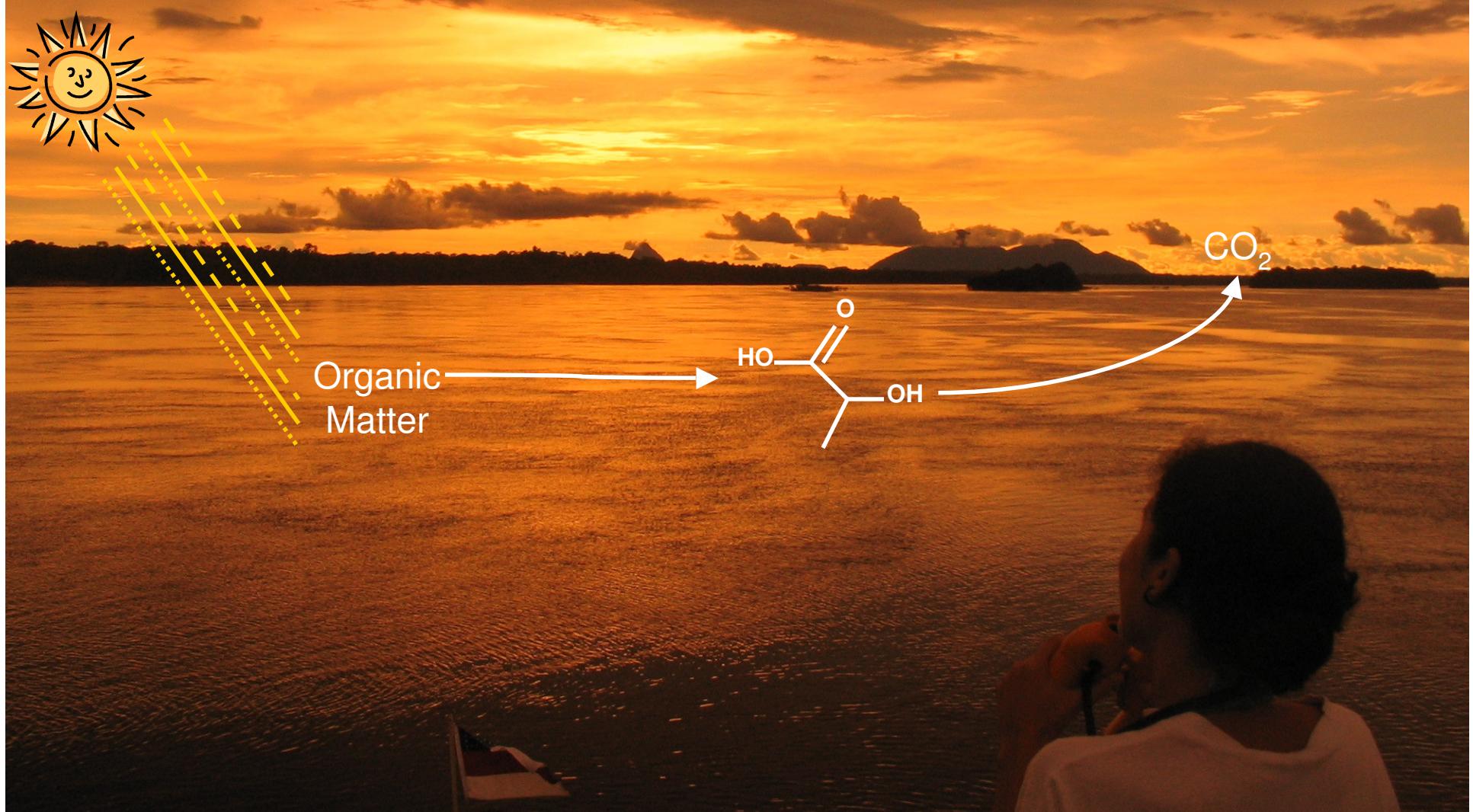


# Photochemical production of low molecular weight organic acids in the Rio Negro

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# Photo-oxidation: The photochemical production of biolabile LMWOAs fuel *in-situ* respiration in the Rio Negro and possibly other rivers of the Amazon basin?

