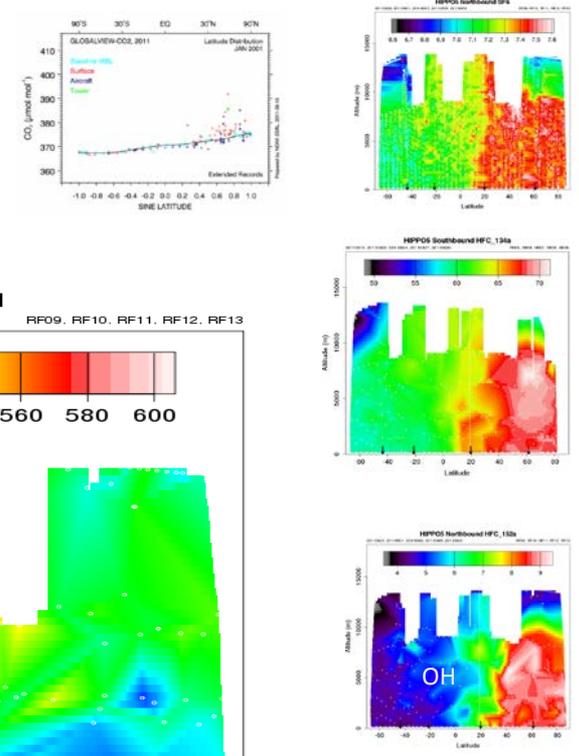
Troposphere tracers: In rapid growth,
 Strong and variable surface source and sinks
 Short lived due to **OH, photolysis, etc..**

- SF₆ > In rapid NH growth (surface source.)
- CO₂ > Strong and variable surface source and sink.
- CH₄ >

~ total lifetime
 (years)

HCFC-143a	47. (OH)
HFC-125	28
HCFC-142b	17
HFC-134a	13
HCFC-22	12
HCFC-141b	9.2
CH ₃ CCl ₃	5.0
HFC-152a	1.5

<u>CH₃Cl</u>	<u>1.0</u>
CH ₃ Br	0.8
CHCl ₃	0.4
CH ₂ Cl ₂	0.4
CH ₂ Br ₂	0.34
C ₂ Cl ₄	0.25



Fine source structure

Free troposphere OH, photolysis loss rates Faster than
 large scale bulk troposphere transport time scales.

Troposphere tracers: In rapid growth,
 Strong and variable surface source and sinks
 Short lived due to OH, photolysis, etc..

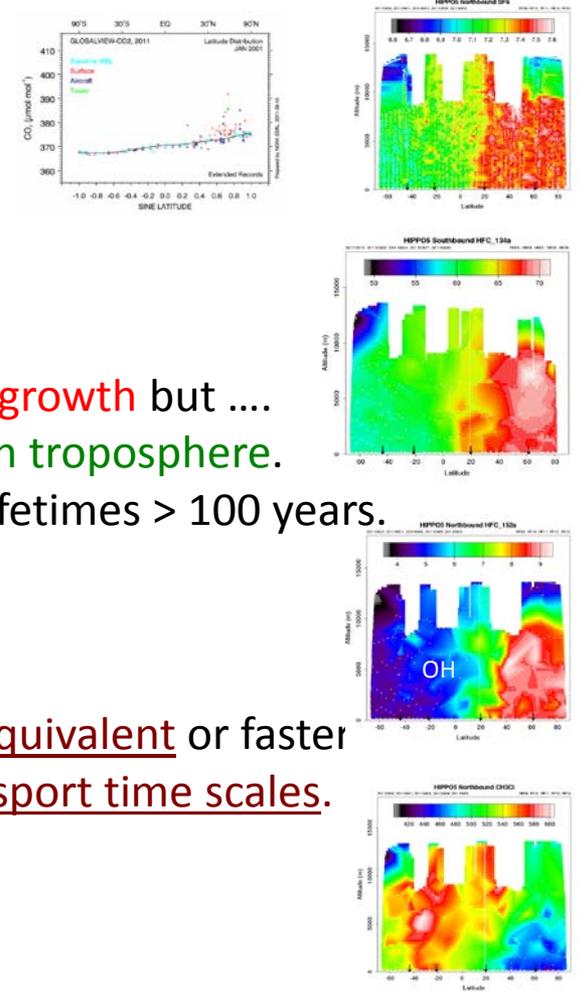
- SF₆ > In rapid NH growth (surface source.)
- CO₂ > Strong and variable surface source and sink.
- CH₄ > “ plus weak OH chemistry.

~ total lifetime
 (years)

HCFC-143a	47. (OH)
HFC-125	28
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CH ₃ CCl ₃	5.0
HFC-152a	1.5
<u>CH₃Cl</u>	<u>1.0</u>
CH ₃ Br	0.8
CHCl ₃	0.4
CH ₂ Cl ₂	0.4
CH ₂ Br ₂	0.34
C ₂ Cl ₄	0.25

Replacement: typically in rapid NH growth but ...
 molecules substantial OH loss in troposphere.
 long stratospheric lifetimes > 100 years.

Free trop OH, photolysis loss rates equivalent or faster
 large scale bulk troposphere transport time scales.



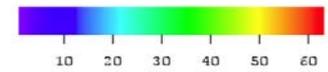
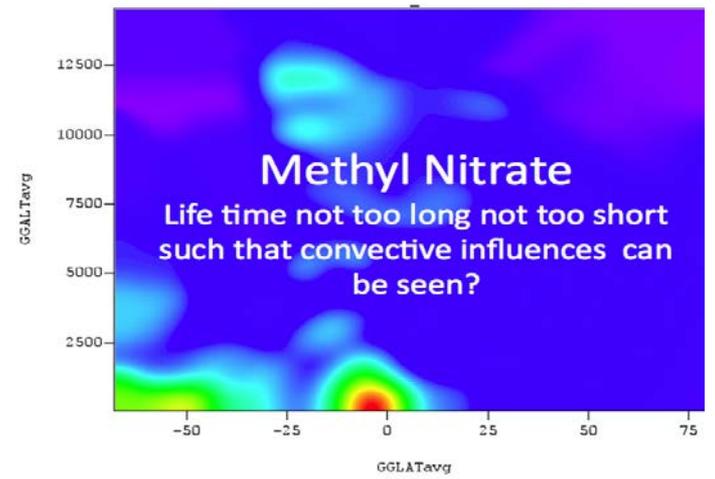
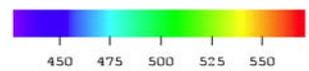
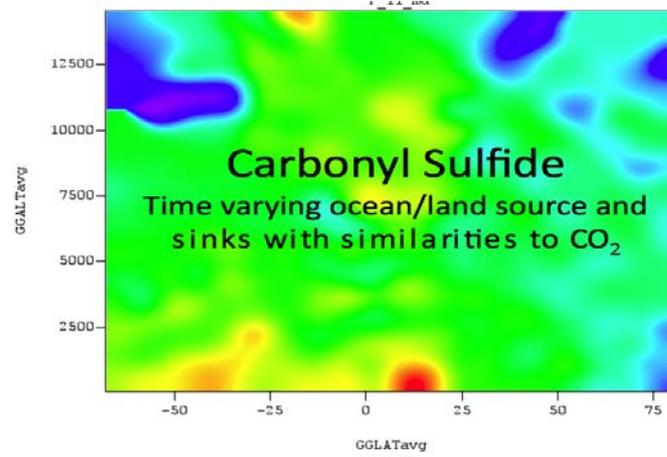
The rest of the tracers: **very short lived**, Atmospheric life times **days to weeks**
 strong and variable **free troposphere source** and **sinks**.
unique surface, land, ocean source and **sinks**.
 often used for **focused** and or **process oriented** studies.

