Using DIC Analysis to Accurately Quantify Estuarine Community Metabolism

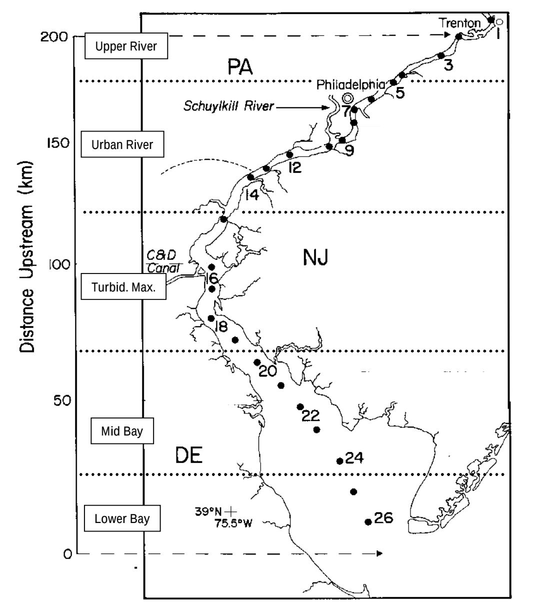
Adam R. Pimenta
Jonathan H. Sharp
University of Delaware
College of Marine and Earth Studies
600 Pilottown Rd. Lewes, DE 19958

Outline

- Community metabolism
  - Quantifying ecosystem function and health
- DIC
  - What it is
  - Why we measure it
  - DIC and metabolism
- Measuring DIC
  - MBARI DIC analyzer
  - Sample handling
  - DIC vs. DO and ^{13}C, ^{14}C
- Previous research
  - Ambient DIC patterns in Delaware Bay
  - DIC incubations in Delaware Bay
  - Different C uptake with DIC vs. ^{13}C

Ecosystem Response vs. Nutrient Concentration

- Delaware Estuary
  - HNLG system (Sharp, 2001)
  - No significant BOD
    - Circulation
    - Turbidity
- Ecosystem response more informative than nutrient concentration
  - Measuring ecosystem response
    - Biomass
    - Primary Productivity
    - Metabolism



The Delaware Estuary with distance axis from head of tide (210 km) to mouth of bay (0 km). Note regions from biogeochemical characterization (Yoshiyama and Sharp, 2006)

Estuarine Metabolic Balance

- Community metabolism
  - Pelagic, microbial community
- Many processes
  - Primary Production
    - Accurately measured since 1940's
  - Respiration
    - Often measured indirectly
  - Chemoautotrophy
    - Insufficiently measured in most estuaries
  - Inorganic processes

Quantifying Community Metabolism

- Microbial, pelagic community metabolism measured directly or using proxies
  - Direct measurements of incubated samples
    - Dissolved Oxygen (DO)
    - Carbon Isotopes (^{13}C, ^{14}C)
    - Dissolved Inorganic Carbon (DIC)
  - Proxy measurements
    - Chlorophyll a
    - Trends in ambient carbon, oxygen measurements

Dissolved Inorganic Carbon

- Speciation
  - HCO_3^- (~89%)
  - CO_3^{2-} (~10%)
  - CO_2 (~1%)
- In low productivity seawater (~35‰) ratios remain relatively constant due to dissociation reactions
- In more productive waters biological activity can alter speciation
- Terriginous and anthropogenic inputs, changing pH will alter speciation