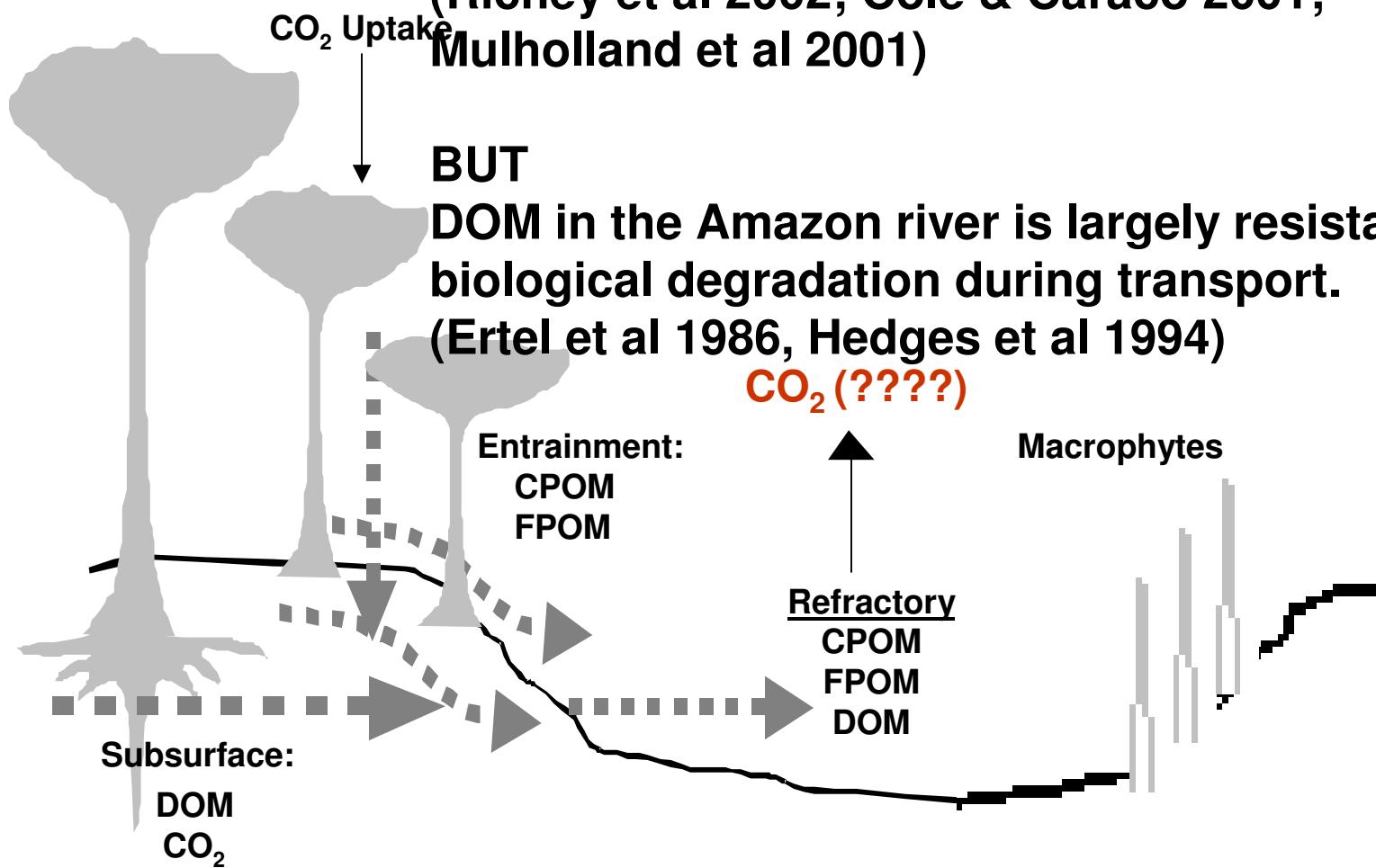


## Motivation

### $\text{CO}_2$ – Respiration Paradox

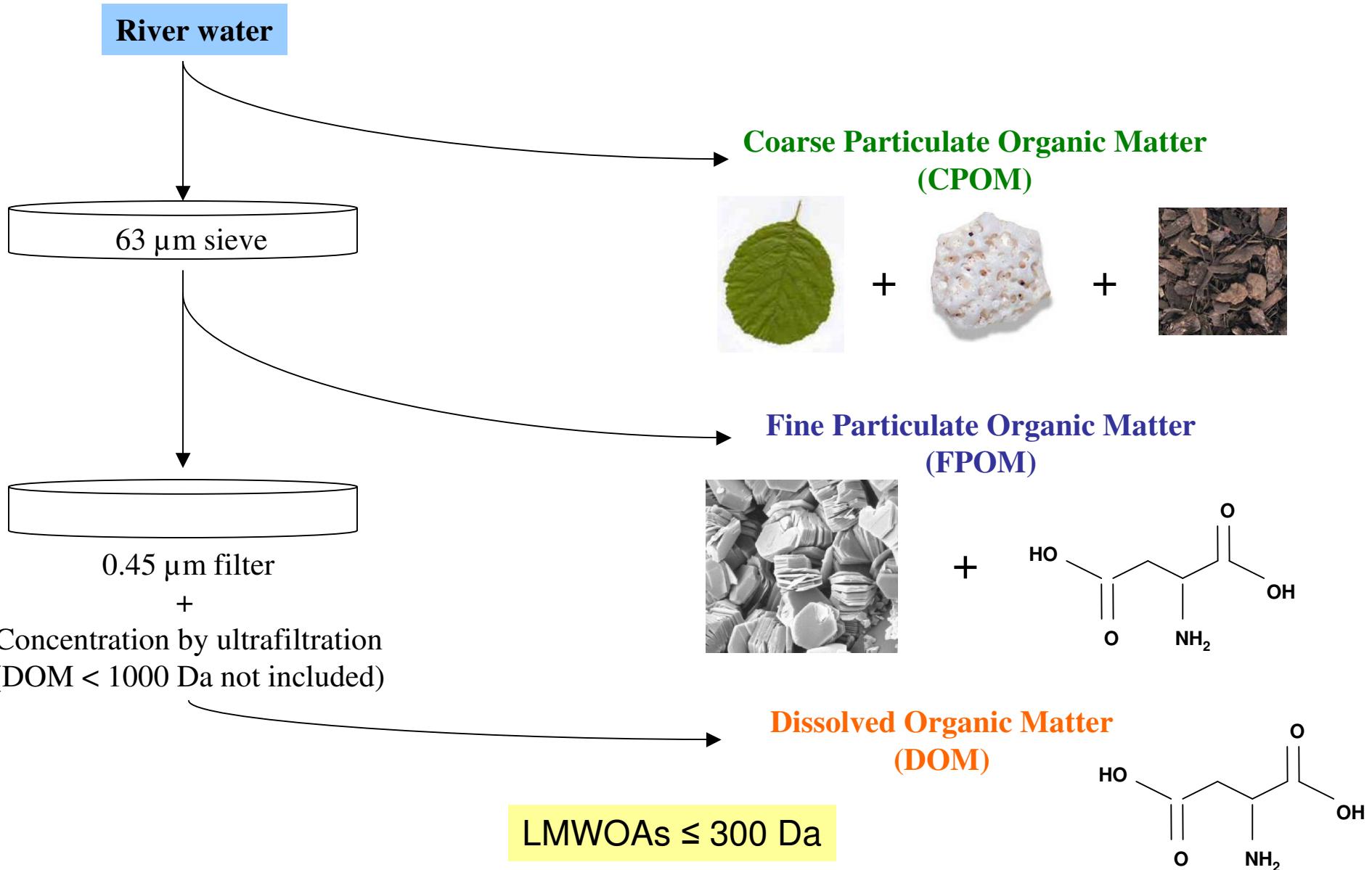
High  $\text{CO}_2$  concentrations in river channels are thought to derive from in-situ respiration of organic matter.

