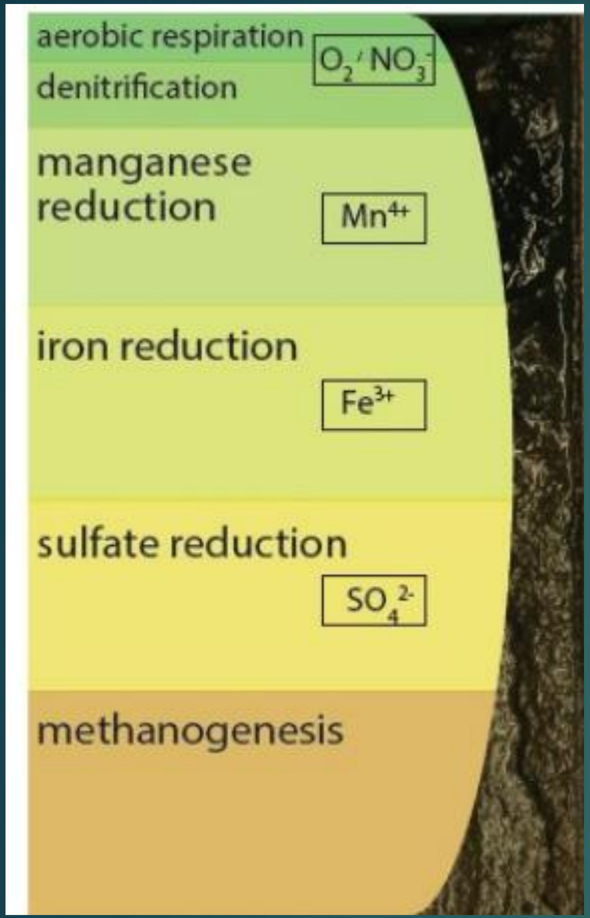
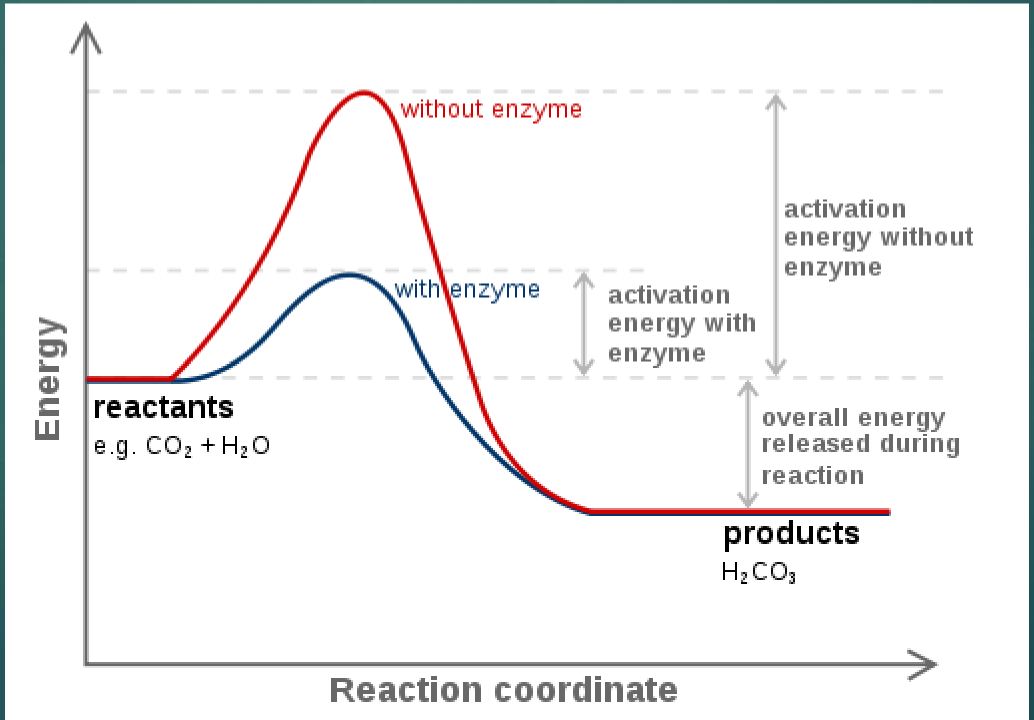
HOW MICROBIAL ACTIVITIES CHANGE THE WATER CHEMISTRY OF LAKES, AND HOW KNOWLEDGE OF THESE AFFECTS POLICIES

CAROL KELLY

Why are microbes so important in determining water chemistry?



- Energy-producing reactions of prokaryotic microbes very <u>diverse</u> (eukaryotes all use oxygen to produce energy)



- Microbial <u>enzymes</u> catalyze many different reactions

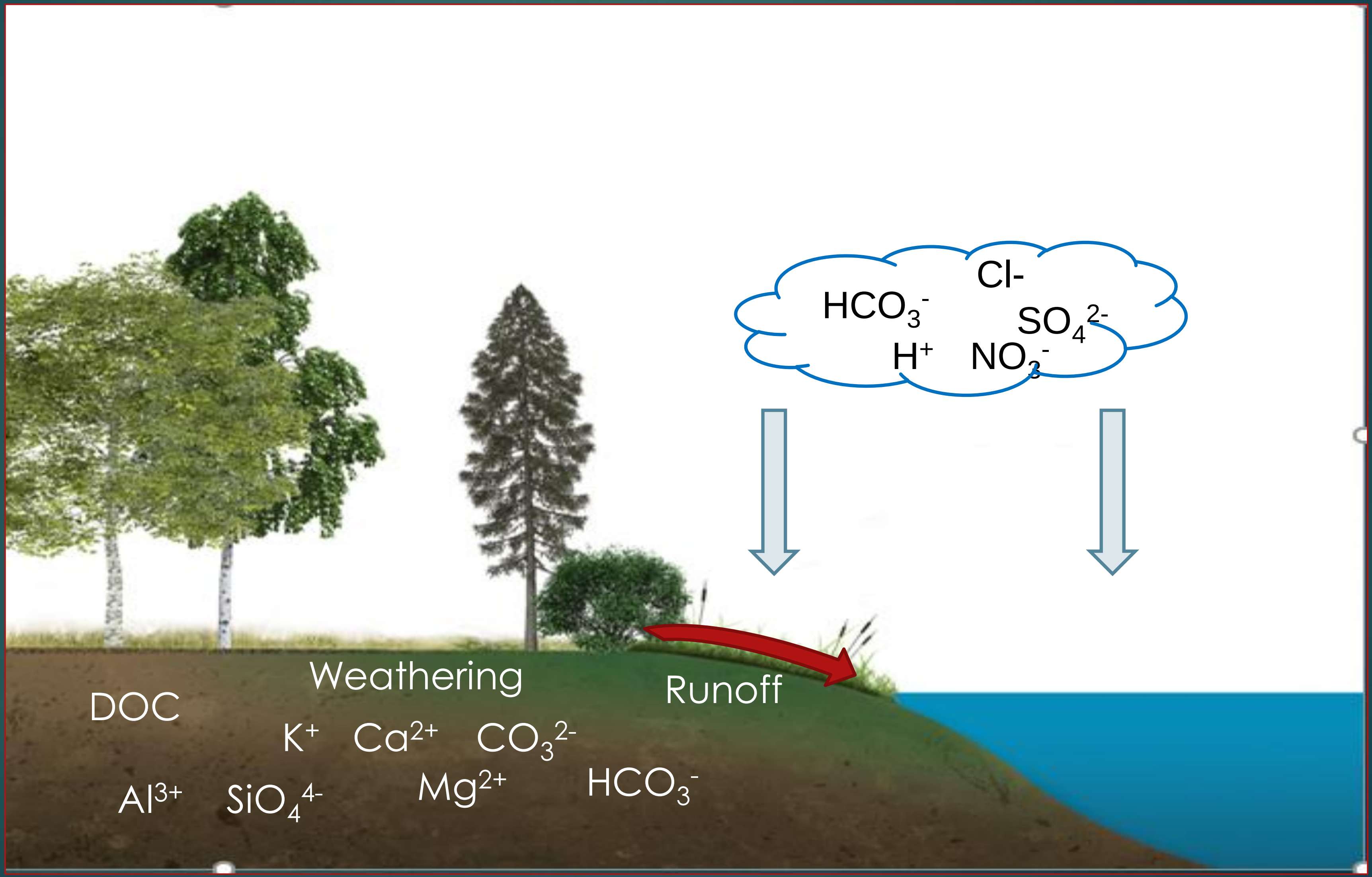
"Acid Rain"

- Sulfur oxides mainly from fossil fuel burning →SO_x's
- Nitrogen oxides from high temperature combustion →NO_x's
- These gases react in the atmosphere to produce H_2SO_4 and HNO_3

- David Schindler
- John Rudd
- Ray Hesslein
- Bob Cook
- Eva Schindler
- Vince St Louis
- Michael Turner
- Akira Furutani
- Morris Holoka
- Mike Stainton
- Jim Prokopovich
- Robert Flett
- John Amaral
- Shirley Richards
- Ken Beatty
- Patricia Ramlal
- Nancy Loewen

ELA’s first acid rain experiment
—addition of known quantities of sulfuric acid (H_2SO_4) to L. 223

For many decades, lake water chemistry and its buffering capacity thought to be determined largely by chemistry of rain and runoff



In lake water, what is buffering capacity?

