Limnology
Chap 10: Geochemistry

Lake Geneva, 2021

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Learning objectives

Today you will learn about :

1. The nutrient cycling
2. Primary production
3. Sedimentation
4. Biogenic calcite precipitations and carbonate system
5. Oxygen depletion

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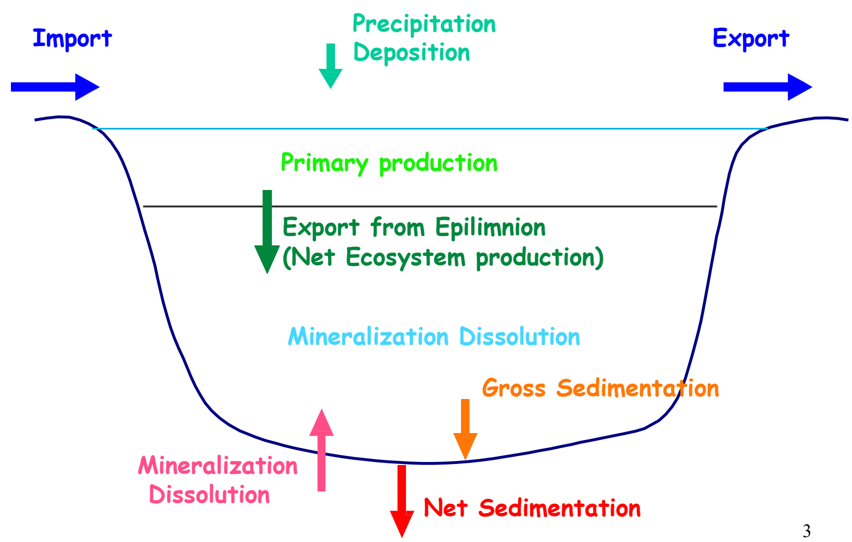
Major biogeochemical processes in lakes



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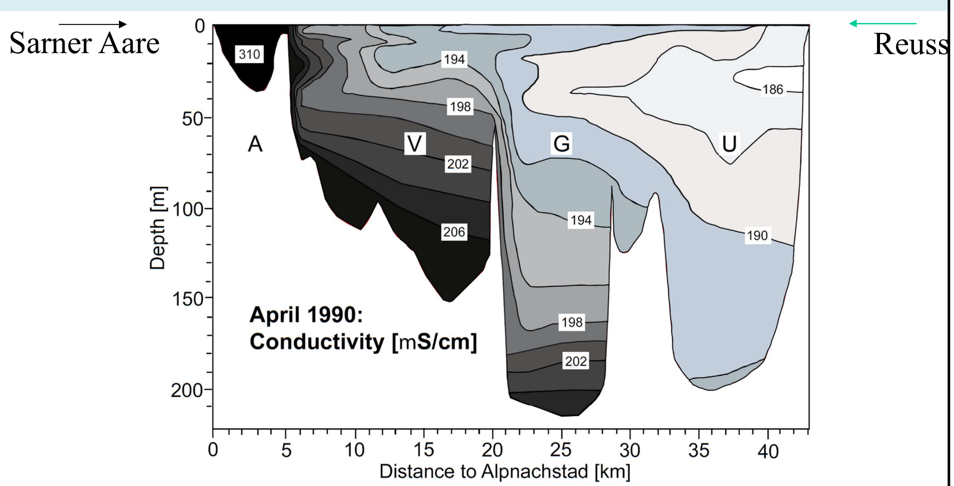
Geology of the catchment determines major ions



	Conductivity µS/cm (20°C)	Alk mmol/L	Ca mmol/L	Mg µmol/L	SO_4^{2-} µmol/L	Si mg/L
Sarner Aa:	224±40	2.42±0.40	1.14±0.18	91±43	140±49	3.4±1.3
Reuss (Seedorf):	90	1.29	0.68	91	96	2.1

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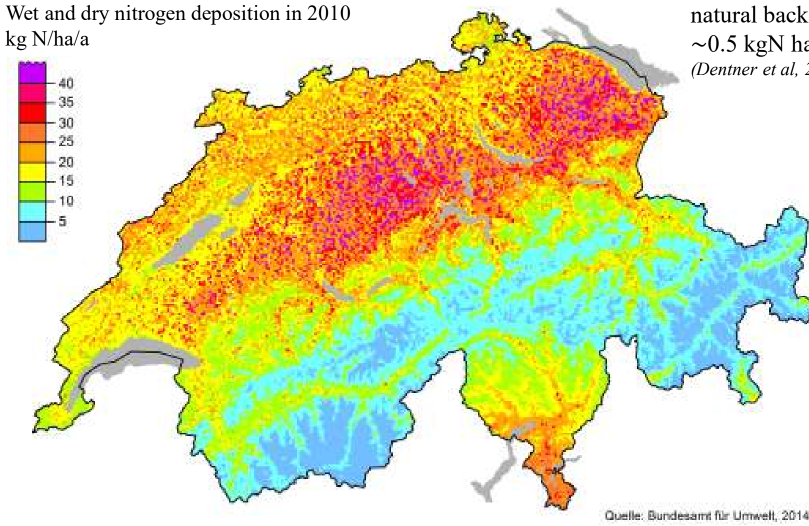
Inputs by atmospheric deposition



natural background
~0.5 kgN $ha^{-1}yr^{-1}$
(Dentner et al, 2006)

Mainly due to anthropogenic contribution

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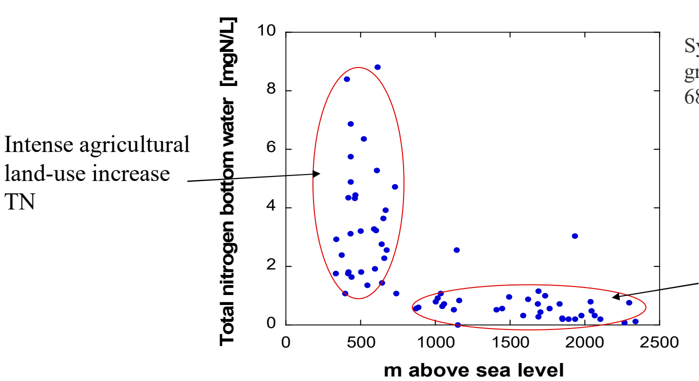
Anthropogenic nitrogen inputs: land use and transport



Systematic concentration gradient with altitude in 68 small Swiss lakes.

