Quantitative Analysis of Air Pollution by Means of
\(^{14}\text{C}\) Concentrations in Plant Leaves

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The air pollution caused by \(\text{CO}_2\) from fossil fuel origin was quantitatively studied by radiocarbon \(^{14}\text{C}\) measurement on the samples of new leaves taken from roadside trees. In the area where concentration of \(\text{CO}_2\) \((^{13}\text{CO}_2 + ^{12}\text{CO}_2)\) of fossil fuel origin was high, the count of \(\text{B}-\text{ray}\) radiation from \(^{14}\text{C}\) tended to be low. The relation between the concentration of sulfur dioxide \((\text{SO}_2)\) in the air and the count of \(\text{B}-\text{ray}\) radiation from the leaf samples could be represented by a linear regression,

\[ Y = (17.568/X) - 67.385; \quad r = -0.995 \]

Where \(Y\) is the \(\text{SO}_2\) concentration in ppb and \(X\) is the \(\text{B}-\text{ray}\) radiation count \((\text{Bq/g-carbon})\).

Key Words: carbon-14, air pollution, plant indicator, sulfur dioxide, nitrogen oxides, plant leaf

1. Introduction

Air pollution has been quantitatively analyzed by determining the concentration of pollutants such as nitrogen oxides \((\text{NO}_x)\), sulfur dioxide \((\text{SO}_2)\) and carbon monoxide \((\text{CO})\). Numerous methods, including plant indicators \(^{1-4}\), have been employed to analyze air pollution. Carbon dioxide \((\text{CO}_2)\) is generated in much larger quantity than other pollutants \(^{5,6}\) by the extensive use of fossil fuel in the industrialized areas and this eventually causes global warming and the heat island phenomena. The influence on the earth environment with \(\text{CO}_2\) from fossil fuel origin is big but very little study has been carried out, for example the local distribution of \(\text{CO}_2\) from fossil fuel.

In this study, the technique of radiocarbon \(^{14}\text{C}\) measurement in plant was applied to analyze the air pollution causing by \(\text{CO}_2\) from fossil fuel origin. If locally occurring \(\text{CO}_2\) from fossil fuel origin mixes with ambient air, the \(^{14}\text{C}\) concentration also changes and would be uniform in the small area. In the city areas where much fossil fuel is consumed, a large amount of \(^{12}\text{CO}_2\) is released into the air and thus the content of \(^{14}\text{C}\) should become relatively lower than other places \(^{7-9}\). Plants assimilate \(\text{CO}_2\) in the air into their tissues through photosynthesis. Therefore, the air pollution caused by fossil fuel can be investigated by determining the relative amount of \(^{14}\text{C}\) in the plant tissues.
2. Methods and Results

Samples of new leaves were taken from roadside trees, namely *Platanus acerifolia*, growing near the Air Pollution Monitoring Stations in Sapporo on August 7, 1994. Samples were immediately dried after collection and later they were synthesized into pure methanol. Carbon in the sample is converted to methanol by the Nystrom formula\(^{10}\):

\[
4\text{CO}_2 + 3\text{LiAlH}_4 = \text{LiAl(OCH}_3\text{)}_4 + 2\text{LiAlO}_2
\]

\[
\text{LiAl(OCH}_3\text{)}_4 + 4\text{ROH} = 4\text{CH}_3\text{OH} + \text{LiAl(OR)}_4
\]

where \(\text{R}\) is buthyl carbitol.

At first plant sample is converted to charcoal in an airtight electric furnace by heating at ca. 800 °C for 2 h. The charcoal is then boiled in a solution of 1% HCl for 1 h, washed well in distilled water, and thoroughly dried.

The charcoal is placed in a quartz tube and subjected to a stream of heated N\(_2\) gas for one hour at 500 °C. Then O\(_2\) is passed through the tube to generate CO\(_2\) gas from the charcoal.

The CO\(_2\) is introduced into mixture of LiAlH\(_4\) and diethyl carbitol for 2 or 3 h until the reaction ends. Enough amounts of buthyl carbitol is added slowly to the mixture and methanol is separated from the mixture by distillation. The methanol was analyzed with a liquid scintillation counter (ALOKA LSC-LB III) for determining the \(\beta\)-ray radiation from \(^{14}\text{C}\).

The \(^{14}\text{C}\) concentrations in the samples are shown in Table 1, and an attempt was made to calculate the amount of \(^{12}\text{CO}_2\) emission from fossil fuels.

The \(^{14}\text{C}\) concentration of the normal air which is not influenced by the local atmospheric pollution is 0.2517±0.0015 Bq/g-carbon\(^{11}\) based on Yamada’s study result.

\[^{14}\text{C}\] concentration from fossil fuel and the \(^{14}\text{C}\) concentration can be expressed in the following simple proportional relation.

