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

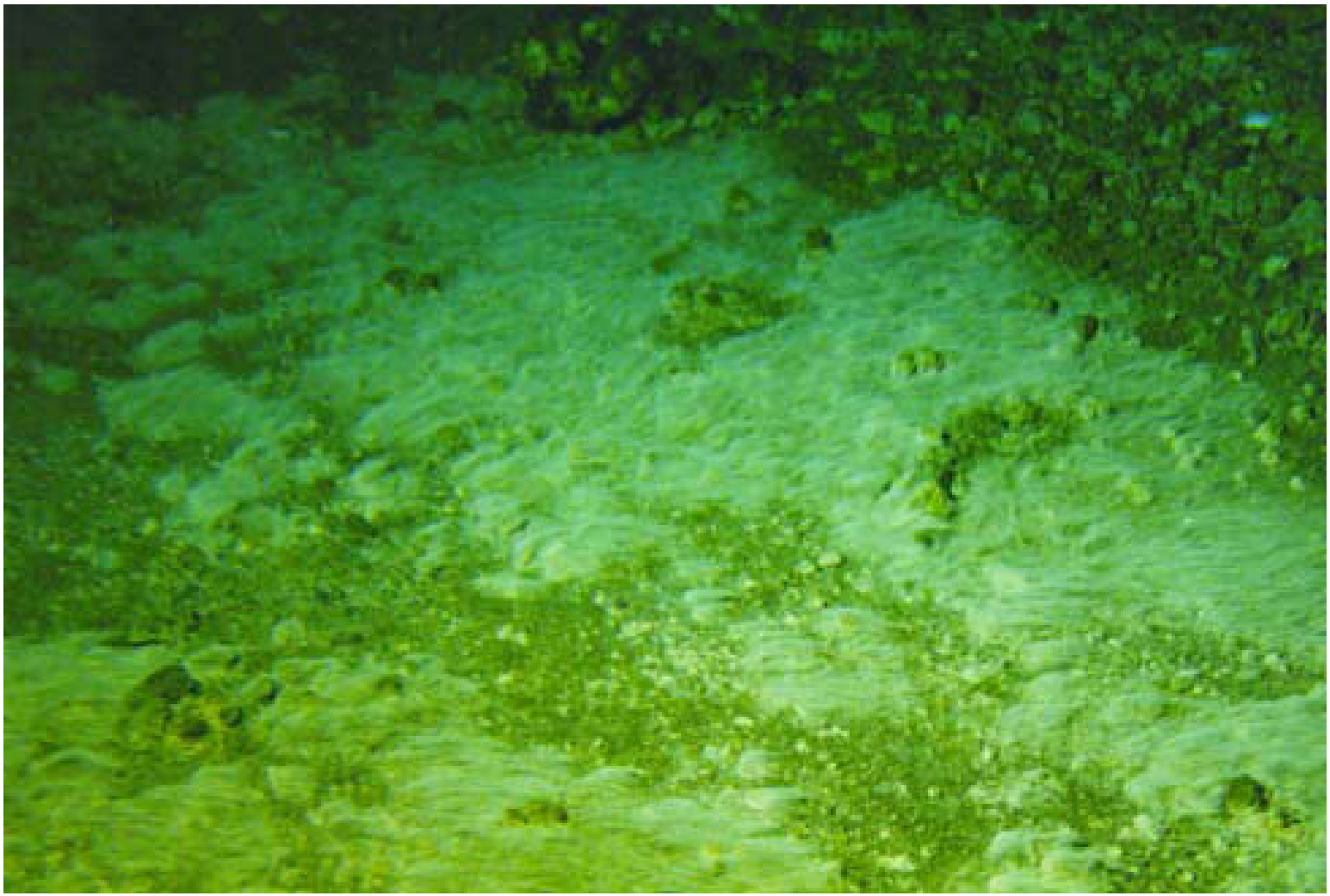
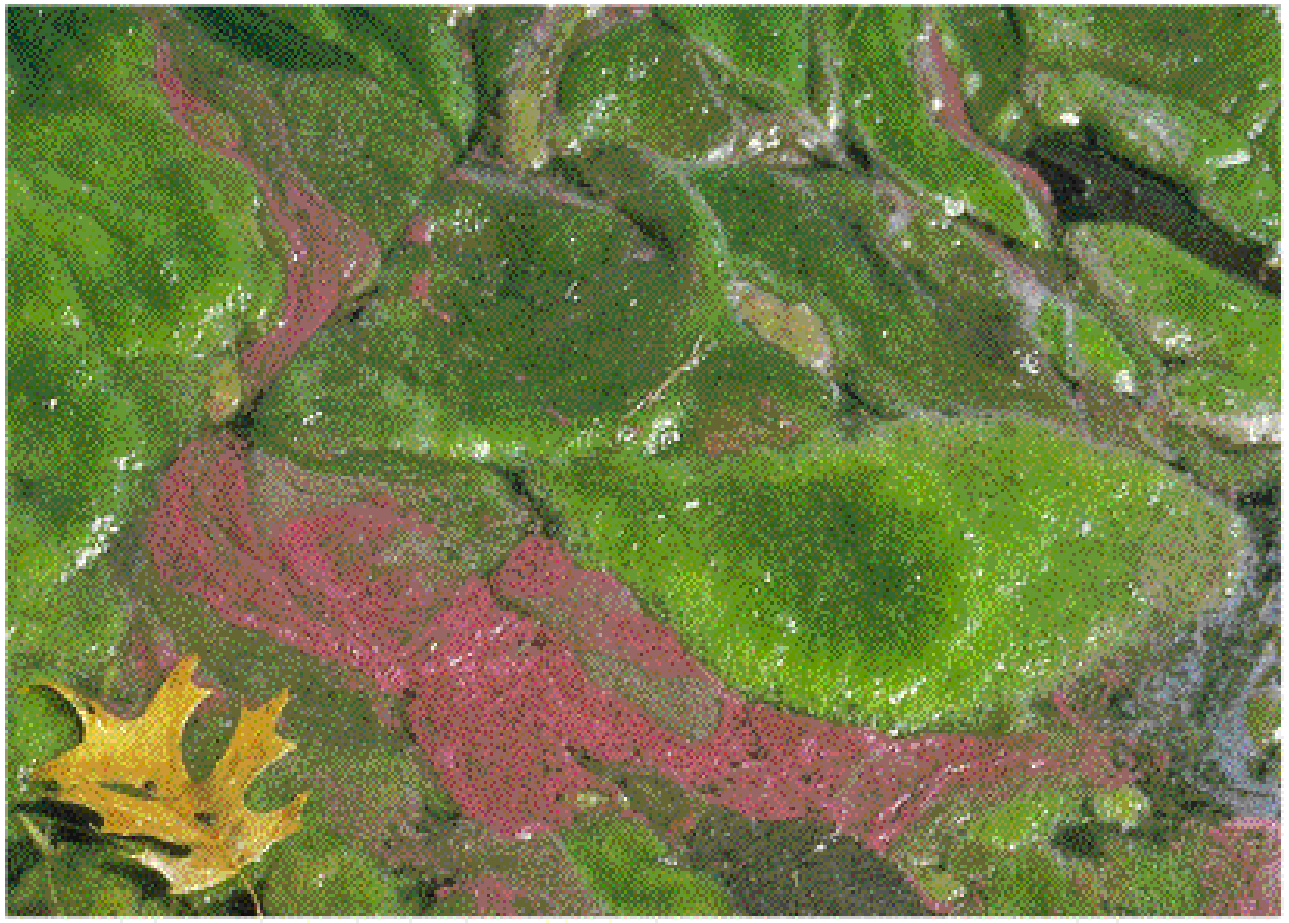


Image courtesy of T.D. Brock

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.).



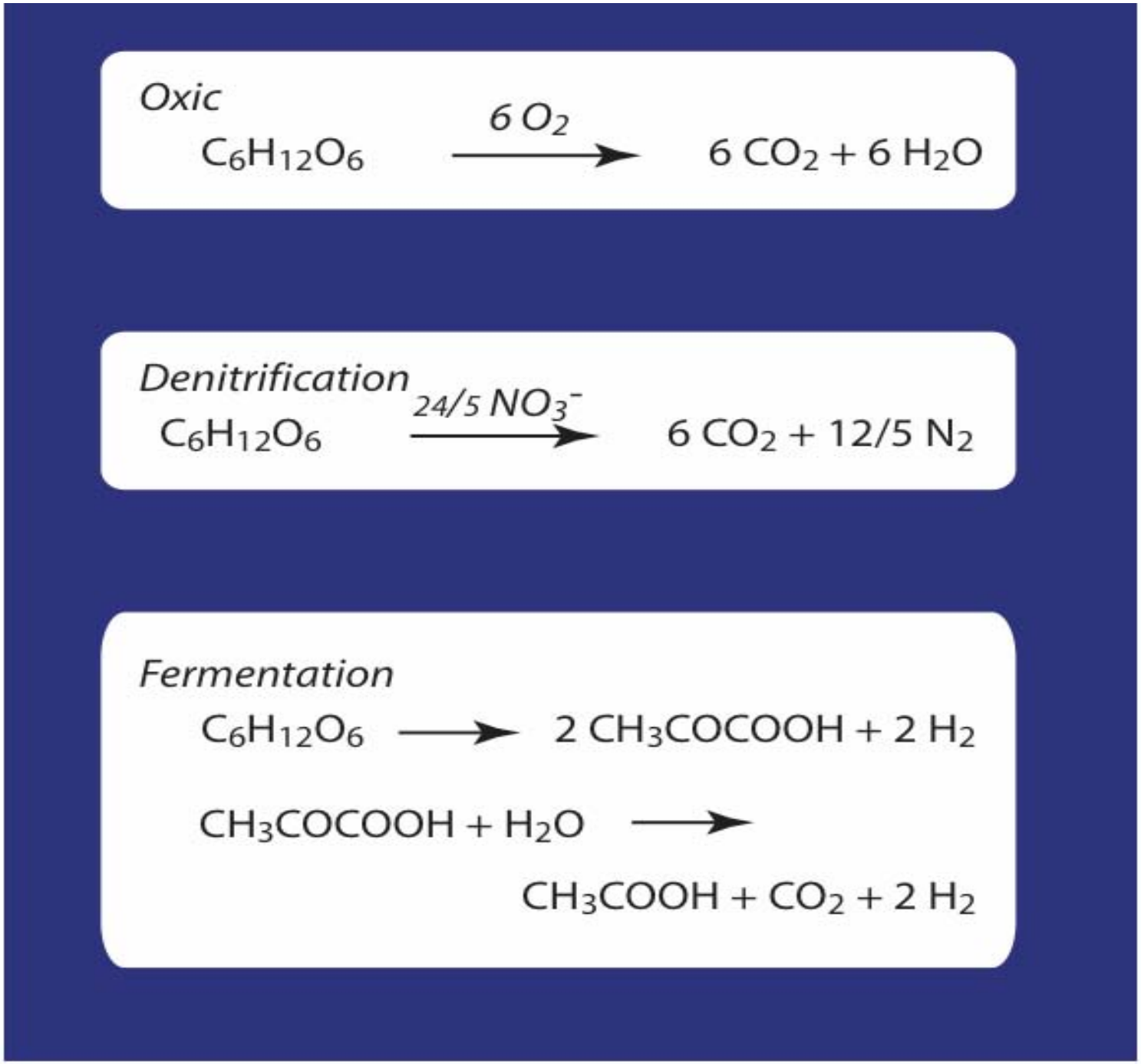
(a)

Courtesy of T.D. Brock. Used with permission.