- ethyne
- benzene
- propane
- Isopentane
- N_butane
- N_pentane
- CH₃I
- CHCl₃
- COS
- H₂
- CO
- O₃
- H₂O
- PAN
- O¹⁸, C¹⁴ (CO₂)

- AWAS data



Eliot Atlas's AWAS data
 substantially adds to this list
 (alternate sampling AWAS
 stainless steel flask and NWAS
 glass flasks)



Vertical and Horizontal Profiles looking for:

* Source/Sinks.

Ocean/Land/Atmospheric with dependency on Pollution/Biology/Chemistry.

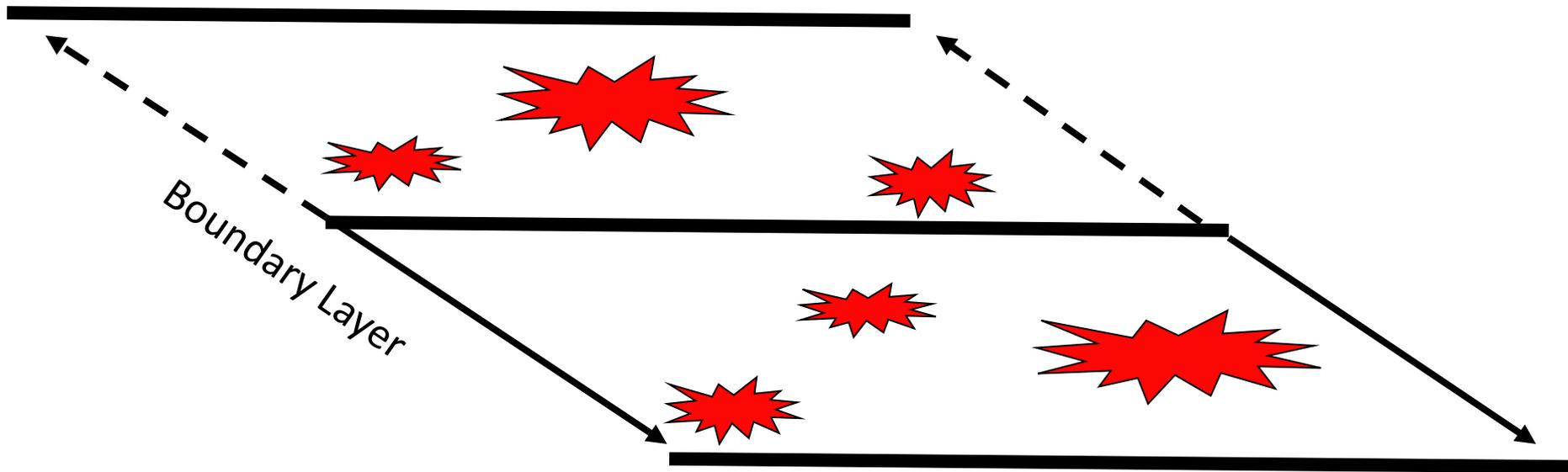
* Coupled with transport.

Upwelling and Mixing.

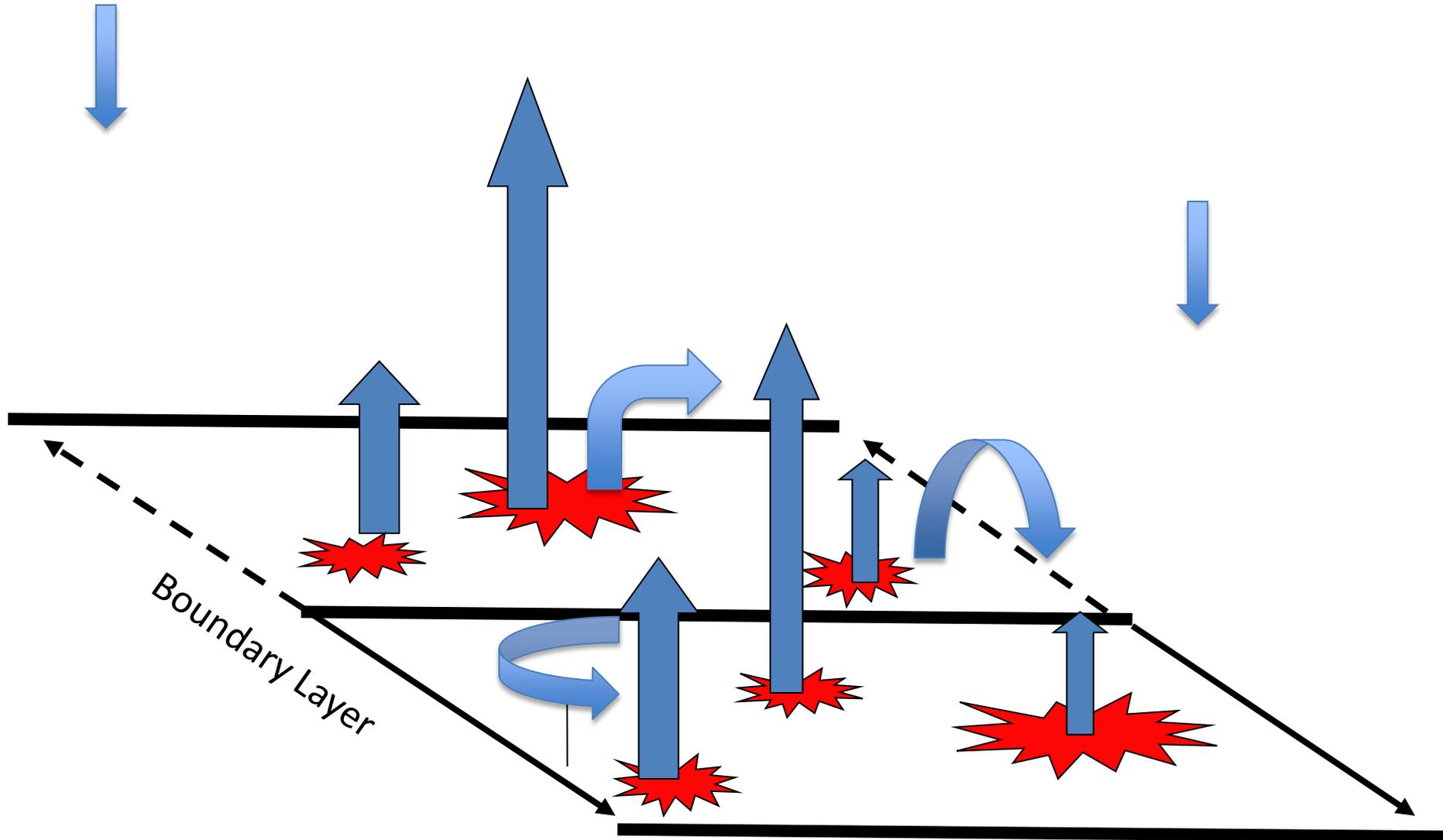
Inter-hemispheric Exchange.