<table>
<thead>
<tr>
<th>Name of the air pollution monitoring station (Sampling station)</th>
<th>NO(_x) concentration (ppb)</th>
<th>SO(_2) concentration (ppb)</th>
<th>(^{14}\text{C}) concentration (Bq/g carbon)</th>
<th>Dead carbon concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>44.75</td>
<td>7.00</td>
<td>0.2360±0.0005</td>
<td>23 280±790</td>
</tr>
<tr>
<td>Shiroishi</td>
<td>28.75</td>
<td>5.00</td>
<td>0.2430±0.0004</td>
<td>12 530±600</td>
</tr>
<tr>
<td>Higashi</td>
<td>21.75</td>
<td>5.75</td>
<td>0.2398±0.0005</td>
<td>17 370±760</td>
</tr>
<tr>
<td>Hushimi</td>
<td>16.75</td>
<td>4.00</td>
<td>0.2467±0.0006</td>
<td>7 090±870</td>
</tr>
<tr>
<td>Shinoro</td>
<td>12.25</td>
<td>4.50</td>
<td>0.2450±0.0008</td>
<td>9 570±1 180</td>
</tr>
<tr>
<td>Asukayama park</td>
<td>10.75</td>
<td>3.75</td>
<td>0.2470±0.0005</td>
<td>6 660±720</td>
</tr>
<tr>
<td>Shinotsu</td>
<td>5.50</td>
<td>3.50</td>
<td>0.2482±0.0005</td>
<td>5 220±720</td>
</tr>
<tr>
<td>Tarukawa</td>
<td>12.25</td>
<td>2.75</td>
<td>0.2498±0.0006</td>
<td>2 660±850</td>
</tr>
<tr>
<td>Oyahuru</td>
<td>6.00</td>
<td>3.00</td>
<td>0.2490±0.0005</td>
<td>3 800±710</td>
</tr>
</tbody>
</table>

The concentrations of NO\(_x\) and SO\(_2\) are the averaged values of monthly mean concentration in the period from growing of the leaf of the load tree (monthly mean temperature >10°C) to the sampling (March–August 1994).

The \(^{14}\text{C}\) concentrations in the atmospheric CO\(_2\) without air pollution; 0.2517±0.0015 Bq/g-carbon. The liquid scintillation counter; ALOKA LSC-LB III. The scintillator; methanol 50 ml + toluene 50 ml. The background 8,03 cpm. The measurement time: 2 800–3 000 min.
\[ 35 \cdot 10^4 : \Delta y = x : x_0 - x \]

Therefore,
\[
\Delta y = 35 \cdot 10^4 \cdot \left( \frac{x_0 - x}{x} \right) = \left( \frac{1}{x} \right) \cdot x_0 - 1 \cdot 35 \cdot 10^4 \text{ (ppb)}
\]

Where \( \Delta y \) is the concentration of local fossil fuel CO\(_2\) \((^{12}\text{CO}_2 + ^{13}\text{CO}_2)\) (ppb) added to the normal air,
\[ 35 \cdot 10^4 \text{ the } \text{CO} \((^{12}\text{CO}_2 + ^{13}\text{CO}_2 + ^{14}\text{CO}_2)\) concentration of normal air (ppb), \]
\[ x \text{ the } ^{14}\text{C} \text{ concentration of the air after mixing the local fossil fuel } \text{CO}_2 \((^{12}\text{CO}_2 + ^{13}\text{CO}_2)\) (Bq), \]
and \( x_0 \) the \(^{14}\text{C} \) concentration of the normal air (Bq).

The results shown in Table 1 indicates that the \(^{14}\text{C} \) concentration tends to be lower at the sampling sites where air pollution is heavy.

The relation between concentration of pollutants and the \(^{14}\text{C} \) concentrations are represented by the following formulae (Fig. 1),
\[
Y = \left( \frac{17.568}{X} \right) - 67.385 \quad r = -0.995 \text{ for } \text{SO}_2 \text{ in ppb}
\]
\[
Y = \left( \frac{145.973}{X} \right) - 578.494 \quad r = -0.900 \text{ for } \text{NO}_x \text{ in ppb}
\]

The following conclusions were drawn from the present results.

1. When a tree grows in the air polluted with fossil fuel, the \(^{14}\text{C} \) concentration in new leaves of the tree is low, indicating mixing of normal air and the polluted one without \(^{14}\text{C} \).

2. It is possible to estimate the mixing ratio of fossil fuel in the air by \(^{14}\text{C} \) concentrations in the plant leaves.

3. A plant can be used as an indicator in the quantitative analysis of air pollution. Since emission of CO\(_2\) \((^{12}\text{CO} + ^{13}\text{CO}_2)\) from fossil fuel is 120–260 times as large as that of \(\text{NO}_x\), the plant

![Fig. 1 Relationships between the \(^{14}\text{C} \) concentration and the concentration of pollutants.](image-url)
indicator seems to be suitable for the analysis of air pollution even at low concentration of the pollutant and give a better precision.

(4) The linear regression of the $^{14}$C concentration with the concentration of NO$_x$, SO$_2$ or other pollutants can be obtained by the analysis of plant leaf samples. Such linear regressions can be used for monitoring of the air pollution caused by the consumption of fossil fuels at different sites and also for the estimation of emission factor of several air pollutants for a wide area.

(5) In Japan, it costs yearly about J ¥30 000 000 to monitor NO$_x$, SO$_2$ or CO at each monitoring station, excluding the maintenance expenditure associated with the operation. On the contrary, the new monitoring technique costs only less than J ¥100 000 per sampling station per 2–3 month period.

(6) The shortcomings of the present method are, first; the leaf samples would not be available during the winter time and, second; the pollution can not be monitored for a short term because the process of plant tissue growth through photosynthesis takes time.

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References