In Switzerland, a maximum annual application to fields of 315 kgN $ha^{-1}yr^{-1}$ is allowed

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(Müller et al. 1998)

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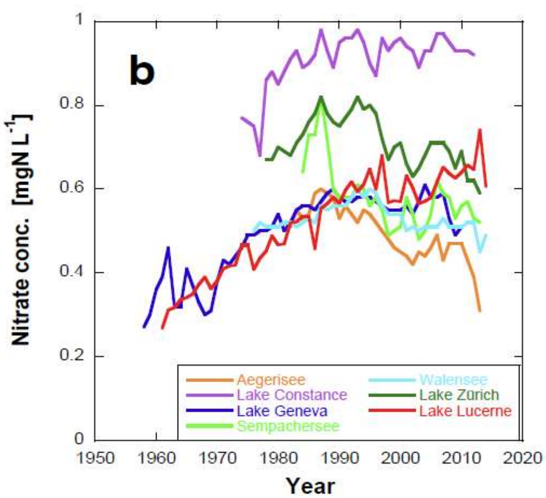
Nitrogen concentrations in lakes



N Sources in Switzerland:

Atmospheric depos. 44 kt N/yr

Mineral fertilizers 52 ktN/yr

Sewage 43 ktN/yr

Manure: legal limit for farming: 315 kg N ha^{-1}

Concentrations of nitrate during seasonal mixing for lakes with peak concentrations <1 mgN L^{-1}

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Lake Kivu: external nutrients inputs (t yr^{-1})

	P	N	Si
Rivers	111	1900	23300
Rain	84	2100	680
Dry deposition	33	1300	660
Total External	230	5300	24600
Upwelling	1800	18400	29500

N, P: Upwelling > External inputs

Si: Riverine inputs = upwelling

(Pasche et al. 2012)

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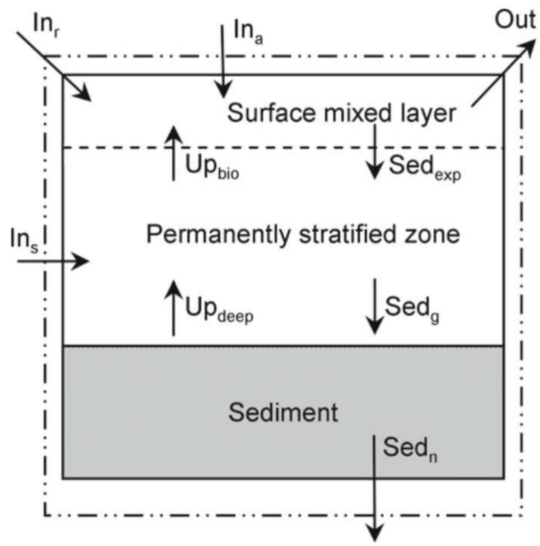
Nutrient cycling: mass balance



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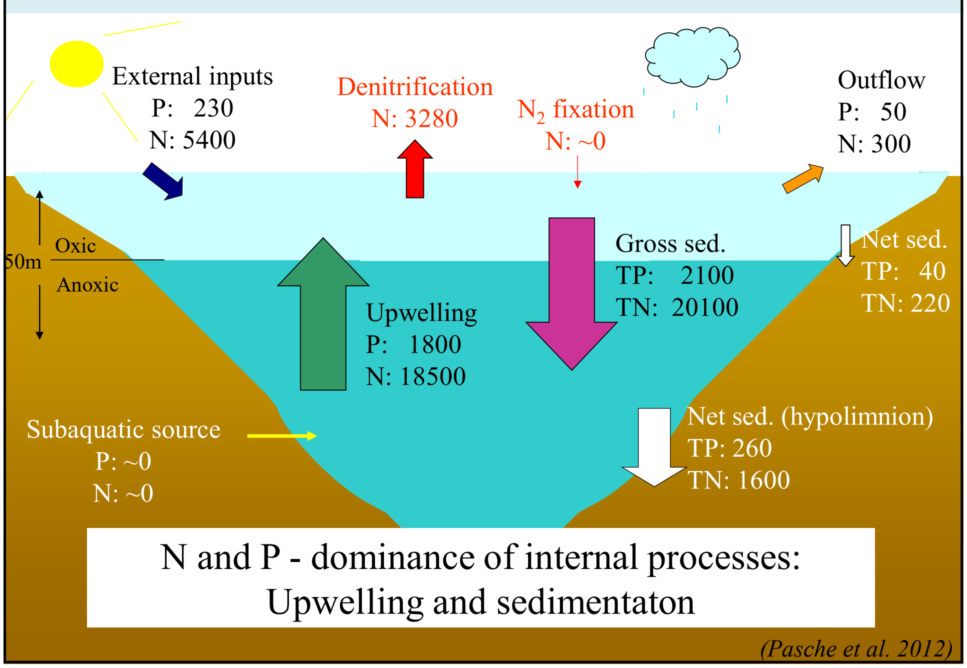
Lake Kivu: N and P cycles (in t yr^{-1})



(Pasche et al. 2012)

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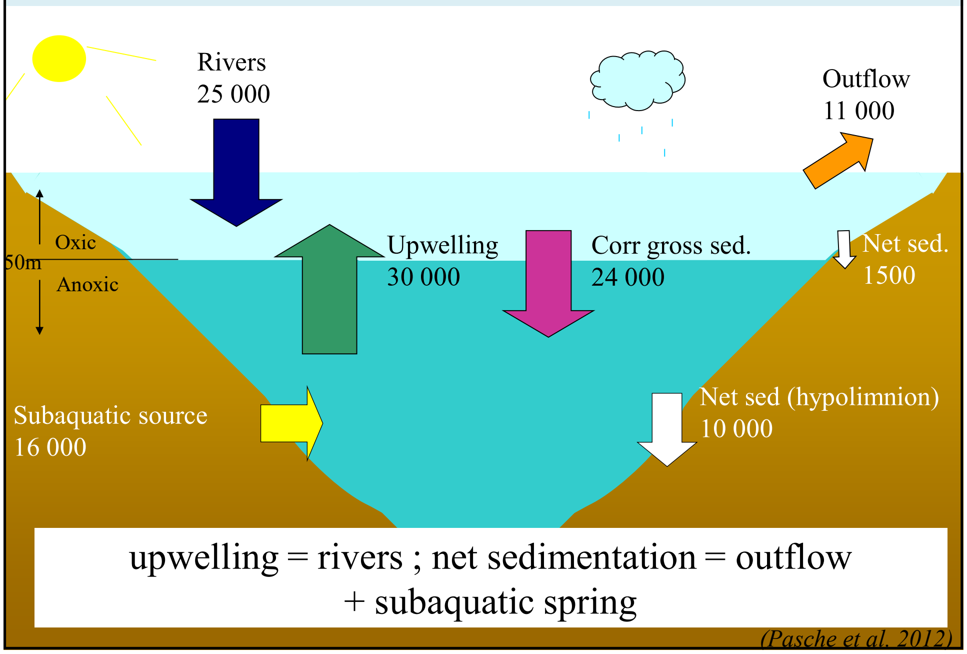
Lake Kivu: Si cycle ($t_{Si}\ yr^{-1}$)



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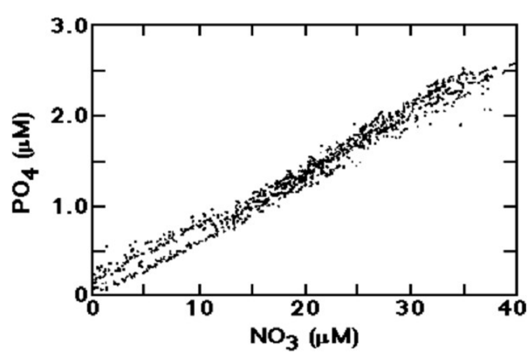
Primary production

N : P – ratio in the World Oceans

Assimilation of C, N, and P:

Analyses of thousands of phytoplankton samples – the ratio agrees with seawater composition

N/P ~ 16:1



Phosphate vs. Nitrate in the Atlantic Ocean during the GEOSECS Program

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Geochemical formulation of Primary Production

$106\ CO_2 + 122\ H_2O + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+$

Production ⇅ Respiration

$\{C_{106}H_{263}O_{110}N_{16}P\} + 138\ O_2$

alternatively:

$\{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)\} + 138\ O_2$

"The authors point out that in seawater and in marine organisms, the C/N/P ratios are close to 106:16:1 everywhere"

Redfield, Ketchum and Richards 1963: **The influence of organisms on the composition of seawater.** In "The Sea" ed. M.N. Hill, pp.26-77, Wiley, Interscience, New York, Vol. 2.

