Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: Anthropogenic and biogenic effects

D. E. Pataki, D. R. Bowing and J. R. Ehleringer

Reporter: Jiaping Xu
1. Background
2. Hypothesis
3. Objectives
4. Method
5. Results and interpretation
6. Critique of their Interpretation
1. Background

1.1 Trends in Carbon dioxide

Fig 1. Here is the longest direct-measurement CO$_2$ time series. [NOAA, 2007]
1. Background

1.1 Trends in Carbon dioxide

Fig 2. CO\textsubscript{2} concentration in UofU.[UofU,2007]
1. Background

1.2 Carbon and oxygen isotope

Isotopes are variants of a particular chemical element. While all isotopes of a given element share the same number of protons, each isotope differs from the others in its number of neutrons.[Li,2009]

Photosynthesis, biogenic respiration, anthropogenic burning give different carbon and oxygen isotope signals which can trace gas exchange in biogeochemical cycles of terrestrial ecosystems. [Francey et al., 1985]
## 1. Background

### 1.2 Carbon and oxygen isotope

Table 1. Stable isotopes of C and O and their mass number and abundance. [Hoefs, 2004; Fry, 2006]

<table>
<thead>
<tr>
<th>Elements</th>
<th>Isotope</th>
<th>Abundance/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>$^{12}$C</td>
<td>98.89</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C</td>
<td>1.11</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}$O</td>
<td>99.759</td>
</tr>
<tr>
<td></td>
<td>$^{17}$O</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>$^{18}$O</td>
<td>0.204</td>
</tr>
</tbody>
</table>
1. Background

1.2 Carbon and oxygen isotope

Table 2. International referrance.[Liu,2009]

<table>
<thead>
<tr>
<th>Medium</th>
<th>configuration</th>
<th>$d^{13}C(%o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomsphere</td>
<td>CO$_2$</td>
<td>-7</td>
</tr>
<tr>
<td>Lake</td>
<td></td>
<td>-8—16</td>
</tr>
<tr>
<td>River</td>
<td></td>
<td>-10</td>
</tr>
<tr>
<td>Sea</td>
<td></td>
<td>0 ± 2</td>
</tr>
<tr>
<td>Terrestrial biology</td>
<td>C</td>
<td>-22</td>
</tr>
<tr>
<td>aquatic in lake</td>
<td>CO$_2$</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-5</td>
</tr>
<tr>
<td>aquatic in river</td>
<td>CO$_2$</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-12</td>
</tr>
<tr>
<td>aquatic in sea</td>
<td>CO$_2$</td>
<td>-24</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0</td>
</tr>
<tr>
<td>Coal</td>
<td></td>
<td>-24</td>
</tr>
<tr>
<td>Natural gas</td>
<td></td>
<td>-40</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td></td>
<td>-20</td>
</tr>
</tbody>
</table>
1. Background

1.2 Carbon and oxygen isotope

Fig 3. The ranges for dissolved carbon and its sources. [Darling, 2005]
1. Background

1.2 Carbon and oxygen isotop

\[ R = \frac{m}{n} \frac{X}{X} \]  

(1)

\[ d = (\frac{R_A}{R_S} - 1) \times 1000 \]  

(2)

- **R** is the carbon isotope ratio of heavy (m) molecules and light (n) molecules.

- **d** is the ratio of R being examined (A) and R of the standard (S), which is dimensionless and is normally adopted as “parts per mil” (‰).
1. Background

Fig 4. Isotopic compositions of the major components. [Yakir, 2000]
1. Background

1.2 Carbon and oxygen isotope

Compared with micrometeorological measurement technology, stable isotope techniques are much more possible to quantify various ecological processes. [Yakir & Sternberg, 2000]

Isotopic measurements can reflect seasonal variability of uptake and release of CO$_2$ as the observed objection. [Ciais et al. 1995, 1997]
1. Background

1.3 Keeling plots

\[ C_a = C_b + C_s \quad (3)[\text{Keeling, 1958}] \]

\[ C_a d_a = C_b d_b + C_s d_s \quad (4) \]

\[ d^{13}C_a = C_b \left( d^{13}C_b - d^{13}C_s \right) \left( 1 / C_a \right) + d^{13}C_s \quad (5) \]

- \( C \): CO\(_2\) concentration.
- \( a \): Atmospheric CO\(_2\) concentration measured in the ecosystem.
- \( b \): The background CO\(_2\) concentration.
- \( s \): The additional CO\(_2\) concentration component produced by the source.
1. Background

1.3 Keeling plots

\[ d_a = d_s + \frac{M}{C_a} \]  \hspace{1cm} (6)

\[ M = C_b \left( d^{13}C_b - d^{13}C_s \right) \]  \hspace{1cm} (7)

Fig 5. Keeling Plots.[Pataki,2003]
1. Background

1.3 Keeling Plot

The plot of $d_a$ versus $1/C_a$ appears a straight line relationship with a slope $M$ and an intercept $d_p$.

