

NEW INSIGHTS INTO CARBON FLUXES IN THE OCEAN: RESULTS FROM MEDFLUX

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**Conundrums and Controversies:
What Contributes to the Vertical Flux of Carbon,
Nitrogen and Phosphorus in Aquatic Ecosystems?
2007 Aquatic Sciences Meeting**



**What we have learned...
(over the past decade)....**

**What we are now learning,
what we know we don't know...
(but know we need to know.....)**

What we have learned... (over the past decade)....

Particle fluxes decrease with depth.

Fluxes vary temporally (in response to upper ocean dynamics).

Fluxes vary spatially (in response to upper ocean dynamics).

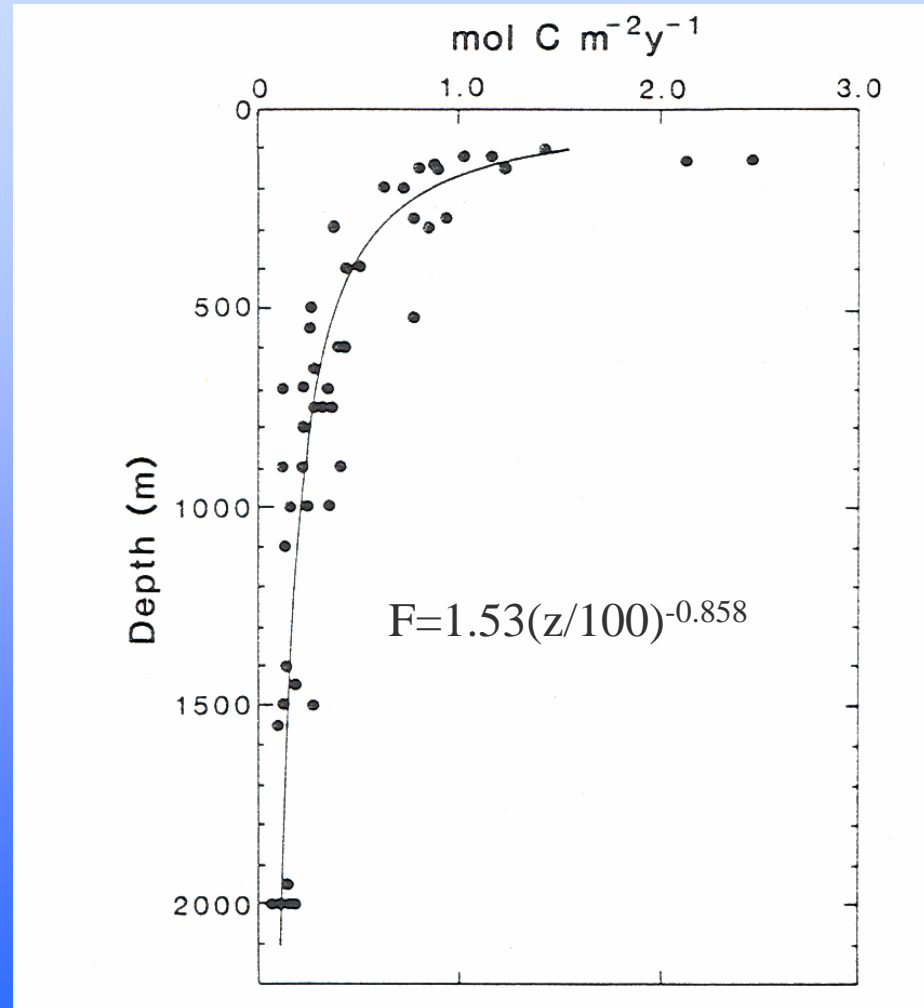
Indicators of organic matter degradation.

Differential degradation vs selective preservation?

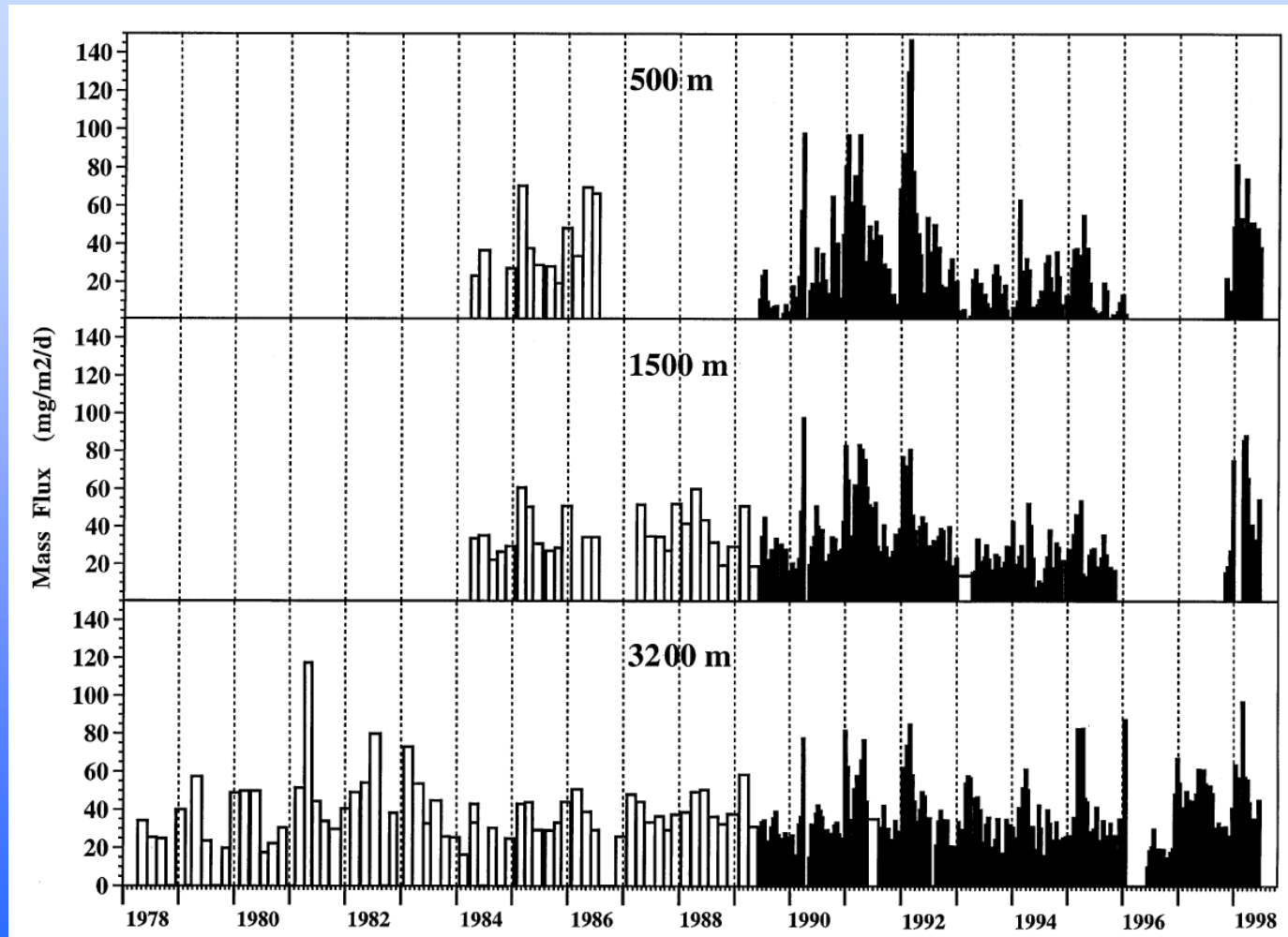
Particle fluxes decrease with depth: Organic matter decomposition + inorganic matter dissolution

Martin Open Ocean Composite Curve –

A first step at
predicting flux....

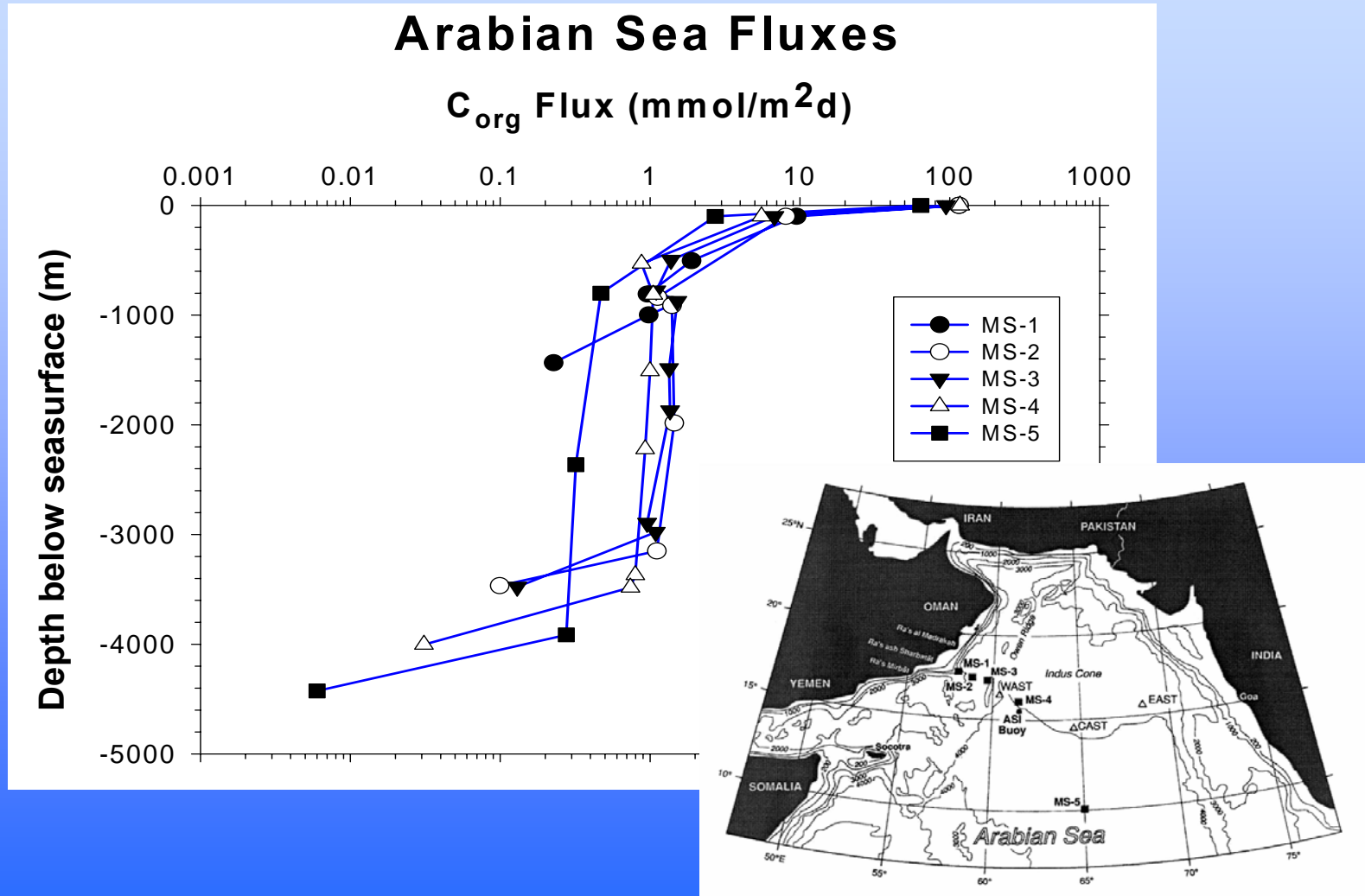


Fluxes vary temporally in response to upper ocean dynamics: 20-year record of flux at Bermuda