"Titratable anions" = HCO_3^- and CO_3^{2-}

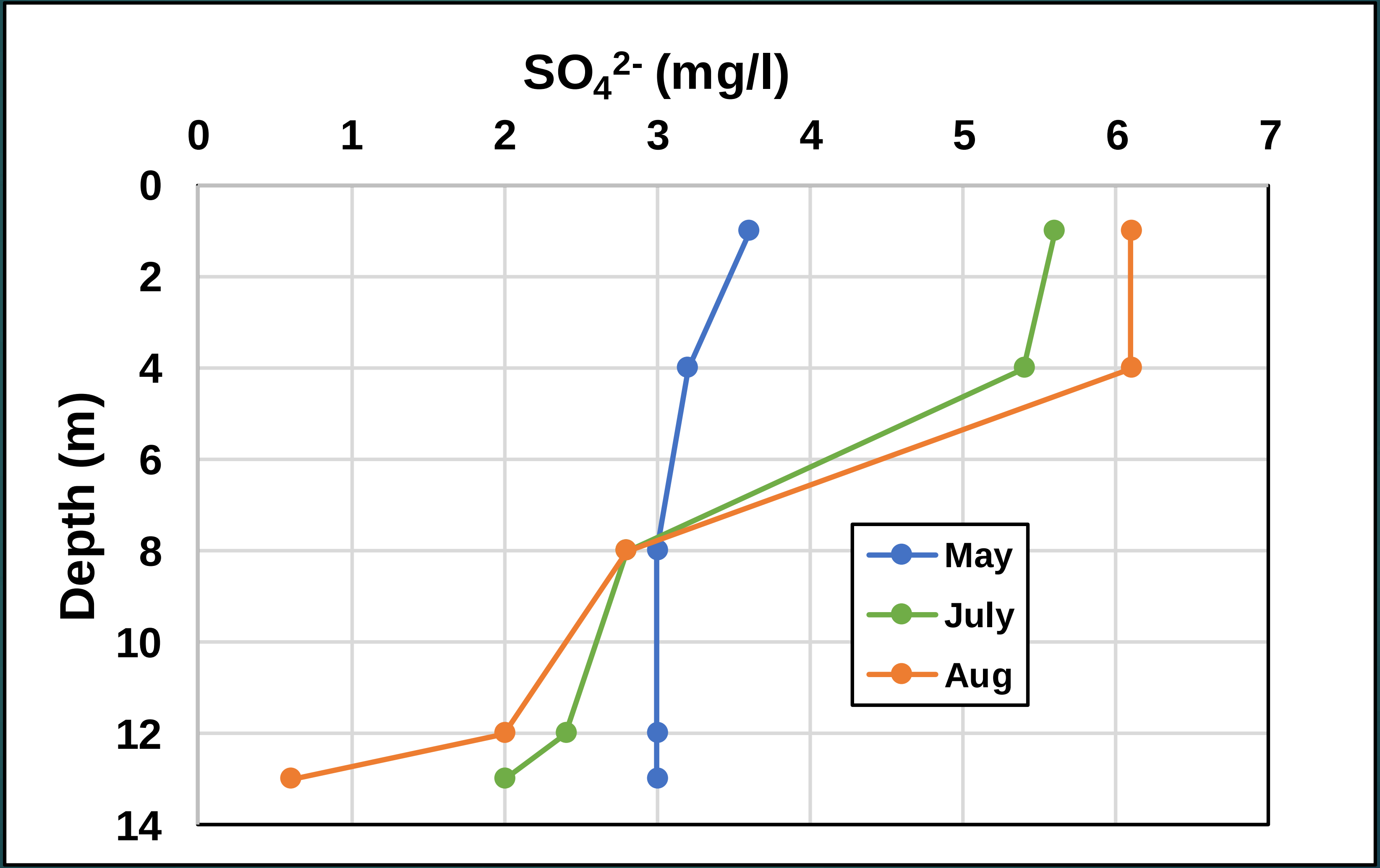
$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

$$H^+ + HCO_3^- \leftrightarrow CO_2 + H_2O$$

Lake 223, First 2 years of experimental acidification with H_2SO_4

	Initial pH	**Predicted (target) pH**	**Actual Final pH**
Year 1	6.65	4.46	6.18
Year 2	6.18	4.60	6.05

Lake 223, 1976



Microbial Consumption of Sulfuric Acid

Sulfate Reducing Bacteria

--Live in anoxic environments

--Use sulfate instead of oxygen in respiration:

$2CH_2O+SO_4^{2-} + 2H^+ \rightarrow H_2S +2\ CO_2 + 2H_2O$

“Biological buffering”

Microbial sulfate reduction was the major consumer of acid in L 223!

Mass balance budgets :

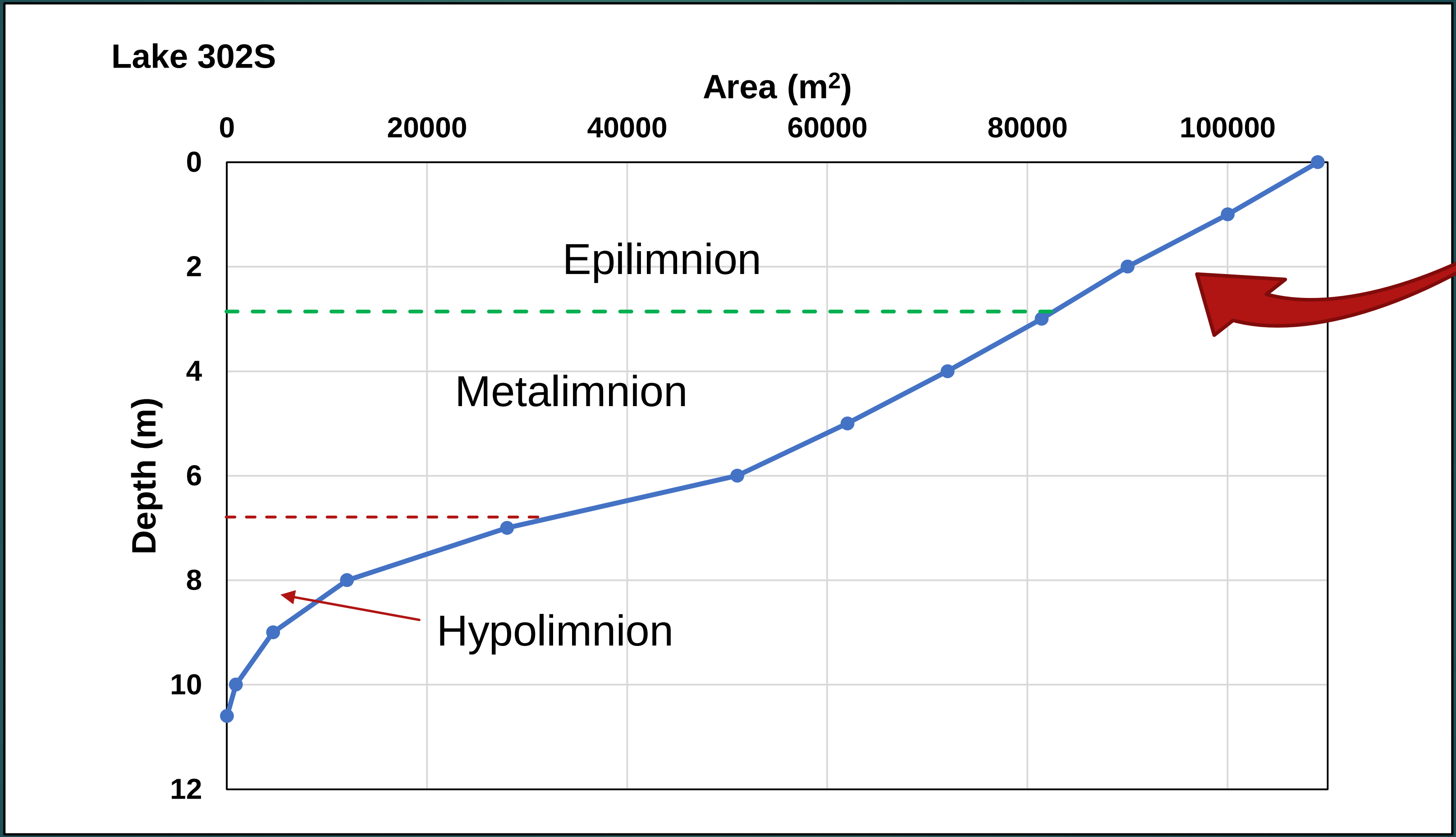
Table 4. Alkalinity generated from reactions of different ions in Lake 223, as deduced from mass-balance budgets. Data are in keq.

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{3+}	Mn^{2+}	NH_4^{+}	SO_4^{2-}	NO_3^{-}	Cl^{-}	Σ cation (C)	Σ anion (A)	C + A	Measured Alk prod.
1976	32.9	2.8	6.7	1.6	2.2	−0.5	1.8	41.5	1.6	5.9	47.5	49.0	96.5	111.7–126.8
1977	13.5	−6.3	−1.1	0.8	7.1	0.3	−2.4	68.4	4.5	−6.3	11.9	66.6	78.5	26.7–109.5
1978	21.0	6.0	14.9	0.5	−10.4	1.7	−1.9	39.5	1.9	16.5	31.8	57.9	89.7	52.0–100.2
1979	6.2	−6.1	−1.3	−0.6	−5.1	3.5	−9.4	5.2	4.5	−18.8	−12.8	−9.1	−21.9	61.6
1980	−16.0	−15.0	−8.6	−4.1	0.4	3.4	−1.4	79.3	6.3	19.8	−41.3	105.4	64.8	105.8
1981	−4.5	−4.6	0.1	−0.9	−13.1	−2.4	−5.4	131.5	8.4	−0.4	−30.8	139.5	108.7	121.8
1982	30.6	−8.8	−2.4	−9.2	9.1	12.6	−10.8	65.1	5.7	9.1	21.1	79.9	101.0	109.4
1983	36.0	−17.2	−5.6	−0.1	−4.1	−4.3	−0.1	105.1	1.5	0.7	4.6	107.3	111.9	66.8
Total	119.7	−49.2	2.7	−12.0	−13.9	14.3	−29.6	535.6	34.4	26.5	32.0	596.5	628.5	655.8–801.9
Total Alk prod. (%)	19	−8	0	−2	−2	2	−5	85	5	4	5	95		

Cook et al., 1986

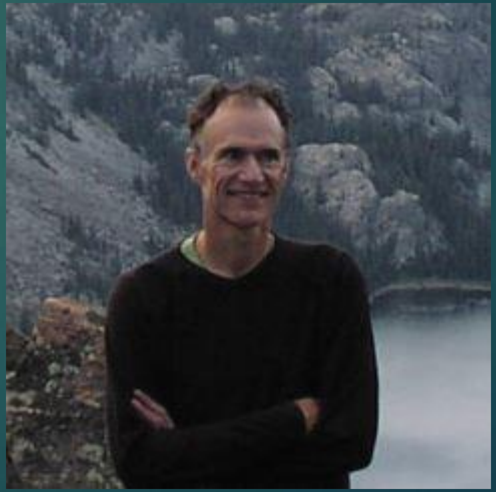
- Not all the sulfate loss was accounted for by the losses in the anoxic hypolimnion (deep water)
- What about epilimnetic (shallow water) sediments overlaid by oxygenated water?

