$^{13}C/^{12}C$ Constraints on Inter- Continental Transport of Fossil fuel CO_2 & Black C Aerosols

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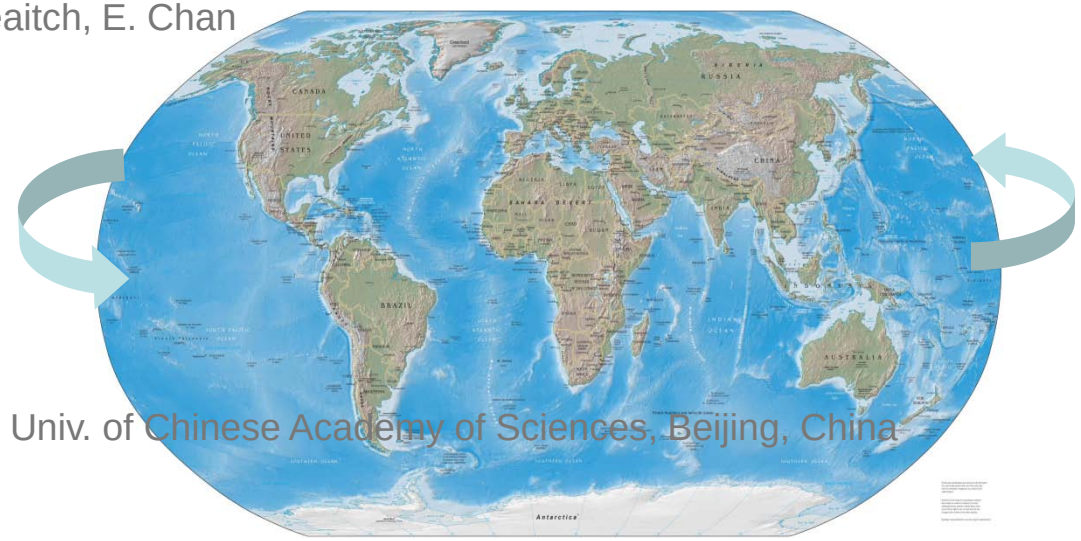


" The world's nations are moving toward agreements that will bind us together in an effort to limit future greenhouse gas emissions. With such agreements will come the need for all nations to make accurate estimates of greenhouse gas emissions and to monitor their changes over time…."

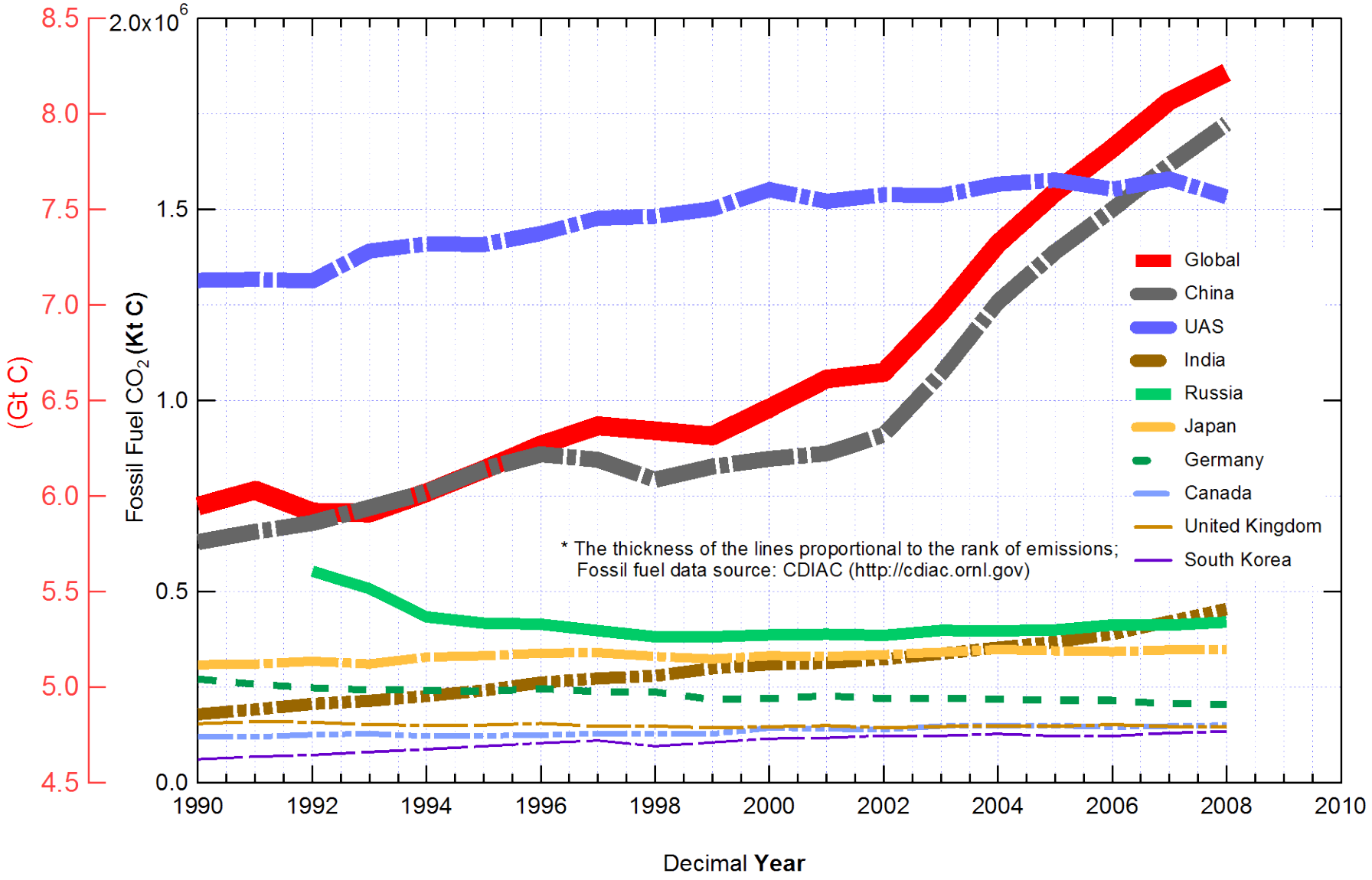
In : Verifying Greenhouse Gas Emissions: Methods to Support International Climate Agreements

By the committee on Methods for Estimating Greenhouse Gas Emissions; National Research Council, 2010
Source: http://books.nap.edu/openbook.php?record_id=12883&page=2

Independent methods for verifying fossil fuel emissions are needed !!

Fossil Fuel CO_2 Emission in Top 9 Emitters

(1990-2008)



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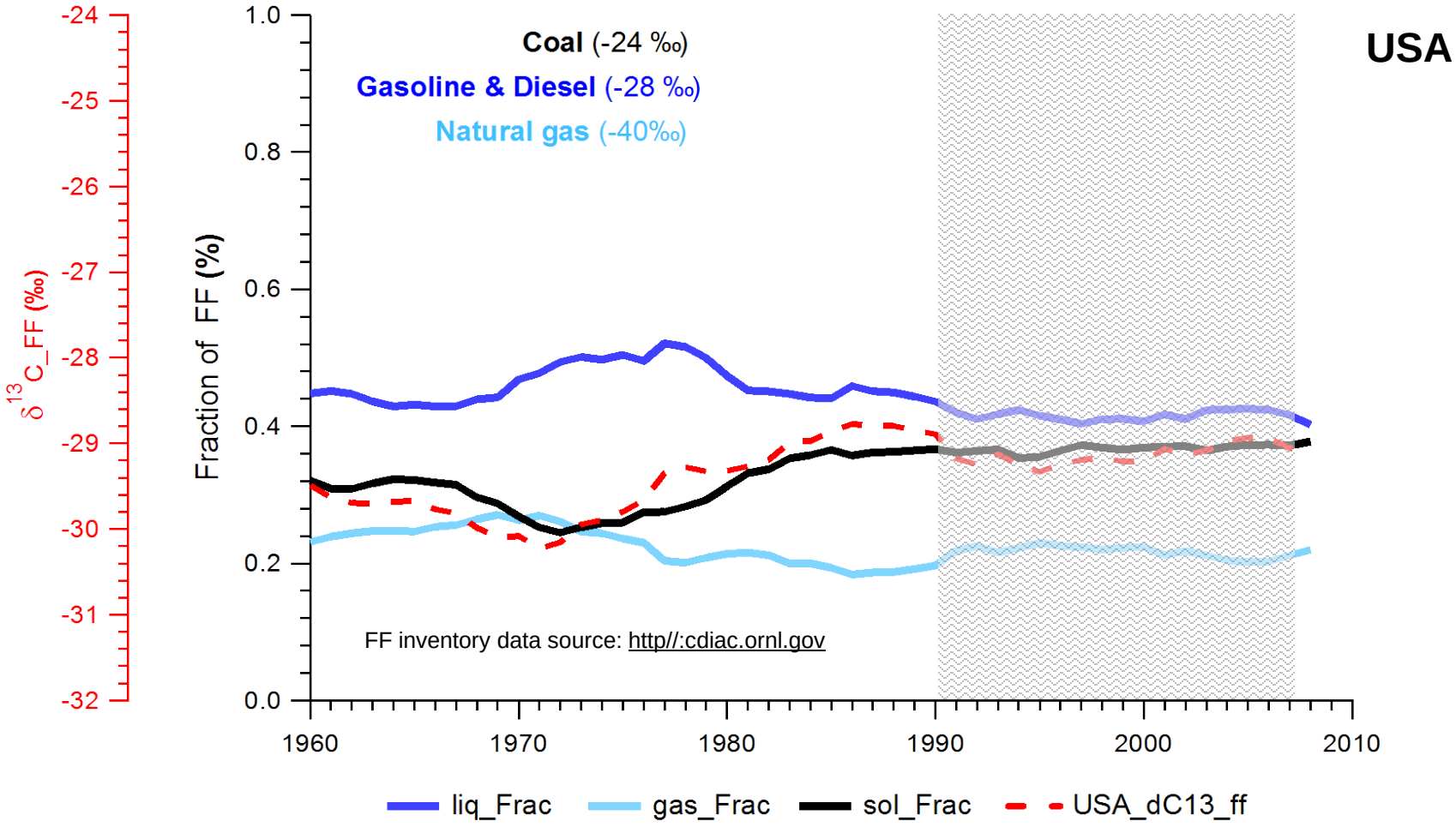
Carbon Isotopic Composition of FF & Energy Structure

(Fossil Fuel Mass Fraction Weighted)



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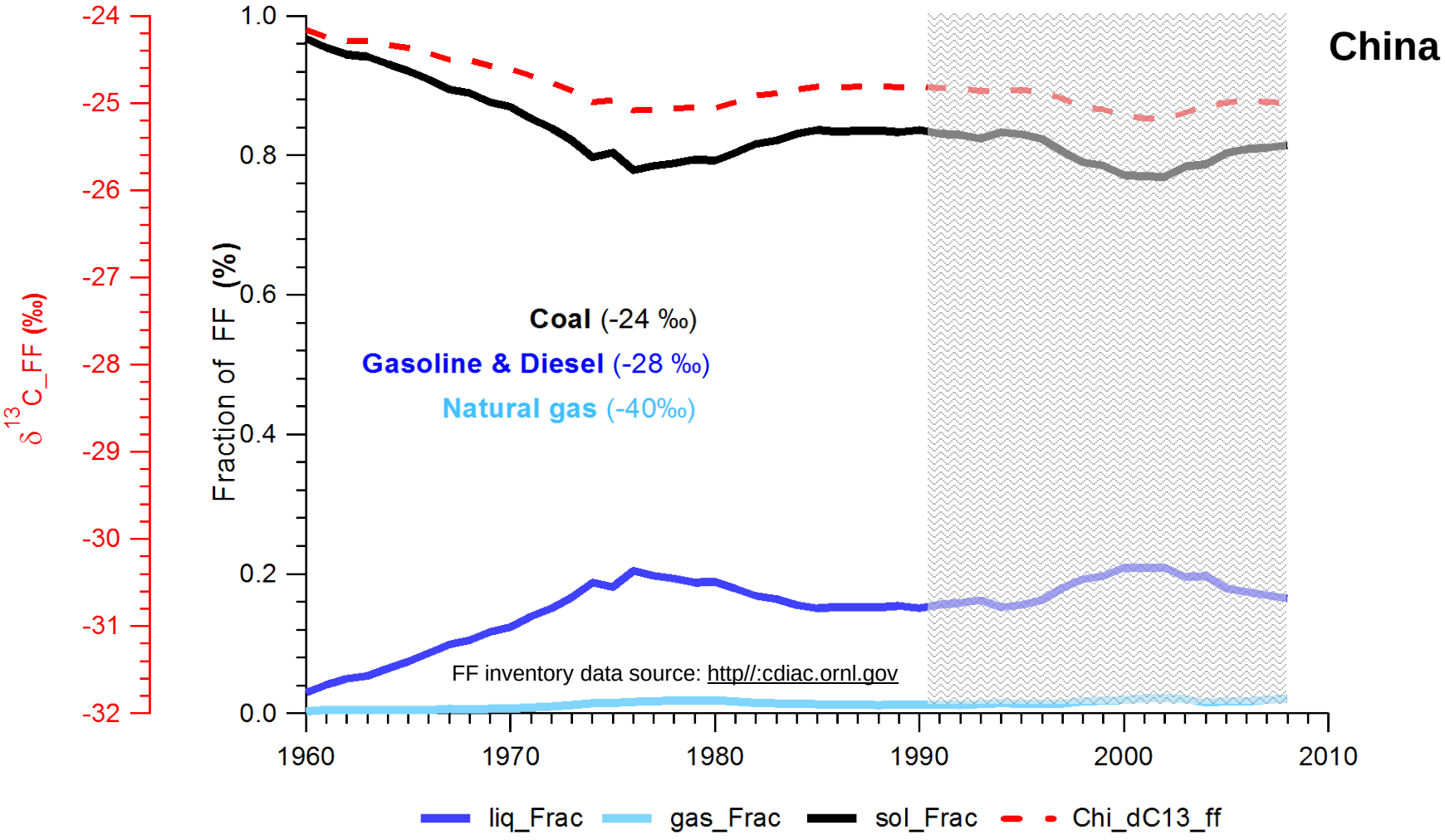
Carbon Isotopic Composition of FF & Energy Structure

(Fossil Fuel Mass Fraction Weighted)