The basis of the Keeling plot method is conservation of mass, which can tell released from urban sources from background. [D. E. Pataki et al. 2003]

By 1960, Keeling et al found that CO$_2$ concentration was not just the diurnal and seasonal variations, but also a year-on-year increase that roughly matched the amount of fossil flues burned per year.
2. Hypothesis

Isotope composition of carbon dioxide can be used to distinct different CO\textsubscript{2} contribution in an urban.
3. Objectives

Using one kind of mass balance model and the Keeling plot method, to partition seasonal cycle of urban CO₂ emission and its isotopic composition without isotope composition of background air.
4. Method

4.1 Site Information
4.2 Experimental Design
4.3 Data Analysis
4.1 Site Information

Fig 6. A photograph of the UofU Site and its environments.[From Google]
4.1 Site Information

Fig 7. A photograph of the UofU Sites and its environments.[from UofU]
4.1 Site Information

Fig 8. A photograph of the Wendover Sites. [From Google]
Fig 9. A photograph of the UofU Site and its environments.[From UofU]
4.2 Experimental Design

4.2.1 Atmospheric measurements:

Fig 10. Illustration of atmospheric measurements.[From UofU]
4.2 Experimental Design

4.2.1 Atmospheric measurements:

The instrument used for carbon dioxide measurement is typically an infrared gas analyzer. These come in many shapes and sizes.

The premise to most infrared gas analyzers is the same. A beam of infrared radiation is shown along a path through which the air sample of interest is passed, while an infrared radiation detector (opposing the beam) measures the quantity of infrared radiation. The greater the quantity of carbon dioxide within the path, the less infrared radiation is detected. Below is a schematic of a simple infrared gas analyzer.

Fig 11. Analysis of atmospheric measurements.[From UofU]
4.2 Experimental Design

4.2.2 Mass balance approach

\[ C_T = C_A + C_S \]  \quad (8)

\[ d_T = c_A (d_A - d_S) (1/c_T) + d_S \]  \quad (9)

\[ d = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 10000 \% \]  \quad (10)

- **T**: The total CO₂ mixing ratio.
- **A**: The background CO₂ mixing ratio.
- **S**: The Urban sources CO₂ mixing ratio.
4.2 Experimental Design

4.2.2 Mass balance approach

\[ f_R + f_G + f_N = 1 \]  \hspace{1cm} (11)

\[ d^{13}C_R f_R + d^{13}C_G f_G + d^{13}C_N f_N = d^{13}C_S \]  \hspace{1cm} (12)

\[ d^{18}O_R f_R + d^{18}O_G f_G + d^{18}O_N f_N = d^{18}O_S \]  \hspace{1cm} (13)

\( R \): Biogenic respiration.

\( N \): Natural gas.

\( G \): Gasoline combustion.
4.3 Data Analysis

- Keeling plot intercept was calculated using geometric mean regression according to Pataki et al. [2003].
- Outliers were removed if the absolute value of the residual for an individual data point was more than 3 standard deviations from the mean residual.
- Intercepts were discarded when the regression model was not significant at $a = 0.01$ according to Flanagan et al. [1997] and Bowling et al. [2003b].
- The standard error of the intercept was calculated by the ordinary least squares, “Model I” regression method [Sokal and Rohlf, 1995].
5. Results and interpretation

Figure 12. The average CO₂ mixing ratio measured at 18m.
5. Results and interpretation

Figure 13. Representative Keeling plots of carbon and oxygen isotope ratio during three discrete sampling periods.
5. Results and interpretation

Figure 14. The carbon isotope ratio of the urban CO₂ source.
5. Results and interpretation

\[ d^{13}C_G = -28.3 \pm 0.1^\circ/oo \]
\[ d^{13}C_N = -37.7 \pm 0.3^\circ/oo \]
\[ d^{13}C_R = -26.2 \pm 0.2^\circ/oo \]
\[ d^{18}O_R = 0.5 \times d^{18}O_{Leaf} + 0.5 \times d^{18}O_{Soil} \]
\[ d^{18}O_G + d^{18}O_N + d^{18}O_S = 21.3^\circ/oo \] (In winter)

Source water value: -15%oo

Water vapor value: -21%oo

The optimal periods to response photosynthetic activity and soil decomposition

Figure 15. (top) A ten-day running average.
(bottom) The oxygen isotope of the urban CO₂ source.
5. Results and interpretation

Figure 16. Components of the nighttime CO$_2$ mixing ratio.