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	→	CO_2	-475	0.85
NO_3^-	→	$N_2 + CO_2$	-448	0.05
Mn(IV)	→	Mn (II)	-349	2-22
Fe(III)	→	Fe (II)	-114	14-28
SO_4^{2-}	→	S^{2-}	-77	56
CO_2	→	CH_4	-58	


Oxic
$C_6H_{12}O_6$ $6\ O_2$ $6\ CO_2 + 6\ H_2O$
Denitrification
$C_6H_{12}O_6$ $24/5\ NO_3^-$ $6\ CO_2 + 12/5\ N_2$
Fermentation
$C_6H_{12}O_6 \longrightarrow 2\ CH_3COCOOH + 2\ H_2$
$CH_3COCOOH + H_2O \longrightarrow$
$CH_3COOH + CO_2 + 2\ H_2$

Sulfate reduction

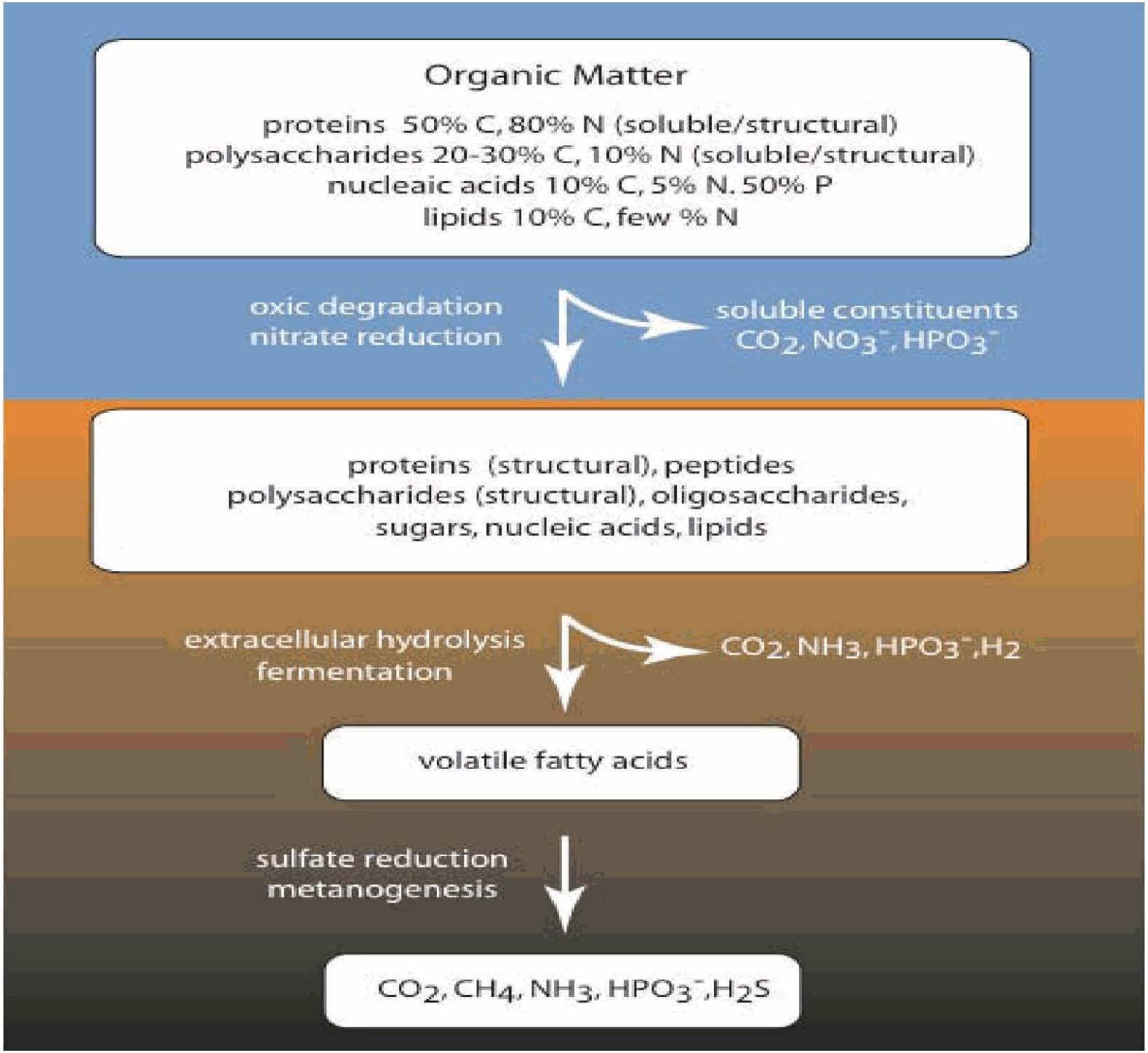
$$CH_3COOH + SO_4^{2-} \longrightarrow 2\,CO_2 + 2\,H_2O + H_2S$$

$$4\,CH_3COCOOH + SO_4^{2-} \longrightarrow 4\,CO_2 + 4\,CH_3COOH + S^{2-}$$

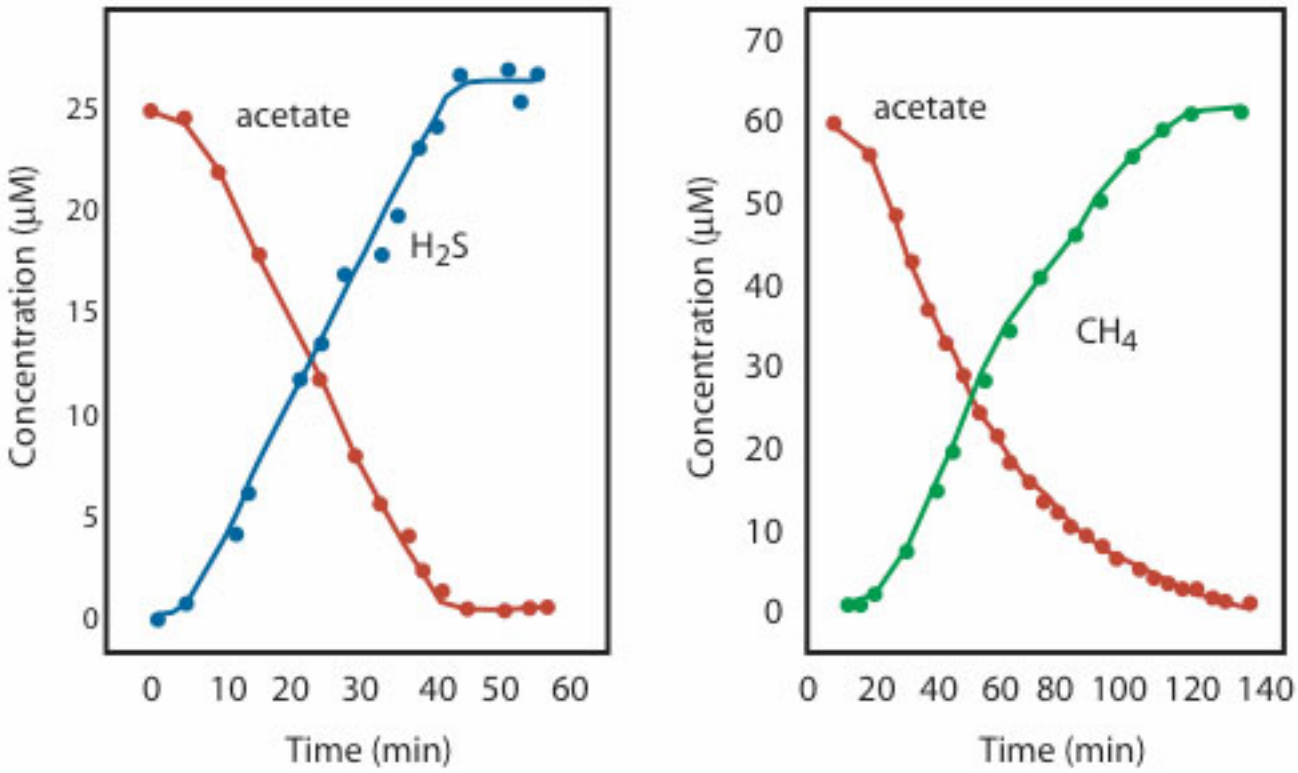
Methanogenesis

$$CH_3COOH \longrightarrow CO_2 + CH_4$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2\,H_2O$$


Organic Matter
proteins 50% C, 80% N (soluble/structural)
polysaccharides 20-30% C, 10% N (soluble/structural)
nucleaic 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
metanogenesis
CO_2, CH_4, NH_3, HPO_3^-, H_2S