DIC and Community Metabolism

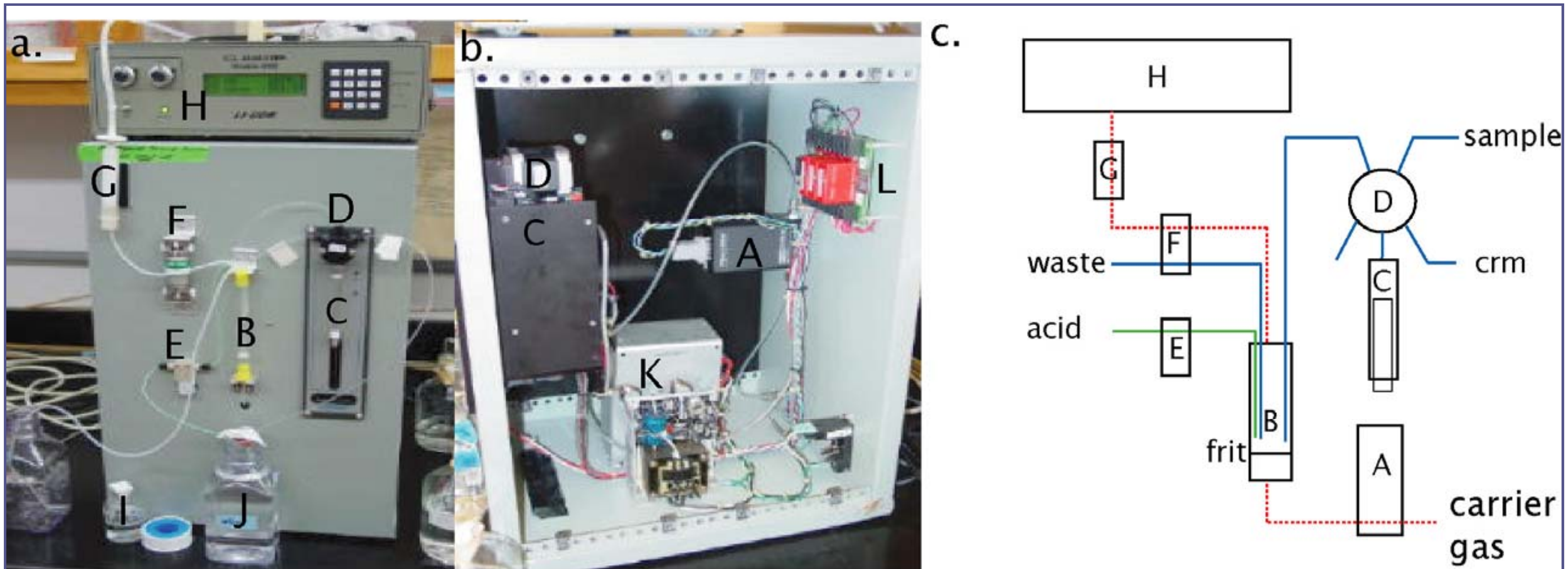
- DIC directly linked to organic carbon pool via photosynthesis, respiration and chemoautotrophy
- Total DIC concentration affected by
  - Primary production
  - Respiration
  - Chemoautotrophic processes
  - Calcification
  - Atmospheric exchange
  - Watershed input

DIC and Community Metabolism

- DIC pool in Delaware Bay
  - ~2000 µmoles C/kg^{-1} at 30‰
  - ~1200 µmoles C/kg^{-1} at 0‰
- 24 hour incubations
  - Light bottle C uptake: 300-400 µM C/day
  - Dark bottle C production: 5-20 µM C/day
- Variable C uptake rates
  - Higher uptake in spring/summer
  - C uptake increases with decreasing turbidity

MBARI DIC Analyzer

- DIC analyzer developed by Gernot Friederich at Monterey Bay Aquarium and Research Institute and described in (Friederich *et al.* 2002)
- Our instrument (modified at UD) is one of three similar instruments
  - University of Delaware, Bermuda Institute of Ocean Sciences, San Francisco State University
- Replicate Precision
  - Oceanic samples: ±0.05 %
  - Estuarine samples: ±0.1-0.2 %