- Most of the water in a lake is in contact with the shallow water sediments
- Harder to measure effects—lots of methods development needed



Core incubations

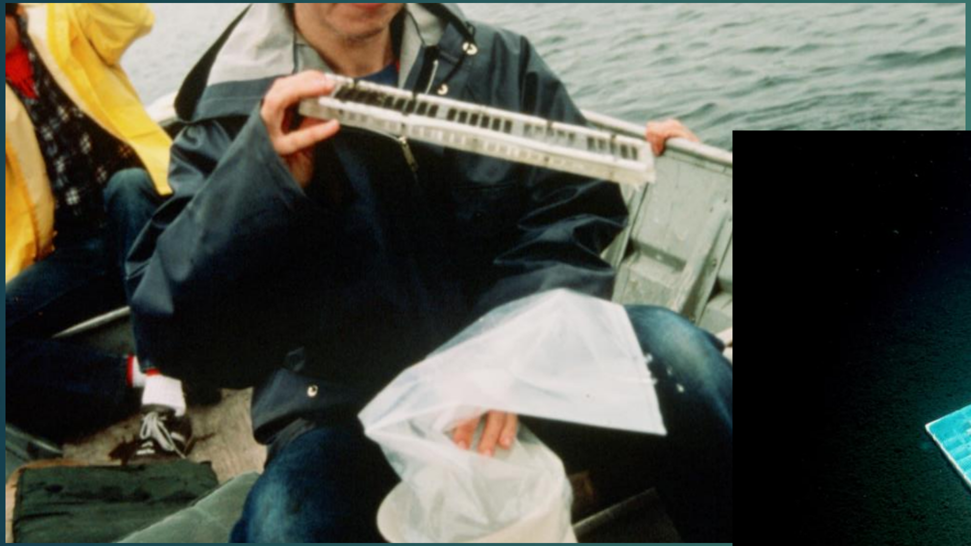
Sulfate reduction -- $^{35}SO_4^{2-}$
Diffusion rates -- $^{3}H_2O$
Denitrification -- $^{15}NO_3$

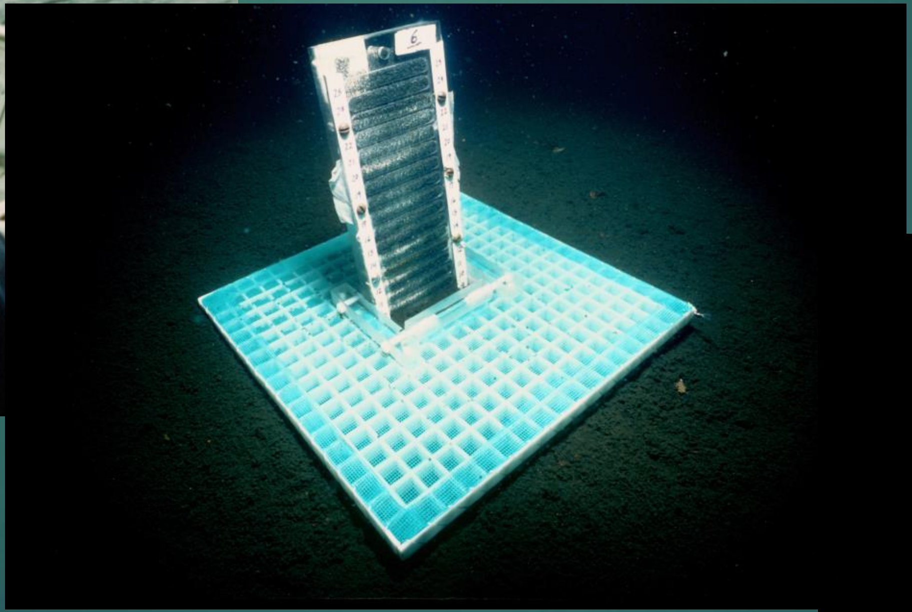


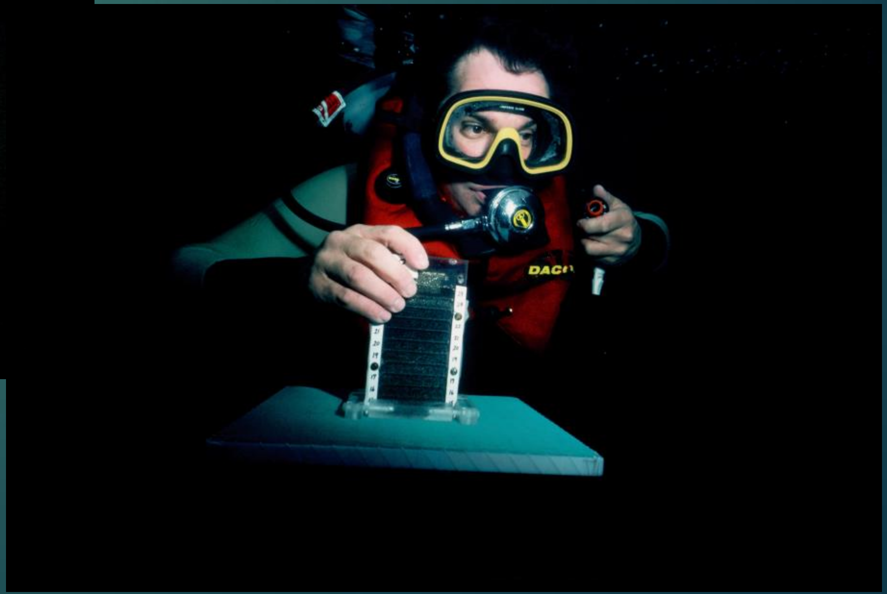
“Flett” probes

- Oxygen
- pH

“Peepers” equilibrate with sediment pore waters







Peeper Analyses:

pH

DIC

CH_4

SO_4^{2-}

NO_3^-

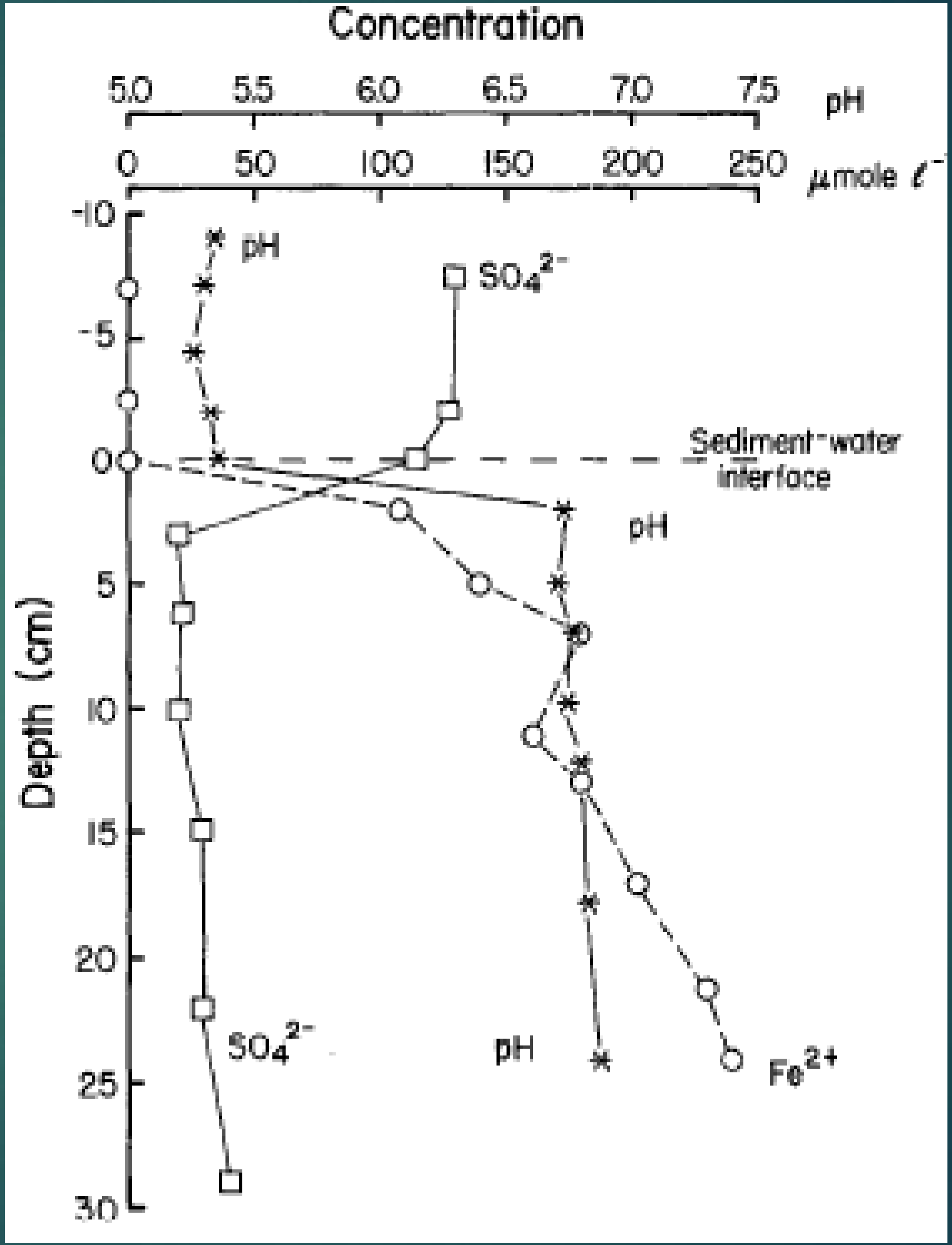
Fe^{2+}

NH_4^+

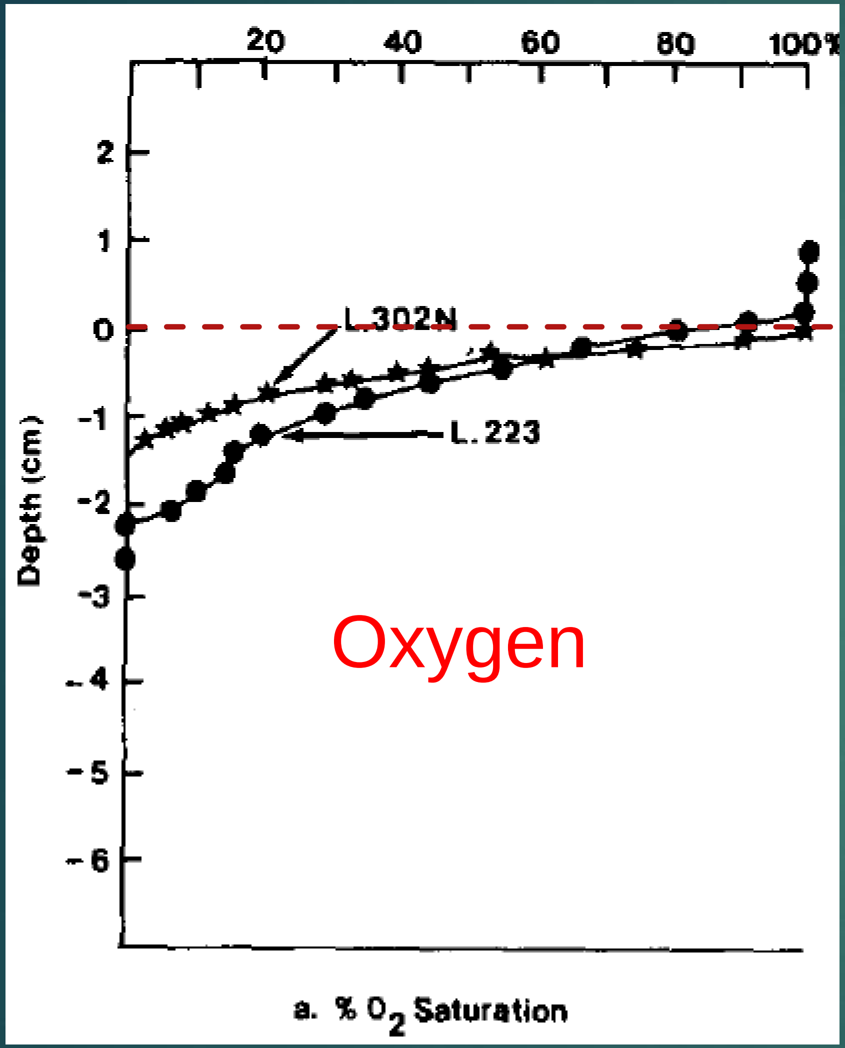
H_2S

L. 223 “Peeper” profile
4 m
August, 1981

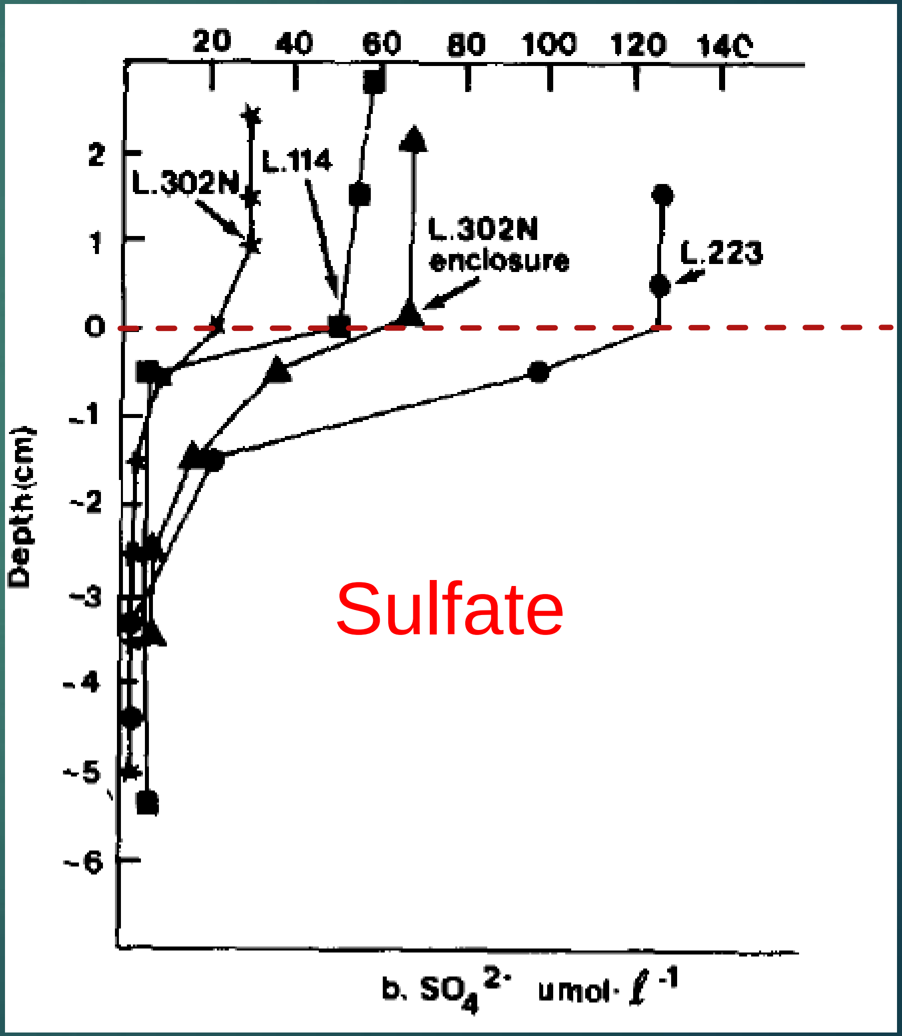
If no microbial activity, profiles would be straight up and down



Shallow water sediments anoxic just below surface

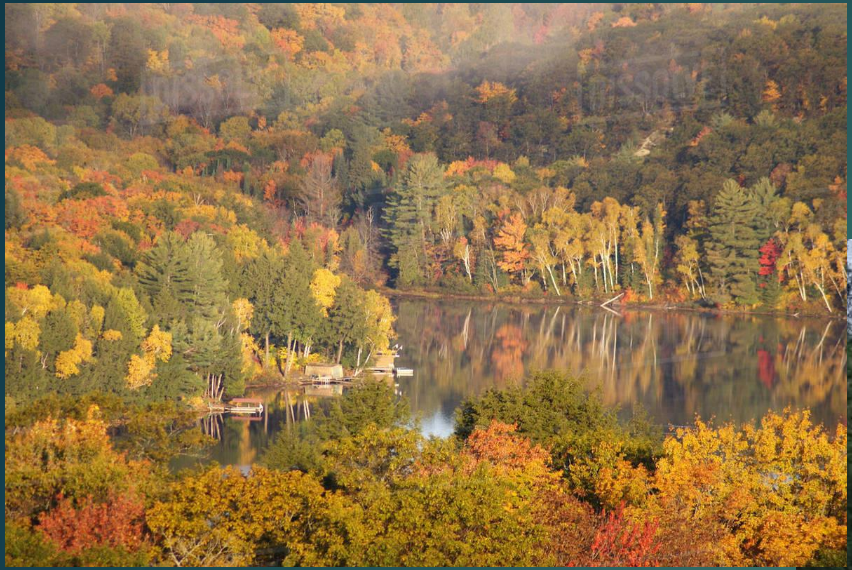


SO_4^{2-} reduction responds to increased SO_4^{2-}



What about non-ELA lakes?

Why did lakes in same depositional region (i.e., same acid rain input) have different pH's?



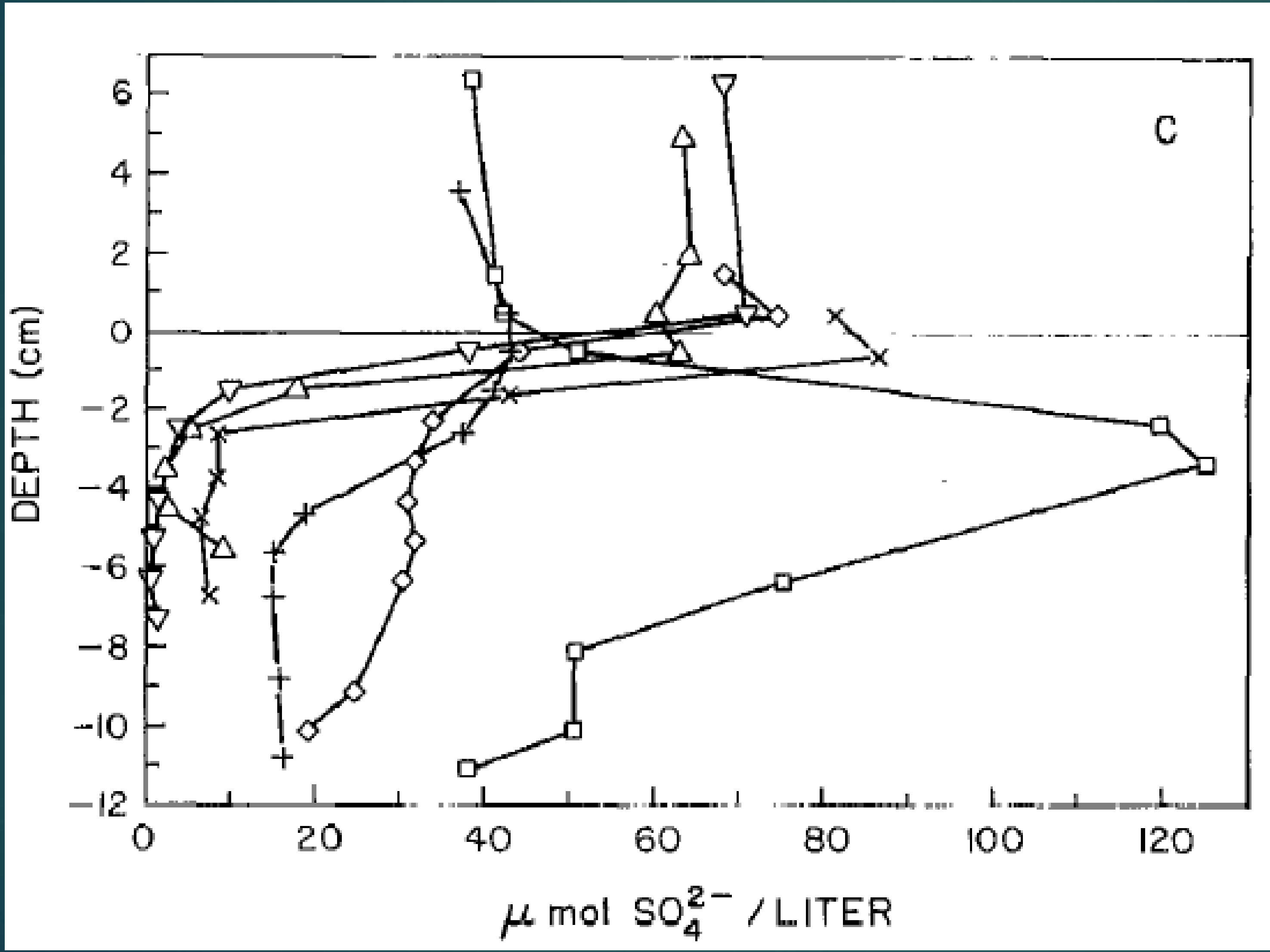
Dorset, ON

Adirondack Mtns, NY

Hovvatn, Norway

Decreasing pH

Profiles of sulfate profiles and pH were similar in other lakes, except at lowest pH in Norway

