Prevention and remediation of advanced (hyper) eutrophication - A case for integrated watershed management

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NUTRIENT IMPACT - Eutrophication

- Photosynthesis is the driving process for primary productivity (euphotic zone)
- In the profundal zone and during night and cloudy days algae respire and impose oxygen demand
- Other important factors are nutrients (N and P), shading, hydraulics and alkalinity
- Hyper-eutrophication is associated with Harmful Algal Blooms, mostly by Cyanobacteria (Cyano - HAB) which behave differently from algae

Cyanobacteria in Lake Mendota (Madison, WI) in 1970s

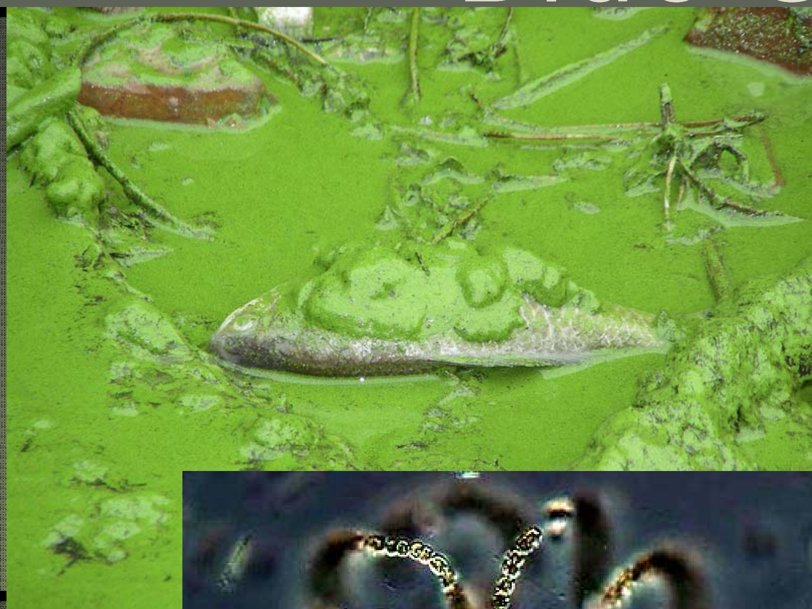
Eutrophication Characteristics*

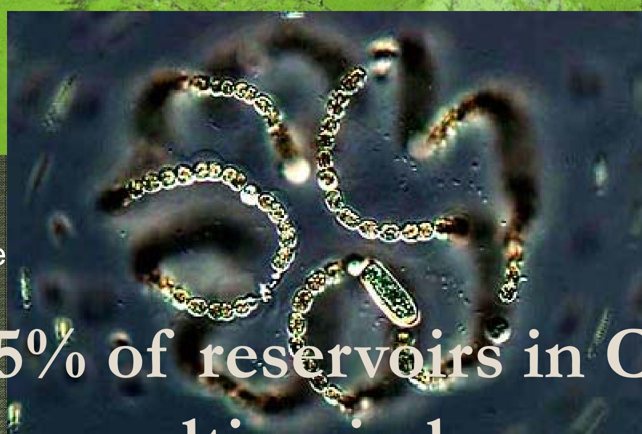
Water Quality	Oligotrophic	Mesotrophic	Eutrophic	Hyper-eutrophic**
Carlson TSI	<40	40 – 50	50-70	>70
Total P (µg/L)	<10	10-24	24-95	> 95
Chlorophyll – *a*	5	5-20	20 - 50	>50
Summer Secchi disc depth (m)	>4	2-4	1-2	<1
Hypolimnetic oxygen (% saturation)	>80	10-80	<10	0

* Original source US Environment Protection Agency (1974)

** Calculated from Carlson (1977) Trophic status index

Hyper-eutrophic catastrophe in Czech Republic and China
Blue Greens





Taihu

Anabaena flos-aquae

Sedlice

Microcystis aeruginosa

In 2005 75% of reservoirs in Czech Republic were hyper-eutrophic, resulting in losses of recreation, water supply, toxins, taste and odor, skin rash


Pea soup. Hans Paerl samples cyanobacteria in ailing Taihu Lake.

ECOLOGY

Doing Battle With the Green Monster of Taihu Lake

In attempting to subdue a vicious algal bloom, scientists aim to restore the health of

PEA SOUP IN CHINA' TAIHU

Taihu area 2338 km^2

Watershed 10000 km^2

Average depth 2 meters

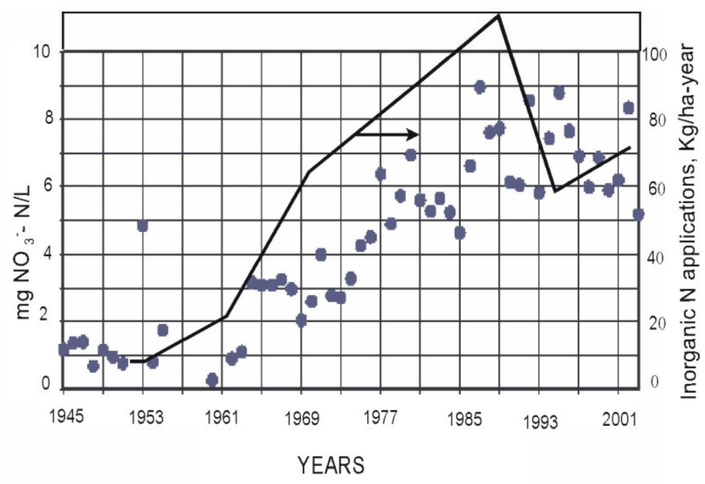
Population in the watershed 40 million, provides water supply to 10 million (Wuxi).

