

Organic matter cycling in anoxic (no oxygen) Marine sediments



There are many examples where oxygen becomes exhausted in sediments

How is organic matter oxidized without oxygen?

What is the origin of petroleum source rocks?

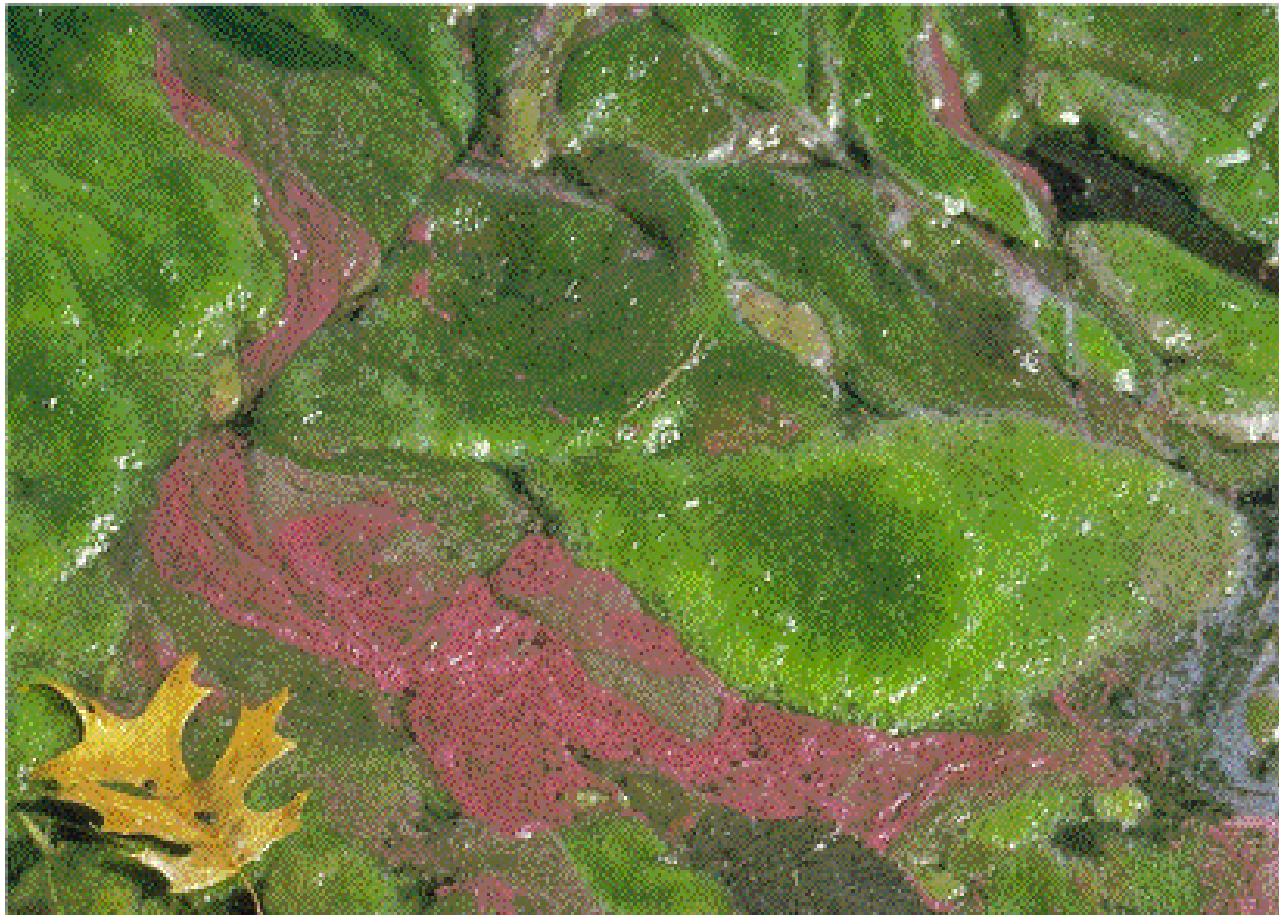
What biological communities can exist in anoxic sediments and how do they function?

How does biogeochemical cycling in anoxic marine sediments affect global C:N:S cycles?

Dysaerobic and anoxic environments are devoid of higher heterotrophic organisms. Biogeochemical cycling, including photosynthesis and C respiration are carried out by bacteria



Bacterial communities are much more metabolically specialized than higher heterotrophs. The communities are strictly segregated according to the environmental conditions. This leads to biogeochemical zoning of microbes and chemical species (nutrients, carbon dioxide, methane, etc.).



(a)

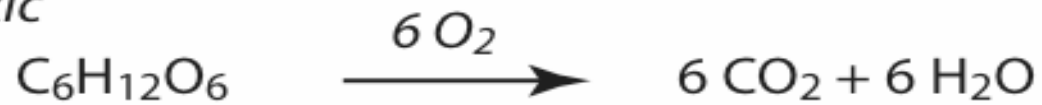
These communities are widespread in the Great Sippewissett Marsh in West Falmouth.



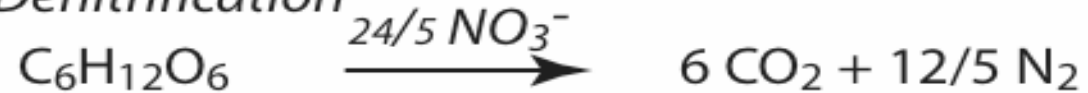
Oxidation of organic matter in marine sediments

| Reaction | ΔE (KJ/mole) | Capacity (mmoles/L sed) |
|-------------------------------------|----------------------|----------------------------|
| $O_2 \longrightarrow CO_2$ | -475 | 0.85 |
| $NO_3^- \longrightarrow N_2 + CO_2$ | -448 | 0.05 |
| $Mn(IV) \longrightarrow Mn(II)$ | -349 | 2-22 |
| $Fe(III) \longrightarrow Fe(II)$ | -114 | 14-28 |
| $SO_4^{2-} \longrightarrow S^{2-}$ | -77 | 56 |
| $CO_2 \longrightarrow CH_4$ | -58 | |

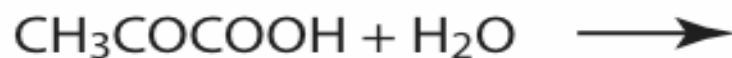
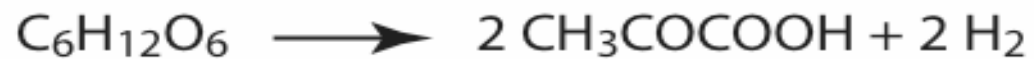
Oxic



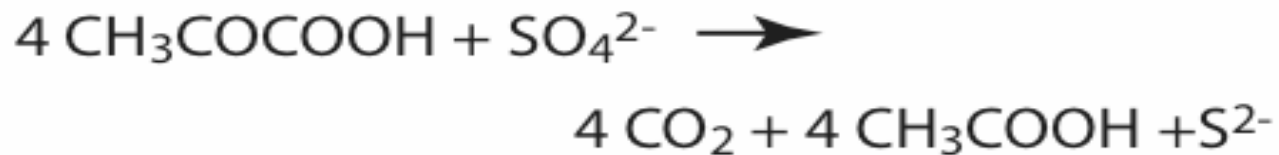
Denitrification



Fermentation



Sulfate reduction



Methanogenesis



Organic Matter

proteins 50% C, 80% N (soluble/structural)
polysaccharides 20-30% C, 10% N (soluble/structural)
nucleic acids 10% C, 5% N, 50% P
lipids 10% C, few % N

oxic degradation
nitrate reduction



soluble constituents
 CO_2 , NO_3^- , HPO_3^-

proteins (structural), peptides
polysaccharides (structural), oligosaccharides,
sugars, nucleic acids, lipids

extracellular hydrolysis
fermentation



CO_2 , NH_3 , HPO_3^- , H_2

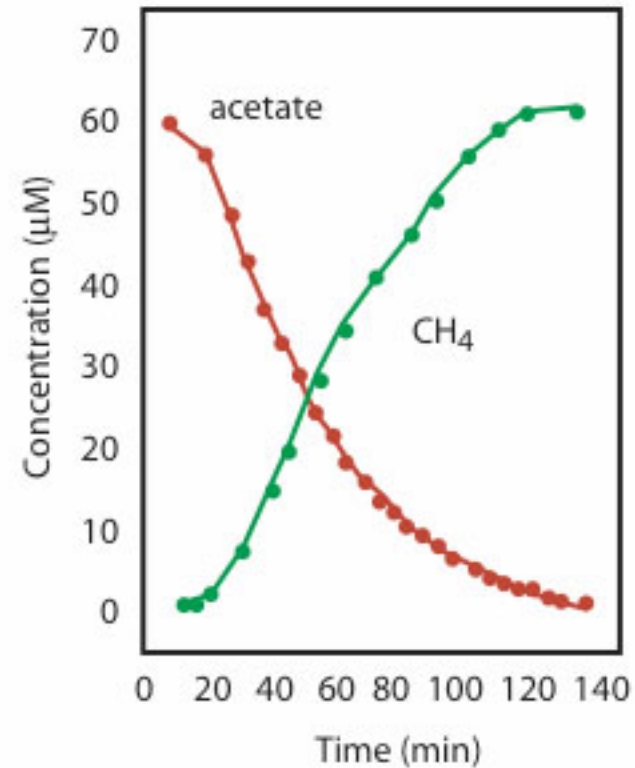
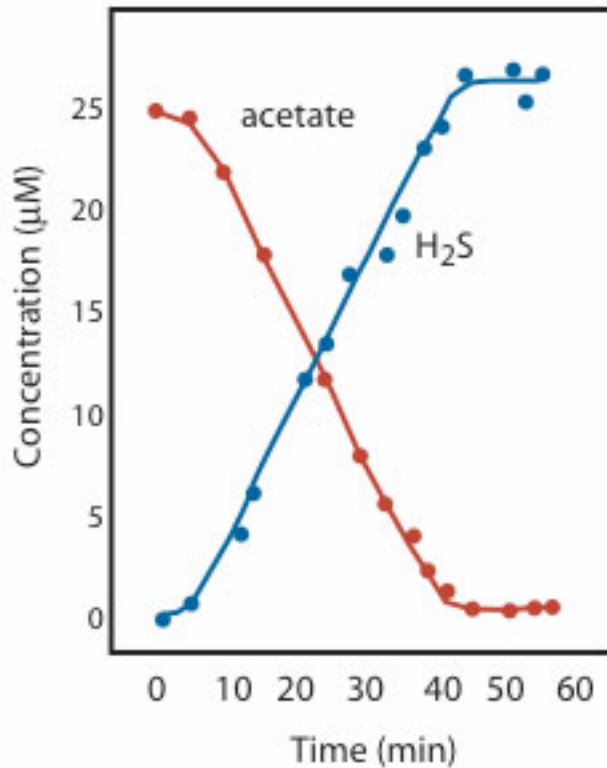
volatile fatty acids