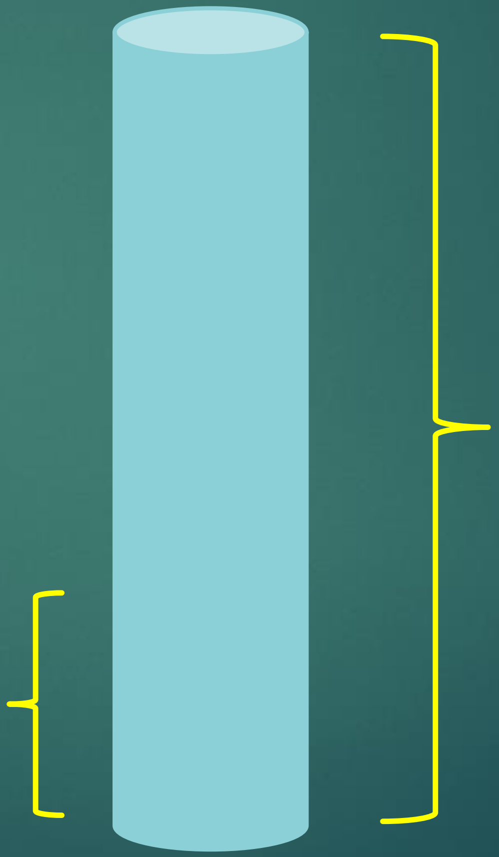


X Chubb Lake (Dorset, ON)
□ Lille Hovvatn Lake, Norway
+ Hovvatn Lake, Norway
◊ Big Moose Lake, NY
Δ Woods L, NY
▼Lake 302S

We calculated relative rates of sulfate reduction by comparing reduction rate to sulfate concentrations:

Mass Transfer Coefficient
for sulfate (S_S) =

Depth of water column
from which sulfate removed
meters per year (m/yr)



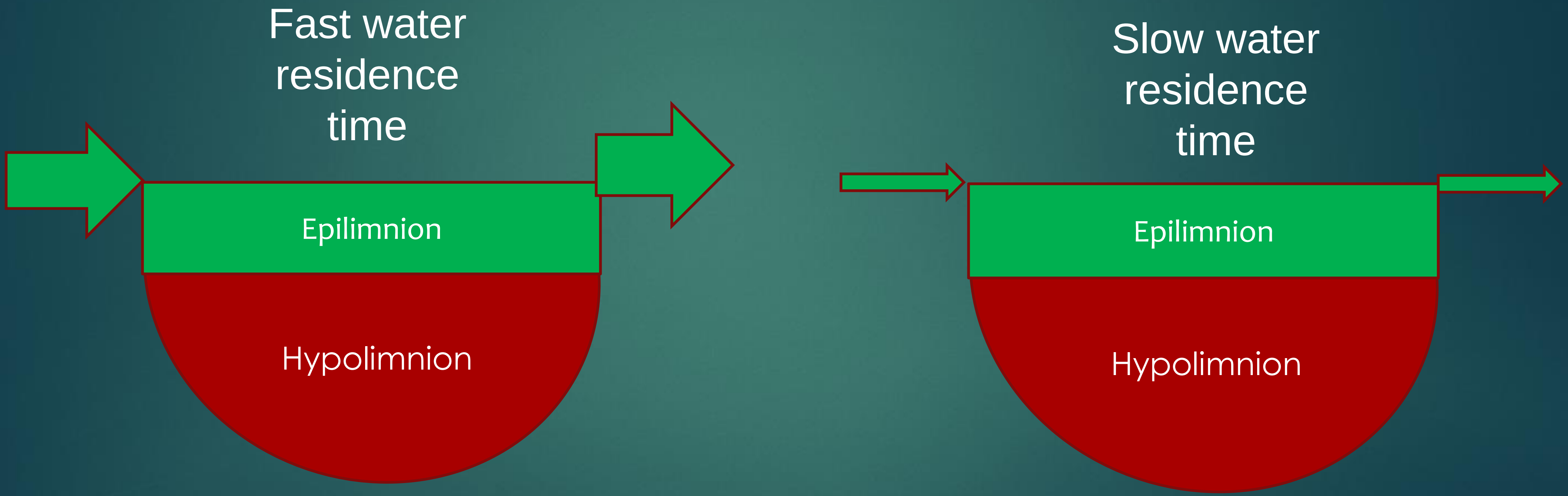
Water Column (meters)
Contains sulfate

Table 2. Measured rates of sulfate reduction* on given dates, and estimates of annual mass transfer coefficients for sulfate (summer rate × 0.5)

Lake	Sampling Depth (m)	Date	SO_4^{2-} $\mu eq \cdot L^{-1}$	SO_4^{2-} reduction rate $\mu eq \cdot m^{-2} \cdot d^{-1}$	Annual S_S $m \cdot yr^{-1}$
302S	1.5	Aug. 1984	136	498	0.65**
223	4	Jul. 1983	236	426	0.33
114	2	Sept. 1981	128	215	0.31
Twitchell	1	Jun. 1984	92	222	0.44
Big Moose	3.5	Jul. 1983	150	400	0.49
Woods	1.5	Jun. 1984	126	362	0.52
Dart's	2.5	Jun. 1984	108	126	0.21
Red Chalk	2	Sept. 1982	176	150	0.16
Chubb	1.5	Sept. 1982	172	270	0.29
Plastic	3.0	Sept. 1982	146	91	0.11
Crystal	6	Jun. 1985	66	100	0.56
					$\bar{x} = 0.36 \pm 0.17$

Inflow to a lake depends on watershed size

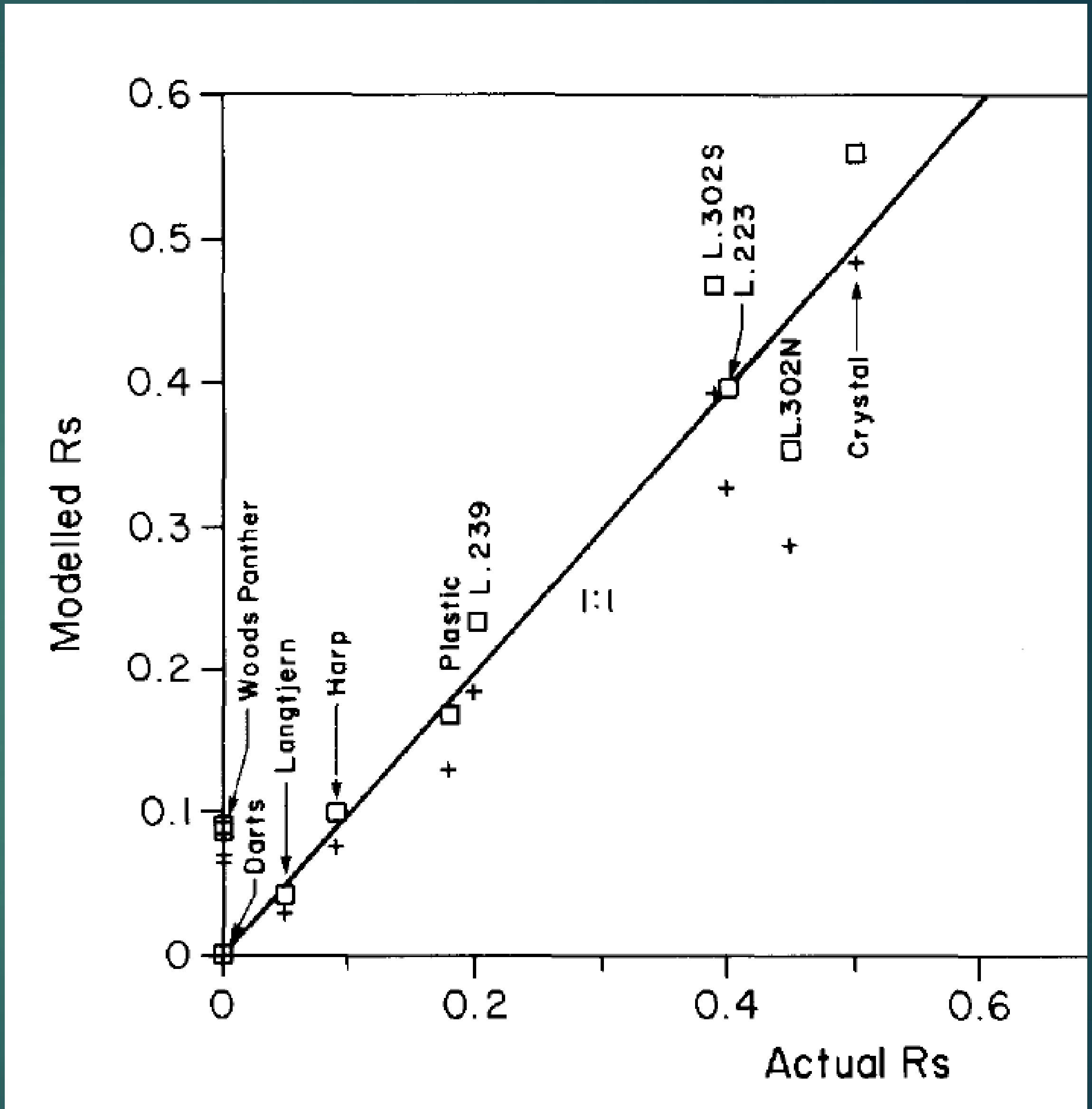
Two lakes of equal volume, but different inflow rates:



R_S = Retention of sulfate
or
Fraction of sulfate "lost" in the lake

Can be modeled if you include water residence time and average S_S

Sulfate loss and acid neutralization is predictable!

