Size Distributions of HULIS in Ambient Aerosols and Fresh Biomass Burning Aerosols in South China

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Humic Like Substances (HULIS)

HULIS consists of a complex, unresolved mixture of water-extracted organic compounds comprising of polycyclic ring structures with hydrocarbon side chains, and hydroxyl, carboxyl and carbonyl groups. (Graber and Rudich, 2006)

- Similar to terrestrial and aquatic humic and fulvic acids in UV, FTIR and NMR characters
- Water-soluble
- Of polyacidic nature
- Hydrophobic
- Molecular weight: 200 ~ 1000 (depend on method)
Objectives

• Abundance of HULIS in ambient and biomass burning aerosols
• Size distributions of HULIS in ambient and biomass burning aerosols
Analytical Methods for HULIS Isolation and Detection Reported in the Literature

<table>
<thead>
<tr>
<th>Studies</th>
<th>Extraction</th>
<th>Separation</th>
<th>Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zappoli et al., 1999</td>
<td>water extraction</td>
<td>Size exclusion chromatography</td>
<td>UV-Vis</td>
</tr>
<tr>
<td>Decesari et al., 2000</td>
<td>water extraction</td>
<td>Ion exchange chromatography</td>
<td>UV-Vis, TOC, H-NMR</td>
</tr>
<tr>
<td>Varga et al., 2001</td>
<td>water extraction</td>
<td>solid-phase extraction cartridge</td>
<td>TOC</td>
</tr>
<tr>
<td>Mayol-Bracero et al., 2002</td>
<td>water extraction</td>
<td>Ion exchange chromatography</td>
<td>TOC</td>
</tr>
<tr>
<td>Limbeck et al., 2005</td>
<td>water extraction</td>
<td>SPE+ ion exchange chromatography</td>
<td>TOC</td>
</tr>
<tr>
<td>Emmenegger et al., 2007</td>
<td>water extraction</td>
<td>SPE+ Size Exclusion Chromatography</td>
<td>ELSD</td>
</tr>
<tr>
<td>Feczko et al., 2007</td>
<td>water extraction</td>
<td>solid-phase extraction</td>
<td>FIA-SAX, TOC</td>
</tr>
<tr>
<td>Krivacsy et al., 2008</td>
<td>water extraction</td>
<td>solid-phase extraction</td>
<td>UV-Vis, TOC</td>
</tr>
</tbody>
</table>

Quantity of HULIS is operationally defined by an isolation method.
Isolation: Solid Phase Extraction (SPE)

Purpose:
Remove: inorganic ions & low MW organic acids
Pre-concentrate

Sample (water extract) Acidified by HCl to PH=2

Rinse with water after sample passed through (collected with effluent together)

Elution with methanol (adjust PH=8.5-9 by NH₄OH)

Eluate
Dryness with N₂
Dissolution in water
ELSD IC

TOC analysis

Oasis-HLB SPE cartridge

Particulates on quartz fiber filter

Method by Varga et al., 2001, with minor modification
Methanol+NH$_4$OH elutes more HULIS than methanol alone

Sample #1

Remarks:
Carbon content determined by ECOC analyzer

Eluate1: 1.5ml solvent
Eluate2: 1.5ml solvent after eluate1
Eluate3: 1.5ml solvent after eluate2
Retained: Retained on SPE cartridge after 3rd elution
Fluorescence property is retained in the methanol/NH4OH eluate (HULIS fraction)

- Over 85% of fluorescence active compounds were collected in the eluate.

- Presence of poly-conjugated structures

- Excitation wavelength 235nm

- Over 85% of fluorescence active compounds were collected in the eluate.
1. **Nebulization**: The liquid passes through a nozzle, mixes with nitrogen gas to form a dispersion of droplets.

2. **Evaporation**: The droplets pass through a heated “drift tube”, where the solvent evaporates, leaving a fine mist of dried particles in solvent vapor.

3. **Detection**: The sample particles pass through a cell and scatter light from a laser beam, generating an electrical signal.

Capable of quantifying mass concentrations of non-volatile analytes of unknown chemical structures.
Direct injection to ELSD

- Mobile phase: 20% ACN & 80% H₂O, FR: 0.6 mL/min
- ELSD nebulizer N₂ FR: 1.5 L/min
  - drift tubing temperature: 90°C
  - RT(DT): 0.6-0.7 min
Calibration curve of ELSD

- ELSD response is based on mass, not on optical or structural characteristics of an analyte.
- Widely used in the field of quantifying unknown mixtures lacking appropriate quantification standards.