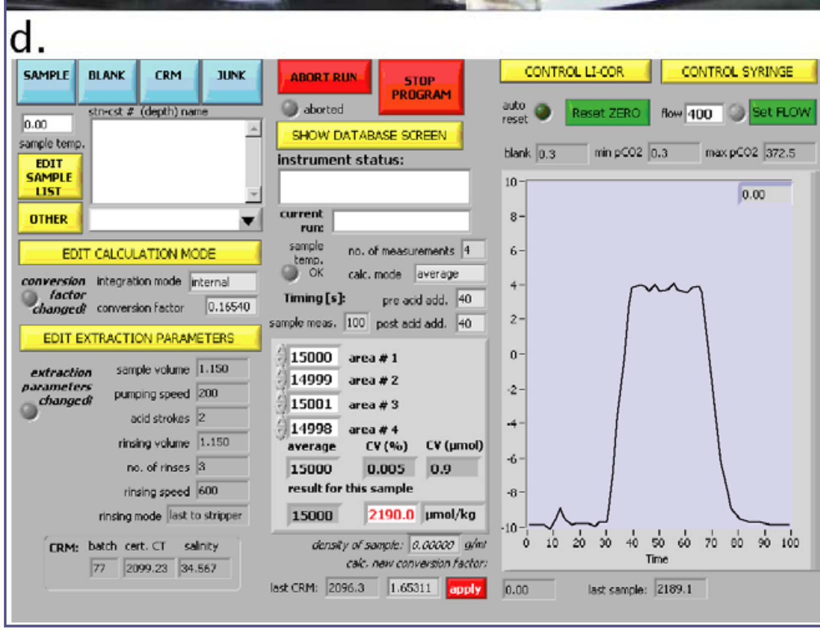


Figure 1. Hardware and software components of the AMICA prototype DIC analyzer. **a.** Front view of the AM ICA prototype. **b.** Side view. **c.** Analitical flow schematic (dark blue line = water; dashed red line = gas line; green line = acid line). **d.** Example of prototype software control and graphical display for the AMICA using LabView. A. Mass flow controller; B. Stripping chamber; C. Kloehn digital syringe; D. 6 way sampling valve. E. Acid injection pump; F. Two-way pinch valve; G. Magmesium perchlorate dryer for the gas stream; H. LiCOR NDIR Analyzer; I. Phosphoric acid reservoir; J. test sample; K.. Power supply, and; L. digital relay switches. Not shown is a laptop computer and carrier gas tank (nitrogen or oxygen).

MBARI DIC Analyzer: Procedure

- Sample injected into sparging cell and acid added
- CO_2 is stripped out using O_2 carrier gas
- CO_2 containing carrier gas passes through drying column
- CO_2 Measured in LI-COR Infrared gas analyzer (IRGA)
- Peak area analyzed using integration program
- Daily standards from SCRIPPS (CRM)
- Analysis of a sample requires slightly more than 20ml.
- ~12 minutes

Sampling

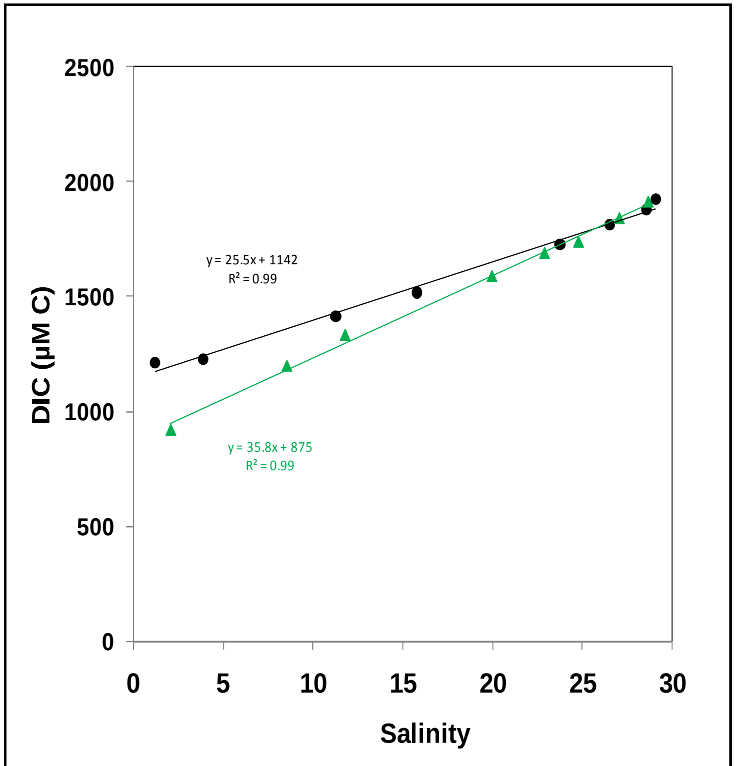
- Ambient measurements
  - Patterns of DIC concentration
  - Spatial and seasonal trends in DIC concentration
  - Measurements throughout the diel cycle allows estimates of soft-tissue metabolic balance
- Incubation measurements
  - Microbial pelagic metabolic rate
  - Depth integrated areal production and respiration
  - Trophic transfer of carbon

