Source and change of tropospheric ozone in China and Pacific Rim

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at

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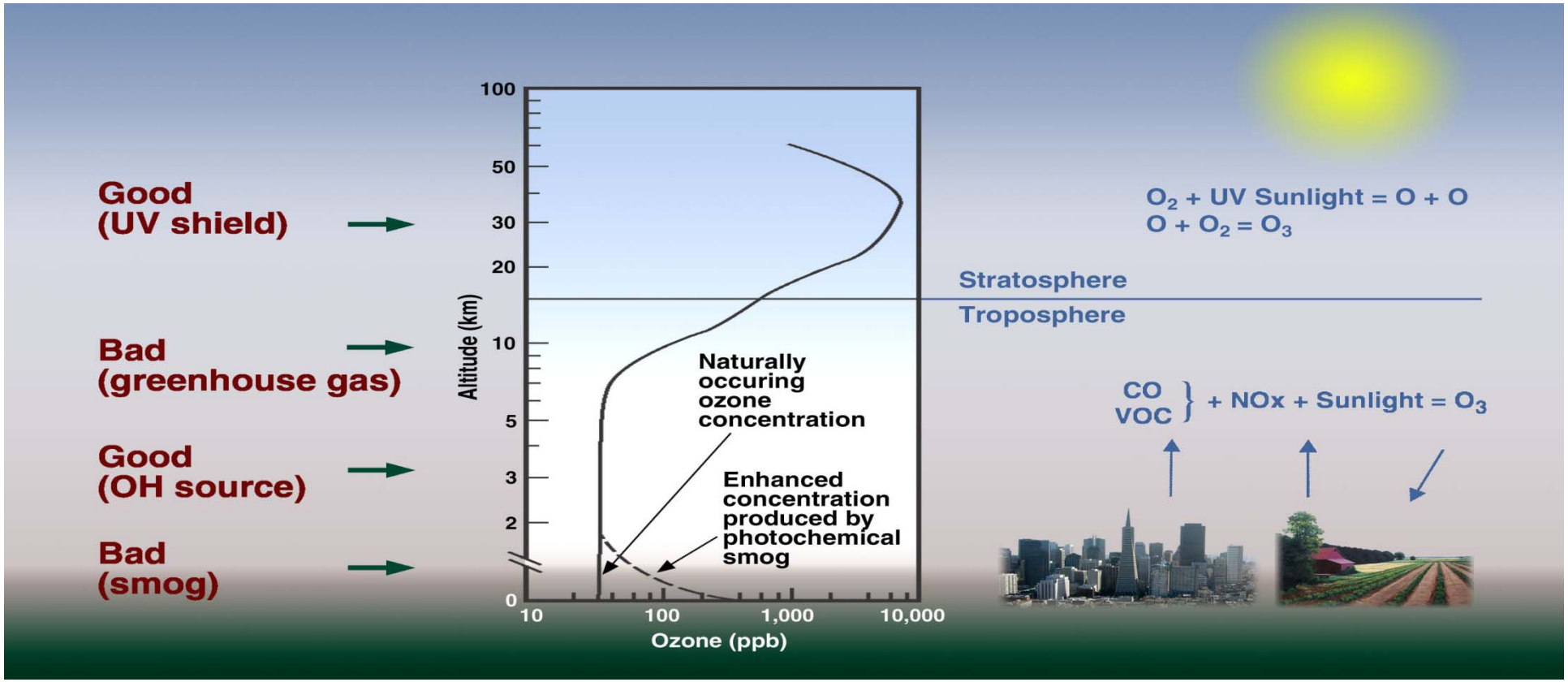
GOOD vs. BAD OZONE



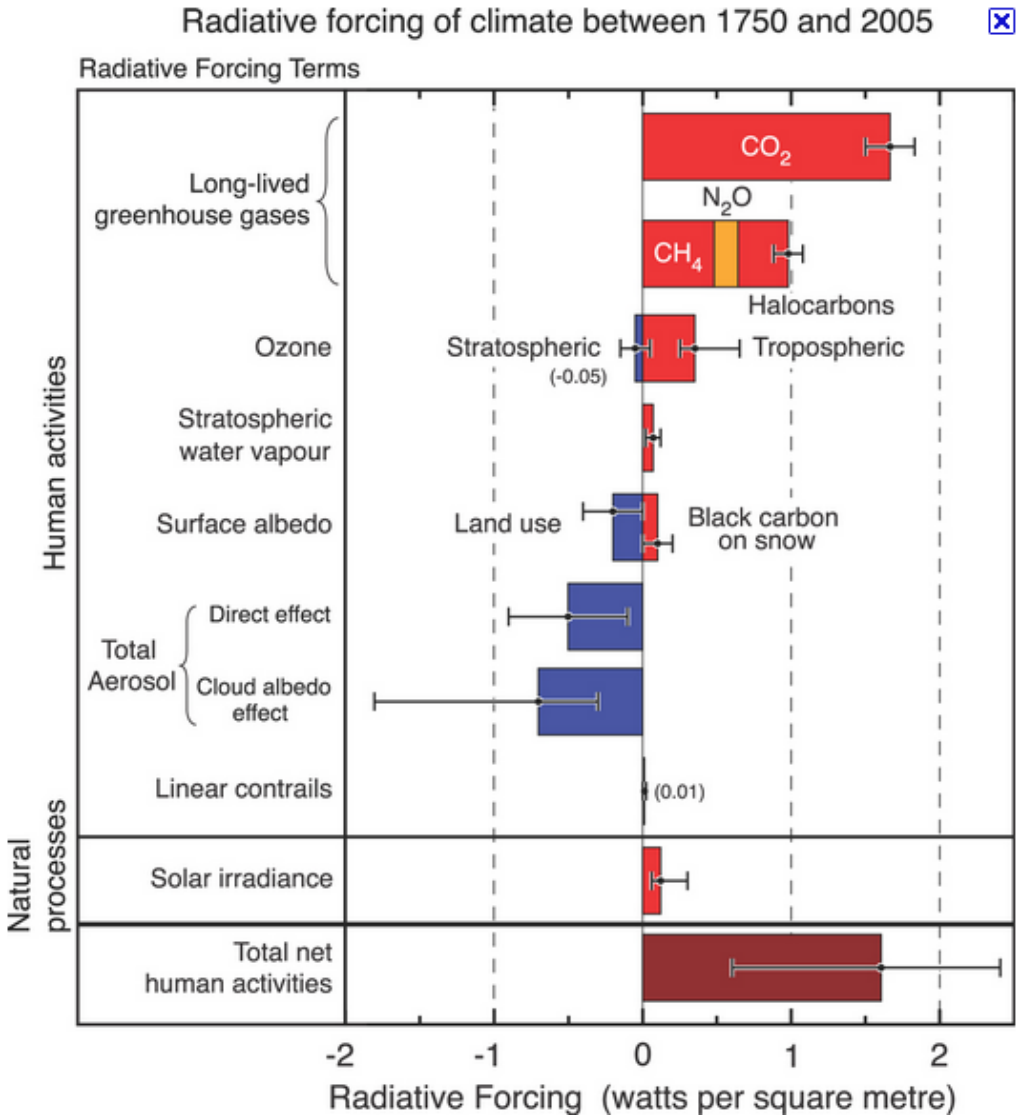
Tropospheric ozone precursors

- Nitrogen oxide radicals; $NO_x = NO + NO_2$
  Sources: combustion, soils, lightning
- Volatile organic compounds (VOCs)
  - Methane
    Sources: wetlands, livestock, natural gas…
  - Reactive VOCs
    Sources: vegetation, combustion
  - Carbon monoxide
    Source: combustion

An important greenhouse gas, especially in the upper troposphere

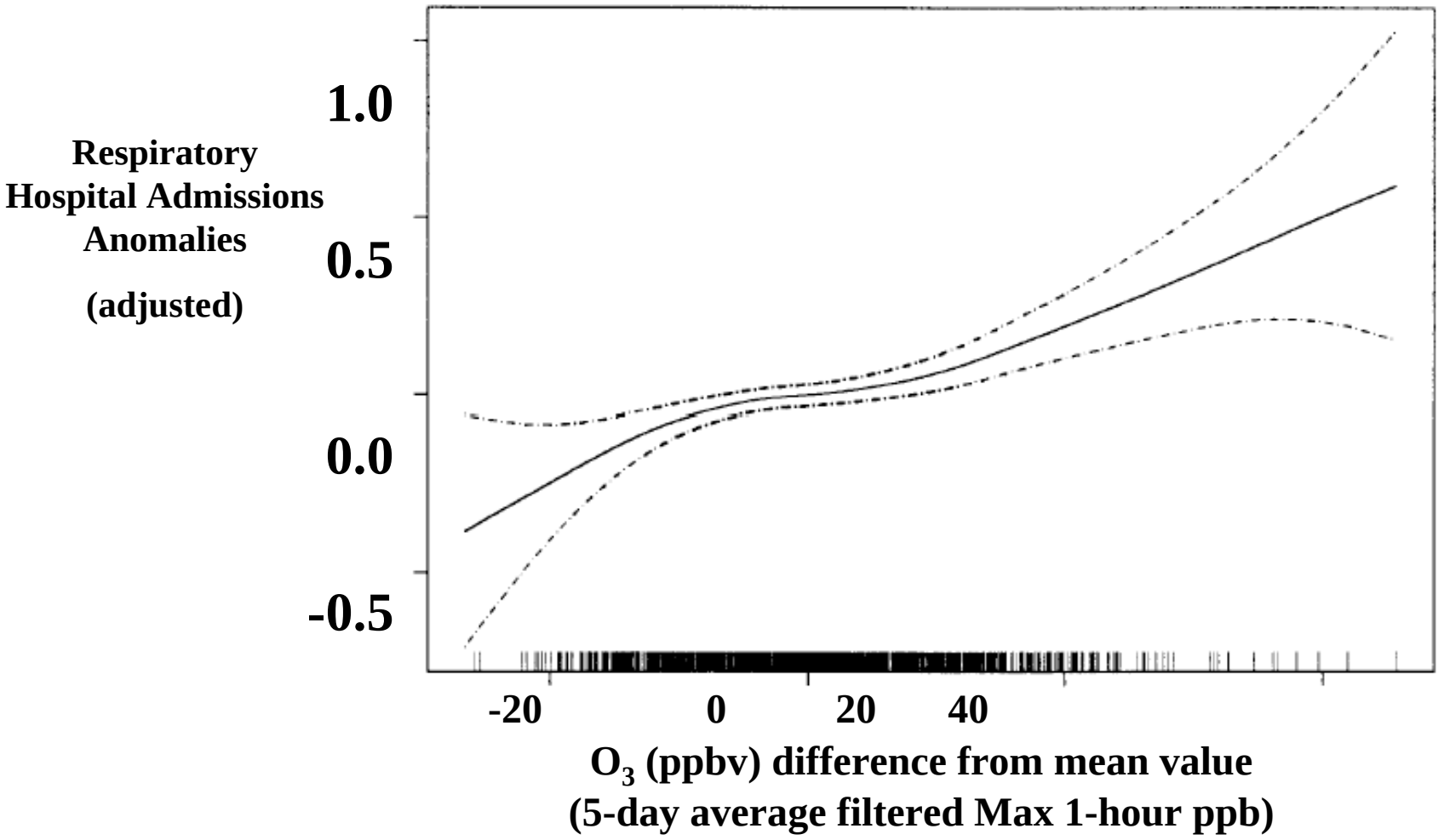
IPCC (2001) RADIATIVE FORCING ESTIMATE:

$\Delta F_{O3} = 0.35 \pm 0.15$ W m^{-2}



IPCC, 2005

Ozone / Hospital Admissions
(Burnett, et al 2001)



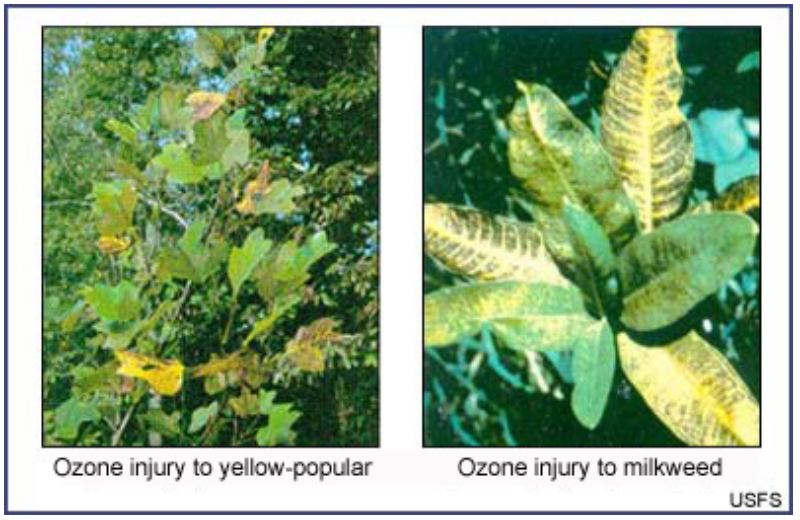
Threat for vegetation

Is ozone pollution affecting crop yields in China?
(W. L. Chameides et al., 1999)

- **Economic:**

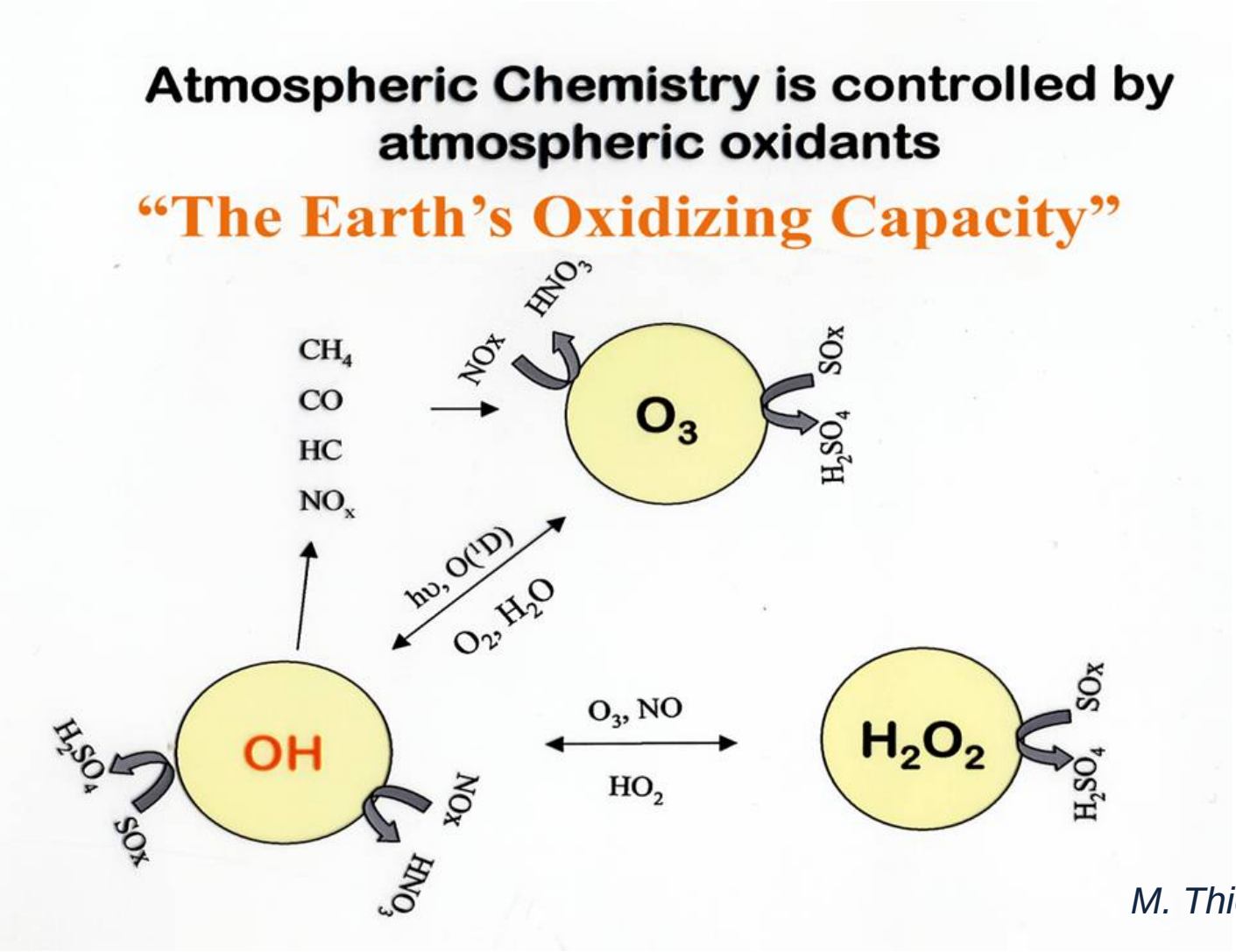
- $1-2 billion lost annually in the U.S. from ozone damage to agriculture and commercial forestry alone.
  - To put this in perspective, PA's total crop production for 2006 was approximately $1.7 billion

- $5 billion in some other countries such as China



http://www.ucar.edu/learn/1_7_1.htm

Ozone plays a pivotal role in the tropospheric chemistry: origin of all oxidants such as OH and H_2O_2 affecting the chemical composition and oxidizing capacity of the atmosphere.

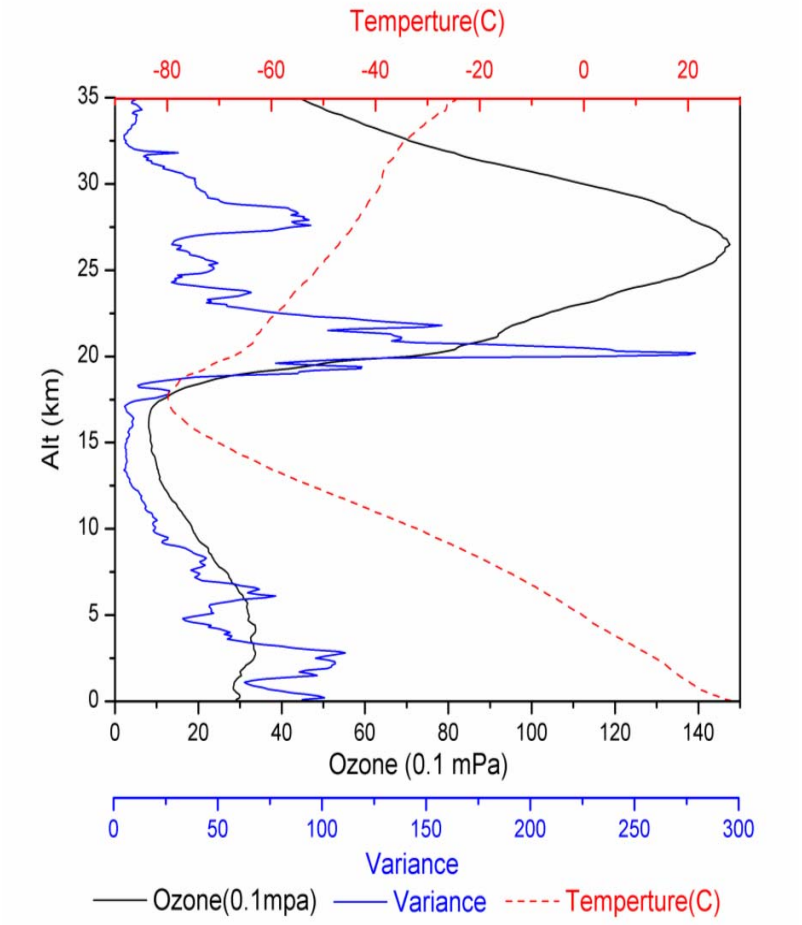


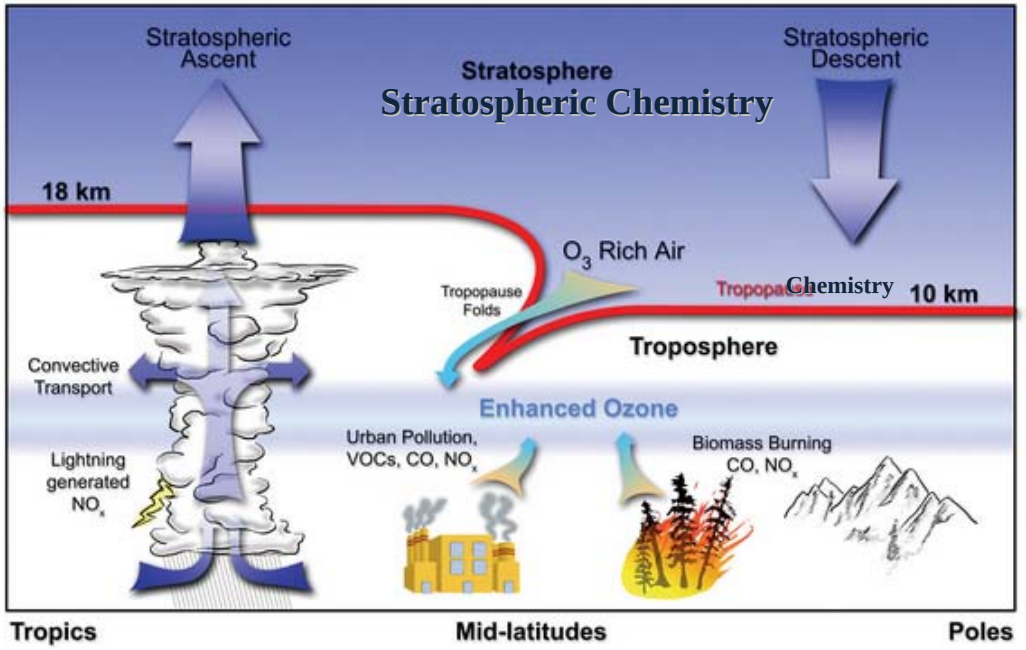
M. Thiemens

Sources of ozone in troposphere

- a dynamic combination of natural (stratospheric) and anthropogenic (from made-made precursors) origin.