HULIS can be determined by ELSD with respect to reference Fulvic acid. The detection limit is about 9 ppm (in solution).
Evaporation in ELSD removes LMW acids

<table>
<thead>
<tr>
<th>compound</th>
<th>separated from HULIS by</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C6 monocarboxylic acids</td>
<td>SPE</td>
</tr>
<tr>
<td>oxalic acid</td>
<td>*</td>
</tr>
<tr>
<td>succinic acid</td>
<td></td>
</tr>
<tr>
<td>malonic acid</td>
<td>*</td>
</tr>
<tr>
<td>gluatric acid</td>
<td>*</td>
</tr>
<tr>
<td>adipic acid</td>
<td></td>
</tr>
<tr>
<td>D,L-malic acid</td>
<td>*</td>
</tr>
<tr>
<td>4-hydroxybenzoic acid</td>
<td></td>
</tr>
<tr>
<td>citric acid</td>
<td>*</td>
</tr>
<tr>
<td>D,L-lactic acid</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>*</td>
</tr>
<tr>
<td>trifluoroacetic acid</td>
<td></td>
</tr>
<tr>
<td>ammonium nitrate</td>
<td>*</td>
</tr>
<tr>
<td>ammonium sulfate</td>
<td></td>
</tr>
</tbody>
</table>

* An asterisk indicates which compound is separated from HULIS during which step.

(Emmenegger et al., 2007, EST)
Most of the inorganic ions are removed by SPE

- $\text{Cl}^- & \text{SO}_4^{2-} : >99\%$
- $\text{NO}_3^- : >98\%$
Recovery test using NAFA and SRFA

Recovery of NAFA vs. Amount of solvent used for elution (mL)
Preliminary Results
Ambient sampling

114.46°E, 23.43°N
~150 km NW to Hong Kong
A small town surrounded by farmland of rice and sugarcane

FIGURE 1. Satellite image taken around 1500 LST on 28 December 1999, which shows the movement of the smoke and haze. The red spots over land correspond to the hill fires. (This figure is reproduced from Fung et al., 2005)
Biomass burning samples

Rice straw field

Sugarcane field
Samples

• Ambient samples
  – 5 sets of PM$_{2.5}$ high-vol samples collected on quartz fiber filter substrate.
    • (HULIS, ECOC, WSOC, major ions)
  – 5 sets of PM$_{2.5}$ mid-volume samples collected on Teflon and quartz fiber filters.
    • (mass)
  – 5 sets of MOUDI samples (0.056-18 µm)
    • (HULIS, ECOC, WSOC, major ions)

• Biomass burning samples
  – 3 sets of samples from rice straw burning smoke (PM$_{2.5}$ and MOUDI)
  – 3 sets of samples from sugar cane leave burning smoke (PM$_{2.5}$ and MOUDI)
## HULIS abundance

<table>
<thead>
<tr>
<th>Sample type</th>
<th>PM$_{2.5}$ (μg/m$^3$)</th>
<th>HULIS (μg/m$^3$)</th>
<th>HULIS/WSOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
<td>143.5</td>
<td>18.1</td>
<td>57%</td>
</tr>
<tr>
<td>Influenced</td>
<td>150.3</td>
<td>16.8</td>
<td>43%</td>
</tr>
<tr>
<td>Ambient</td>
<td>40.2</td>
<td>5.9</td>
<td>67%</td>
</tr>
<tr>
<td></td>
<td>54.6</td>
<td>6.1</td>
<td>61%</td>
</tr>
<tr>
<td></td>
<td>136.2</td>
<td>12.1</td>
<td>48%</td>
</tr>
<tr>
<td><strong>Mean ± std</strong></td>
<td><strong>105 ± 53</strong></td>
<td><strong>11.8 ± 5.8</strong></td>
<td><strong>55±10%</strong></td>
</tr>
</tbody>
</table>

- **Sugarcane burning** *(n=3)*
  - 2921±617
  - 221±50
  - 31±2%

- **Ricestraw burning** *(n=3)*
  - 9537±839
  - 1178±246
  - 28±1%

WSOM=WSOC*2.1 (based on Kiss et al., 2002)
<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Method</th>
<th>HULIS (μg/m³)</th>
<th>HULIS/WSOM</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po Valley, Italy, polluted rural site</td>
<td>Water extracted, SEC, UV-VIS detection</td>
<td>0.6~2.5</td>
<td>19~50%</td>
<td>Zappoli et al., 1999</td>
</tr>
<tr>
<td>Amazon, rural site, forest fire affected</td>
<td>Water extracted, IEC, TOC</td>
<td>1.52~27.9</td>
<td>14~29%</td>
<td>Mayol-Bracero et al., 2002</td>
</tr>
<tr>
<td>K-puszta, background rural</td>
<td>Water extracted, SPE, TOC</td>
<td>4.4 (winter)</td>
<td>34~65%</td>
<td>Kiss et al., 2002</td>
</tr>
<tr>
<td>Six background site in Europe</td>
<td>Water extracted, SPE, FIA-SAX, TOC</td>
<td>0.076~1.77</td>
<td>8.1~22%</td>
<td>Feczko et al., 2007</td>
</tr>
<tr>
<td>New Zealand, marine urban site</td>
<td>Water extracted, SPE, UV-VIS detection, TOC</td>
<td>0.46~10.34</td>
<td>31~46%</td>
<td>Krivacsy et al., 2008</td>
</tr>
</tbody>
</table>

WSOM=WSOC*2.1, HULIS=HULIS-C*1.9 (based on Kiss et al., 2002)
### HULIS/K⁺ ratio in PM$_{2.5}$: Ambient $>>$ fresh BB aerosols