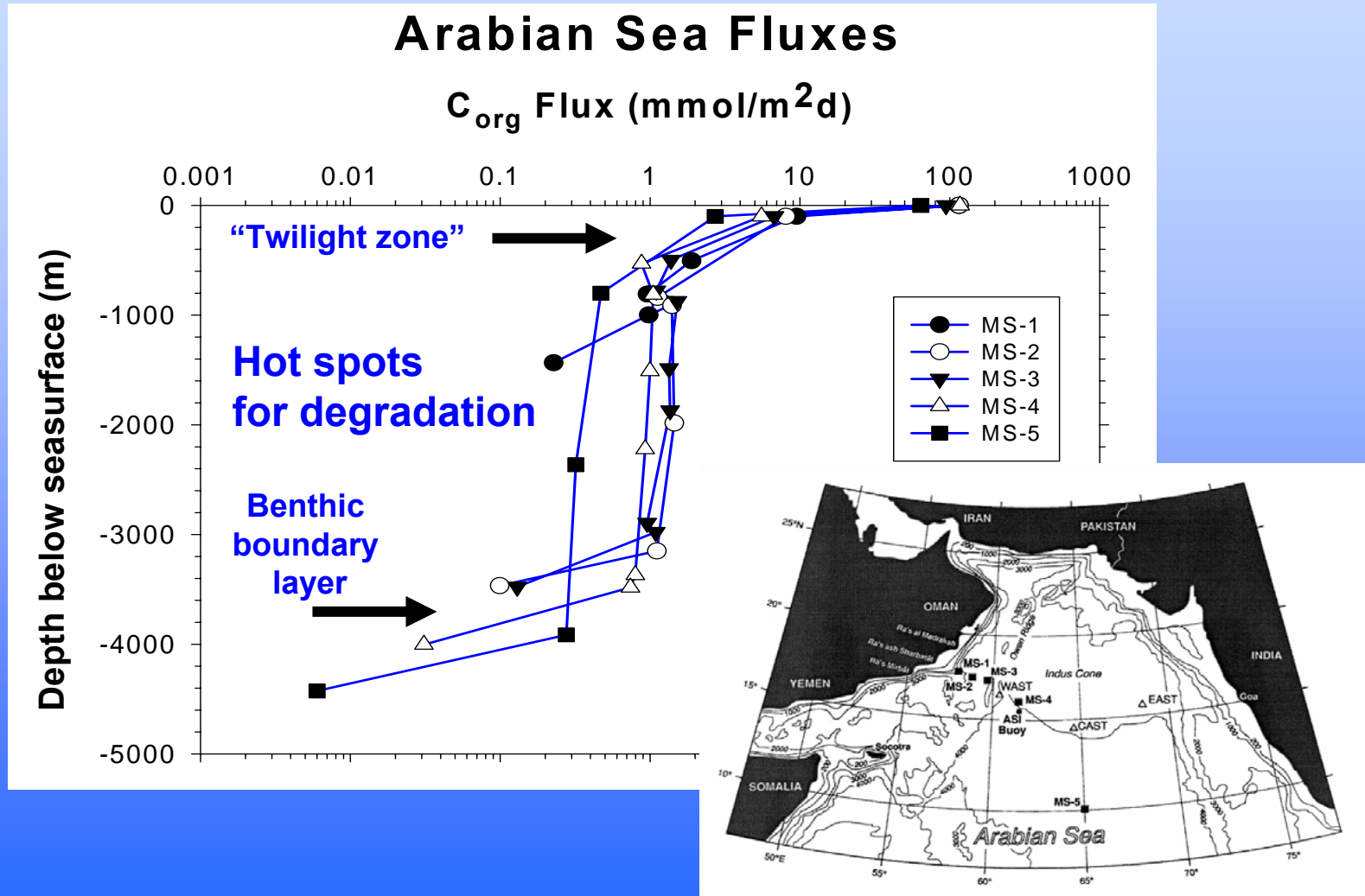
(Conte, M. H., N. Ralph, E. H. Ross. 2001. Season and interannual variability in deep ocean fluxes at the Ocean Flux Program (OFP)/ Bermuda Atlantic Time Series (BATS) site in the western Sargasso Sea near Bermuda. *Deep-Sea Res. II*, 48, 1471-1505)

Fluxes vary spatially in response to upper ocean dynamics: Monsoonal physical forcing in the Arabian Sea



(C. Lee, D. W. Murray, R. T. Barber, K. O. Buesseler, J. Dymond, J. I. Hedges, S. Honjo, S. J. Manganini, J. Marra, C. Moser, M. L. Peterson, W. L. Prell, S. G. Wakeham. 1998. Particulate organic carbon fluxes: Results from the U.S. JGOFS Arabian Sea Process Study. *Deep-Sea Res. II* 45: 2489-2501)

Fluxes vary spatially in response to upper ocean dynamics: Monsoonal physical forcing in the Arabian Sea

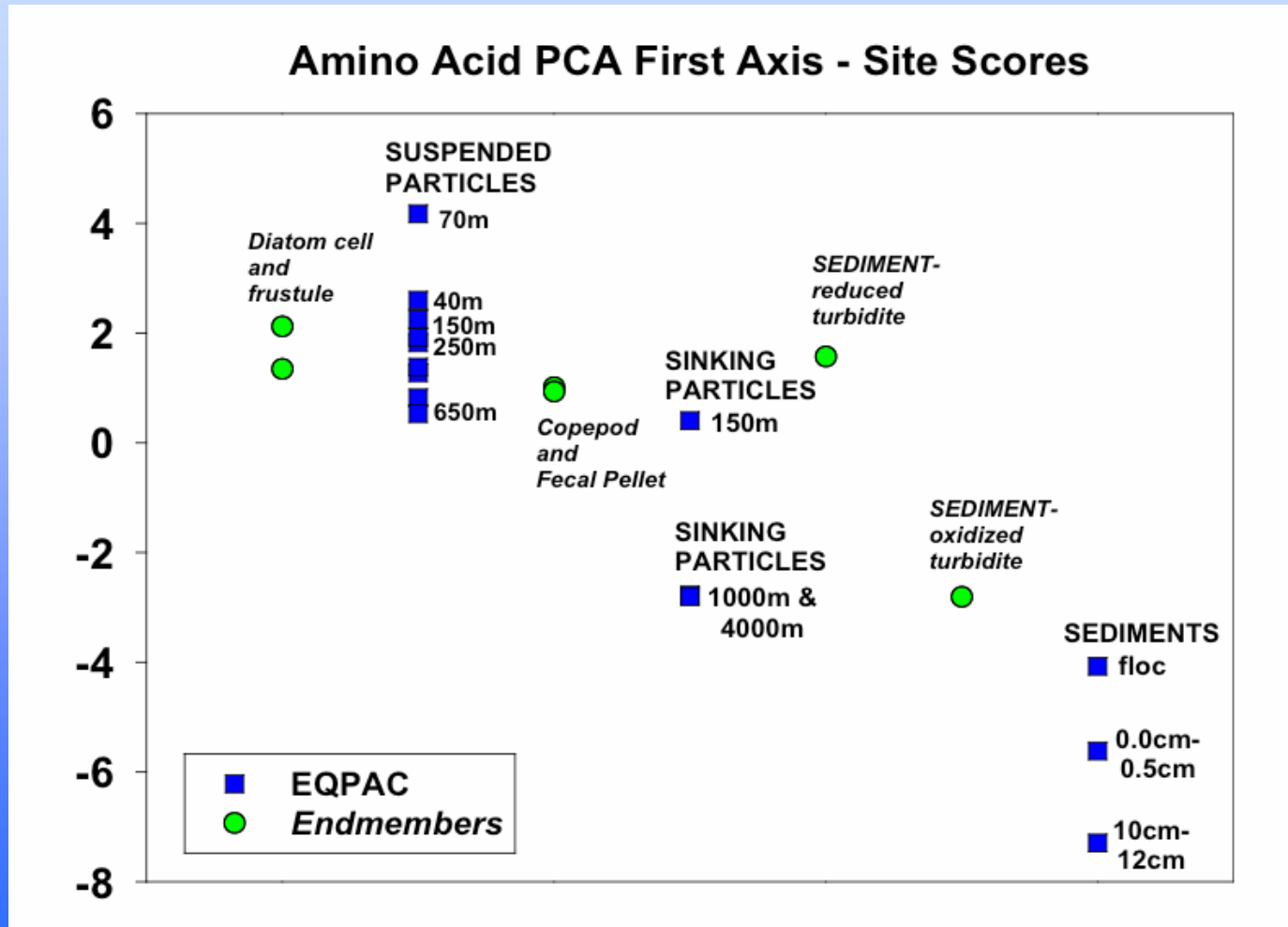


(C. Lee, D. W. Murray, R. T. Barber, K. O. Buesseler, J. Dymond, J. I. Hedges, S. Honjo, S. J. Manganini, J. Marra, C. Moser, M. L. Peterson, W. L. Prell, S. G. Wakeham. 1998. Particulate organic carbon fluxes: Results from the U.S. JGOFS Arabian Sea Process Study. *Deep-Sea Res. II* 45: 2489-2501)

Indicators of organic matter degradation

Amino acid Degradation Index (DI)

(*sensu* Dauwe and Middelburg)