sulfate reduction
methanogenesis



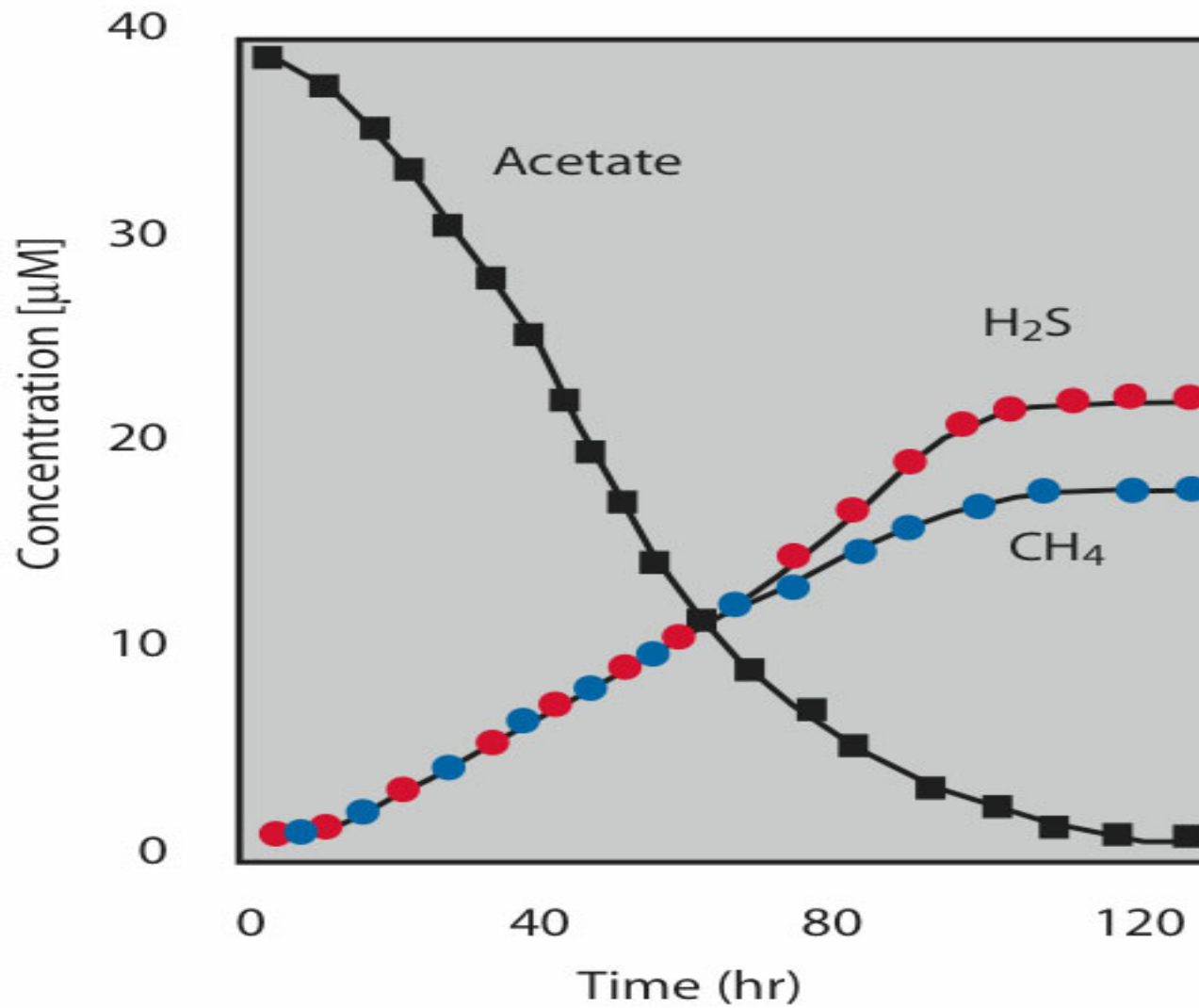
CO_2 , CH_4 , NH_3 , HPO_3^- , H_2S

Consumption of acetate by sulfate reducing and methanogenic bacteria



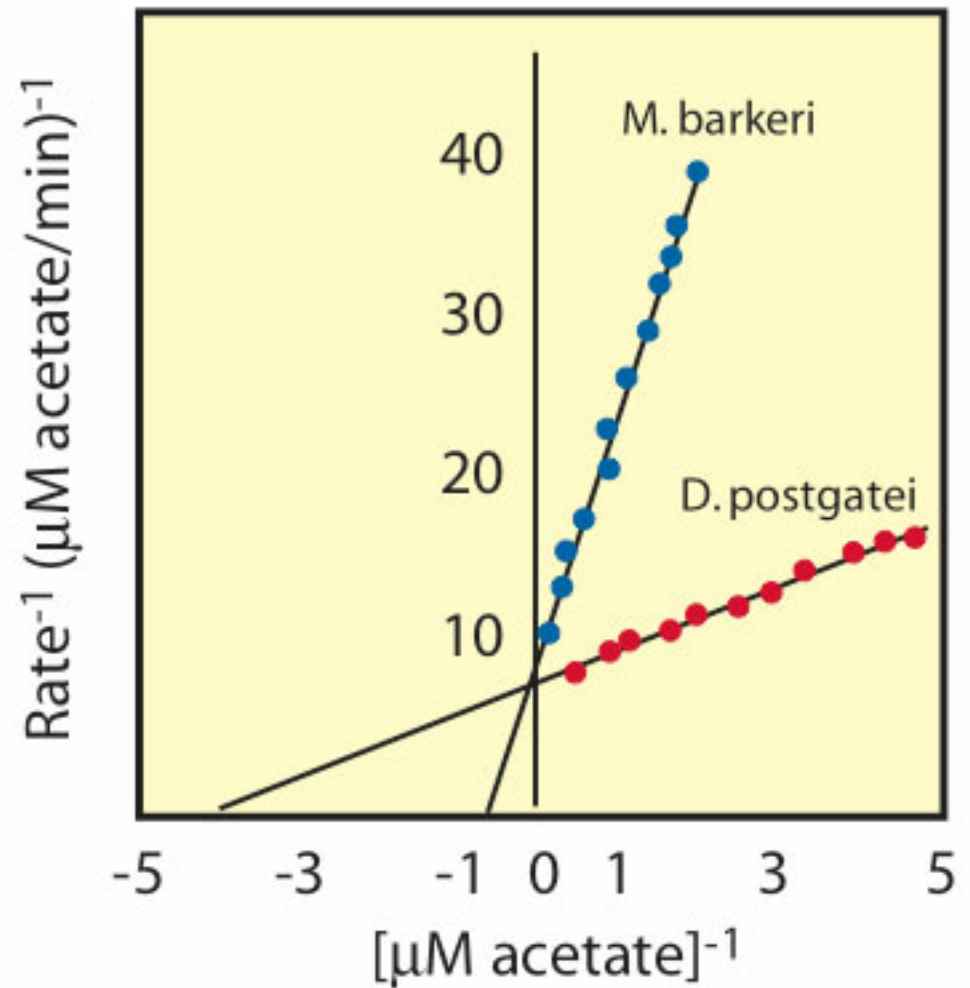
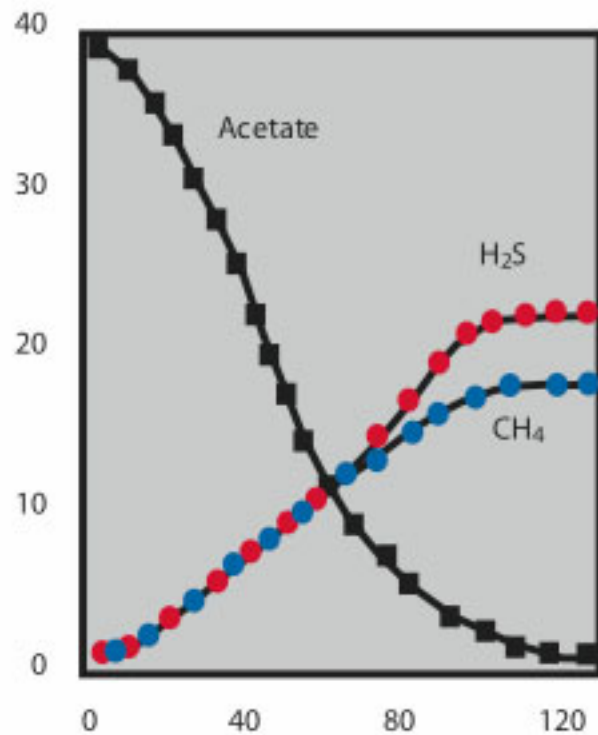
Acetate = CH₃COOH
Volatile Fatty Acid (VFA) = CH₃RCOOH

Competition for acetate between
Desulfobacter postgatei and *Methanosarcina bakerii*