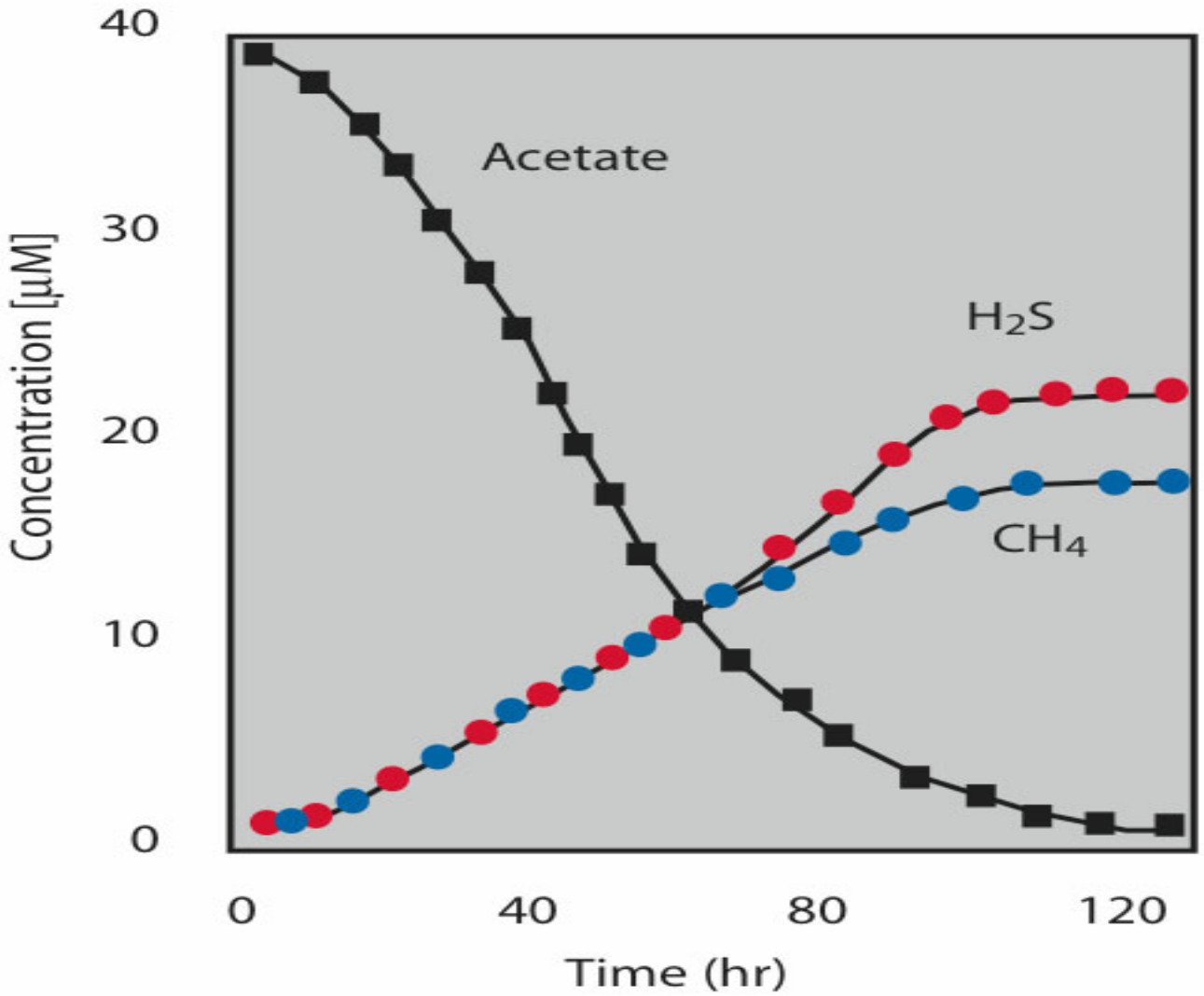
Consumption of acetate by sulfate reducing and methanogenic bacteria



Acetate = CH_3COOH

Volatile Fatty Acid (VFA) = CH_3RCOOH

Competition for acetate between
Desulfobacter postgatei and *Methanosarcina bakerii*



Competition for acetate between
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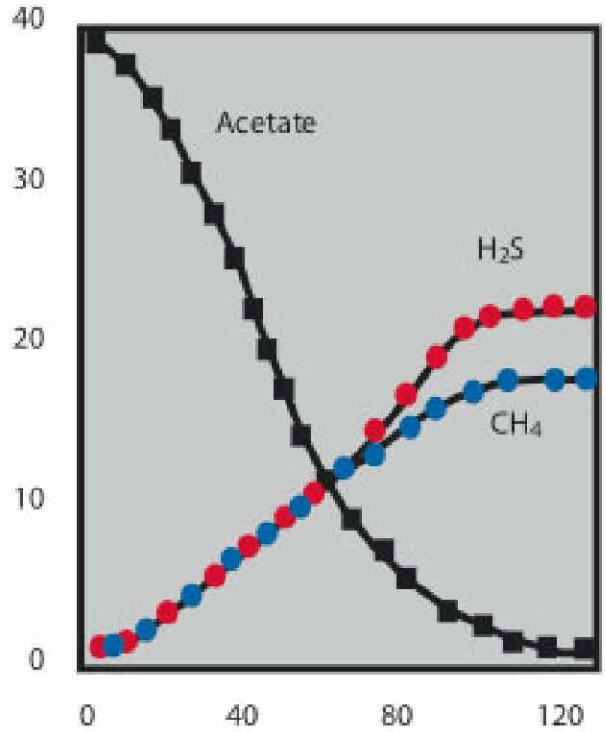
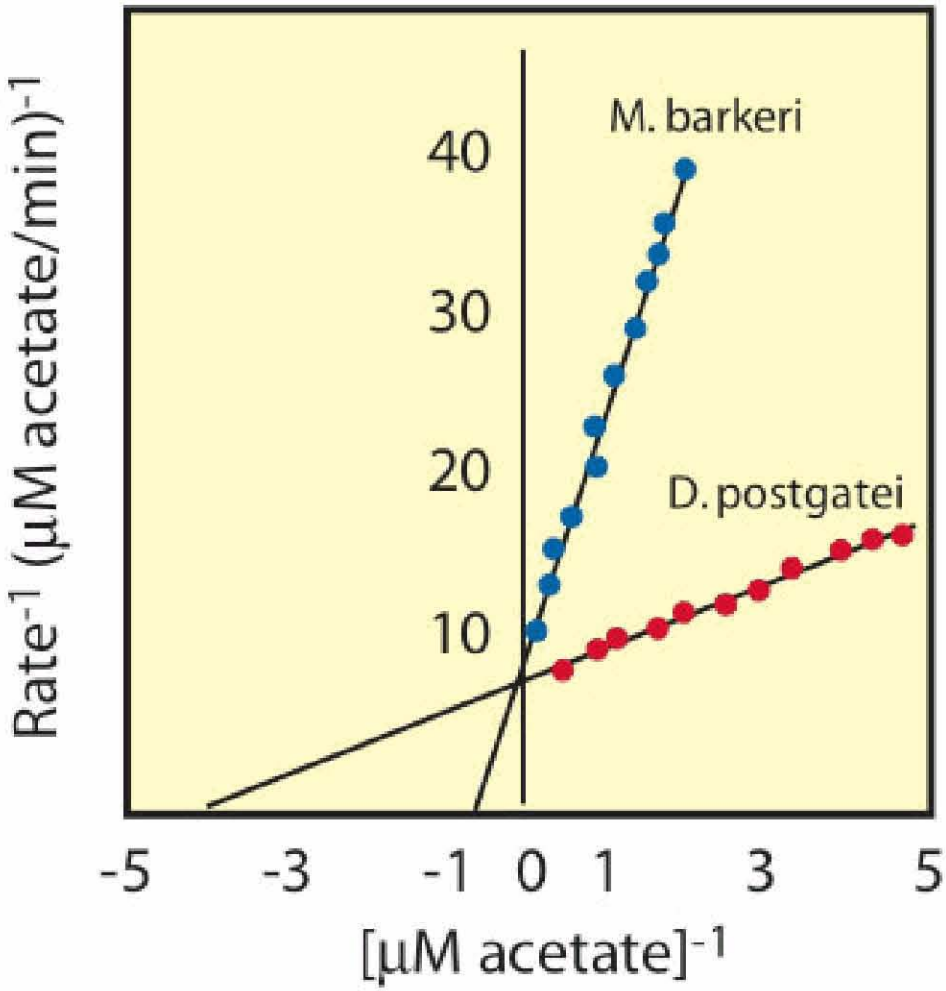
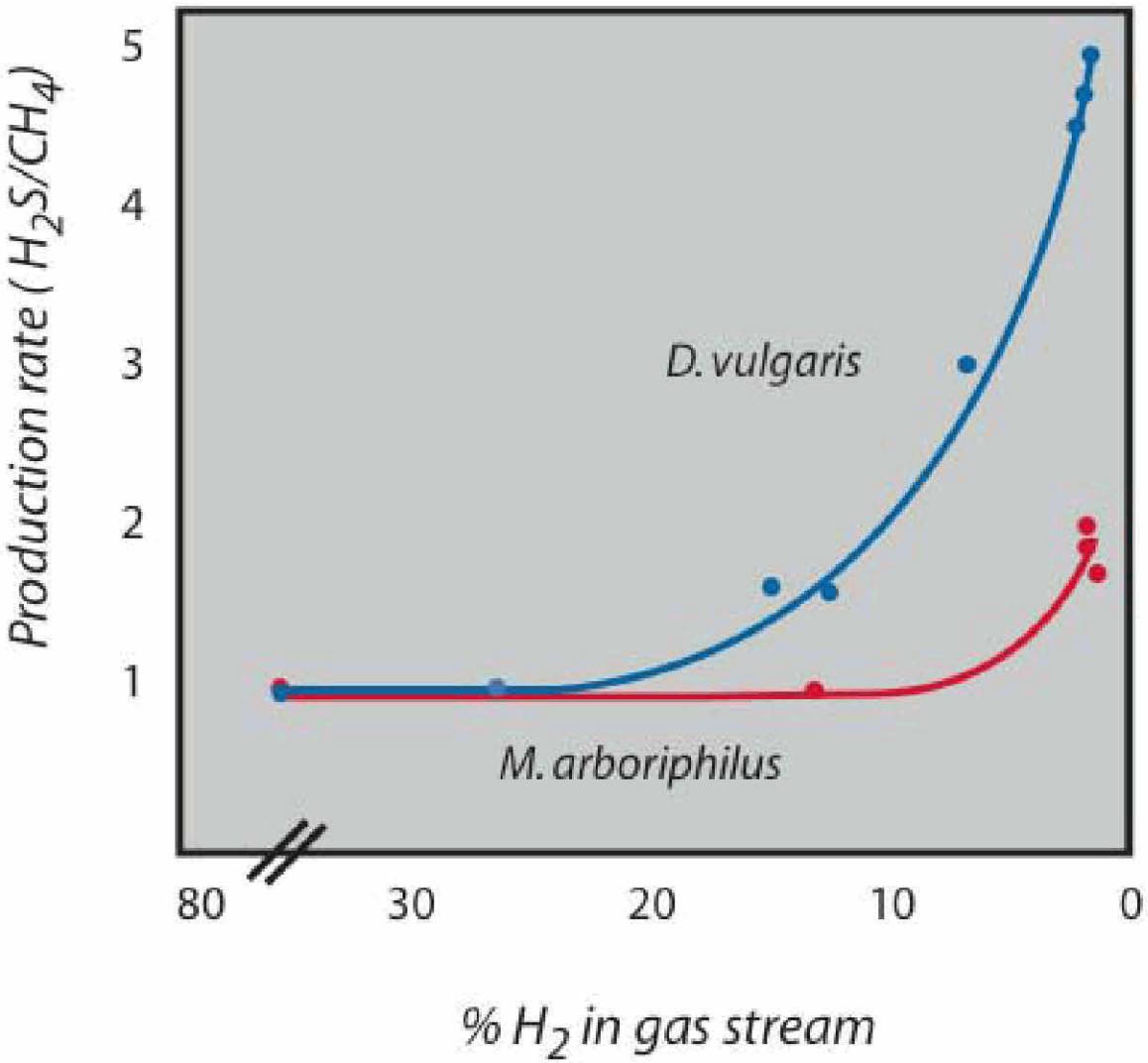
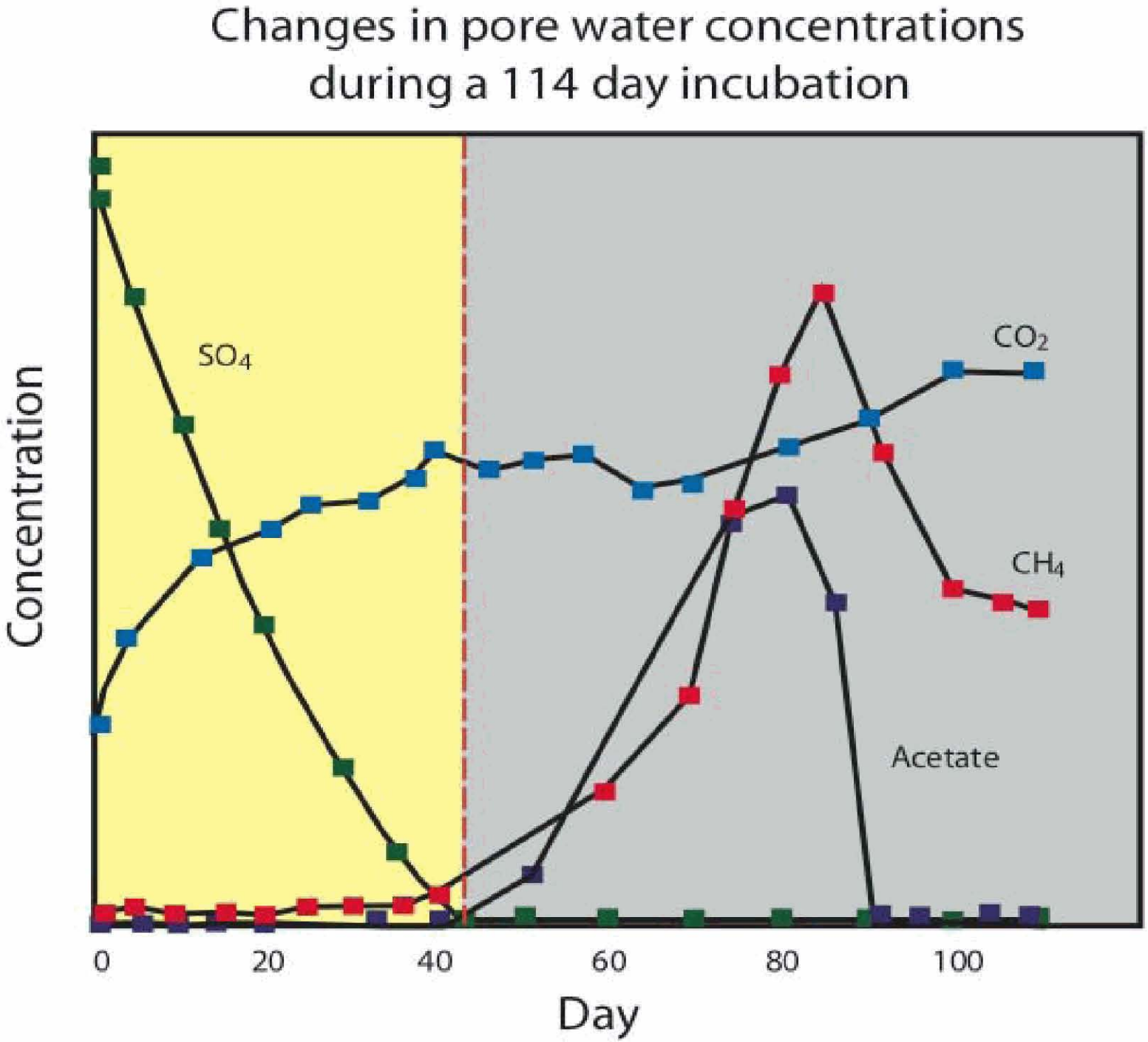