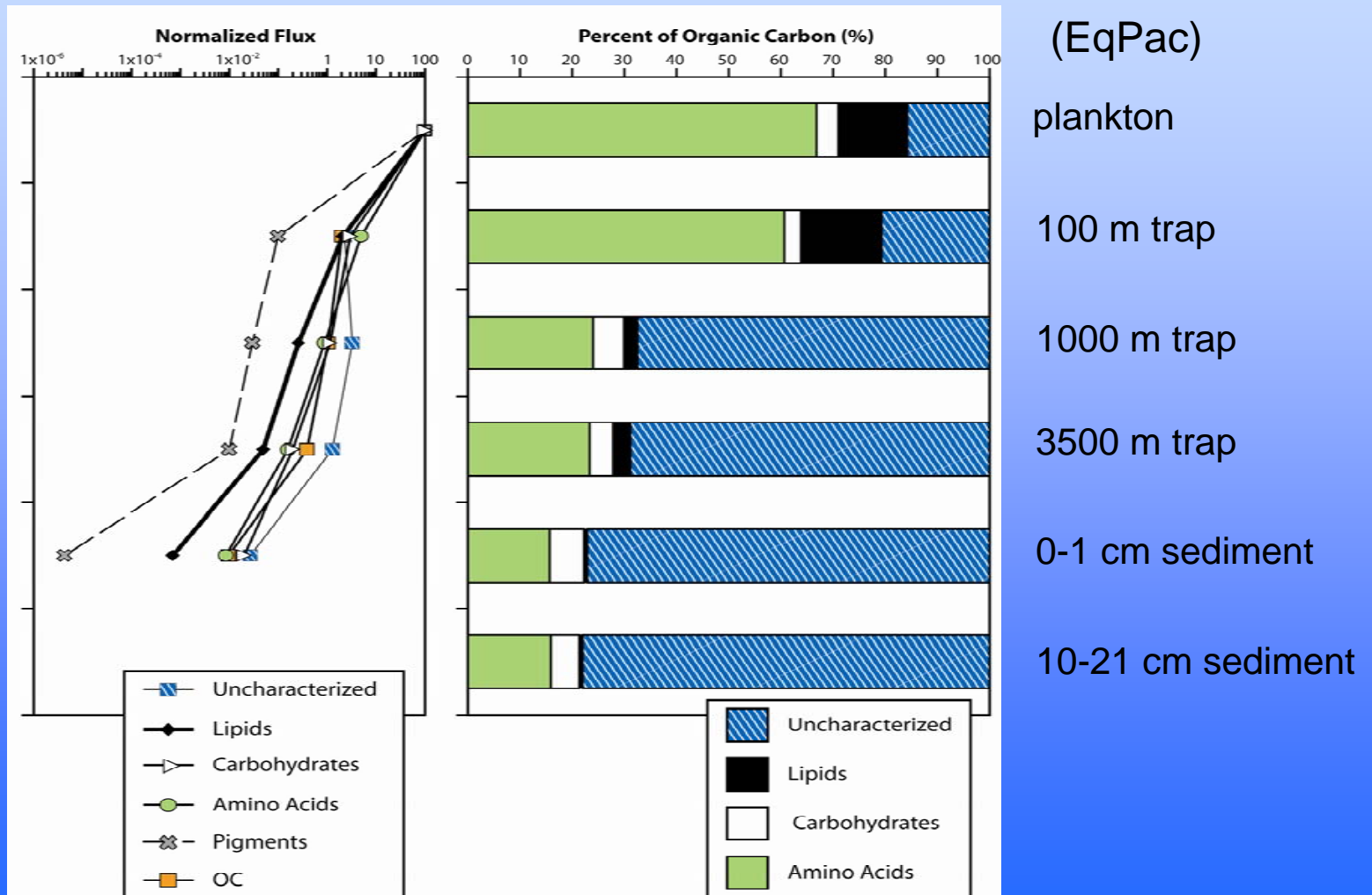


(Sheridan C.C., C. Lee, S.G. Wakeham, J.K.B. Bishop. 2002. Suspended particle organic composition and cycling in surface and midwaters of the equatorial Pacific Ocean. *Deep-Sea Res.* 49: 1983-2008)

Differential degradation

Organic compounds behave differently...

Preferential degradation???

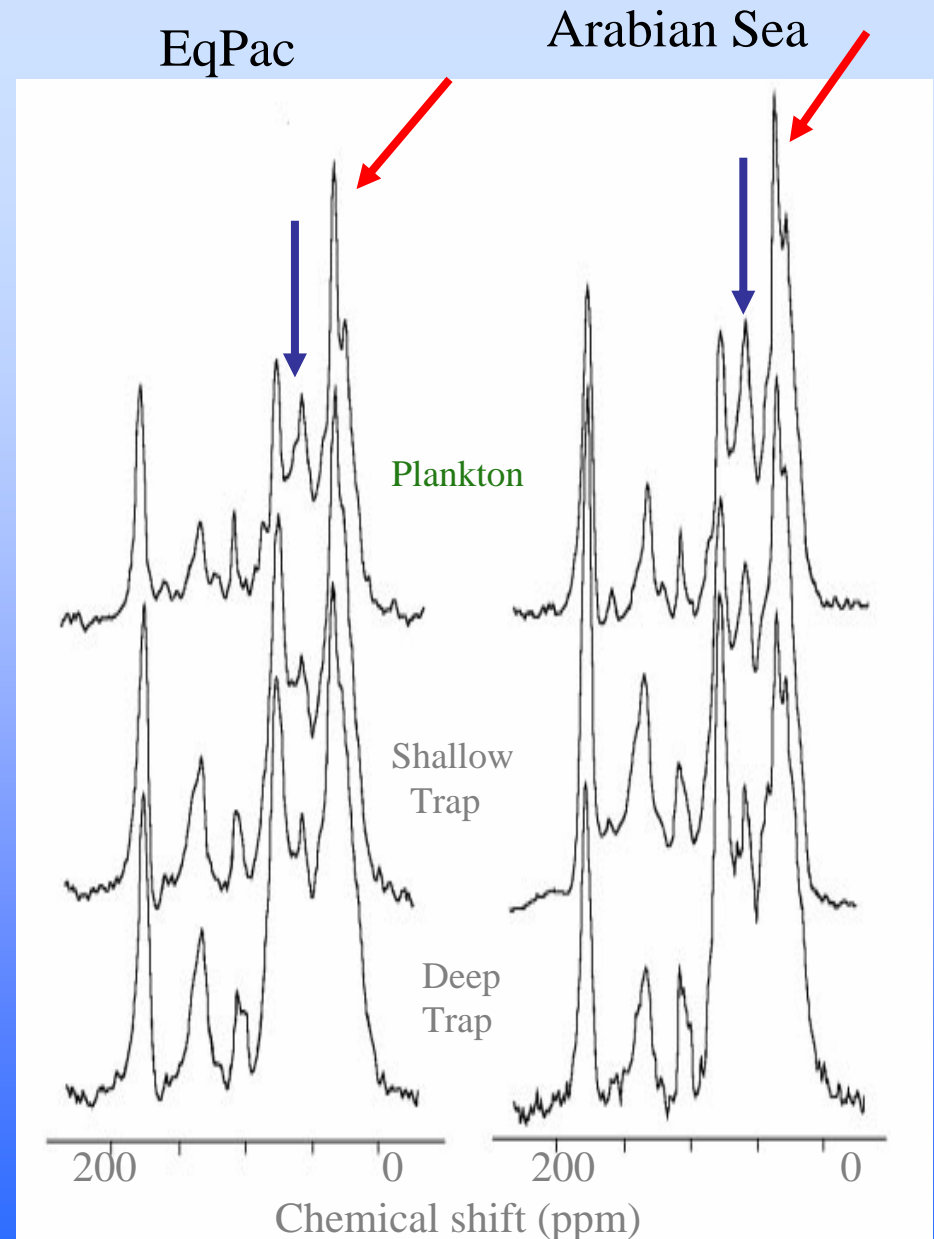


(Lee, C., Wakeham, S. G., Arnosti, C. 2004. Particulate organic matter in the sea: the composition conundrum. *Ambio* 33, 565-575)

But – bulk compositional analysis (^{13}C -NMR) shows something else!

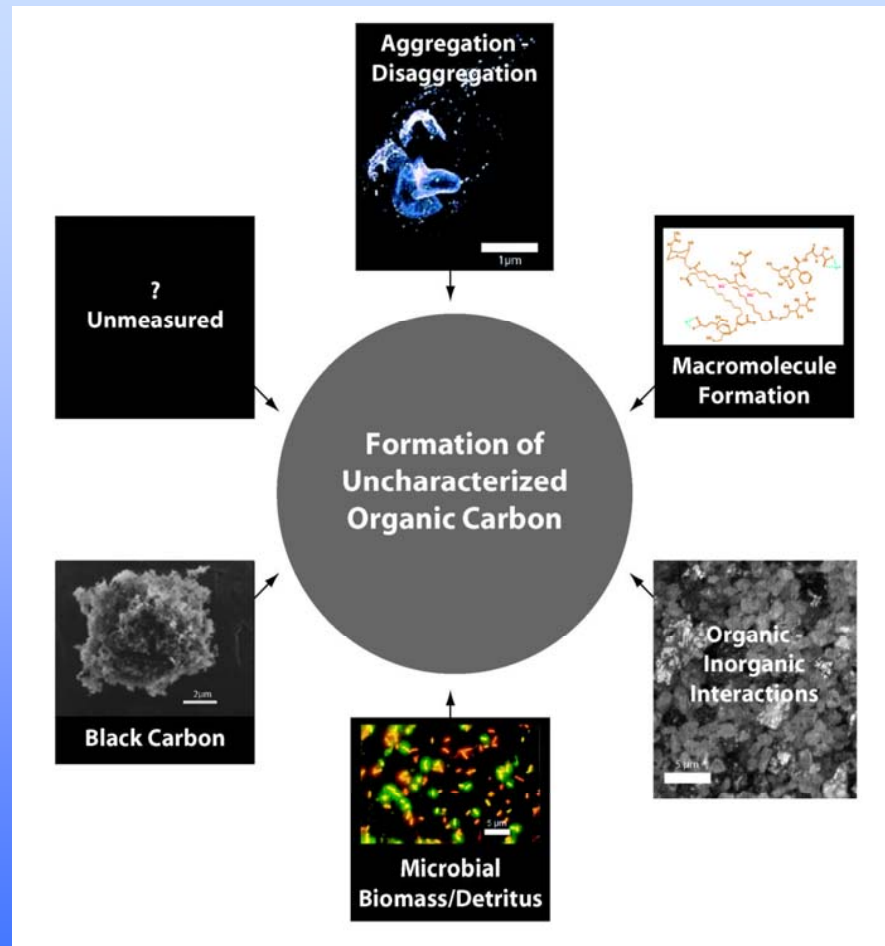
Amino acid-like and **alkyl** materials dominate, but there is minimal change in composition down the water column.

Selective preservation??



(Hedges, J. I., J. A. Baldock, Y. Gelinas, C. Lee, M. L. Peterson, S. G. Wakeham. 2001. Non-selective preservation of organic matter in sinking marine particles. *Nature* 409: 801-804)

How does “molecularly-characterized” OM become “molecularly-uncharacterized” OM?