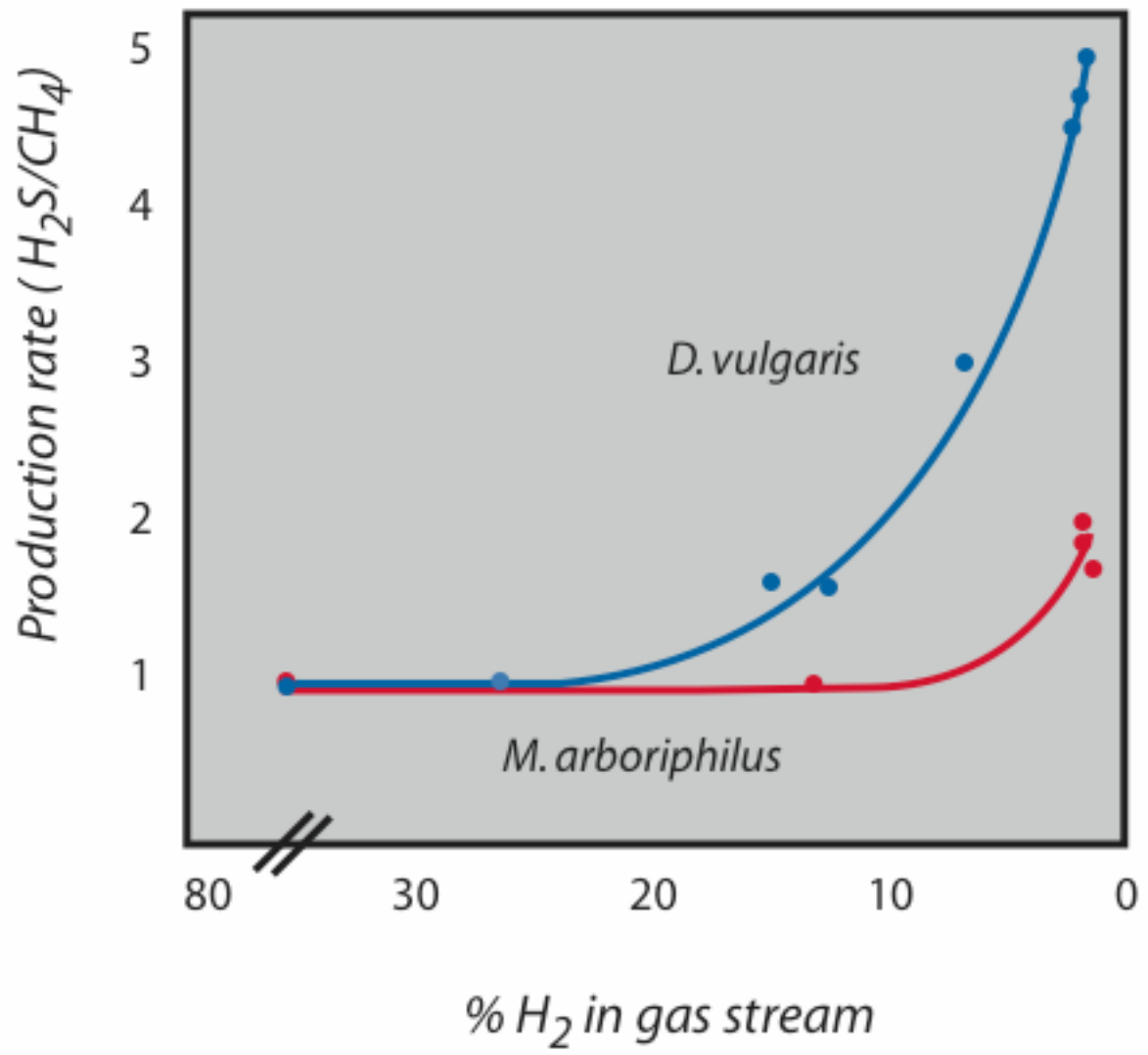


Double reciprocal plot of rate vs Acetate concentration

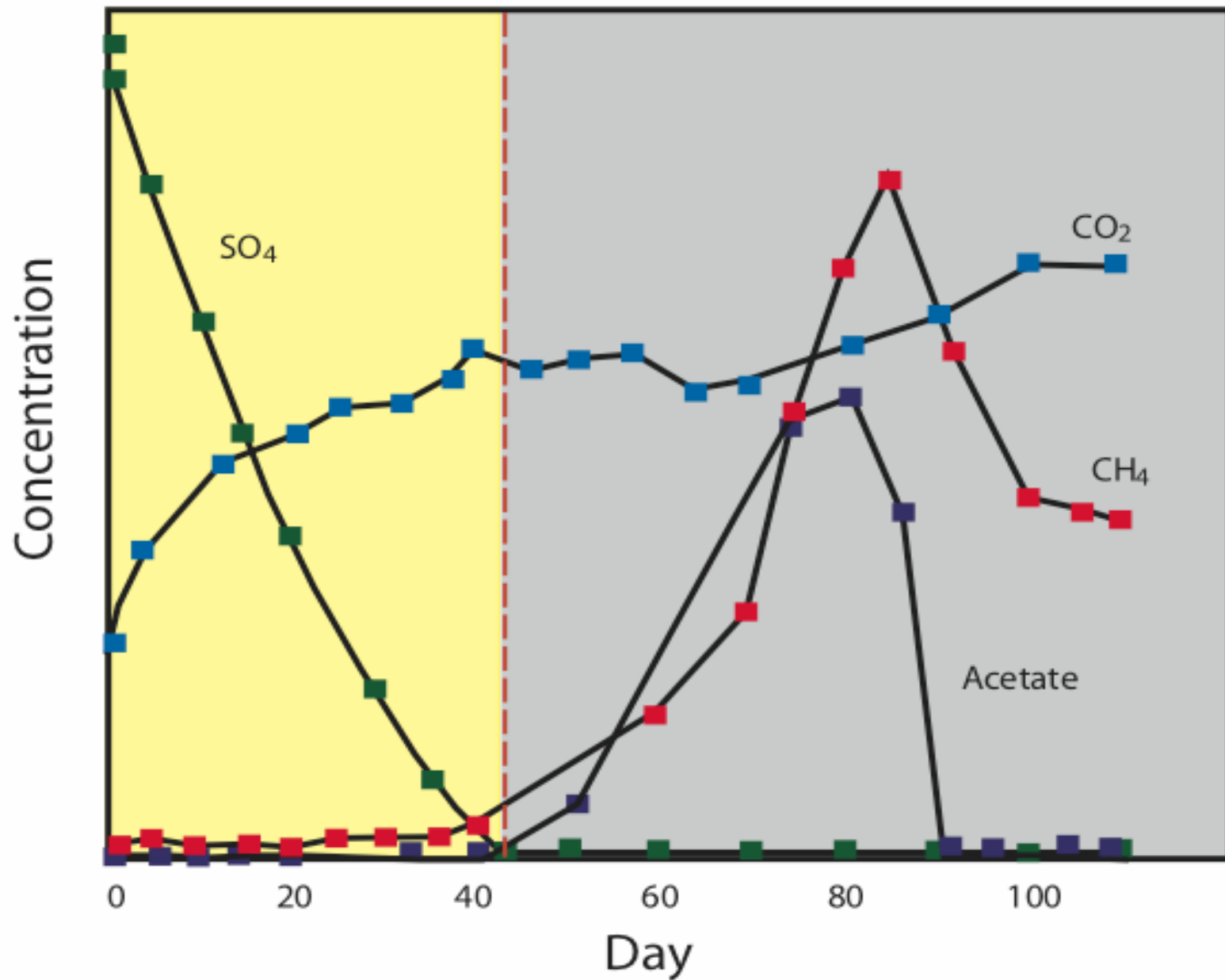
Competition for acetate between
Desulfobacter postgatei and *Methanosarcina barkeri*



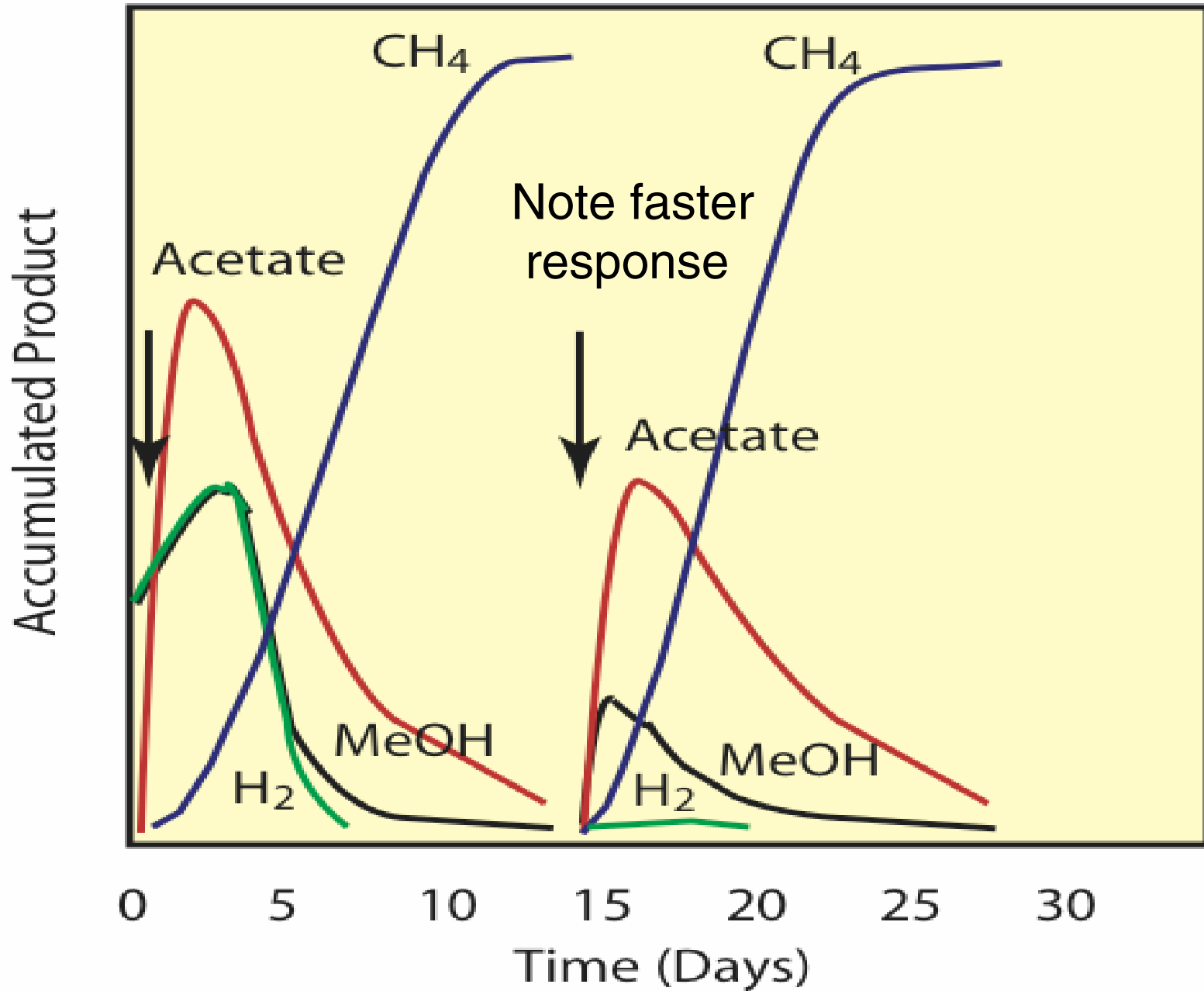
Competition for hydrogen between sulfate reducing and methanogenic bacteria



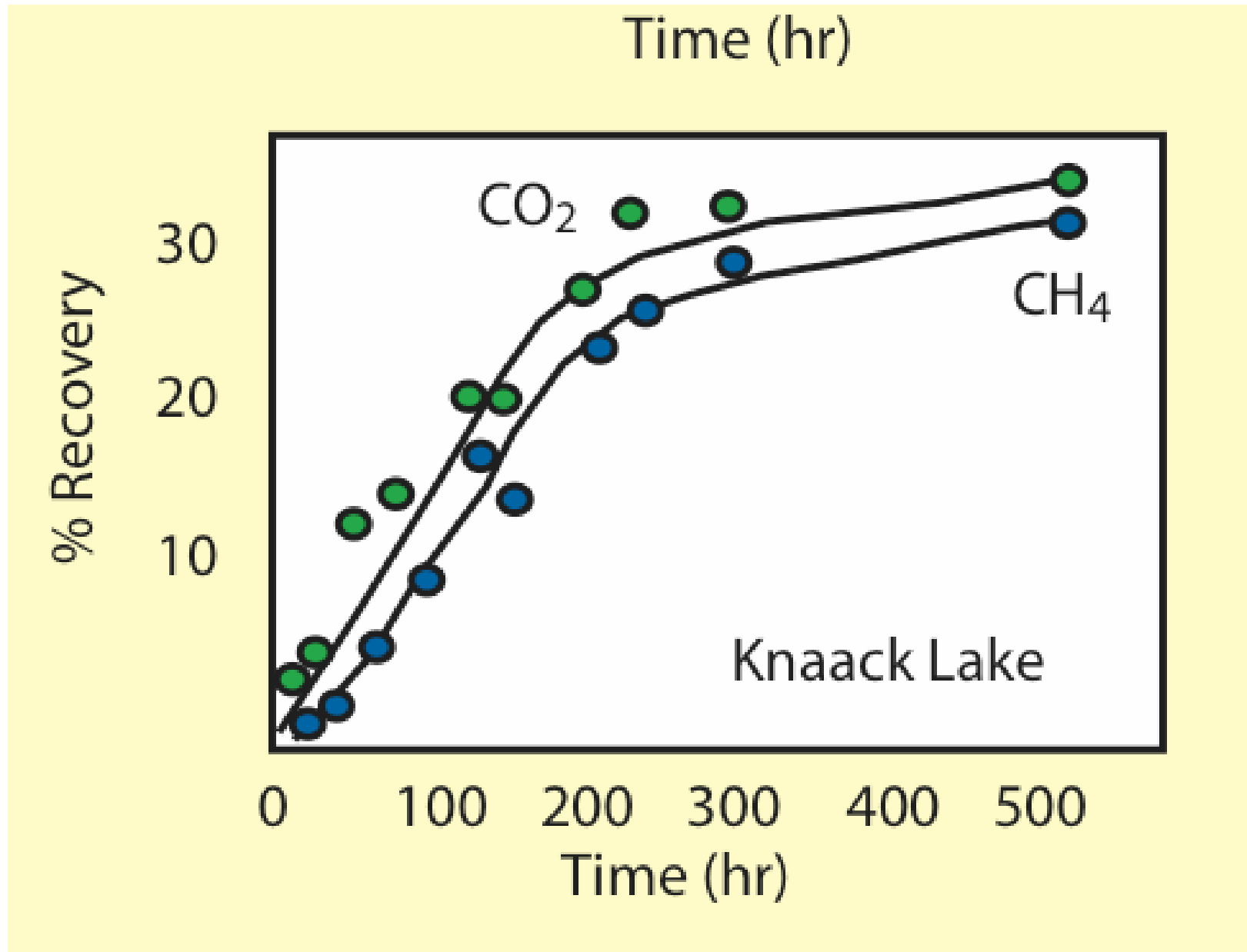
Changes in pore water concentrations during a 114 day incubation