Saya, Hainan, spring 2004





Tropospheric ozone chemistry

Initiation:

R1: $O_3 + h\nu \rightarrow O(^1D) + O_2$

R2: $O(^1D) + H_2O \rightarrow 2OH$

Chain propagation:

		Multipliers
R3:	$CO + OH + O_2 \rightarrow HO_2 + CO_2$	m
R4a:	$HO_2 + NO \rightarrow NO_2 + OH$	m_1
R4b:	$HO_2 + O_3 \rightarrow OH + 2O_2$	m_2
R5:	$NO_2 + O_2 + h\nu \rightarrow NO + O_3$	m_1

$m = m_1 + m_2$

Termination:

R6: $OH + NO_2 + M \rightarrow HNO_3 + M$

R7: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Net (R1 – R5):

R8: $O_3 + H_2O + mCO + (2m_1\text{-}m_2\text{-}1)O_2 \rightarrow mCO_2 + 2OH + (m_1\text{-}m_2)O_3$

Net Production of O_3:	**$m_1 > m_2+1$**
O_3 neutral:	**$m_1 = m_2+1$**
Net destruction of O_3:	**$m_1 \leq m_2$**

Tropospheric ozone production cycle

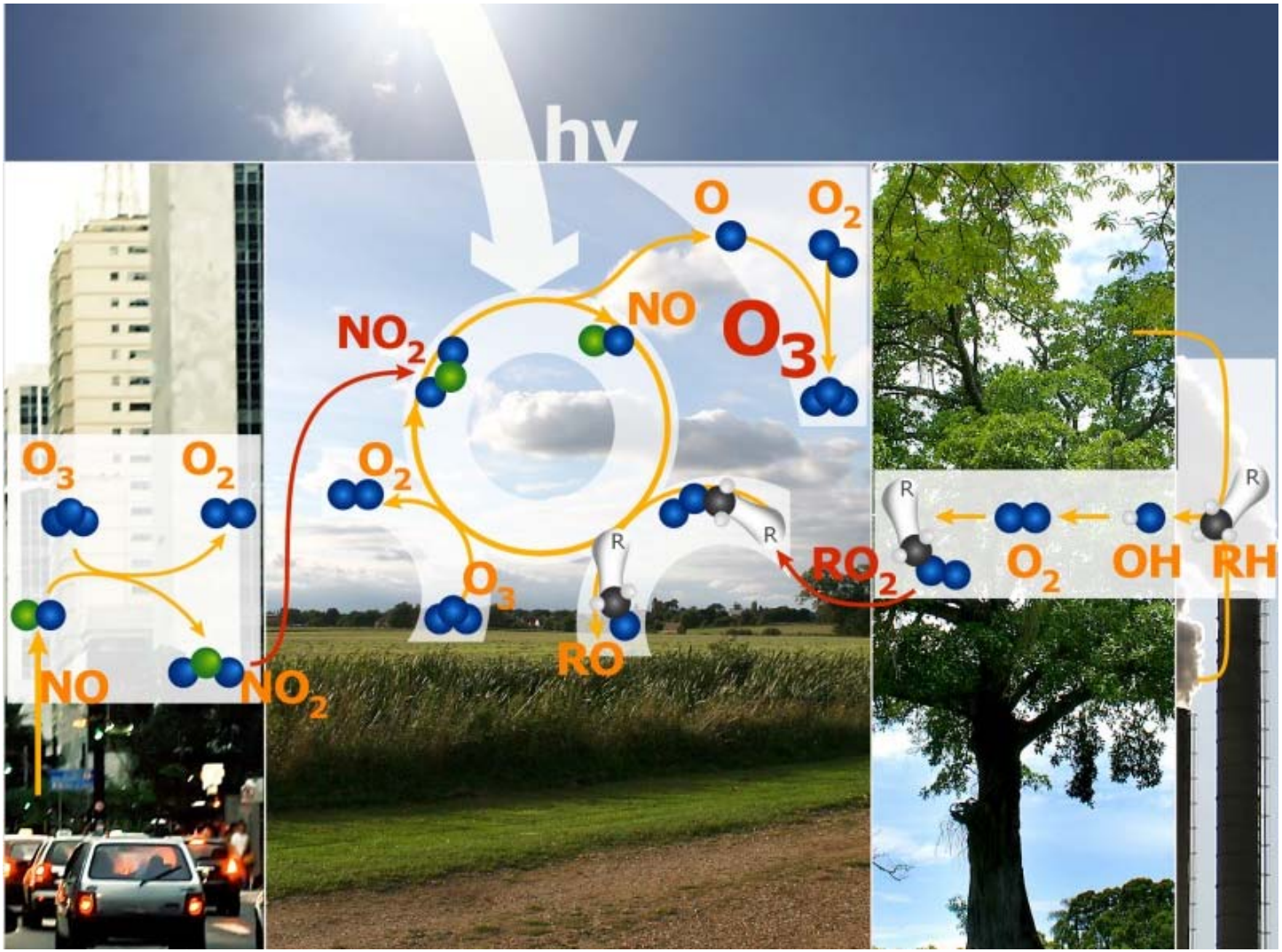


Image: Anja Kaiser. From www.atomsphere.mpg.de/enid/1442

Photochemical ozone production

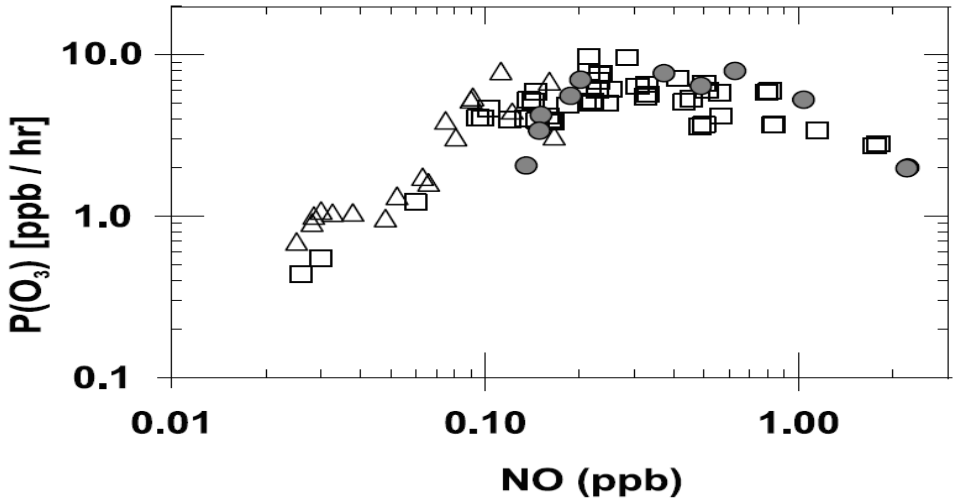
- photolysis of ozone is most significant source of OH

- atmospheric oxidation of hydrocarbons, CO and CH_4 (in descending order) initiated by OH radical
  - production of peroxy radicals (HO_2, RO_2) which interact with O_3-NO-NO_2 cycle to photo-chemically produce ozone
  - produce carbonyl compounds (aldehydes and ketones) which undergo further oxidation
  - recycling of OH

- termination by formation of nitric acid (OH + $NO_2 \equiv HNO_3$) or peroxides (H_2O_2, ROOH)

Nonlinear ozone chemistry upon NOx

- NO_x concentrations almost always low enough that ozone production is NO_x limited ([NO_x] > ~20 pptv)



- for [NO_x] < ~20 pptv, chemistry results in net ozone destruction: no NO_x to turn-over the NO-NO_2 cycle

$$O_3 + h\nu \equiv O(^1D) + O_2$$
$$O(^1D) + H_2O \equiv 2\ OH\cdot$$

– Also $HO_2\cdot + O_3 \equiv OH\cdot + 2\ O_2$

– important in tropical marine boundary layer

Estimates global NO_x emissions for early 1990s (Tg-N/year).

Technological	23 - 27
Aircraft	0.5
Biomass burning	7.0 - 8.0
Soils	5.0 - 12.0
Lightning	3.0 - 20.0

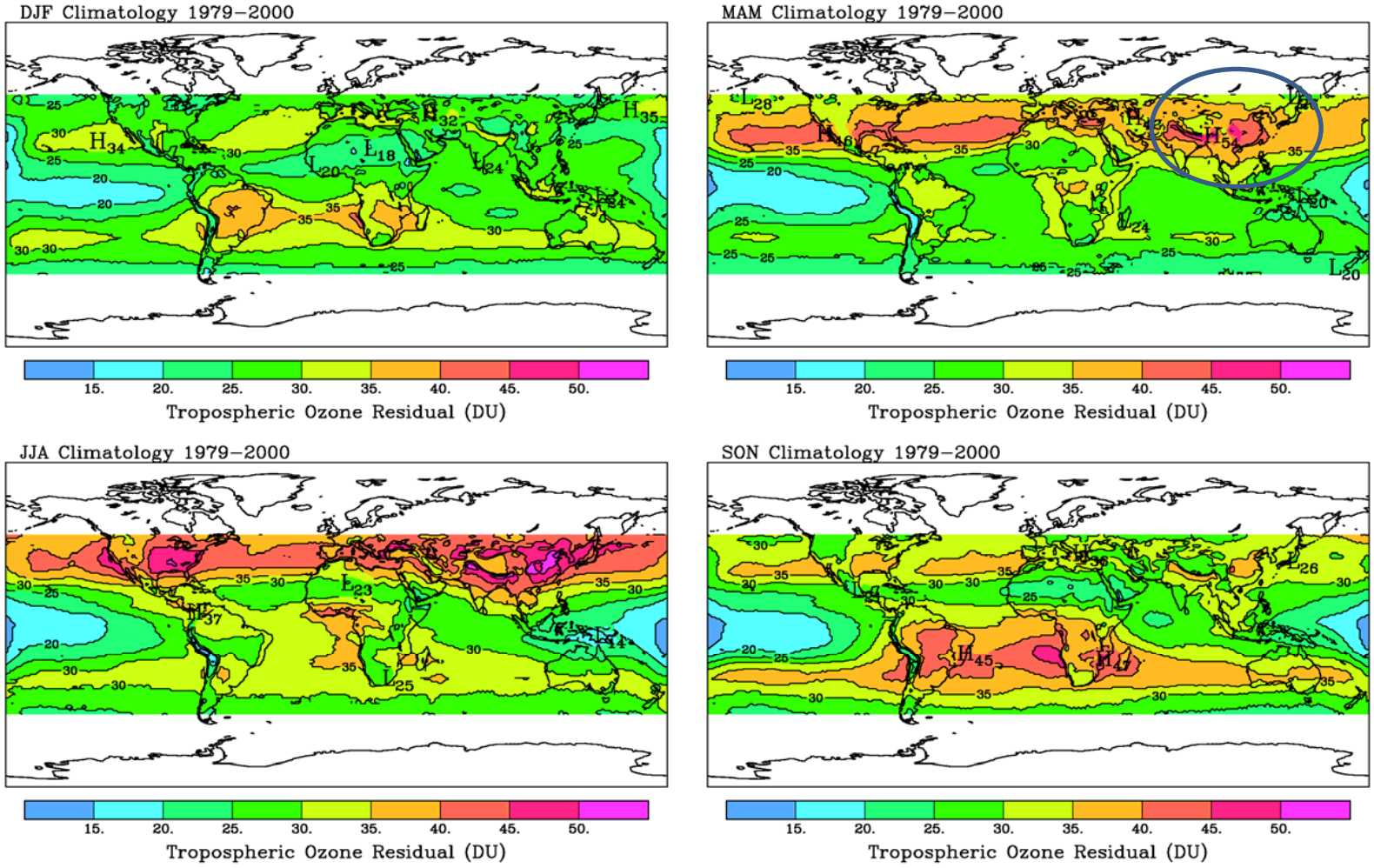
- Biomass burning includes savannah burning, tropical deforestation, temperate wildfires and agricultural waste burning

- lifetime from ~ 6 hours in planetary boundary layer (PBL) to several days to a week in the upper troposphere (UT)

- from 10s ppbv in urban areas to 10s pptv in remote regions (UT and remote MBL), give rise to different chemical regimes and control local ozone chemistry

Global tropospheric residual ozone

Tropospheric ozone column from satellite



Data from asd-www.larc.nasa.gov/TOR/data.html (Fishman *et al.*, 2003).

Surface O_3 levels in various regimes

Natural background (pre-industrial):	10-20 ppb
Remote locations in the Northern Hemisphere:	20-40 ppb (varying by season and latitude)
Rural areas during region-wide pollution events	80-100 ppb
Peak O_3 in urban areas during pollution events	120-200 ppb
Maximum urban O_3 (Los Angeles, Mexico City)	490 ppb
Stratospheric ozone layer	15000 ppb
USEPA health standard for ozone	85 ppb, 8 hour exposure
HKAQO	122 ppb

Scientific and interesting questions

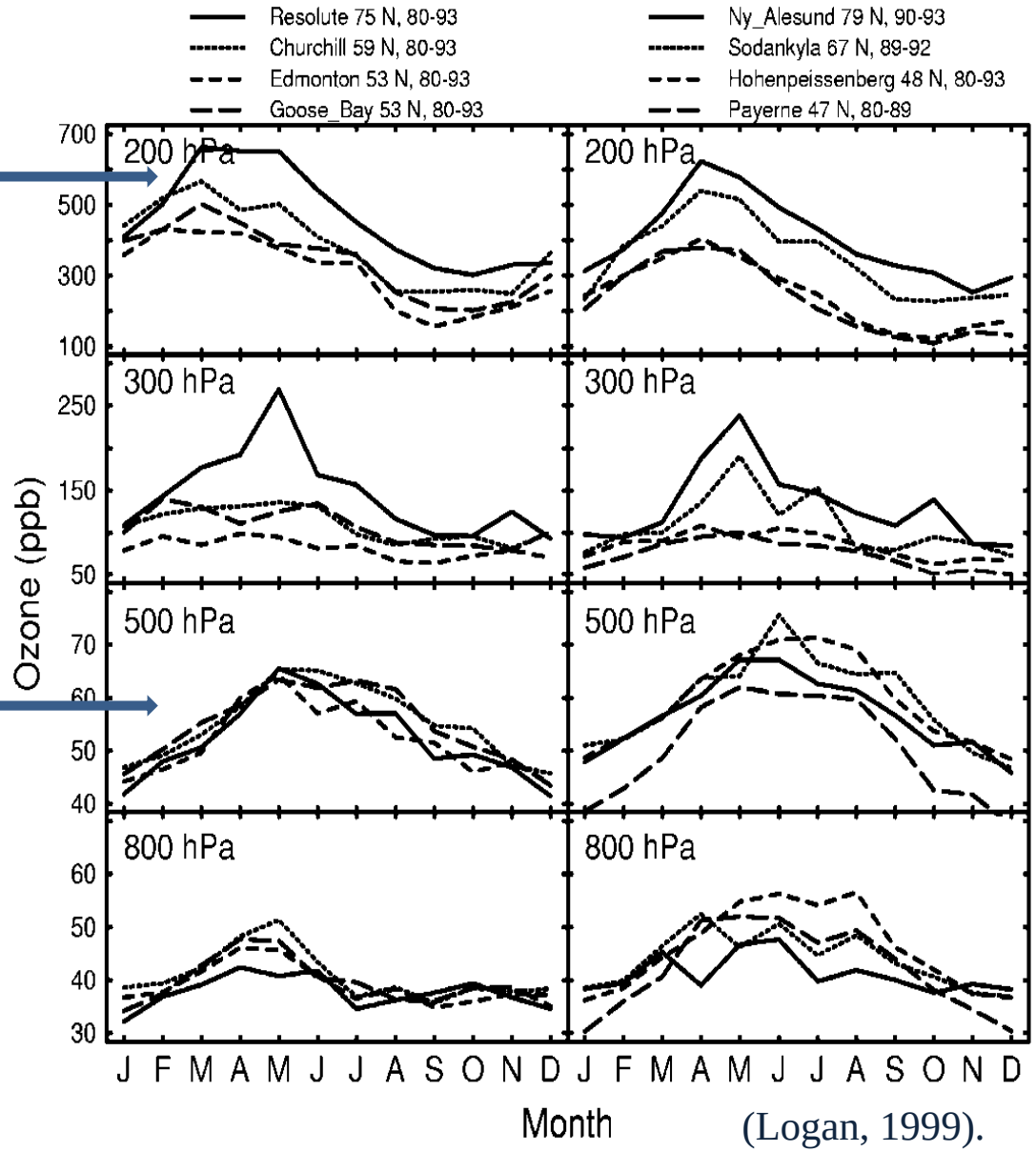
- In Europe and N. America, increases of photochemical ozone produced from pollution has resulted in change of seasonal cycle of tropospheric ozone, and thus oxidizing capacity of the atmosphere.
- What happens in Asia? How this will impact on the regional air quality, atmospheric chemistry and eco-climate system?
- To understand the issues, we HAVE TO separate natural ozone and anthropogenic ozone from pollution to tropospheric ozone budget, especially the seasonal maximum.
- Challenges: very limited systematic and long-term ozone measurements in Asia and there is still no a good method.

Source of spring-summer tropospheric ozone maximum in Asia

Debate on sources of ozone maximum

Dynamic processes: strat-trop exchanges, such as tropopause folding

Chemical processes: formation from industrial and urban pollution

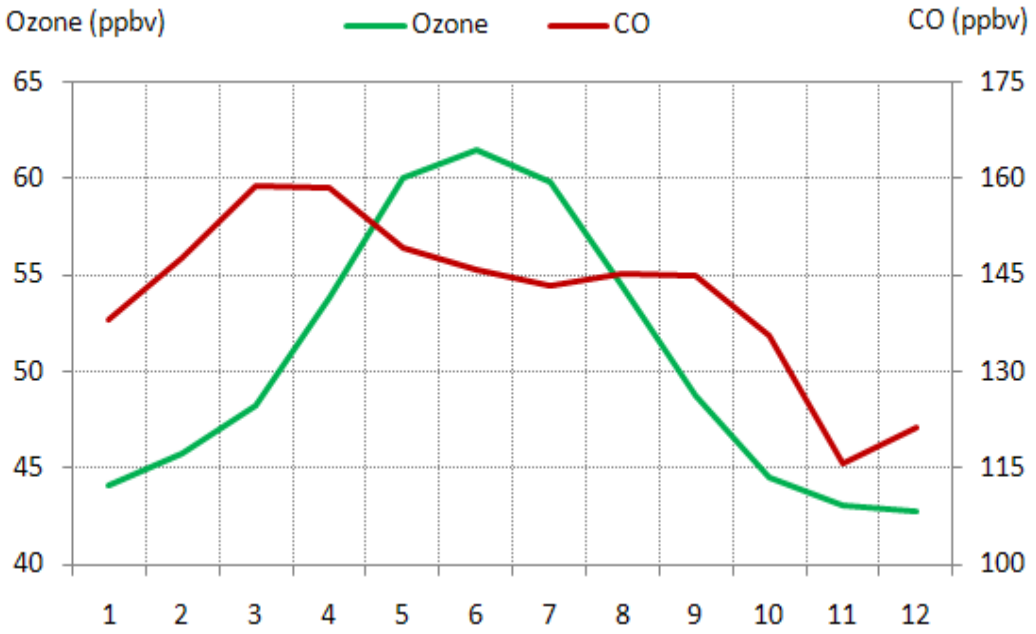


Seasonal cycle of O_3 at different pressure levels (eight different stations of northern hemisphere)

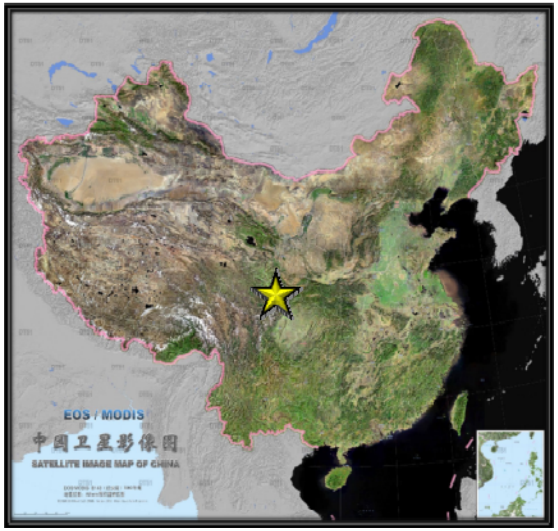
(Logan, 1999).

Debate on sources of summer ozone maximum

- natural strat. ozone (Ding et al)
- long-range transport from Eurasia (Zhu et al.)
- transport of from east China (Akimoto)
- combination of both (Zheng et al.)

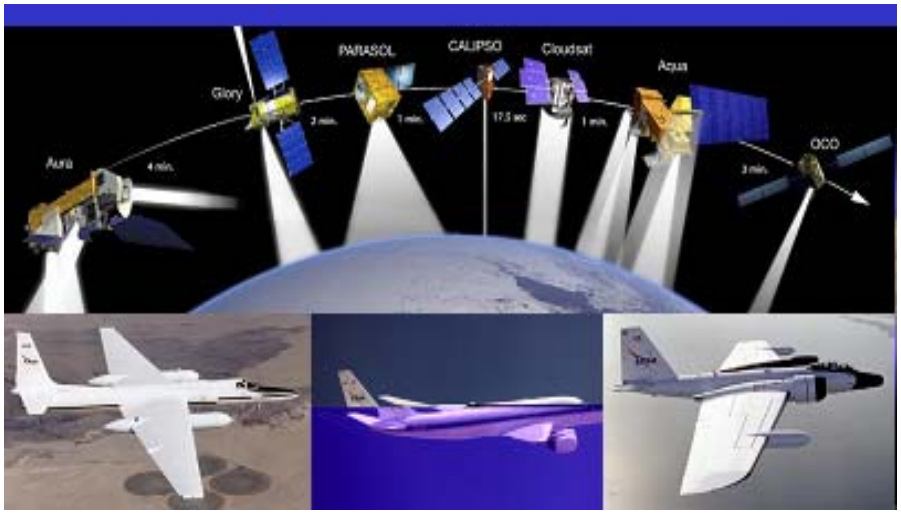


Waliguan Observatory
2001-2009



NASA's Aircraft Mission- Global Tropospheric Experiment (GTE) Program

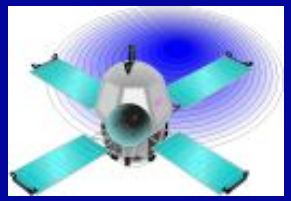
- The Transport and Chemical Evolution over the Pacific (TRACE-P) in March/April 2001



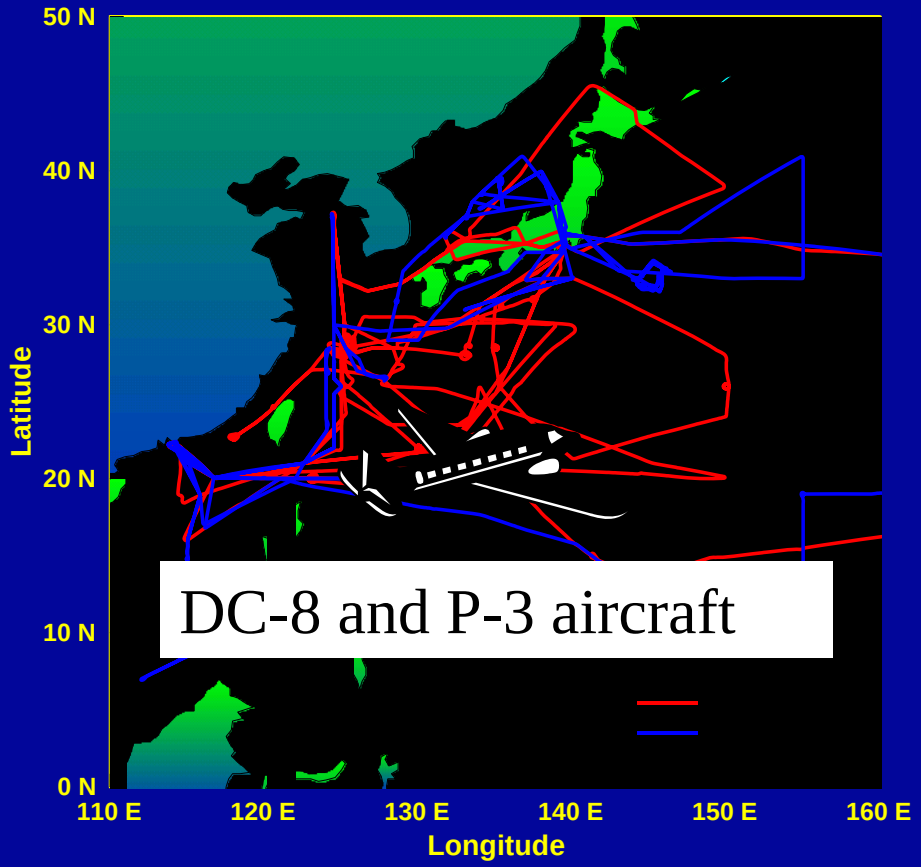
- Objectives to determine:
  - chemical composition of the Asian outflow over the western Pacific in spring in order to understand and quantify the export of chemically and radiatively important gases and aerosols, and their precursors, from the Asian continent
  - chemical evolution of the Asian outflow over the western Pacific in spring and to understand the ensemble of processes that control the evolution, focusing on tropospheric O3 and aerosols.