(Richey et al 2002; Cole & Caraco 2001;  
Mulholland et al 2001)



## Motivation

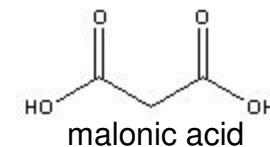
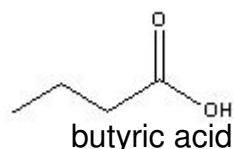
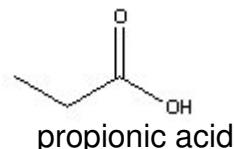
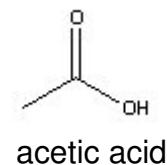
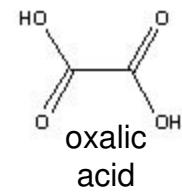
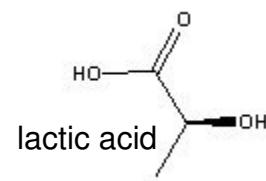
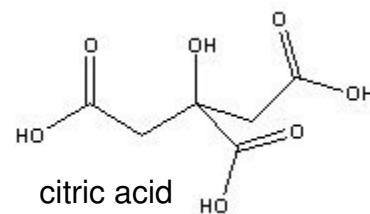
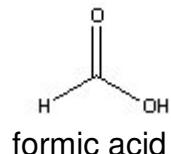
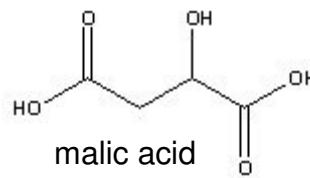
Is unmeasured organic matter (“Mystical” Organic Carbon) fueling *in-situ* respiration?



Pre-concentration methods for organic analyses omit 25 – 40 % of the DOM transported by the Amazon river.

# What are LMWOAs and which are important in rivers?

LMWOA	Production Process (based on published papers)
Acetic acid	anaerobic, photochemical, soils, rain
Formic acid	photochemical, rain
Lactic acid	anaerobic
Butyric acid	anaerobic
Propionate acid	anaerobic, soils
Oxalate acid	photochemical, soils
Malonate acid	photochemical, soils
Malic acid	soils
Citric acid	soils



## Motivation

### Soils: Ambient LMWOA concentrations are low, but fluxes are high.

- Low LMWOA concentrations (1 – 2 % of total DOC) but rapid cycling in soils.
- Estimated to provide labile substrate to fuel 30 % of total soil CO<sub>2</sub> respiration flux. vanHees et al 2005; Soil Biology & Biochemistry)

### Oceans and Lakes: Photochemical degradation of DOM produces labile by-products.

- In a humic lake, photochemical production of LMWOAs > microbial utilization = accumulation at surface. (Bertilsson & Tranvik 1998; L&O)
- Photochemical degradation may be mechanism for removal of refractory, terrestrial DOM from the ocean. (Mopper et al 1991; Nature)
- Other photochemical products include CO<sub>2</sub> (Graneli et al 1996; L&O) & nutrients (Bushaw et al 1996; Nature)