Interactions between Boundary-Layer <-> Troposphere <-> Stratosphere.

Challenge: Source region is distributed and in most cases has uncertain boundary.



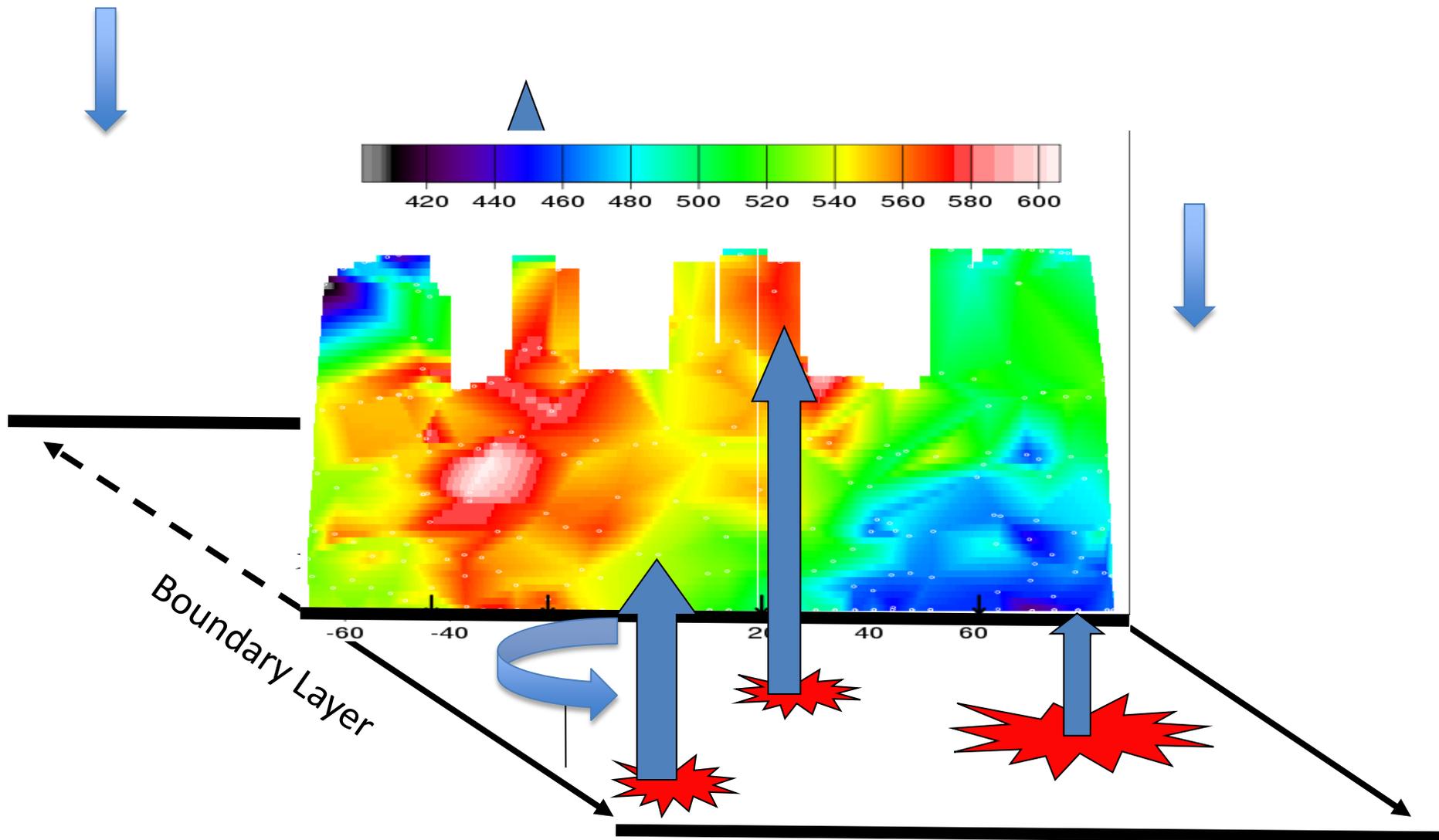
Challenge: **Distributed** and in most cases uncertain boundary **source** region.
Coupled variable **transport** and in most cases variable **chemistry**.



Challenge: **Distributed** and in most cases uncertain boundary **source** region.

Coupled variable **transport** and in most cases variable **chemistry**.

Data only exist on a sheet down the pacific though with good seasonal coverage.



Challenge: Distributed and in most cases uncertain boundary source region.

Coupled variable transport and in most cases variable chemistry.

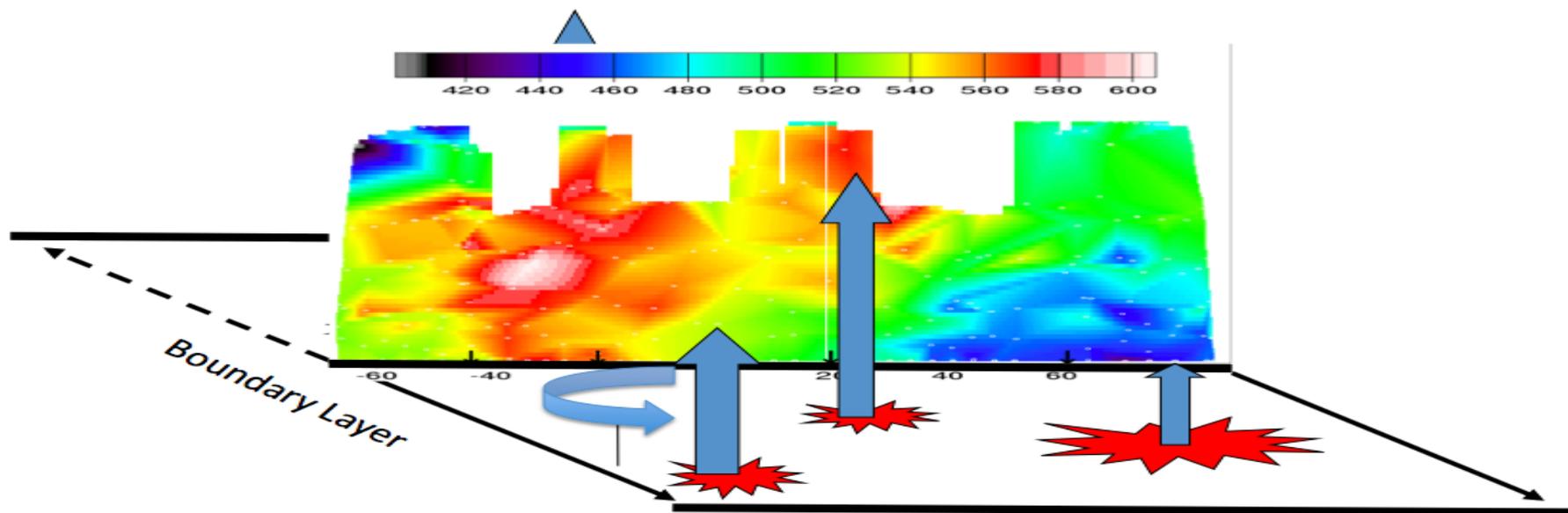
Data only exist on a sheet down the pacific though with good seasonal coverage.