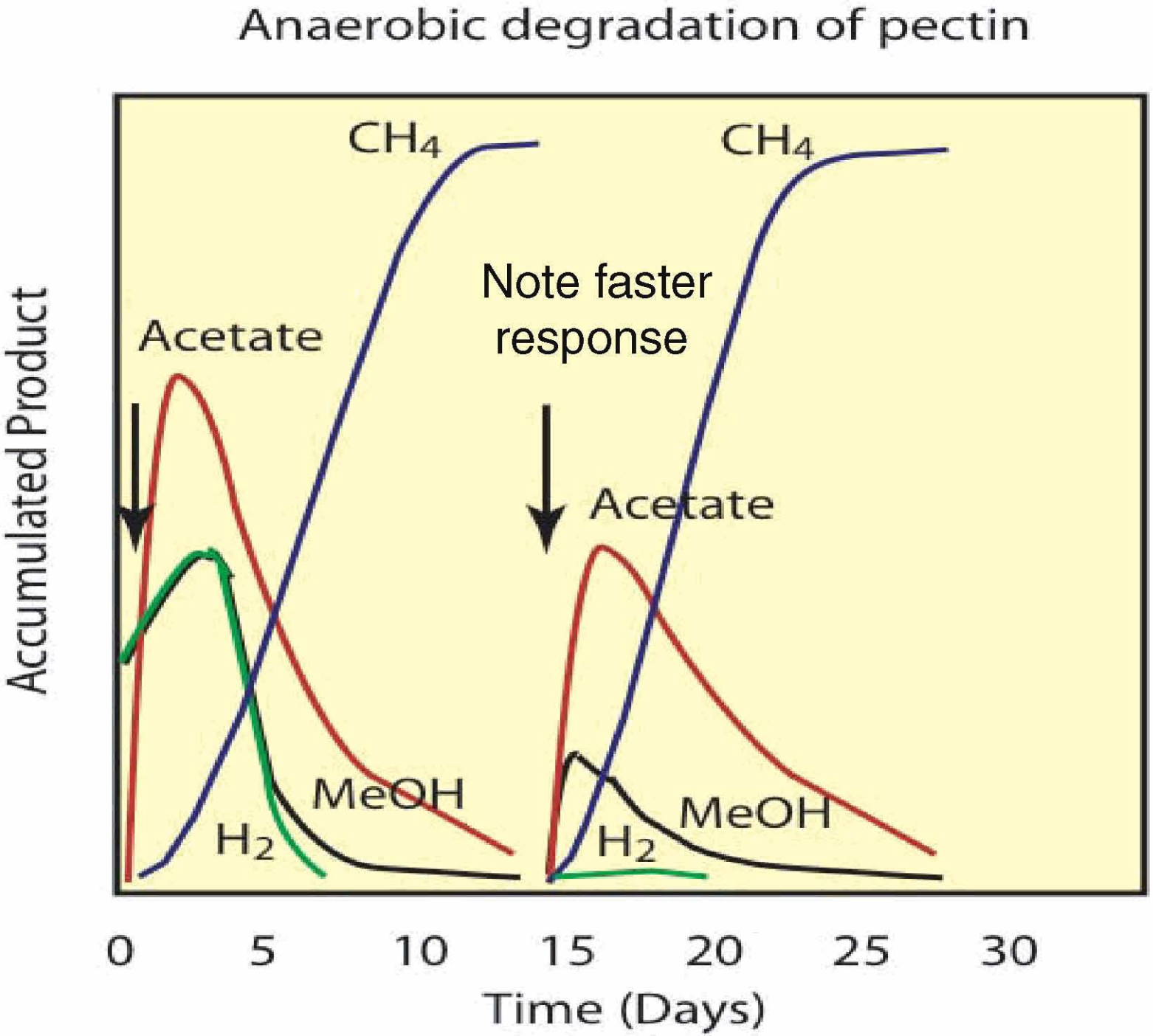
Double reciprocal plot of rate vs Acetate concentration



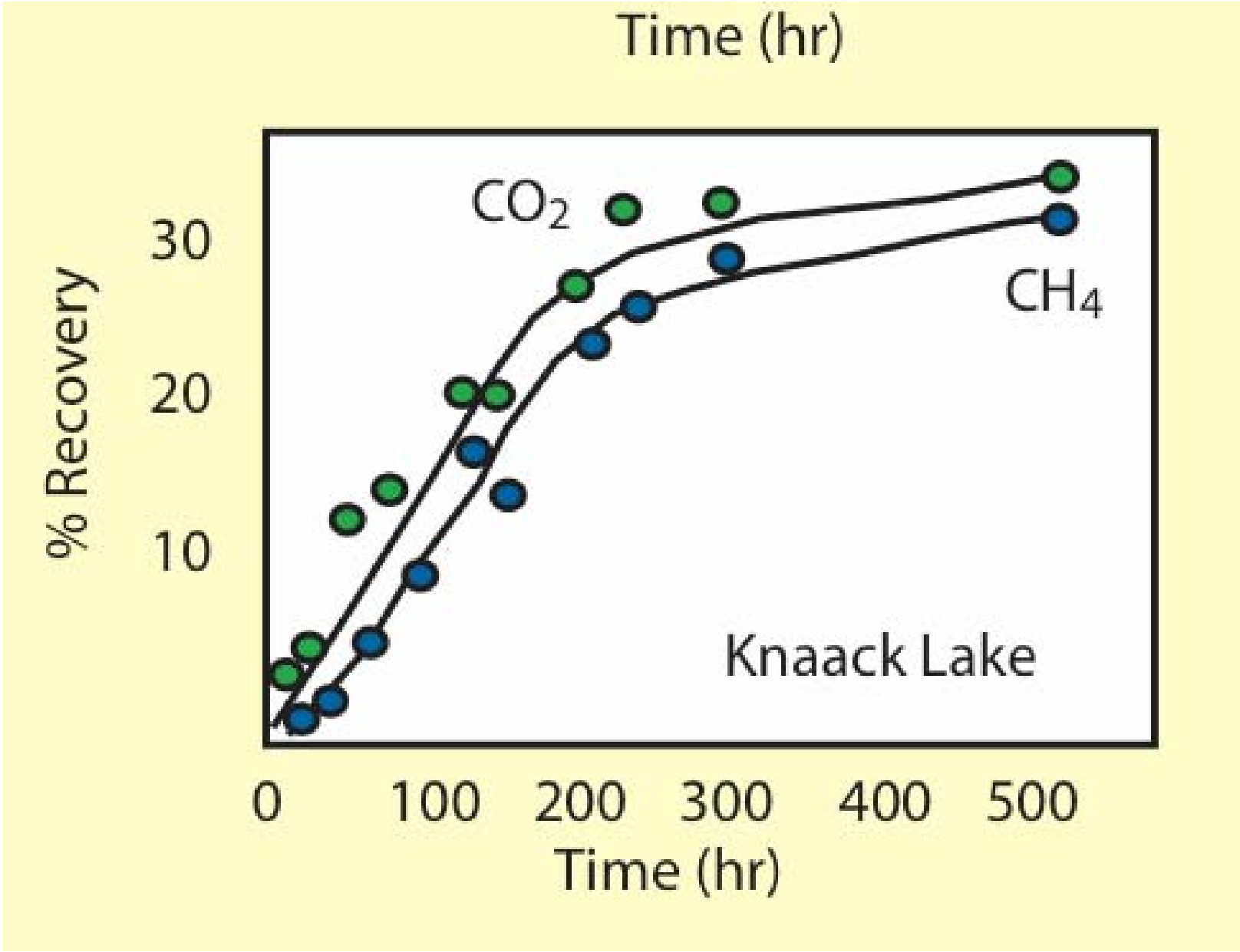
Competition for hydrogen between sulfate reducing and methanogenic bacteria