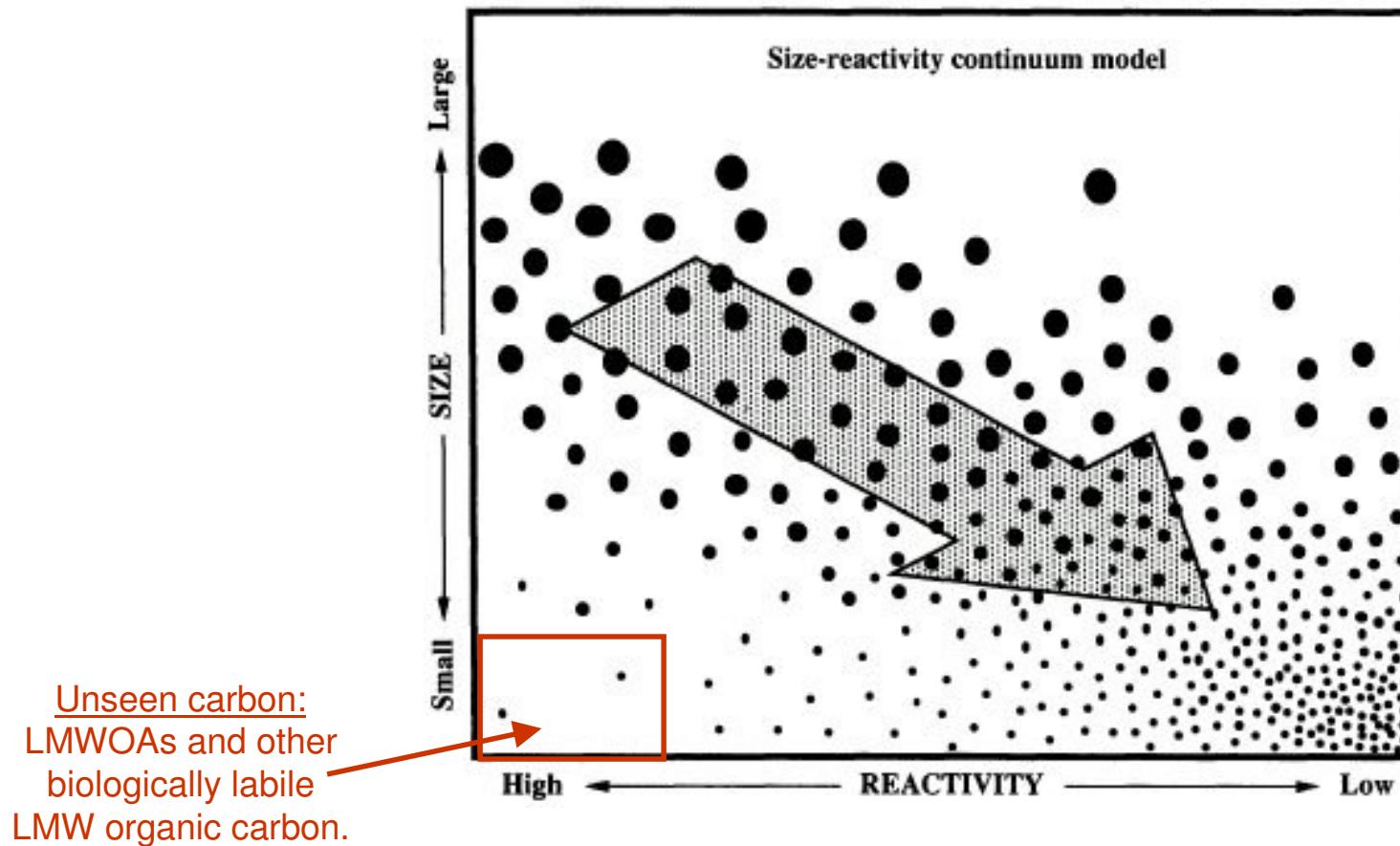
### Could LMWOA dynamics be similar in rivers?

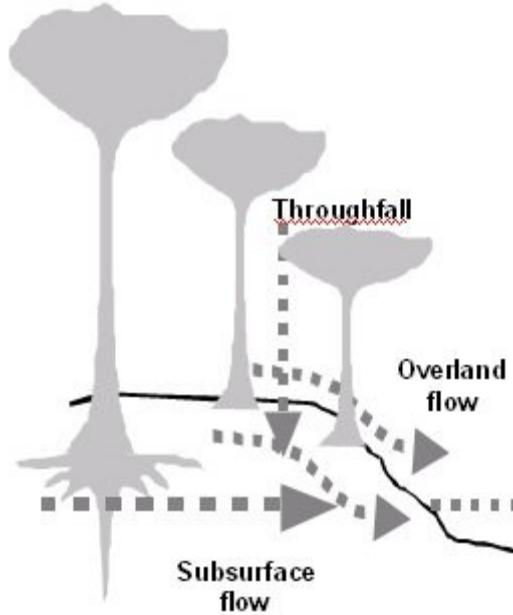
- Riverine humic DOM is photochemically labile (Bertilsson et al 1999)
- Riverine POM is also photochemically labile (Mayer et al 2006)

# Significance

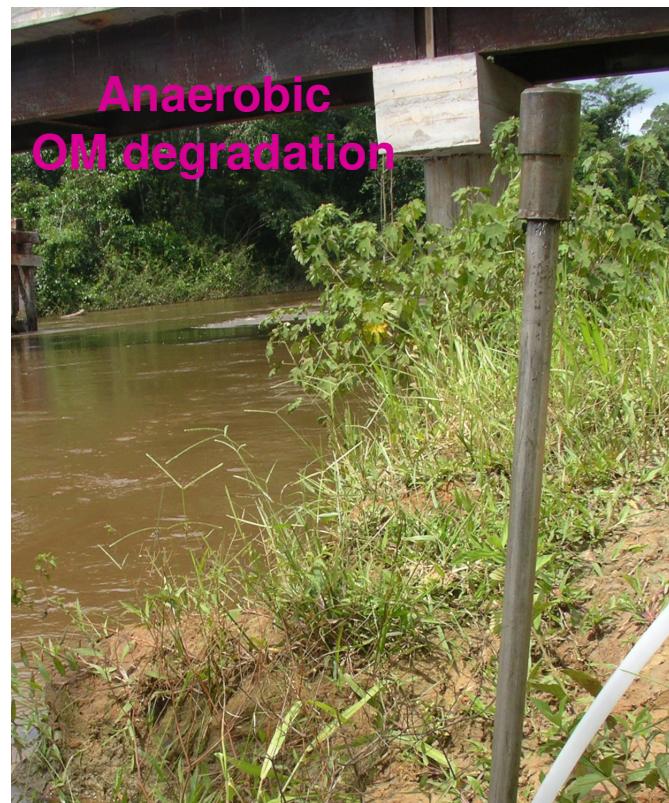
**H<sub>0</sub>:** LMWOA concentrations in the Amazon river are low, but rapid turnover times result in a large contribution to *in situ* respiration & direct CO<sub>2</sub>