Run 3D- model simulations:

Propagate estimates of **surface sources/sinks** and **atmospheric chemistry** onto the **HIPPO data** set.

Use **agreement / disagreement** to improve estimates of surface sources/sinks, **chemistry** and **model transport**.

Already too many HIPPO **model studies** to list N_2O , CH_4 , Br-loading, OH, SF_6 -Trop Age, PAN, H_2



Can anything be accomplished outside the 3D-models?

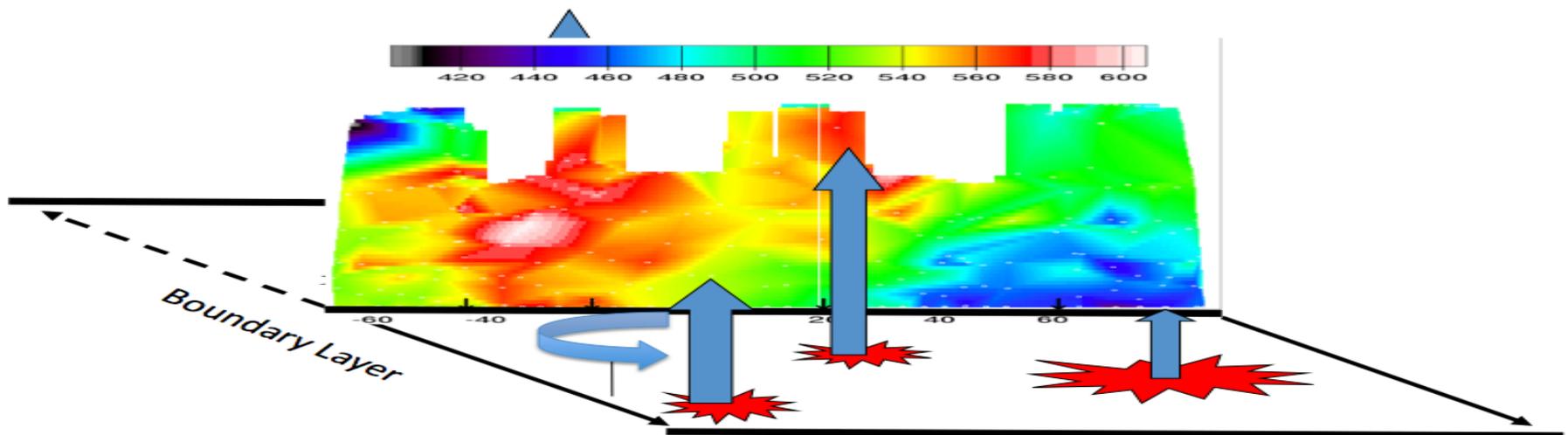
correlated data set:

- > many with surface source correlations .
- > all species in air parcel measured by HIPPO share a common path
- > all species in air parcel share correlated chemical fields etc.

process oriented studies... proposed example.

Link tropical transport to inter hemispheric exchange ?

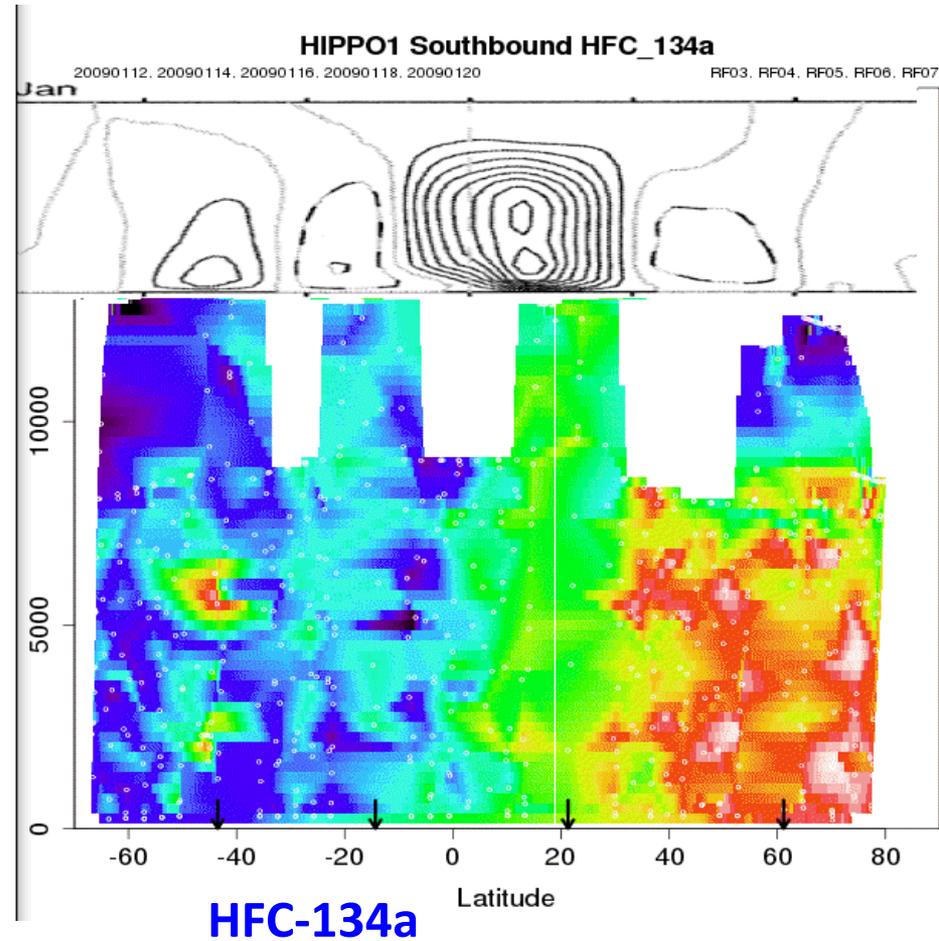
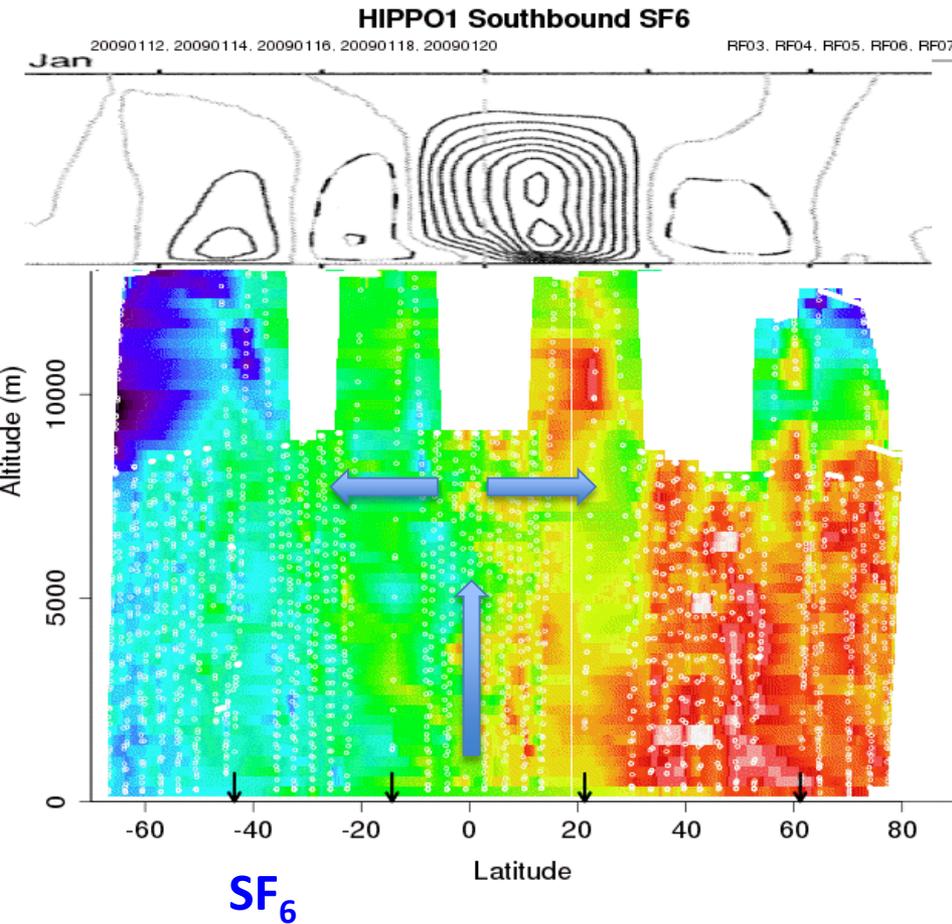
Leverage inter hemispheric exchange to distributed OH loss ?