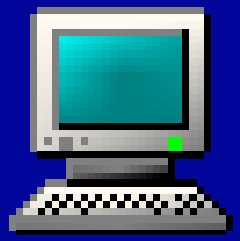
NASA/TRACE-P Aircraft Mission to the Pacific Rim (March-April 2001)

Quantifying the export of Asian pollution



Satellite data:
MOPITT (CO)
TOMS (ozone)
SEAWIFS,
TOMS (aerosols)





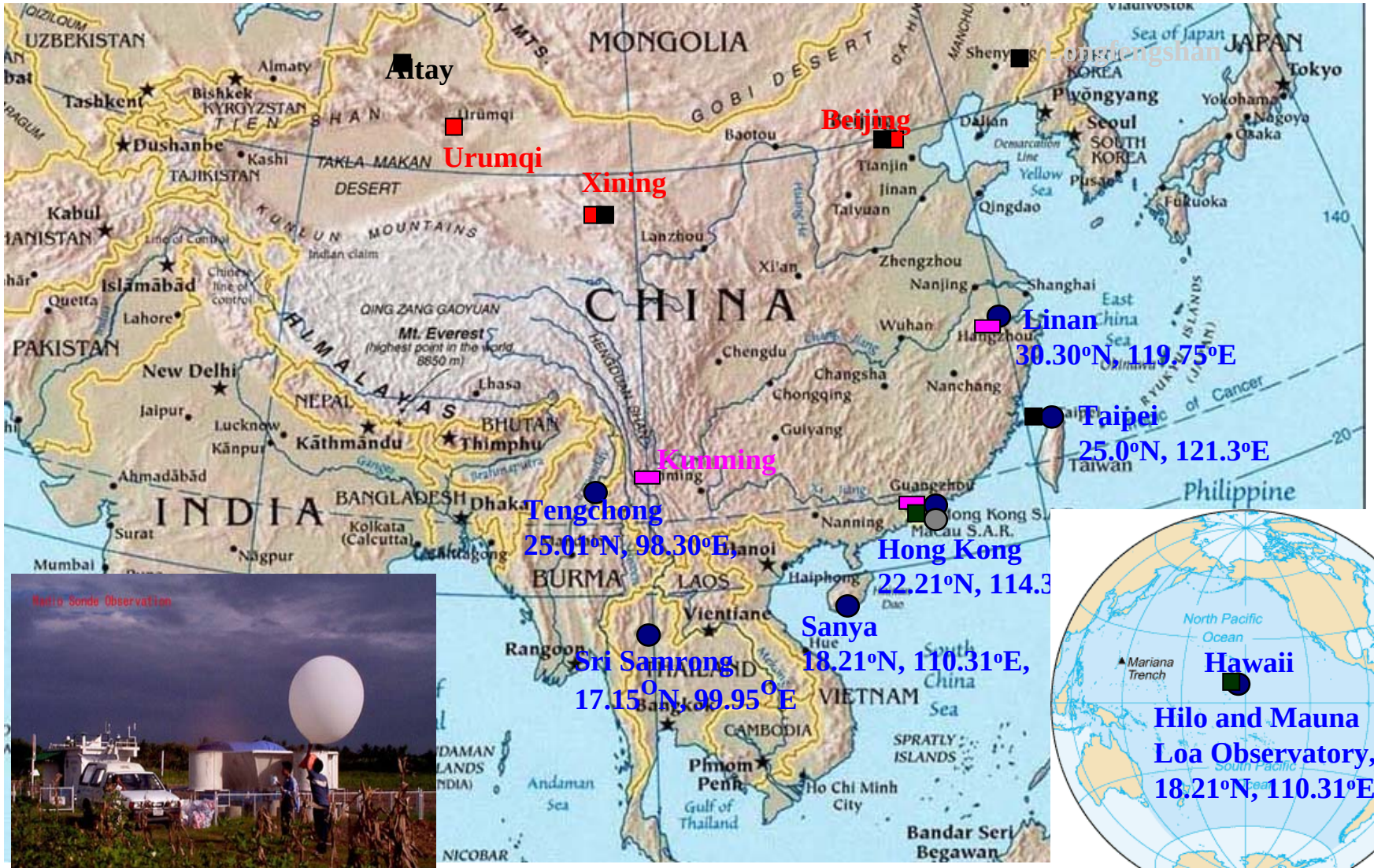
3-D chemical transport model forecasts

Flight tracks were designed to optimize model testing and satellite validation

Jacob et al., 2003

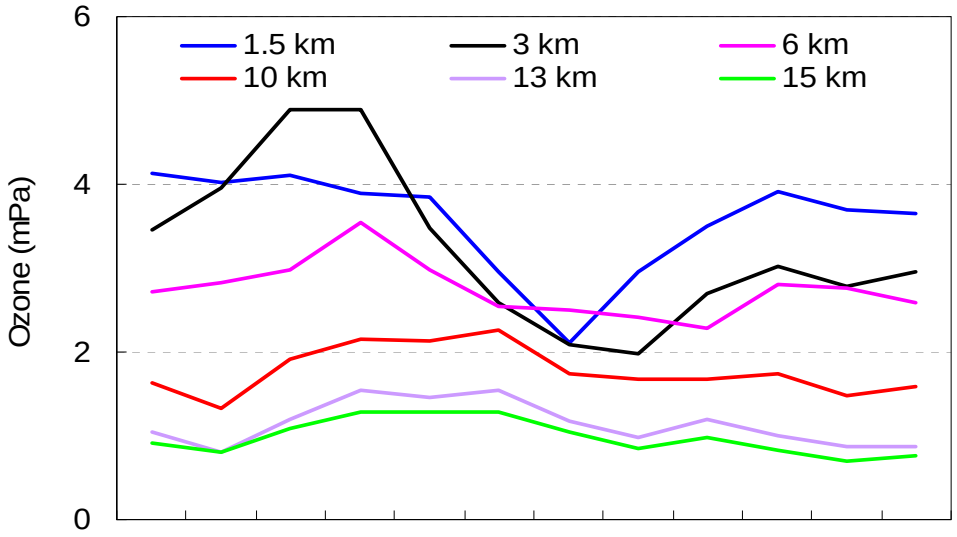
Ozonesonde experiment programs

- Since 1993 and 1994; NASA TRACE-P: spring 2001; NASDA PEACE-A: winter 2002;
- TAPTO: spring 2004; TAPTO: spring 2005

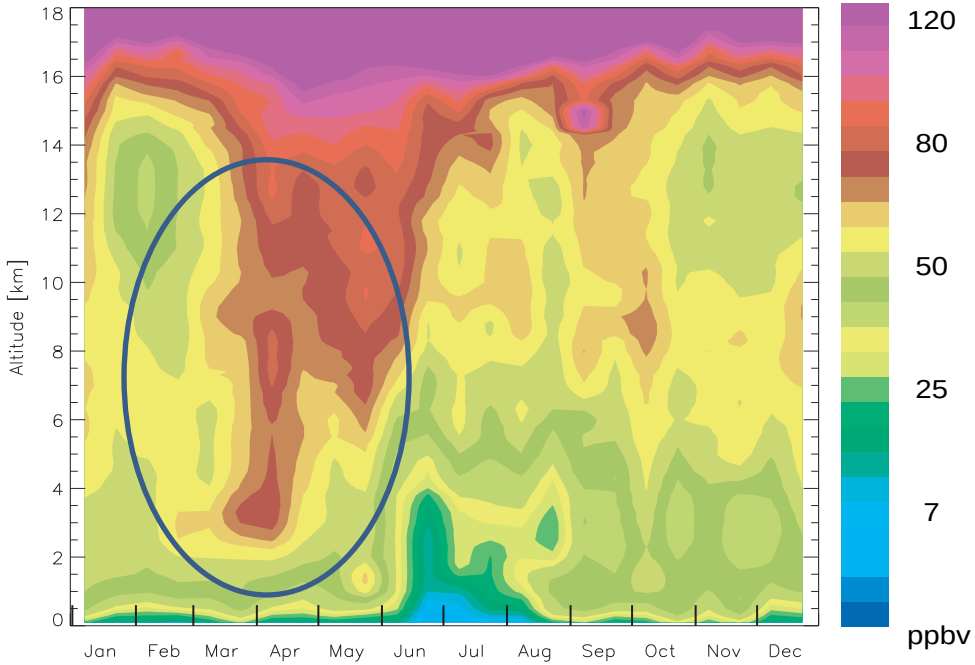


Tropospheric ozone over Asia

Hong Kong (22.4 ºN) (1994-2007)

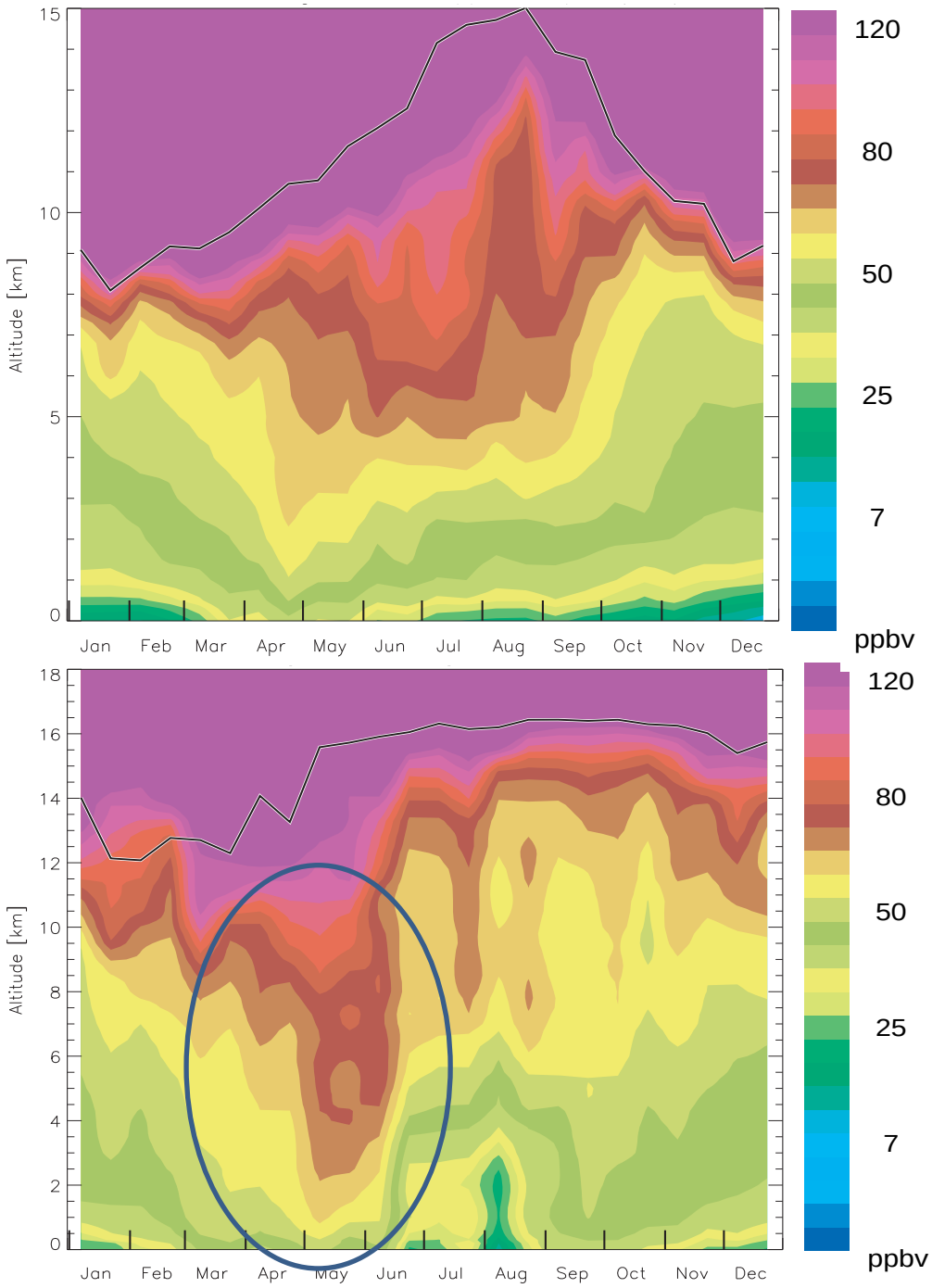


Hong Kong (22.4 ºN) (2000-2001)



Sapporo, Japan (43°N) (2000-2001)

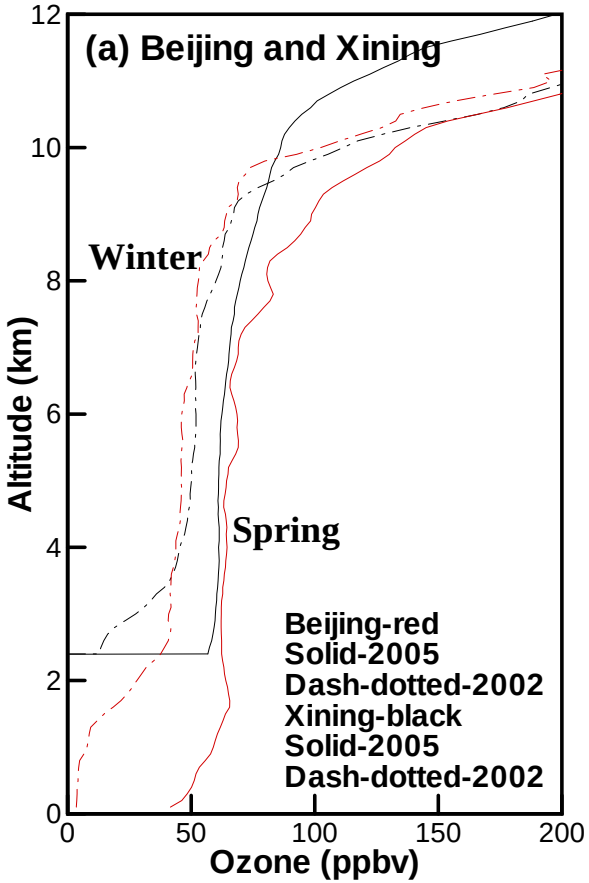
Kagoshima, Japan (32°N) (2000-2001)



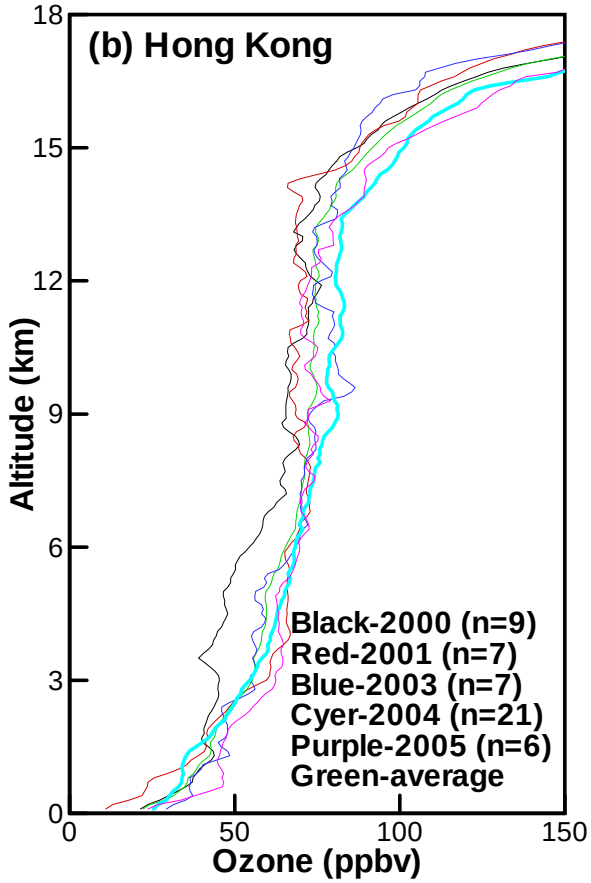
Change of ozone profiles

Winter: 2002 - (Jan-Feb)

Spring: 2005 - (April-May)



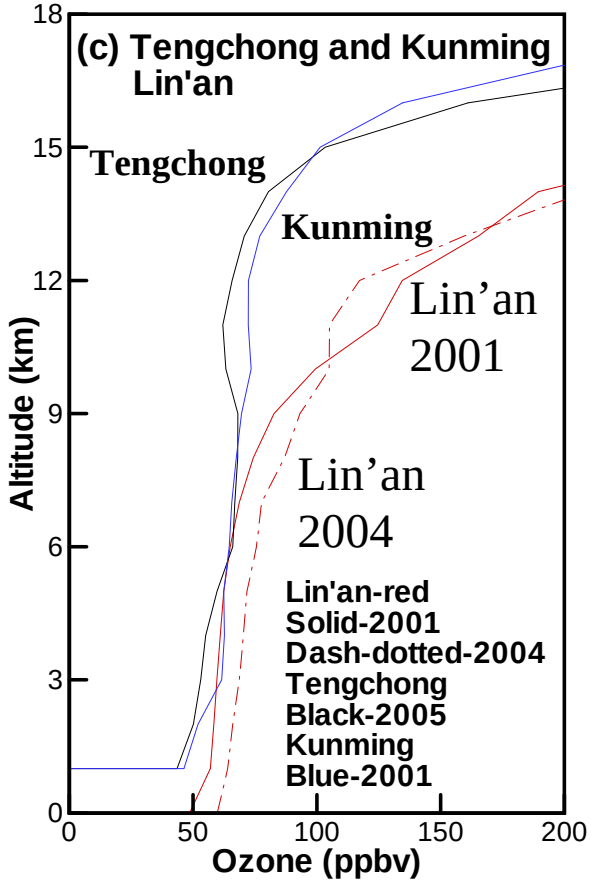
Spring (April-May)



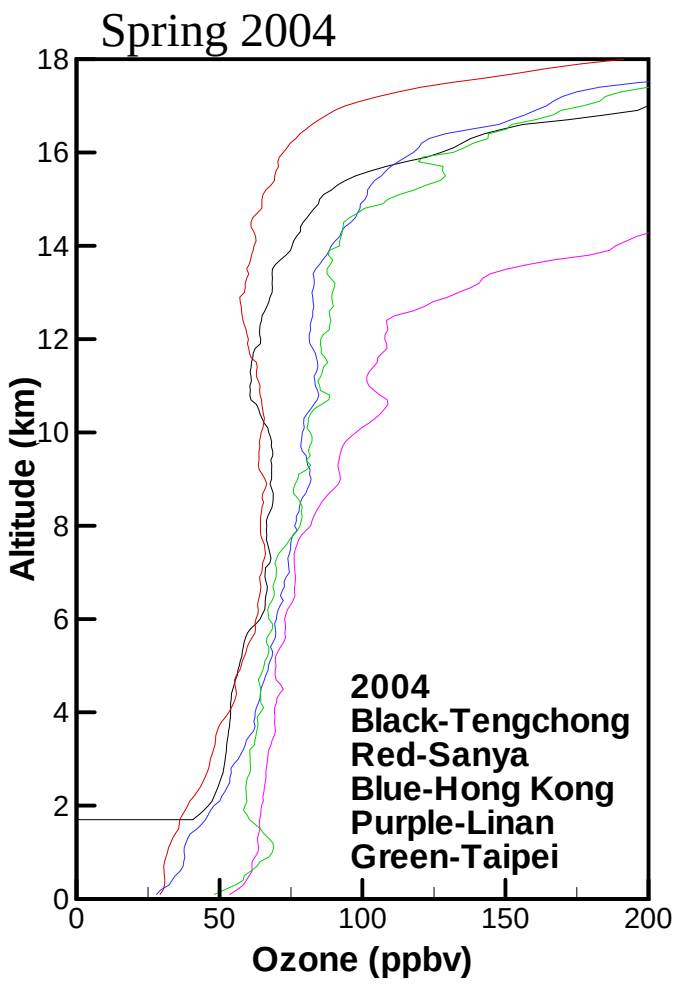
Spring:

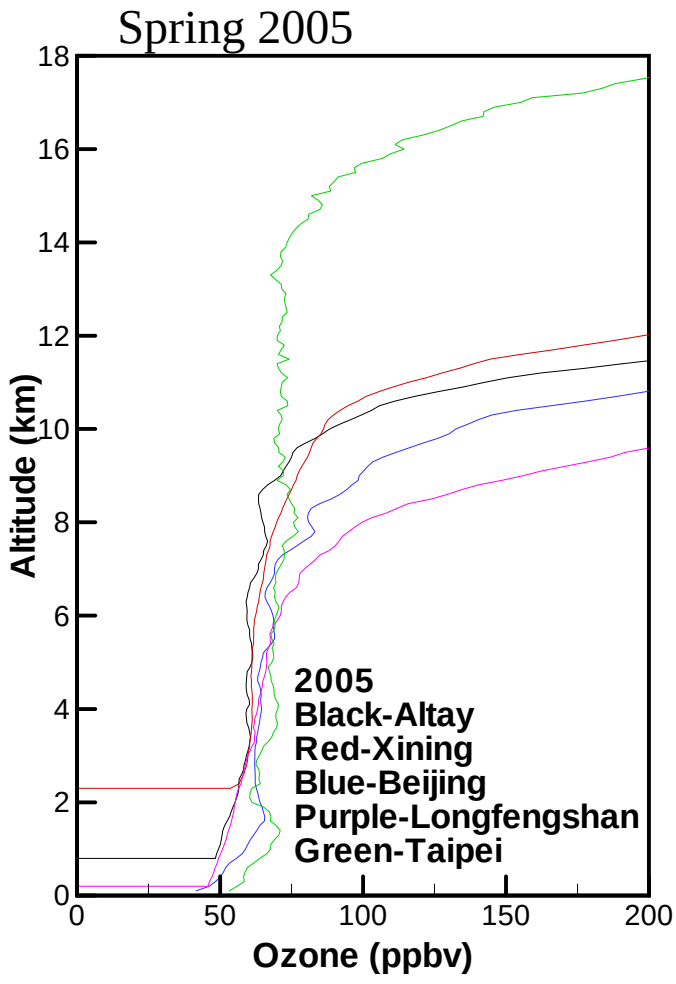
2001 - (March-April)

2004 - (April-May)

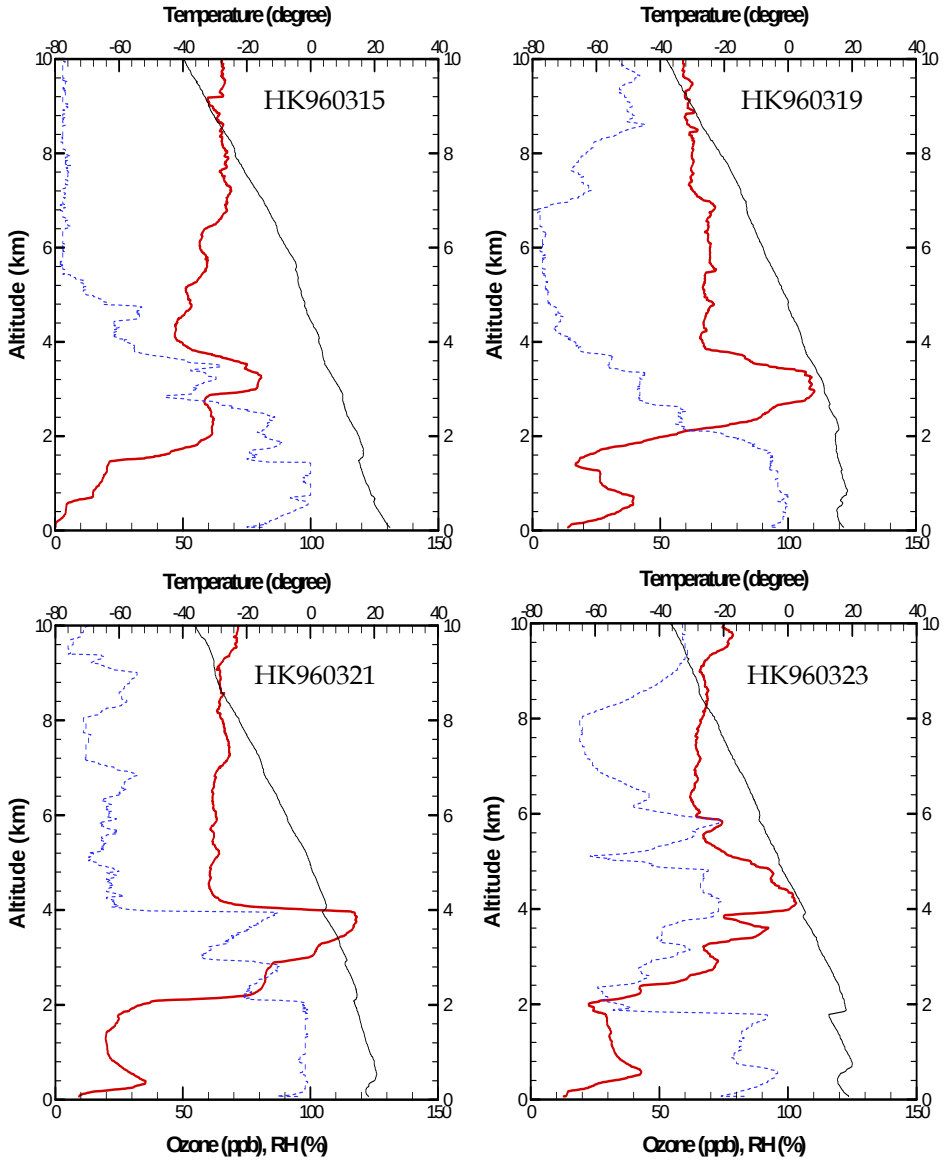


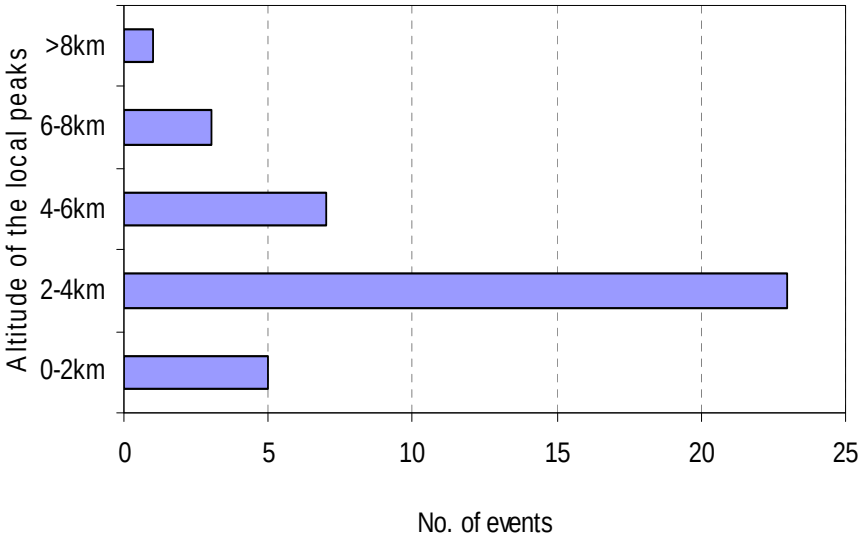
Characteristics of ozone profiles in south and north transport pathways





SE Asian biomass burning and ozone enhancements over the Pacific



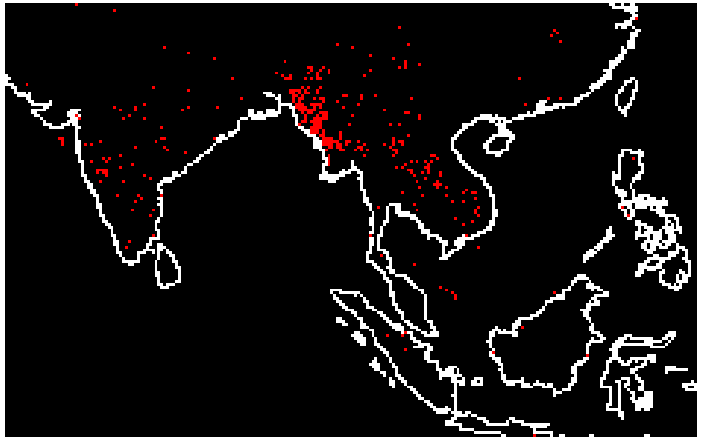


The seasonal distribution of the ozone enhancement cases and the vertical distribution of local ozone peaks over Hong Kong from 1993 to 1999.

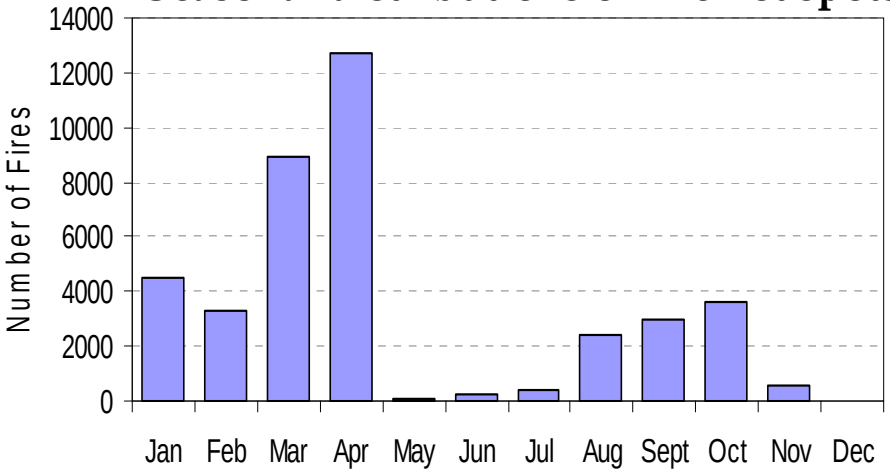
Chan et al., 2001, 2003

Biomass burning activity in SE Asia

Fire counts in April 2001

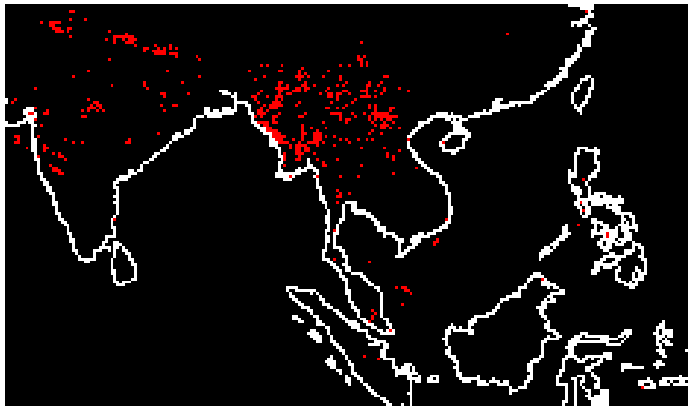


Seasonal distributions of fire hot spots



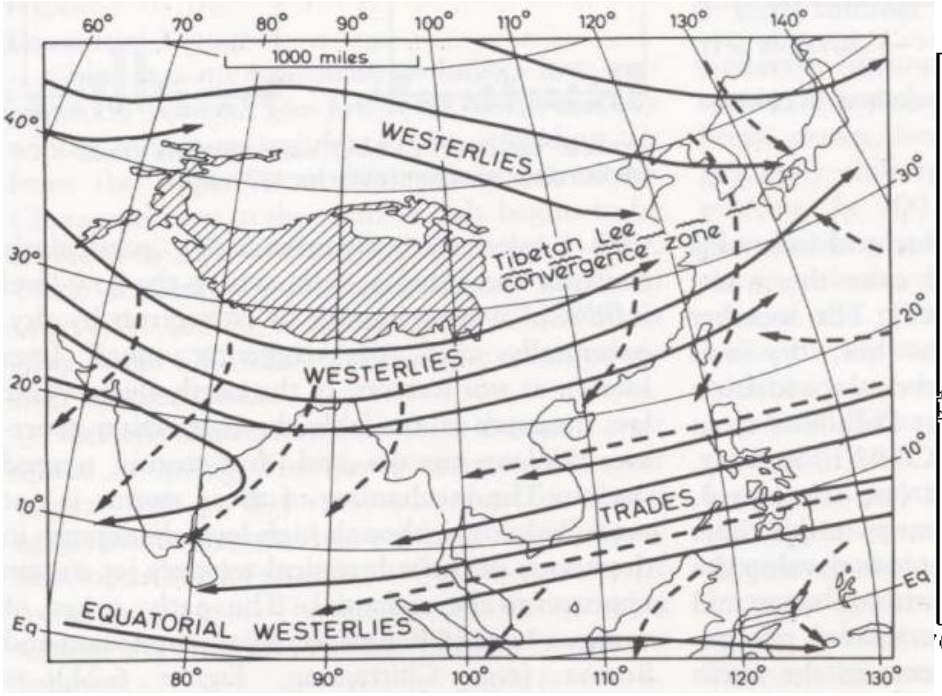
SE Asia (-10º to 30º N and 60º to 150º E).

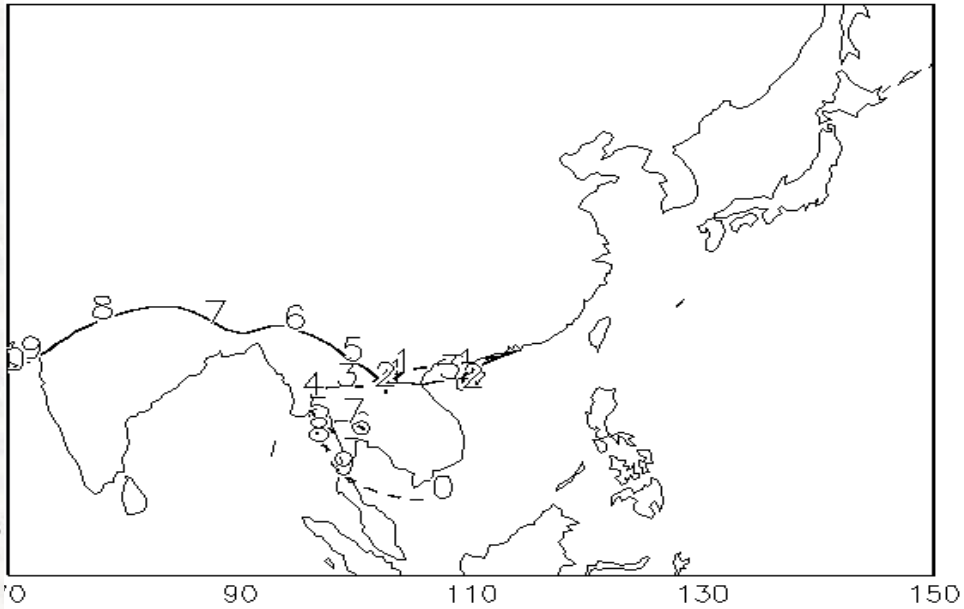
Fire counts in March 2001



Source: ESA

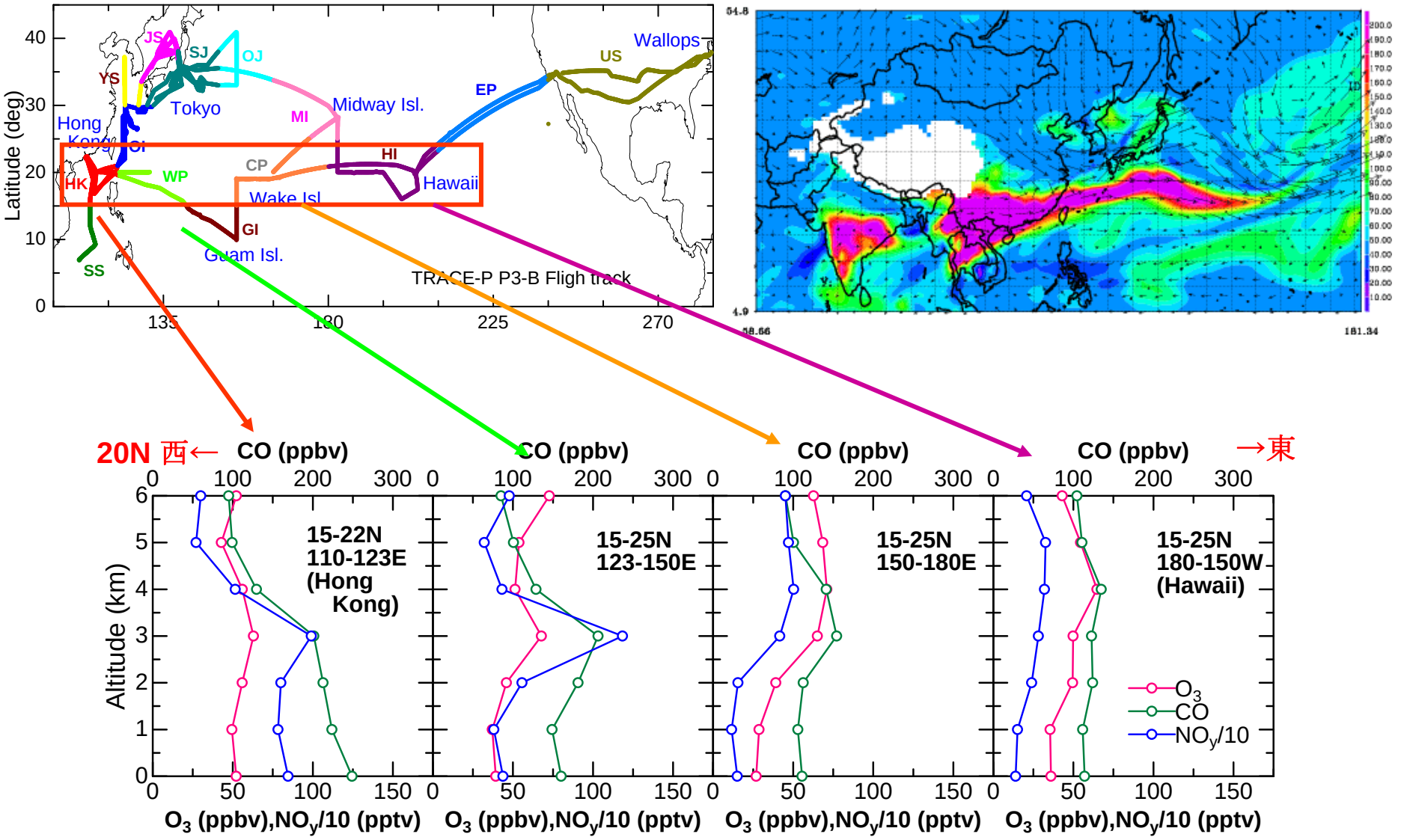
Typical transport patterns of ozone-rich air masses following the transport pathways of upper westerly wind from the fire hot spot regions in SE Asia.