LMWOAs and the size reactivity continuum model (Amon & Benner 1996)





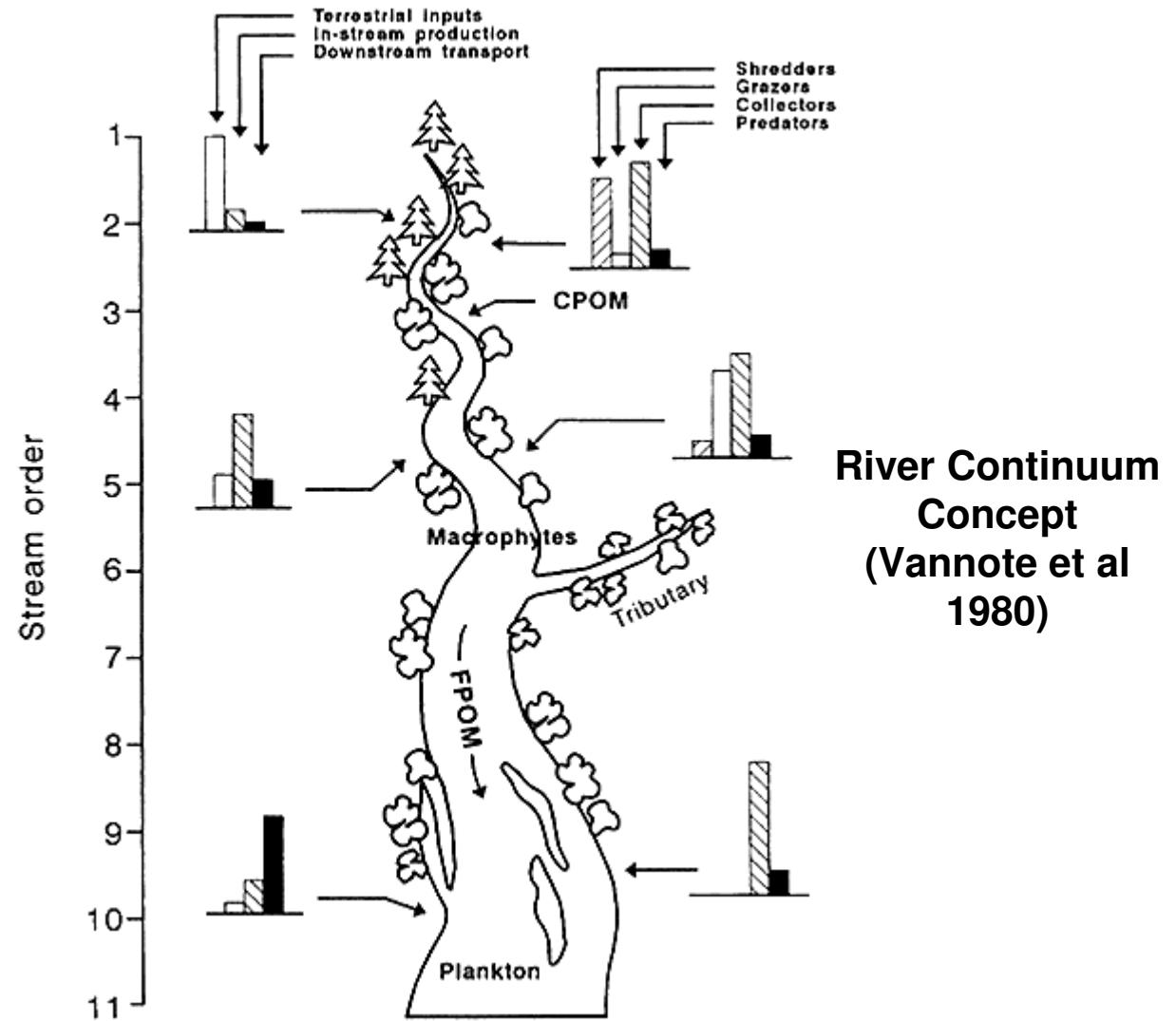
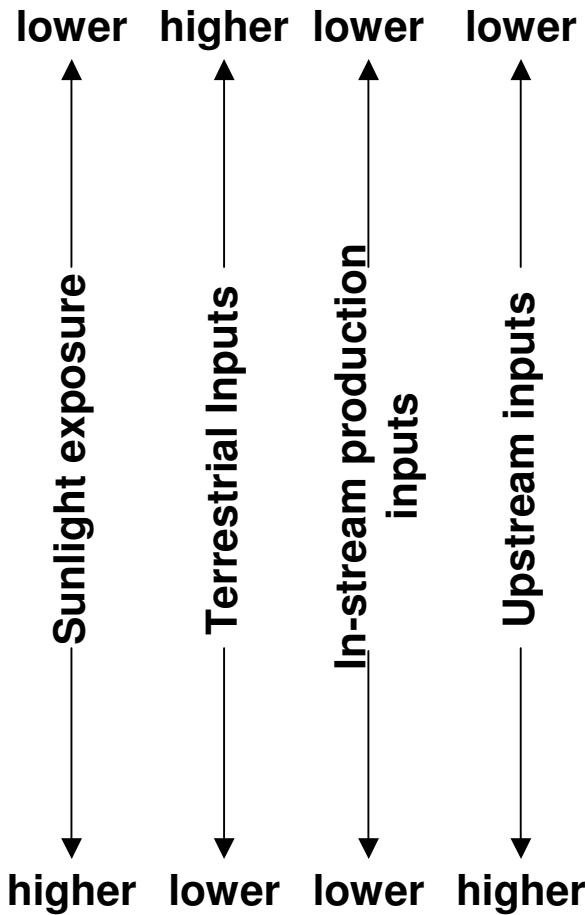
## Potential Sources