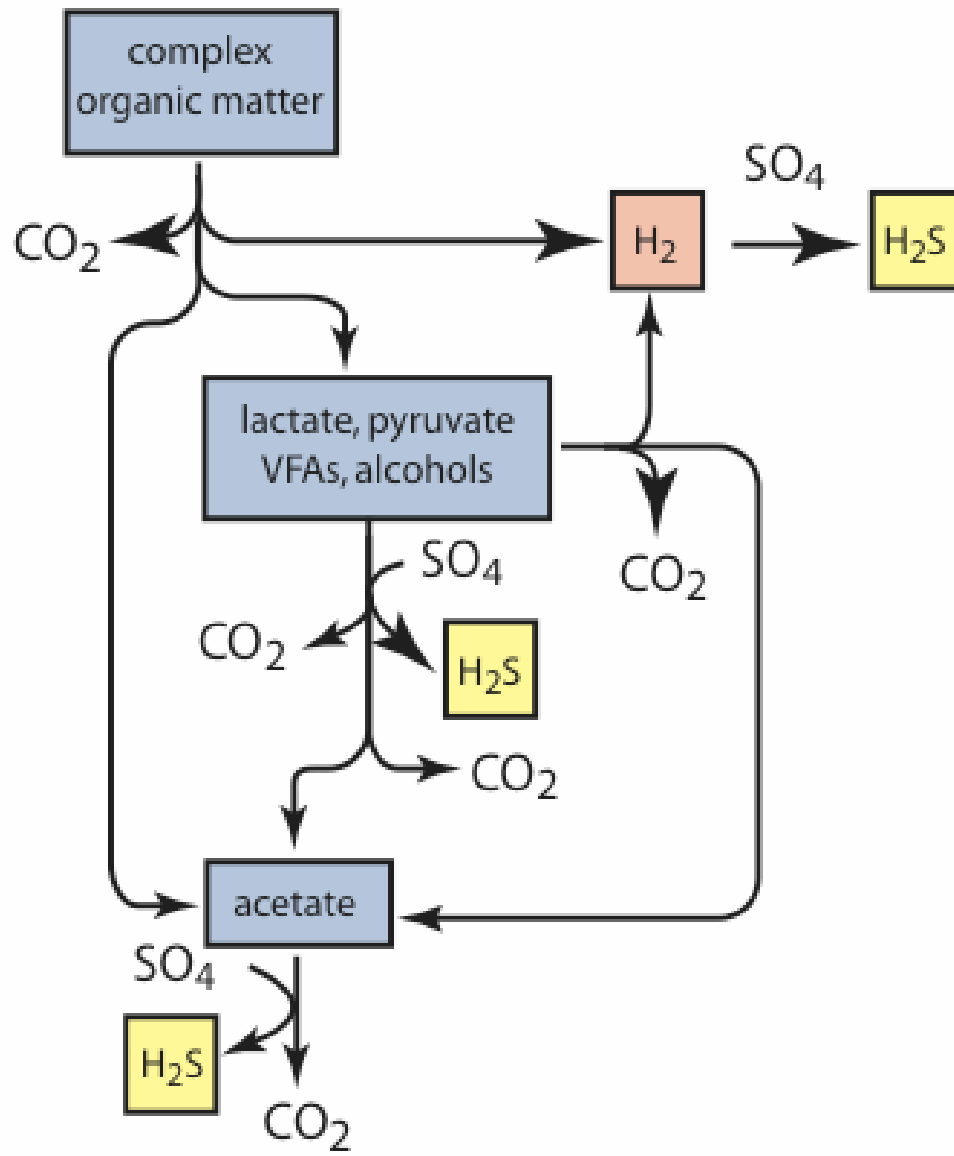
Anaerobic degradation of pectin



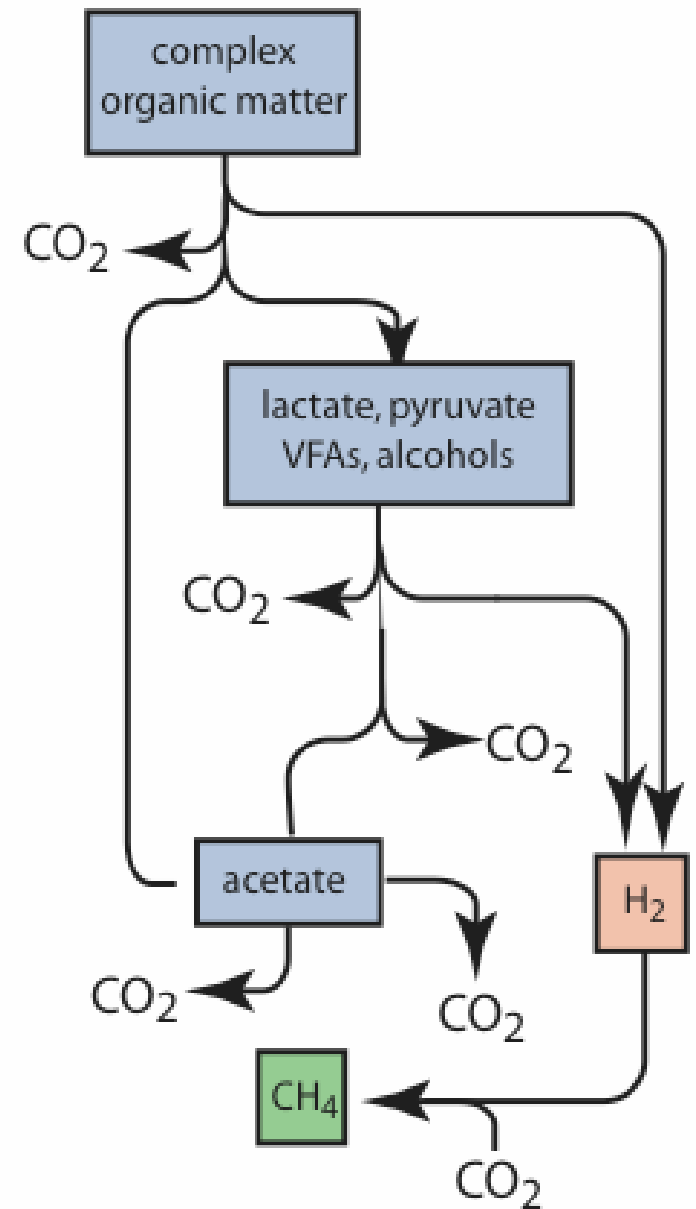
Degradation of pectin in Knaack Lake sediments



Sulfate Present



Sulfate Absent

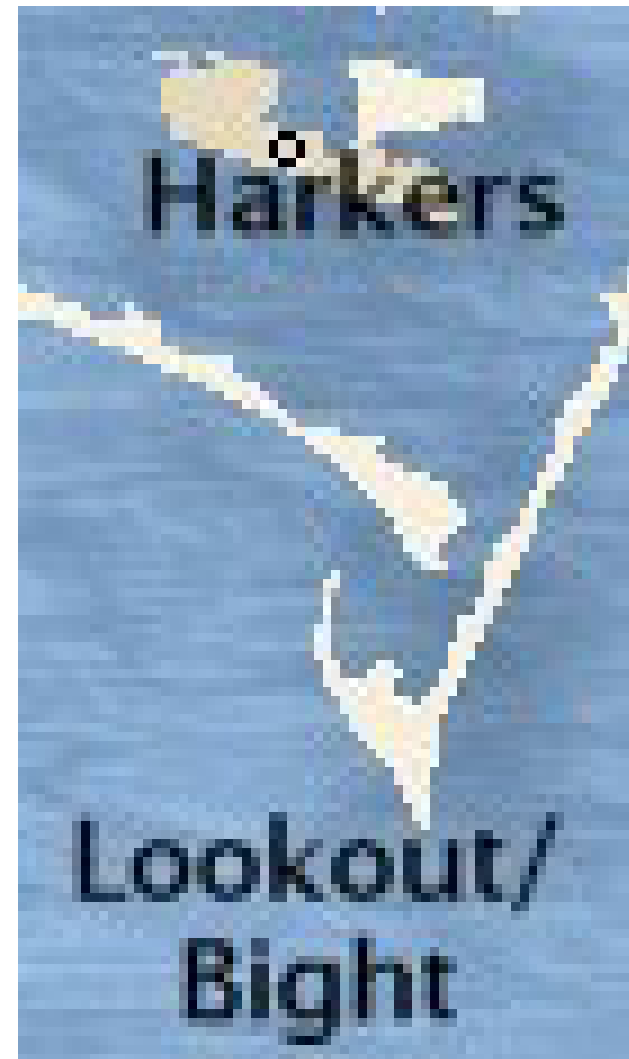
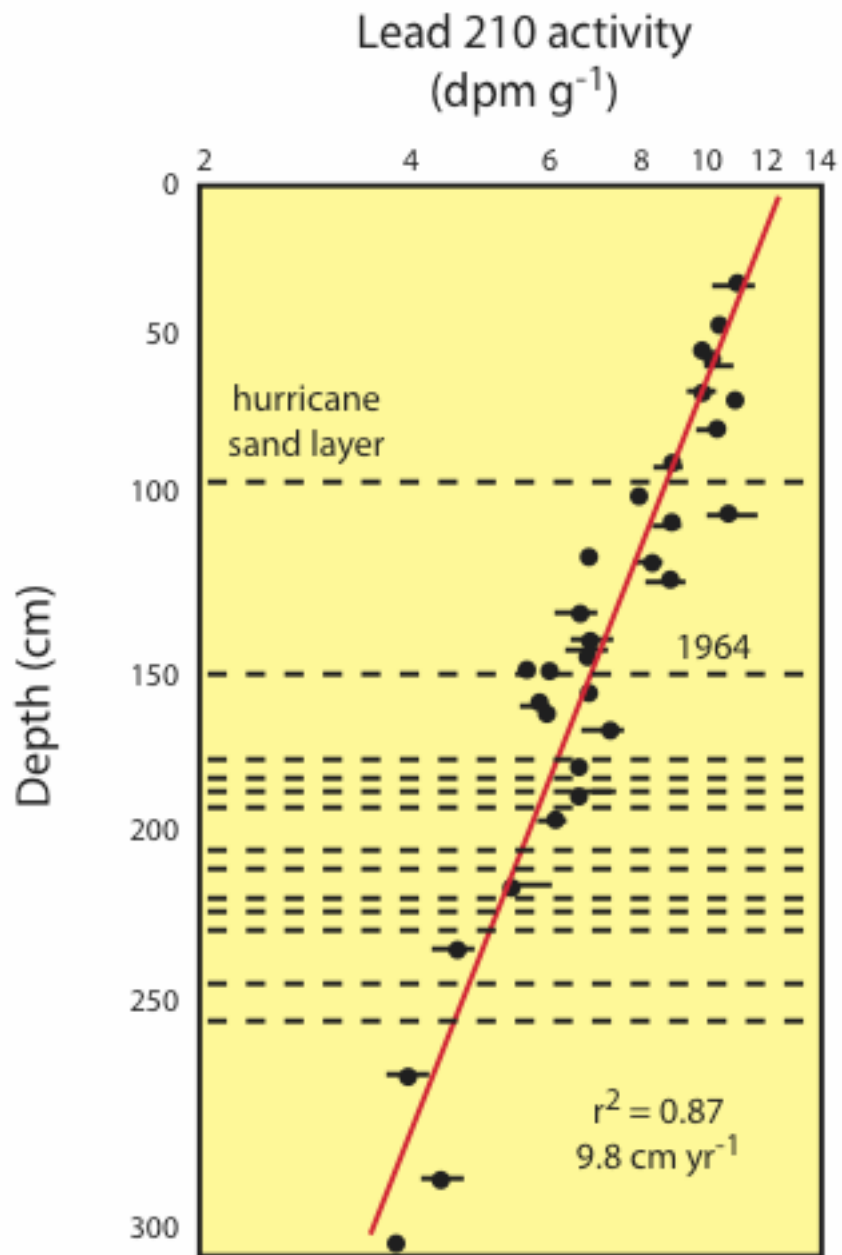