L.Y. Chan et al., 2000

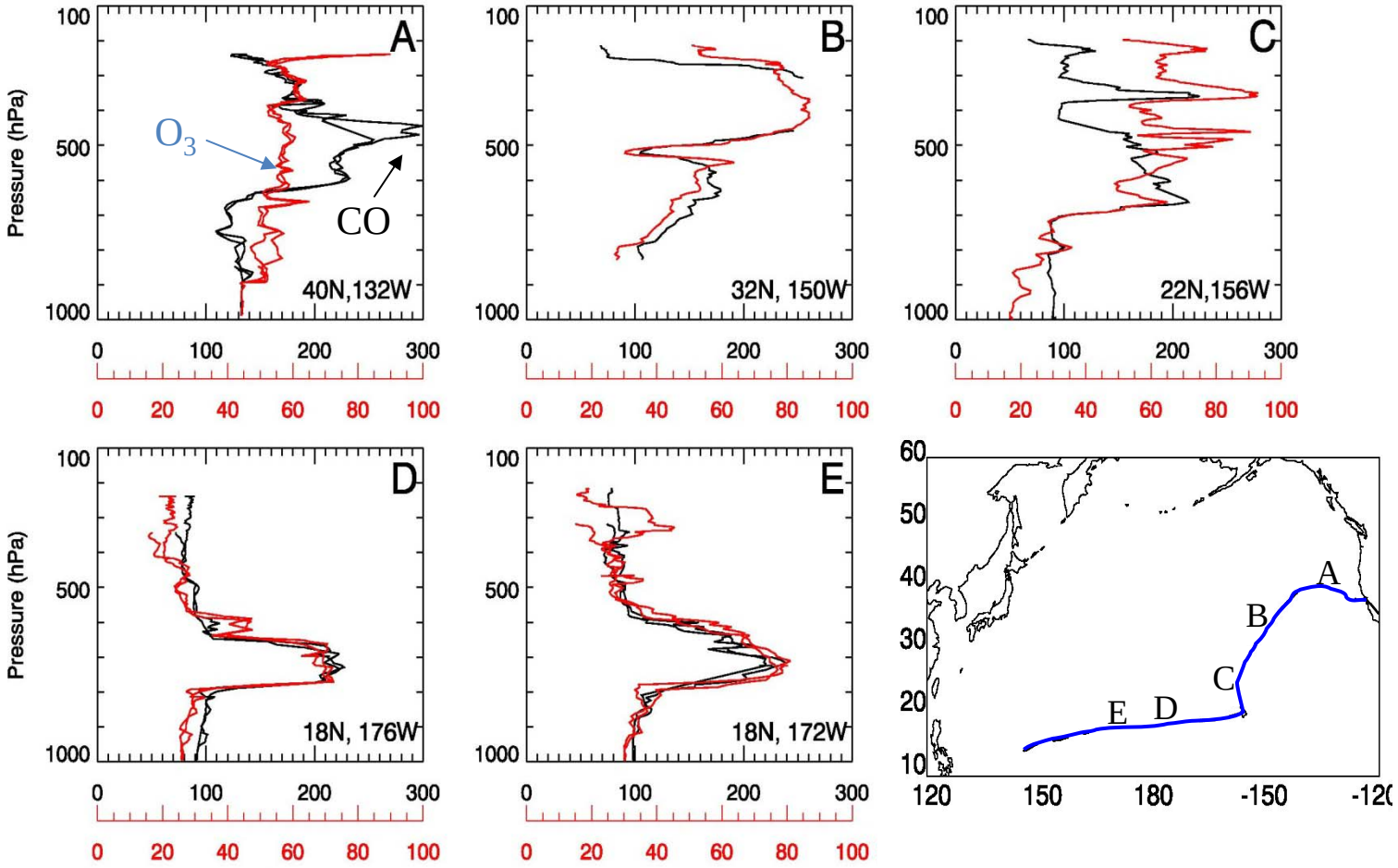
TRACE-P biomass burning plume



TRACE-P biomass burning plume

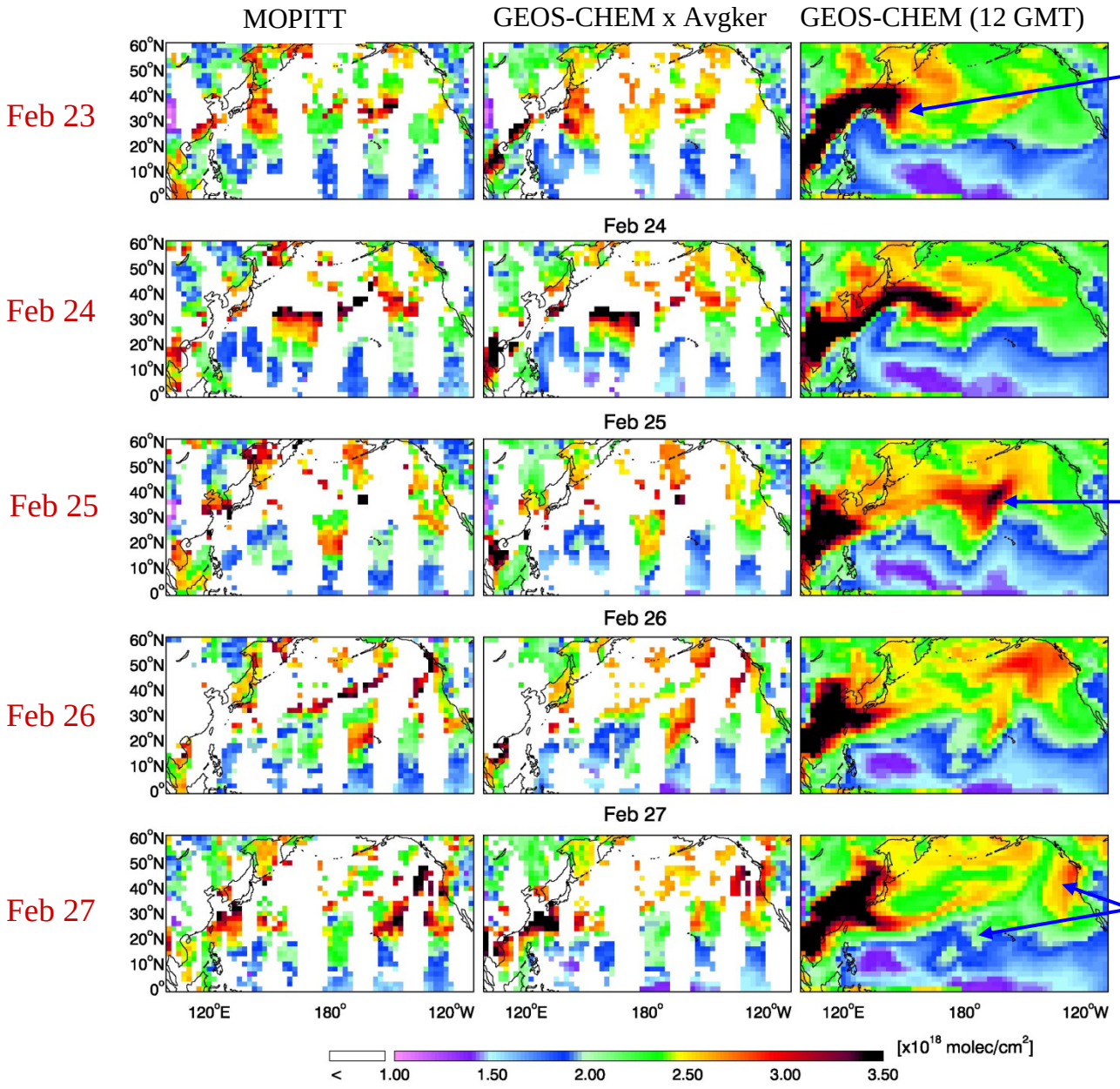
Feb. 22-27, 2001

- Aircraft observations during outbound trans-Pacific TRACE-P flights observed elevated levels of CO (and O_3)



Jacob et al., 2003

MOPITT OBSERVATIONS OF A TRANSPACIFIC PLUME
Total column CO

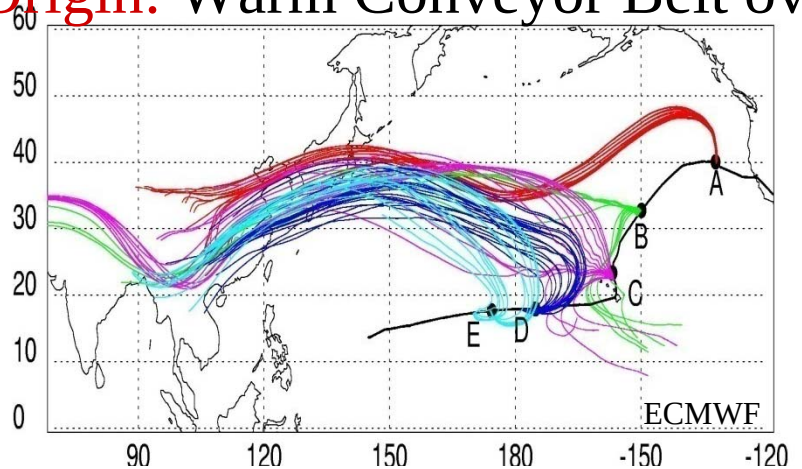


Asian pollution exported via cold front

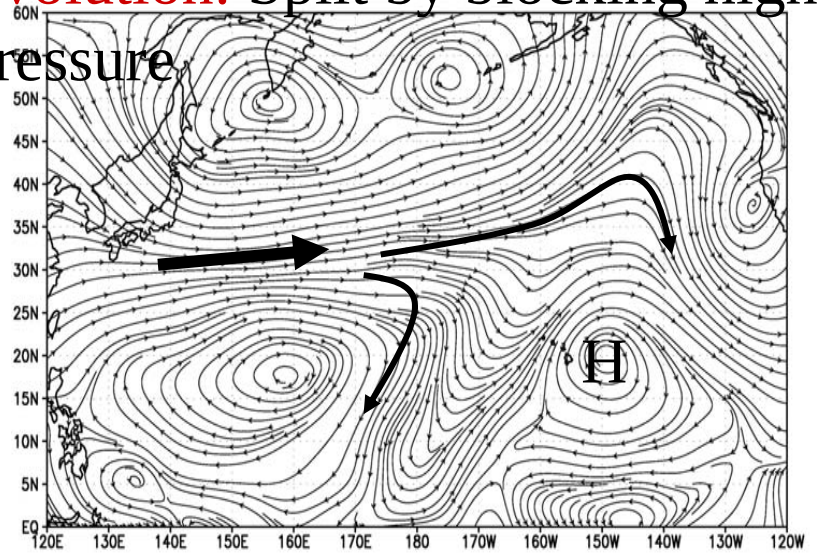
Plume encounters a blocking H Pressure System and splits

Elevated CO reaches North America
Southern branch at low latitudes produces O_3

Origin: Warm Conveyor Belt over Asia



Evolution: Split by blocking high pressure



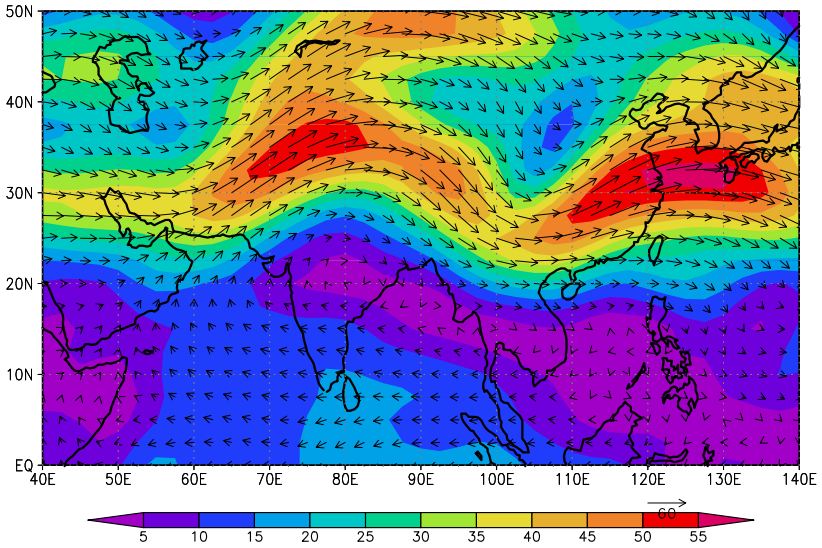
Scientific questions: Impact of Asian pollution over Pacific and N. America

- *Since 1990s, Jaffe, Yienger and others suggested that the observed oxidant, trace gas and aerosol compositions increases in eastern Pacific and North America are due to transboundary transport of pollutants from Asia .*

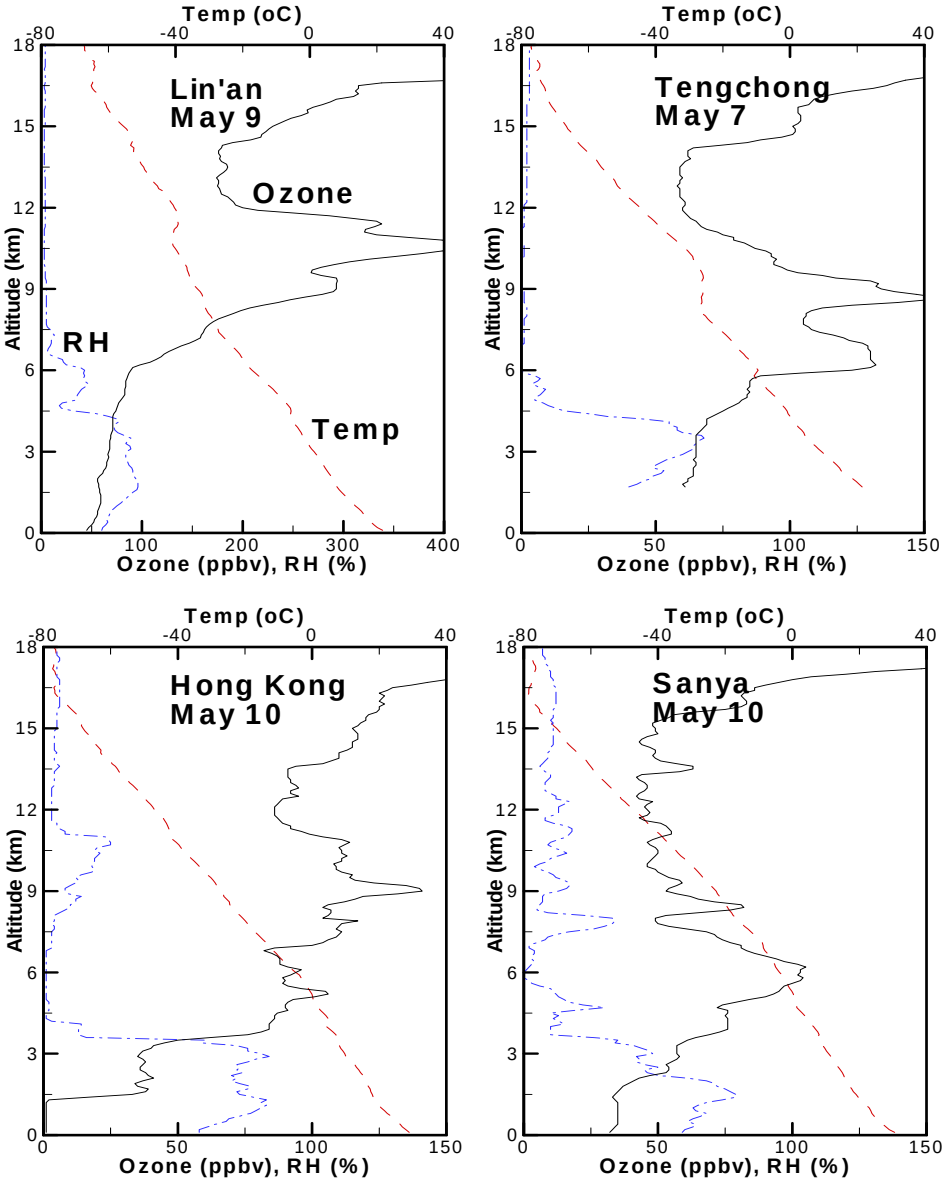
- *Jacob et al. pointed out that the surface ozone increases in America are results of cross-Pacific transport of ozone of anthropogenic ozone from Asia .*

- *Oltmans et al. however reported that ozone increases at Mauna Loa Observatory in Pacific during springtime when transport of pollutants from Asia is more significant is insignificant. On the contrary, most apparent increases occur during the fall and winter of 1980-2000 due to large scale change in air mass flow pattern in the Pacific.*

Ozone enhanced by Stratosphere-Troposphere Exchange

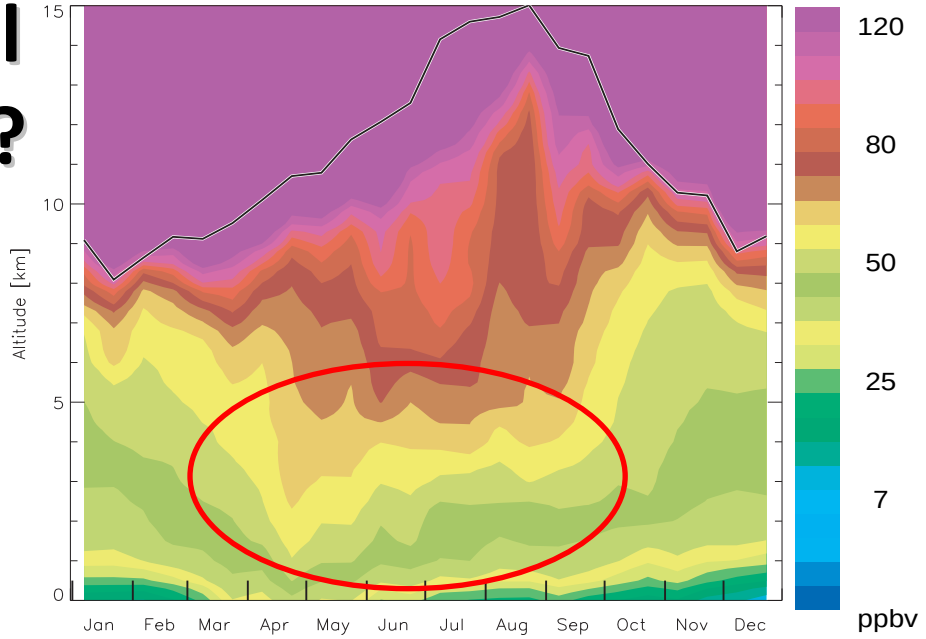


May 7

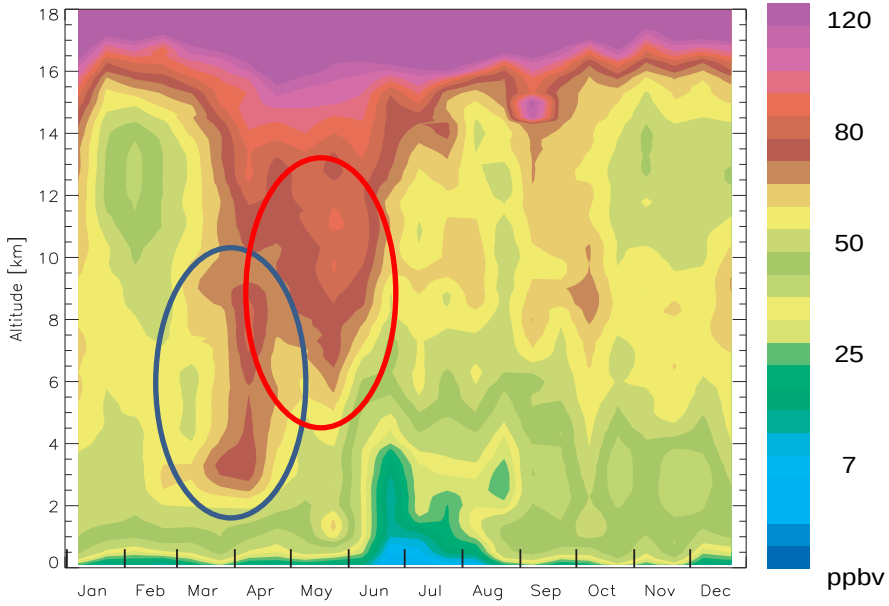


How to distinguish natural and anthropogenic ozone?

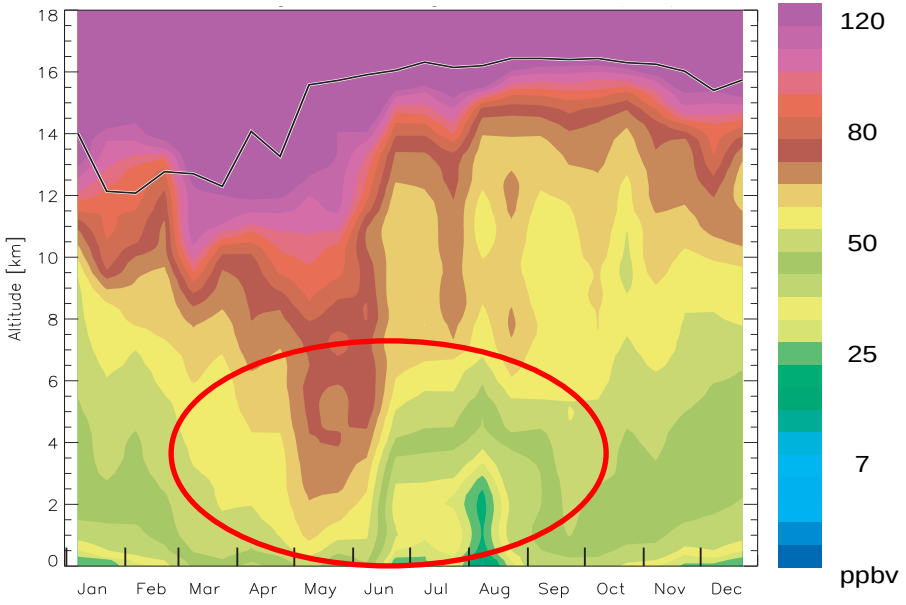
Sapporo, Japan (43°N) (2000-2001)

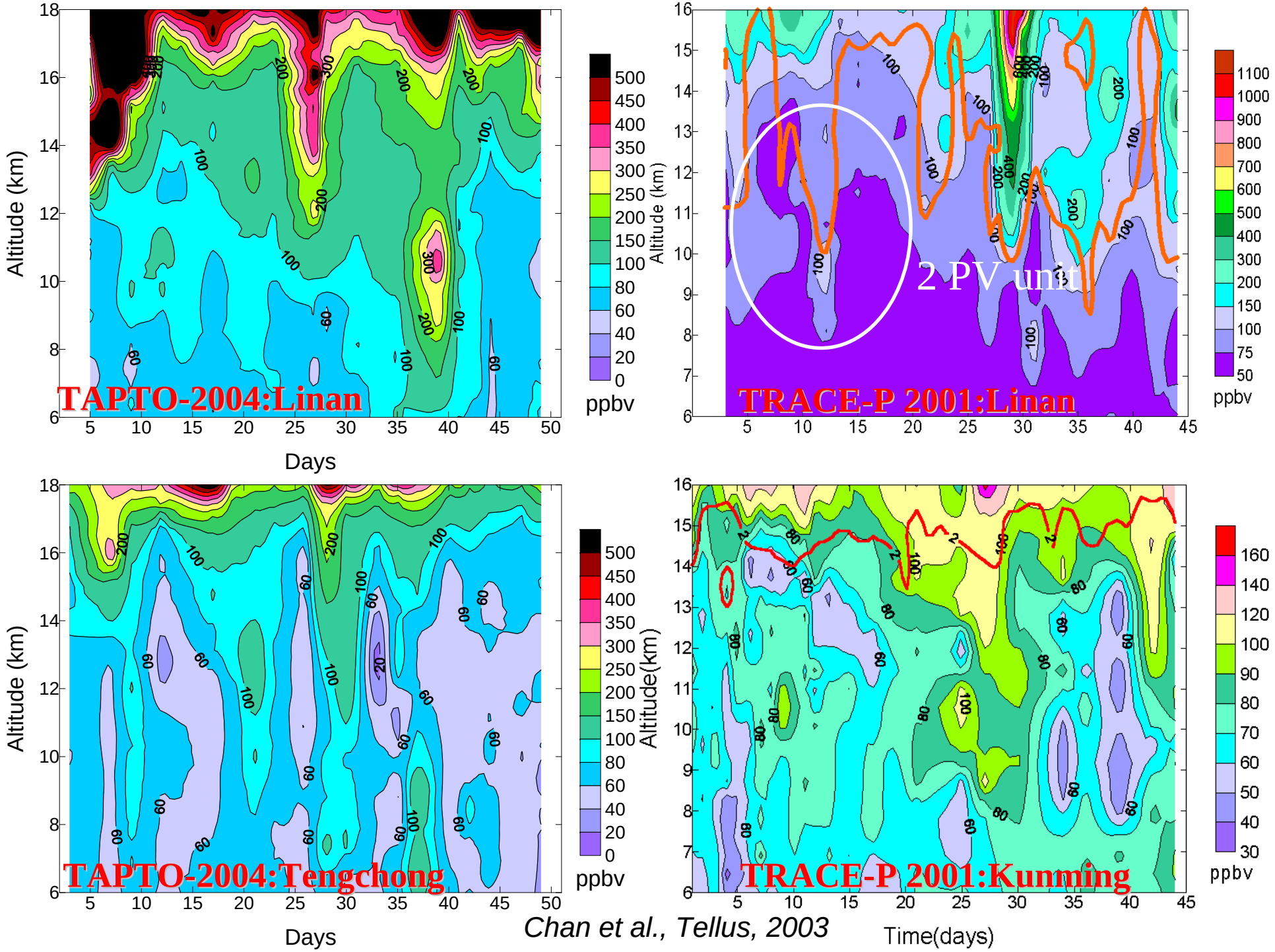


Hong Kong (22.4 °N) (2000-2001)



Kagoshima, Japan (32°N) (2000-2001)





Chan et al., Tellus, 2003

Scientific hypothesis:

- *Natural ozone due to stratospheric-tropospheric exchange process is one of the candidates that mix with anthropogenic ozone and pollution and being transported to the downwind Pacific and America and resulted in ozone increases there.*