## LMWOAs



# Sources are scale-dependent

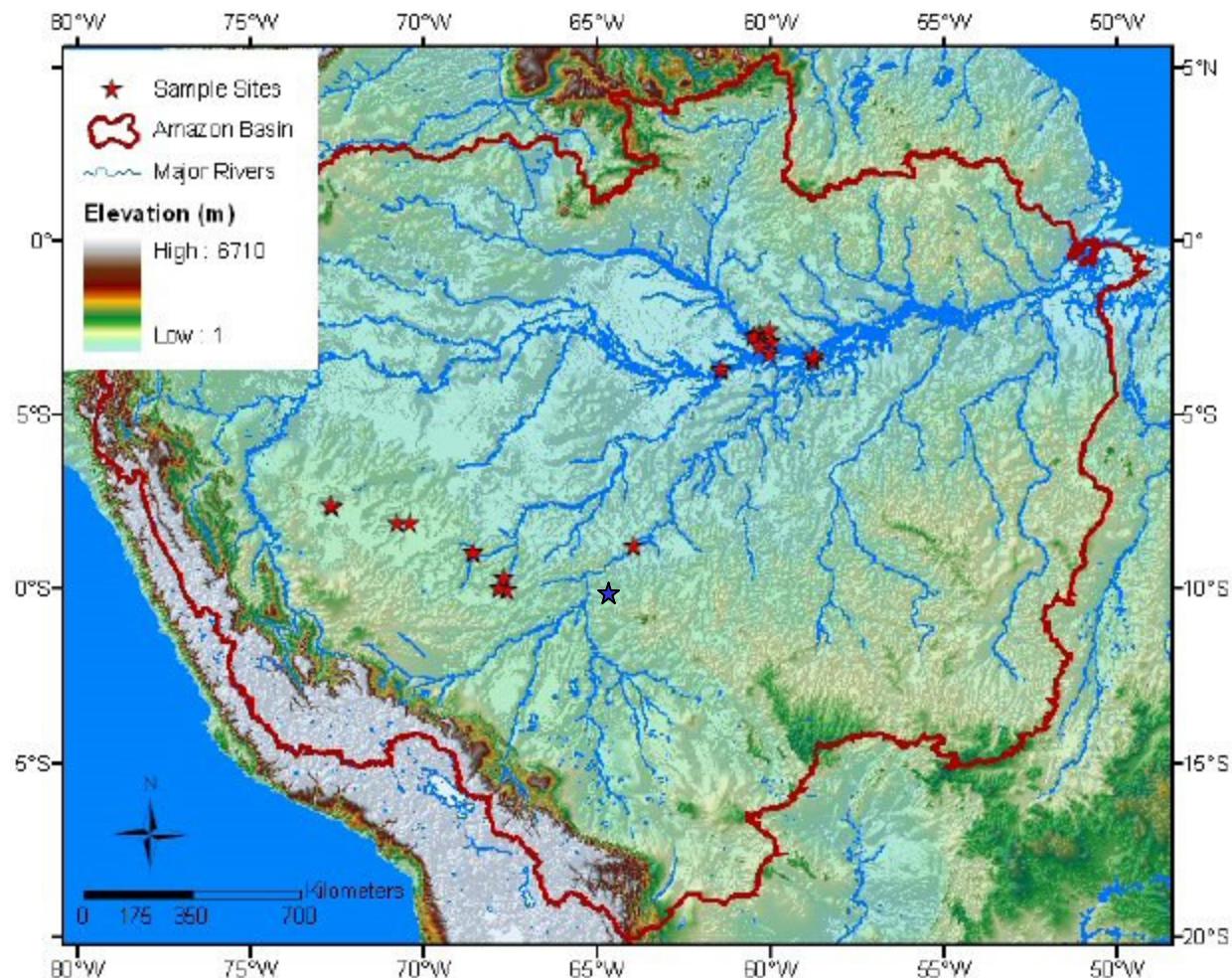


- At small scales, discrete storm events supply large quantities of LMWOAs to streams.
- At large scales, LMWOAs fueling *in situ* respiration must be produced in or very near river cl