- Preponderant in Winter
- Negligible in Summer
- Similar with $d^{18}O$
- Wendover
5. Results and interpretation

Table 3. Sensitivity analysis of calculations of the mean fractional contribution of $f_R$, $f_G$, and $f_N$ to the total CO$_2$ source during winter and the growing season.

<table>
<thead>
<tr>
<th>Case Description</th>
<th>January 1 to April 15</th>
<th>April 16 to November 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>$f_R$ = 0.02, $f_G$ = 0.42, $f_N$ = 0.57</td>
<td>$f_R$ = 0.32, $f_G$ = 0.43, $f_N$ = 0.25</td>
</tr>
<tr>
<td>1% depletion $\delta^{13}$C$_R$</td>
<td>$f_R$ = 0.02, $f_G$ = 0.42, $f_N$ = 0.56</td>
<td>$f_R$ = 0.32, $f_G$ = 0.47, $f_N$ = 0.21</td>
</tr>
<tr>
<td>1% depletion $\delta^{13}$C$_G$</td>
<td>$f_R$ = 0.02, $f_G$ = 0.47, $f_N$ = 0.52</td>
<td>$f_R$ = 0.32, $f_G$ = 0.48, $f_N$ = 0.19</td>
</tr>
<tr>
<td>1% depletion $\delta^{13}$C$_N$</td>
<td>$f_R$ = 0.02, $f_G$ = 0.47, $f_N$ = 0.51</td>
<td>$f_R$ = 0.32, $f_G$ = 0.46, $f_N$ = 0.22</td>
</tr>
<tr>
<td>30% soil respiration</td>
<td>$f_R$ = 0.01, $f_G$ = 0.42, $f_N$ = 0.56</td>
<td>$f_R$ = 0.26, $f_G$ = 0.51, $f_N$ = 0.23</td>
</tr>
<tr>
<td>70% soil respiration</td>
<td>$f_R$ = 0.03, $f_G$ = 0.40, $f_N$ = 0.57</td>
<td>–</td>
</tr>
<tr>
<td>30% plant respiration</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7.2% kinetic fraction of soil diffusion</td>
<td>$f_R$ = 0.02, $f_G$ = 0.41, $f_N$ = 0.57</td>
<td>$f_R$ = 0.34$^b$, $f_G$ = 0.43$^b$, $f_N$ = 0.23$^b$</td>
</tr>
<tr>
<td>3% enrichment of soil water</td>
<td>$f_R$ = 0.02, $f_G$ = 0.42, $f_N$ = 0.57</td>
<td>$f_R$ = 0.35$^b$, $f_G$ = 0.40$^b$, $f_N$ = 0.25$^b$</td>
</tr>
<tr>
<td>No enrichment of leaf water at night</td>
<td>$f_R$ = 0.00, $f_G$ = 0.42, $f_N$ = 0.58</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$Calculations are from equations (4)–(6). Baseline refers to the calculations shown in Figure 5 and described in the text. In analyses $i$–$iii$, the carbon isotope ratios of ecosystem respiration ($\delta^{13}$C$_R$), gasoline combustion ($\delta^{13}$C$_G$), or natural gas combustion ($\delta^{13}$C$_N$) were decreased by 1% from the baseline simulation. The remaining analyses are changes to the assumptions in the model of the oxygen isotope ratio of ecosystem respiration ($\delta^{18}$O$_R$). A dash indicates that a solution was less than 0 for much of the season; i.e., the solution was invalid.

$^b$Values of $f_G$ were negative in April.
6. Critique of their interpretation

- The sampling site can’t really represent urban environment, because energy structure in campus and its surroundings differs with urban regions.

- The C-G model based on steady-state hypothesis, which is hard to reach and is controlled by relative humidity in short time scale. In addition to Peclet effect and various inner leaves in spatial, the evaluation will be higher than real value.

- Keeling plot only can depart two sources at a time. Due to this reason, it’s hard to accurate partitioning urban sources into component part.
Thank You