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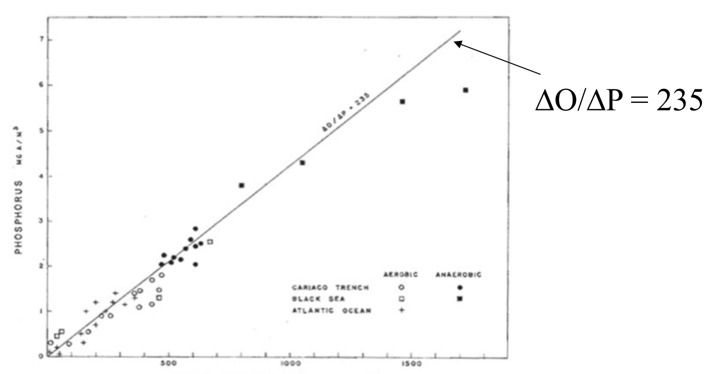
Mineralization: O_2 consumption at the release of P

$\{C_{106}H_{263}O_{110}N_{16}P\} + 138\ O_2 \rightarrow 106\ CO_2 + 122\ H_2O + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+$



organic matter. The figure shows that as increasing quantities of organic matter decompose in the water the utilization of oxygen increases approximately in the ratio of 235 atoms for each atom of phosphorus set free [3]. After the phosphorus content reaches a little more than 2 mg

(AC Redfield 1958)

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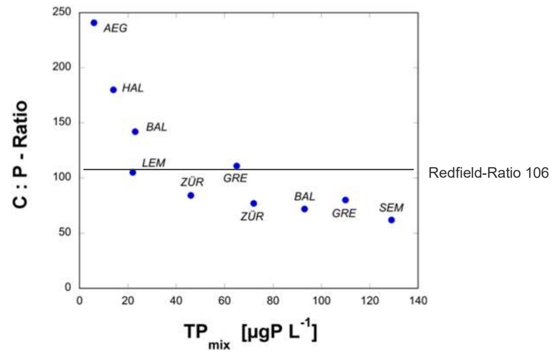
Is there a Redfield Ratio for Lakes?

Data from **sediment traps** suggest that phytoplankton assimilates P according to availability.



The phytoplankton community can adjust to varying concentrations of P:

- variation of the species composition
- luxury consumption (→ fatten up)
- or tighten the belt (→ slender)

(Müller et al 2019) 15

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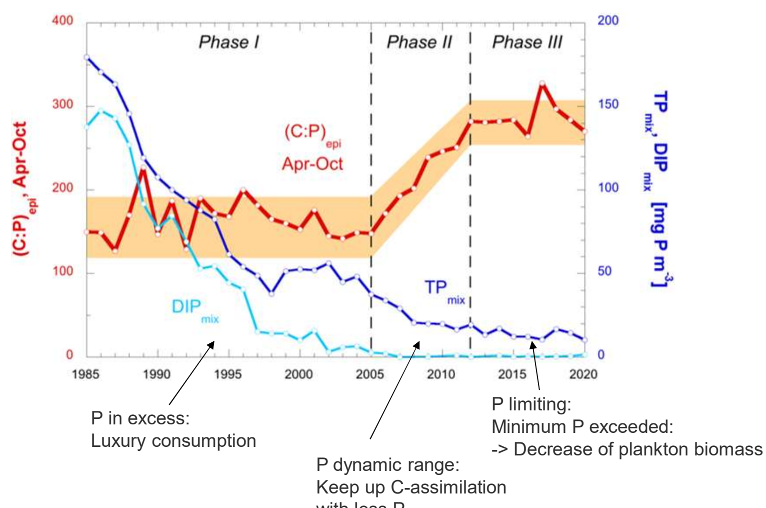
Is there a Redfield Ratio for Lakes?

Data from **Lake Hallwil seston during Re-oligotrophication**



→ **C:P ↑ during reoligotrophication**

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(Müller et al. 2021)

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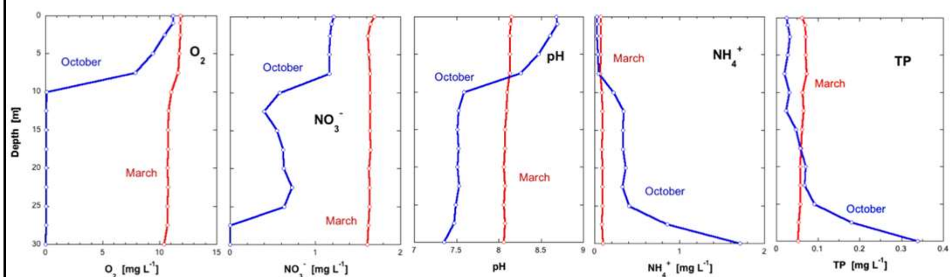
Primary production and mineralization

$106\,CO_2 + 122\,H_2O + 16\,NO_3^- + HPO_4^{2-} + 18\,H^+ \Rightarrow \{C_{106}H_{263}O_{110}N_{16}P\} + 138O_2$



March = replenishment after deep mixing

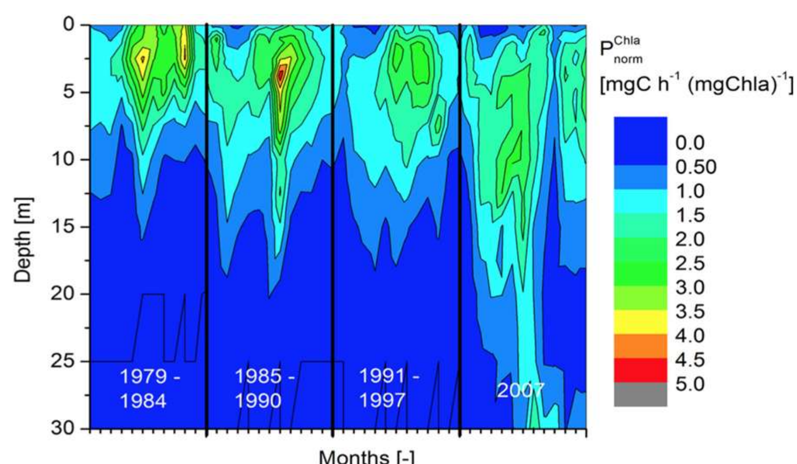
October = total use after productive season

$\{C_{106}H_{263}O_{110}N_{16}P\} + 138O_2 \Rightarrow 106\,CO_2 + 122\,H_2O + 16\,NO_3^- + HPO_4^{2-} + 18\,H^+$

Lake Greifen 17

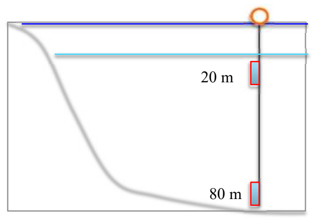
Primary production during reoligotrophication

Lake Lucerne: another reason for high PP in spite of decreasing P (apart from increasing C:P ratio)



(Finger et al. 2013)

Net ecosystem production / gross sedimentation



Flux rates [gC $m^{-2}a^{-1}$]	Lower trap	TP_{mix} [µgP L^{-1}]
Lake Baldegg 1994-1996	90	100
Lake Baldegg 2013-2014	90 – 95	28
Lake Sempach 1984-1992	73 ± 28	130
Lake Hallwil 2014-2016	44 – 54	14
Lake Aegeri 2014	28	6

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In class exercice:

1) Nutrient cycling in lakes

a) What are the nutrient inputs into the lake epilimnion?

b) What are the nutrient outputs from the lake epilimnion?

c) Which additional process do you need to take into account for nitrogen?

d) What is the main difference between the external and internal nutrients inputs?