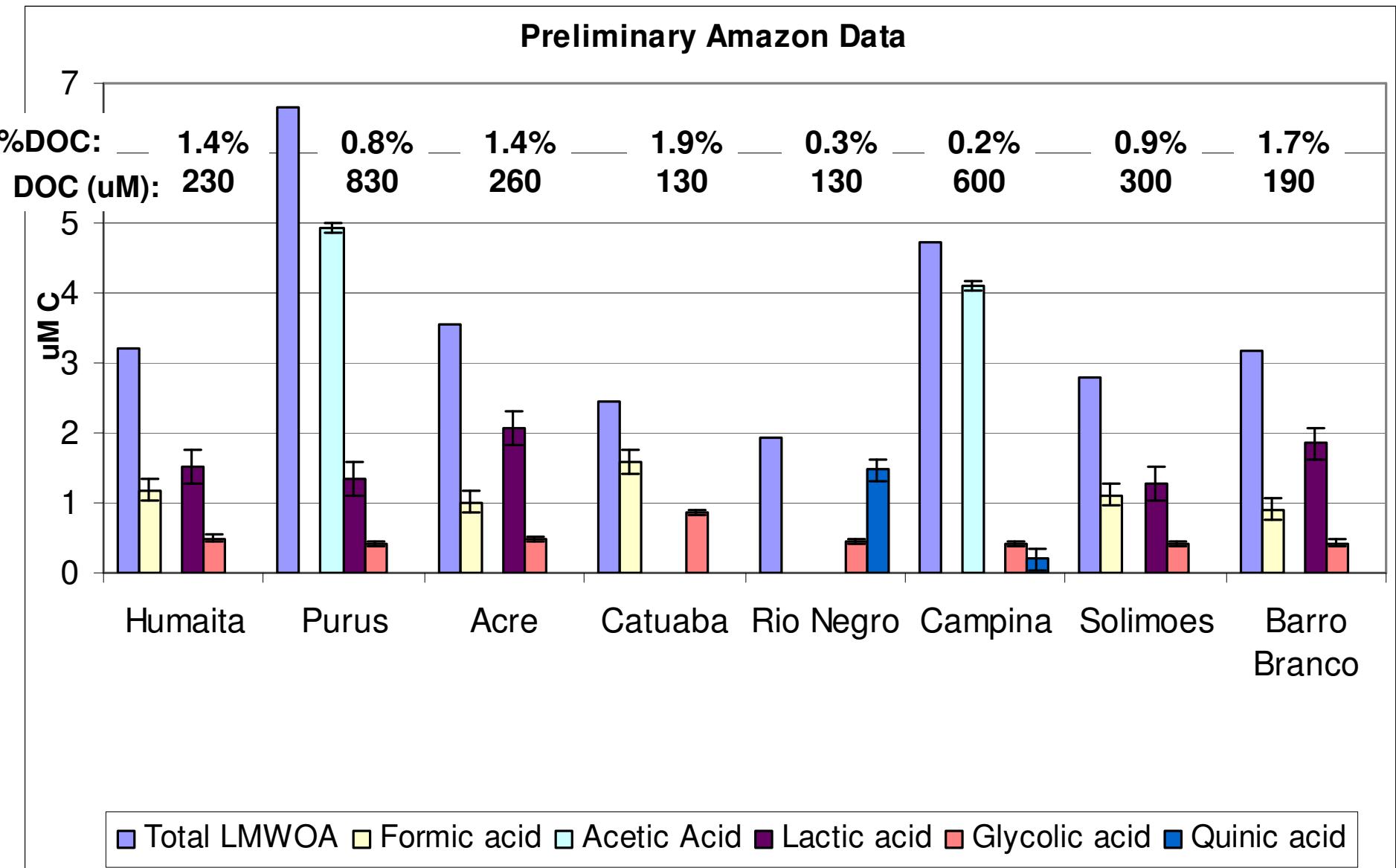
# Study Sites

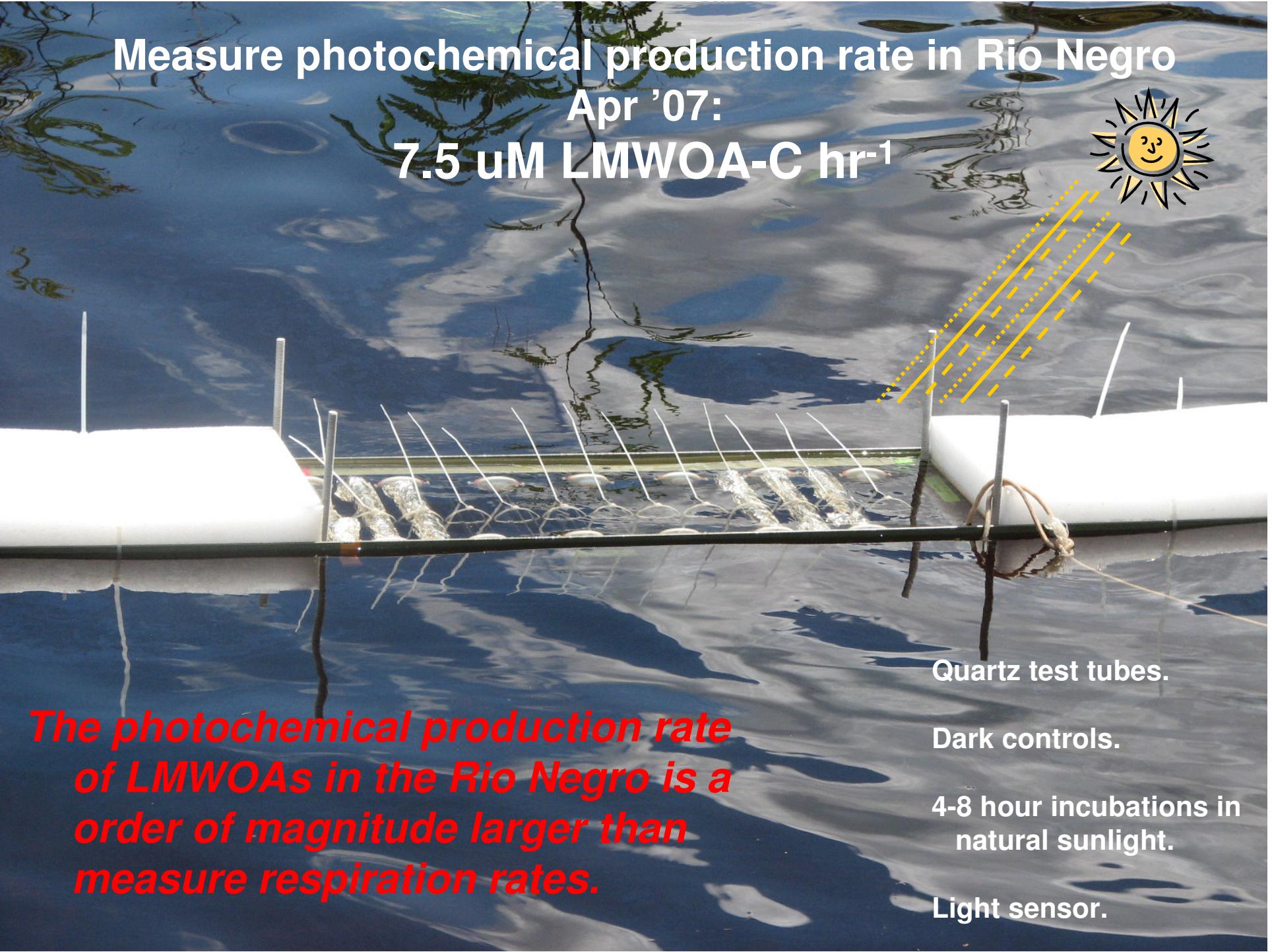
★ Rio Negro  
Rio Solimoes  
Campinas  
Barro Branco  
Rio Purus  
Rio Acre  
Humaita  
Catuaba