How do we determine the composition of this “uncharacterized” fraction?

What we have learned... (over the past decade)....

Particle fluxes decrease with depth.

Fluxes vary temporally (in response to upper ocean dynamics).

Fluxes vary spatially (in response to upper ocean dynamics).

Indicators of organic matter degradation.

Differential degradation vs selective preservation?

What we are now learning, what we know we don't know... (but know we need to know.....)

Sampling issues – still!

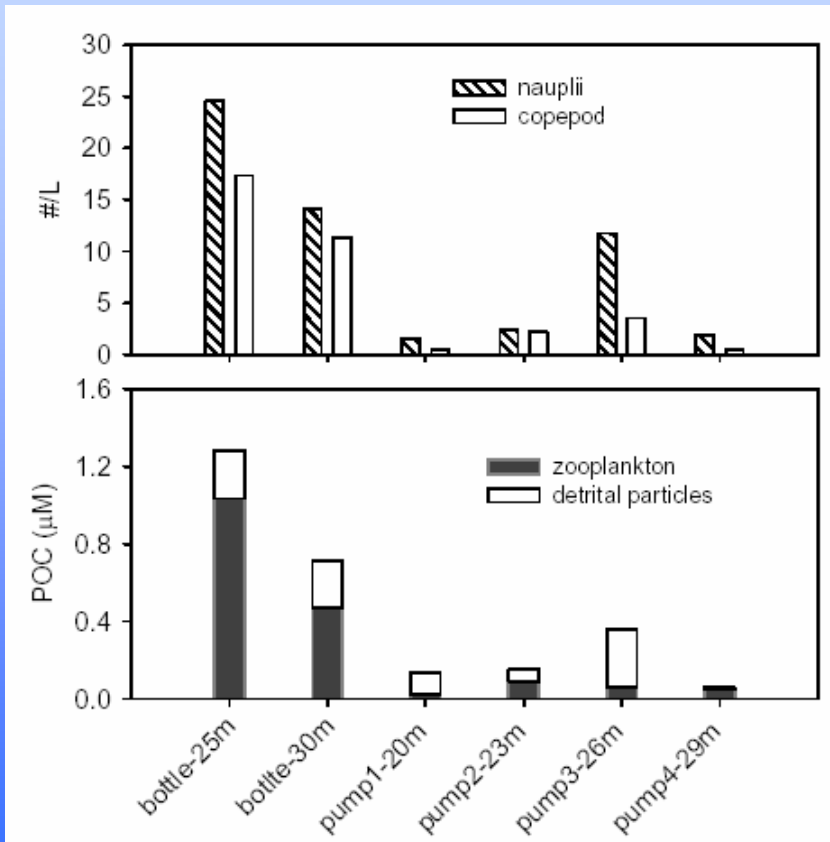
What makes particles sink – ballast?

How fast do particles sink *in-situ*?

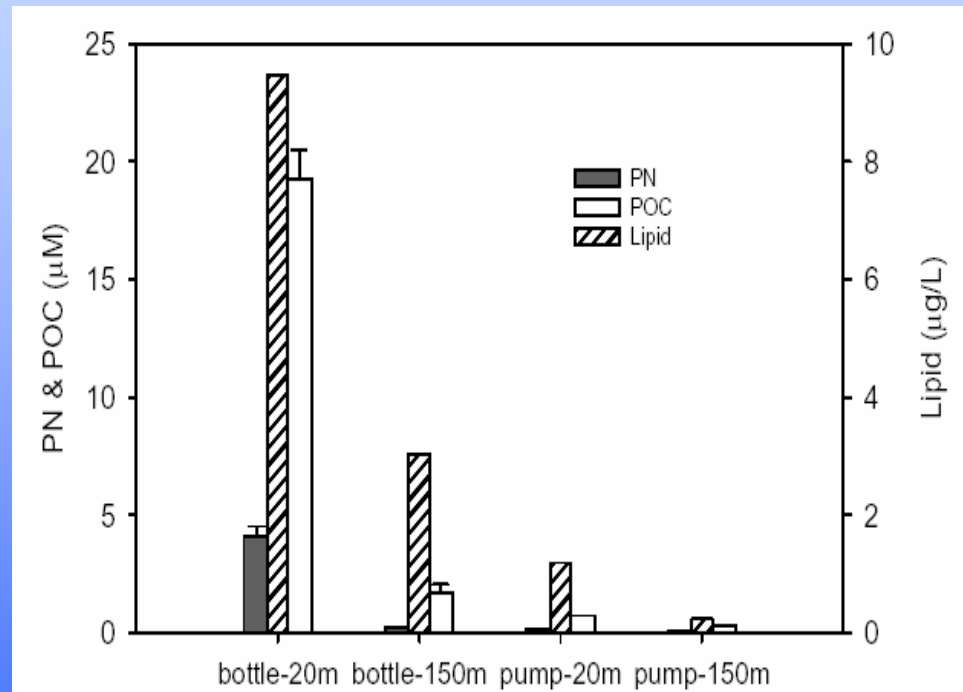
Particle decomposition – organic matter and ballast?

What is the correct POC measurement? The same old question of bottles vs pumps....

MedFlux 2005



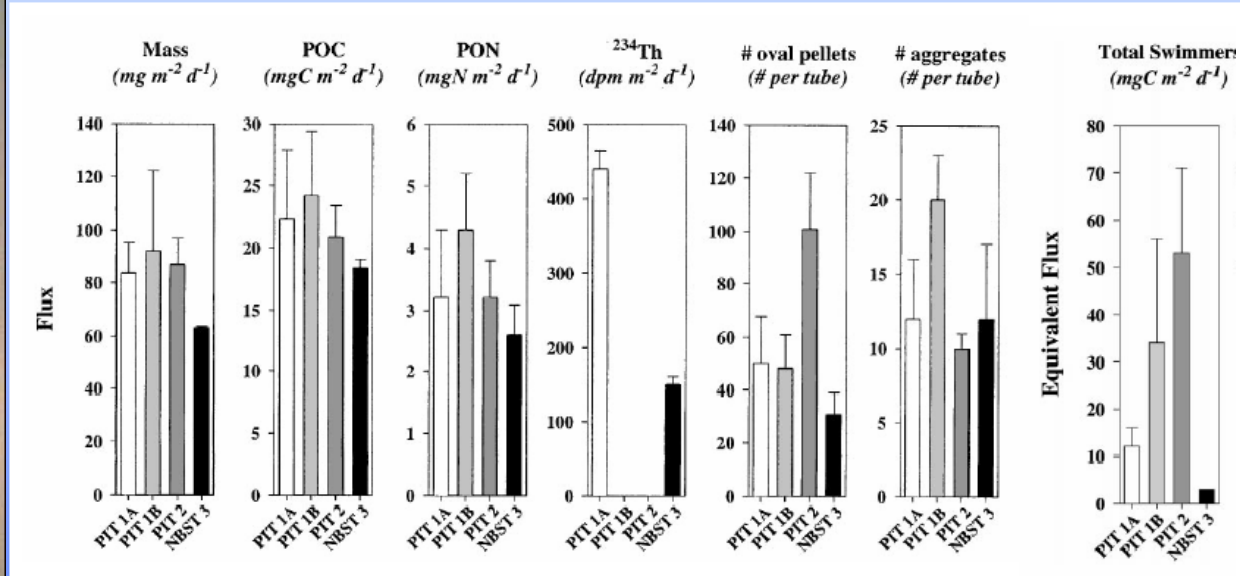
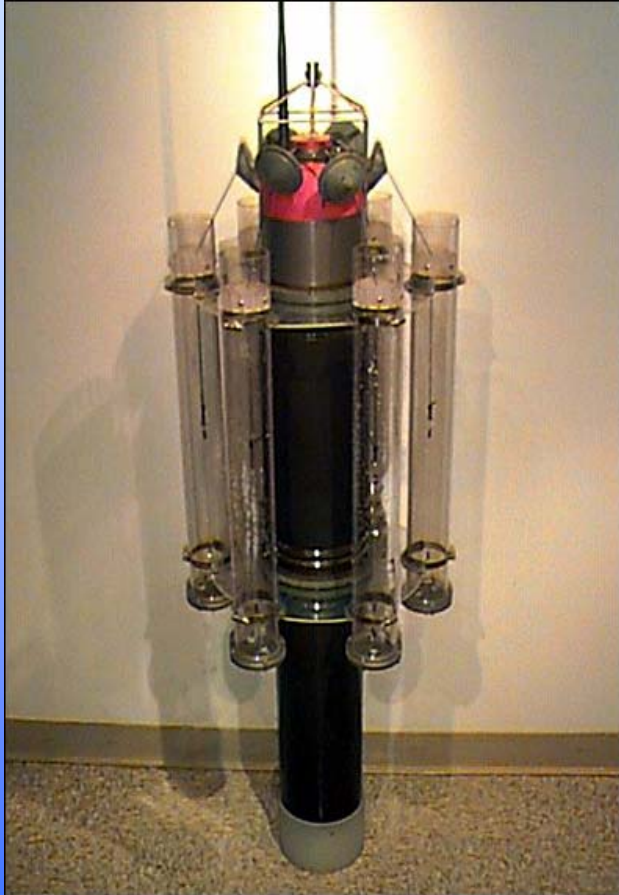
MedFlux 2006



(Liu, Z., J., Cochran, C. Lee, B. Gasser, J. C. Miquel, S. G. Wakeham (submitted) Contribution of zooplankton to particulate organic carbon concentrations measured in Niskin bottles compared to *in-situ* pumps. Deep-Sea Res. II)

Measuring a flux accurately is still a non-trivial task!