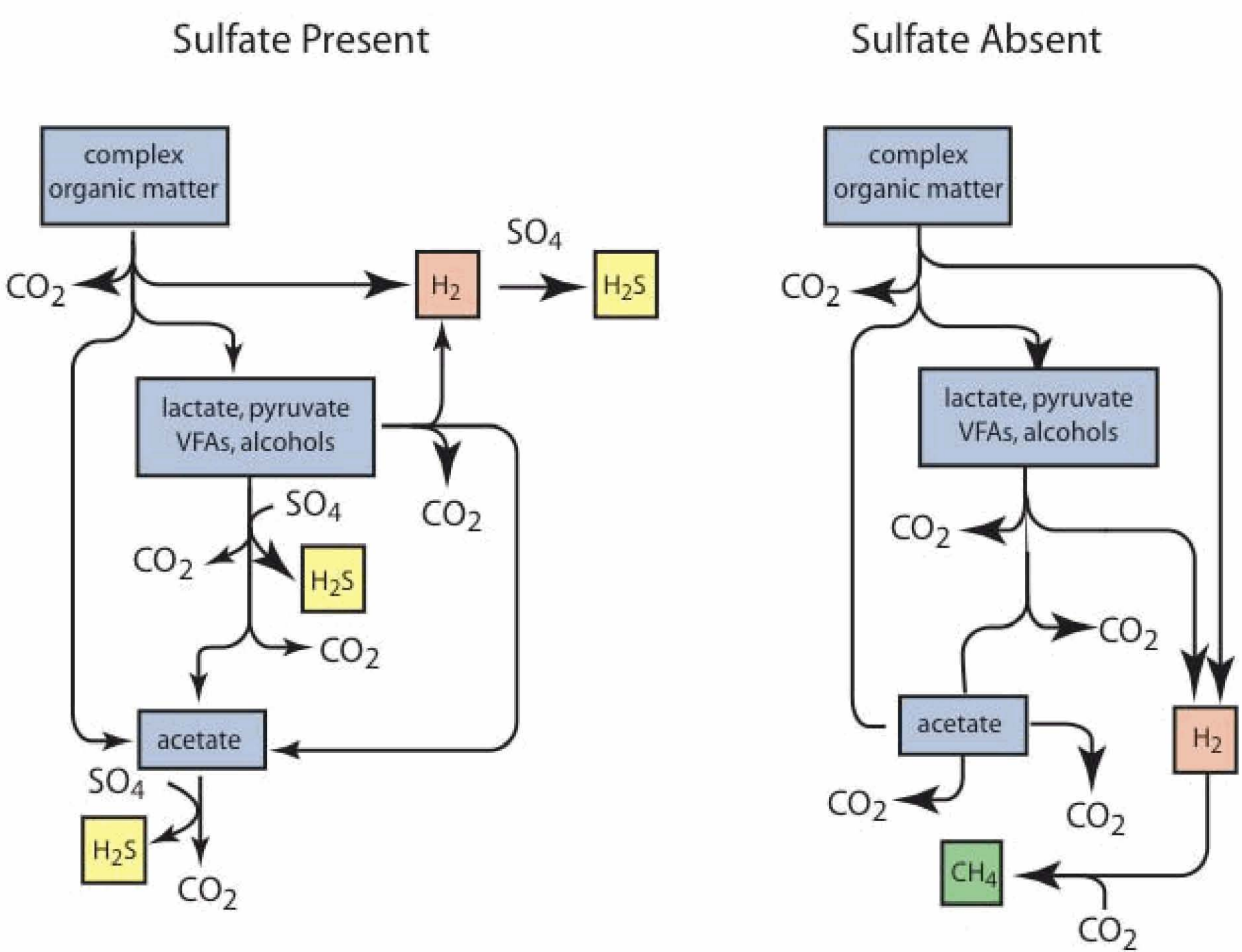



Changes in pore water concentrations
during a 114 day incubation
Concentration
SO4
CO2
CH4
Acetate
0
20
40
60
80
100
Day


Anaerobic degradation of pectin
CH4
CH4
Note faster response
Acetate
Acetate
MeOH
MeOH
H2
H2
Accumulated Product
0
5
10
15
20
25
30
Time (Days)

Degradation of pectin in Knaack Lake sediments

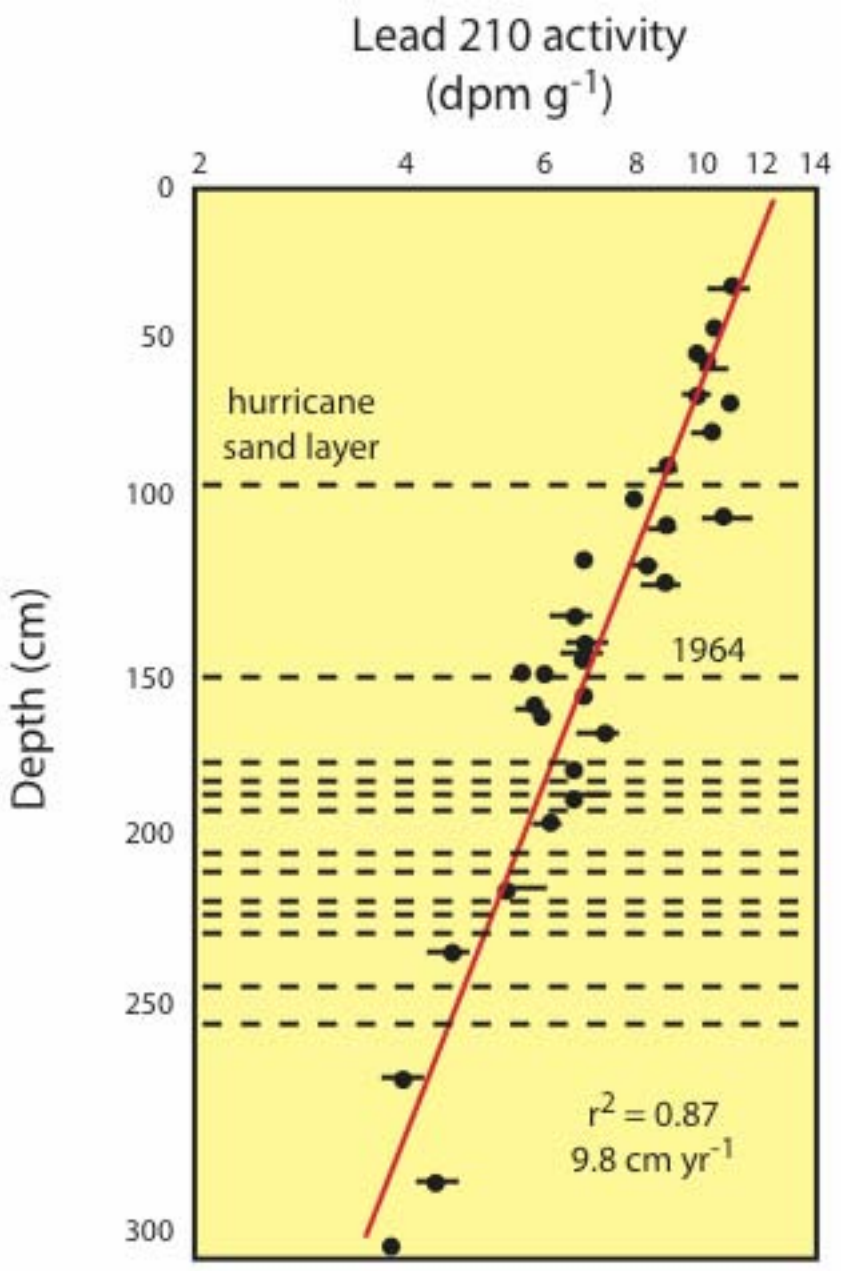



Sulfate Present
complex organic matter
CO_2
H_2
SO_4
H_2S
lactate, pyruvate VFAs, alcohols
CO_2
SO_4
CO_2
H_2S
CO_2
acetate
SO_4
H_2S
CO_2
Sulfate Absent
complex organic matter
CO_2
lactate, pyruvate VFAs, alcohols
CO_2
CO_2
acetate
H_2
CO_2
CO_2
CH_4
CO_2

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 methanogensis.

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

Biogeochemical cycling in Cape Lookout Bight Sediments

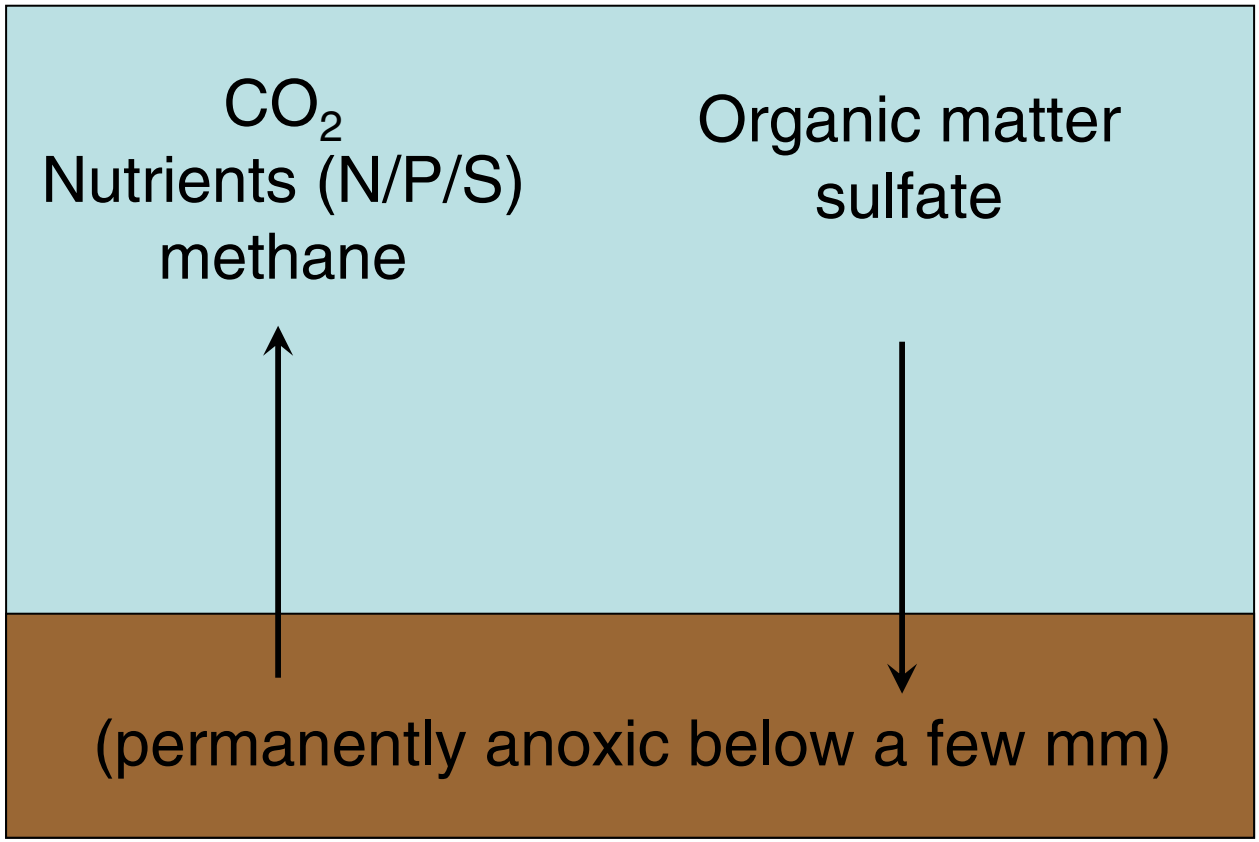


Map of Cape Lookout Bight.