Chemical thermodynamics and pure culture studies of anaerobic micro-organisms suggest that the oxidizing capacity of sediments is >>> than [O₂].

We predict that sulfate and ultimately carbon dioxide will be used as electron acceptors during organic matter oxidation. We also predict that sulfate reduction will occur before methanogenesis.

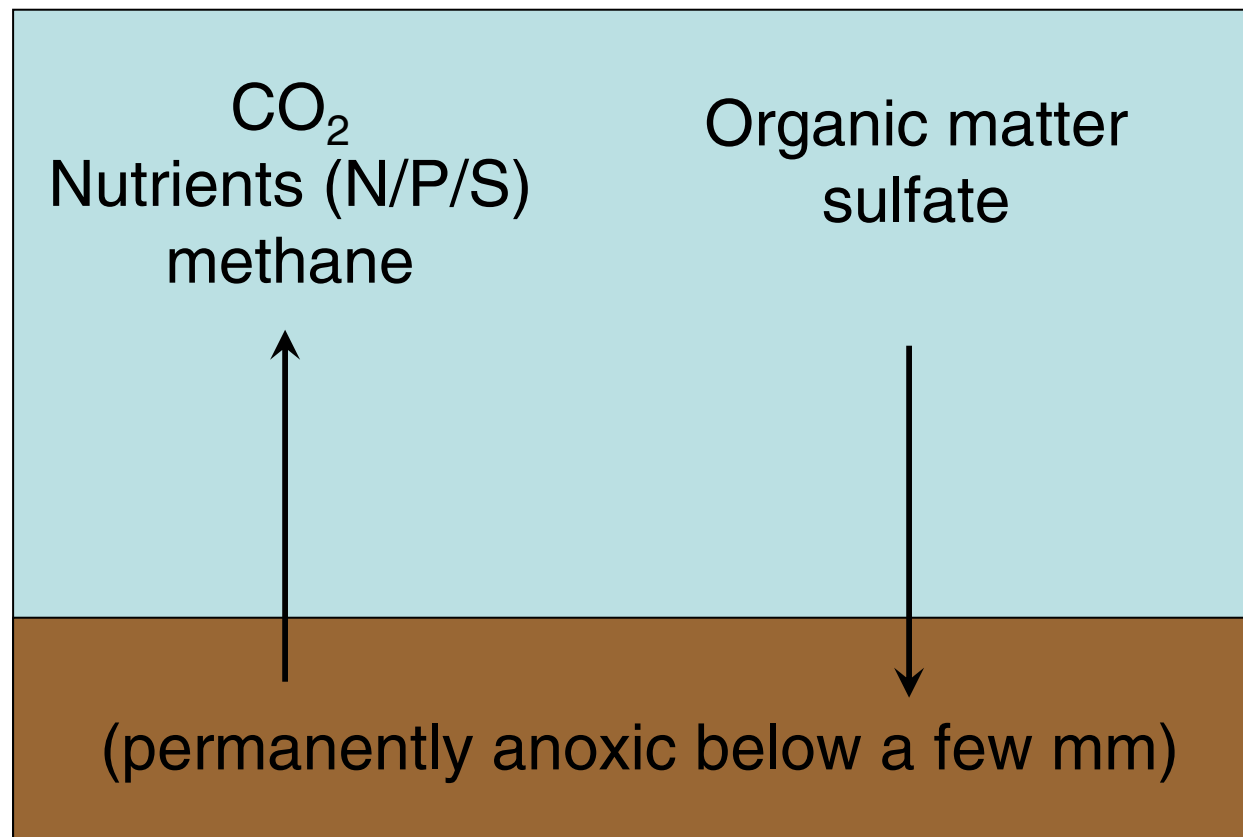
Can we observe the consequences of these factors
And model their impact on organic matter oxidation?