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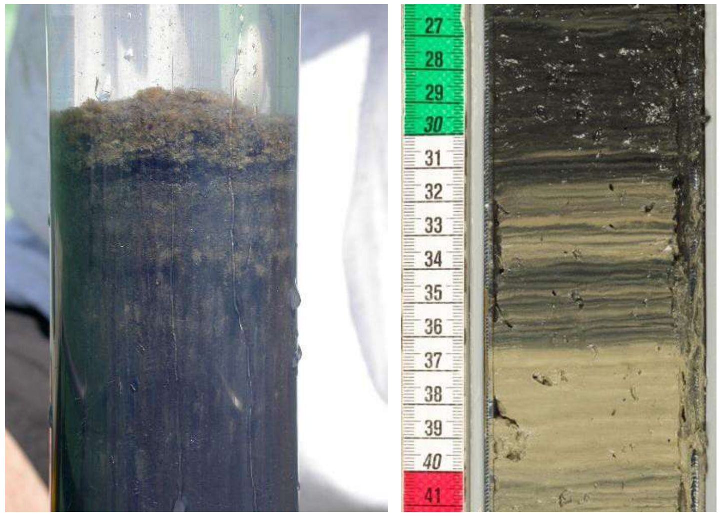
Sediment archives



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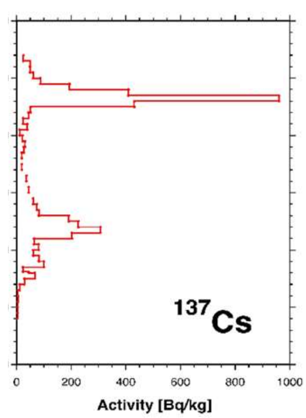
Traces in the sediment



Tchernobyl 1986

Nuclear bomb tests 1963

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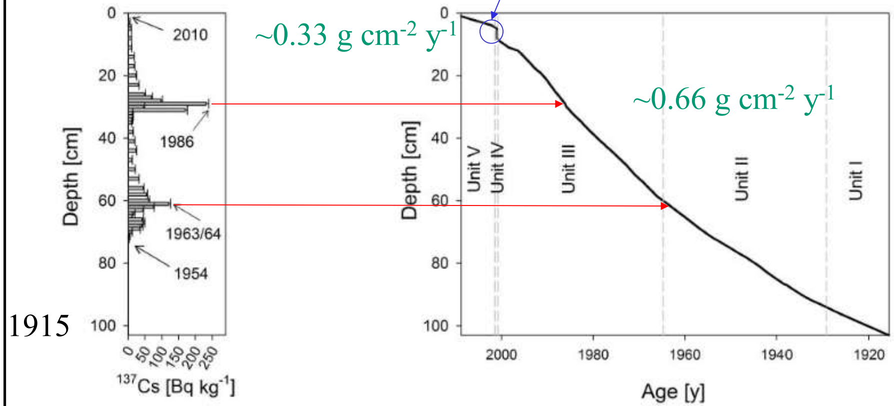
Age model for the sediment of Lake Geneva

Transfer work of the WWTP outlet pipe in 2001

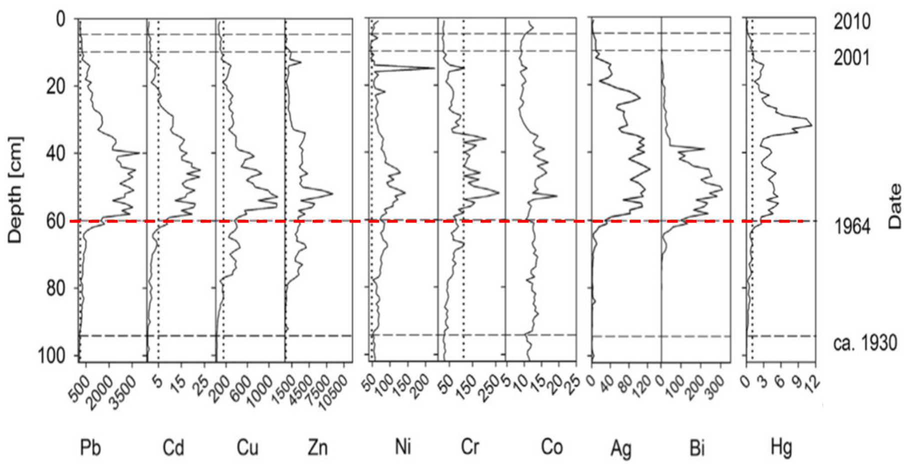


Sedimentation accumulation rates

(*Gascon Diez et al. 2017*)

Traces element in the sediment of Lake Geneva

Implementation of WWTP in Vidy Bay → increased contamination with trace metals



(*Gascon Diez et al. 2017*)

Sediment analyses: net sediment rates

Use Mass Accumulation Rates (Deposition rates) instead of only contents

Requires: Dating (^{210}Pb and/or ^{137}Cs) ➔ *cm/yr*

Estimation of porosity (via water content) ➔ *Vol/Vol*

Requires: *Estimation of sediment dry density* ➔ *g/cm³*

Requires: Measurement of carbon content

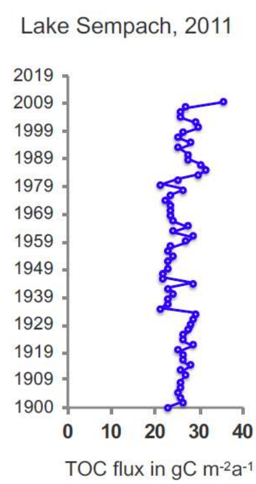
$g\ m^{-2}\ yr^{-1}$ instead of $mg\ g^{-1}$

Mineralization in the sediment (early diagenesis)

Gross sedimentation versus net sedimentation

C-flux from sediment traps
(gross sedimentation): 73 gC $m^{-2}a^{-1}$

Av. TOC-Flux from sediment analysis
(net sedimentation): 26 gC $m^{-2}a^{-1}$



About $^{2}/_{3}$ mineralized, $^{1}/_{3}$ buried

Early diagenetic processes in the sediment

E_H [V]