- *Will the recovery of stratospheric ozone layer cause increases of tropospheric ozone due to frequent STE processes? Will such natural ozone reaches surface and impacts on air quality?*

- *How to distinguish this natural ozone and to quantify this natural ozone at surface?*

New evidence and isotope mass independent fractionation method for assessing stratospheric air at surface

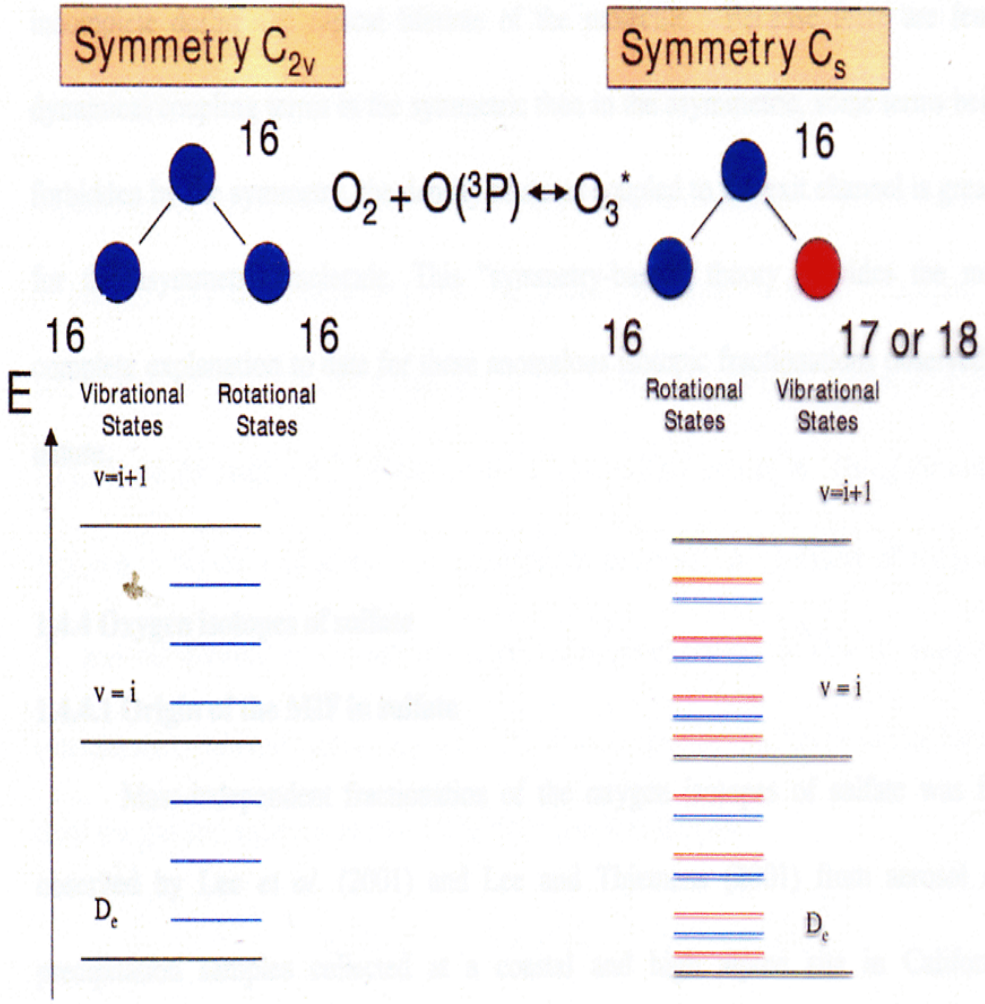


FIGURE 1.14 Diagram showing that the asymmetric C_s ozone molecule has a greater number of rotational states superimposed on its vibrational levels, resulting in greater stability in the O_3^* intermediate.

Chemical interaction of O_3 and CO_2

– a source of mass independent fractionation of stable oxygen isotopes in CO_2

- $O+O_2 + M \rightarrow O_3 + M$ (M=N_2, O_2, etc.) (1)
- $O_3 + hv \rightarrow O_2 + O(1D)$ (2)
- $O_2 + hv$ (Lyman-α) $\rightarrow O(^3P) + O(^1D)$ (3)
- $O(^1D) + CO_2 \rightarrow CO_3^* \rightarrow CO_2 + O(^3P)$ or $O(^1D)$ (4)

- significant sources of $\delta\,^{17}O$ and $\delta\,^{18}O$ in CO_2 at stratosphere and mesosphere

SOURCE OF ANOMALOUS CARBON DIOXIDE

$$^{18}O(^{1}D) + CO_2 \text{ ----> } CO_3^* \text{-----> }$$

$$^{16}O(^{3}P) + CO_2$$

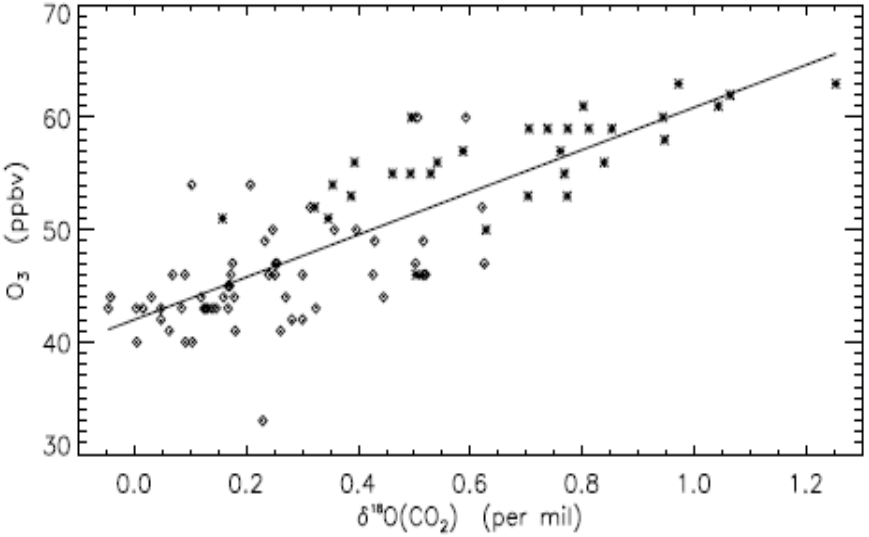
Thus, the oxygen isotopic anomaly in carbon dioxide reflects ozone photochemical activity. Coupled to trace species measurements, this is a new, highly sensitive means to study stratospheric and mesospheric chemistry.

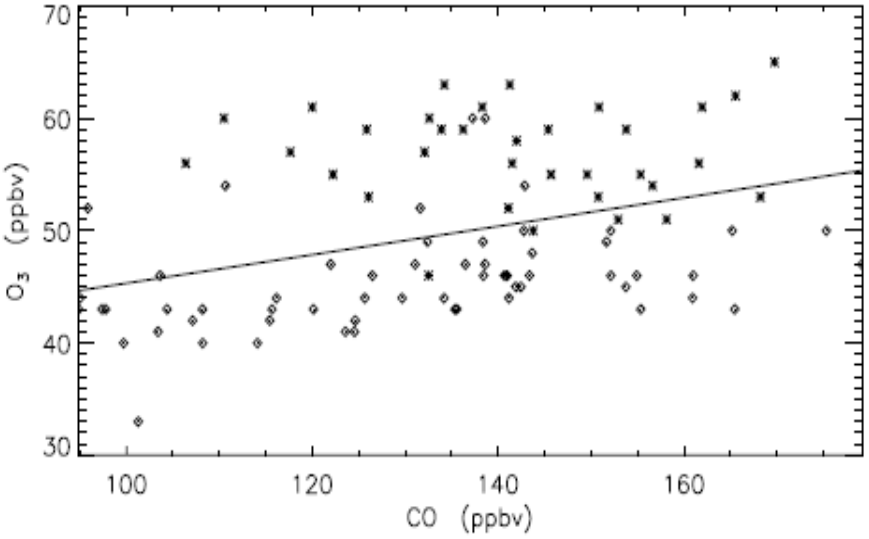
Also
effective measure of
stratosphere-troposphere
mixing

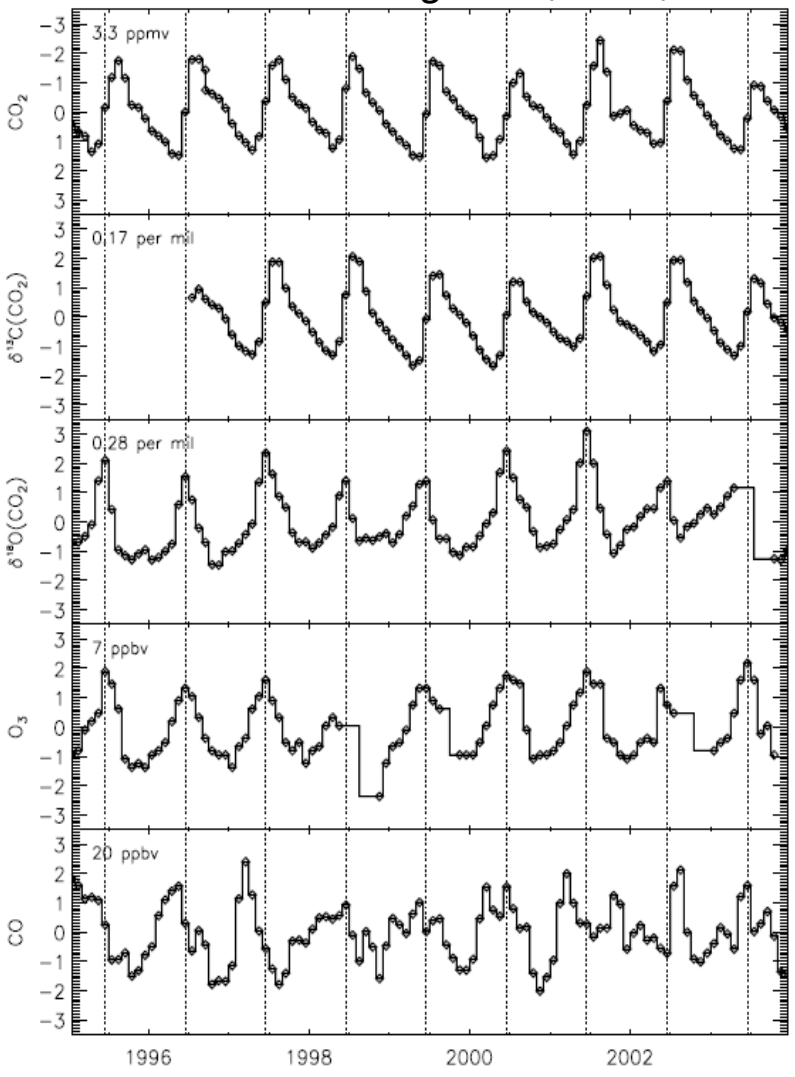
M. Thiemens

New evidence from $\delta\,^{18}O_{CO2}$ – contribution from stratosphere at surface

Liang et al., GRL, 2007







Relationship between $\triangle^{17}O_{CO2}$ and stratospheric air tracers ($\triangle^{17}O_{CO2} = \delta\,^{17}O\text{-}0.516\times\,\delta\,^{18}O$)

NASA - *ER-2* High Altitude Airborne Science Aircraft

-

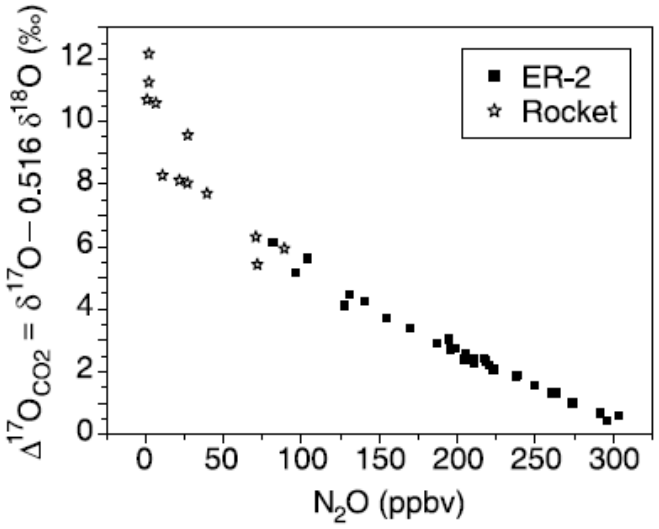


Figure 3. $\Delta^{17}O_{CO2}$ vs N_2O mixing ratio from the ER-2 and rocket [*Thiemens et al.*, 1995b].

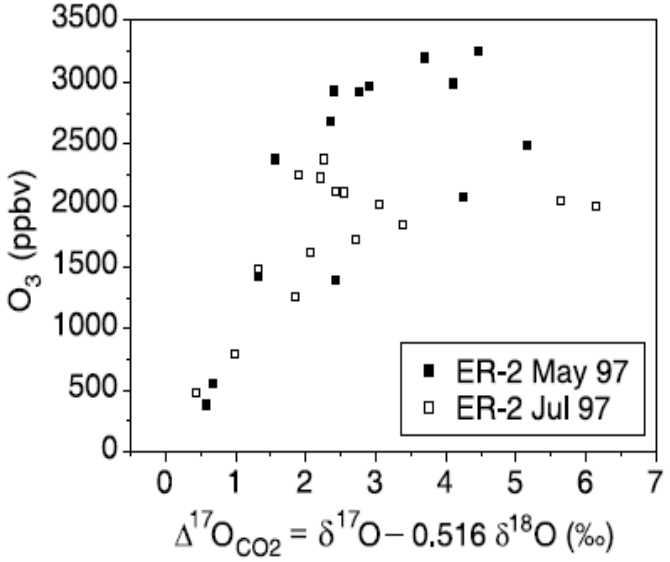
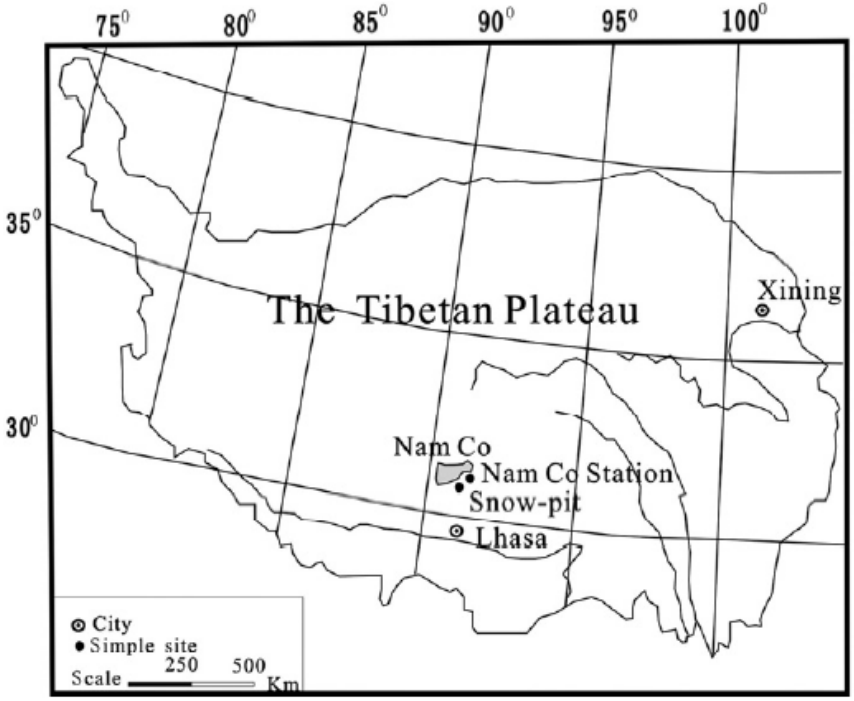


Figure 4. O_3 mixing ratios vs $\Delta^{17}O_{CO2}$ from the ER-2.

(Source: Boering et al., 2004, GRL)

Can the simultaneous measurements of $\Delta^{17}O(CO_2)$, $^{35}SO_2$, $^{35}SO_4^{2-}$ and O_3 constrain the dynamic of STE process and its impacts?



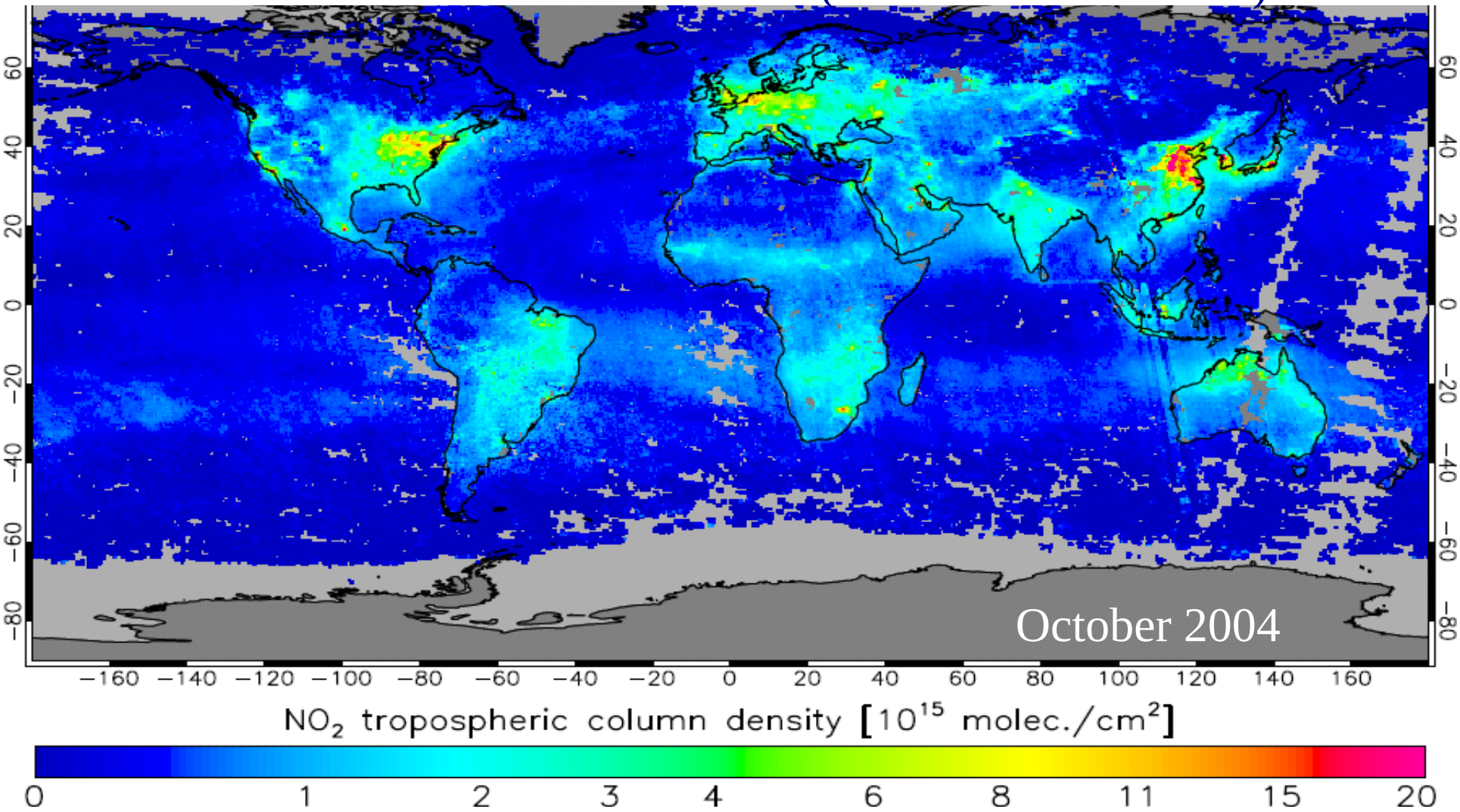
Considering the high altitude of Tibetan Plateau (with an average of 4000m a.s.l.), it would be easier to catch the signature of STE there. Such study is being conducted in Nam Co Station (4730m a.s.l.). Results are going to come out in the following months.