January

large tropical transport
drives inter hemispheric exchange

Mean Stream function - NCEP-NCAR reanalysis (I M Dima and JM Wallace 2002)



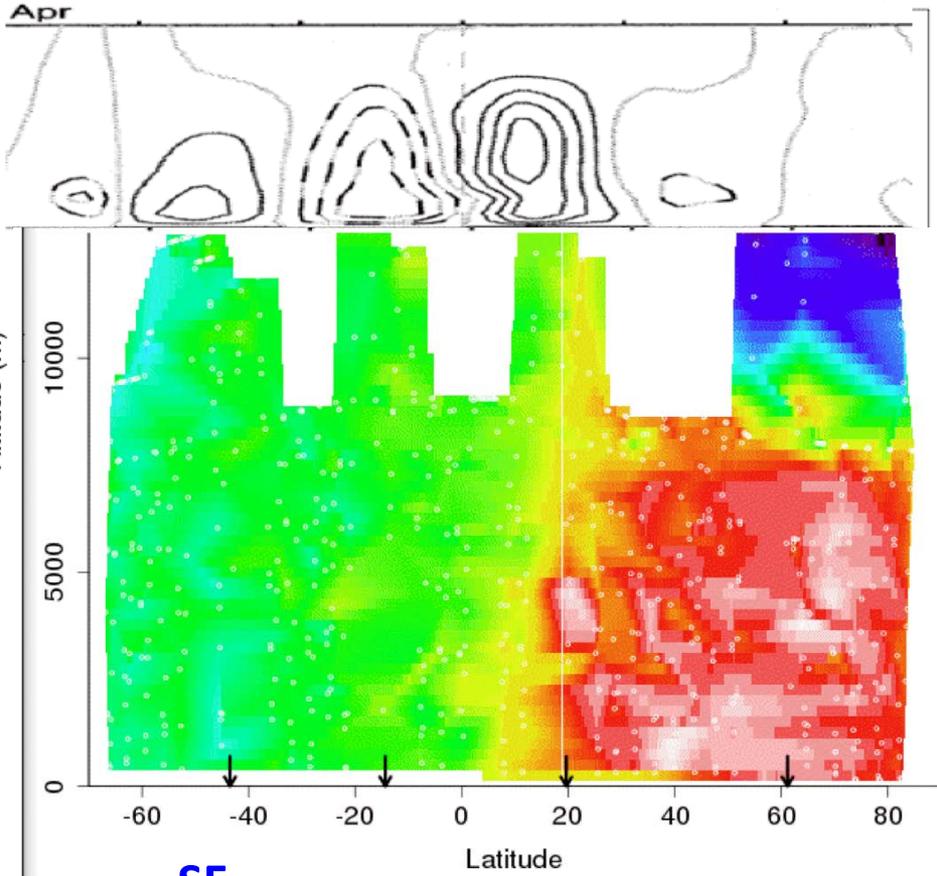
April

tropical transport slows down
hemispheres homogenize

HIPPO3 Northbound SF6