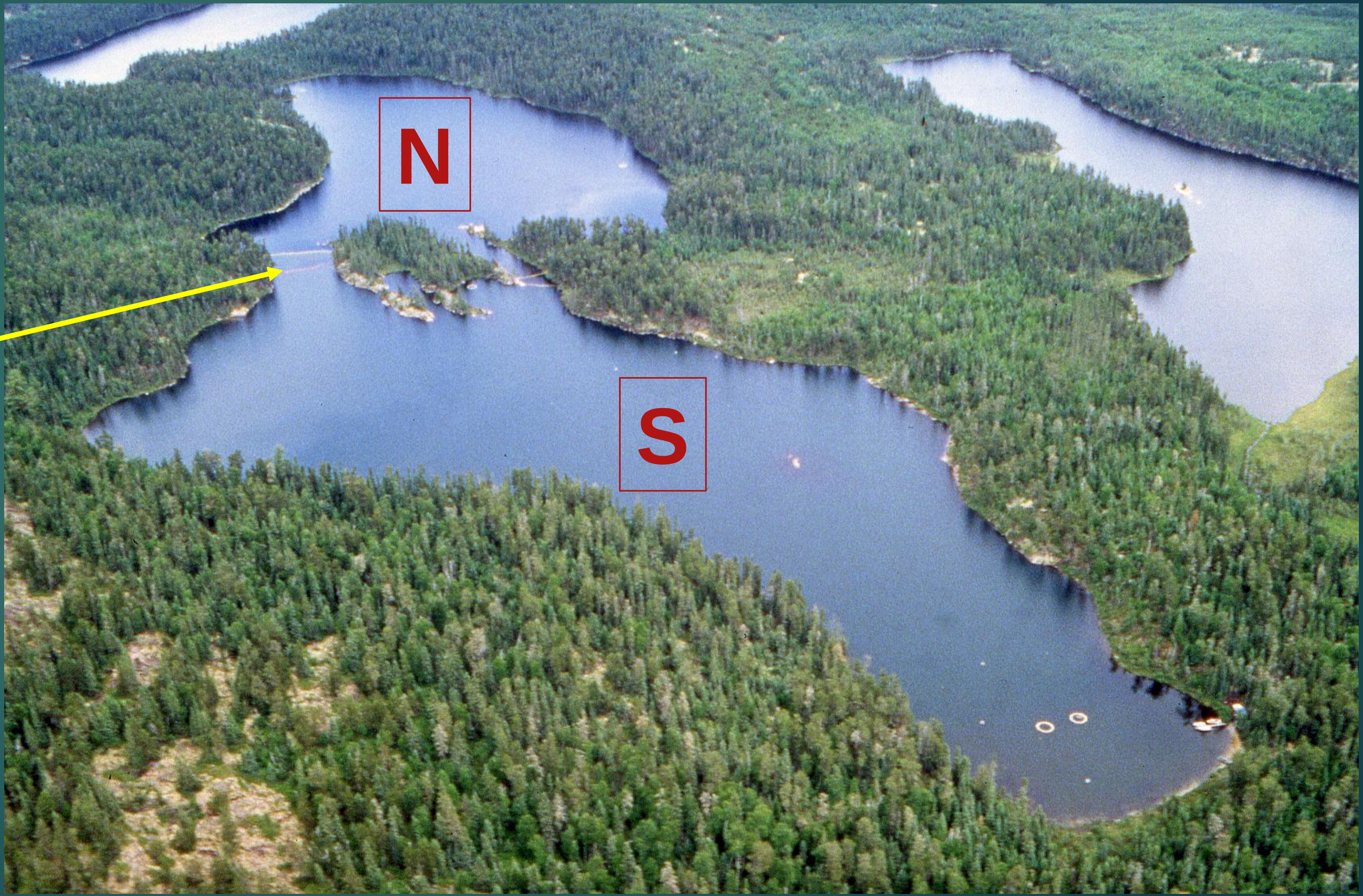


Acid Rain has both Sulfuric Acid (H_2SO_4) and Nitric Acid (HNO_3)

DO THEY BOTH NEED TO BE REGULATED TO THE SAME DEGREE?

Lake 302 North (Nitric acid) and South (Sulfuric Acid)

Curtain dividing
the two basins



Microbial Consumption of Nitric Acid (HNO3)

Algae

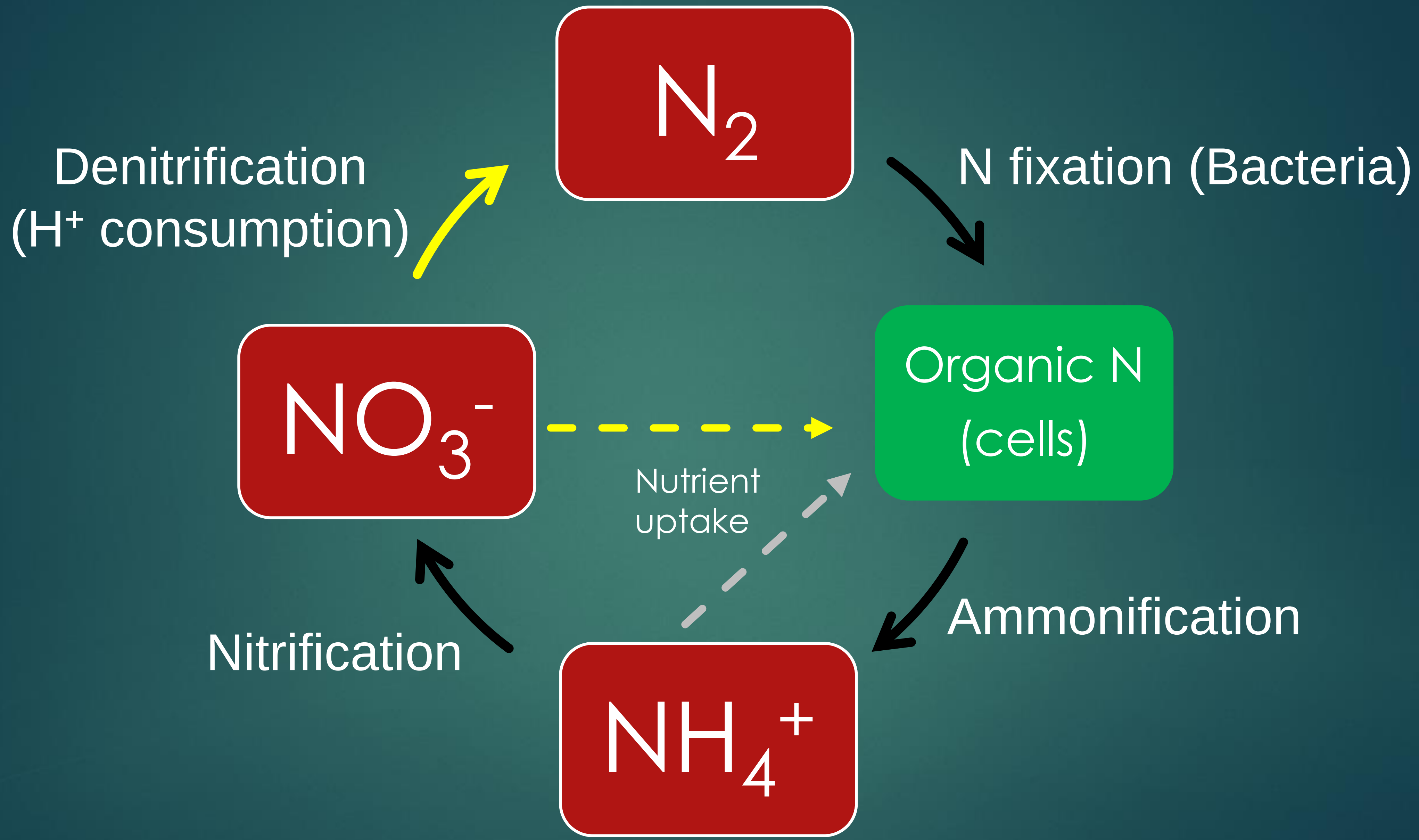
--Take up NO_3^- as a nutrient

Denitrifying Bacteria

--Live in near-anoxic environments

--Use nitrate instead of oxygen in respiration:

$$2\ NO_3^- + 2\ H^+ + \text{organic carbon} \rightarrow N_2 + 2H_2O + CO_2$$



N_2
N fixation (Bacteria)
Denitrification
(H^+ consumption)
NO_3^-
Organic N
(cells)
Nutrient
uptake
Nitrification
Ammonification
NH_4^+

Sediment traps collect algal cells as they sediment to bottom of lake

Nitrate additions did not increase algal productivity

Table 4. Sedimentation rates of C, N, and S (μmol m^{-2} d^{-1}) in summer 1982 and 1984 from the epilimnia of the north and south basins of Lake 302.

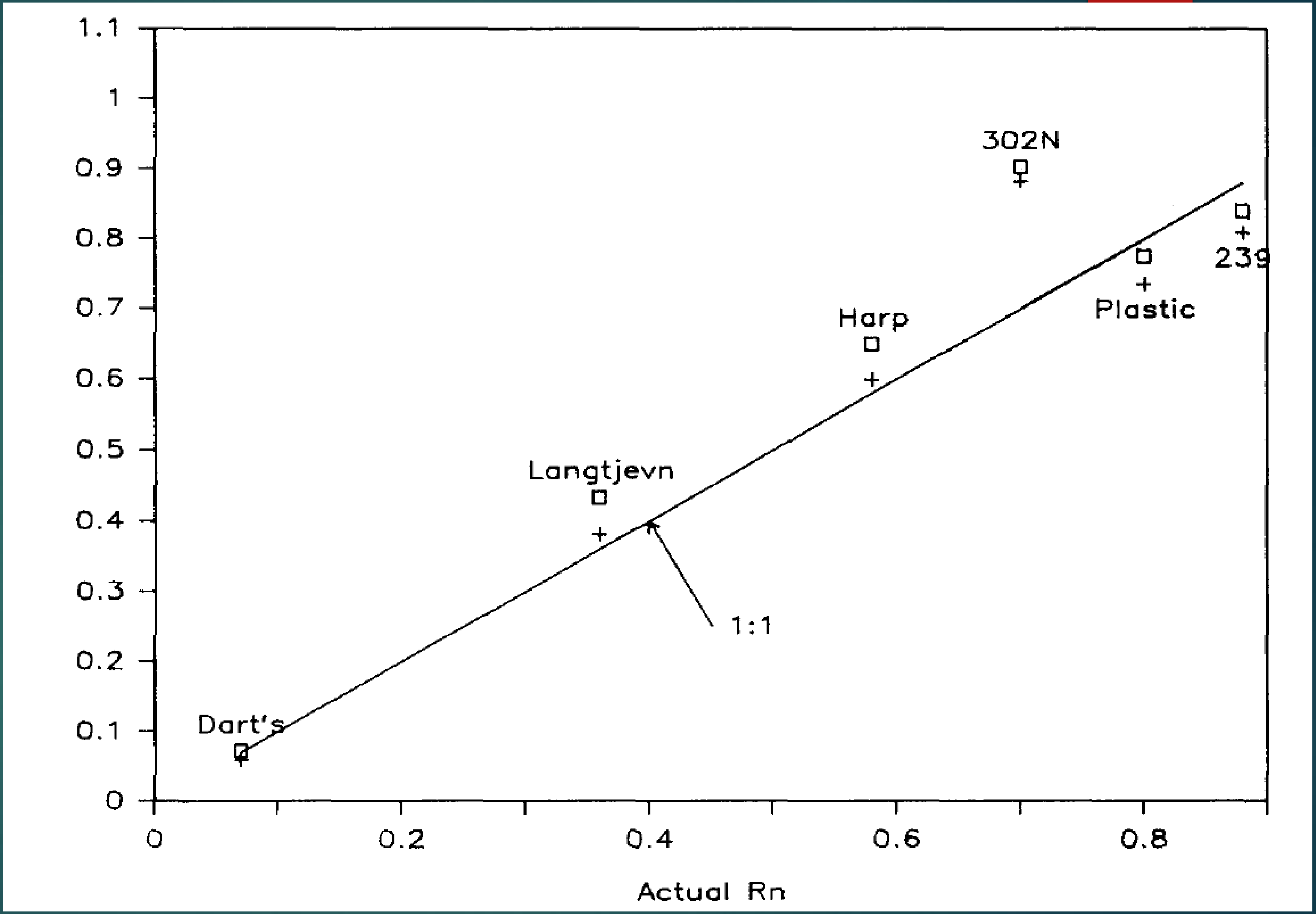
	C	N	S*
1982†			
North basin	14	1.3	0.086
South basin	18	2.5	0.11
1984‡			
North basin	22	1.9	0.14
South basin	25	3.0	0.16