Biogeochemical cycling in Cape Lookout Bight Sediments

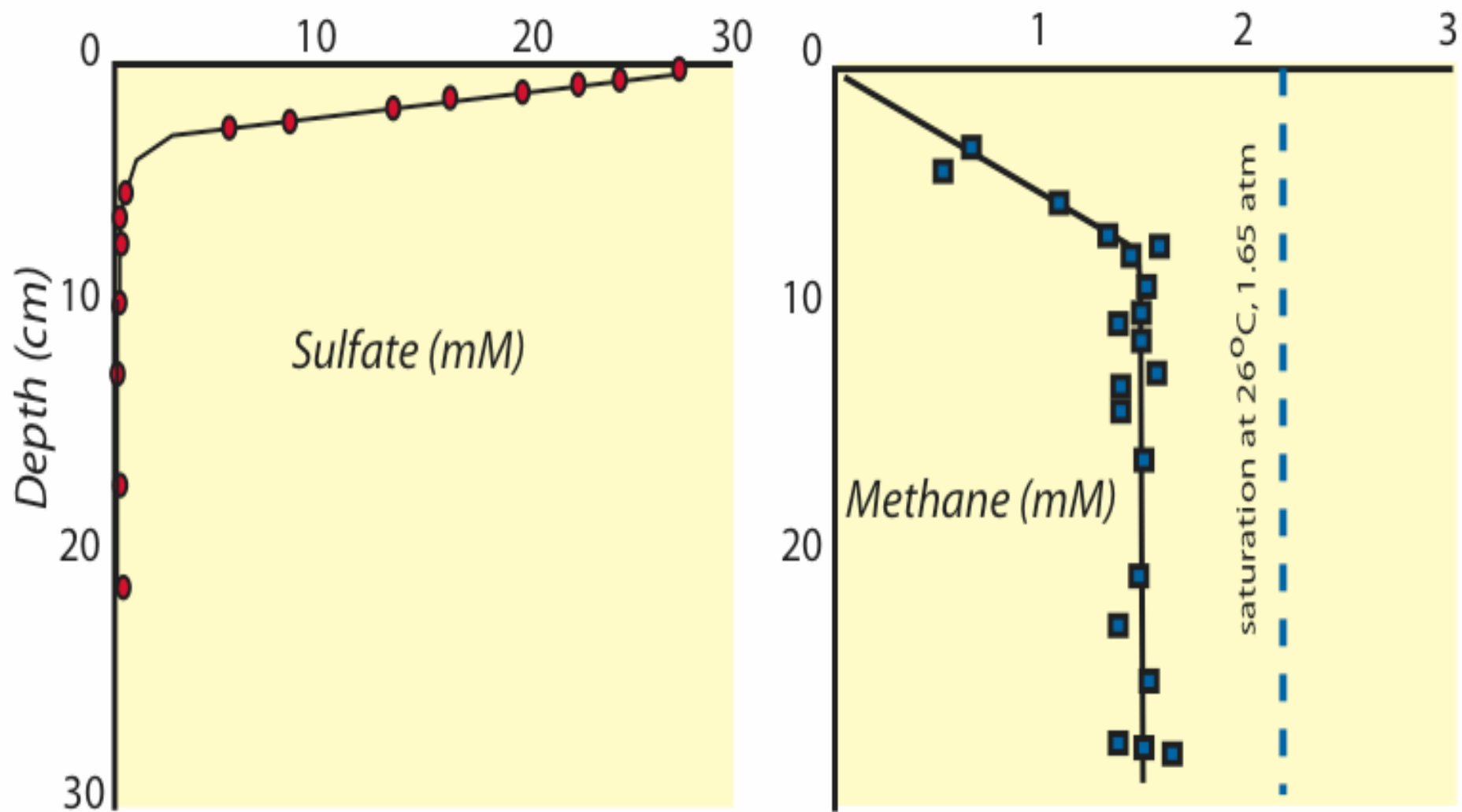


Biogeochemical cycling in Cape Lookout Bight

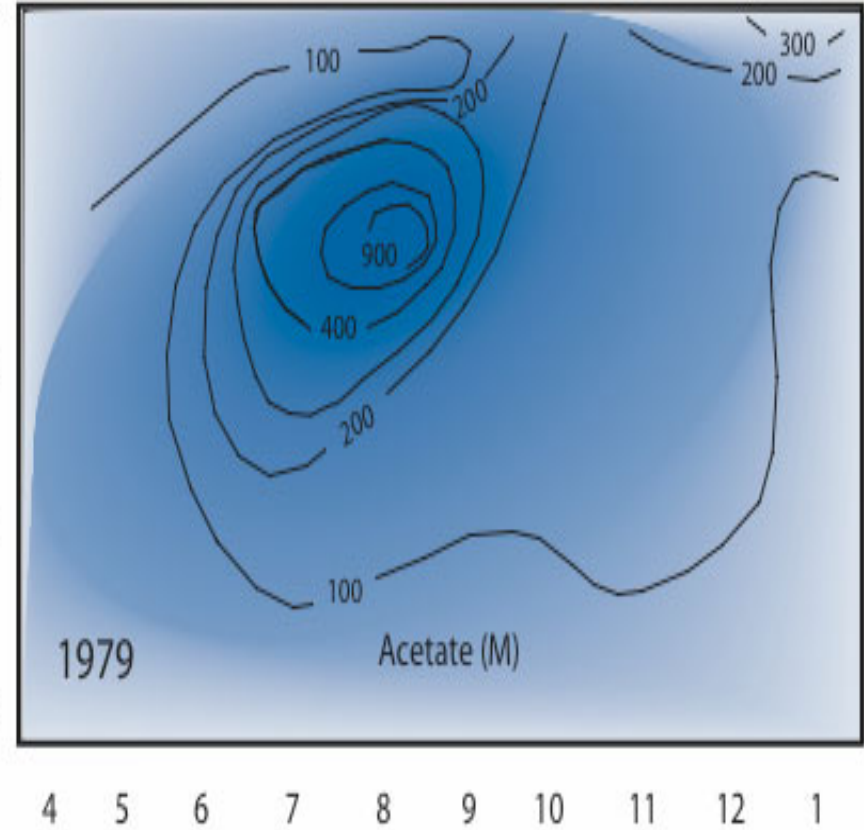
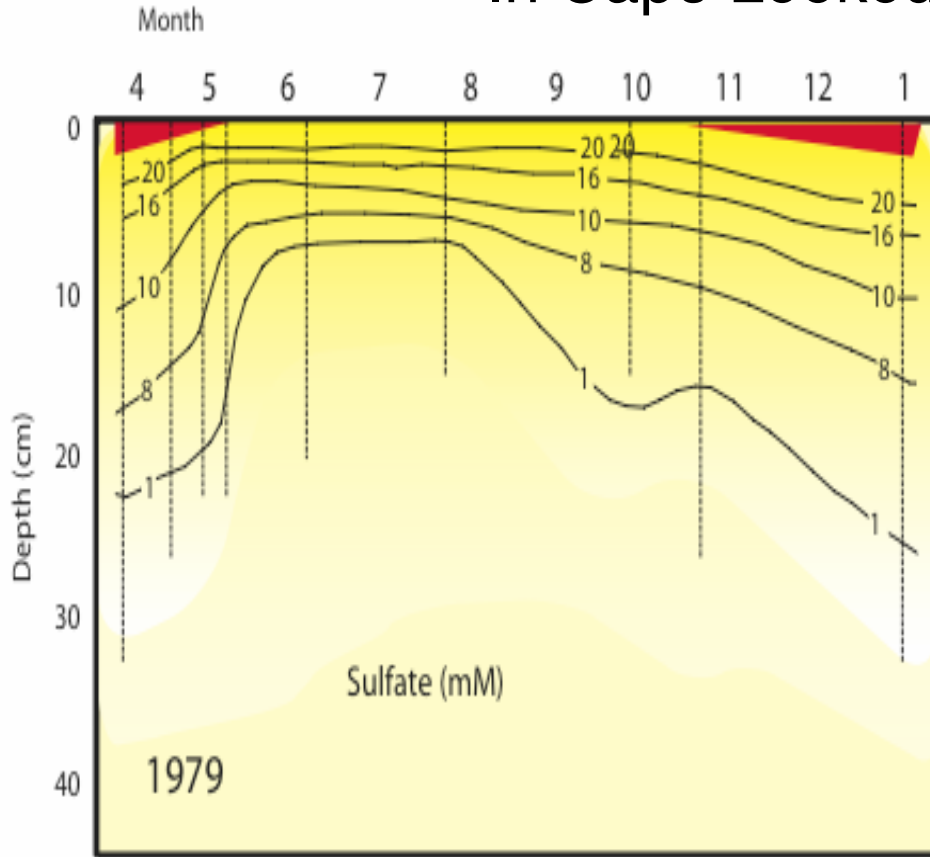
Can we achieve chemical balance if the system is at steady state?



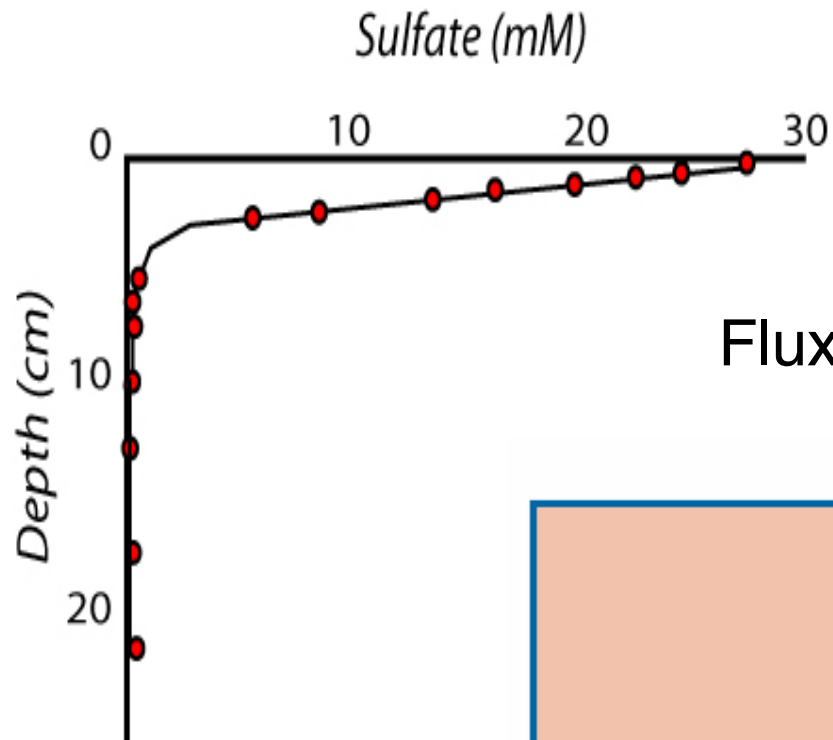
Sulfate and Methane in CLB sediments (August)



Seasonal distribution of sulfate and acetate In Cape Lookout Bight sediments



Note that sulfate is exhausted closer to the sediment/water interface in summer due to enhanced rate of sulfate reduction. Acetate accumulates only when sulfate reaches low concentrations

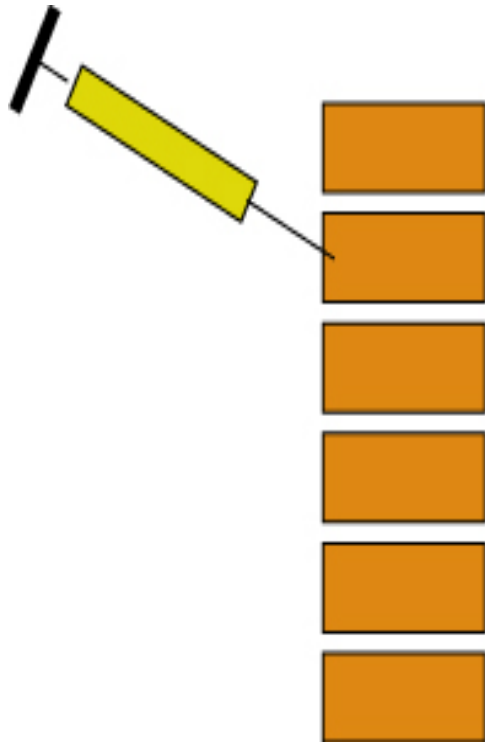


How can we calculate C
reminerlization from
sulfate reduction?

$$\text{Flux} = k (\delta C / \delta z)$$

| | Sulfate Reduction Rate | | |
|---------------------------|------------------------|------|----------|
| | DS | D'S | measured |
| Kinetic model | 13.1 | 15.5 | |
| Computer gradient | 12.1 | 16.2 | |
| Linear gradiaent | 12.1 | | |
| sediment incubation | | | 15.6 |
| ³⁵ S reduction | | | 16.6 |

Measurement of sulfate Oxidation using ^{34}S



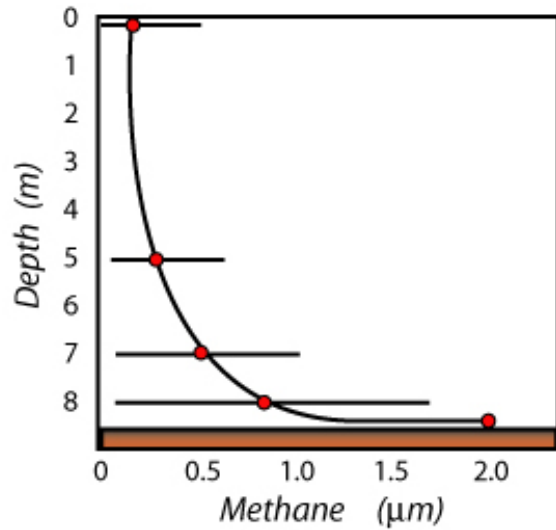
Moles of sulfate reduced
($\text{m}^{-2} \text{yr}^{-1}$)

| | tube | ^{35}S |
|------|------|-----------------|
| Jan | 8.0 | 12.2 |
| Feb | 7.7 | 13.3 |
| Mar | 11.4 | 12.7 |
| Apr | 15.2 | 7.4 |
| May | 11.8 | 16.4 |
| Jun | 16.8 | 20.9 |
| July | 22.0 | 25.4 |
| Aug | 27.2 | 30.0 |
| Sept | 26.2 | 23.3 |
| Oct | 17.5 | 16.2 |
| Nov | 8.7 | 10.0 |
| Dec | 6.4 | 11.1 |
| | 15.1 | 16.6 |