Benefits of DIC Method Over DO and ^{13}C, ^{14}C Method

- Ease of Use
- Sample stability
- No toxic Chemicals
- Permitting issues
- Cost of system

Ambient DIC Distribution

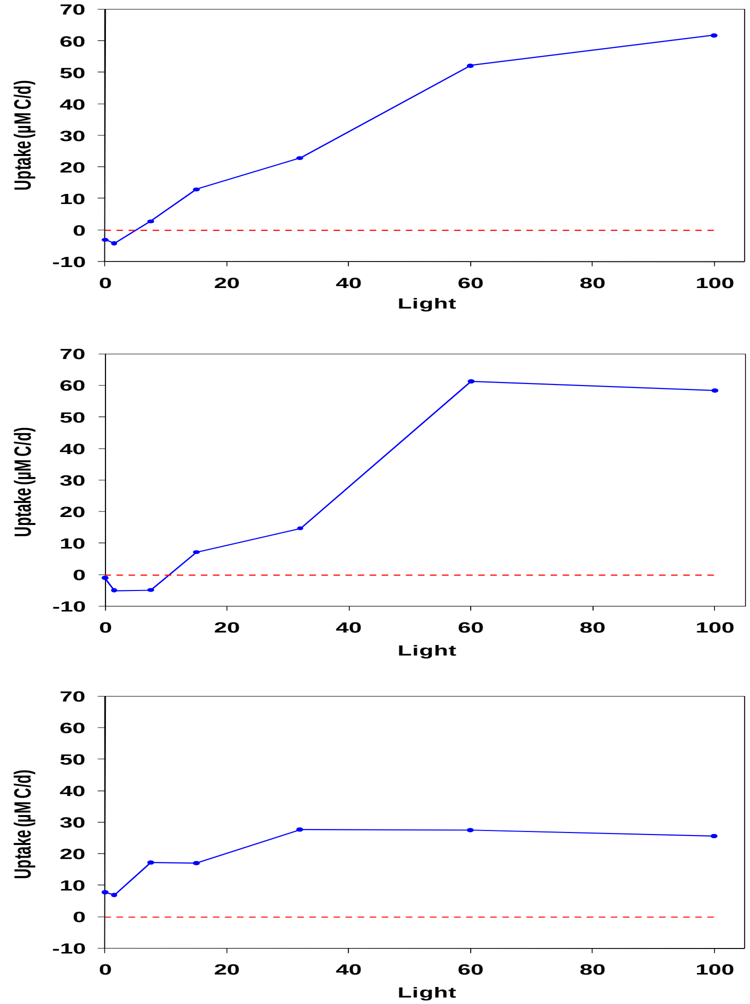
- Delaware estuary transects
  - June 2006
  - September 2007
- Relatively linear pattern with salinity
- Uniform coastal endmember
- Variability at low salinity is due to differences in watershed input



DIC vs salinity for individual Delaware Estuary cruises in September 2007 (circles) and June 2006 (triangles).