NO3- removal by denitrifying bacteria was much slower than by algae

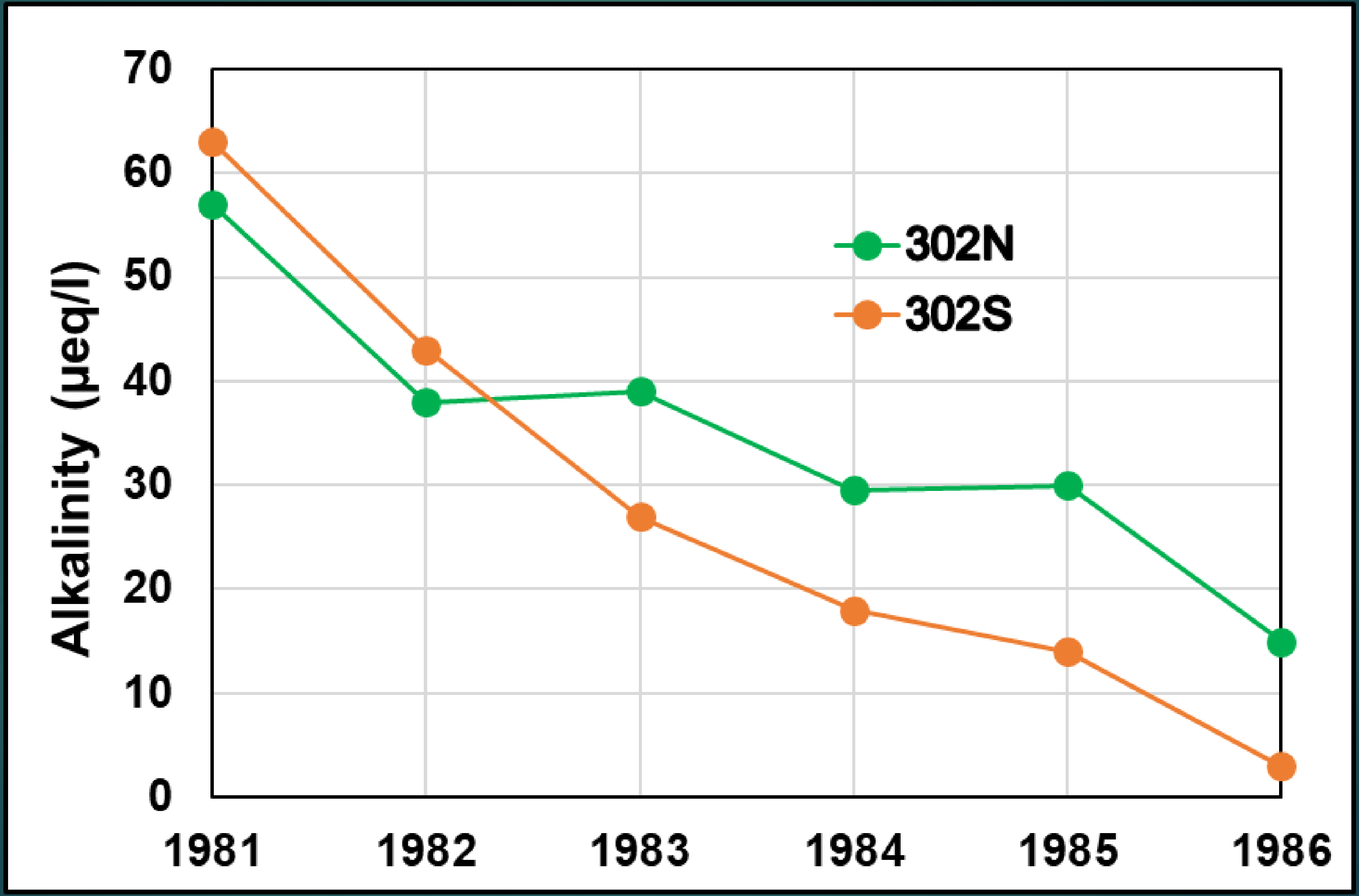
Lake	Years	Midsummer NO_3^- µmol L^{-1}	% NO_3^- Removed	t_w yr	S_N m yr^{-1}
302 South (pre-acid)	1981	0.13	120	8.3	440[b]
302 North (pre-acid)	1981	0.14	130	5.8	220[b]
227	1971-1982	0.45	100	4.1	210[c]
Crystal	1984	ND	99	25	42[c]
223	1976-1983	<0.4	98	8.7	25[b]
Plastic	1984-1986	<0.15	81	3.0	11[c]
239	1981-1983	0.2	57	2.5	6.8[c]
Harp	1984-1986	<0.15 to 1.2	57	2.5	6.8[c]
Langtjern	1972-1978	2	36	0.2	6.8[c]
302 South (acid added)	1982-1985	0.8 to 1	89-93	8.3	6-9[b,d]
302 North (acid added)	1982-1985	20 to 40	69	5.8	5[b]
Dart's	1982-1984	20	7	0.6	0.89[c,e]

Modeled nitrate removal (R_N)

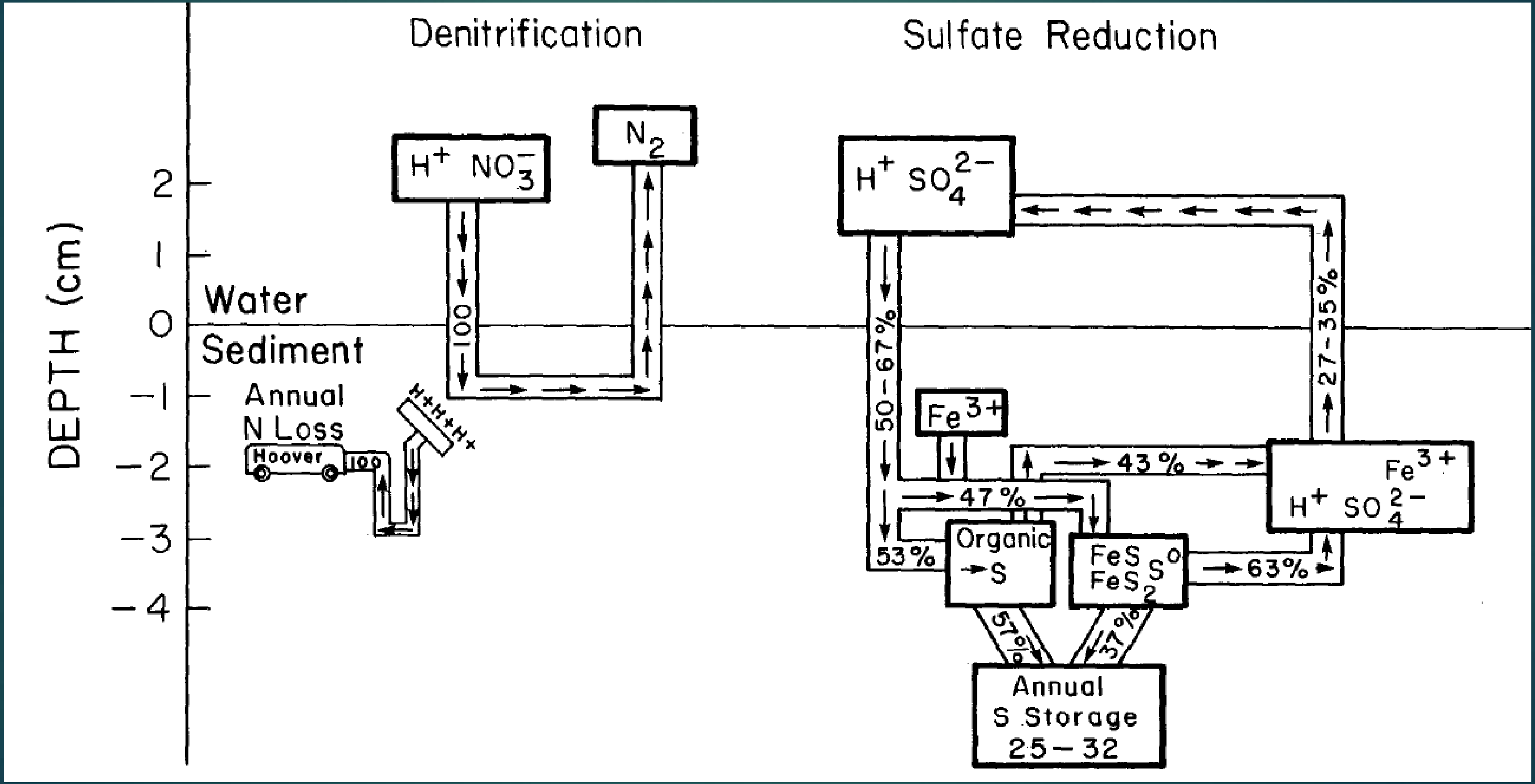
Using water residence time and average S_N



Nitric acid did acidify, but only half as efficient as sulfuric acid in acidifying a lake