+800mV

O_2	→ H_2O	Respiration
NO_3-	→ N_2	Denitrification
Mn(IV)	→ Mn(II)	Mn-Reduction
NO_3^-	→ NH_4^+	Nitrate reduction
CH_2O	→ CH_3OH	Fermentation
Fe(III)	→ Fe(II)	Fe-reduction
SO_4^{2-}	→ S(-II)	Sulfate reduction
CO_2	→ CH_4	Methane formation
H^+	→ H_2	Hydrogen formation

-400mV

{CH_2O} +

All microbially mediated

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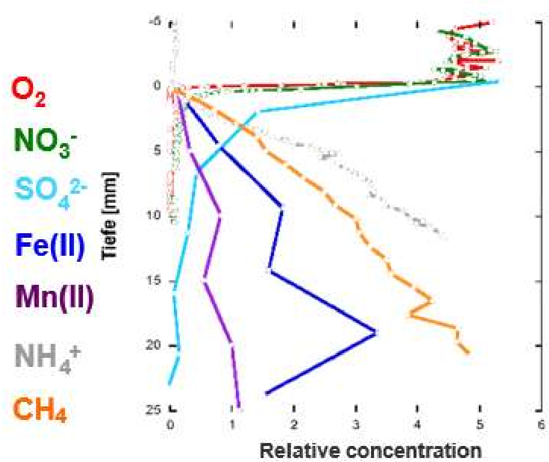
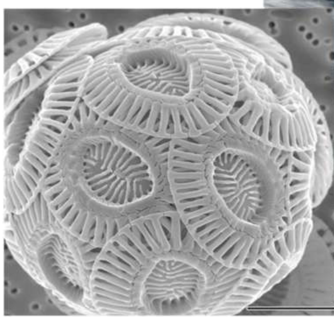
Early diagenetic processes in the sediment

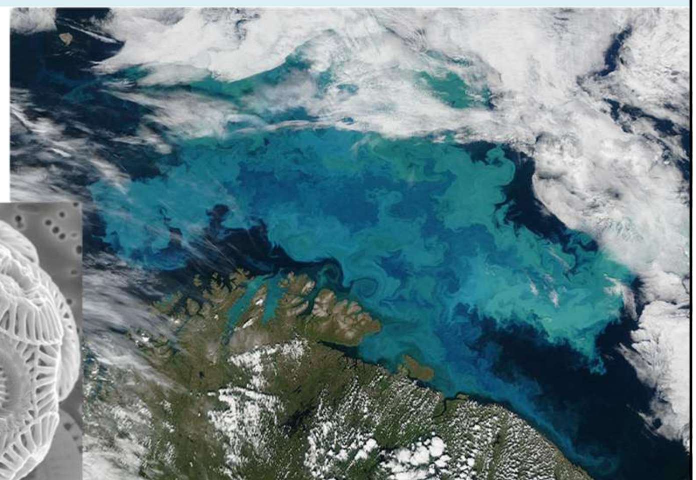
Mineralization of organic matter



Biogenic calcite precipitation in lakes

Emiliana Huxleii





Coccolithophore bloom in the Barents Sea

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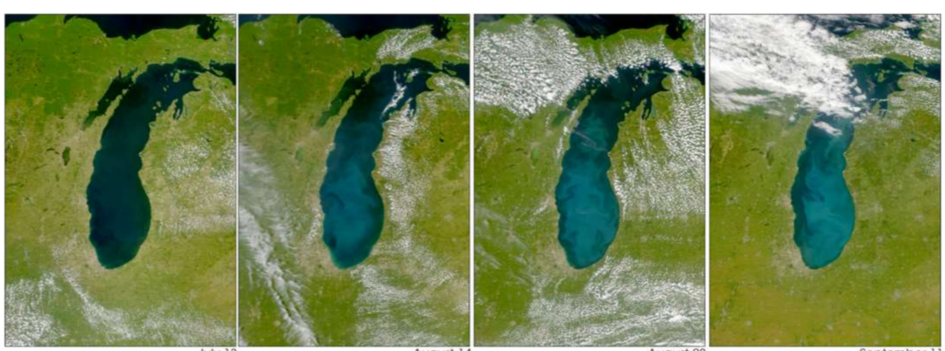
Biogenic calcite precipitation in lakes

Whiting event in Lake Michigan induced by T-increase – abiotic



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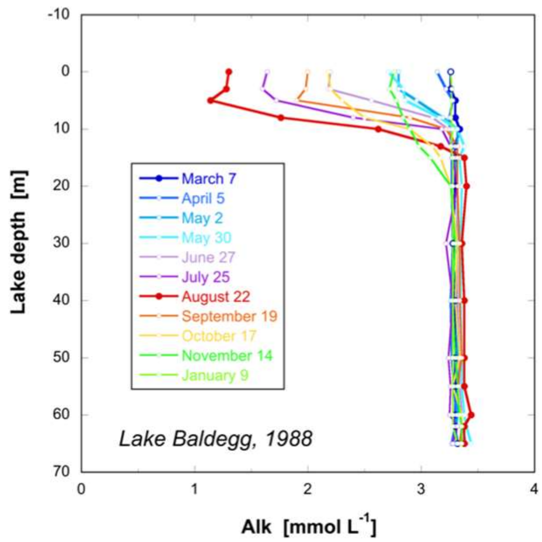
Biogenic calcite precipitation in lakes



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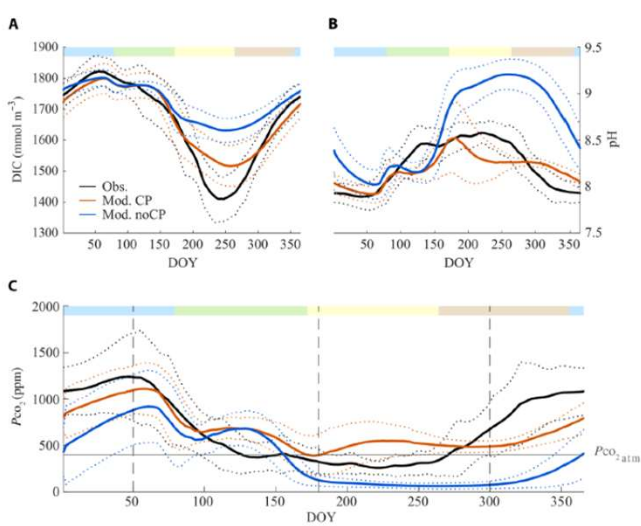
Calcite precipitation: The forgotten piece of lakes' carbon cycle

(Many et al. 2024)



As calcite precipitates, it reduces the water's alkalinity
→ increase in CO_2 concentration and subsequent outgassing.