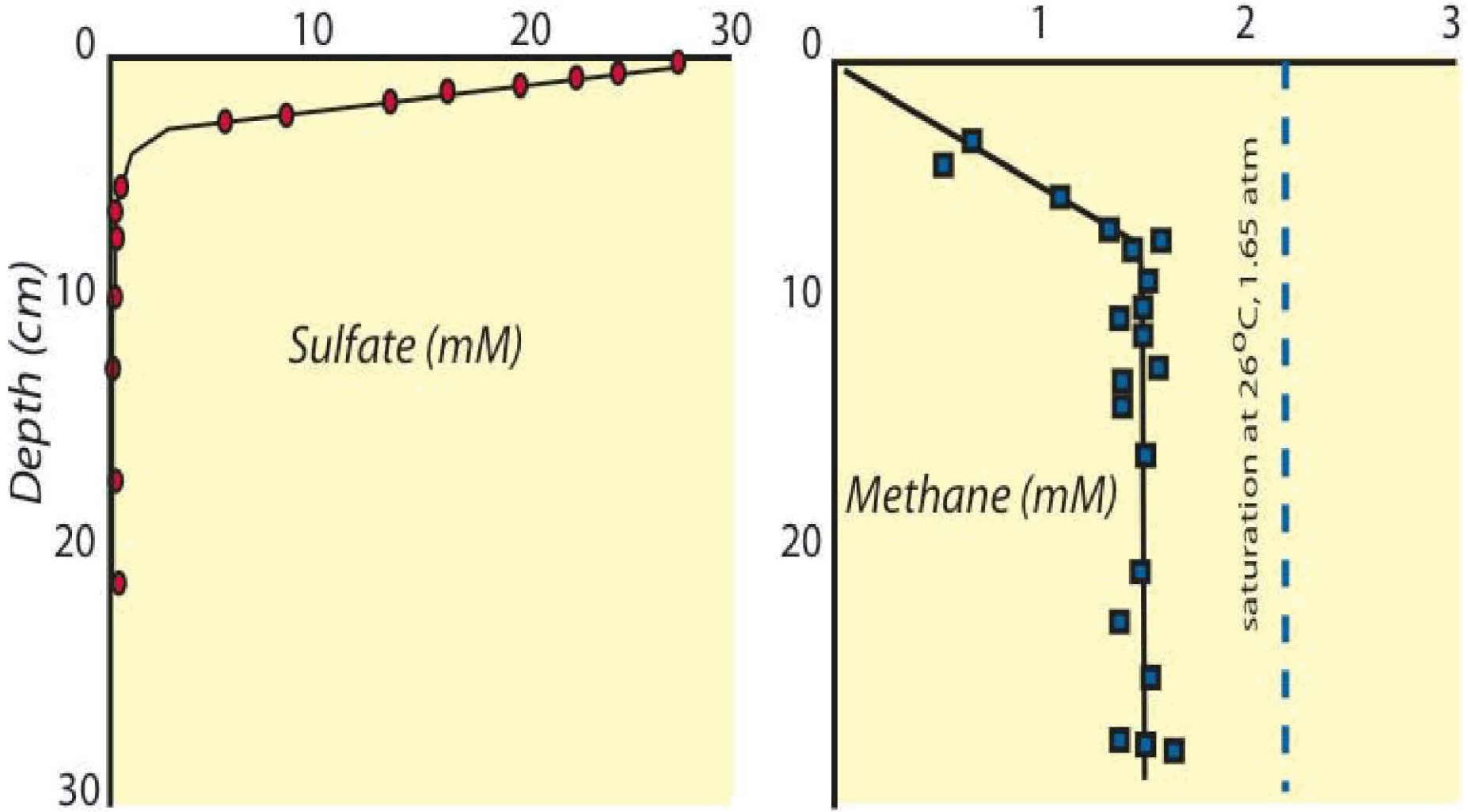
Map removed due to copyright restrictions.

Biogeochemical cycling in Cape Lookout Bight

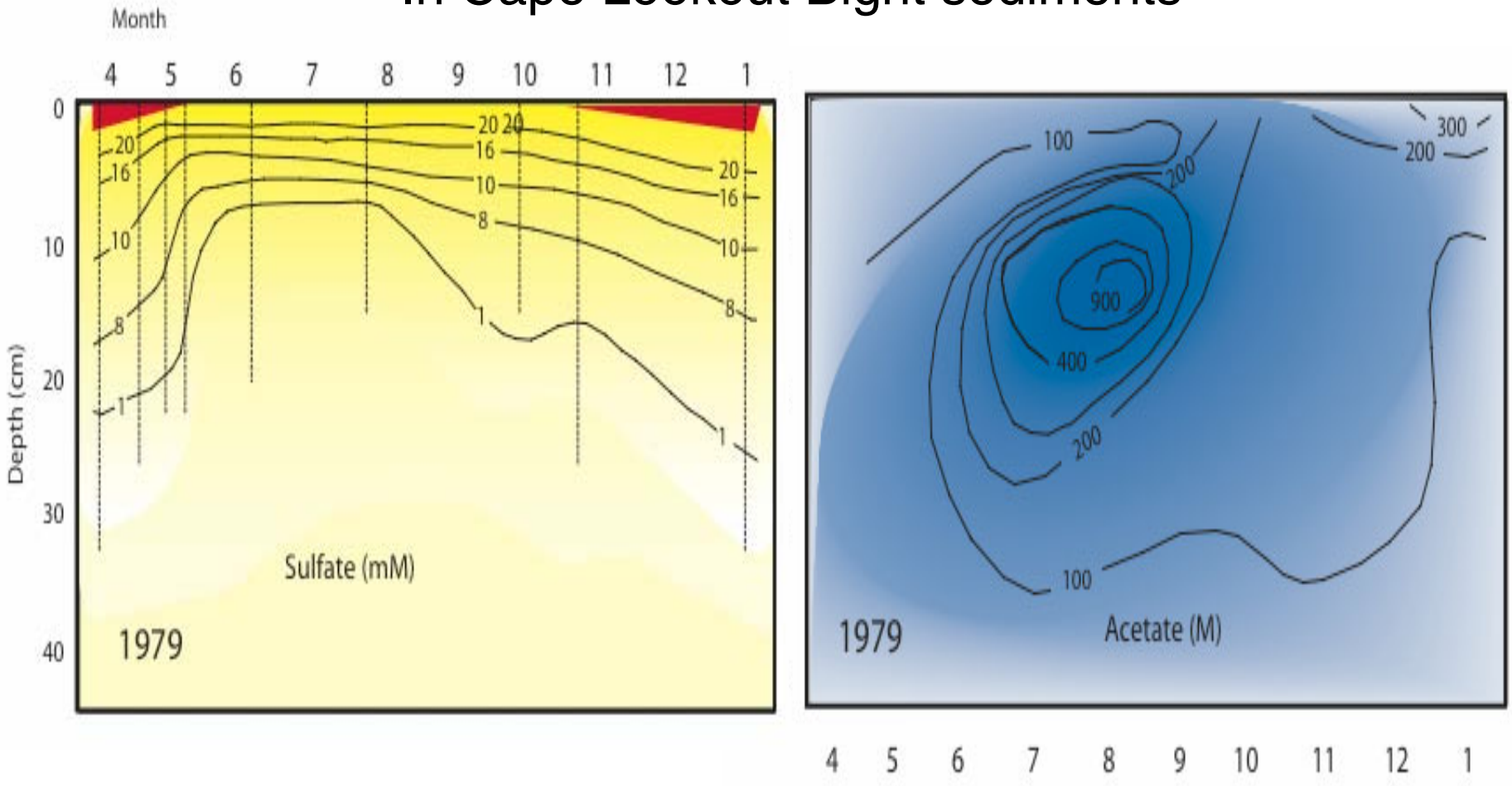
Can we achieve chemical balance if the system is at steady state?



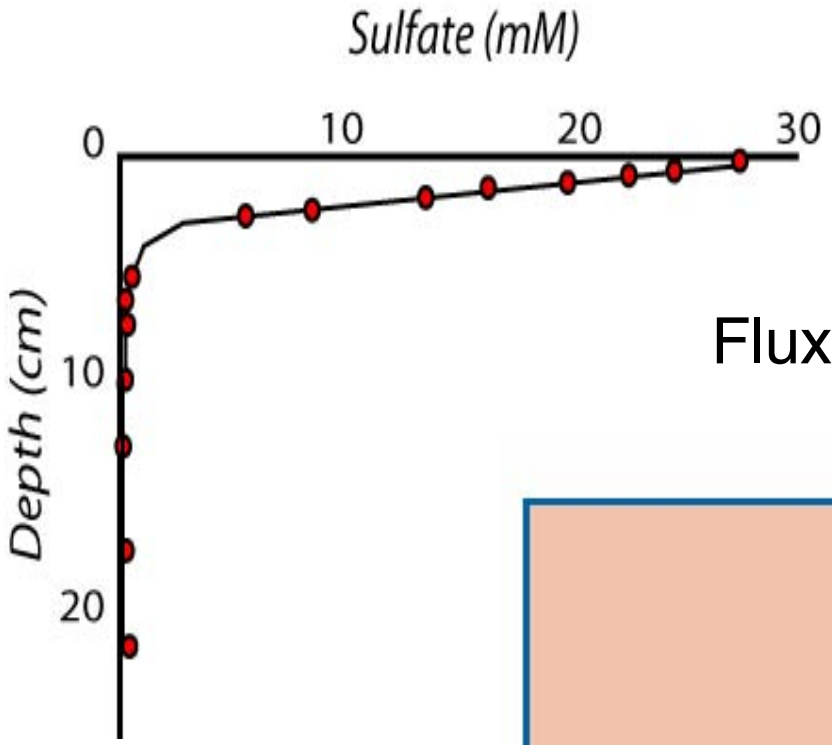
Sulfate and Methane in CLB sediments (August)



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



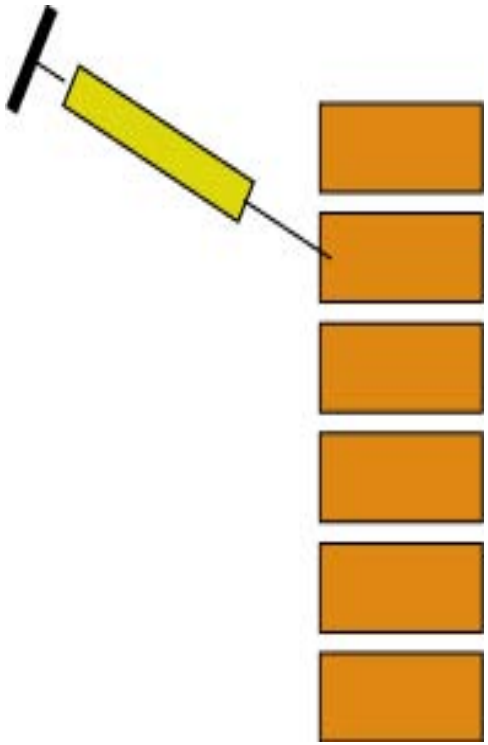
How can we calculate C remineralization from sulfate reduction?