20100405, 20100408, 20100410, 20100413, 20100415

RF06, RF07, RF08, RF09, RF10

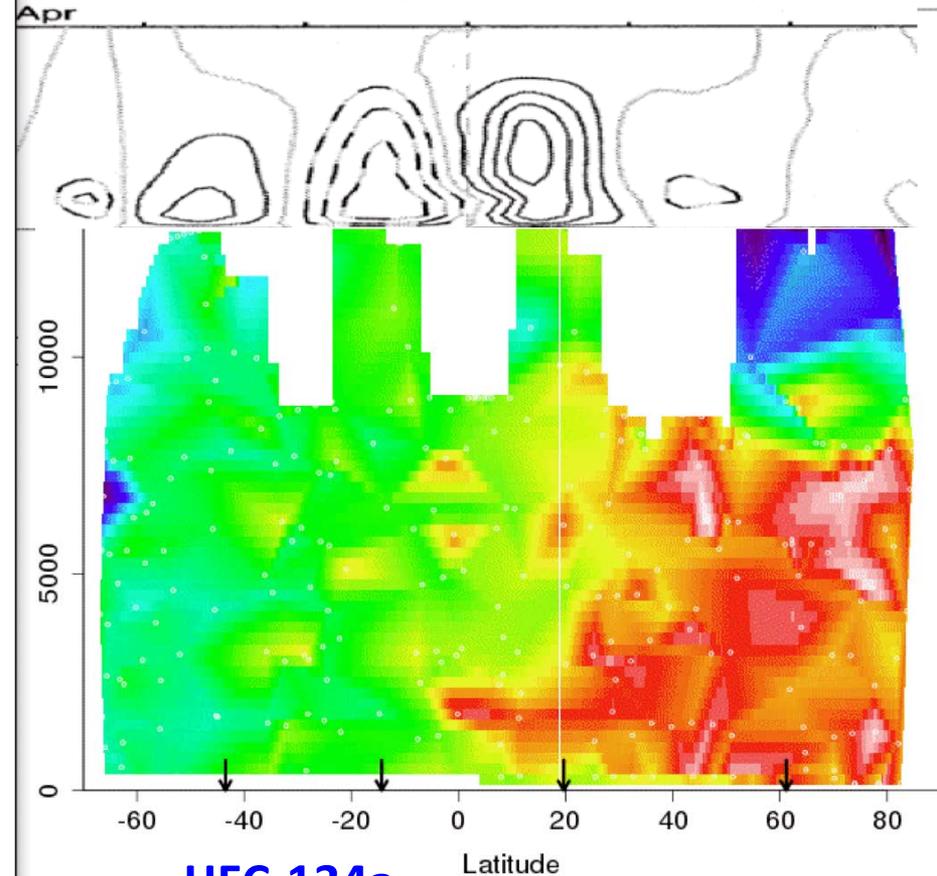


SF₆

HIPPO3 Northbound HFC_134a

20100405, 20100408, 20100410, 20100413, 20100415

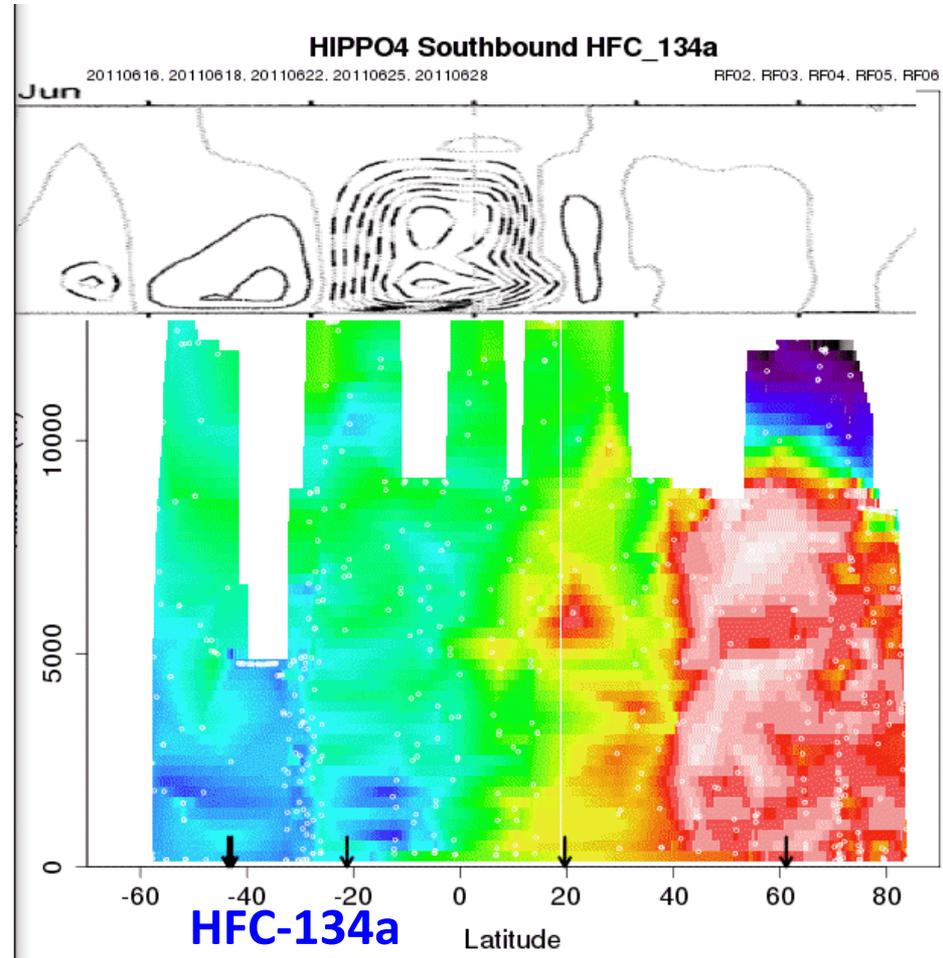
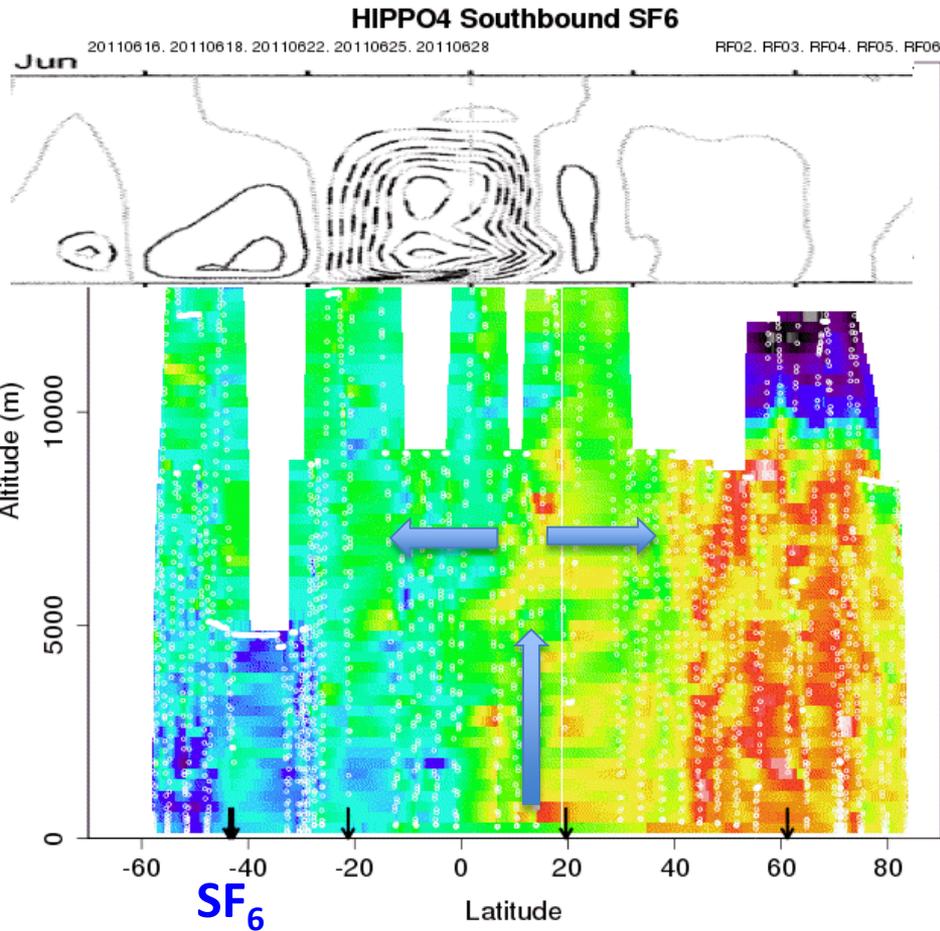
RF06, RF07, RF08, RF09, RF10