<table>
<thead>
<tr>
<th>Sample type</th>
<th>HULIS/K⁺</th>
<th>HULIS-C/WSOC</th>
<th>HULIS-C/OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.93</td>
<td>63%</td>
<td>30%</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>4.92</td>
<td>47%</td>
<td>28%</td>
</tr>
<tr>
<td>Influenced</td>
<td>4.62</td>
<td>74%</td>
<td>32%</td>
</tr>
<tr>
<td>Ambient</td>
<td>4.09</td>
<td>67%</td>
<td>34%</td>
</tr>
<tr>
<td>Mean ± std</td>
<td>4.3±0.5</td>
<td>61±11%</td>
<td>30±4%</td>
</tr>
<tr>
<td>Sugarcane burning</td>
<td>0.54±0.11</td>
<td>31±2%</td>
<td>15±2%</td>
</tr>
<tr>
<td>(n=3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice straw burning</td>
<td>1.0±0.3</td>
<td>34±3%</td>
<td>15±2%</td>
</tr>
<tr>
<td>(n=3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HULIS-C = HULIS/1.9 (based on Kiss et al., 2002)
HULIS ambient size distributions

Condensation mode: 10%
Droplet mode: 78%
Coarse mode: 12%
HULIS is dominant in droplet mode particles

<table>
<thead>
<tr>
<th></th>
<th>Droplet HULIS /Total HULIS</th>
<th>Droplet HULIS-C /Droplet TOC</th>
<th>Droplet HULIS /Droplet TWSM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient 01</td>
<td>70%</td>
<td>57%</td>
<td>25%</td>
</tr>
<tr>
<td>Ambient02</td>
<td>77%</td>
<td>64%</td>
<td>22%</td>
</tr>
<tr>
<td>Ambient03</td>
<td>72%</td>
<td>64%</td>
<td>19%</td>
</tr>
<tr>
<td>Ambient04</td>
<td>77%</td>
<td>65%</td>
<td>19%</td>
</tr>
<tr>
<td>Ambient05</td>
<td>65%</td>
<td>52%</td>
<td>22%</td>
</tr>
<tr>
<td>Ambient mean±std</td>
<td>72±5%</td>
<td>60±7%</td>
<td>22±3%</td>
</tr>
</tbody>
</table>

TWSM: total water soluble matters (TOC*2.1+inorganic ions)
Ambient HULIS/K\(^+\) in individual size modes exceed the corresponding ratios in fresh BB smoke.

Graphs showing the distribution of HULIS and K\(^+\) in different size modes for Sugarcane and Ricestraw.
Summary

• HULIS is an abundant component of ambient particles in the PRD region, China.
  – ~55% of water soluble organic matter in PM$_{2.5}$

• Size distribution: the droplet mode HULIS accounts for ~78% of the total HULIS and contributes 60% of WSOC and 22% of water soluble organic matter in this mode, suggesting its important role in the cloud processing of aerosols.

• Biomass burning is a major source of HULIS in the PRD
  – ~30% of water soluble organic matter in fresh biomass burning particles was contributed by HULIS.

• The differences in HULIS/K$^+$ ratio between ambient and biomass burning samples indicated that there are additional sources of HULIS.
  – Condensation mode: Secondary HULIS from acid-catalyzed particle-phase reaction?
  – Droplet mode: Secondary HULIS formed from in-cloud processing?
  – Coarse mode: Soil-derived HULIS?
Acknowledgement

• Thank Dr. Lingyan He, Dr. Xiaofeng Huang and Eric Xue’s for helping with sampling.

• Funding support from Hong Kong Research Grants Council.
Suggested origins of HULIS

- Biomass burning
  - Direct emission
- Condensation
- Soot
- Low volatile products
  - Decomposed by microbe
- Cloud processing
  - Polymerization
  - Acid catalyzed particle phase reactions
- HULIS
- H$_2$SO$_4$
- NO$_x$, photooxidation
- Direct emission
- Oxidation
- Condensation
- OH, H$_2$O$_2$
- Acid catalyzed particle phase reactions
- Modified from Andreas Gelencser presentation, Organic Speciation Workshop

- Kalberer et al., 2004
- Jang et al., 2002
- Dommen et al., 2006
- Deceari et al., 2002
- Mayol-Bracero et al., 2002
- Holmès et al., 2007
- Gelencser et al., 2002
Test sample:
100ppm NAFA+Na$_2$SO$_4$ acidified by HCl

- More than 99% Cl$^-$ & SO$_4^{2-}$ are removed.
- But the recovery is poor by using only methanol for elution

Change the solvent to ACN can not help for more elution (16%)
Theory: Retention Factor [k] vs. pH for Acids, Bases, and Neutrals

- **Acid Retained**
  - Acid [HA]
  - Neutrals
  - pKᵦ = 4.8

- **Base Retained**
  - Base [B]
  - Base [BH⁺]
  - Acid [A⁻]
  - pKᵦ = 9.0

- **Low Retention for Base**
  - Recommended pH range for silica

- **Low Retention for Acid**
  - Recommended pH range for Oasis® Sorbents

- **Recommended pH range for silica**
  - 2 to 8

- **Recommended pH range for Oasis® Sorbents**
  - 0 to 14