Therefore 32 moles C by sulfate oxidation

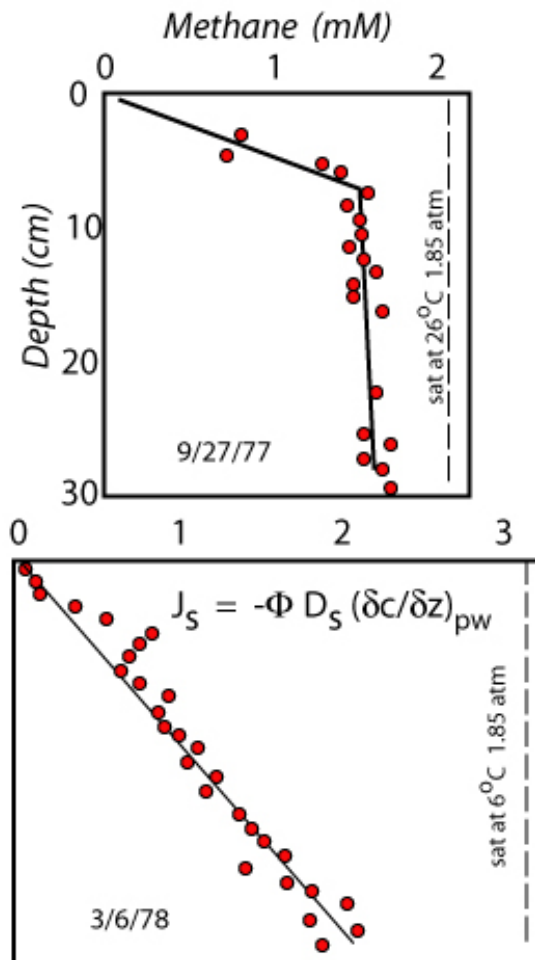
Methane fluxes from CLB sediments

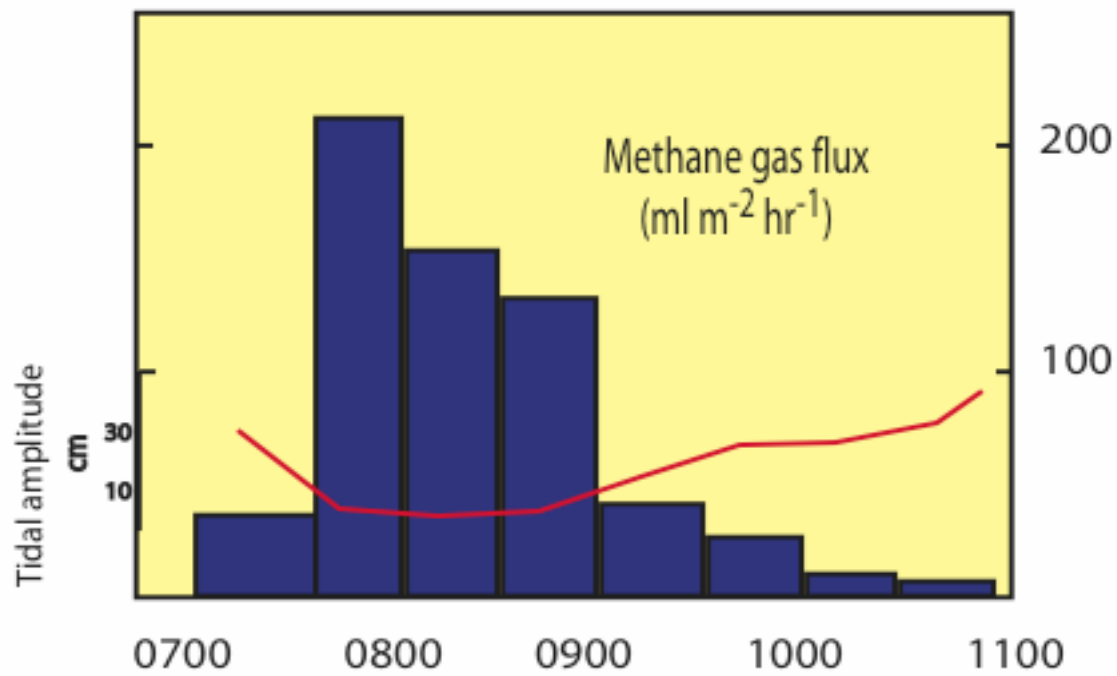
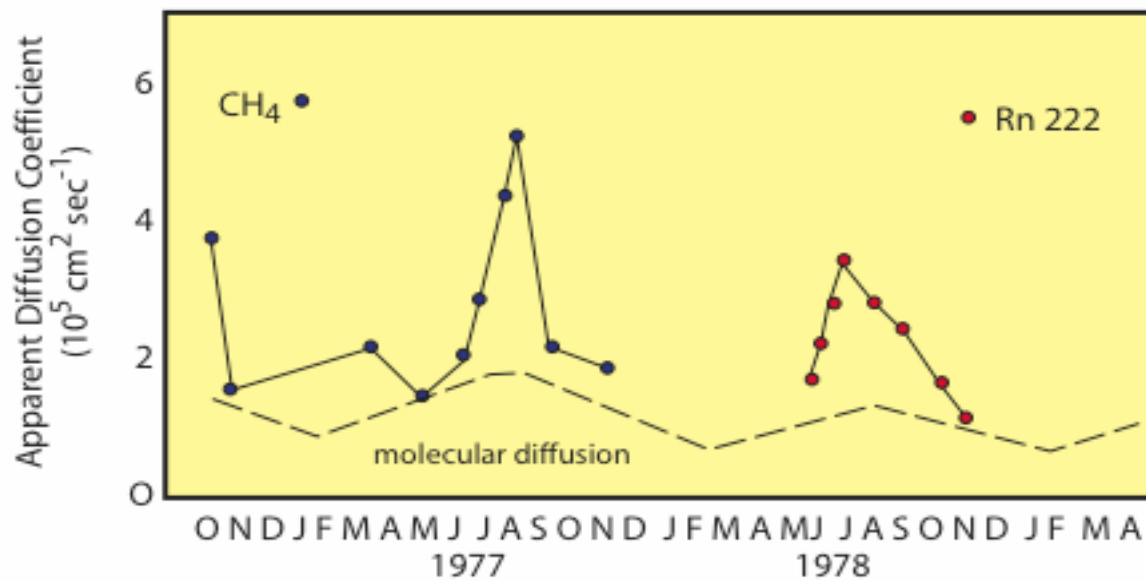


Methane diffusive fluxes

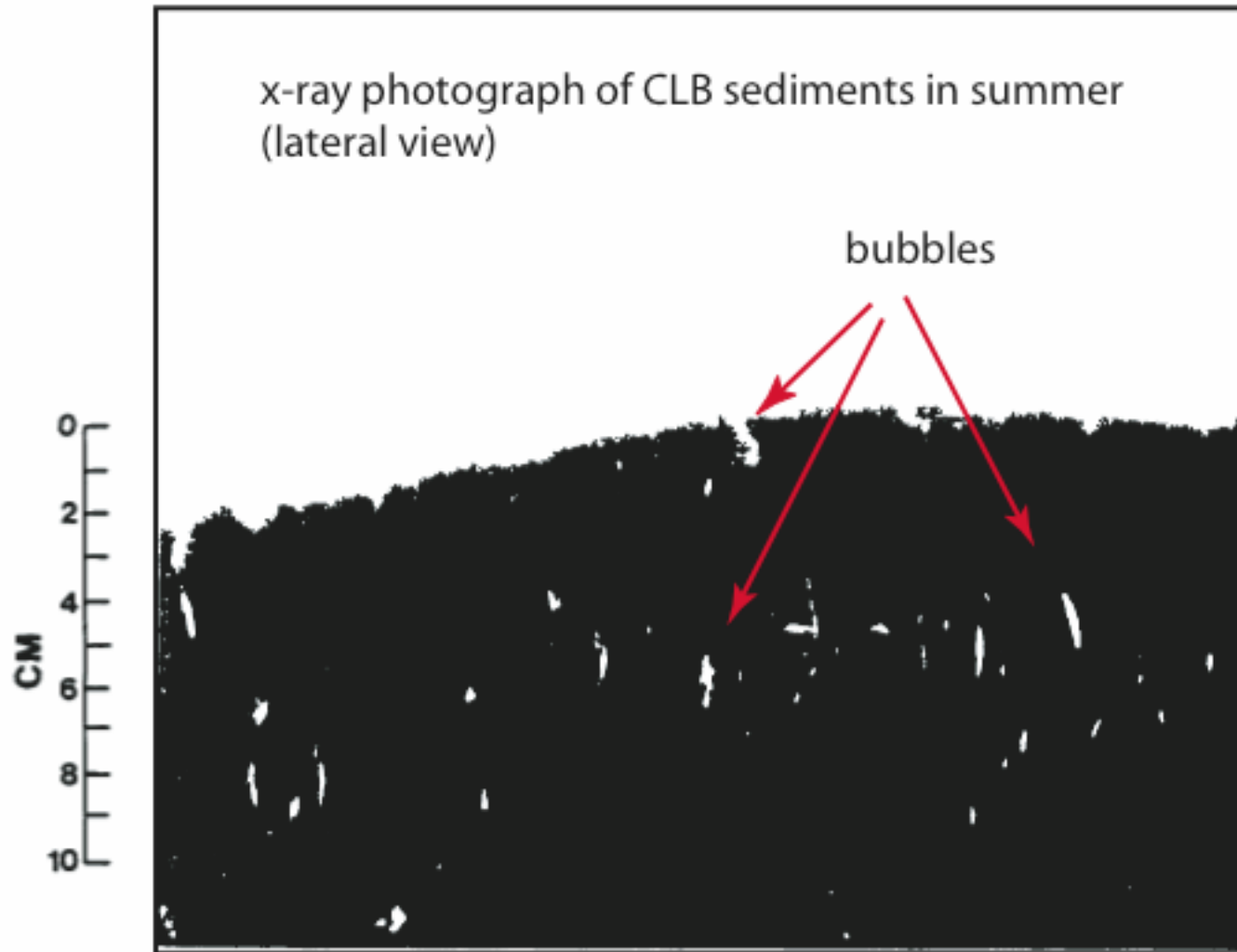
| Date | J_s | J_{theor} | J_{excess} |
|-----------------|-------|--------------------|---------------------|
| 16 October 76 | 84 | 31 | 53 |
| 6 November 76 | 30 | 26 | 4 |
| 25 March 77 | 51 | 27 | 24 |
| 16 May 77 | 48 | 50 | 0 |
| 27 June 77 | 82 | 69 | 13 |
| 13 July 77 | 130 | 78 | 52 |
| 5 August 77 | 274 | 115 | 159 |
| 22 August 77 | 393 | 129 | 264 |
| 20 September 77 | 186 | 160 | 25 |
| 17 November 77 | 66 | 46 | 20 |

Calculation of Methane flux from CLB sediments





Methane concentrations build up to saturation values and form bubbles that remove CO₂ and methane from sediments



ΣCO_2 fluxes
 $\mu\text{m m}^{-2} \text{hr}^{-1}$

CH_4 fluxes
 $\mu\text{m m}^{-2} \text{hr}^{-1}$

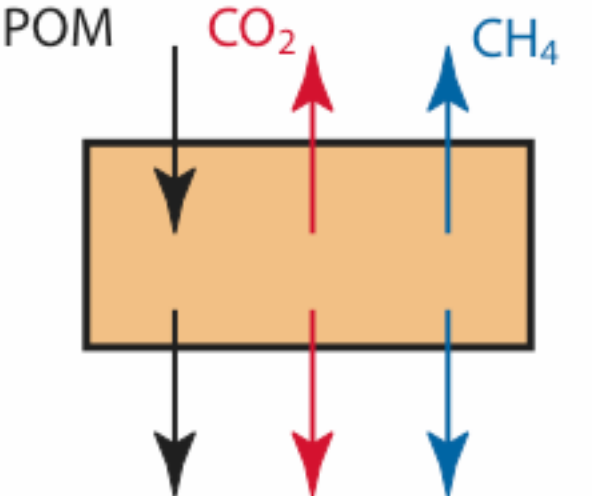
| Month | diff | bubble | Total | diff | bubble | Total |
|-------|------|--------|-------|------|--------|-------|
| Jan | 1900 | 0 | 1900 | 50 | 0 | 50 |
| Feb | 1900 | 0 | 1900 | 50 | 0 | 50 |
| March | 1900 | 0 | 1900 | 51 | 0 | 51 |
| April | 1900 | 0 | 1900 | 50 | 0 | 50 |
| May | 3825 | 0.6 | 3826 | 48 | 52 | 100 |
| June | 5400 | 5.6 | 5406 | 82 | 480 | 562 |
| July | 6000 | 20 | 6020 | 130 | 1740 | 1870 |
| Aug | 6300 | 26 | 6326 | 334 | 2250 | 2484 |
| Sept | 4900 | 18 | 4918 | 184 | 1500 | 1684 |
| Oct | 2700 | 6.5 | 2707 | 84 | 560 | 644 |
| Nov | 2200 | 0.8 | 2201 | 48 | 65 | 113 |
| Dec | 1900 | 0 | 1900 | 50 | 0 | 50 |

Average 3400 6.5 **3407** 97 544 **651**

mean monthly flux ($\text{mole m}^{-2} \text{yr}^{-1}$)