Trends of tropospheric ozone and precursors

TROPOSPHERIC NO_2 MEASUREMENTS FROM SPACE

map the distribution of NO_x emissions

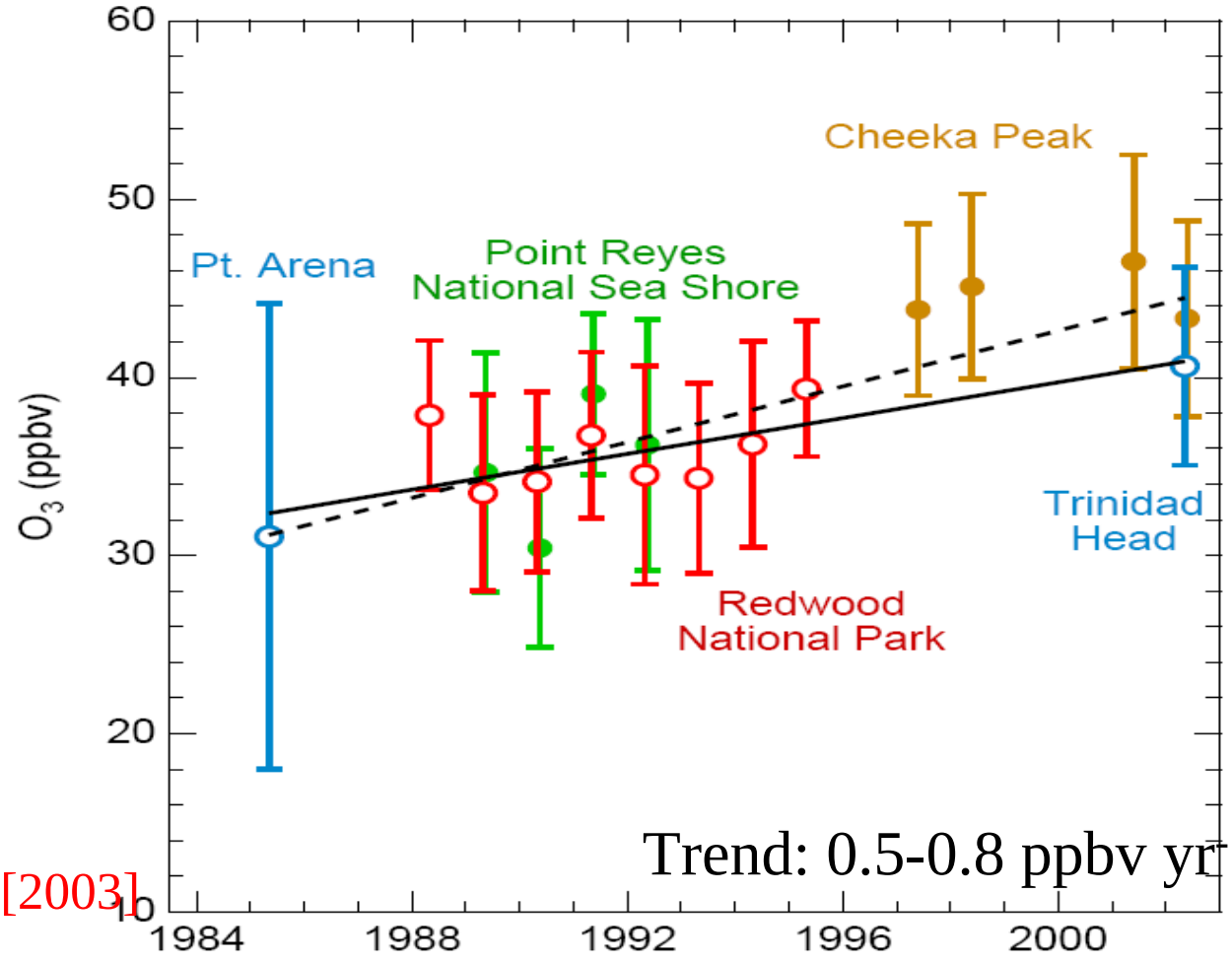
OMI satellite instrument (13x24 km^2 resolution)



Boersma et al. [JGR, submitted]

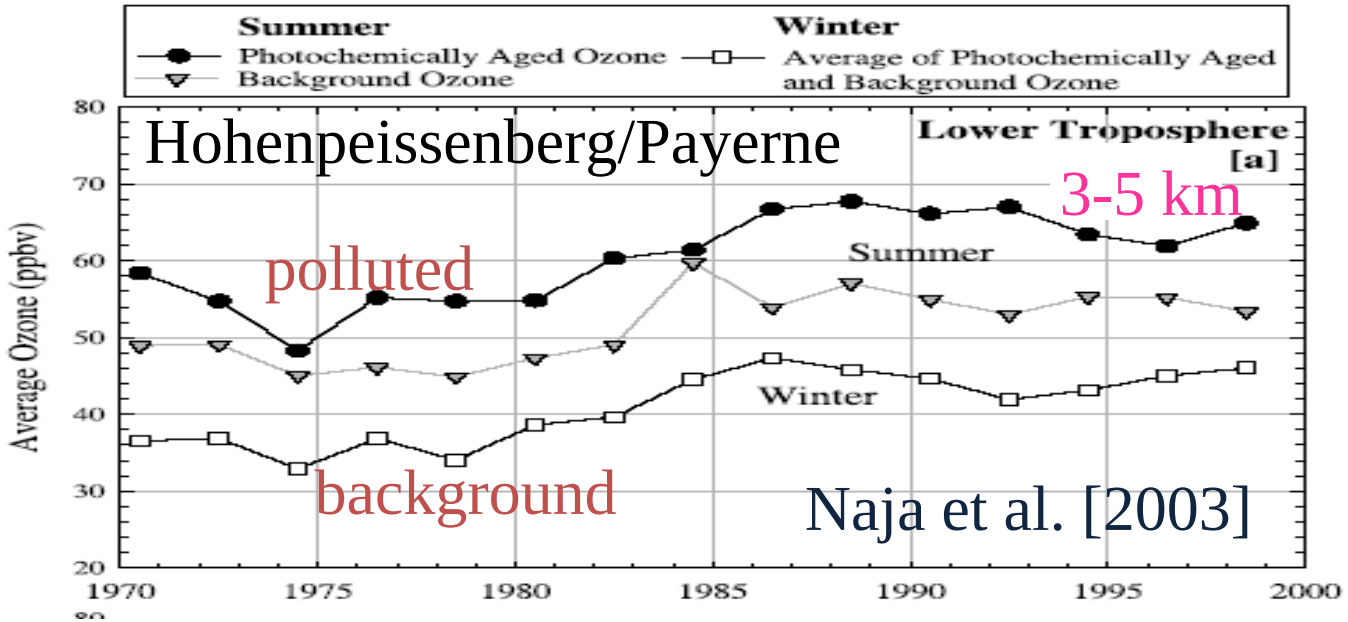
Recent trends of tropospheric ozone

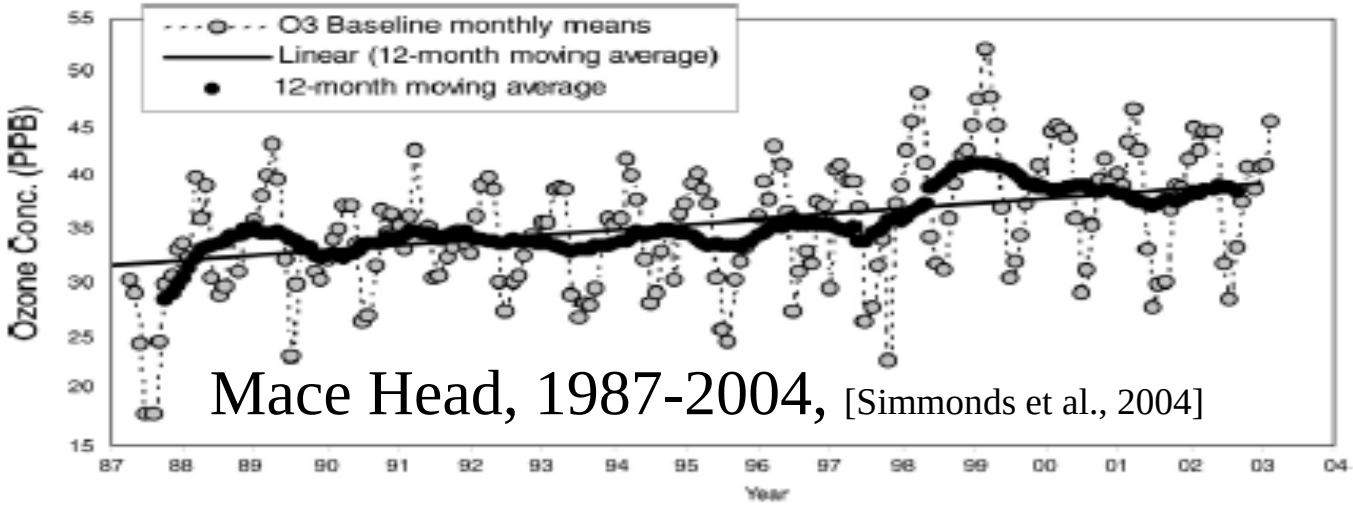
Ozone background trend over California in spring
10-15 ppbv increase over past 20 years



Jaffe et al. [2003]

Rising background ozone in Europe

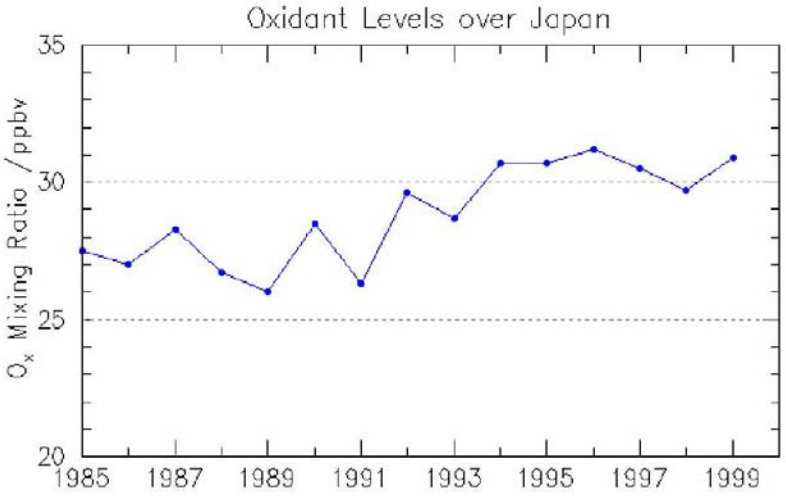




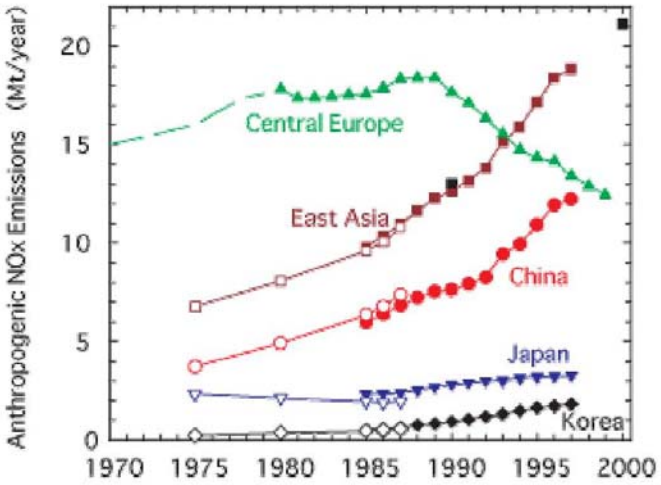
Mace Head, 1987-2004, [Simmonds et al., 2004]

Recent trends of ozone over Japan

Background O_3 over Japan is Rising



Ohara and Sakata, 2003: Data at 341 stations



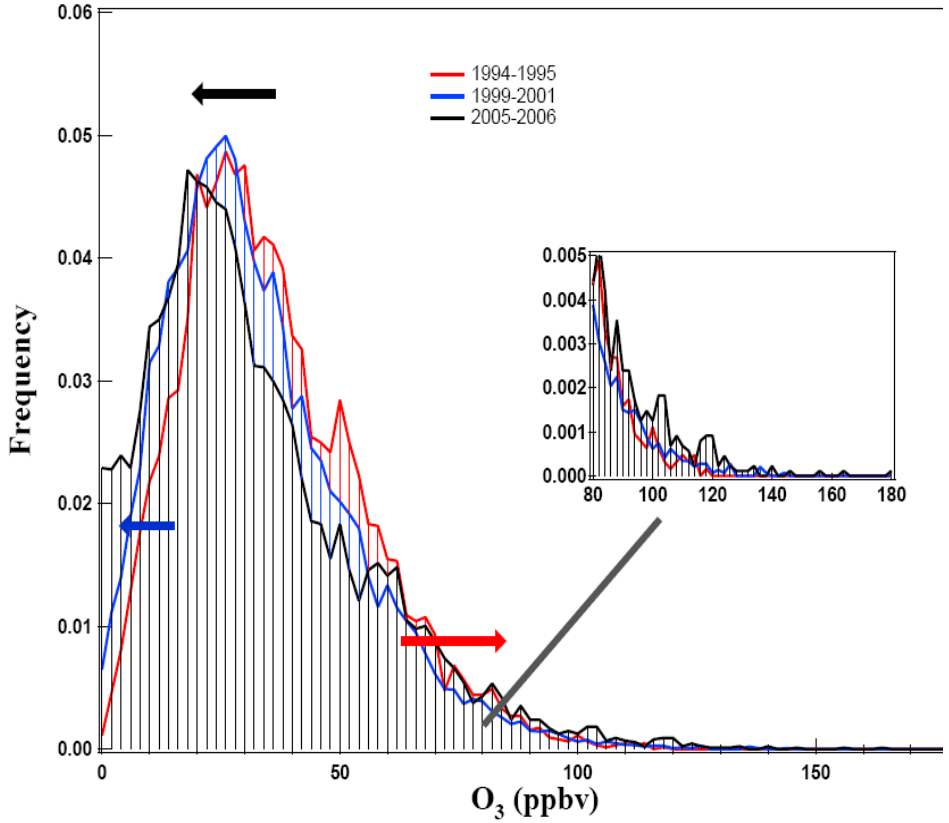
Naja and Akimoto, 2004

Why is Japanese O_3 rising?

- Emissions in Japan are almost stabilized
- Rising NO_x/CO/NMVOCs emissions over East Asia?

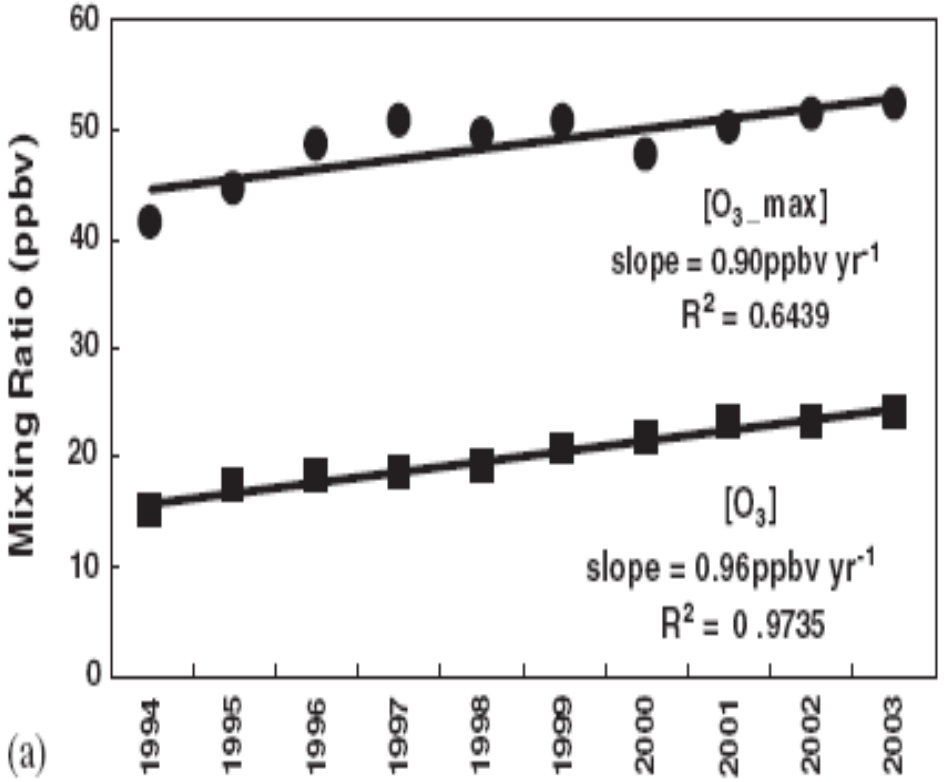
National Institute for Environmental Studies

Linan, Yangtze River Delta



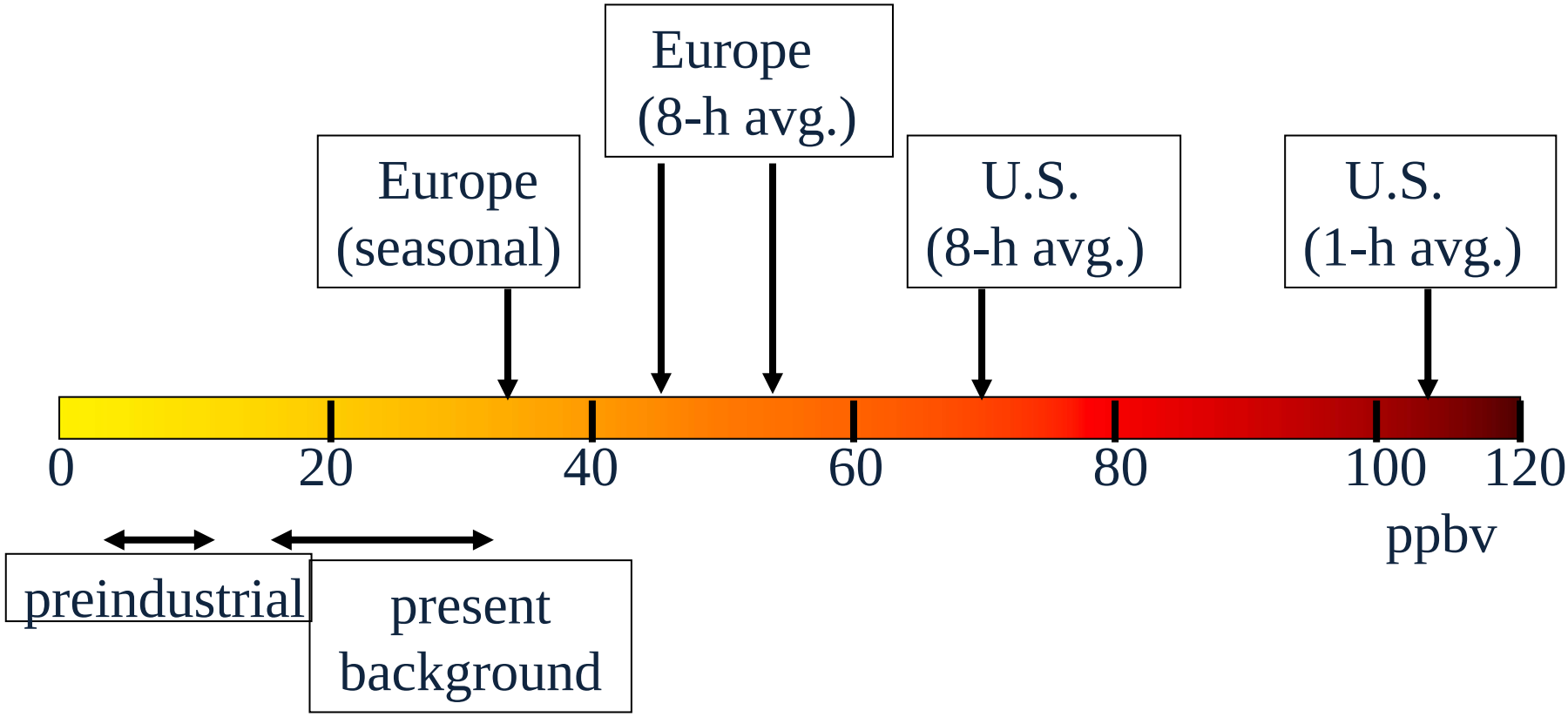
Xu et al., 2009

Taipei

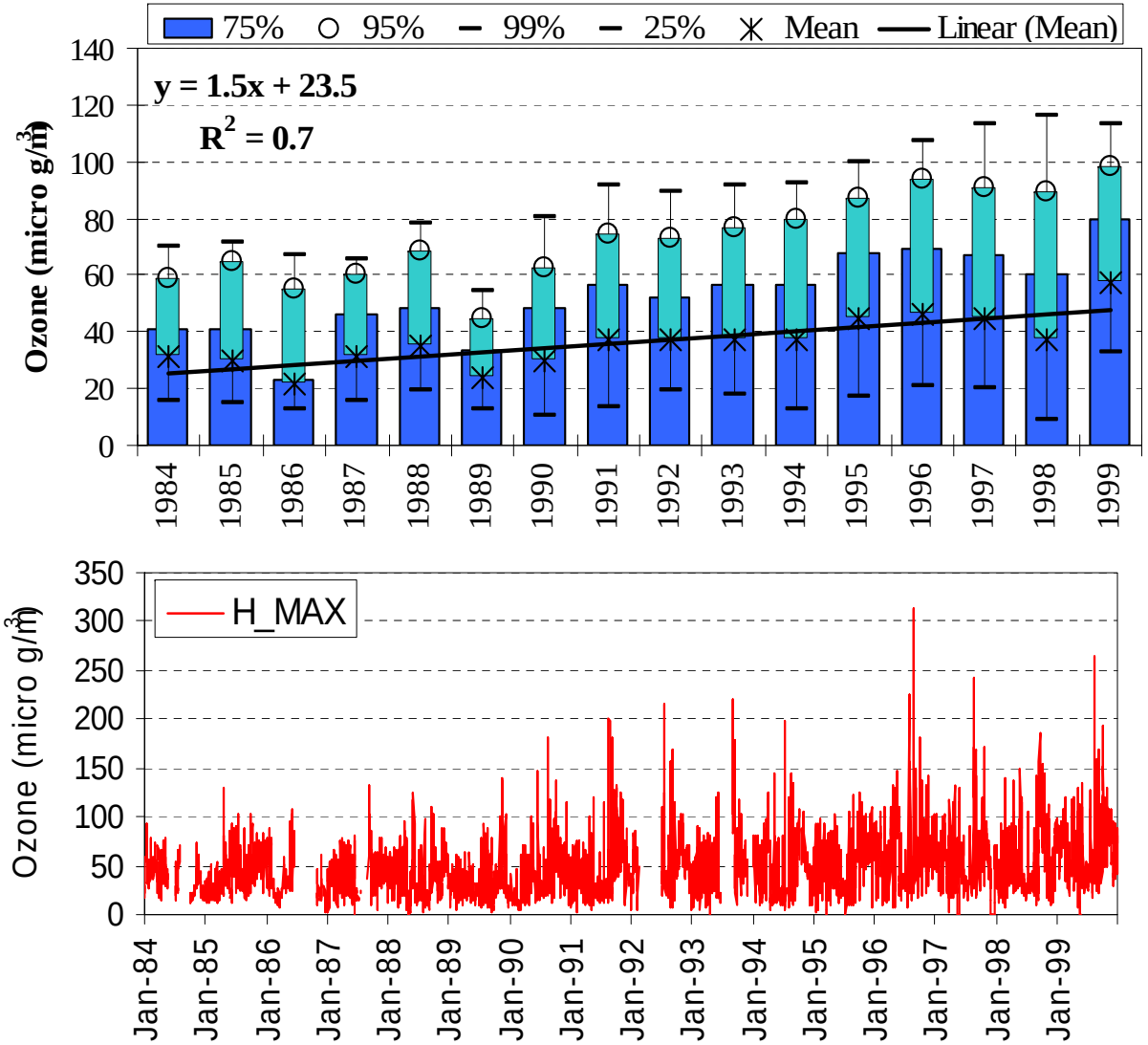


Chou et al., 2006

Present background ozone is sizable increment towards violation of U.S. air quality standards