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

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



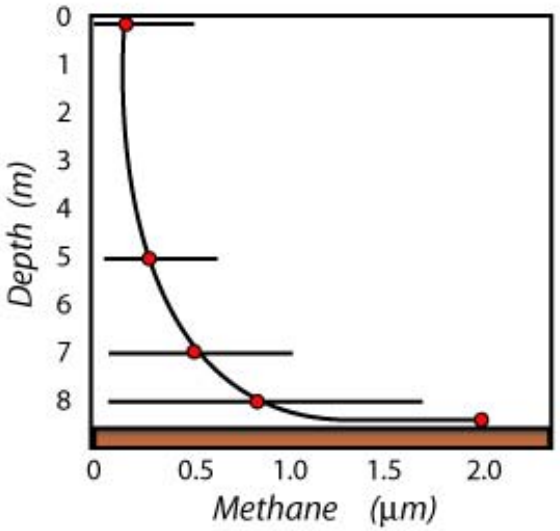
Moles of sulfate reduced ($m^{-2}\ yr^{-1}$)

	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

$$2CH_2O + SO_4^{=} \longrightarrow 2CO_2 + H_2S + H_20$$

Therefore 32 moles C by sulfate oxidation

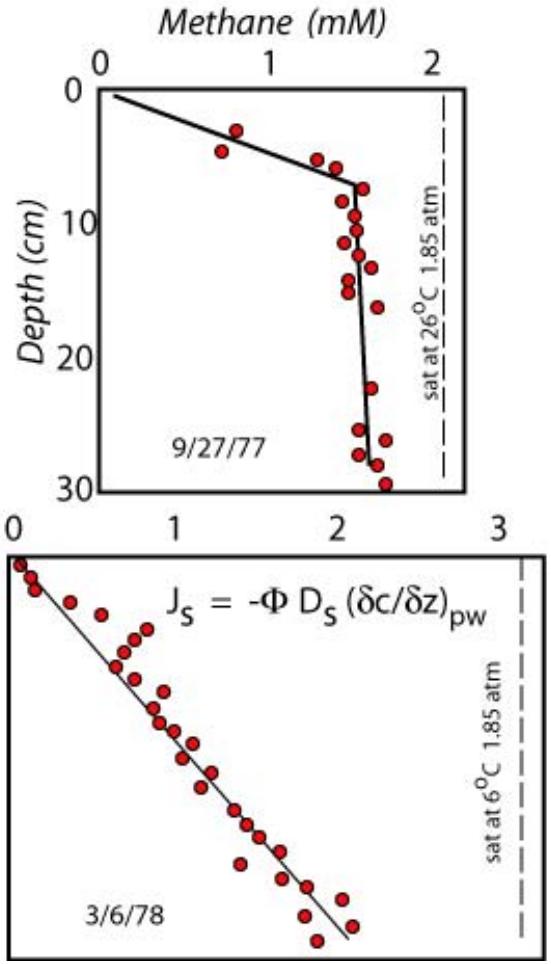
Methane fluxes from CLB sediments

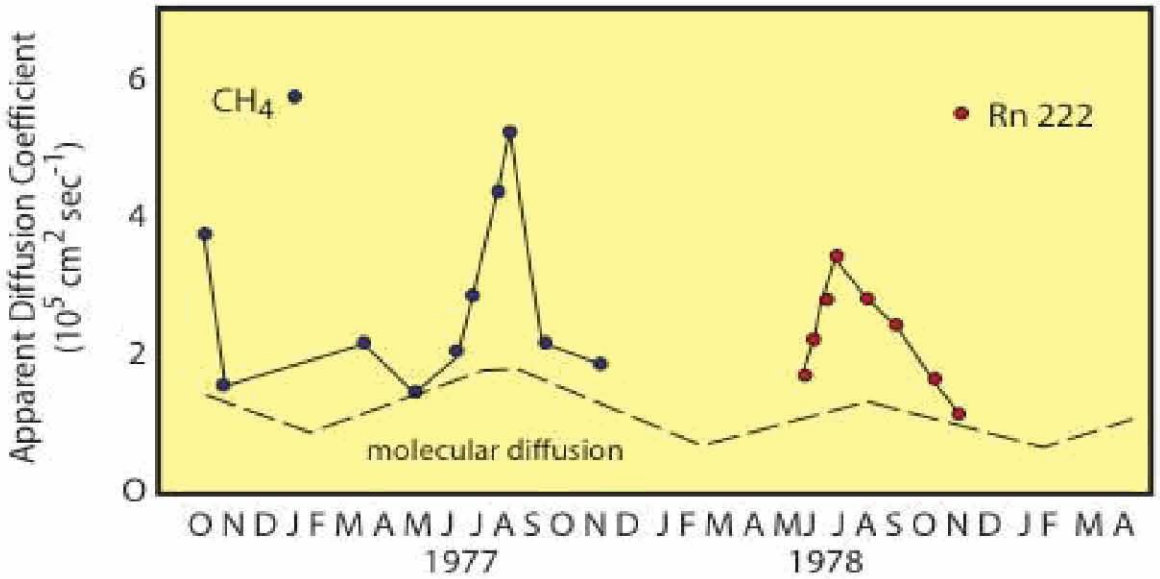


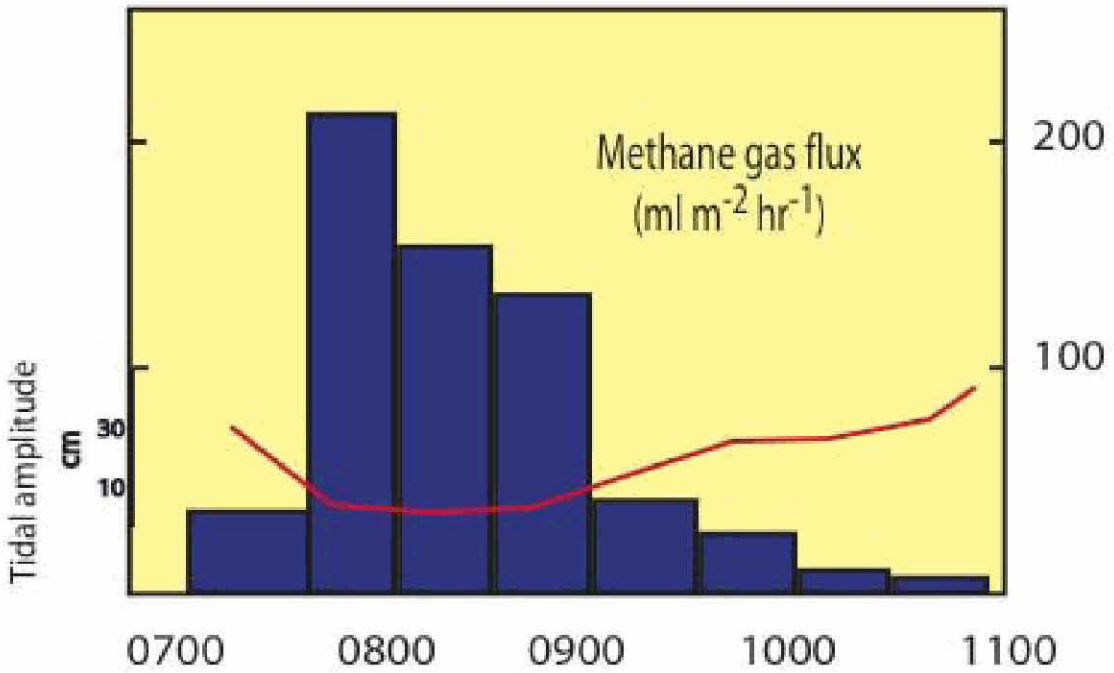
Methane diffusive fluxes

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

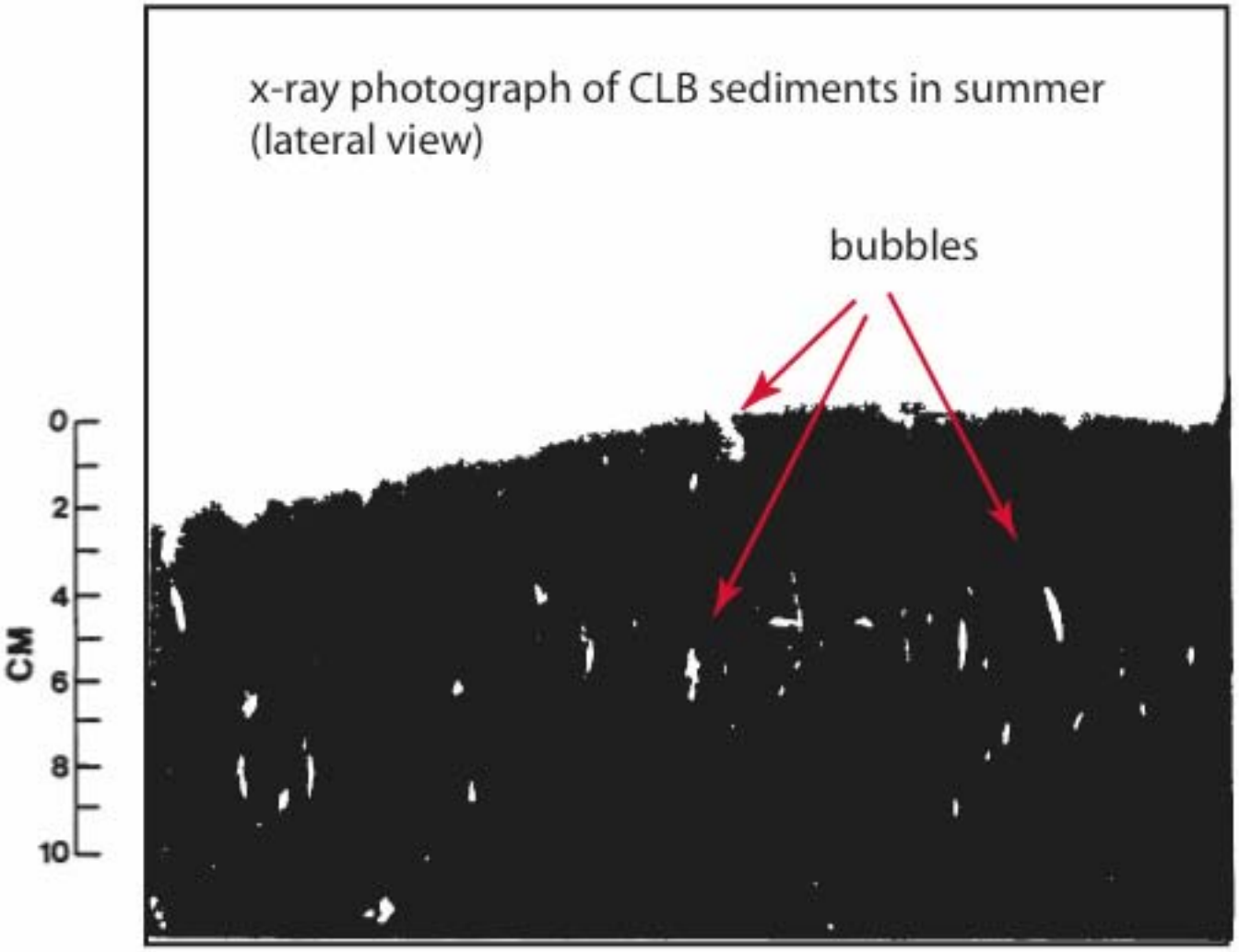
Calculation of Methane flux from CLB sediments