Neutrally-buoyant trap to Reduce hydrodynamic biases



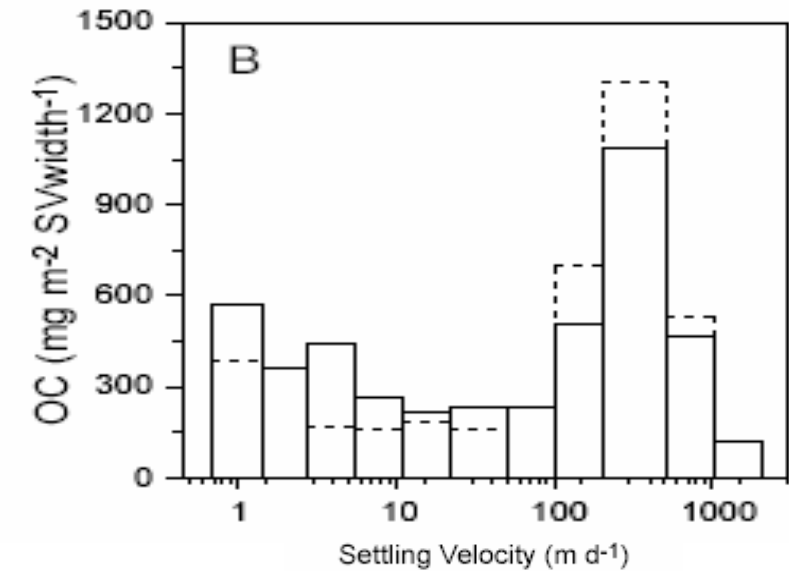
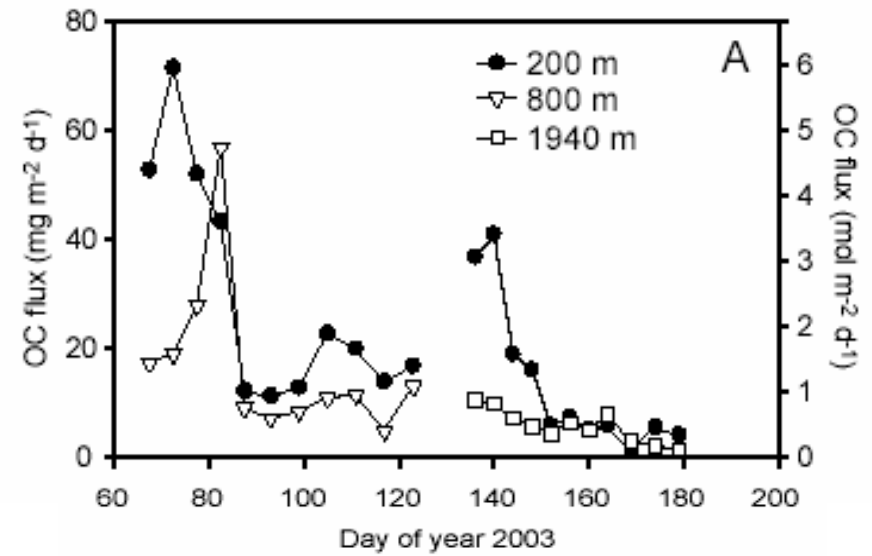
(Buesseler, K. O., et al., 2002. A comparison of the quantity and composition of material caught in a neutrally buoyant versus surface-tethered sediment trap *Deep-Sea Res. I* 47 277-294)

(Valdes, J. R., J. F. Price 2000. A Neutrally buoyant, upper ocean sediment trap. *J. of Atmos. Oceanogr. Technol.*, 17: 62-68)

**Indented-rotating sphere (IRS) valve-
reduces swimmers, allows *time-series*
and *settling velocity* collections**

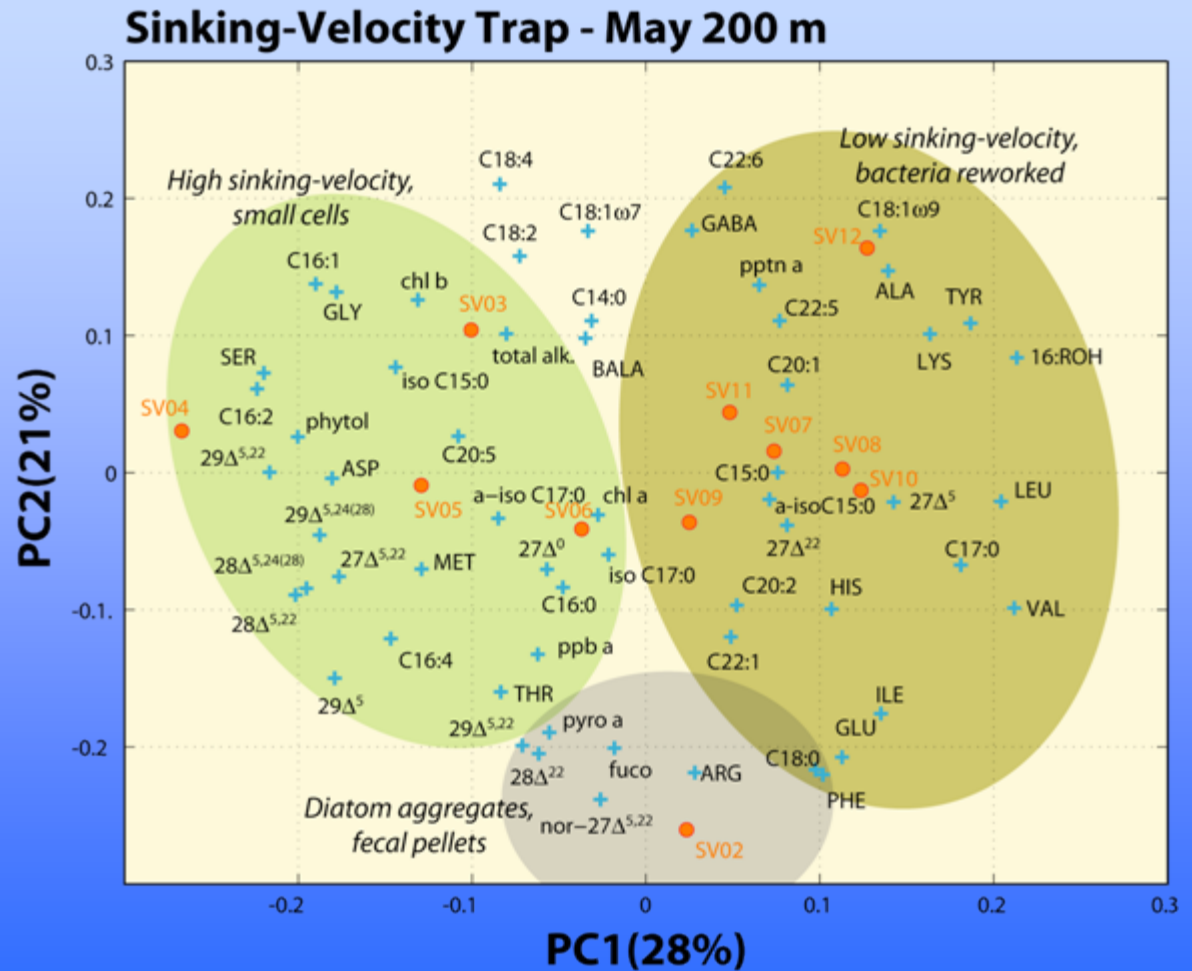
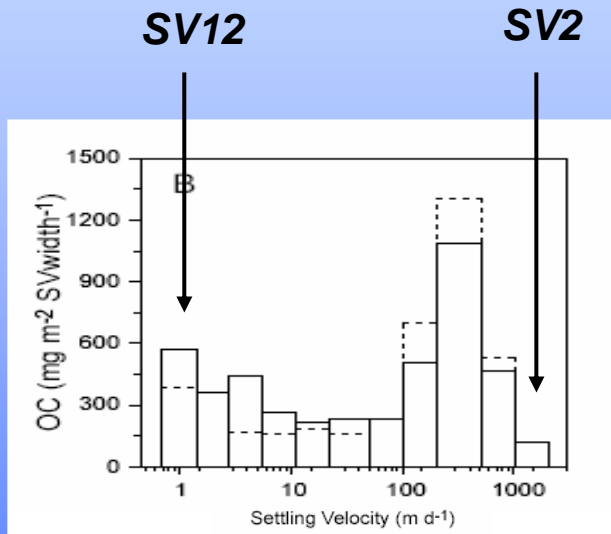


(Peterson, M. L., S. G. Wakeham, C. Lee, M. A. Askea J. C. Miquel. 2005. Novel techniques for collection of sinking particles in the ocean and determining their settling rates. *Limnol. Oceanogr. Methods* 3, 520-532)



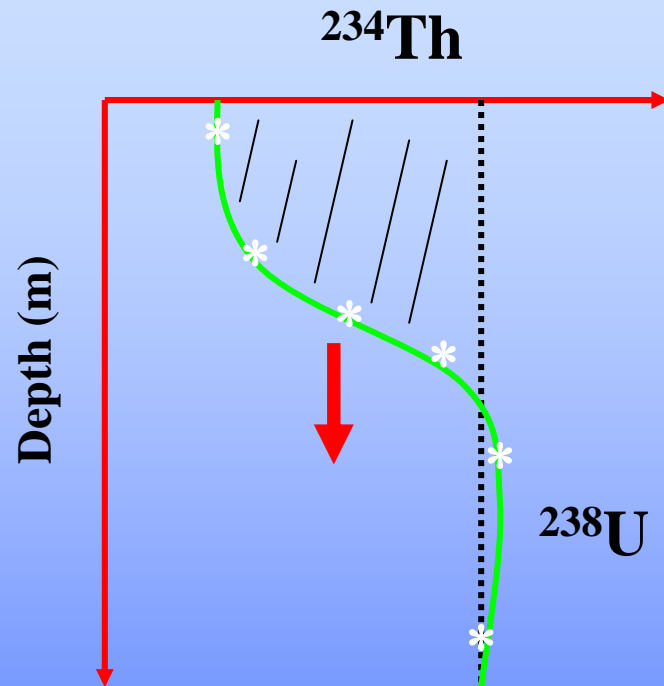
(Wakeham, S. G., C. Lee, M. L. Peterson, Z. Liu, J. Szlosek, I. F. Putnam and J. Xue. Organic compound composition and fluxes in the Twilight zone – Time series and settling velocity sediment traps during MedFlux. Submitted to *Deep-Sea Res II*)

Particles with different sinking velocities have different organic compositions



(Wakeham, S. G., C. Lee, M. L. Peterson, Z. Liu, J. Szlosek, I. F. Putnam and J. Xue. Organic compound composition and fluxes in the Twilight zone – Time series and settling velocity sediment traps during MedFlux. Submitted to Deep-Sea Res II)

Thorium-234 approach for estimating particle export



At Steady State:

$$(^{238}\text{U} - ^{234}\text{Th}) \lambda * Z = ^{234}\text{Th} \text{ Export (dpm m}^{-2} \text{ d}^{-1})$$