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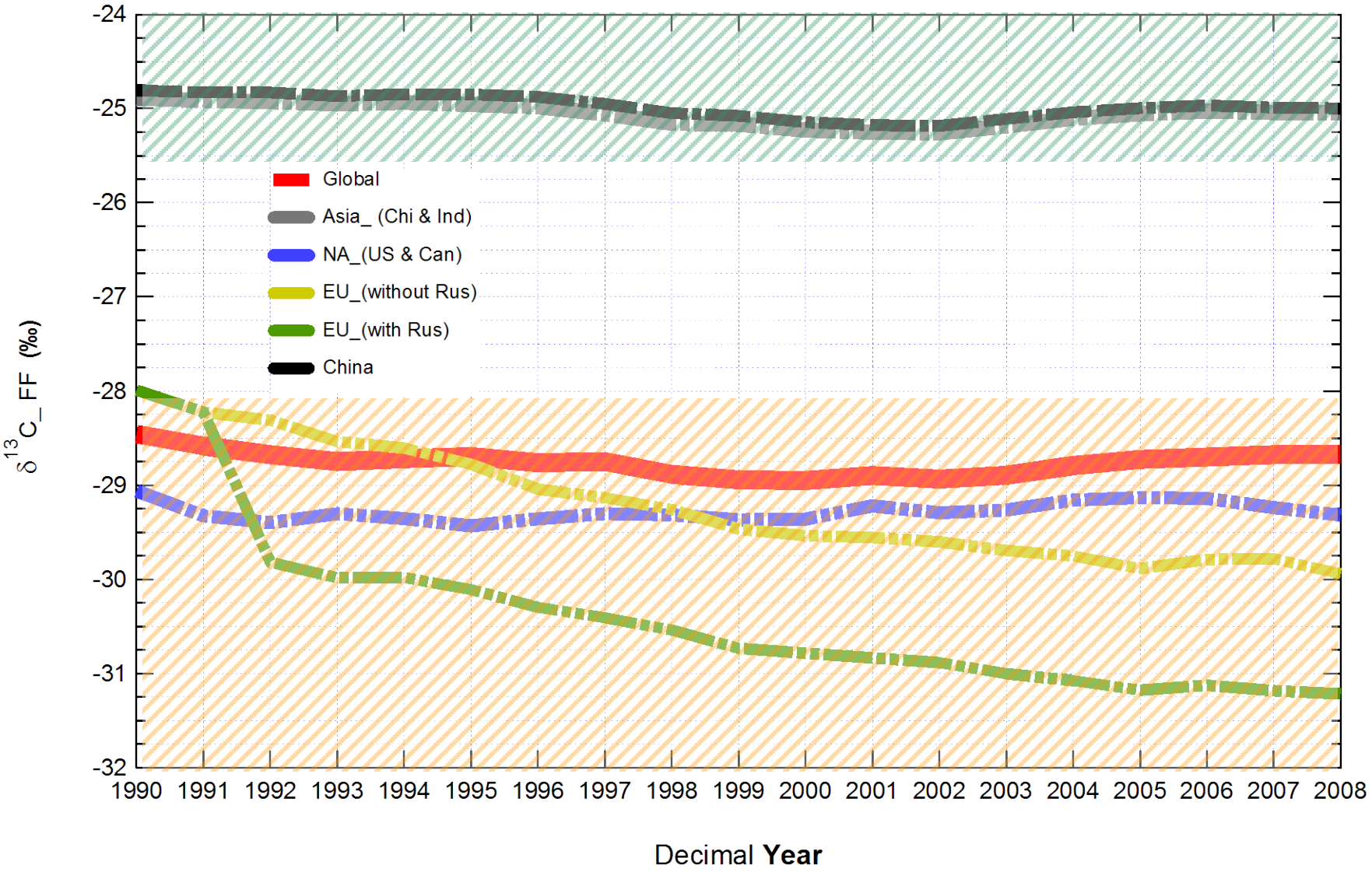
C isotopic Compositions of Fossil Fuel at Regional Scale

(fossil fuel mass fraction weighted)



Coal (-24‰) **Gasoline & Diesel** (-28‰) Natural gas (-40‰)

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$^{13}C/^{12}C$ in air CO_2 and BC aerosols

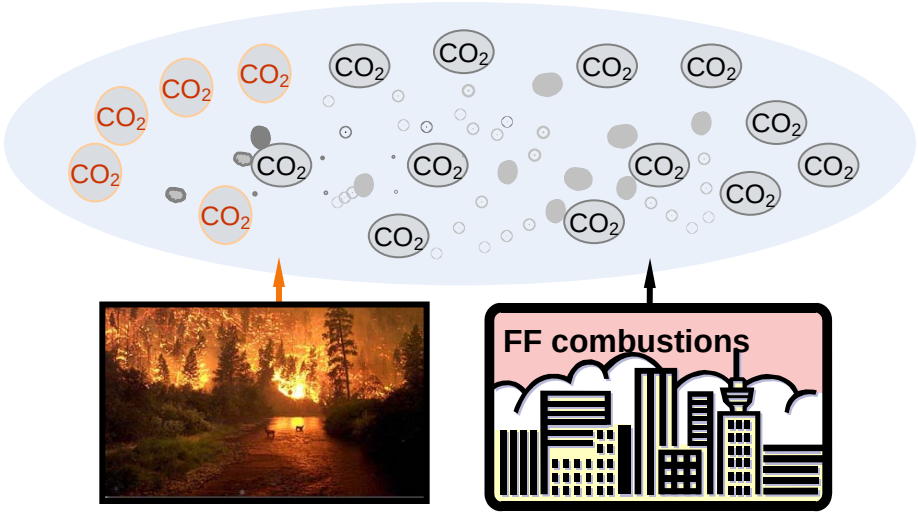
***CO_2 & BC** (or elemental carbon) are*

- Important Components affecting radioactive forcing on global and regional scales
- One of the major common emission sources: FF combustions

Different atmospheric life time:

***CO_2 :** ~ 200 years*

***BC:** ~ 7-10 days*



Assumptions:

- ✓ Very small isotopic fractionations in FF combustions
- ✓ No processes modifying isotopic compositions after their emissions;
- ✓ $\delta^{13}C_{FF} \approx \delta^{13}C_{FF(CO2)} \approx \delta^{13}C_{FF(BC)}$

Implications of $\delta^{13}C_{mea(BC)}$ and $\delta^{13}C_{mea-(CO2)}$

- ✓ *$\delta^{13}C_{FF(BC)}$ values can be directly inferred from $\delta^{13}C_{mea(BC)}$*
- ✓ *$\delta^{13}C_{FF(CO2)}$ can be only derived from $\delta^{13}C_{mea(CO2)}$ and $C_{mea-CO2}$ values with an assumption of a two-end member mixing*

Observation sites of $^{13}C/^{12}C$ in Atmospheric CO_2 & Black Carbon Aerosols

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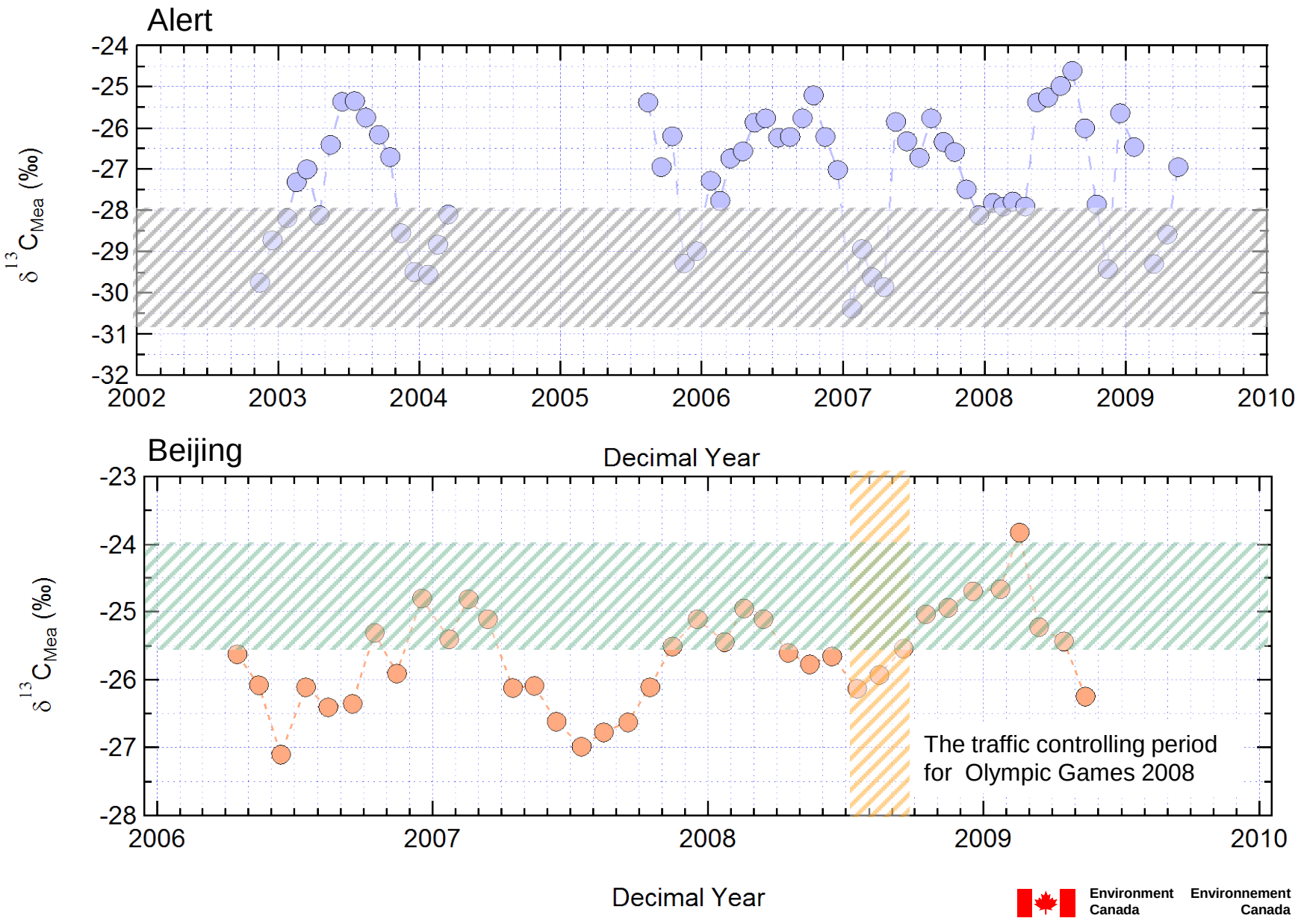
Carbon Isotopic Compositions ($\delta^{13}C_{mea\_BC}$) of **EC** at Alert & Beijing



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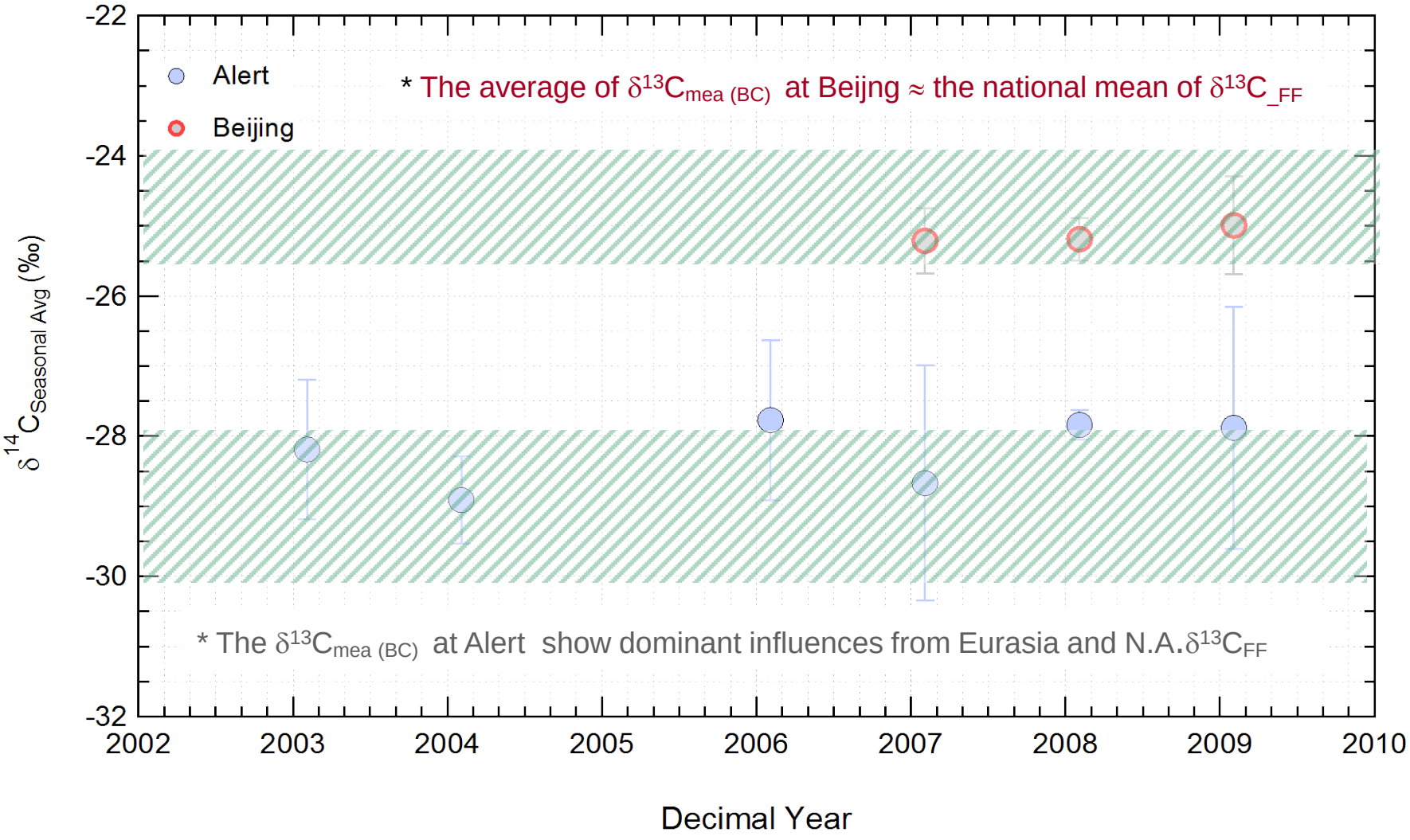
Seasonal Average (Nov – Apr) of $\delta^{13}C_{mea\_BC}$ in **EC** at Alert & Beijing



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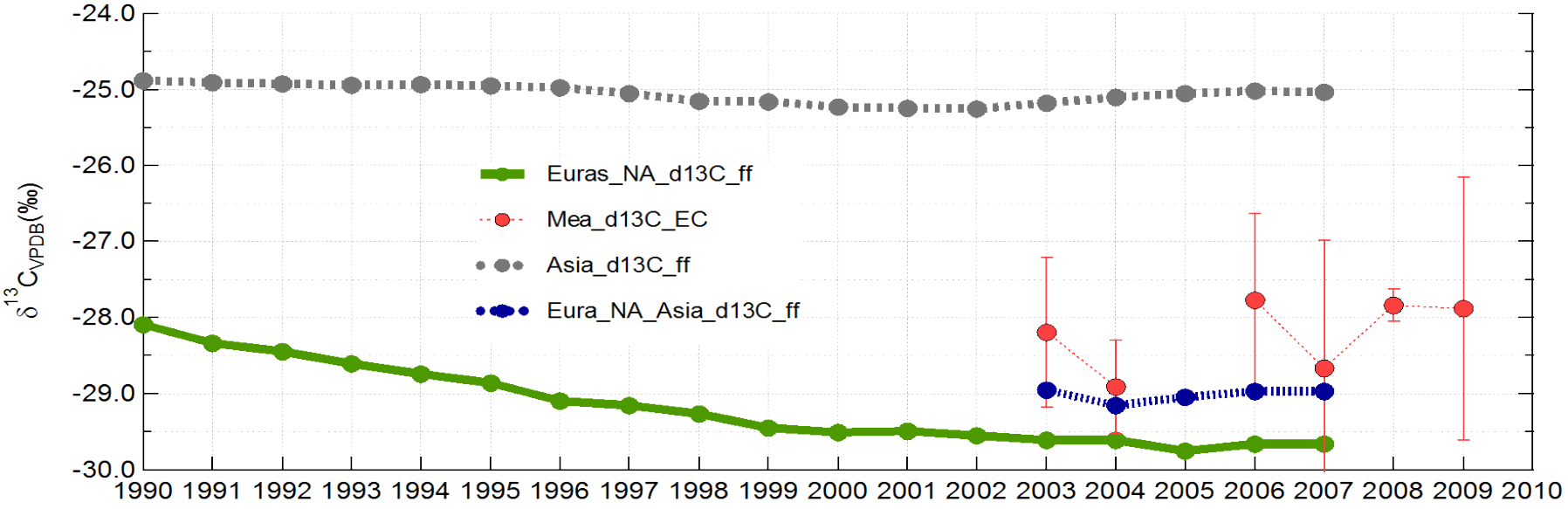
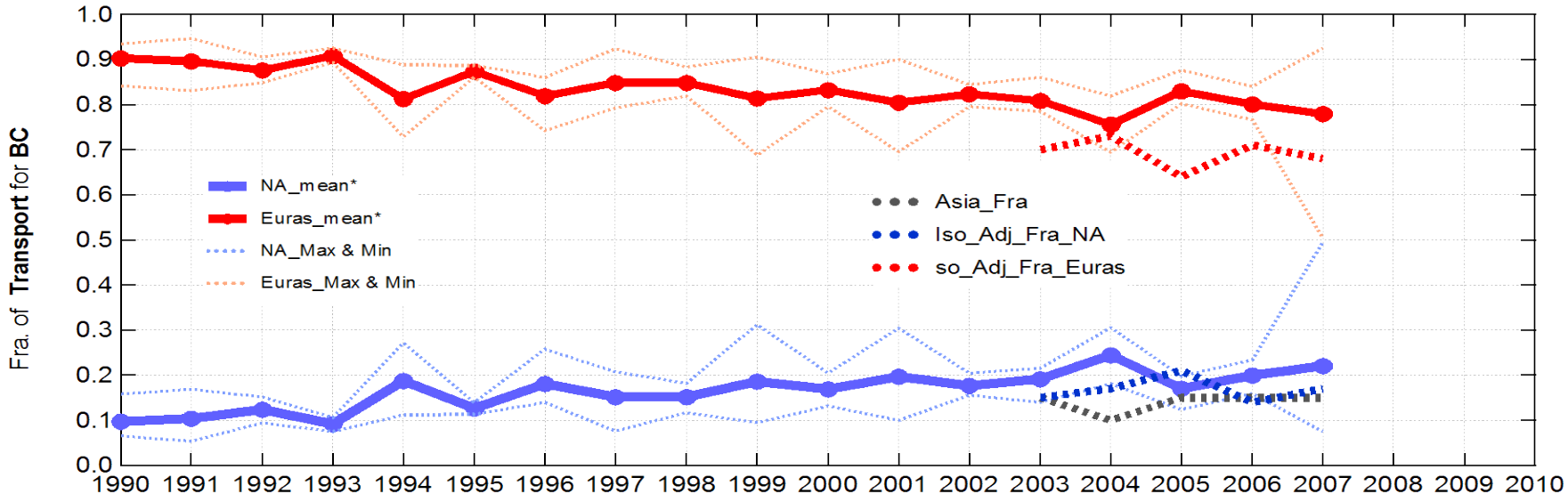
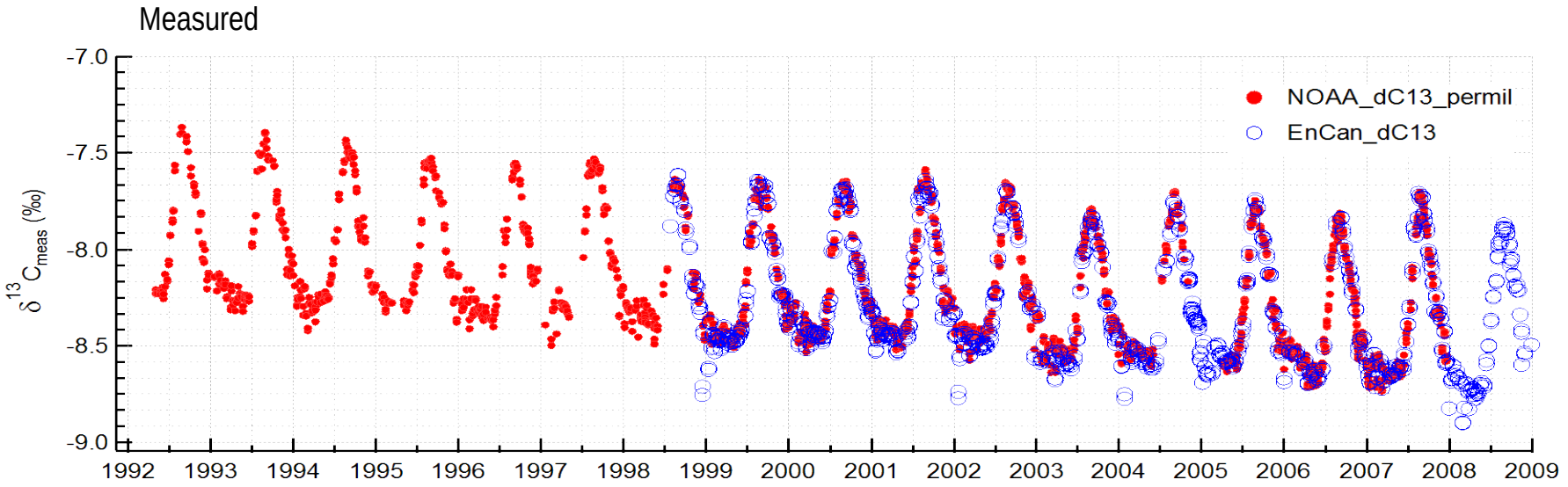
$^{13}C/^{12}C$ Constraints on Inter-Continental Transport of Fossil Fuel BC to Alert

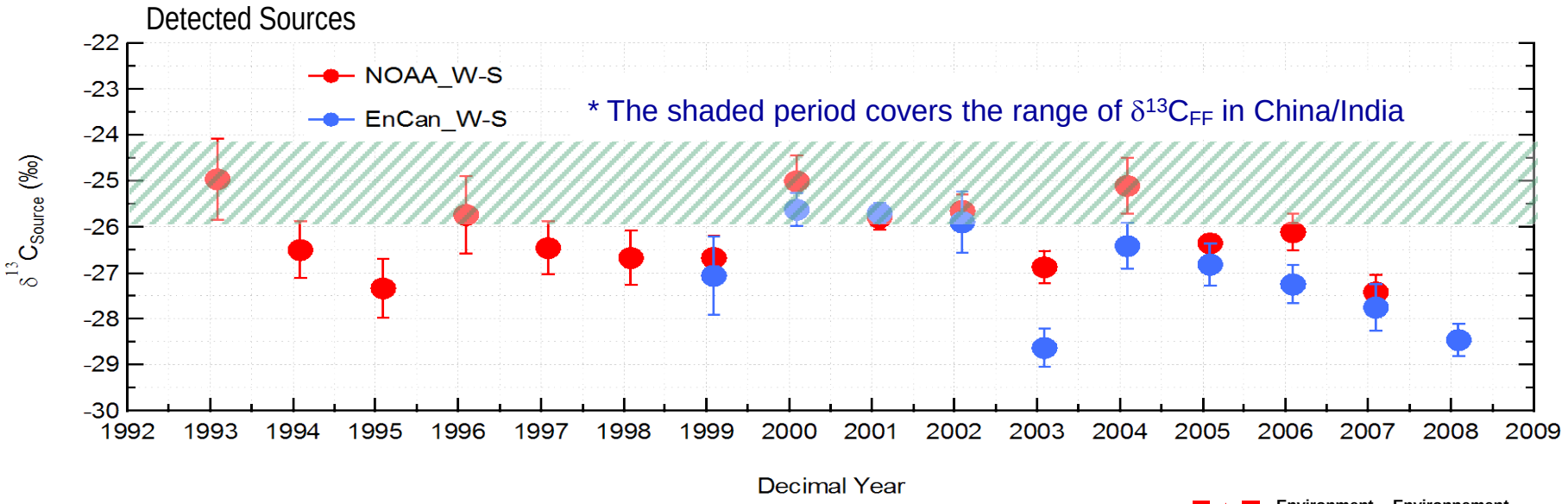
(Nov – Apr)





Carbon Isotopic Composition of **Detected Source CO_2 at Alert**





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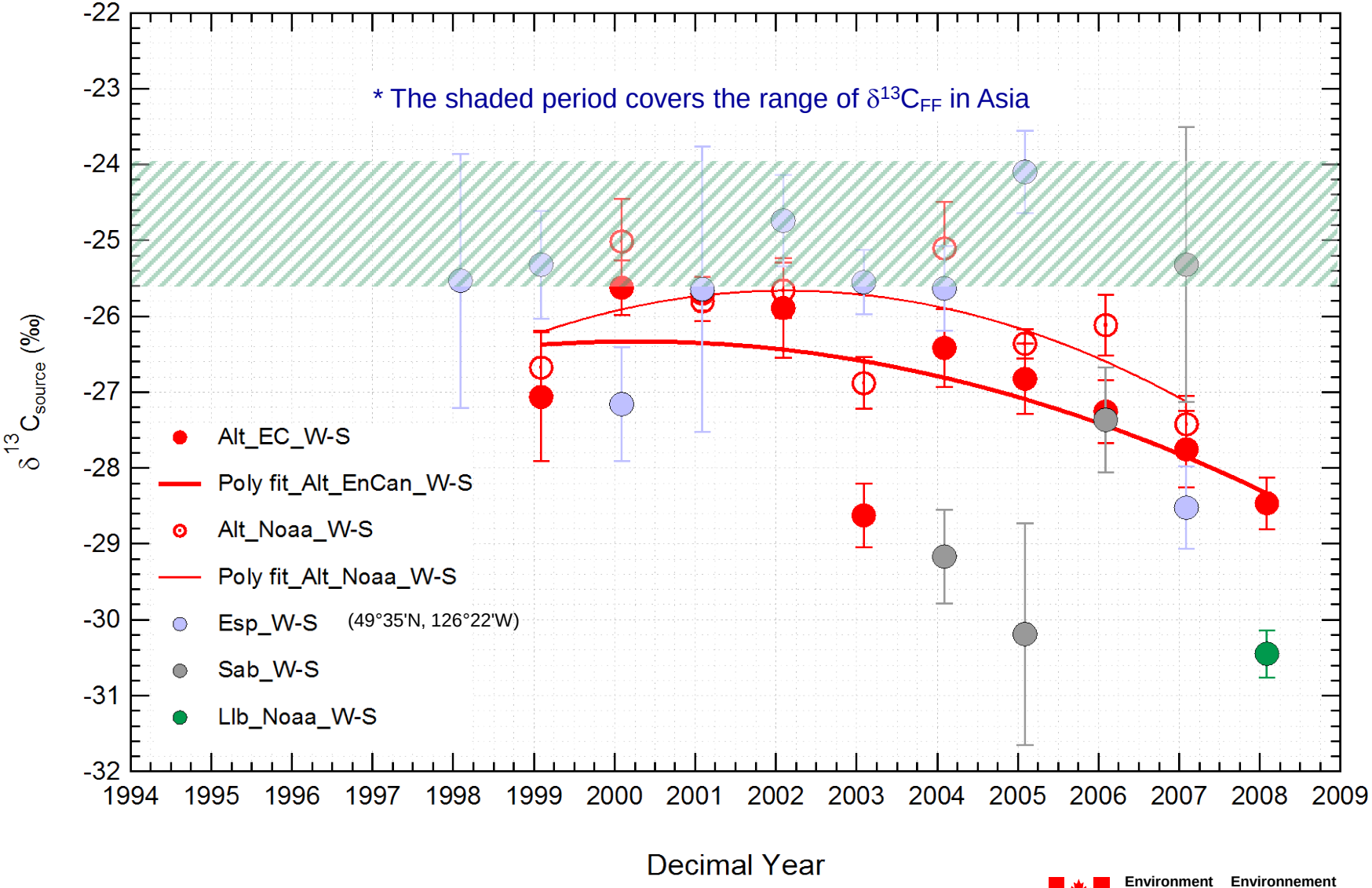
Carbon Isotopic Composition of
Detected Source CO_2 over Canada



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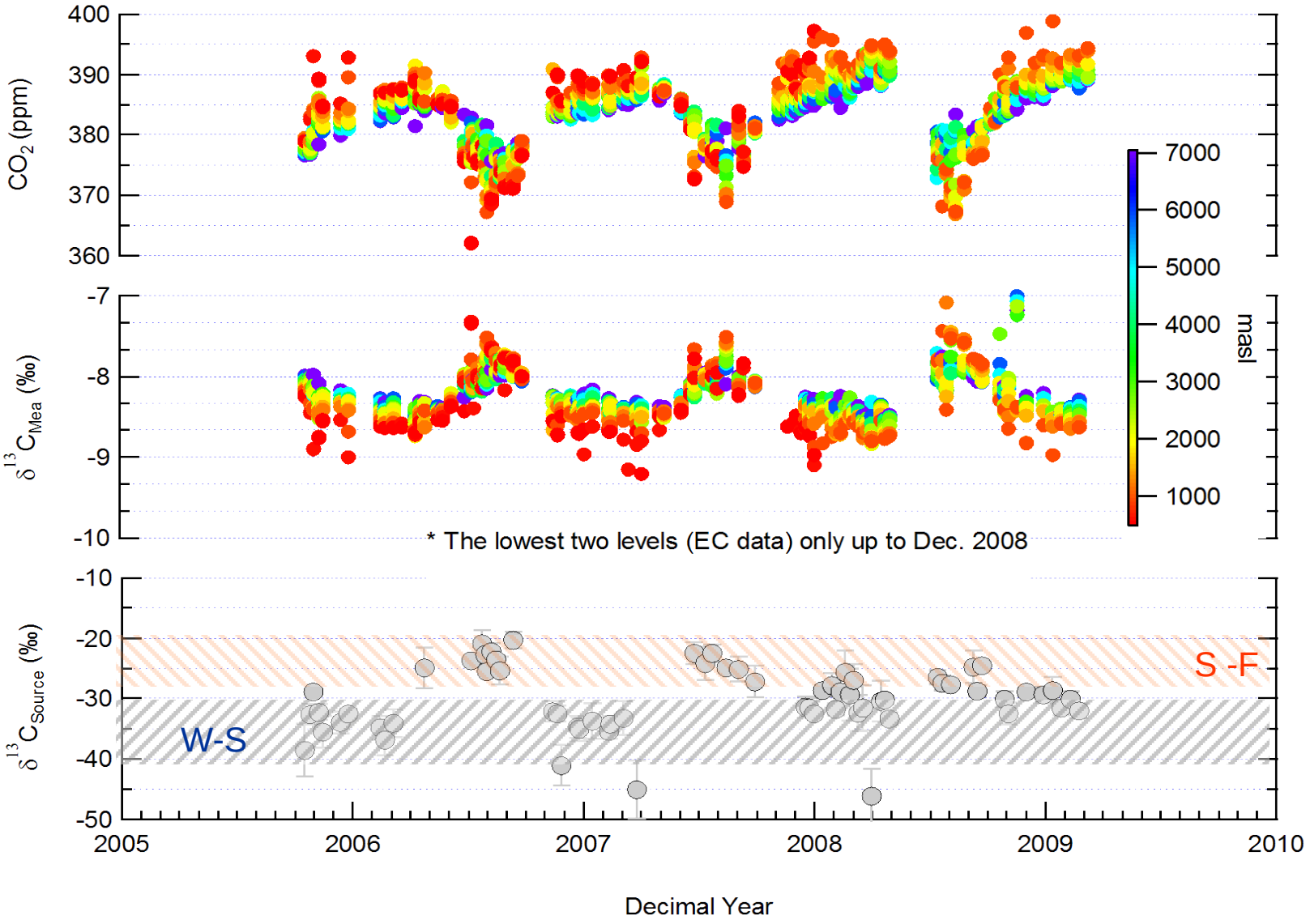
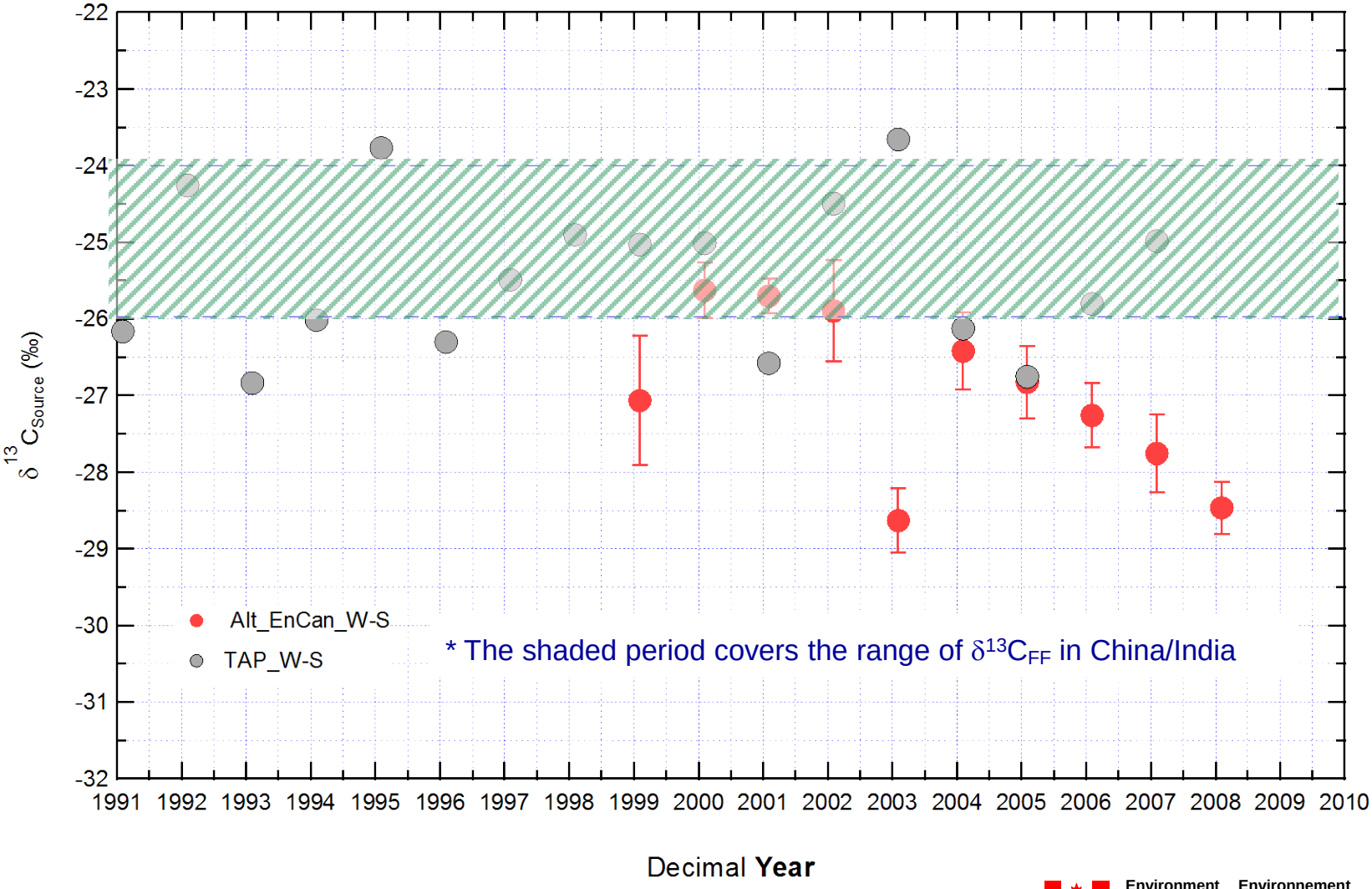

Carbon Isotopic Composition of
Detected Source CO2 via Vertical Profiles at Berms*
(53°59'N,105°7'W, Close to Prince Albert, SK)
CO2 (ppm)
400
390
380
370
360
δ13CMea (‰)
-7
-8
-9
-10
7000
6000
5000
4000
3000
2000
1000
masl
* The lowest two levels (EC data) only up to Dec. 2008
δ13CSource (‰)
-10
-20
-30
-40
-50
S -F
W-S
2005
2006
2007
2008
2009
2010
Decimal Year

Carbon Isotopic Composition of **Detected Source CO_2** at TAP, South Korea

(36.73°N, 126.13°E)



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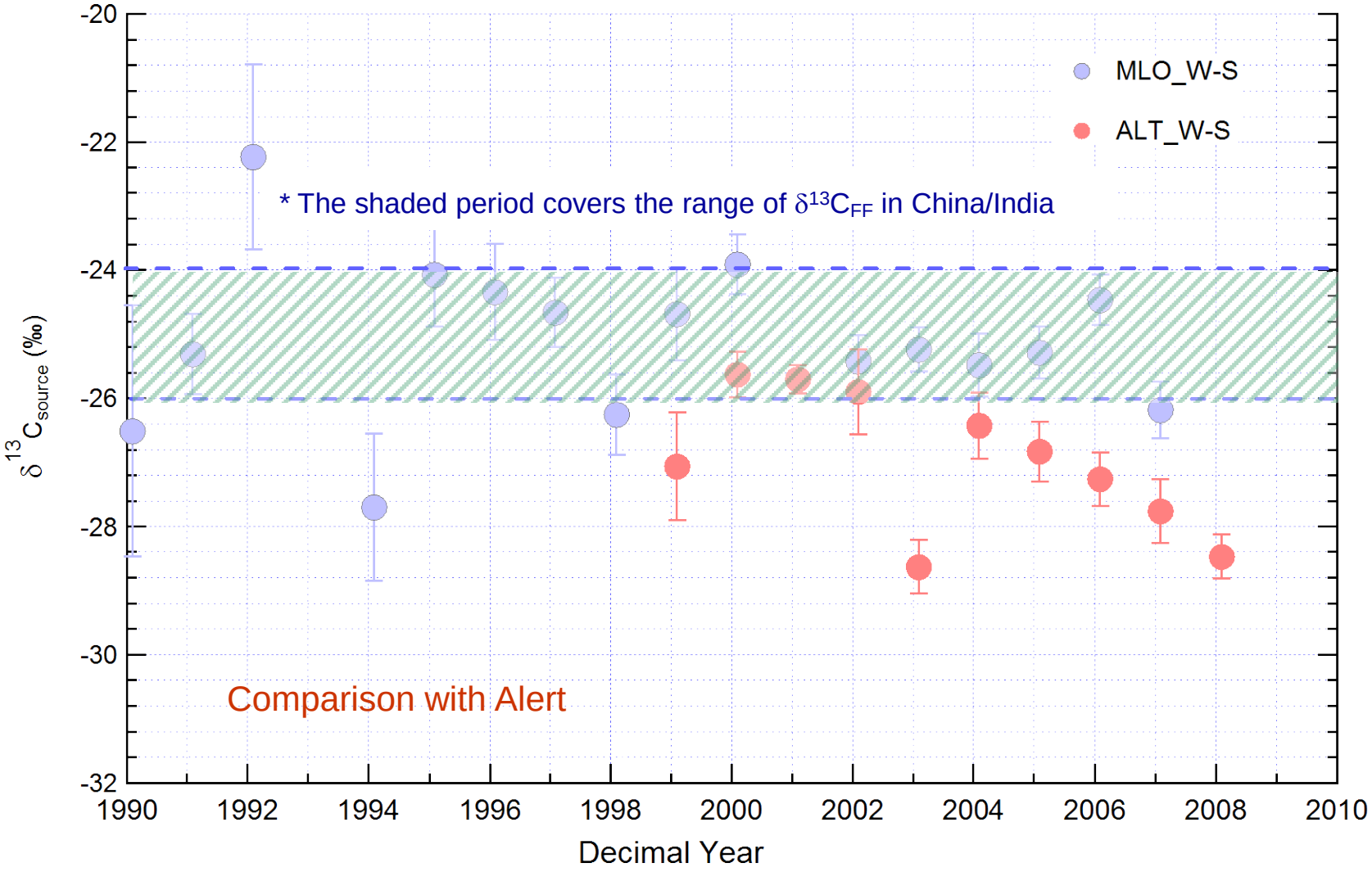
Carbon Isotopic Composition of
Detected Source CO_2 at Mauna Loa, Hi

(19.54°N, 155.58°W, 3397masl)



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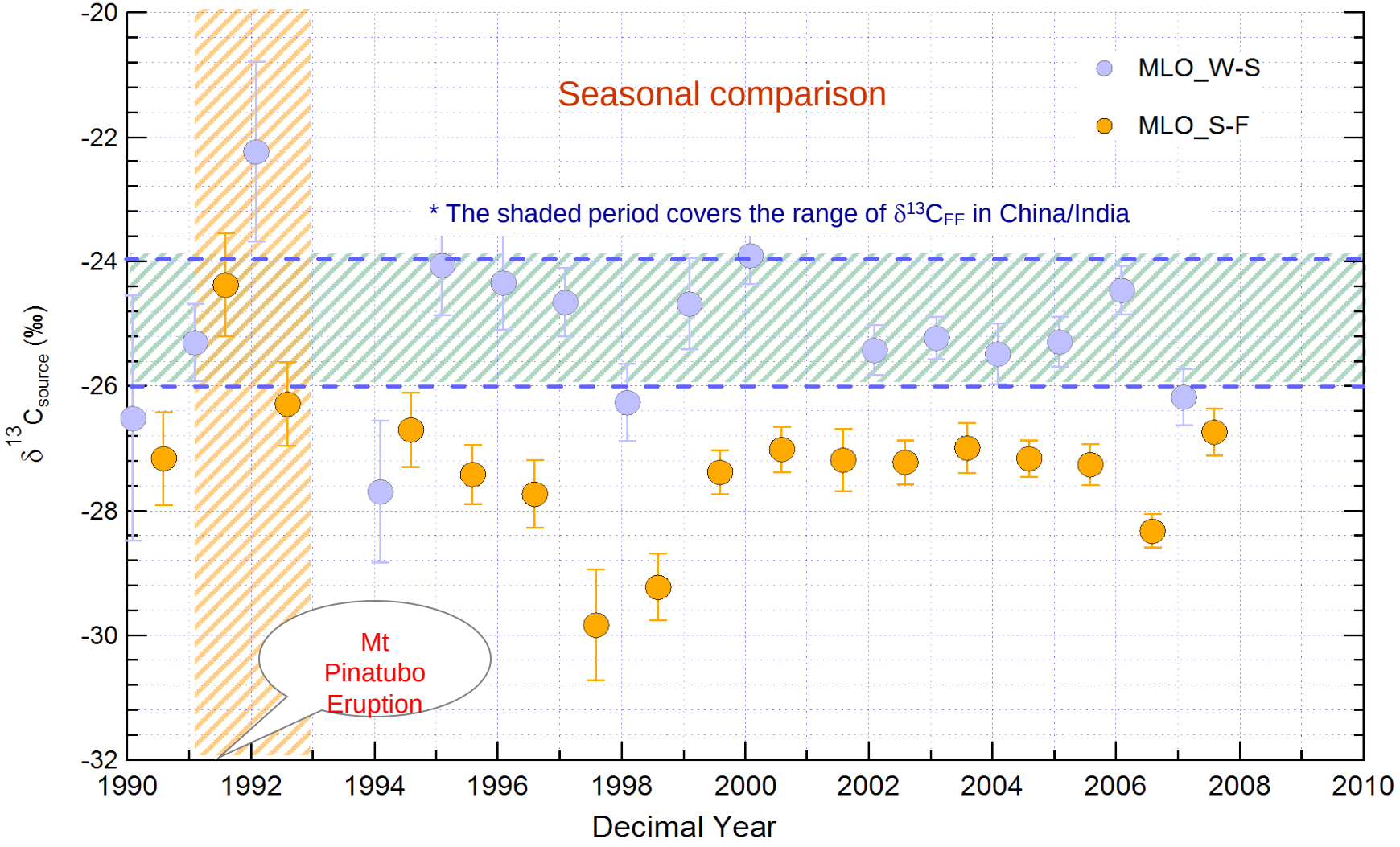
Carbon Isotopic Composition of
Detected Source CO_2 at Mauna Loa, Hi

(19.54°N, 155.58°W, 3397masl)



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What we have learn

- The $\delta^{13}C_{mea(BC)}$ values obtained from Beijing (~ -25 ‰) during win-spr time (2006-09) are obviously different from those at Alert (~ -28‰). The former are close to the mean value of $\delta^{13}C_{FF}$ in China, indicating a similar FF usage structure as the national mean of the country. Whereas, the latter show the dominant influence (< -28‰) from Eurasia (Europe + Russia) and NA.

- The majority of the detected $\delta^{13}C_{FF(CO2)}$ values derived from the $\delta^{13}C_{mea(CO2)}$ measurements at TAP, South Korea (1991- 2007) are within the range from -24‰ to -26‰, indicating major influences of $\delta^{13}C_{FF}$ from the China/India region. Whereas, most of $\delta^{13}C_{FF(CO2)}$ at Alert (1999 - 2008) are < -26‰, suggesting much more FF contributions reaching Alert from Eurasia and NA than those from Asia (i.e. China/India). This is consistent with the results from $\delta^{13}C_{mea(BC)}$ at Alert.

What we have learn

- In contrast with the $\delta^{13}C_{FF(CO2)}$ obtained at the arctic region (i.e., Alert), the $\delta^{13}C_{FF(CO2)}$ values from the lower latitudes (e.g., EPT and PTA) on the west coast of NA and at Mauna Loa in North Pacific Ocean, are mainly within the range from -24‰ to -26‰ or even more positive, inferring that the FF CO_2 signals from Asia could be transported across Pacific Ocean to North America.

- High precision C isotope measurements in flask and filter samples can be used, as independent methods, to identify and verify FF signals and their influences on both regional and global scales as long as the corresponding emission sources are isotopically distinguishable.

- The results of this work could be also used to constrain transport models for qualifying the relative contributions of air masses from different source regions.


Alert
Canada
BRW
Ak, US
LLB
Canada
BRM
Canada
ESP
Canada
SAB
Canada
PTA
Ca, US
MLO
Hi, US
Beijing
China
TAP
South Korea
Mt. Pinatubo
Thanks !

Acknowledgement

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Thomas J. Conway, Patricia M Lang
for CO_2 measurements

Kenneth Masarie for data processing

Financial support:

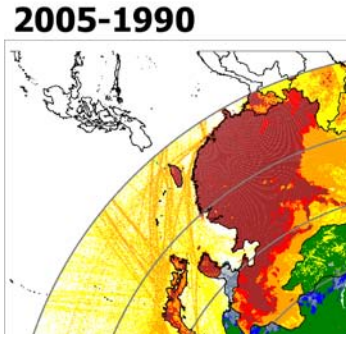
Climate Research fund, Environment Canada

NOAA Research fund

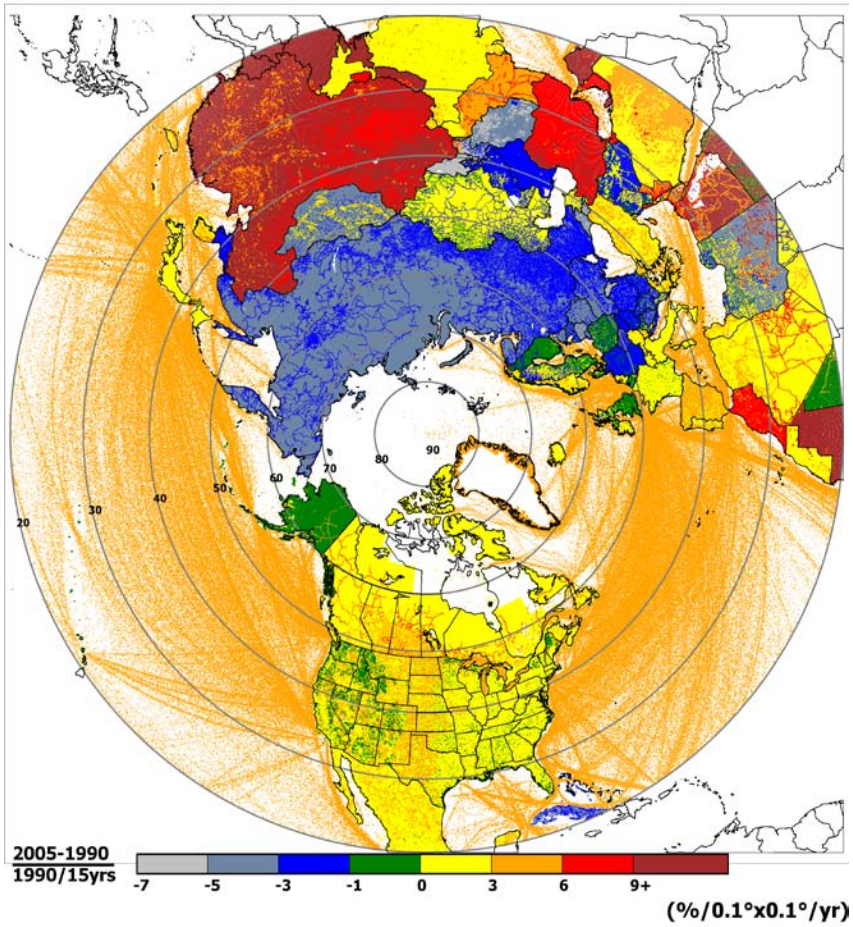
Absolute & Relative Changes (1990 – 2005) in total CO_2 Emissions from Edgar Database

(http://edgar.jrc.ec.europa.eu/index.php)

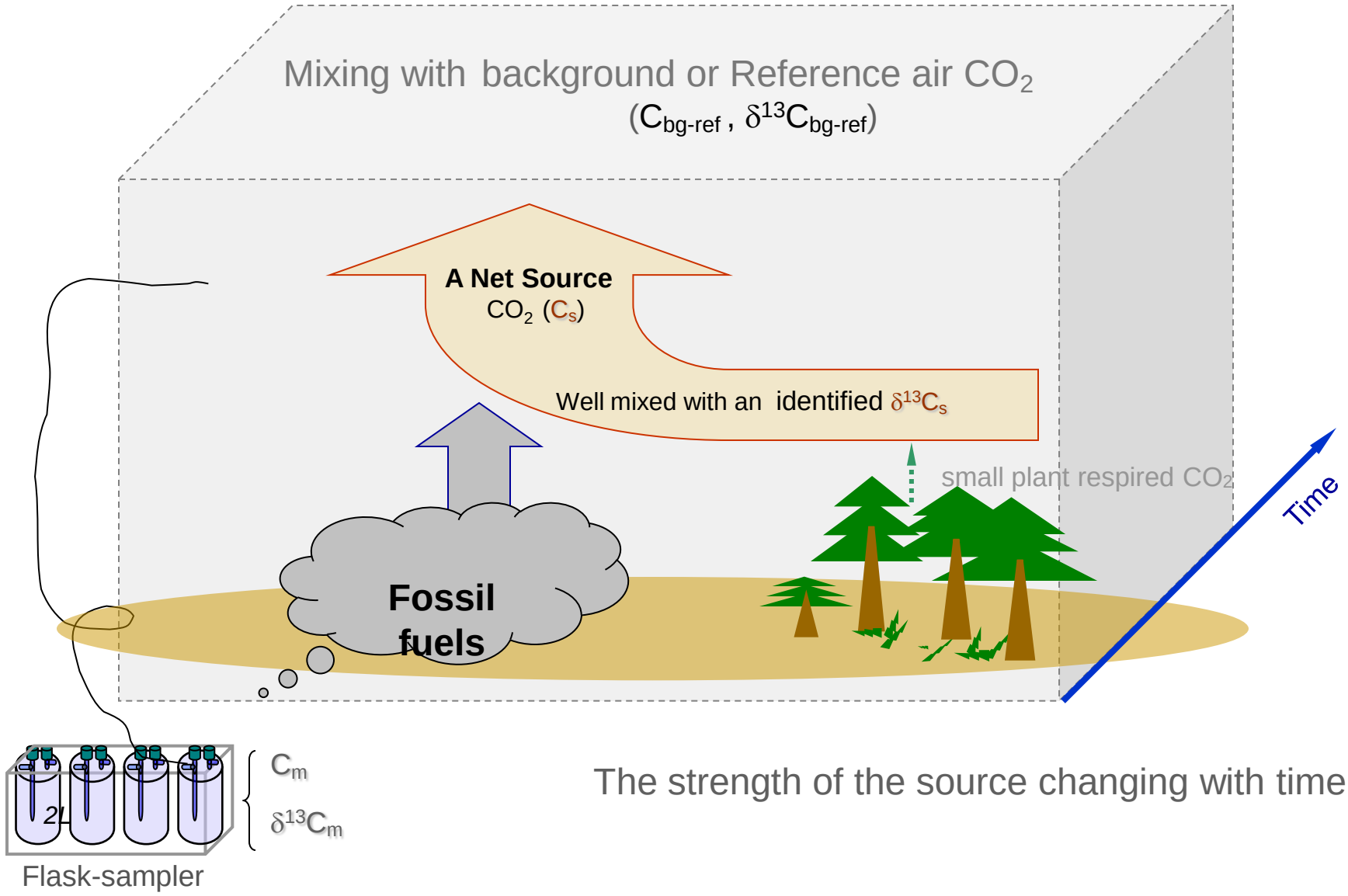
Absolute Changes



Relative Changes



Schematic of Two–end Member Mixing of Atmospheric CO_2



The strength of the source changing with time

Derivation of $\delta^{13}C_s$ in Atmospheric CO_2 Measurements ($\delta^{13}C_m$, C_m)

Mass Balance

$$\begin{cases} C_m = C_{bg\text{-}ref} + C_s \\ \delta^{13}C_m * C_m = \delta^{13}C_{bg\text{-}ref} * C_{bg\text{-}ref} + \delta^{13}C_s * C_s \end{cases}$$

Linear function

$$\delta^{13}C_m = (\delta^{13}C_{bg\text{-}ref} - \delta^{13}C_S) * C_{bg\text{-}ref}/C_m + \delta^{13}C_s$$

$$\delta^{13}C_m = \mathbf{b} * (1/C_m) + \mathbf{a}$$

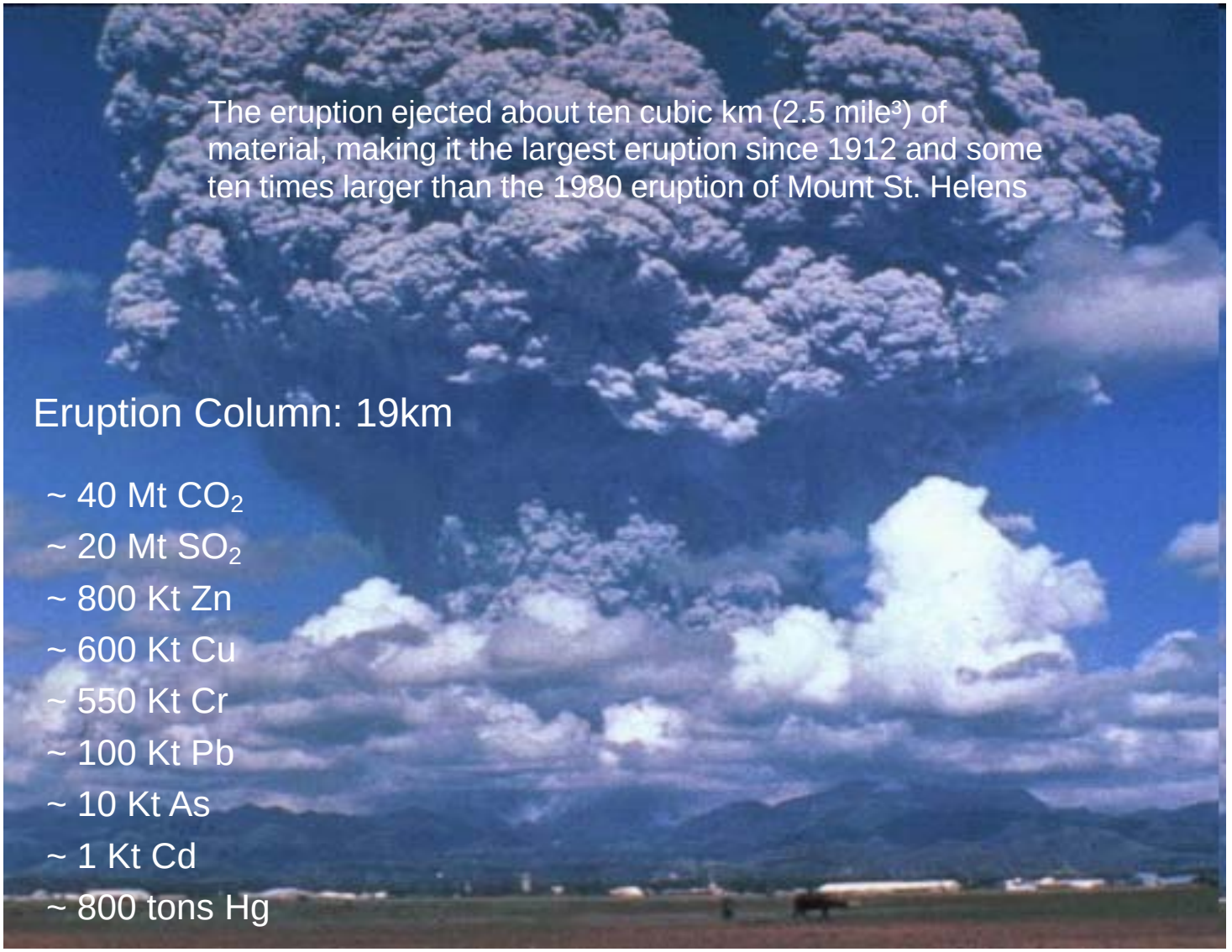
$$\mathbf{b} = (\delta^{13}C_{bg\text{-}ref} - \delta^{13}C_s) * C_{bg\text{-}ref} \qquad \mathbf{a} = \delta^{13}C_s$$

Assumptions:

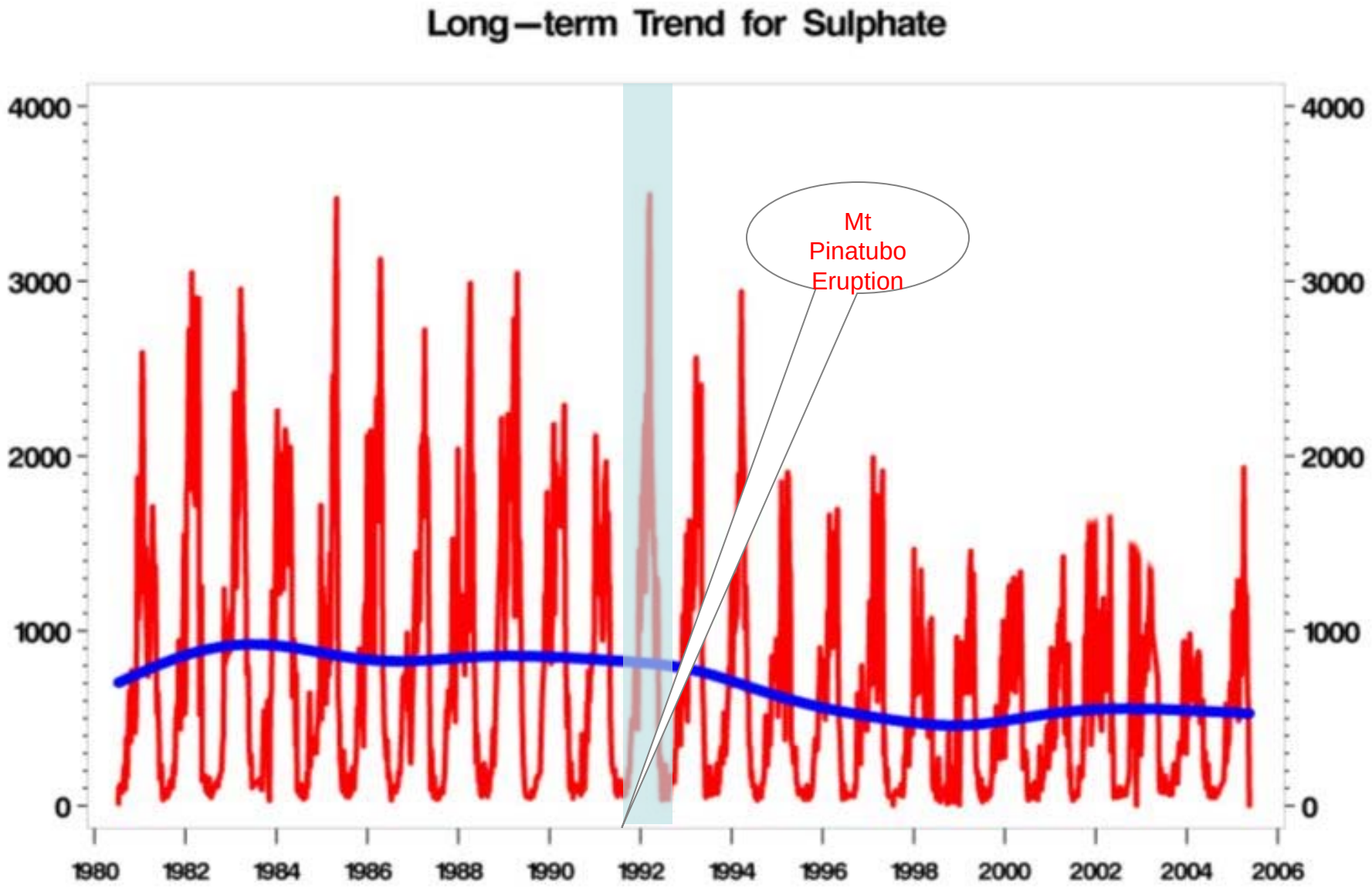
- The net source CO_2 is well mixed with a distinguishable isotopic composition ($\delta^{13}C_s$)
- $C_{bg\text{-}ref}$ changes are only caused by C_s

Mount Pinatubo Eruption, Philippines

(15.14°N, 120.35°E)

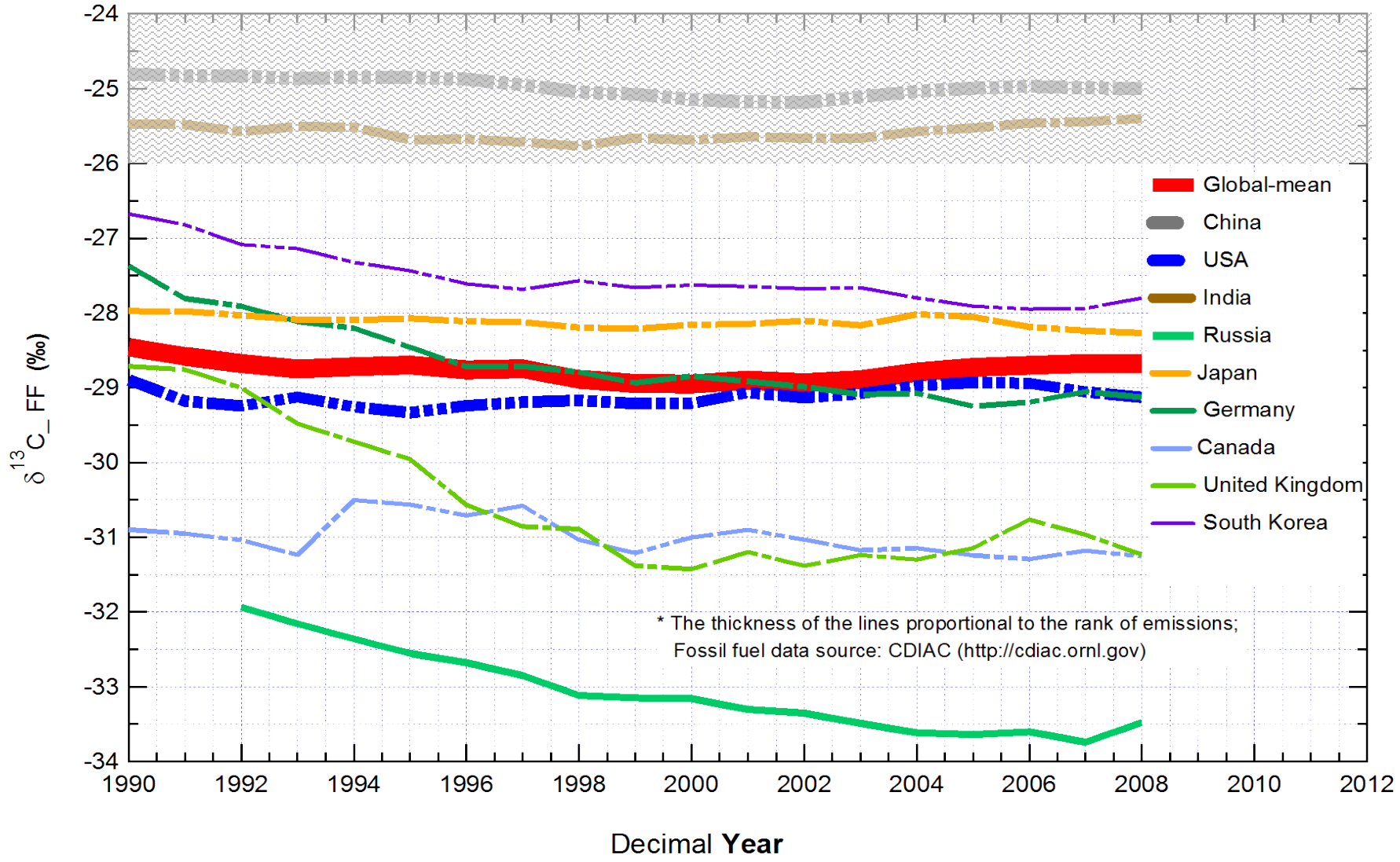


Source: http://pubs.usgs.gov/pinatubo, http://vulcan.wr.usgs.gov/Projects/Emissions/Reports/Pinatubo/pinatubo_abs.html


Long—term Trend for Sulphate
4000
3000
2000
1000
0
Mt
Pinatubo
Eruption
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006

C isotopic Compositions of Fossil Fuel in Top 9 Emitters

(fossil fuel mass fraction weighted)



Coal (-24‰) **Gasoline & Diesel** (-28‰) Natural gas (-40‰)

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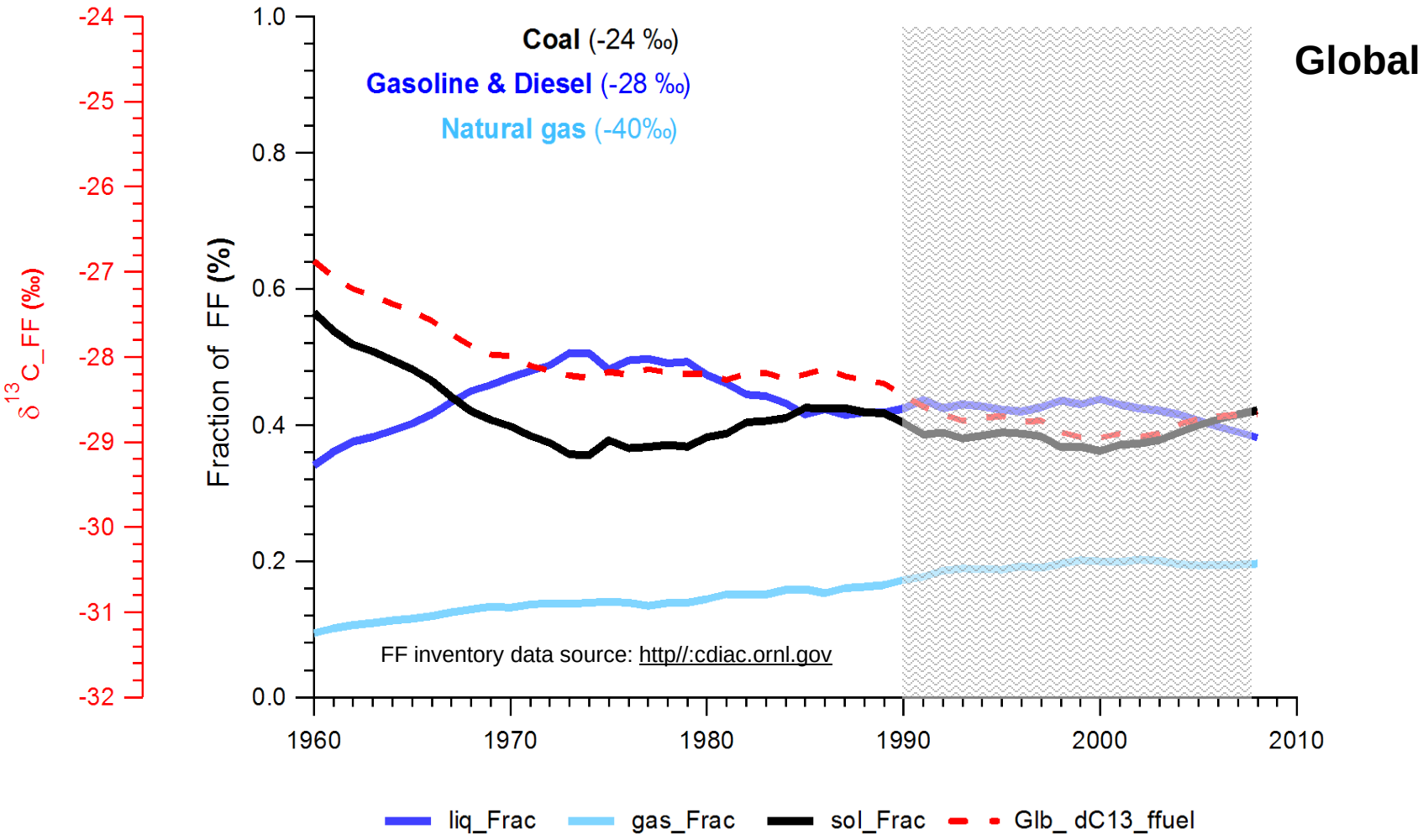
Carbon Isotopic Composition of FF & Energy Structure

(Fossil Fuel Mass Fraction Weighted)



* The shaded period can be compared with the observations

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Tracing Sources and Process via Stable Carbon Isotopes

$R_S = (^{13}C/^{12}C)_s$

Physical

Photochemical

Biological

$R_{Ob} = (^{13}C/^{12}C)_{Ob} = \alpha * R_S$

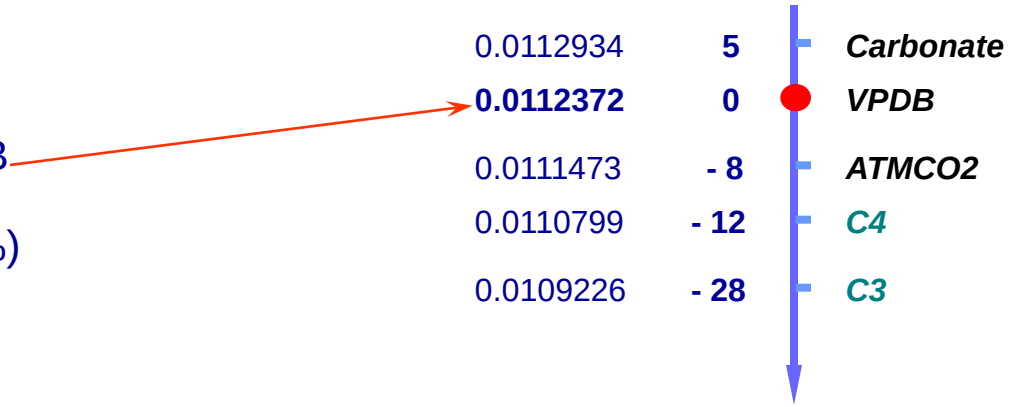
Sources **Processes** **Observations**

$\alpha = R_{Ob} * R_S$

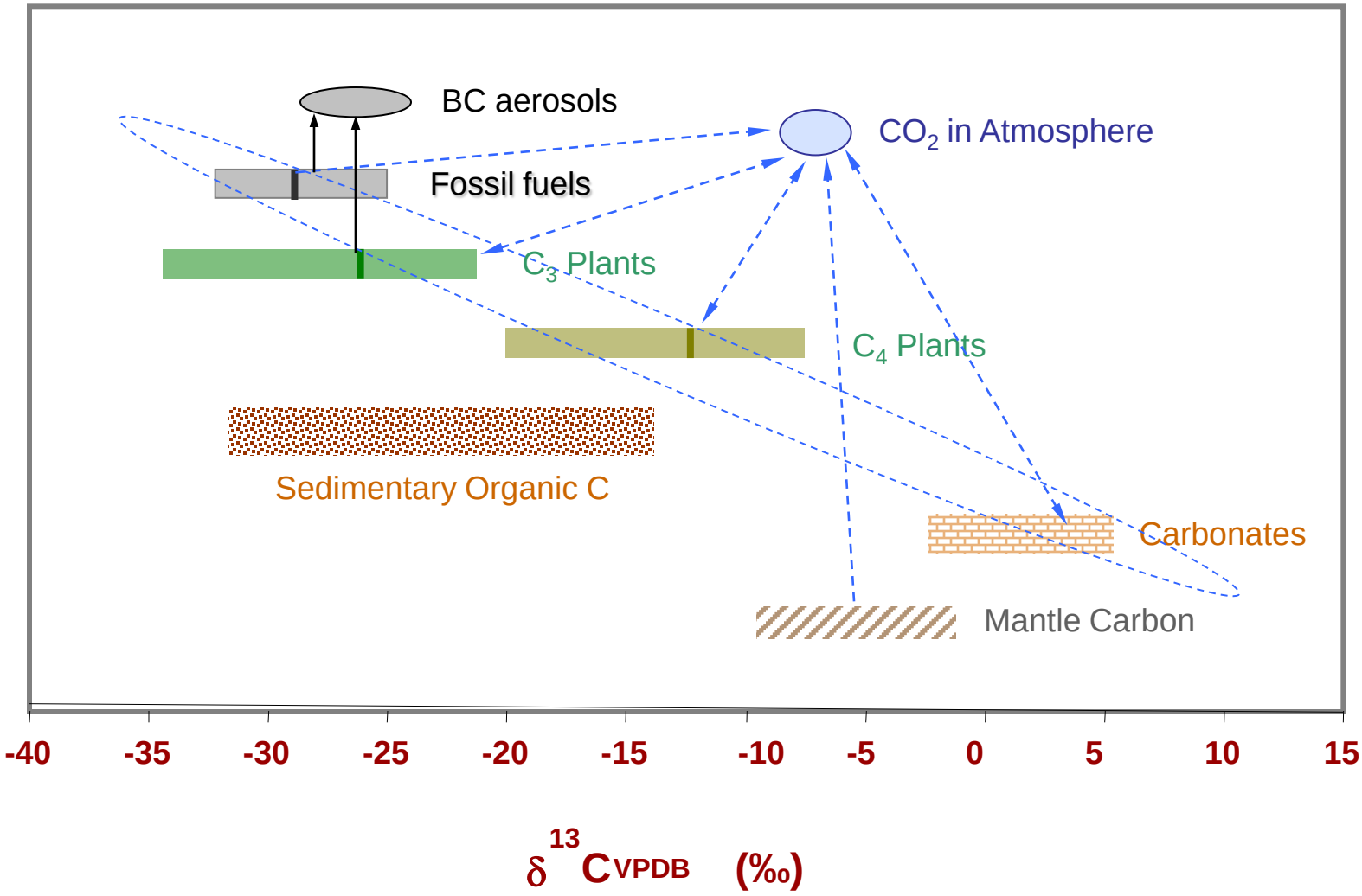
* Assuming no processes modifying the C isotopic compositions of **CO_2** and **BC** after their emissions into the atmosphere. Here, only the mixing from different sources is considered. Mixing/dilution processes won't change isotopic compositions.

Terminology

- $R = {}^{13}C/{}^{12}C$
- The Primary Standard: VPDB
- $\delta^{13}C = [(R_{sam}/R_{Std}) - 1]*10^3$ (‰)

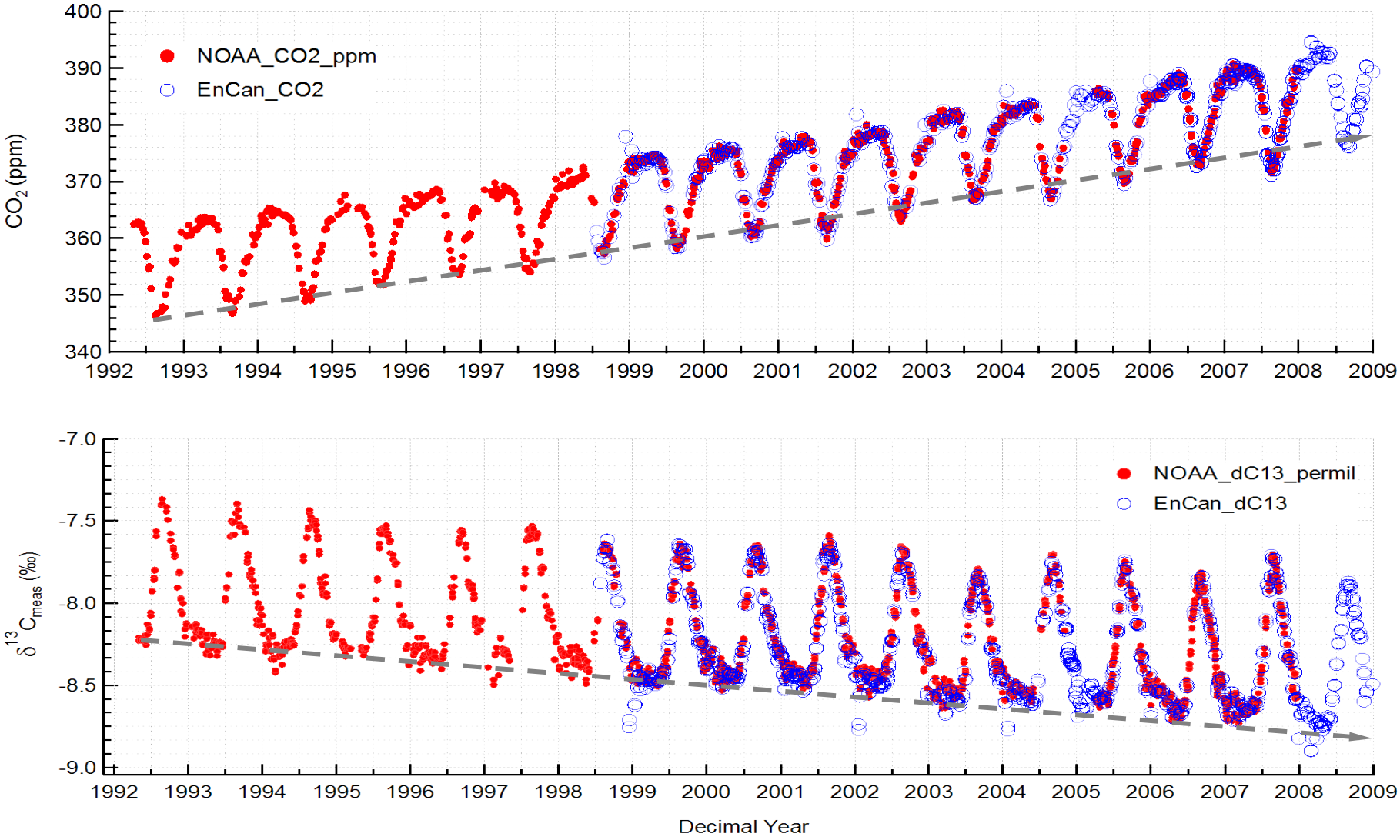


$\delta^{13}C$ values of Important Reservoirs/Sources in the Earth



CO_2 Concentration & Isotope ($\delta^{13}C_m$) at Alert

(82°27'N, 62°31'W)



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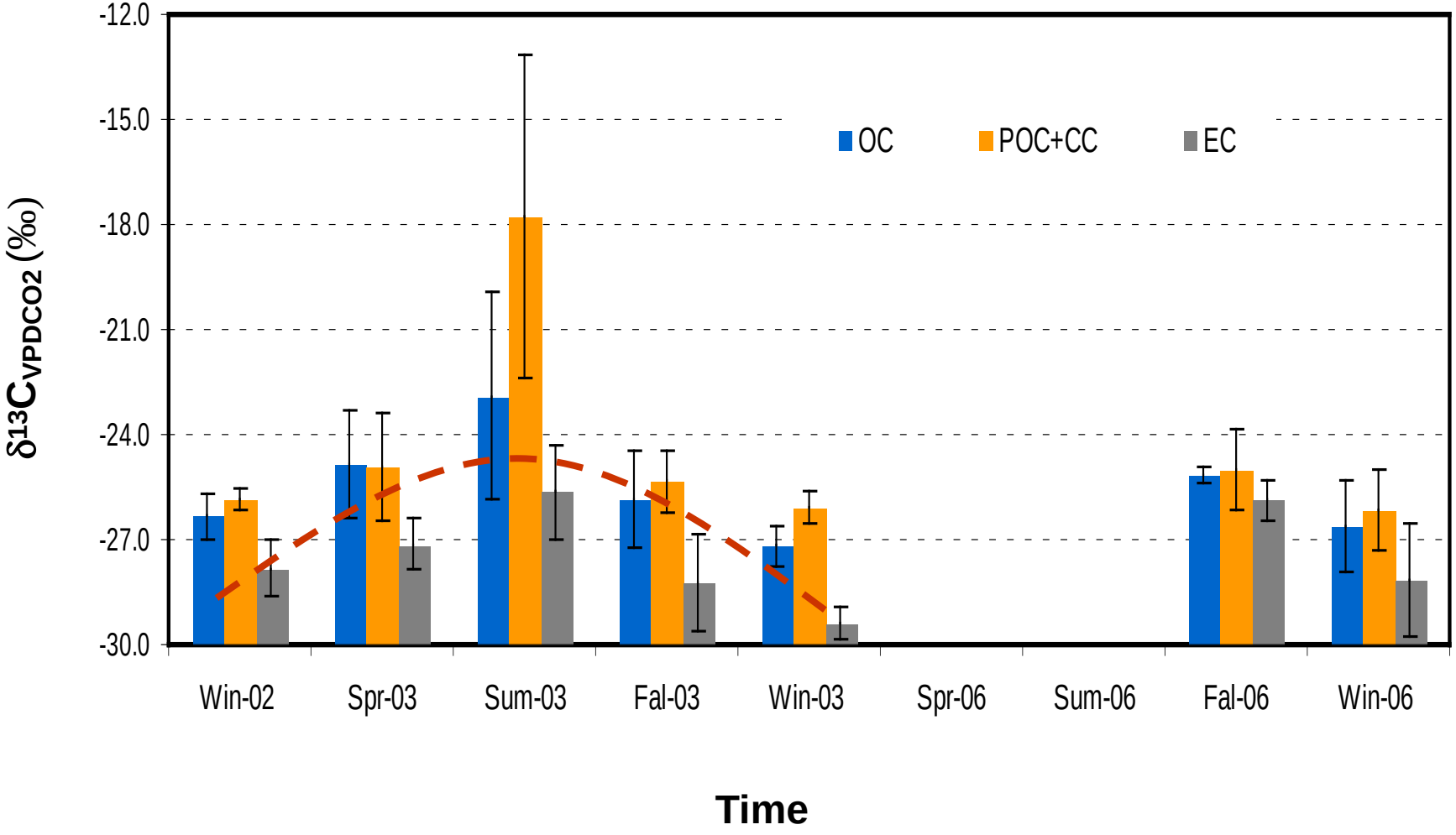
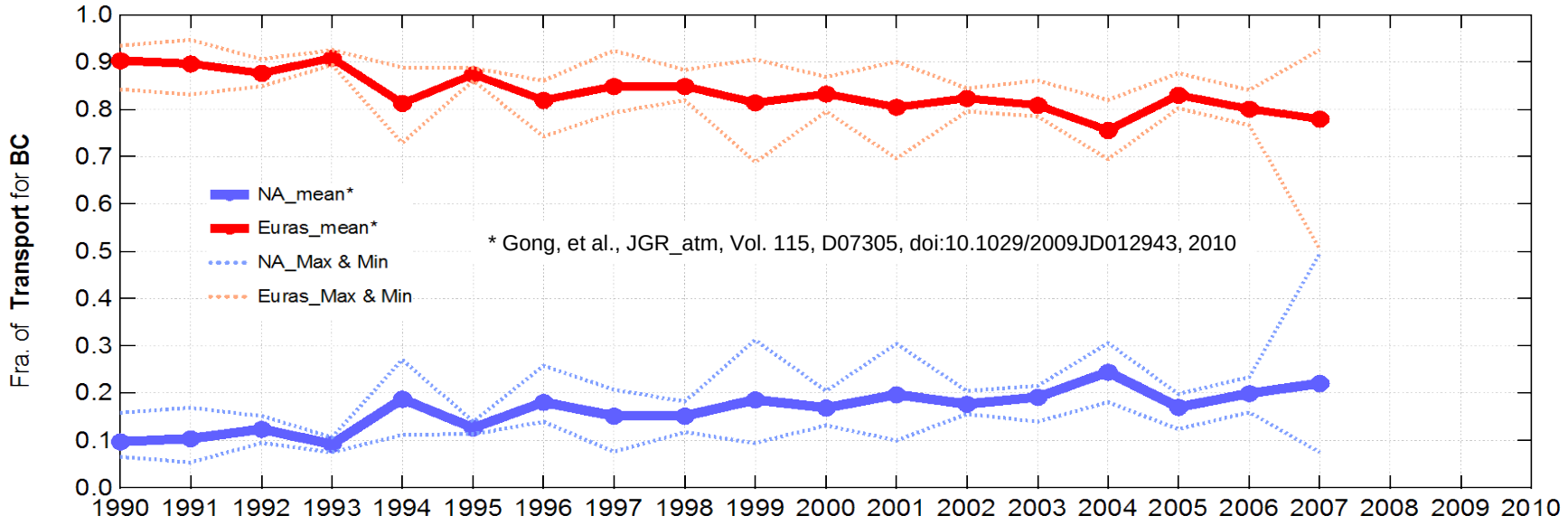
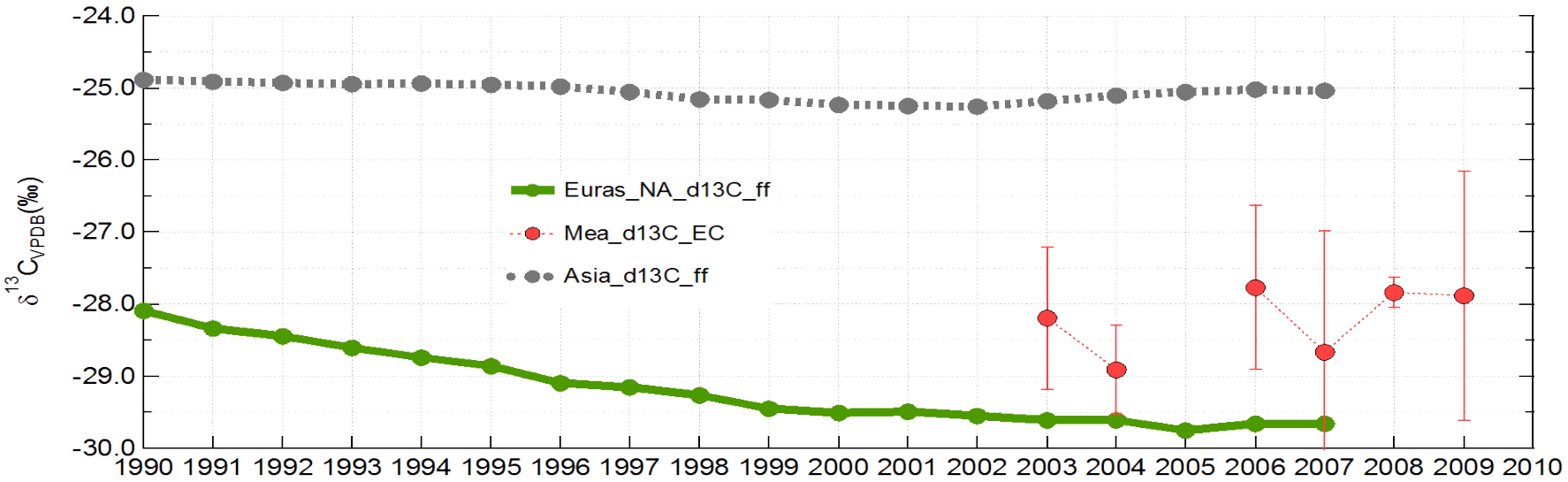
OC-EC Isotopic Compositions in fine PM at Alert (82°27'N, 62°31'W) (2002-06)



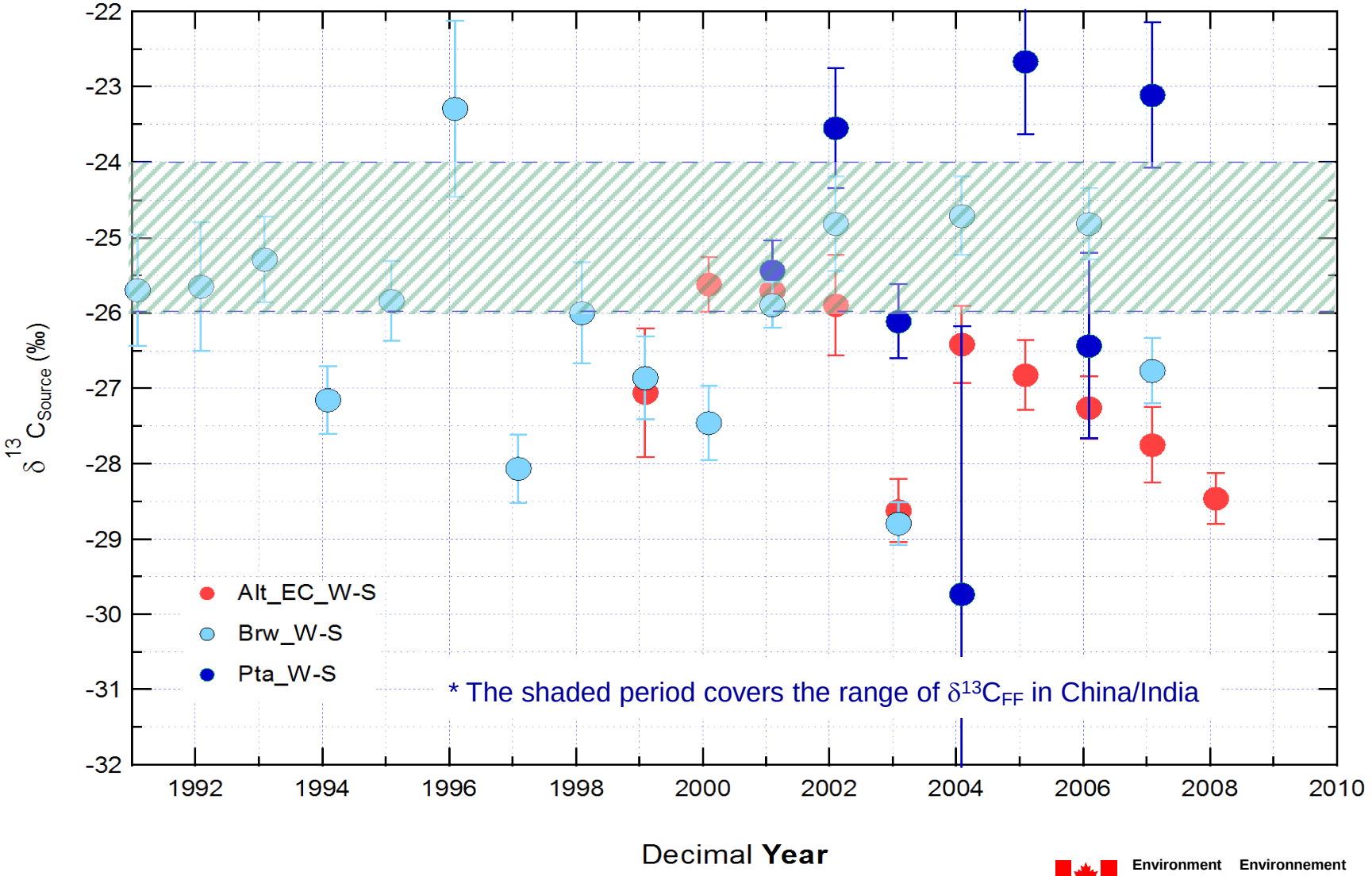
$^{13}C/^{12}C$ Constraints on Inter-Continental Transport of Fossil Fuel BC to Alert

(Nov – Apr)





Carbon Isotopic Composition of
Detected Source CO_2 at Barrow, AK and Point Arena, Ca



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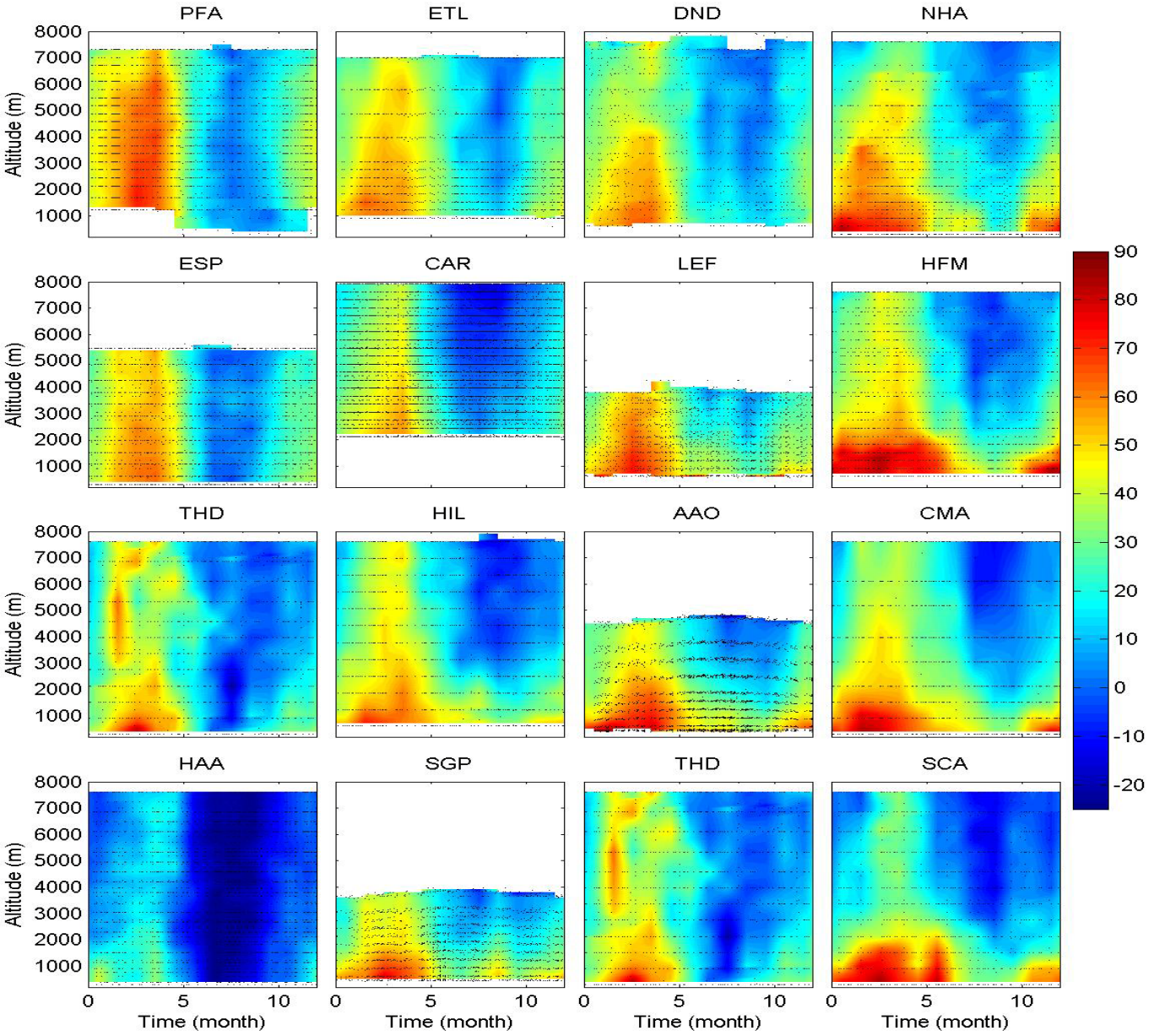
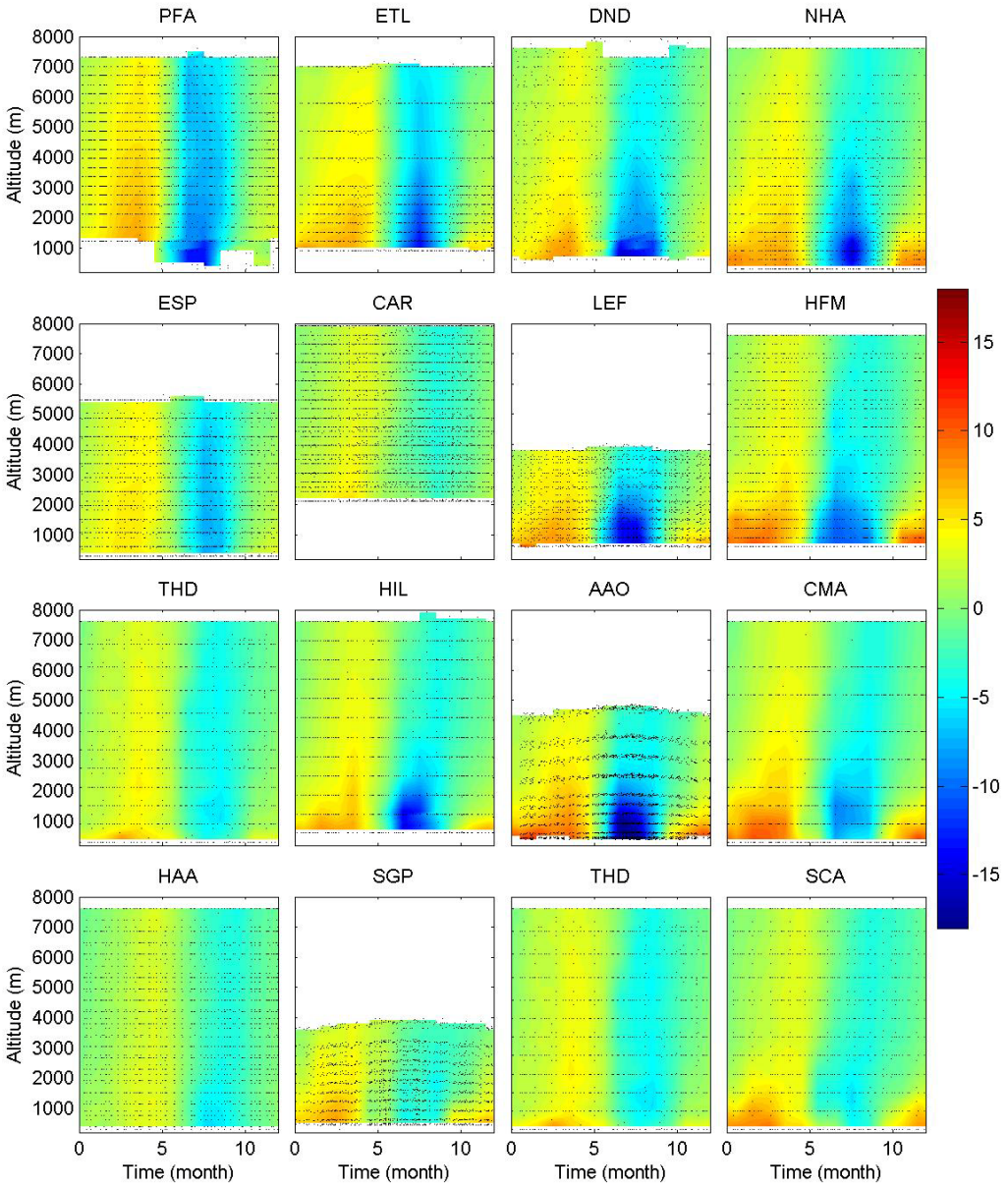
CO

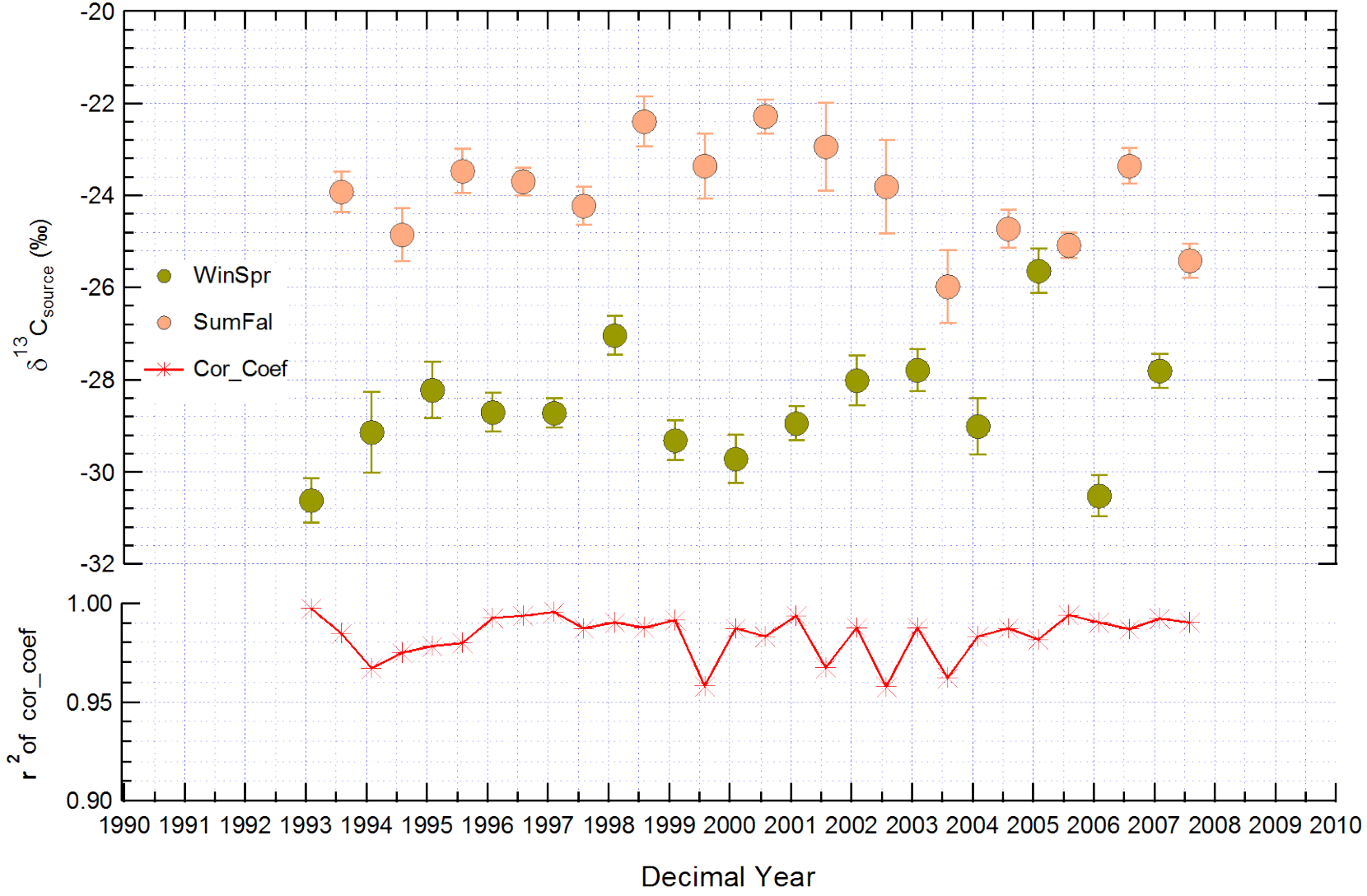

PFA
ETL
DND
NHA
ESP
CAR
LEF
HFM
THD
HIL
AAO
CMA
HAA
SGP
THD
SCA
Altitude (m)
8000
7000
6000
5000
4000
3000
2000
1000
0
5
10
Time (month)
90
80
70
60
50
40
30
20
10
0
-10
-20

CO2


PFA
ETL
DND
NHA
ESP
CAR
LEF
HFM
THD
HIL
AAO
CMA
HAA
SGP
THD
SCA
Altitude (m)
8000
7000
6000
5000
4000
3000
2000
1000
0
5
10
Time (month)
15
10
5
0
-5
-10
-15

Carbon Isotopic Composition of **Detected Source CO_2** at Hegyhatsal, Hungary

(46.95°N, 16.65°E, 248masl)



Carbon Isotopic Composition of
Detected Source CO_2 at Mauna Loa, Hi

(19.54°N, 155.58°W, 3397masl)