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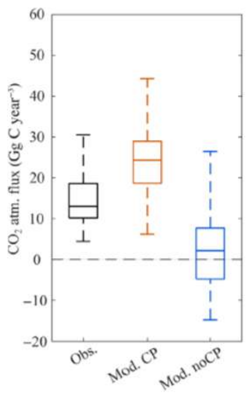
Calcite precipitation: The forgotten piece of lakes' carbon cycle



Annual CO_2 fluxes in Lake Geneva (1981-2021)

Implications & Future Directions

- **Reevaluating Carbon Budgets**
- **Policy and Management**:
- **Further Research**

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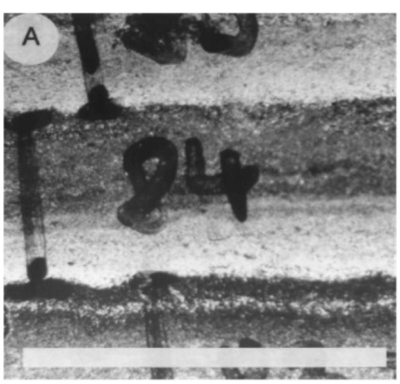
Pattern in the sediments

Calcite precipitation in Spring
Settling organic matter in Summer/Fall

In case of anoxia = no bioturbation

⇒ **Varved sediments**



Lake Baldegg

Lake Zürich, 2013

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Biogenic calcite precipitation in lakes

$106\ CO_2 + 122\ H_2O + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+ \leftrightarrow \{C_{106}H_{263}O_{110}N_{16}P\} + 138\ O_2$

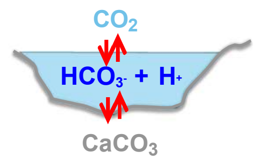
Calcite precipitation induced by pH increase: **CO_2 is a Lewis acid**

$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3$ K_H

$H_2CO_3 \leftrightarrow HCO_3^- + H+$

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

$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_{3(s)}$



$$CO_{2(g)} + CaCO_{3(s)} + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$$

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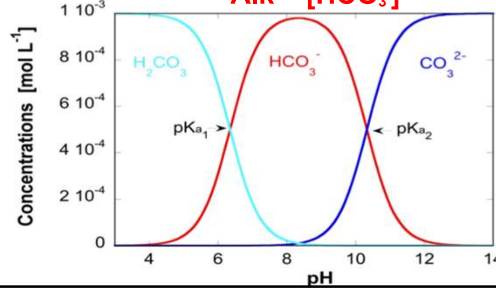
The concept of alkalinity

Acid-neutralizing capacity:

$$Alk = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH] - [H^+]$$

→ Direct access to the CO_2-Calcite system:
CO_2, HCO_3^-, CO_3^{2-}, Ca^{+2}, pH,
precipitation and dissolution of carbonates

Alk ≈ $[HCO_3^-]$



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The properties of alkalinity

- determined with a simple acid-base titration (mmol L^{-1})
- Together with pH, alkalinity describes the whole inorganic carbon system in natural waters
- conservative chemical parameter (independent of temperature and pressure)
- Alkalinity does not change when H_2CO_3, or CO_2 or other substances change (neither acids nor bases)
- Many redox processes consume (oxidations) or produce (reductions) alkalinity

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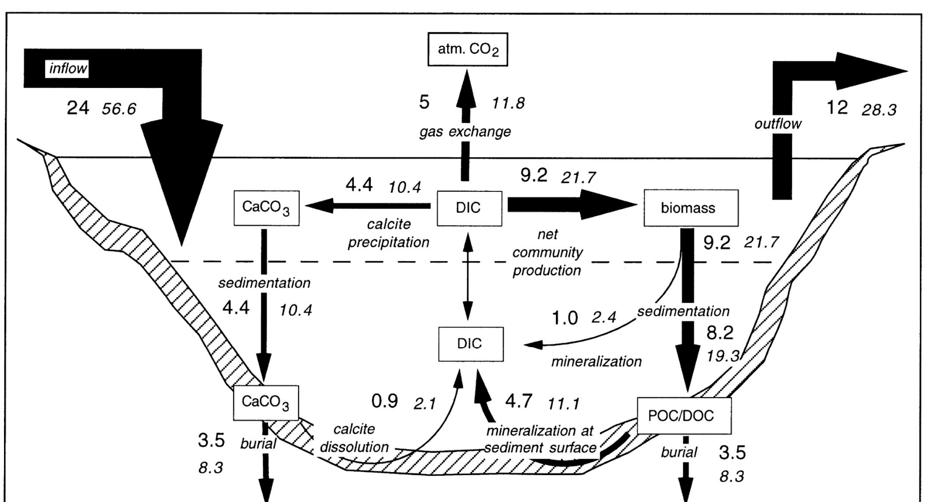
Carbon budget in Lake Soppen



Gruber et al. 2000 [mol m^{-2} yr^{-1}] *[10^5 mol yr^{-1}]*

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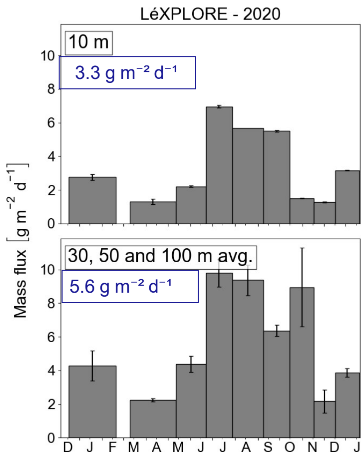
In class exercice:

2) Sedimentation in Lake Geneva

In the figure below, the flux of the total mass of settling particles in Lake Geneva were measured at a depth of 10 m, and averaged at depths of 30, 50 and 100 m, using sediment traps.

a. How do these fluxes vary seasonally? How can you explain these seasonal variations?
b. How would you explain the higher flux below 30 m (mean 5.6 g m^{-2} d^{-1}) compared to the flux at 10 m (mean 3.3 g m^{-2} d^{-1})?



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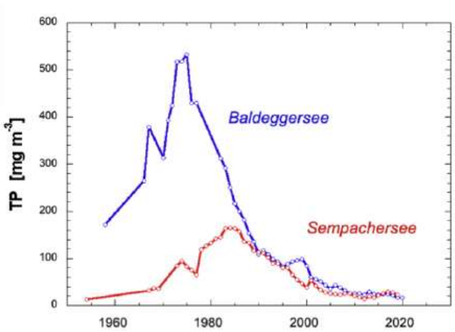
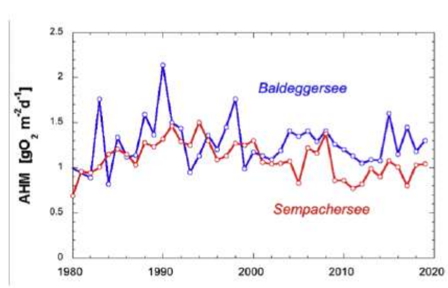
Oxygen depletion in lakes: the paradox

Fighting eutrophication successfully





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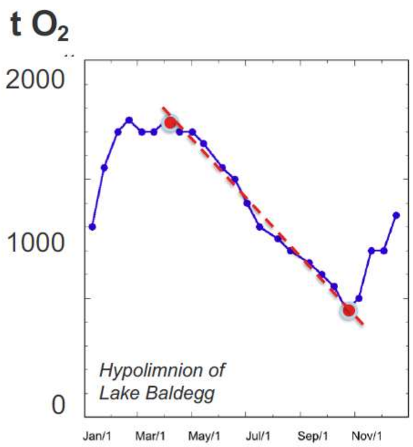
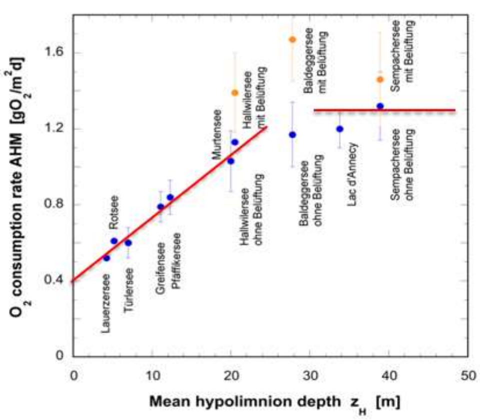
Oxygen consumption rate in the hypolimnion