DIC uptake in the Delaware Estuary

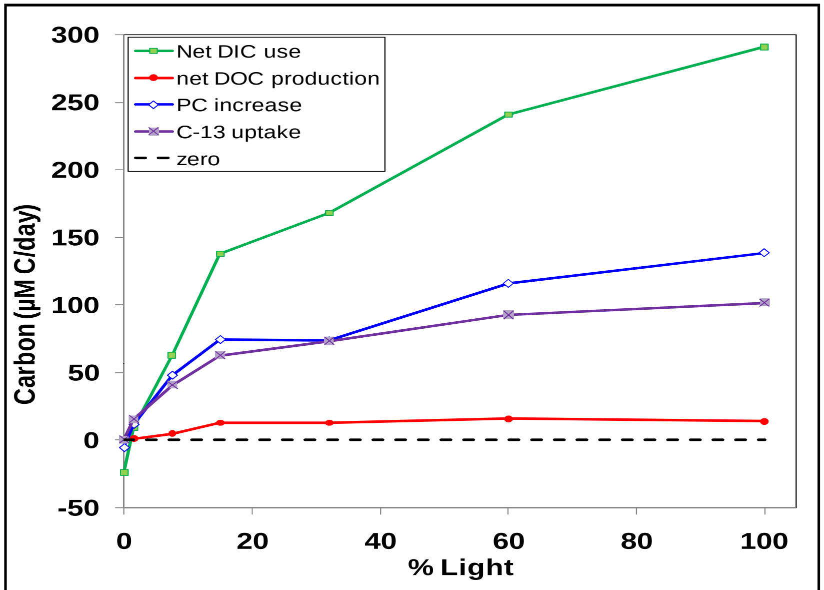
- DIC uptake in Delaware Bay
  - 24 hour incubation
  - Samples subjected to seven different light levels
  - Depth integrated productivity
- Compensation point
  - DIC increase in dark bottle
  - Compensation light level varies within estuary
  - Compensation light level between 1.5% and 7.5% light in lower bay
  - Compensation light level higher in turbidity maximum region
  - Dark bottle DIC uptake in urban river region



DIC uptake in lower bay (top), turbidity maximum (middle) and urban river region (bottom). Data from DF-5 cruise, September, 2008.

Future Work

- Discrepancy between DIC and ^{13}C uptake rates
- ^{13}C and particulate carbon (PC) show dark bottle C uptake
- C uptake based on ^{13}C and PC measurements is approximately 50% less than DIC measurements
  - Possible ^{13}C incorporation lost in smaller size classes
  - DIC in form of CO_2 lost in headspace
  - Possible recycling of ^{13}C over 24 hour incubation



Simulated in-situ carbon uptake at Murderkill River, station 10: DIC flux, ^{13}C uptake, particulate carbon increase, and DOC production (including dark). The dashed line indicates zero carbon flux.

Conclusion

- Community metabolism well suited to assessing estuarine function and health
- DIC is an effective parameter for measuring estuarine community metabolism
  - Directly produced and consumed during normal metabolic processes
- MBARI instrument allows for high precision and easy to use analysis
- Previous work in Delaware Bay and Murderkill River demonstrates applicability of DIC measurements
- Work remains to be done to reconcile DIC measurements with ^{13}C uptake rates

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Acknowledgements

- We acknowledge the US National Science Foundation for an OTIC grant that has supported much of our DIC research; we acknowledge a grant from the Kent County Levy Court (DE) for support of our Murderkill River research project, we also acknowledge the support provided by the DuPont Clear into the future program and Delaware DNREC for assistance with samples where we have applied and experimented with DIC incubations." We thank Kelly Peeler and Yoana Voynova for assistance on some of the experiments reported here