HFC-134a

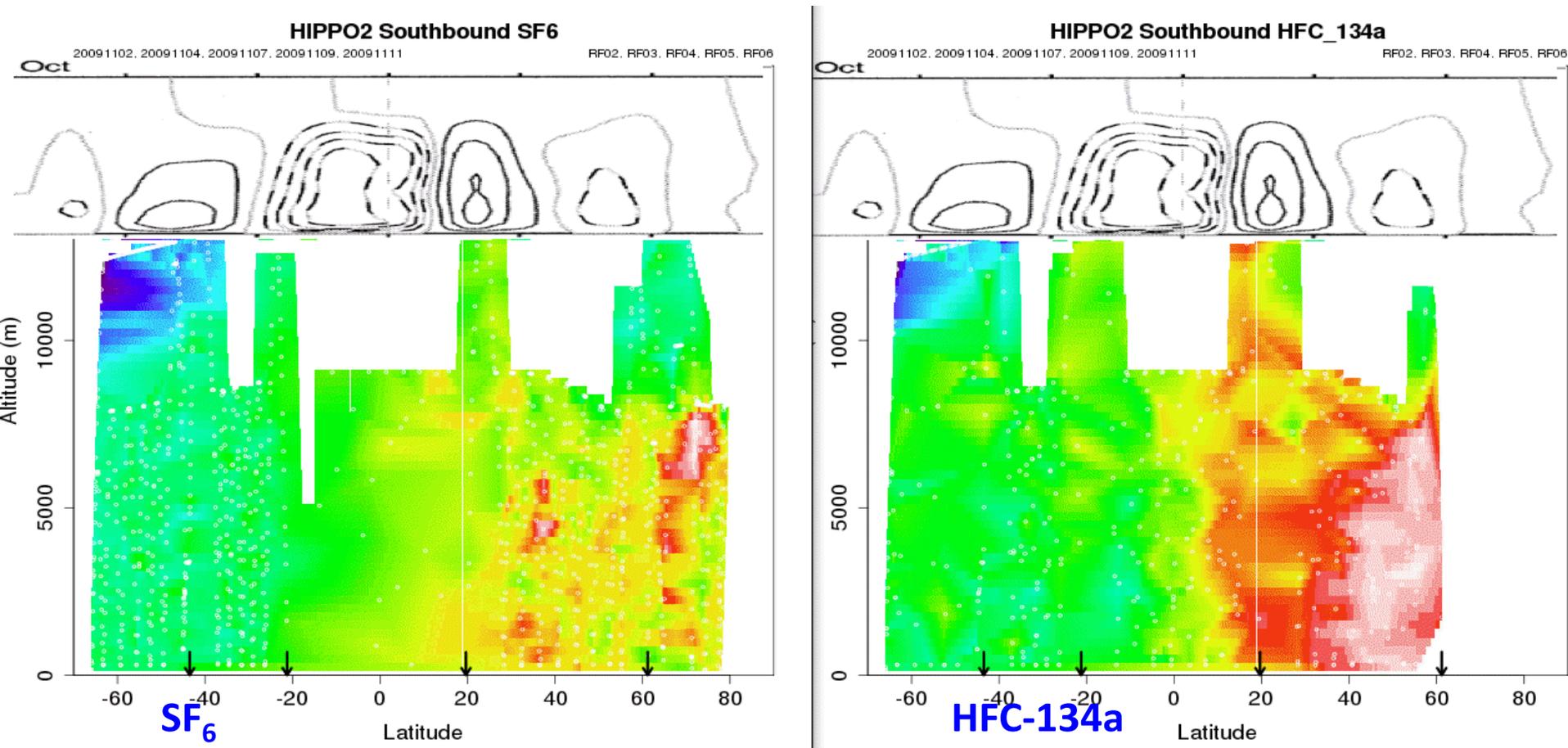
June

large tropical transport
drives inter hemispheric exchange



October

tropical transport slows down
hemispheres homogenize



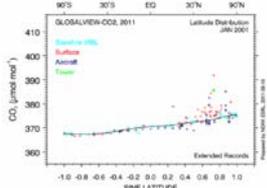
- Note:** that HFC-134a etc. have Northern Hemispheric sources in growth, similar to SF₆.
- If we **normalize** each tracer to their **respective growth rate**.
 - **Then** (in the absence of OH loss) they would have the **same inter hemispheric gradient**.
 - Differences in these **normalized gradient** are then a **measure of loss**.

Correlated Data Set:

- > all species in air parcel measured share common path
- > all species in air parcel share correlated chemical fields.

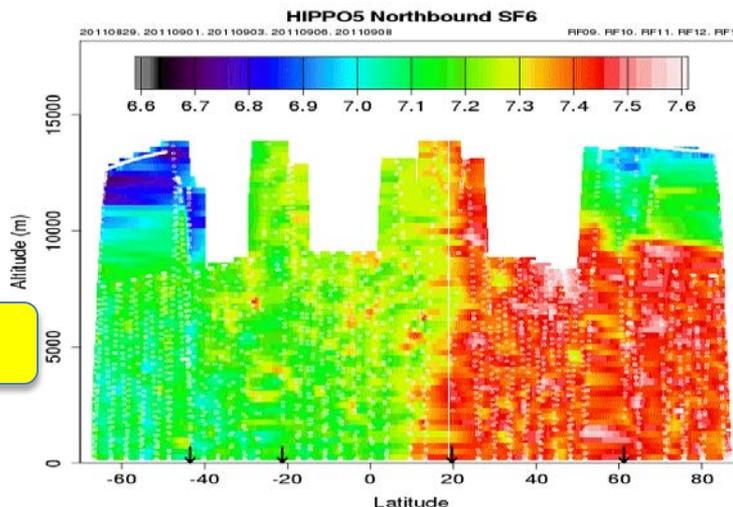
SF₆ > NH growth

CO₂
CH₄

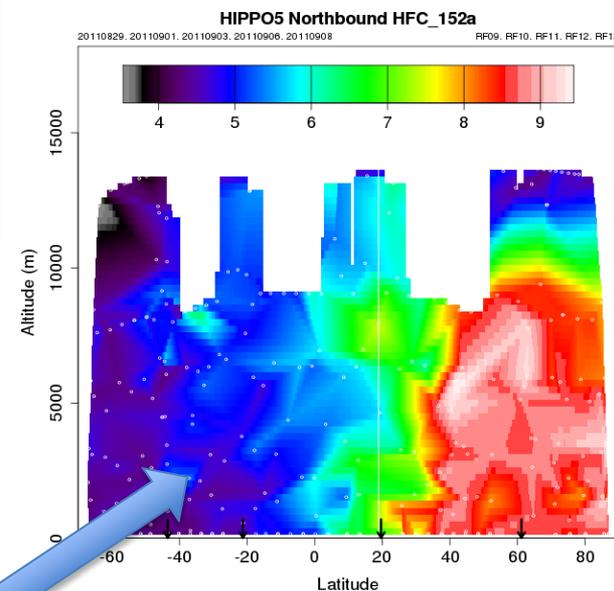


NH growth

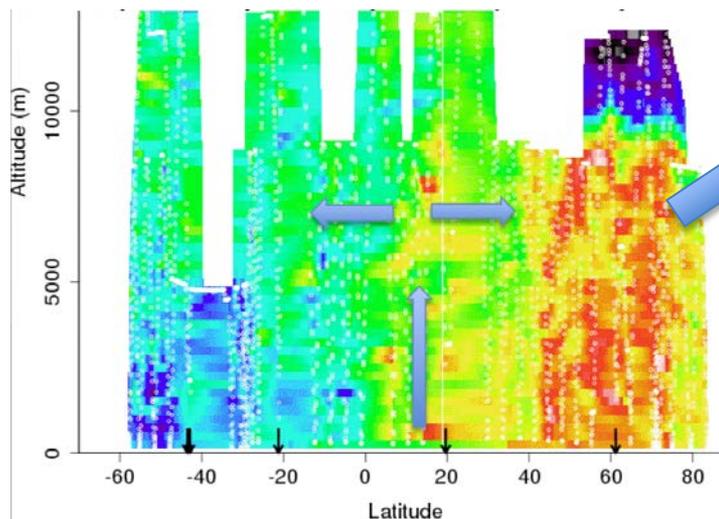
HCFC-143a	47.
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<u>HFC-152a</u>	<u>1.5</u>
CH ₃ Cl	1.0
CH ₃ Br	0.8
CHCl ₃	0.4
CH ₂ Cl ₂	0.4
CH ₂ Br ₂	0.34
C ₂ Cl ₄	0.25



~ total lifetime
(years)



Transition time
~ 1 month



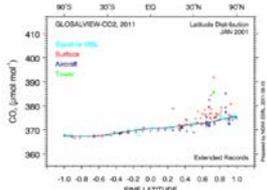
Remove gradient
due solely to transport

Correlated Data Set:

- > all species in air parcel measured share common path
- > all species in air parcel share correlated chemical fields.