29.8 0.057 **29.9** 0.85 4.85 **5.70**

Total C remineralization in CLB sediments



remineralization = C flux

| out of top | out of bottom |
|----------------------------|---------------------------|
| $\Sigma\text{CO}_2 = 29.9$ | $\Sigma\text{CO}_2 = 5.7$ |
| $\Sigma\text{CH}_4 = 5.7$ | $\Sigma\text{CH}_4 = 0.1$ |
| <hr/> | <hr/> |
| 35.6 | 5.8 |

Total C remineralization
 41.4 moles m⁻² yr⁻¹

Total Carbon flux = 41.4

Methane flux = 5.8

total C remineralization due to methanogenesis:

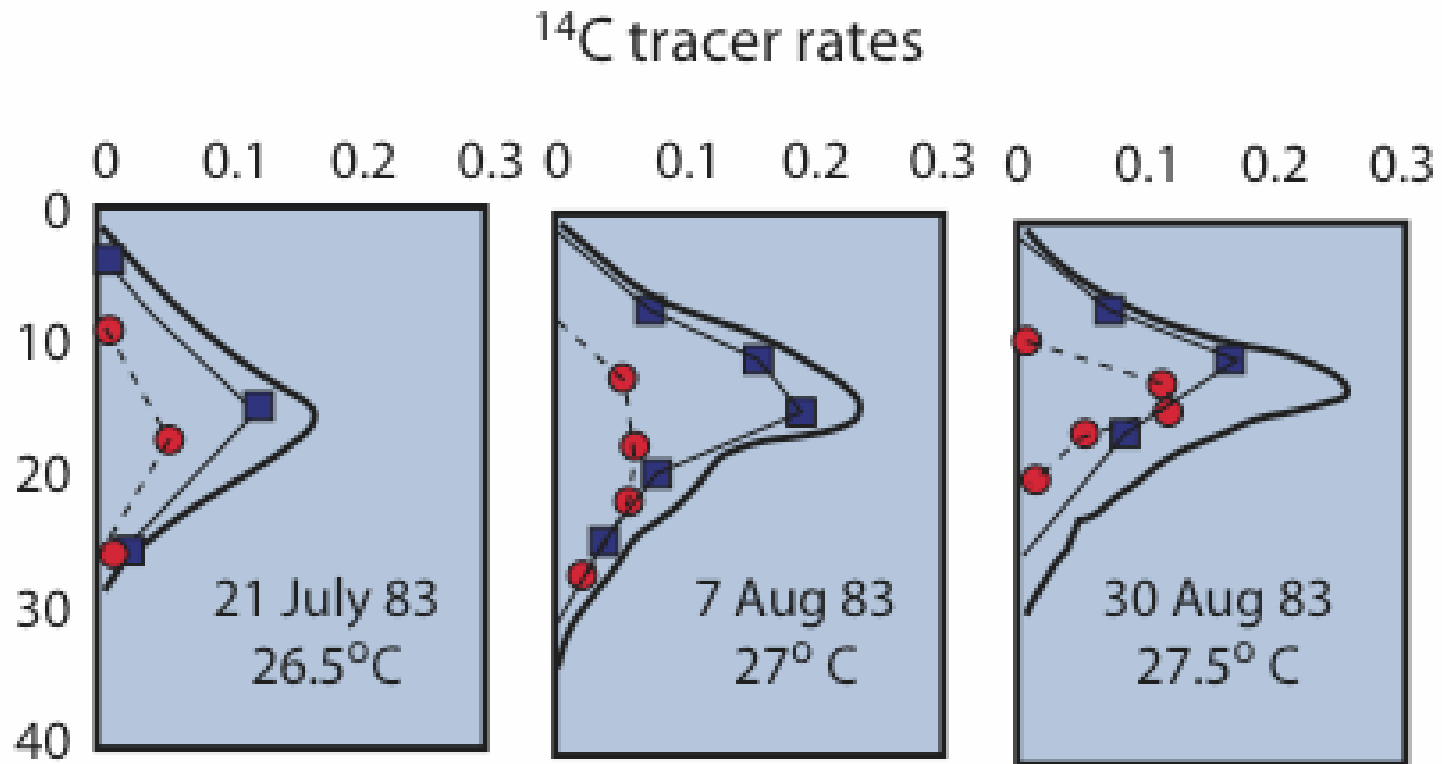
$5.8 \times 2 = 11.6$ moles $m^{-2} yr^{-1}$ or 28%

C remineralization due to sulfate reduction is:

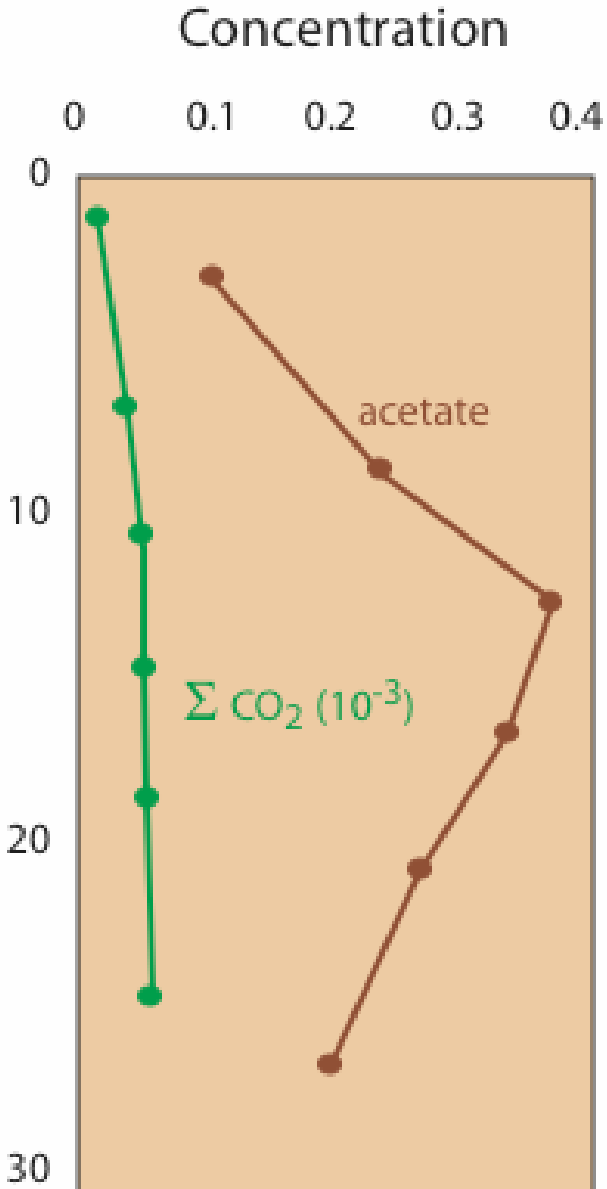
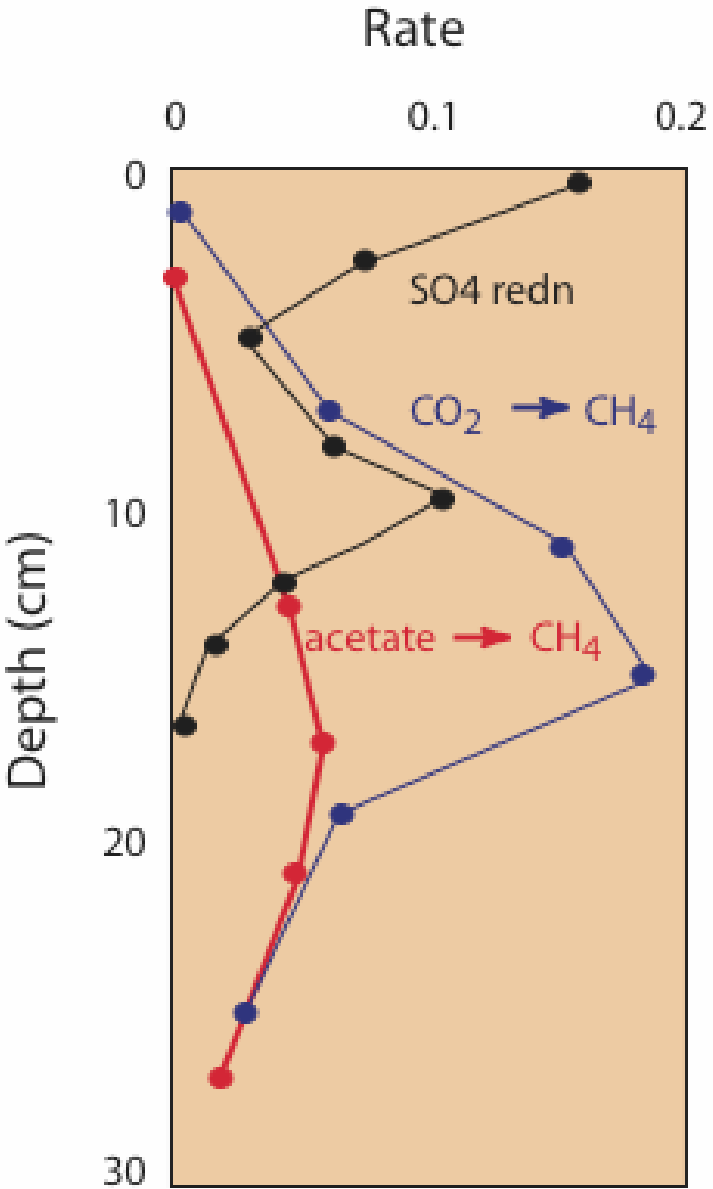
$$\begin{array}{r} 41.4 \\ - \underline{11.6} \\ \hline 29.8 \text{ moles C } m^{-2} yr^{-1} \text{ or } 72\% \end{array}$$

Sulfate reduction measured or calculated from tube/tracer incubations and sulfate gradient is 30-36 moles yr^{-1}

Production of methane from acetate and CO₂
in CLB sediments. ¹⁴C tracer studies.



Rates of C remineralization in CLB sediments



Integrated (0-35 cm) rates of methane production
and sulfate reduction in CLB sediments

| Date | T°C | CH ₄ | SO ₄ |
|-------------|-----|-----------------|-----------------|
| 21 Feb. 81 | 11 | 0.04 | 1.00 |
| 24 April 81 | 17 | 0.03 | 2.40 |
| 19 May 80 | 23 | 0.05 | |
| 29 May 80 | 25 | 0.56 | 0.96 |
| 2 Jul. 81 | 23 | 1.60 | |
| 2 Aug. 81 | 27 | 2.00 | 2.60 |
| 30 Aug. 81 | 26 | 1.00 | 2.90 |
| 5 Oct. 80 | 26 | 0.79 | 4.40 |
| 8 Oct. 79 | 22 | 1.10 | 3.60 |
| 9 Nov. 81 | 19 | 0.02 | 1.70 |

mmol m⁻² h⁻¹

Summary:

Terminal electron acceptors are used in the order of free E yields (O_2 , Fe/Mn, SO_4 , CO_2)

Anoxic sediments are biogeochemically zoned according to e- acceptors

Organic matter is oxidized by microbial consortia - no single organism degrades complex organic matter to CO_2 . Instead, fermentation produces VFAs which are used by acetophiles to yield CO_2 and methane.

Methane is produced by two reactions CO_2 redn with Hydrogen, and disproportionation of acetic acid.