Sources and Composition of Dissolved and Particulate Organic Matter in the Delaware Estuary

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Overview

• Introduction
  – Estuarine Carbon Cycle

• Study Site
  – Delaware River and Bay Watershed
  – Sampling Locations

• Methods

• Results
  – Terrestrial – to – Aquatic Ratio for Fatty Acids
  – Radiocarbon Ages of Lipid Fractions

• Summary
Objectives

• Evaluate the sources and ages of different lipid fractions across the river-estuary-coastal ocean gradient in DE Bay

Approaches Used:

• **Lipid biomarker composition of surface water POM and UDOM**: sources of OM
  • $\text{TAR}_{\text{FA}}$
  • **Radiocarbon**: identify ages of POM and UDOM
    • Today: neutral and polar total lipid extract (TLE)
    • Still to come: identify ages of POM lipid fractions, source specific biomarkers
Delaware Watershed OM

• Potential OM end-members (and ages) include:
  – Estuarine primary production algae and marsh plants (modern)
  – Runoff from pastureland, farmland, and forests (modern/intermediate)
  – Wastewater effluent (intermediate)
  – Marsh sediments (intermediate)
  – re-exposed Pleistocene sediments (ancient)
  – Marcellus Shale and fossil fuels (ancient)
Sampling Locations

- **5 cruises – Surface water collection**

- **Fixed Locations**
  - River, Bay Mouth, Coastal Ocean

- **Variable Locations**
  - ETM, Chl a Max, High Chl a
Sample Collection Methods

Bulk Water (100 – 1100 L)

POM > 0.7μm

Filtered water

UDOM 0.1μm to 1 kDa

ASE Extract

Neutral TLE

Radiocarbon Sample

Polar TLE

Same as POM

Lipid Composition Sample

Fatty Acid Derivatization

Identify Compounds GC and GC/MS

Radiocarbon Select FA compounds

Same as Neutral

UDOM from Chl a Max Site
October 2011
Photo Courtesy K. Hossler

Filter from Bay Mouth Site
October 2010
Lipids as Biomarkers

- Biomarkers are used to determine organic matter sources and reactivity
  - Lipid biomarkers = fatty acids
- Terrestrial-to-Aquatic ratio ($TAR_{FA}$) can show contributions of terrestrial and aquatic OM
  - $TAR_{FA} = \frac{(C_{24:0} + C_{26:0} + C_{28:0})}{(C_{14:0} + C_{16:0} + C_{18:0})}$
  - ($TAR_{FA} = 1$ equal terrestrial and aquatic FA) (Meyers, 1997)
Results – Terrestrial – to – Aquatic Ratio $R_{FA}$

- Surface water POM and UDOM dominated by aquatic OM (i.e., $R_{FA} < 1$)

- ↑ $R_{FA}$ at River and ETM for POM

- ↑ $R_{FA}$ in Oct. 2010 than Mar. 2011
Motivation: Lipid Ages

- TOC radiocarbon age reflects average of all biochemical compound classes
- Biochemical classes range in radiocarbon age
- DE River UDOM lipid fraction oldest compound class

modified from Wang et al. 2006
• Lipid older than POC
• Neutral TLE aged relative to Polar TLE
Results – Radiocarbon

- Lipid older than POC
- Neutral TLE aged relative to Polar TLE
- **POM is younger than UDOM**
Results – Radiocarbon

October 2010

Endmember boxes based on Loh et al. 2004 and references therein, Griffith et. al 2009
Results – Radiocarbon

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Summary

• Marine primary production – main contributor to surface water FA

• Greater difference in age between neutral and polar TLE in UDOM than in POM

• Isotope bi-plot suggests bulk POC reflects a mixture of plankton and terrigenous sources along estuary but lipids reflect a range of source and age composition
  – POM TLE:
    • ETM/ Bay Mouth – mixture of sources
    • River/ Chl a max – similar to petroleum source
  – UDOM TLE:
    • Neutral TLE – similar to petroleum and black carbon
    • Polar TLE – mixture of sources
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Questions?
Results – POM Fatty Acid Distribution

- Saturated and polyunsaturated FA were most abundant
Results – UDOM Fatty Acid Distribution

- FA Concentrations much lower in UDOM
- Dominated by saturated FA
- Opposite trend to POM – Highest nitrogen uptake seaward

Distance from Bay Mouth (km)