Apparent Diffusion Coefficient
(10^5 cm^2 sec^{-1})
6
4
2
O
CH_4
Rn 222
molecular diffusion
O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A
1977
1978

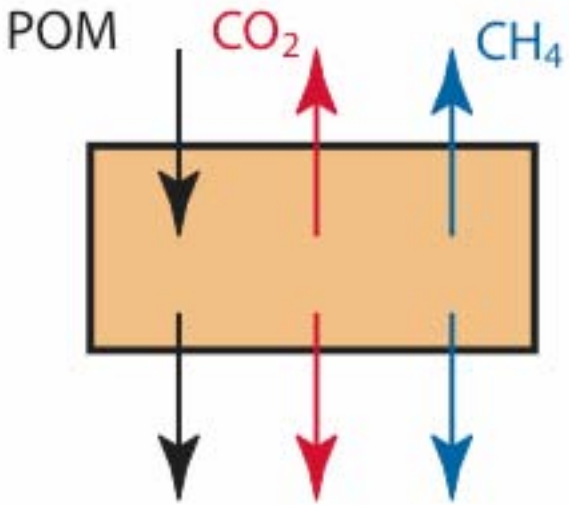

Methane gas flux
(ml m^{-2} hr^{-1})
200
100
Tidal amplitude
cm
30
10
0700
0800
0900
1000
1100

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



	ΣCO_2 fluxes $\mu m\ m^{-2}\ hr^{-1}$			CH_4 fluxes $\mu m\ m^{-2}\ hr^{-1}$		
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 (mole $m^{-2}\ yr^{-1}$)						
	29.8	0.057	**29.9**	0.85	4.85	**5.70**

Total C remineraliztion in CLB sediments



remineralization = C flux

out of top	out of bottom
$\Sigma CO_2 = 29.9$	$\Sigma CO_2 = 5.7$
$\Sigma CH_4 = 5.7$	$\Sigma CH_4 = 0.1$
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 remineraliztion due to methanogenesis:

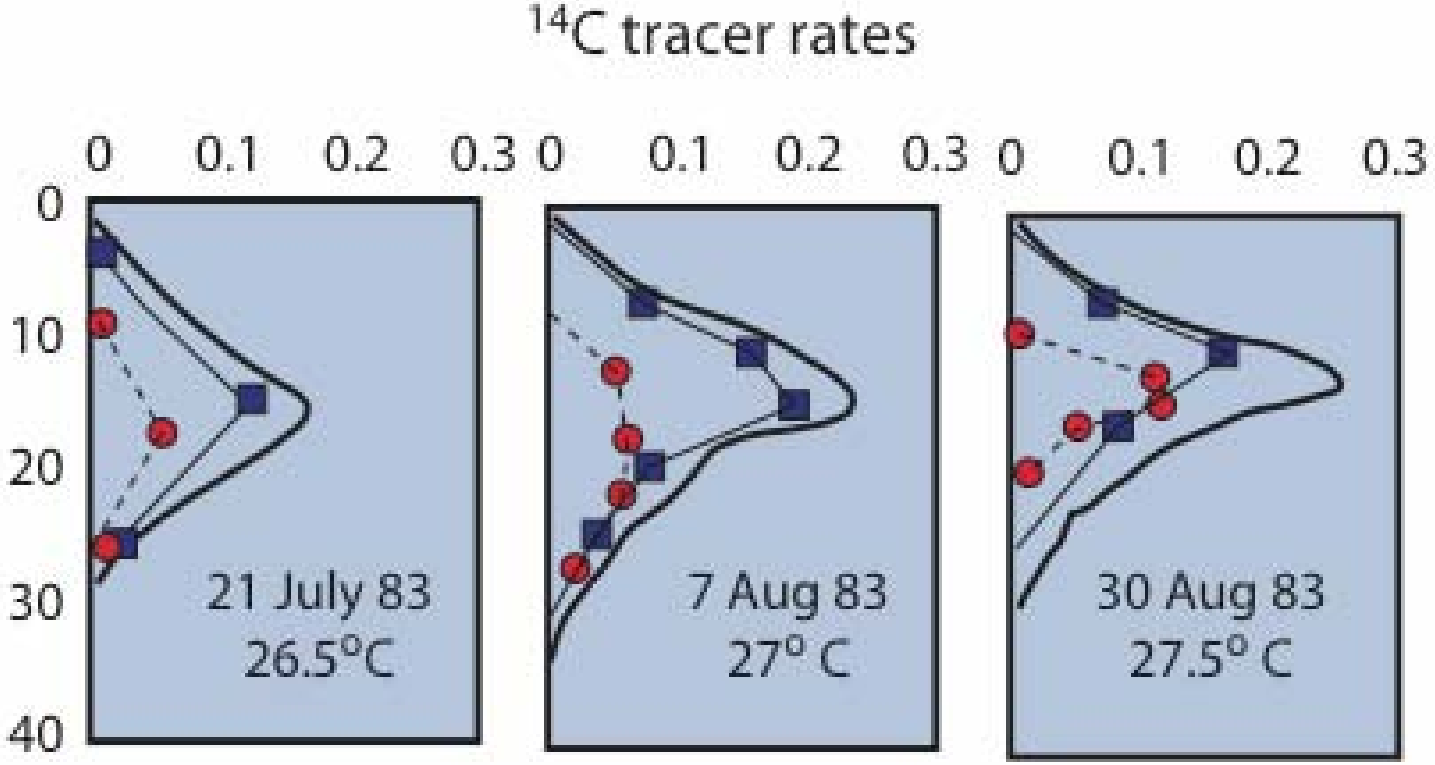
5.8 x 2 = 11.6 moles m-2 yr-1 or 28%

C reminerealization due to sulfate reduction is:

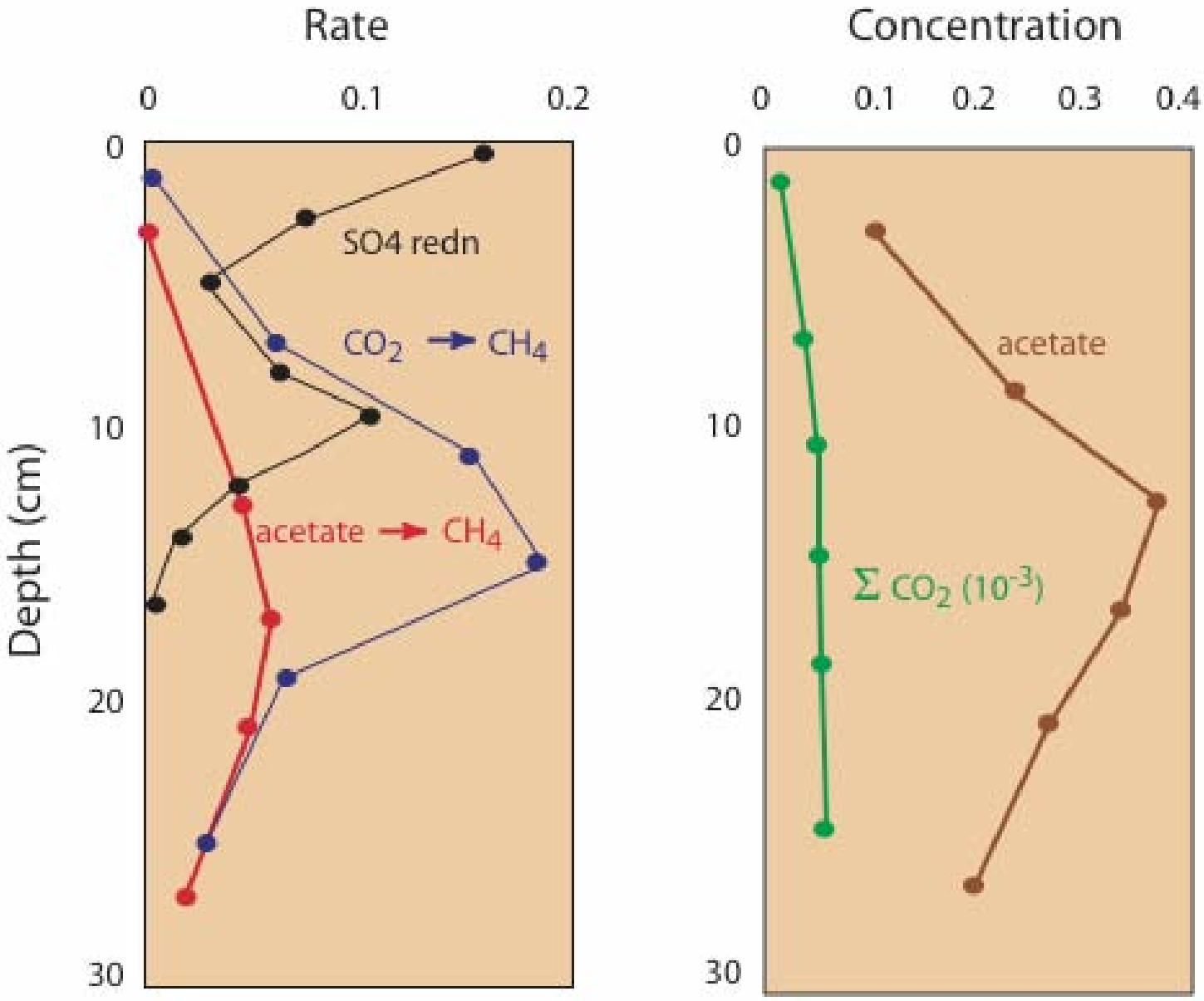
41.4
- 11.6
29.8 moles C m-2 yr-1 or 72%

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

Production of methane from acetate and CO_2 in CLB sediments. ^{14}C 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.