Recent trends of ozone in China



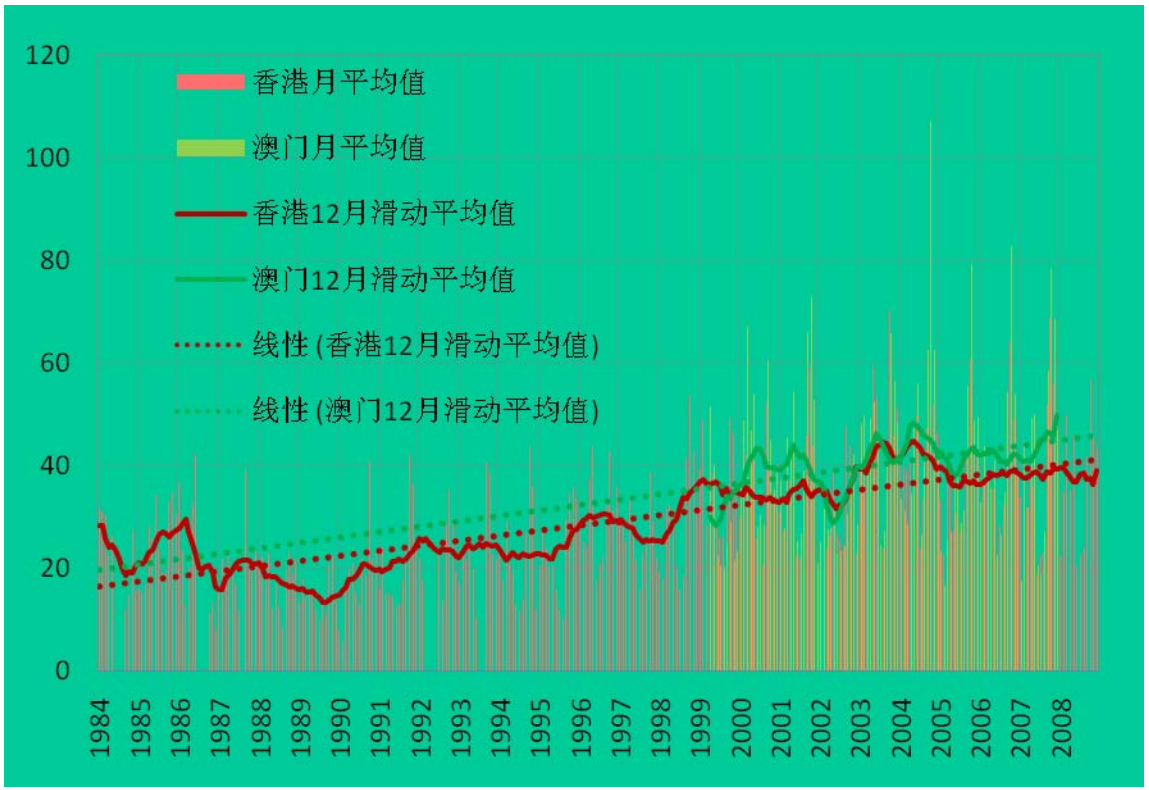
(winter monsoon period: October-April; early morning 01-05 am data)

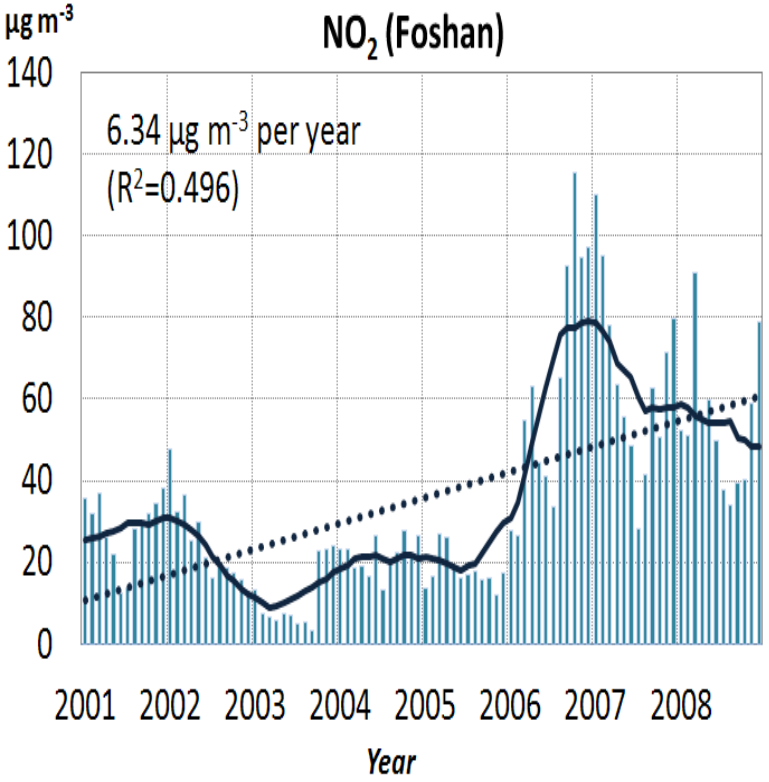
Chan et al., OSE, 2004

Recent trends in Pearl River Delta

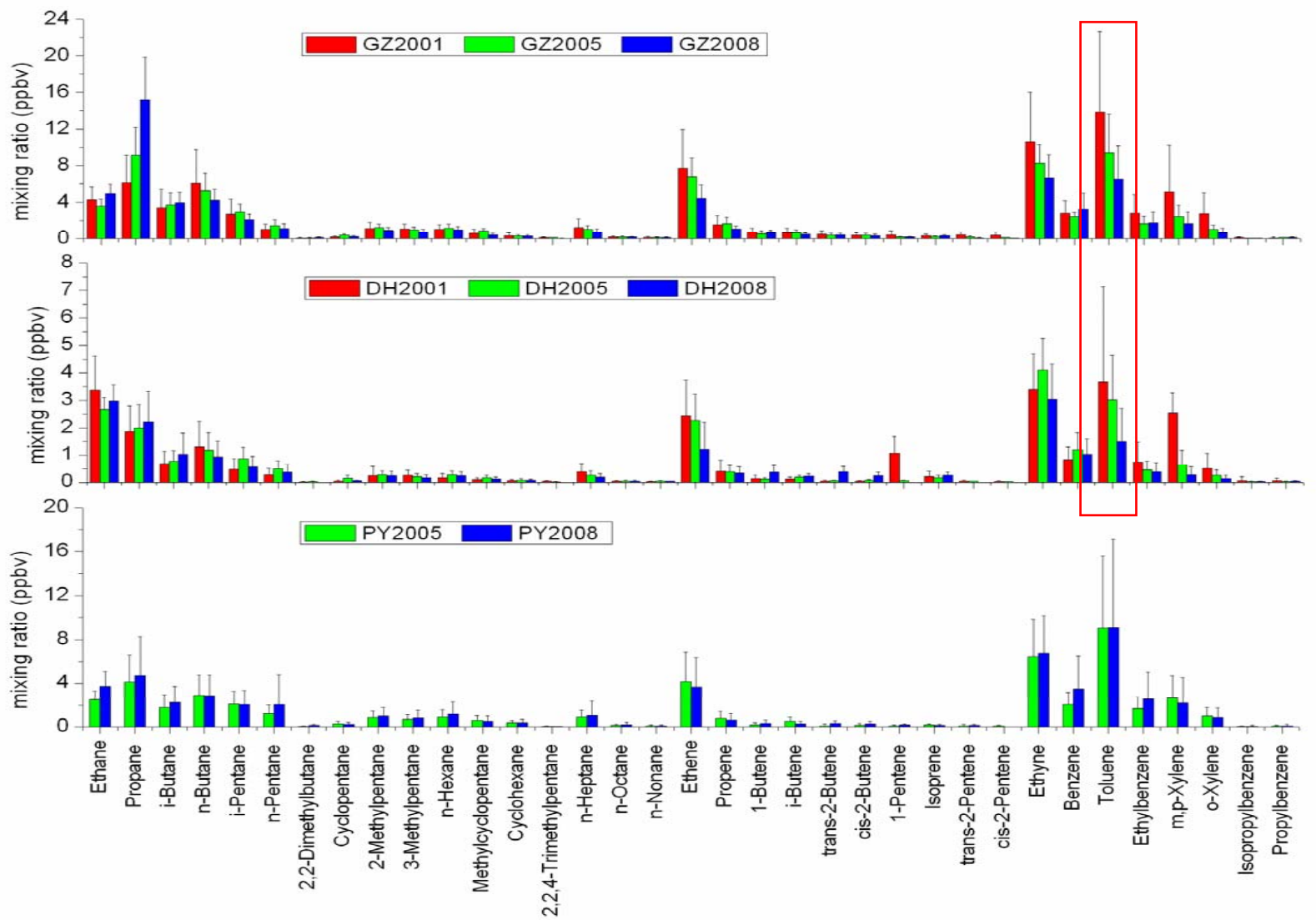
- Increases in NOx in China is especially significant due to growth in vehicle and traffic

HK and Macao, Pearl River Delta



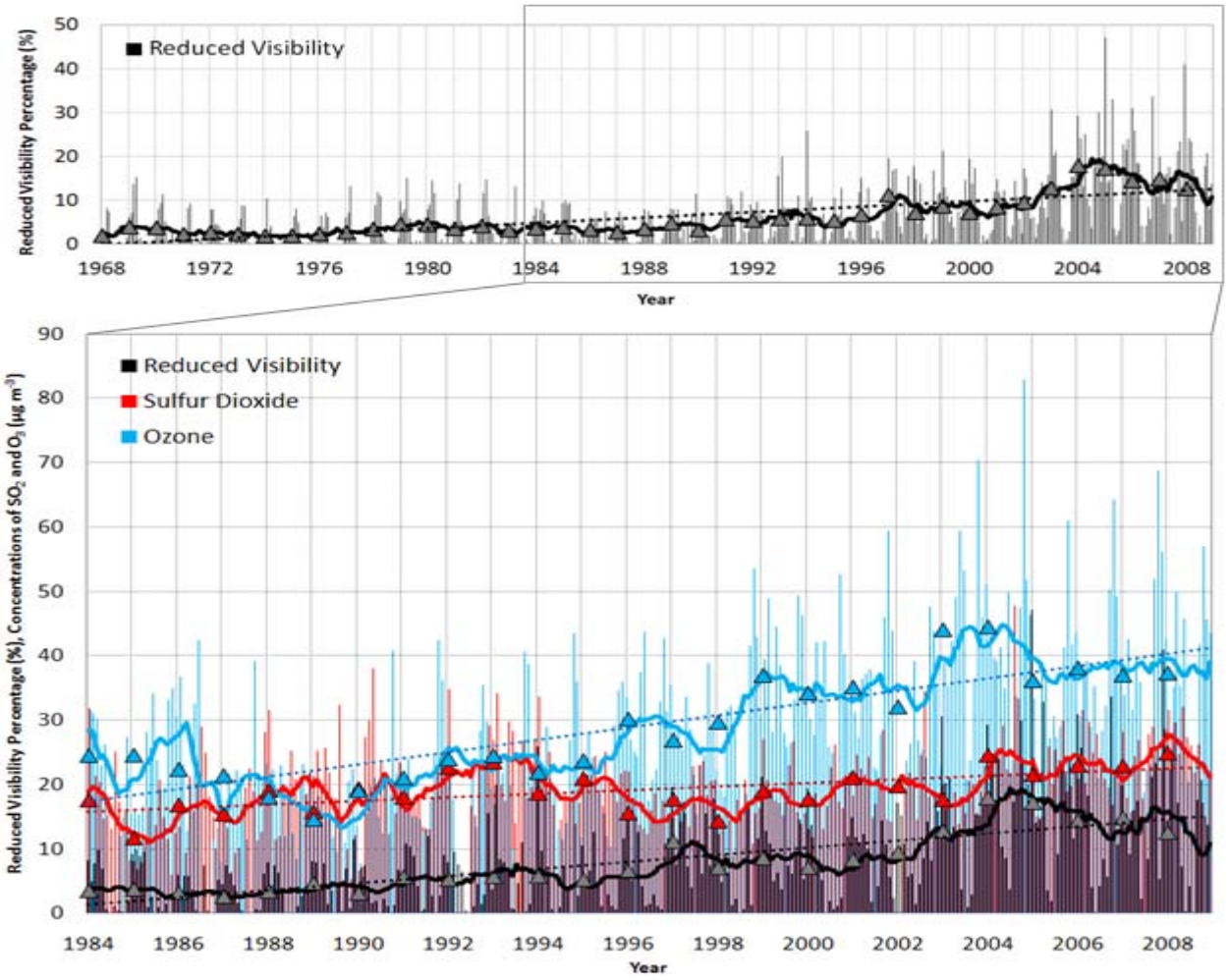


- Substantial changes in hydrocarbons



Impacts of ozone increases on atmospheric environmental quality

Time series of RV, concentrations of SO_2 and O_3 in HK



Impacts of ozone increases on atmosphere

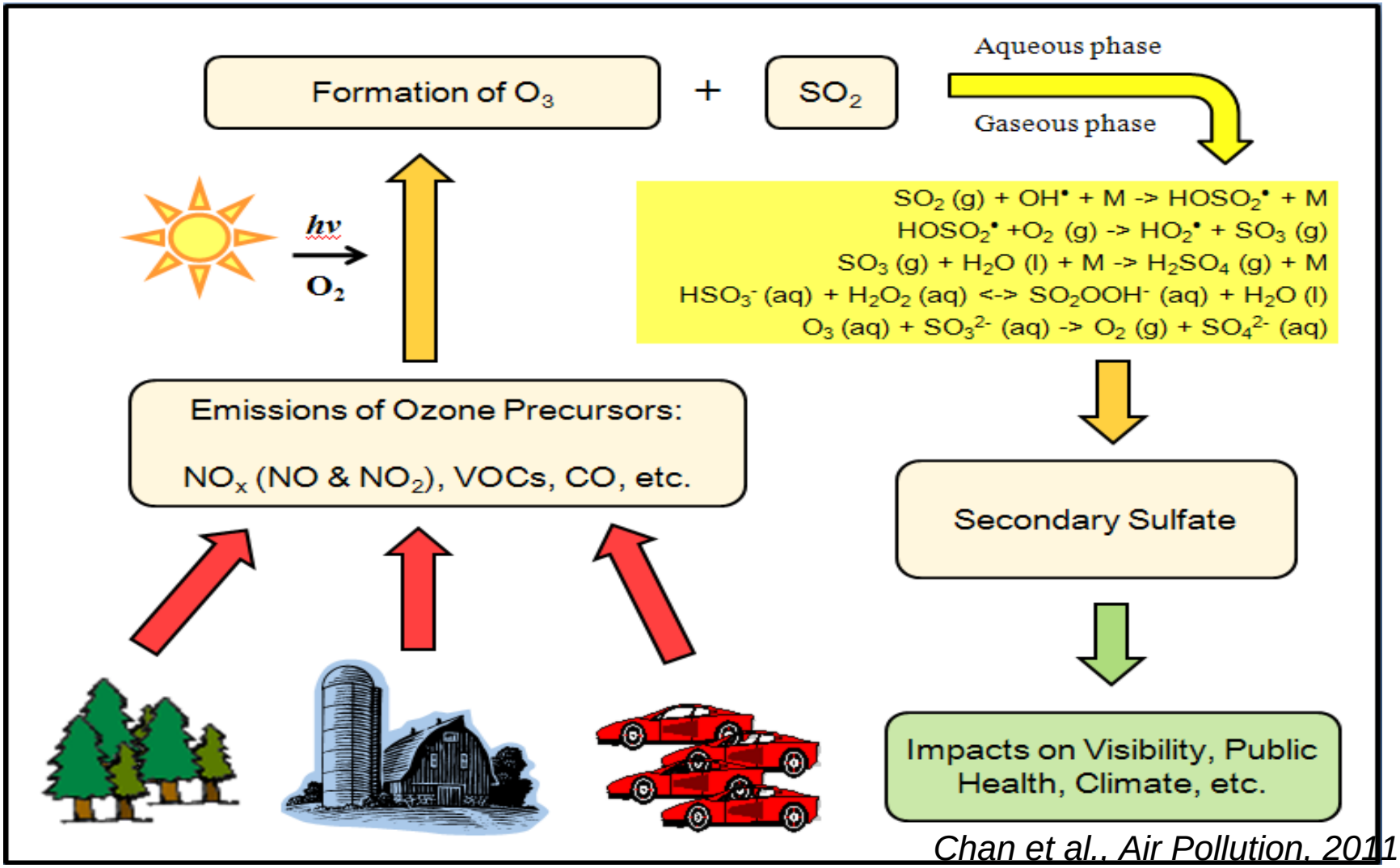
Multiple linear regression equations of RV (%) and pollutant conc. (μ g m^{-3})

Regression Model	Independent Variables	Equation[a]
1 (Hong Kong 1993 – 2008)	O_3, SO_2, NO_x, NO_2, PM_{10}	[RV] = 0.28 [SO_2] + 0.27 [NO_2] + 0.15 [O_3] – 15.80
2 (Macao 1999 - 2007)	O_3, SO_2, NO_2, PM_{10}	[RV] = 0.33 [PM_{10}] – 5.70
3 (Foshan 2001 - 2008)	SO_2, NO_2, PM_{10}	[RV] = 0.14 [NO_2] + 0.50 [PM_{10}] - 21.24

Hong Kong

Regression Model	Period	Independent Variables	Equation
Model 1	1993 – 2008	O_3, SO_2, NO_x, NO_2, PM_{10}	[RV] = 0.28 [SO_2] + 0.27 [NO_2] + 0.15[O_3] – 15.80
Model 2	1984 – 2008	O_3, SO_2, NO_x, NO_2	[RV] = 0.26 [SO_2] + 0.13 [NO_2] + 0.25 [O_3] – 12.21
Model 3	1993 – 2008	O_3, SO_2, NO_x, NO_2	[RV] = 0.29 [SO_2] + 0.33 [NO_2] + 0.17 [O_3] – 16.87
Model 4	1984 – 1992	O_3, SO_2, NO_x, NO_2	[RV] = 0.11 [NO_x] – 0.09 [NO_2] – 1.12

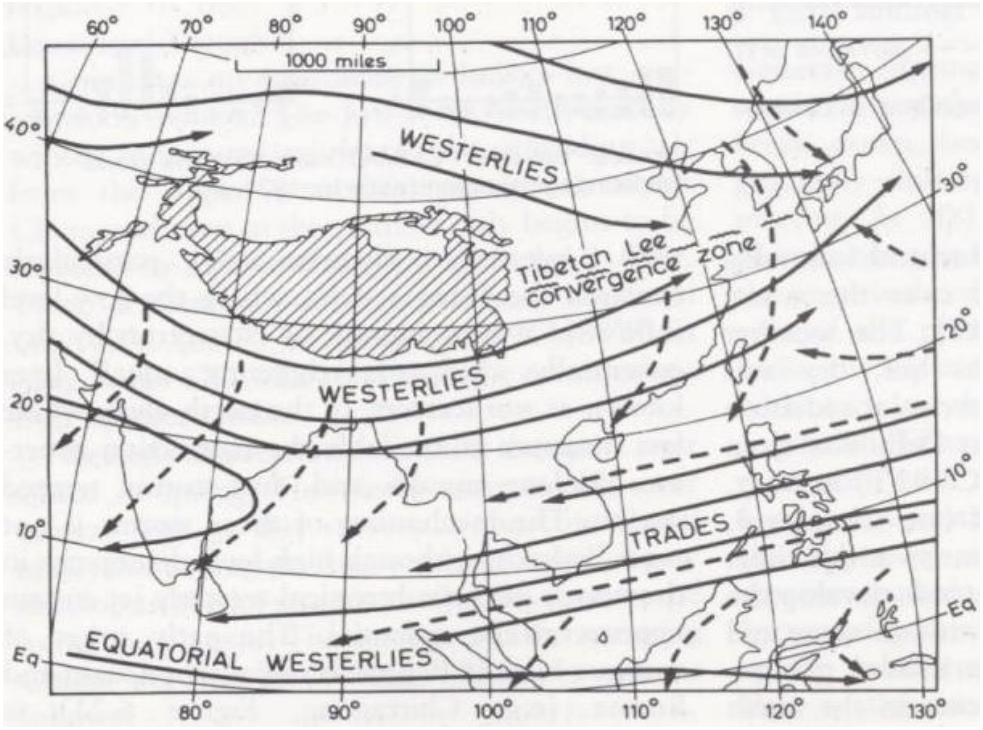
Schematic diagram of ozone impact on sulfate formation and visibility degradation



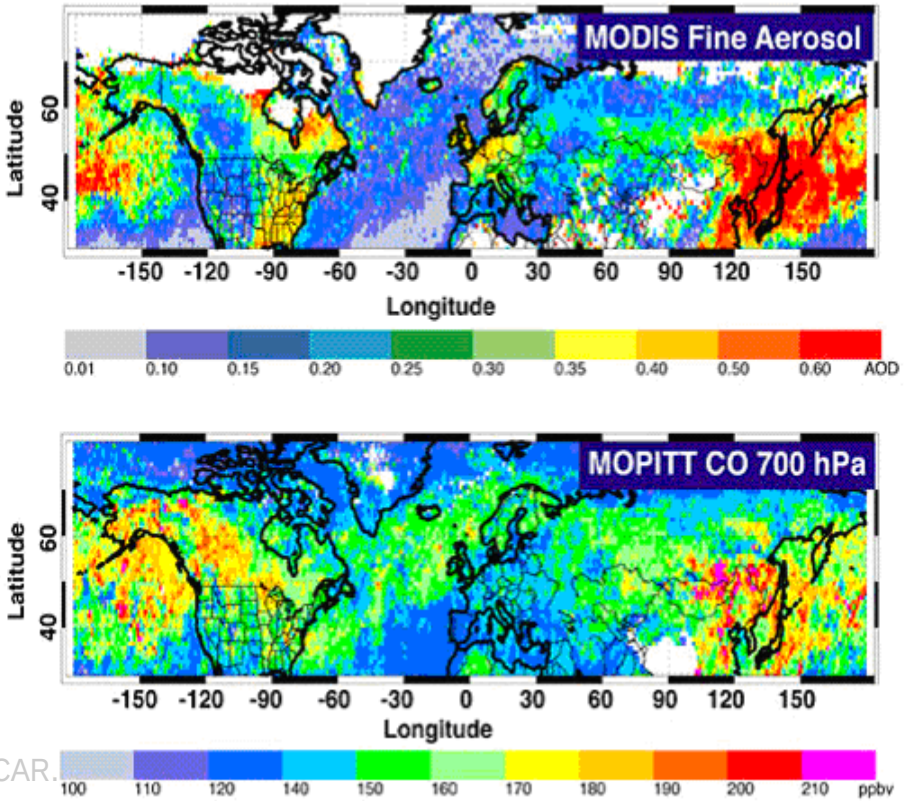
Chan et al., Air Pollution, 2011

What other impacts can be?

- ozone in the BL has a lifetime of ~ 2 weeks;
- transported of increased ozone to tropical SE Asia from east Asian coast is possible;
- what will be the impacts on air quality degradation and crop yield ?



May, 2003. Measured on Terra satellite.



Source: David Edwards, NCAR.