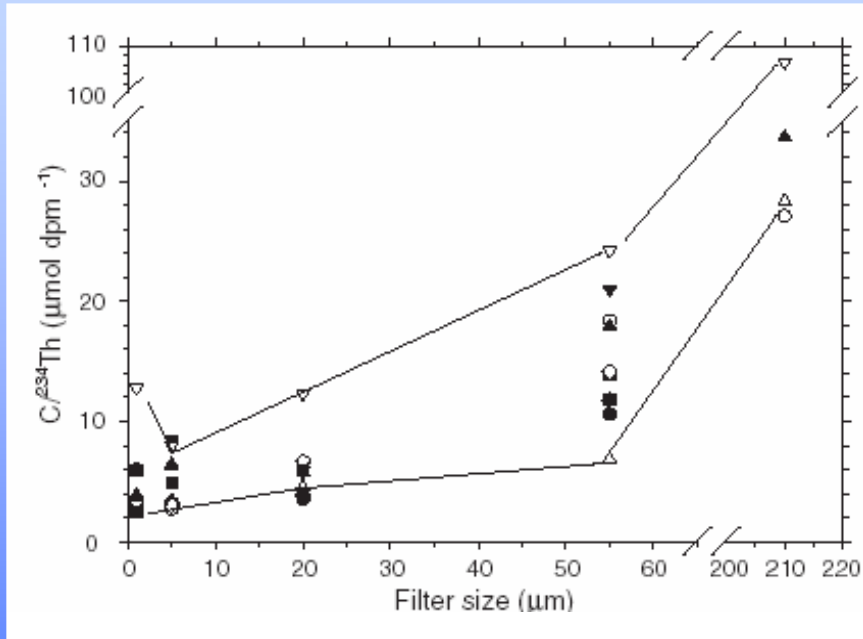
Measure $C/^{234}\text{Th}$ on sinking particles

--> **Carbon Export**

(After Claudia Benitez-Nelson, 2004. History of ^{234}Th and particle export, Future Applications of ^{234}Th in Aquatic Ecosystems (FATE) Workshop)

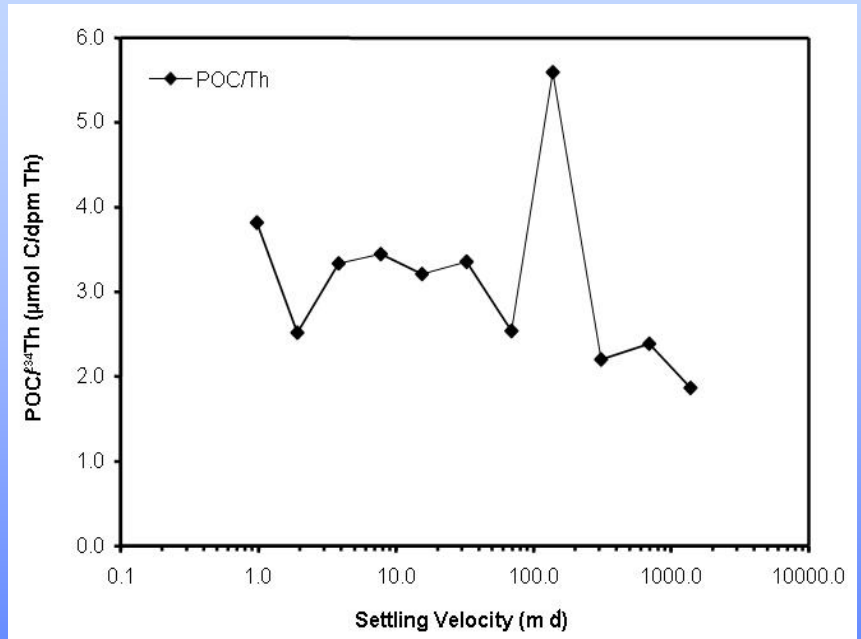
Estimating OC flux using ^{234}Th requires the OC/ ^{234}Th

In-situ pump filters, Sub-Antarctic
(Australian Sector)



(Buesseler, K.O. et al. 2006. An assessment of particulate organic carbon to thorium-234 ratios in the ocean and their impact on the application. *Mar. Chem.* 100: 213–233)

MedFlux 2003 SV traps



(Szlosek, J.E., Cochran, J.K. Miquel, J.C., Masqué, P., Armstrong, R.A., Fowler, S.W.. Particulate Organic Carbon- ^{234}Th relationships in particles separated by settling velocity in the Northwest Mediterranean. Submitted to *Deep-Sea Res. II*)

There is also variability in OC/ ^{234}Th as a function of depth sampled, sampling device (pumps vs traps), and region sampled (Buesseler et al, 2006).

Why do particles sink?

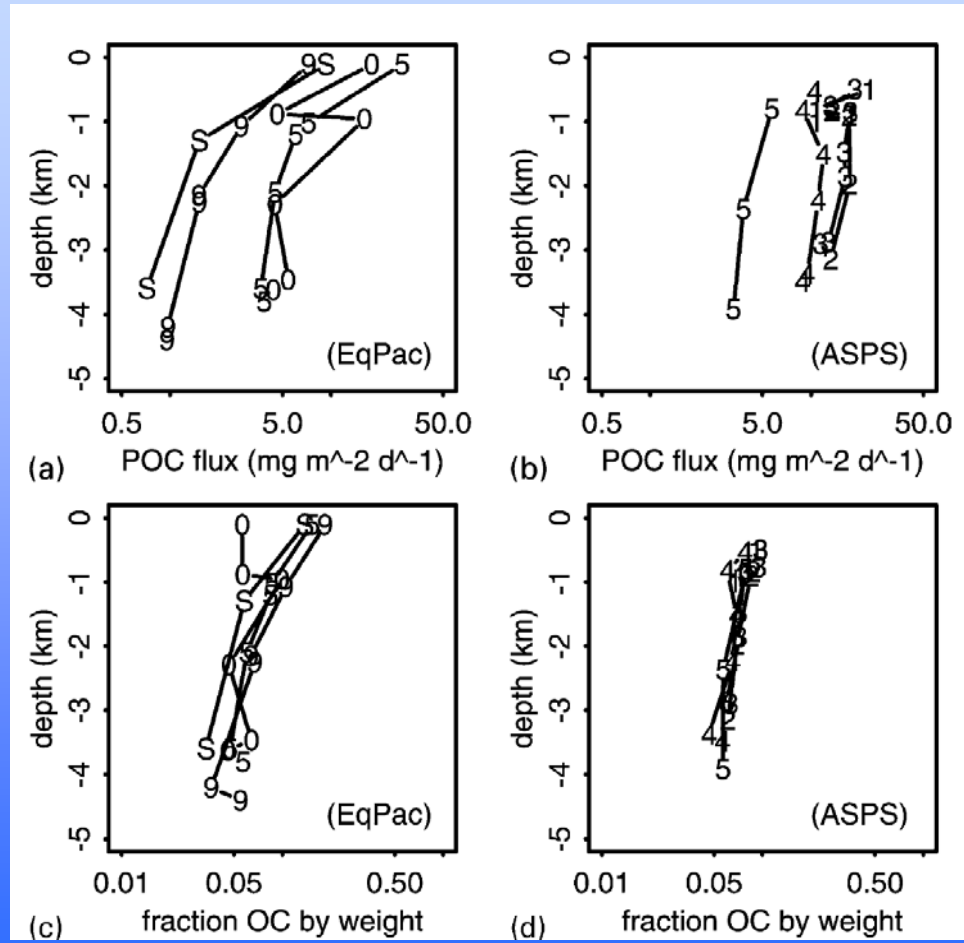
Organic matter will not sink without mineral ballast

$$[\rho_{OM} \sim 0.9-1.05; \rho_{bio-silica} 2.0 \text{ g/cc}; \rho_{carbonate} 2.3]$$

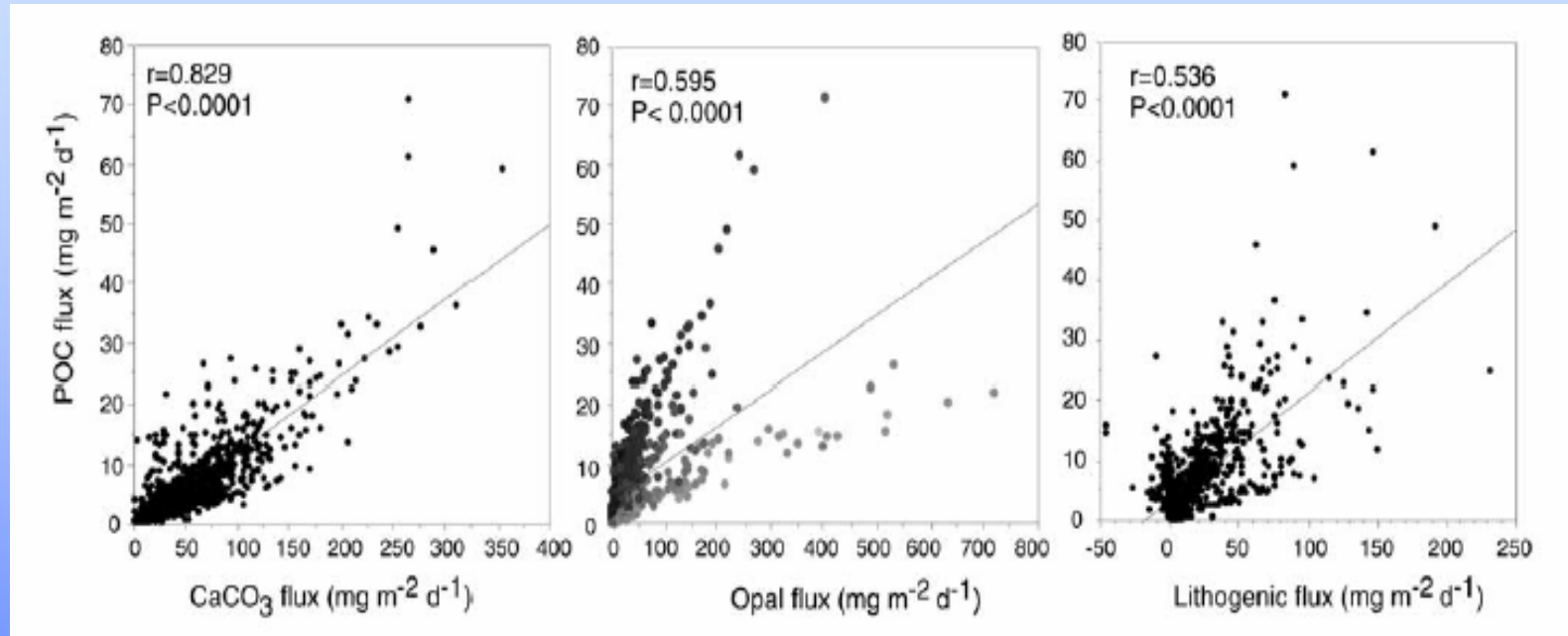
Organic carbon fluxes decrease with depth to varying degrees at different locations.

The percent of total mass made up by organic carbon reaches a constant value at depth, ~5%.

The Ballast Hypothesis



Which mineral ballast carries most of the POC flux?



(Klaas C. and D.E Archer. 2002. Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global Biogeochem. Cycles* 16: Art. No. 1116)

But the story is not yet complete... and there is no consensus -
e.g., at Bermuda, carbonate does not seem to have a greater
carrying capacity than opal and lithogenic material
(Boyd and Trull, *Progress Oceanogr.* in press).