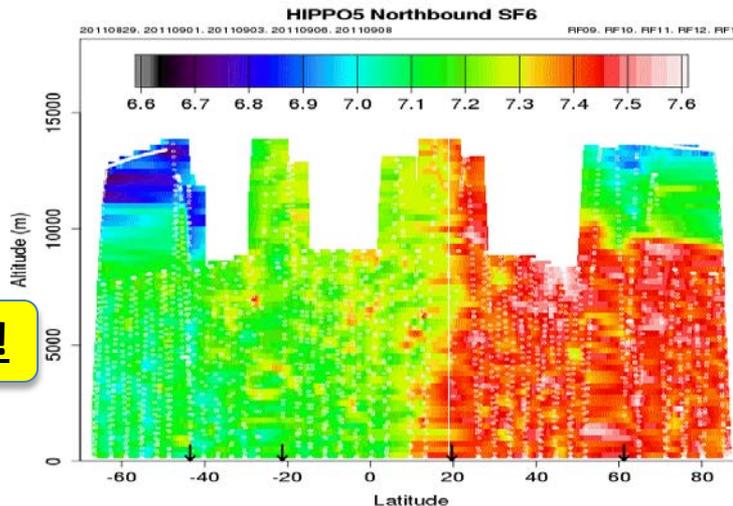
SF₆ > NH growth

CO₂
CH₄

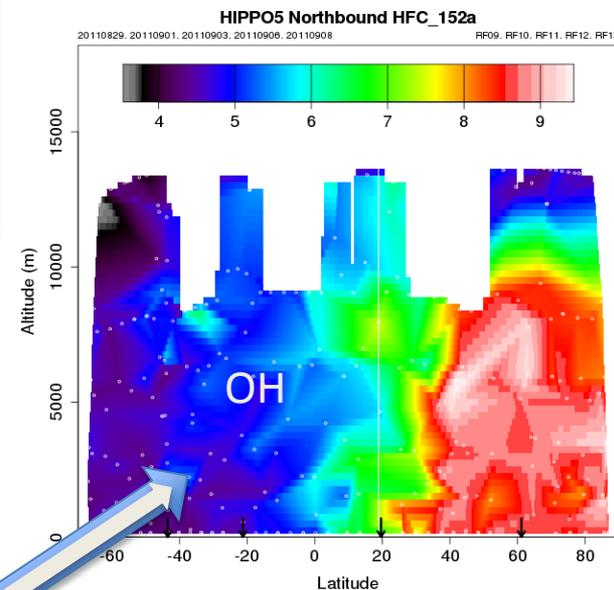


NH growth and OH loss!

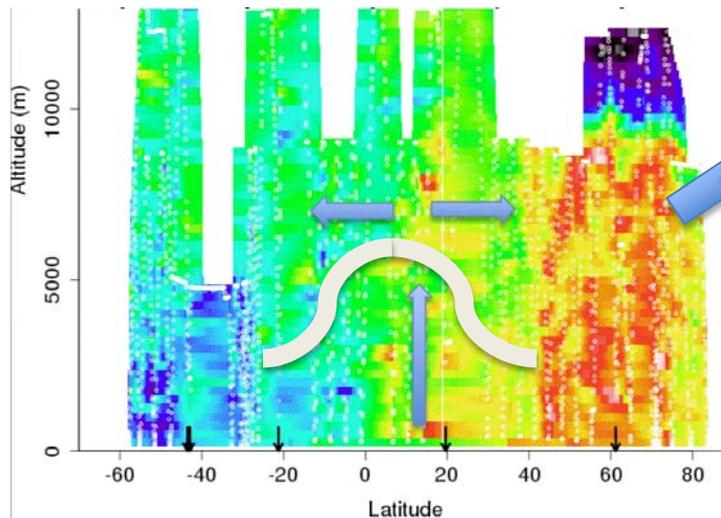
HCFC-143a	47.
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~ total lifetime
(years)



Transition time
~ 1 month



Identify and quantify OH loss
Coupled to transport

Summary

HIPPO unique and valuable data set:

Good Seasonal and Spatial Coverage.

Large and diverse set of correlated trace gas measurements.

Producing Science:

Suited well for 3D Model studies.

Process oriented Model independent studies.

If you like and or use this data set.....

- .
- .
- .

Please support ATom proposal,

HIPPO like with added chemistry and aerosols.

Pacific and Atlantic.

NASA DC-8.

NOAA_GMD generates **8** separate submission **files** for each flight.

GCMS-M2_	Mass Spec Flask Data.	<i>S. Montska et al.</i>
MAGICC_gmd_	Carbon Cycle Group Flask Data (CO ₂ , CO, CH ₄ , H ₂ , SF ₆ , N ₂ O)	<i>C. Sweeney et. al.</i>
SIL_isotopes_	Isotope Flask Data. (¹⁸ O , ¹³ C on CO ₂)	<i>(J. White and B. Vaughn INSTARR)</i>
UCATSO3_	2B Photometer (O ₃)	<i>J. Elkins et. al.</i>
UCATSGC_	In Situ Chromatograph-ECD (N ₂ O, SF ₆ , CH ₄ , CO, H ₂)	<i>J. Elkins et. al.</i>
UCATSH20_	MayComm TDL (H ₂ O)	<i>J. Elkins et. al.</i>
GC_ECD_	In Situ Chromatograph-ECD (N ₂ O, SF ₆ , CH ₄ , CO, H ₂ , CFC-11, -12, -131, halon-1211, PAN)	<i>J. Elkins et. al.</i>
GC_MSD_	In Situ Chromatograph-MSD (CH ₃ Cl, CH ₃ Br, CH ₃ I, HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, OSC, CS ₂)	<i>J. Elkins et. al.</i>

Sample Volume information:

Integrate
over
Fast Data sets.

PFP Flask data is altitude targeted (on dives) with ~ 10-20 seconds of sample width.
(24 to 36 flask samples per flight).

(target precision 0.05% on up depending on species)

In situ MDS data are similar to flask data except for a higher 3 min. data rate and a sample width integration of ~ 150 sec , or about an 80% sample duty cycle.

(target 1% precision)

Correlate
with
Fast Data sets.

In situ ECD data have even higher data rate of 1 or 2 min (2-3 second sample width).
(target 0.5% precision)

O₃ (0.1 Hz) (target 2% +2 ppb precision)

H₂O (1 Hz) (target 3% + 1 ppb precision)

Redundant data sets:

