$^{13}\text{C}/^{12}\text{C}$ 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

Independent methods for verifying fossil fuel emissions are needed!!
Fossil Fuel CO₂ Emission in Top 9 Emitters (1990-2008)

* The thickness of the lines proportional to the rank of emissions; Fossil fuel data source: CDIAC (http://cdiac.ornl.gov)
Carbon Isotopic Composition of FF & Energy Structure
(Fossil Fuel Mass Fraction Weighted)

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

USA

NOAA_GMD Annual Conference, May, 2010
Carbon Isotopic Composition of FF & Energy Structure
(Fossil Fuel Mass Fraction Weighted)

China

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

FF inventory data source: http://cdiac.ornl.gov

NOAA_GMD Annual Conference, May, 2010
C isotopic Compositions of Fossil Fuel at Regional Scale

(fossil fuel mass fraction weighted)

Coal (-24‰)  Gasoline & Diesel (-28‰)  Natural gas (-40‰)
$^{13}\text{C}/^{12}\text{C}$ 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;
- $\delta^{13}\text{C}_{\text{FF}} \approx \delta^{13}\text{C}_{\text{FF(CO}_2)} \approx \delta^{13}\text{C}_{\text{FF(BC)}}$

Implications of $\delta^{13}\text{C}_{\text{mea(BC)}}$ and $\delta^{13}\text{C}_{\text{mea(CO}_2)}$

- $\delta^{13}\text{C}_{\text{FF(BC)}}$ values can be directly inferred from $\delta^{13}\text{C}_{\text{mea(BC)}}$
- $\delta^{13}\text{C}_{\text{FF(CO}_2)}$ can be only derived from $\delta^{13}\text{C}_{\text{mea(CO}_2)}$ and $C_{\text{mea-CO}_2}$ values with an assumption of a two-end member mixing
Observation sites of $^{13}$C/$^{12}$C in Atmospheric CO$_2$ & Black Carbon Aerosols

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

NOAA_GMD Annual Conference, May, 2010
Carbon Isotopic Compositions ($\delta^{13}C_{\text{mea-BC}}$) of EC at Alert & Beijing
Seasonal Average (Nov – Apr) of $\delta^{13}C_{\text{mea}}_{\text{BC}}$ in **EC** at Alert & Beijing

* The average of $\delta^{13}C_{\text{mea}}_{\text{BC}}$ at Beijing ≈ the national mean of $\delta^{13}C_{\text{FF}}$

* The $\delta^{13}C_{\text{mea}}_{\text{BC}}$ at Alert show dominant influences from Eurasia and N.A. $\delta^{13}C_{\text{FF}}$
Carbon Isotopic Composition of Detected Source CO₂ at Alert

The shaded period covers the range of $\delta^{13}\text{C}_{FF}$ in China/India.
Carbon Isotopic Composition of Detected Source CO₂ over Canada

* The shaded period covers the range of $\delta^{13}C_{FF}$ in Asia

![Graph showing carbon isotopic composition over Canada with specific years and locations marked.](image)
Carbon Isotopic Composition of Detected Source CO₂ via Vertical Profiles at Berms*
(53°59'N, 105°7'W, Close to Prince Albert, SK)

* The lowest two levels (EC data) only up to Dec. 2008
Carbon Isotopic Composition of Detected Source CO$_2$ at TAP, South Korea (36.73°N, 126.13°E)

* The shaded period covers the range of $\delta^{13}$C$_{FF}$ in China/India
Carbon Isotopic Composition of Detected Source CO₂ at Mauna Loa, Hi
(19.54°N, 155.58°W, 3397 masl)

* The shaded period covers the range of δ¹³C_FF in China/India

Comparison with Alert
Carbon Isotopic Composition of Detected Source CO$_2$ at Mauna Loa, Hi
(19.54°N, 155.58°W, 3397masl)

Seasonal comparison

* The shaded period covers the range of $\delta^{13}$C$_{FF}$ in China/India

Mt Pinatubo Eruption
The $\delta^{13}$C_{mea(BC)} values obtained from Beijing ($\sim -25$‰) during win-spr time (2006-09) are obviously different from those at Alert ($\sim -28$‰). 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.
In contrast with the δ^{13}C_{FF(CO2)} obtained at the arctic region (i.e., Alert), the δ^{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.
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Absolute & Relative Changes (1990 – 2005) in total CO₂ Emissions from Edgar Database