→ $gO_2\ m^{-2}\ d^{-1}$

Oxygen consumption rate in the hypolimnion

Calculation of O_2 consumption rates:



The areal consumption rate is similar in all (eutrophic) lakes

O_2 consumption rate increases with mean hypolimnion depth

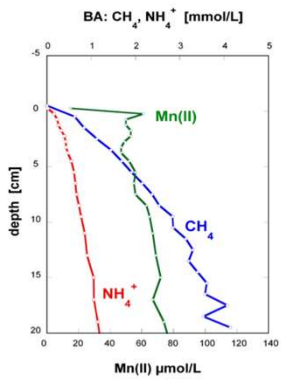
Mineralization in the sediment should be similar in all (eutrophic) lakes

O_2 consumption rates are higher when lakes were artificially aerated

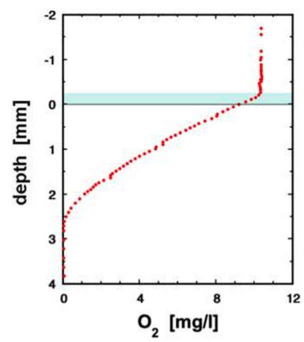
Two processes must be responsible for O_2 consumption in eutrophic lakes

Oxygen depletion in lakes by two processes

Reduced substances diffusing from the sediment:



Diffusive transport of O_2 across the benthic boundary layer:



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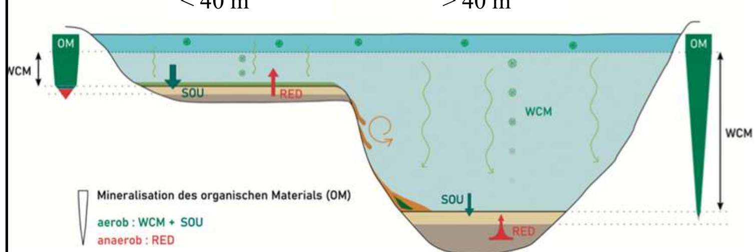
In deep lakes: water column mineralization

Shallow lakes
< 40 m

Deep lakes
> 40 m



O_2 Exchange with Atmosphere

Primary Production

Net Ecosystem Production

Aerobic Mineralization in the water column (WCM)

Settling Particles

O_2 Diffusion to the sediment (SOU)

Production of reduced substances (F_{red})

→ three essential locations for O_2 consumption

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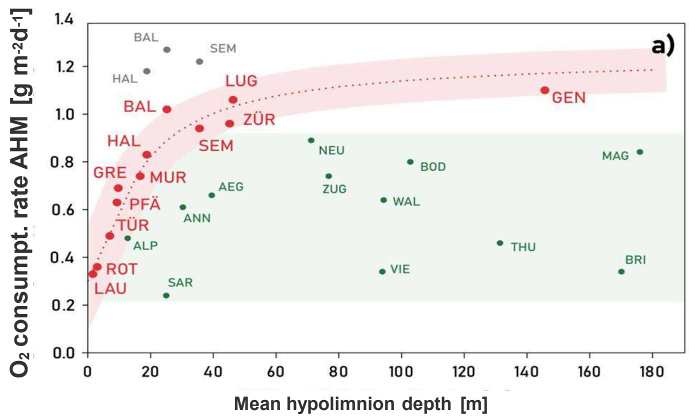
Eutrophic and oligotrophic lakes



O_2 consumption in eutrophic lakes <40m => O_2 limited → OC stored in sed

O_2 consumption in deep lakes (or oligotrophic lakes) is not limited by the O_2 concentration but by settling organic matter

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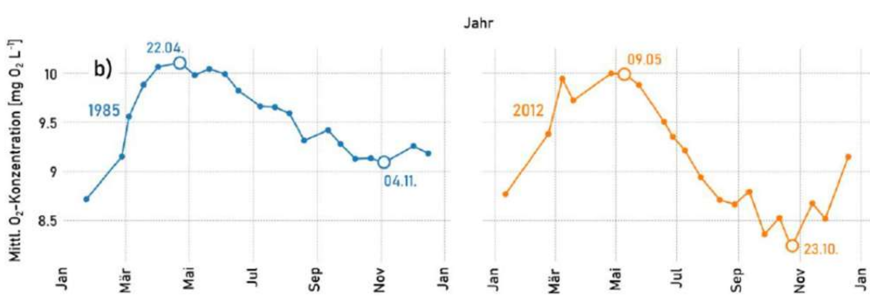
Estimating the oxygen consumption rate AHM



$$AHM(z_H) = \frac{z_H}{\Delta t_{strat}} \times \left(O_2^{Frühjahr} - O_2^{Herbst}\right)$$

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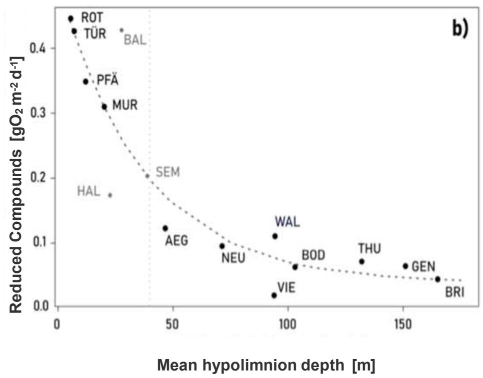
Consequences for the sediment of an eutrophic lake

High sedimentation of C_{org} but not enough O_2 for complete mineralization:

- Deposition in the sediment – low anaerobic mineralization
- Slow formation of reduced compounds (CH_4, NH_4^+)
- Slow diffusion of CH_4/NH_4^+ from the sediment and oxidation



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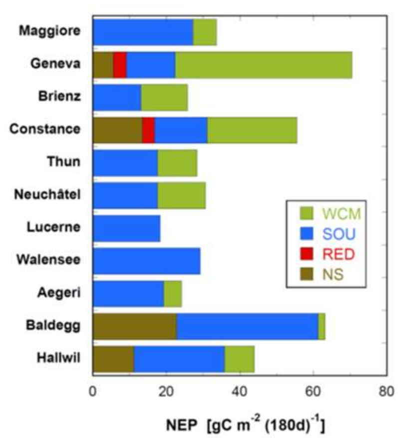
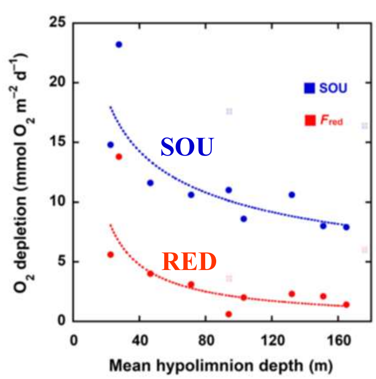
Contribution of the different oxygen sinks





(Steinsberger et al. 2021)