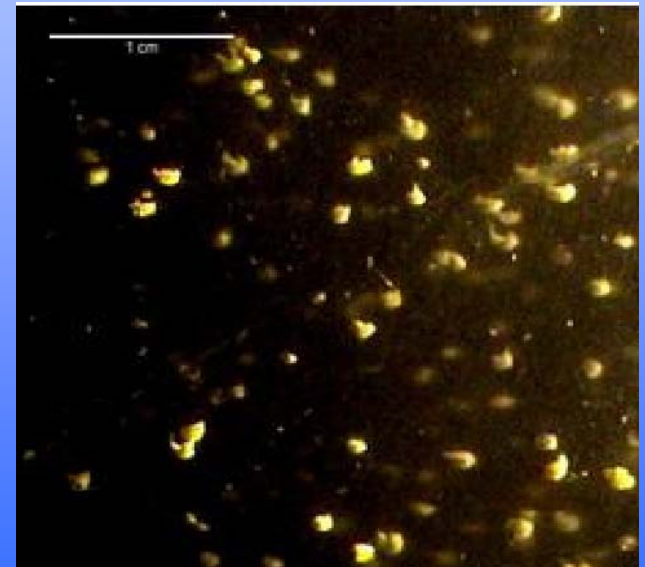
Effect of mineral on particle dynamics:

Calcifying cells (*E. huxleyi*) aggregated faster, were smaller, had higher settling velocities and excess density and mass than non-calcifying cells.

Experiments comparing calcified aggregates with showed a greater ballasting effect than for silicified aggregates (diatoms).



Uncalcified *E. hux.*



Calcified *E. hux.*

(Engel, A., J. Szlosek, L. Abramson, Z. Liu, and C. Lee. (Submitted) Investigating the effect of ballasting by CaCO₃ in *Emiliana huxleyi*: I. Formation, settling velocities and physical properties of aggregates. Deep- Sea Res. II)

(Engel, A., L. Abramson, J. Szlosek, Z. Liu, G. Stewart, D. Hirschberg, and C. Lee. (Submitted) Investigating the effect of ballasting by CaCO₃ in *Emiliana huxleyi*: II. Decomposition of particulate organic matter. Deep- Sea Res. II)

How fast do particles sink?

To compare different locations and times, we normalized for the different size SV bins:

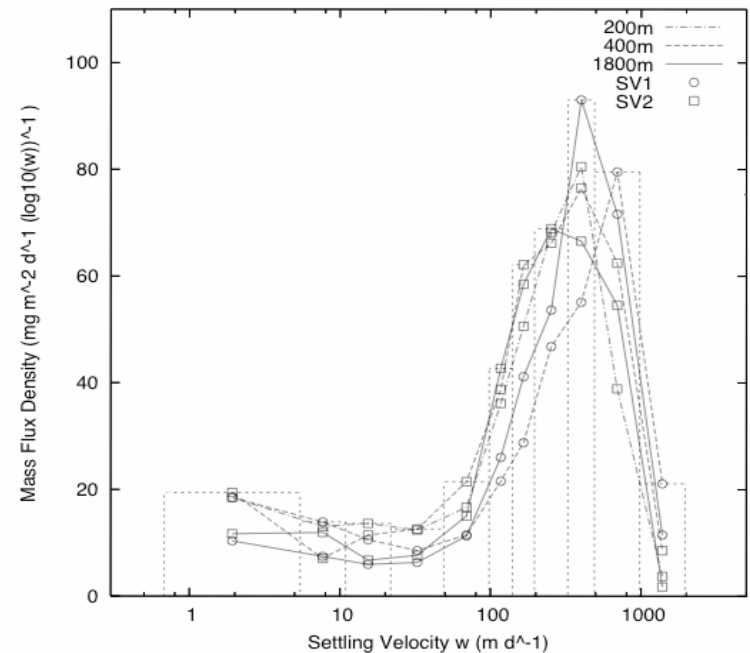
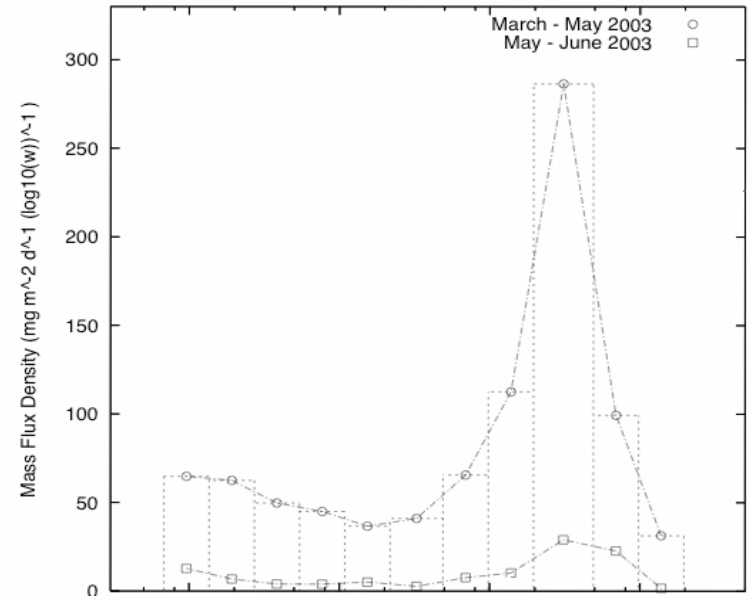
Mass flux density has the same relationship to mass flux that probability has to probability density: the area under the bar is mass flux, while the height of the bar is mass flux density.

The MFD-SV pattern was the same in March-May and May-June despite the large difference in mass flux.

In 2005, we had mass flux density as a function of settling velocity at 200, 400 and 1800m during March-April, the spring bloom period.

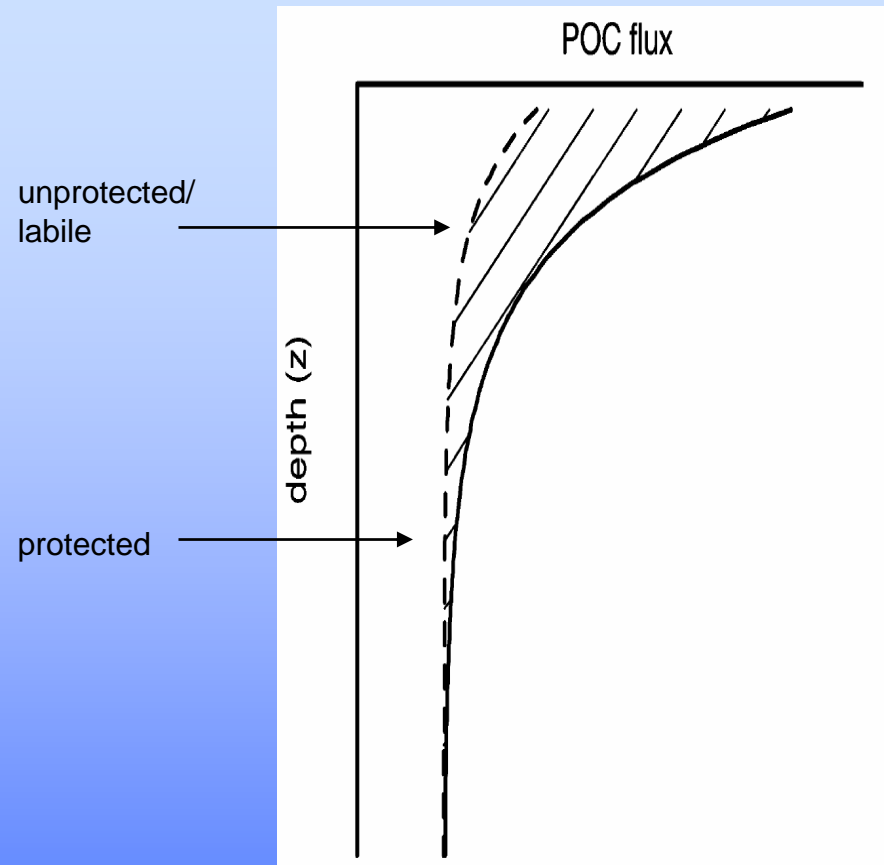
At this site at this time, the spectra are almost identical!

(Armstrong, R. A., C. Lee, M. L. Peterson, J. K. Cochran, S. G. Wakeham. 2007. Sinking velocity spectra and the ballast ratio hypothesis. Submitted to Deep Sea Research II)



Mineral – organic matter interactions??

What if ballast minerals on sinking particles physically protect a fraction of their associated organic matter, and that the ratio of organic carbon to ballast is key to predicting variability in export fluxes and sinking velocities of organic carbon.



OM-mineral aggregates can sink, but dissolution of the mineral ballast may slow the sinking, and/or degradation of an organic “glue” may allow aggregates to disaggregate and slow sinking.

Effect of mineral on particle degradation:

Calcifying cells (*E. huxleyi*) aggregated faster, were smaller, had higher settling velocities and excess density and mass than non-calcifying cells.

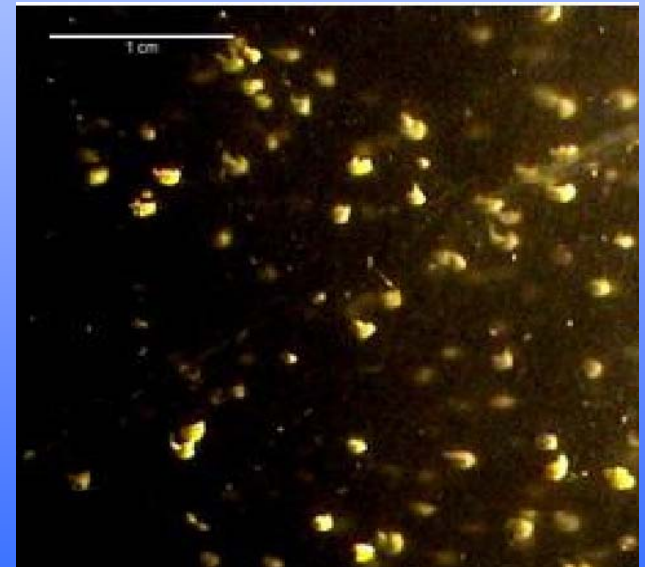
Experiments comparing calcified aggregates with showed a greater ballasting effect than for silicified aggregates (diatoms).

Cells without a shell were more subject to loss of OM than calcified cells.

Biogenic calcite helps in the preservation of POM by offering structural support for organic molecules.