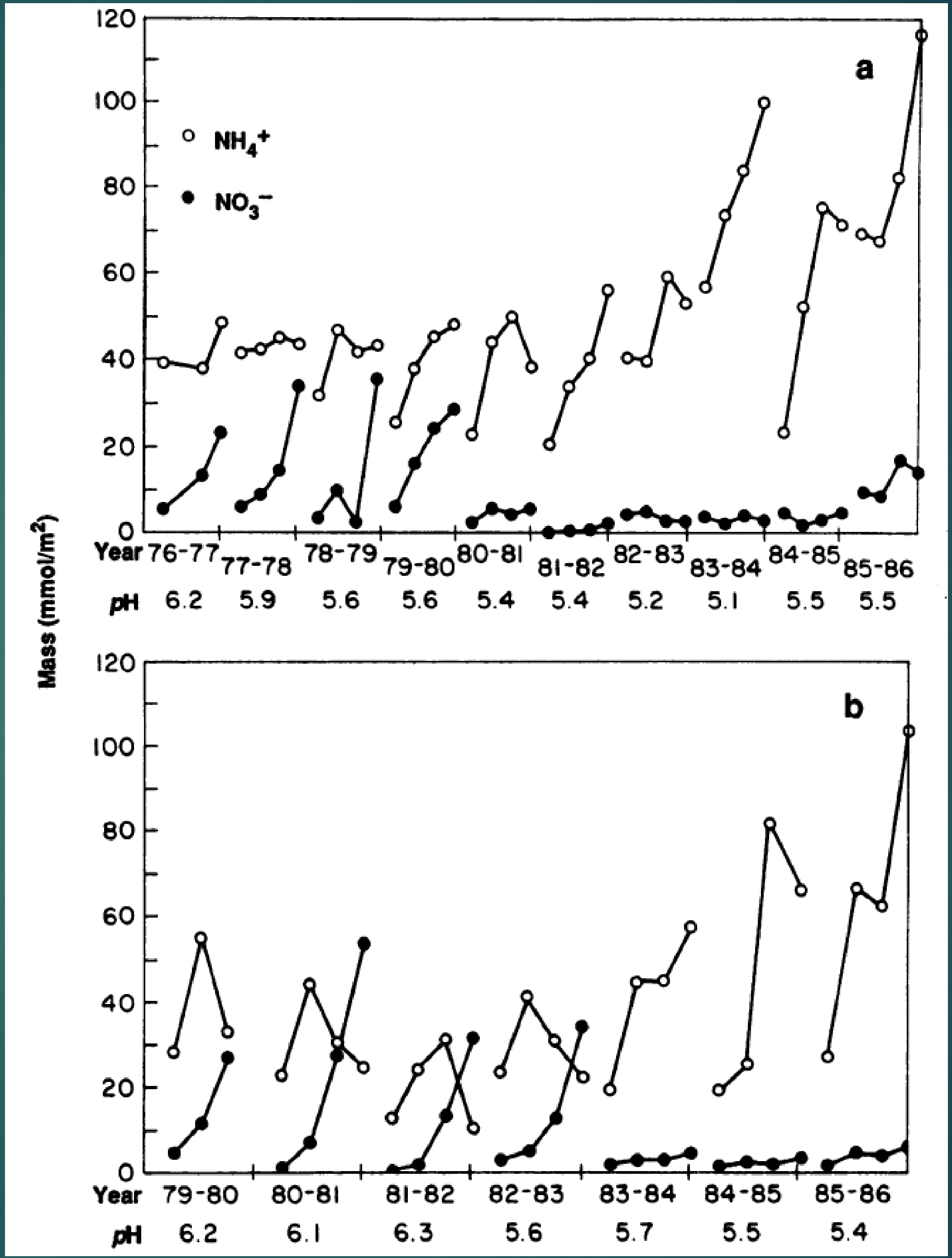
Why did nitric acid acidify less efficiently?

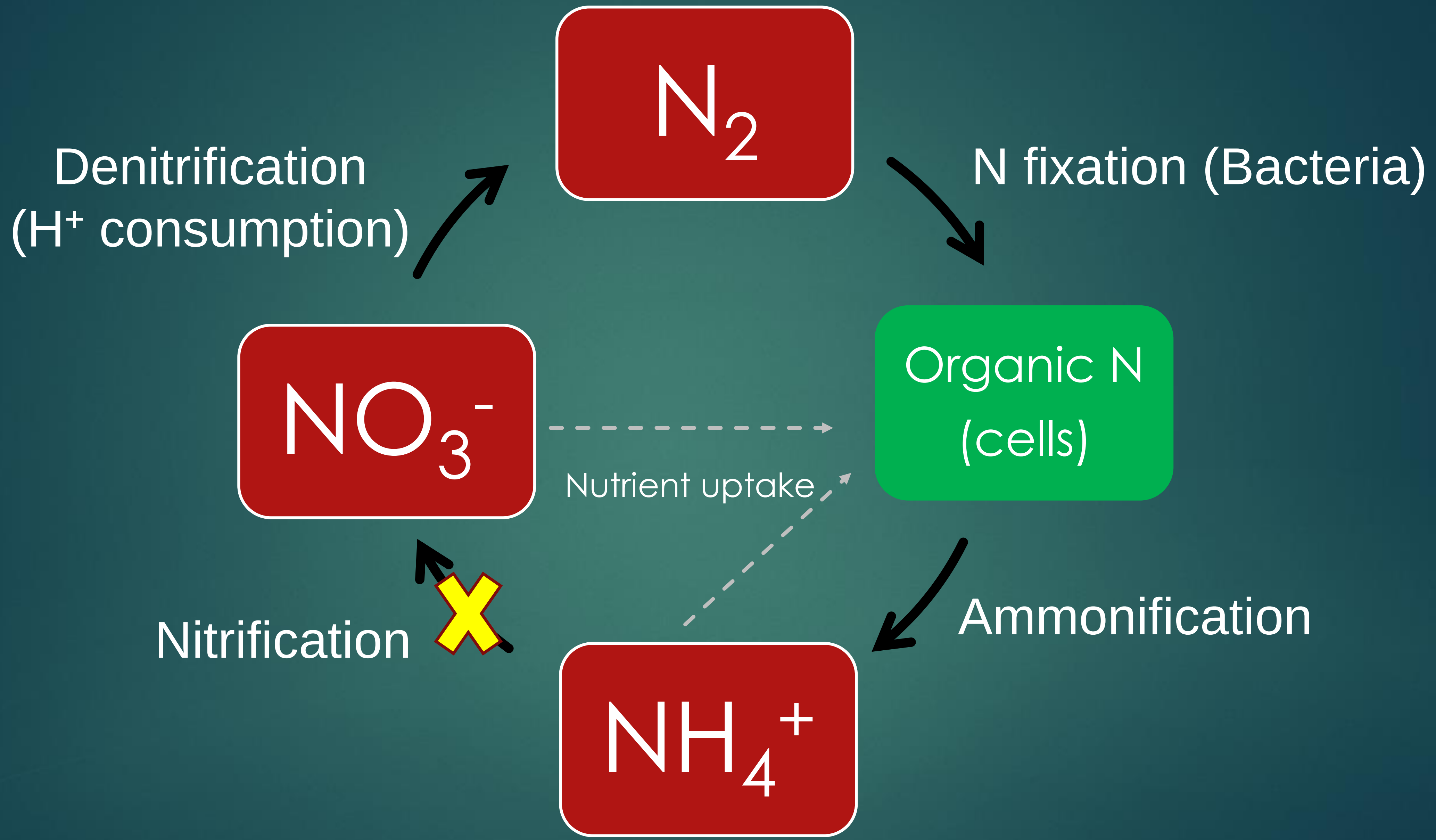


What happens at really low pH?

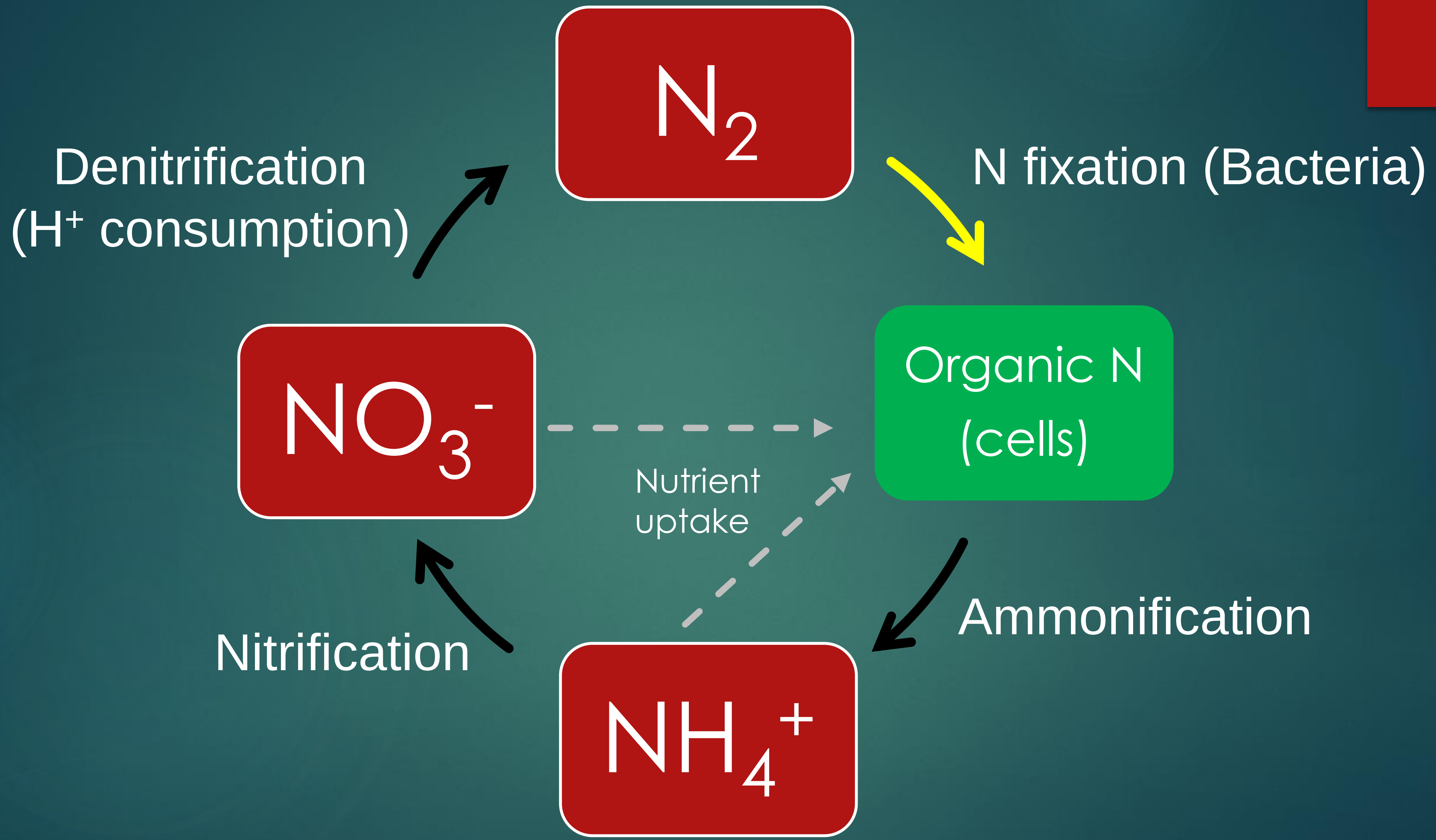
Nitrogen cycle was disrupted at low pH

NH_4^+ accumulated





N2
N fixation (Bacteria)
Denitrification
(H+ consumption)
NO3-
Organic N
(cells)
Nutrient uptake
Nitrification
Ammonification
NH4+



N2
Denitrification
(H+ consumption)
N fixation (Bacteria)
NO3-
Organic N
(cells)
Nutrient
uptake
Nitrification
Ammonification
NH4+

MICROBIAL ACTIVITIES,
WATER CHEMISTRY , AND POLICIES

- ELA experiments, changing one thing at a time, were crucial in understanding fate of acid rain in lakes

- These experiments provided means to develop understanding of mechanisms, and methods that could be used to transfer understanding to other lakes