Schematic of Two–end Member Mixing of Atmospheric CO₂

Mixing with background or Reference air CO₂

\( (C_{bg-ref}, \delta^{13}C_{bg-ref}) \)

A Net Source CO₂ \( (C_s) \)

Well mixed with an identified \( \delta^{13}C_s \)

Fossil fuels

small plant respired CO₂

\( C_m \)

\( \delta^{13}C_m \)

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**

\[
\begin{align*}
C_m &= C_{bg-ref} + C_s \\
\delta^{13}C_m \times C_m &= \delta^{13}C_{bg-ref} \times C_{bg-ref} + \delta^{13}C_s \times C_s
\end{align*}
\]

**Linear function**

\[
\delta^{13}C_m = (\delta^{13}C_{bg-ref} - \delta^{13}C_s) \times C_{bg-ref}/C_m + \delta^{13}C_s
\]

\[
\delta^{13}C_m = b \times (1/C_m) + a
\]

\[
b = (\delta^{13}C_{bg-ref} - \delta^{13}C_s) \times C_{bg-ref} \quad a = \delta^{13}C_s
\]

**Assumptions:**

- The net source CO$_2$ is well mixed with a distinguishable isotopic composition ($\delta^{13}C_s$)
- $C_{bg-ref}$ changes are only caused by $C_s$
Mount Pinatubo Eruption, Philippines
(15.14°N, 120.35°E)

The eruption ejected about ten cubic km (2.5 mile³) of material, making it the largest eruption since 1912 and some ten times larger than the 1980 eruption of Mount St. Helens.

Eruption Column: 19km

- ~ 40 Mt CO₂
- ~ 20 Mt SO₂
- ~ 800 Kt Zn
- ~ 600 Kt Cu
- ~ 550 Kt Cr
- ~ 100 Kt Pb
- ~ 10 Kt As
- ~ 1 Kt Cd
- ~ 800 tons Hg

C isotopic Compositions of Fossil Fuel in Top 9 Emitters
(fossil fuel mass fraction weighted)

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

*The thickness of the lines proportional to the rank of emissions; Fossil fuel data source: CDIAC (http://cdiac.ornl.gov)*
Carbon Isotopic Composition of FF & Energy Structure
(Fossil Fuel Mass Fraction Weighted)

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

* The shaded period can be compared with the observations

FF inventory data source: http://cdiac.ornl.gov

Global
Tracing Sources and Process via Stable Carbon Isotopes

\[ R_S = \left( \frac{^{13}C}{^{12}C} \right)_S \]

\[ R_{Ob} = \left( \frac{^{13}C}{^{12}C} \right)_{Ob} = \alpha \times R_S \]

**Sources**
- **Physical**
- **Photochemical**
- **Biological**

**Processes**
\[ \alpha = R_{Ob} \times R_S \]

**Observations**

* Assuming no processes modifying the C isotopic compositions of CO₂ 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**
- \( R = \frac{^{13}C}{^{12}C} \)
- The Primary Standard: VPDB
- \[ \delta^{13}C = \left[ \frac{R_{sam}}{R_{Std}} - 1 \right] \times 10^3 \ (\%o) \]

<table>
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</table>

*Carbonate*

*VPDB*

*ATMCO2*

*C4*

*C3*
$\delta^{13}$C values of Important Reservoirs/Sources in the Earth

![Diagram showing the distribution of $\delta^{13}$C values across various carbon reservoirs and sources.](image)
CO₂ Concentration & Isotope ($\delta^{13}C_m$) at Alert
(82°27'N, 62°31'W)
OC-EC Isotopic Compositions in fine PM at Alert (82°27'N, 62°31'W) (2002-06)
$^{13}\text{C}/^{12}\text{C}$ Constraints on Inter-Continental Transport of Fossil Fuel BC to Alert

(Nov – Apr)

Carbon Isotopic Composition of Detected Source CO₂ at Barrow, AK and Point Arena, Ca

* The shaded period covers the range of $\delta^{13}C_{FF}$ in China/India
CO
Carbon Isotopic Composition of Detected Source CO2 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)