Uncalcified *E. hux.*



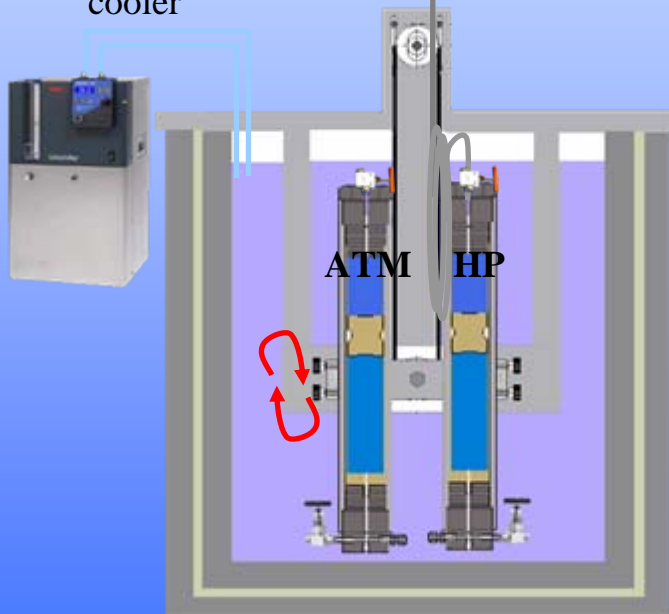
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Are degradation (or dissolution) rates constant as particles sink? What really are *in-situ* degradation rates – does increasing pressure slow degradation?

PASS: PArTicle Sinking Simulator

2) Temperature cooler



3) Piloted pressure generator

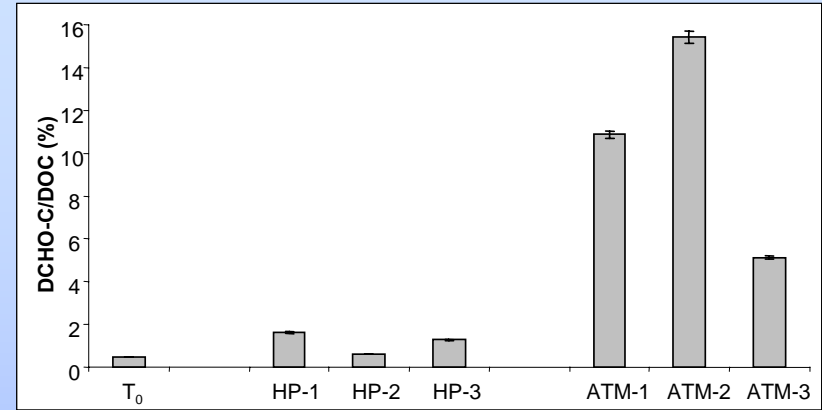
1) HPBs fitted within the revolving system incubated in water bath

(Tamburini, C., M. Goutx, C. Guigue, M. Garel, D. Lefèvre, B. Charrière, R. Sempéré, S. Pepa, C. Lee, B. Moriceau, M. L. Peterson, S. Wakeham. Novel technique to simulate fall of particles through the water column to evaluate effect of pressure on prokaryotic mineralization. Submitted to Deep-Sea Res. II)

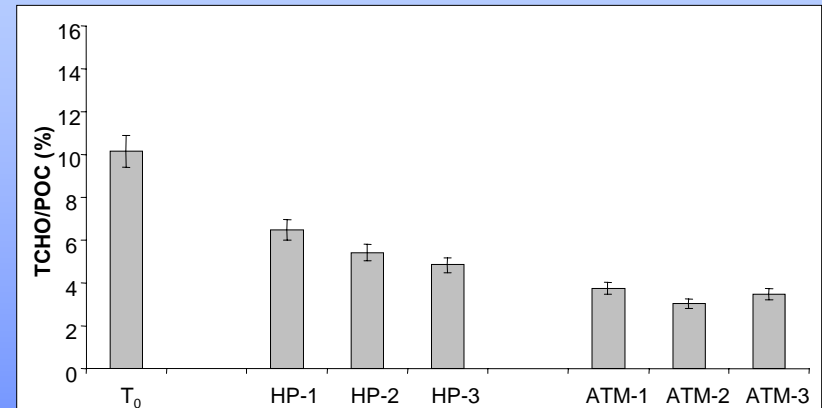
Comparison of high pressure vs. atmospheric pressure incubations show considerable difference in organic matter compositions.

Therefore incubation experiments carried out at atmospheric pressure may not accurately represent degradation as sinking particles are exposed to increasing ambient pressures. (Is more polysaccharide “glue” produced at higher pressures?)

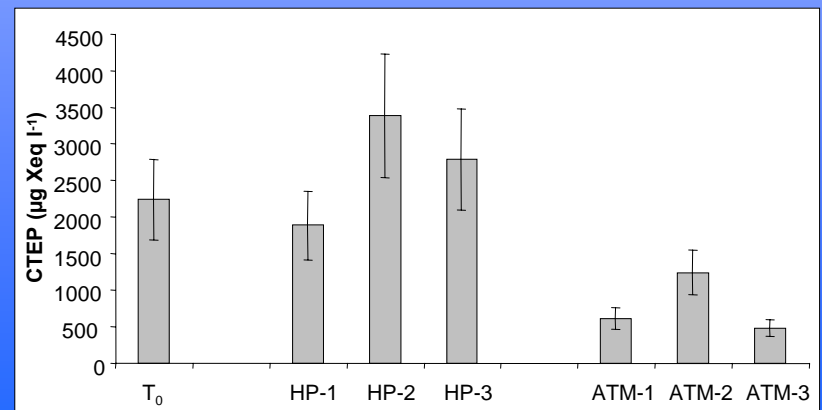
a)



b)



c)



(Tamburini, C., M. Goutx, C. Guigue, M. Garel, D. Lefèvre, B. Charrière, R. Sempéré, S. Pepa, C. Lee, B. Moriceau, M. L. Peterson, S. Wakeham. Novel technique to simulate fall of particles through the water column to evaluate effect of pressure on prokaryotic mineralization. Submitted to Deep-Sea Res. II)

Some final thoughts –

Particle dynamics:

Slowly sinking particles collide with other particles to form larger aggregates, but when they get too large and start sinking too quickly, they fall apart because of the high shear.

Sinking velocities:

Basically, particle size and sinking velocity adjust to changes in particle density, always yielding the same sinking velocity spectrum.

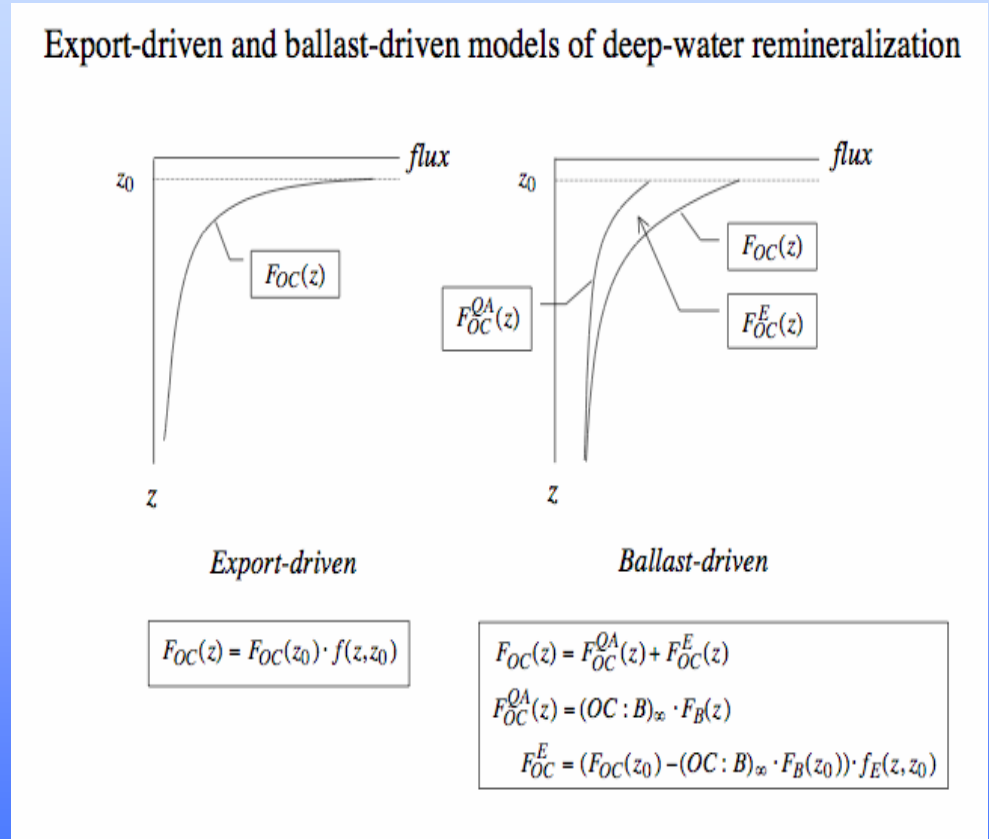
Decomposition:

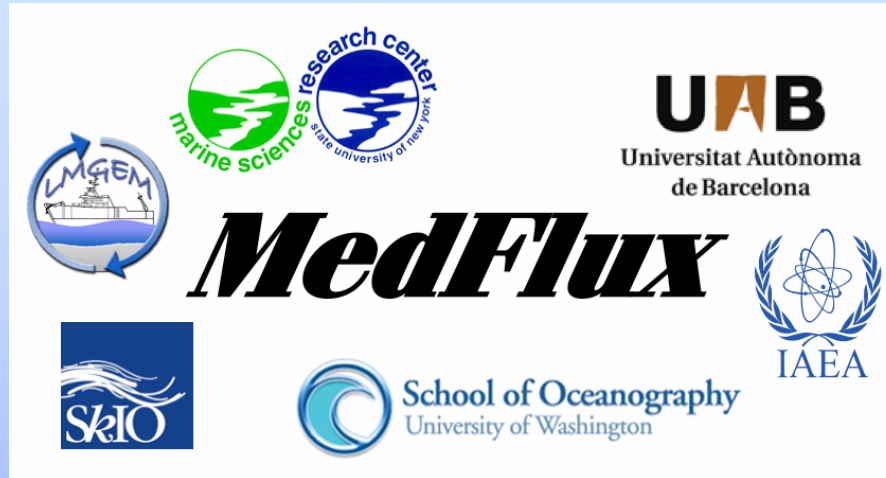
Because of this constancy, remineralization time is directly proportional to depth in remineralization profiles, enabling calculation of absolute rates.

More final thoughts –

Export-driven flux: particulate organic carbon (POC) fluxes are determined uniquely by the POC flux at some "export horizon", independent of any other factors. Example: the "Martin curve."

Ballast-driven flux: There are two dominant components to POC flux, one quantitatively associated with, and perhaps protected by, ballast (silicate and carbonate minerals, and dust) and two, a labile POC phase that is remineralized as a function of depth only.





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See <http://www.msrc.sunysb.edu/MedFlux/> for more information.

