Solid-phase extraction of dissolved organic matter (SPE-DOM) from river, estuarine and open ocean waters

Gerhard Kattner¹, Thorsten Dittmar², Boris Koch¹, and Norbert Hertkorn³

¹Alfred Wegener Institute for Polar and Marine Research, Ecological Chemistry, Bremerhaven, Germany
²Florida State University, Department of Oceanography, Tallahassee, USA
³GSF-National Research Centre for Environment and Health, Institute of Ecological Chemistry, Neuherberg, Germany
Extraction methods

• Solid-phase extraction (SPE)
  using XAD resins
  using sequential combination of different XAD resins
  using various sorbents
  using pre-packed cartridges and discs with silica-C18 sorbent
• Ultrafiltration with a 1 kDa cutoff
• Combination of ultrafiltration and SPE
• Sequential combination of reversed osmosis and electrodialysis
# Properties of the solid phase sorbents

(according to manufacturer's (Varian) information)

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Structure</th>
<th>Pore size</th>
<th>Retention properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18</td>
<td>octadecyl bonded phase, silica-based</td>
<td>60 Å</td>
<td>retention of non-polar compounds</td>
</tr>
<tr>
<td>C18EWP</td>
<td>octadecyl bonded phase, silica-based</td>
<td>500 Å</td>
<td>more efficient retention of large molecules, compared to C18</td>
</tr>
<tr>
<td>C18OH</td>
<td>non-endcaped octadecyl bonded phase, silica-based, with active silanol groups</td>
<td>150 Å</td>
<td>enhanced retention of basic compounds, compared to C18</td>
</tr>
<tr>
<td>C8</td>
<td>octyl bonded phase, silica-based</td>
<td>60 Å</td>
<td>not as retentive for non-polar compounds as C18</td>
</tr>
<tr>
<td>PPL</td>
<td>styrene divinyl benzene polymer</td>
<td>150 Å</td>
<td>retention of highly polar to non-polar substances from large volumes of water</td>
</tr>
<tr>
<td>ENV</td>
<td>styrene divinyl benzene polymer</td>
<td>450 Å</td>
<td>similar to PPL, larger pore size</td>
</tr>
</tbody>
</table>
Scheme for the isolation of SPE-DOM from seawater

1. Prepare sample
   Sample → Inline filter (1 cartridge volume)
   collect and add HCl (adjust pH=2)

2. Rinse adsorber
   Methanol (filtered and acidified, <50 L)

3. Extract DOM
   Sample → PPL
   Waste

4. Remove salt
   0.01 M HCl (2 cartridge volumes)
   <40 mL min⁻¹

5. Dry adsorber
   Air or N₂ (ca. 5 min)

6. Elute sample
   Methanol (1 cartridge volume)
   <2 mL min⁻¹
   SPE-DOM

* choose size of PPL cartridge according to sample volume and DOC concentration: do not exceed 2 mmol DOC or 10 L sample per g adsorber
Extraction procedure abord
PPL-Extracts
Extraction efficiencies for the isolation of SPE-DOM using different sorbents

North Brazil coastal zone and shelf
North Brazil shelf and coastal zone

C/N ratio

- Bulk DOM
- PPL
- C18

delta $^{13}$C

- Marine
- Terrestrial
- PPL
- C18
Composition of combined hydrolysable amino acids (North Sea)

- Asp
- Glu
- Ser
- Thr
- Gly
- Arg
- Ala
- GABA
- Tyr
- Val
- Leu

- original
- PPL
- C18

Total AA

(%)
Percentage of D-amino acids (North Sea)

- D-Asp
- D-Glu
- D-Ser
- D-Ala
- D total

Graph showing the percentage of D-amino acids in different samples: original, PPL, C18.
Reversed-Phase High-Performance Liquid Chromatography (HPLC)

Comparison of PPL and C18 sorbent

Fluorescence and DAD detection

Fluorescence detector:
- ex: 260 nm; em: 430 nm
- DAD contour plot: 200-400 nm (700 nm)

All other parameters are identical, e.g.
- amount of enriched sample, elution volume, injection volume
Location of samples and DOC concentration

<table>
<thead>
<tr>
<th>Location</th>
<th>DOC (µM) in seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Apalachicola River and tributaries</td>
<td>150 ± 5</td>
</tr>
<tr>
<td>B Apalachicola salt marshes</td>
<td>350 ± 10</td>
</tr>
<tr>
<td>C North Brazil shelf and coastal zone</td>
<td>120 ± 4</td>
</tr>
<tr>
<td>D Gulf of Mexico deep sea</td>
<td>80 ± 2</td>
</tr>
<tr>
<td>E Weddell Sea (surface to bottom)</td>
<td>60 ± 3</td>
</tr>
</tbody>
</table>
Extraction efficiency and C/N ratio of SPE-DOM (PPL)

A  Apalachicola River and tributaries
B  Apalachicola salt marshes
C  North Brazil shelf and coastal zone
D  Gulf of Mexico deep sea
E  Weddell Sea (surface to bottom)
Summary

Simple and robust method

PPL extracts >60% of coastal and >40% of deep-sea DOC

PPL retains a major fraction of N-containing compounds

Complete desalting of the sample
  NMR
  Ultra high resolution MS
  Various HPLC- and GC-MS-MS methods
  Fractionation of samples

Autonomous extraction with pumps from ship or on moorings
I urgently propose a workshop to decide on extraction methods for DOM.

Thank you.
Caeté Estuary (Brazil)
Concentration of total amino acids
Extraction efficiencies for the isolation of SPE-DOM using different sorbents

Estuary and on the North Brazil shelf (distance offshore)
Concentration of amino acids

- Org
- PPL
- C18

(μmol/L)

Asp | Glu | Ser | Thr | Gly | Arg | Ala | GABA | Tyr | Val | Leu

Total AA