CHARACTERIZATION OF THE ORGANIC FRACTION OF ATMOSPHERIC AEROSOLS

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SPECIES CONTRIBUTIONS TO PM MASS CONCENTRATIONS

• The concentration of particulate organics is generally estimated by multiplying the measured concentration of organic carbon (OC) by a factor of 1.2 to 1.4.

• This factor, which is an estimate of the average molecular weight (OM) per carbon weight for the organic aerosol (OM/OC), stems from very limited studies conducted during the 1970s (Grosjean and Friedlander, 1975).

• Recent investigations suggest that 1.4 is the lowest reasonable estimation for the OM/OC value for an urban aerosol, and that 1.4 does not accurately represent the OM/OC value for a non-urban aerosol (Turpin and Lim, 2001).
SPECIES CONTRIBUTIONS TO PM MASS CONCENTRATIONS

• Based on a recent literature review (Turpin and Lim, 2001), ratios of 1.6 for urban aerosols and 2.1 for non-urban aerosols appear to be more accurate (non-urban aerosols tend to be more oxygenated).

<table>
<thead>
<tr>
<th>COMPOUND CLASS</th>
<th>MWt/CWt</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-Alkanes (C23-C34)</td>
<td>1.2</td>
</tr>
<tr>
<td>Aliphatic dicarboxylic acids (C2-C9)</td>
<td>1.7 – 3.8</td>
</tr>
<tr>
<td>Multifunctional aliphatic acids (C3-C6)</td>
<td>2.5 – 3.1</td>
</tr>
<tr>
<td>Aromatic polycarboxylic acids (C8-C10)</td>
<td>1.7 – 2.1</td>
</tr>
<tr>
<td>PAHs (C6-C24)</td>
<td>1.0 – 1.1</td>
</tr>
<tr>
<td>Carbonyls (C2)</td>
<td>2.4</td>
</tr>
<tr>
<td>Sugars (levoglucosan, C6)</td>
<td>2.3</td>
</tr>
</tbody>
</table>

OBJECTIVES

• Development of an **analytical methodology** to characterize the organic component of the atmospheric aerosols.

• Estimation of the organic molecular weight per carbon weight ratio for the Pittsburgh area (**OM/OC ratio**).

• **Qualitative analysis** of the different fractions of the organic PM.
DETERMINATION OF OM/OC FOR THE PAQS SAMPLES

24-hour samples (July 2001-August 2002)

PM2.5 Inlet

8”×10” baked QFF

65 samples were selected throughout the year…

…sonicated for 15min in a mixture of HEXANE, DICHLOROMETHANE, and ACETONE (1:1:2)…

…and Soxhlet extracted in the same mixture of solvents

The extracts were filtered…

…and applied on the top of a glass column packed with Silica Gel
DETERMINATION OF OM/OC FOR THE PAQS SAMPLES

Nitrogen stream

Mass recoveries varied between 76 and 97%

Average mass recovery = 80%

30×0.7cm glass column

1.5g of silica gel (Merck, 0.040-0.063 mm, activated at 150 °C for 3h).

1.4ml/min

HEXANE (15ml)

DICHLORO METHANE (15ml)

ETHYL ACETATE (15ml)

ACETONE (15ml)

METHANOL (15ml)

Average mass recovery = 80%

OM

OC

OM

OC

OM

OC

OM

OC

OM

OC

OM

OC

OM

OC
DETERMINATION OF OM/OC FOR THE PAQS SAMPLES

- All extracts/fractions were also analyzed by ion-chromatography (IC) to determine the amount of inorganic species present in each extract/fraction.

\[
\cdot (\text{OM})_{\text{extract/fraction}} = (\text{OM}_{\text{extract/fraction}} - \text{OM}_{\text{blank}} - \text{inorganics})
\]

\[
\cdot (\text{OC})_{\text{extract/fraction}} = (\text{OC}_{\text{extract/fraction}} - \text{OC}_{\text{blank}})
\]
THE DIFFERENT FRACTIONS

- The mass percentage of the acetone-soluble and the methanol-soluble fractions (4+5) varied between 45 and 74%.

- The mass percentage of the dichloromethane-soluble and the ethylacetate-soluble fractions (2+3) varied between 7 and 35%.

- The mass percentage of the hexane-soluble fraction (1) varied between 25 and 46%.
• The results confirm that **OM/OC increases with the polarity of the fraction** (the most polar compounds tend to be more oxygenated).
• Two independent OM/OC estimates were obtained for each sample: one estimate from the analysis of the extracts and one estimate from the analysis of the fractions. These independent OM/OC estimates are in good agreement.
THE DIFFERENT FRACTIONS

Polarity of the fractions

\[
\left( \frac{OM_{\text{fraction}}}{\sum OM_{\text{fractions}}} \right) \times 100
\]

\[
\left( \frac{OC_{\text{fraction}}}{\sum OM_{\text{fractions}}} \right) \times 100
\]
• OM/OC seems to be positively correlated with the amount of secondary OC estimated during PAQS (Cabada et al., 2004, Polidori et al., in preparation). However, the variation of OM/OC may also be affected by other factors (e.g. wood smoke production).
CONCLUSIONS

• The average OM/OC ratio for the Pittsburgh area was estimated to be 1.9

• The lowest estimated OM/OC value was 1.3 and the highest was 2.8

• Between 45 and 74% of OM was in the two most polar fractions

• OM/OC seems to be positively correlated with the amount of secondary OC estimated during PAQS
AKNOWLEDGEMENTS

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