★ Rancho  
Grande



## Ambient LMWOA concentrations are low relative to total DOC concentration.





Measure photochemical production rate in Rio Negro

Apr '07:  
7.5  $\mu\text{M}$  LMWOA-C  $\text{hr}^{-1}$



Quartz test tubes.

Dark controls.

4-8 hour incubations in  
natural sunlight.

Light sensor.

*The photochemical production rate  
of LMWOAs in the Rio Negro is a  
order of magnitude larger than  
measure respiration rates.*

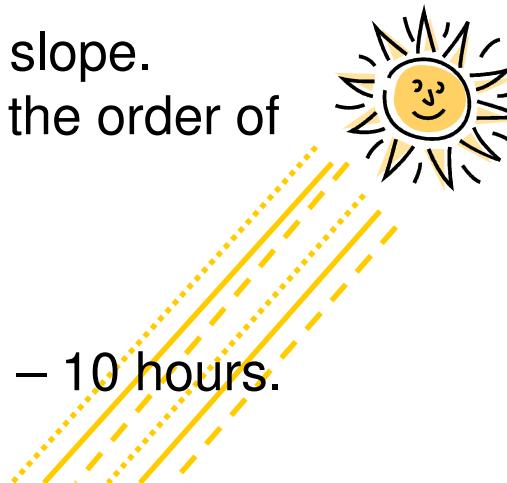
# Future Work

**Does photochemical degradation of DOM at the river surface produce enough LMWOAs to fuel respiration throughout the water column?**

## Surface renewal rate:

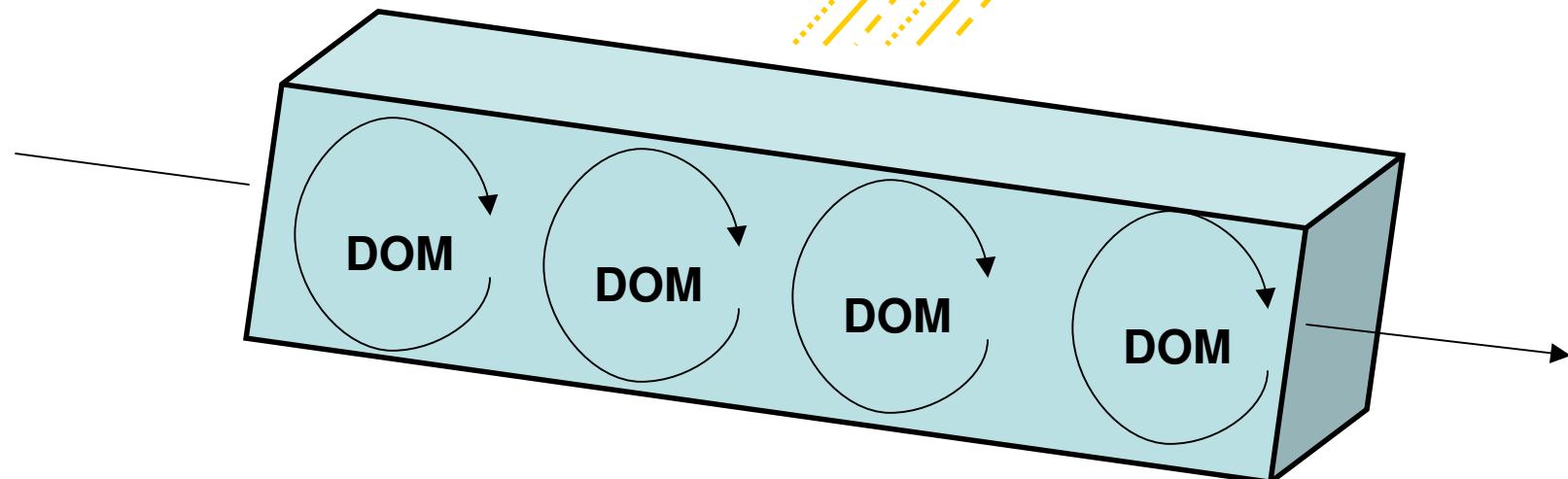
Use current velocity, depth and surface slope.

Vertical mixing time for Rio Negro is on the order of hours.



## In soils:

Mean residence time of LMWOAs = 1 – 10 hours.



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