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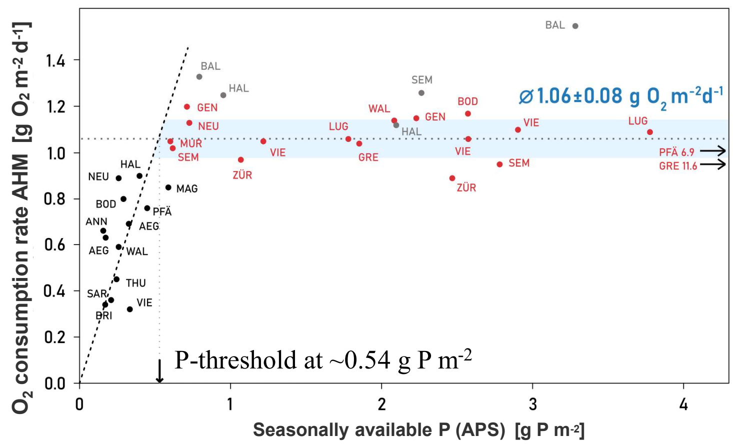
Oxygen Consumption and Phosphorus Availability

APS and AHM are related below **P-threshold**

AHM above P-threshold is constant, independent of P!

AHM only decreases at APS < P-threshold



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Oxygen depletion: conclusions

- **Shallow lakes**
  - O_2 consumption is maximal and controlled by mean hypo depth (O_2 concentration above the sediment)
    - maximum consumption by the sediment
    - Reduced compounds from the sediment
  - high organic carbon legacy in the sediment
  - hardly any reaction to declining P
  - very slow improvement of O_2 concentrations in the hypolimnion

- **Deep lakes**
  - O_2 consumption is controlled by the amount of settling organic carbon (primary production)
  - low content of organic carbon in the sediment – even in eutrophic lakes
  - fast reaction to declining P

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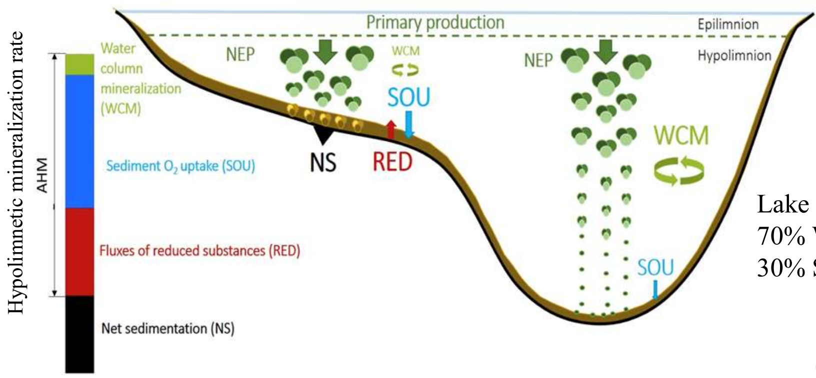
Estimating net ecosystem production

Export ratio = $\frac{\text{Sinking flux of OC}}{\text{Primary production}}$ = 34%



Lake Geneva:
70% WCM
30% SOU

NEP = AHM + NS

Works well for Lake Constance and Geneva

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Steinsberger et al. 2021

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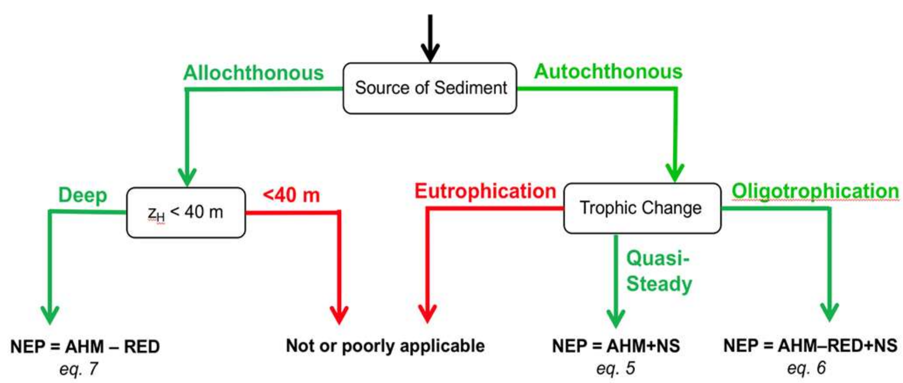
Estimating net ecosystem production



Lakes Maggiore, Brienz, Thun, Neuchâtel, Lucerne, Walen, Aegeri

Lakes Geneva, Constance

Lakes Baldegg, Halwill

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Steinsberger et al. 2021

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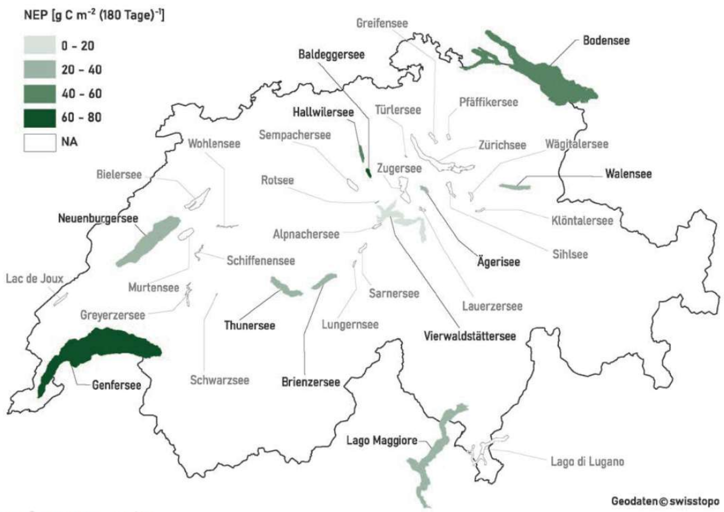
Estimation of the net ecosystem production



$$NEP\ [g\ C\ m^{-2}\ (180\ Tage)^{-1}] =$$
$$[(AHM - RED) \times \frac{106}{138} \times \frac{12\ g\ C\ mol^{-1}}{32\ g\ O_2\ mol^{-1}} \times 180\ Tage] + NS$$

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Take home message

1. The nutrients cycling make the balance between the inputs, outputs and internal recycling.
2. The primary production has a C:P ratio that can vary strongly depending on P concentrations.
3. The analyses of sediment cores reveals the lake history, and is an active zone for mineralization of organic matter.
4. Calcite can precipitate if it is oversaturated and nucleus are available. It is often linked to PP, which increase the pH.
5. The oxygen consumption occurs in the water column and in the sediment, where O_2 is directly consumed and to oxidize the reduced substances diffusing out of the sediment.
6. Above the P-threshold, the oxygen depletion is constant, but becomes proportional to P below this threshold at 0.54 gP m^{-2}

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In class exercice:

3) Oxygen depletion and net ecosystem production in Lake Geneva

a) Estimate AHM of Lake Geneva in 1985. The stratification started on 22.04 with 10.09 gO_2 m^{-3} and ended on 4.11 with 9.08 gO_2 m^{-3}. The mean hypolimnion depth is 151 m.

b) Estimate the NEP of Lake Geneva in 1985. The net sedimentation over the productive season is 5.5 gC m^{-2}