VICIOUS ALGAL BLOOMS

Over the last 30 years trophic status progressed from mesotrophic diatom dominated water body to hyper-eutrophic dominated by toxins producing *Microcystis* harmful blooms. During blooms bottled water was provided to people of WuXi at a price up to $7/bottle

Credit Washington Post – Associated Press September 22, 2012

Suspected Causes of the Problem



Želivka River in Czech Republic

Agricultural erosion without soil conservation is 2-3 orders of magnitude greater than natural erosion

- Green revolution in agriculture based on unbalanced overuse of industrial fertilizers
- Monocultural agriculture fed by industrial chemicals
- Increased erosion by plowing up an down the slope all the way to the water bodies
- Lack of best management practices to control nonpoint sources of N & P
- Discharges from point sources of nutrients with little P and N removals.
- Combined sewers with uncontrolled CSOs
- Phosphate detergents
- Very high soil and groundwater contamination by N (nitrate) and high P and N in surface waters

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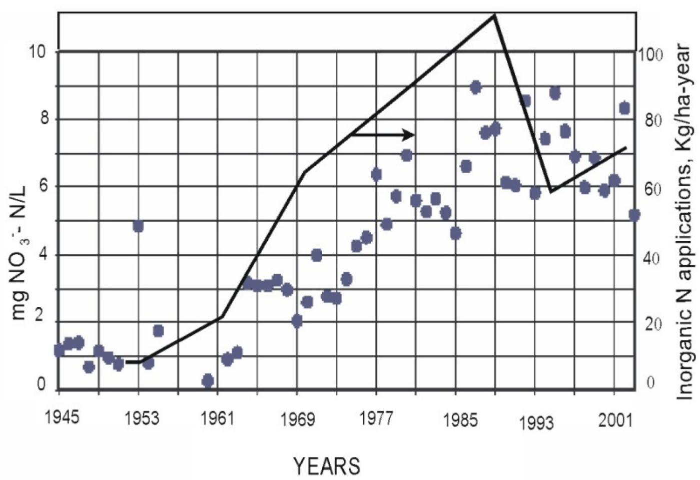

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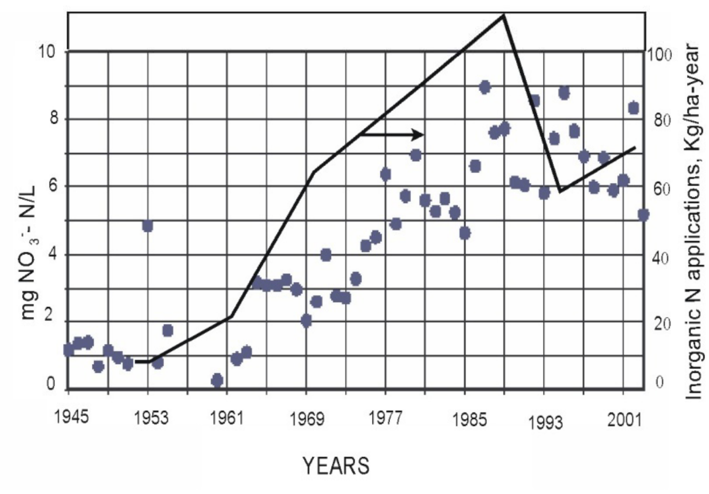

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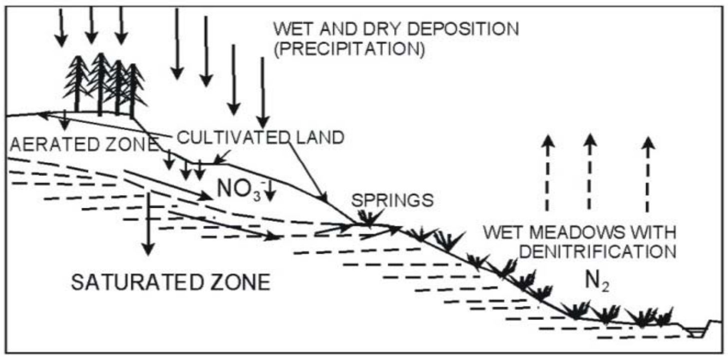
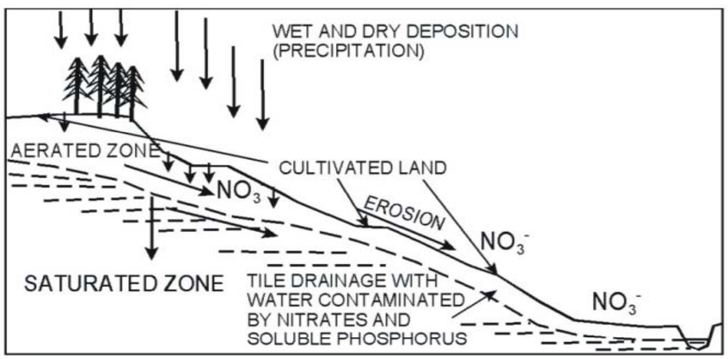
Serious problems with HABs in Texas, Florida, California, Great Lakes states, New York State, Charles River in Boston , and elsewhere

Riparian wetland drainage and upland erosion



A) Water and nutrient regime before tile drainage



B) Water and nutrient regime after tile drainage

Source: Laxa at al (2008) *Vodni Hospodarstvi*

- Low land (alluvial and plains) wetlands were drained
  - change of the reduced conditions of soil to oxygenated which converted less mobile organic N and ammonium to highly mobile nitrate
- Loss of denitrification
- Nitrate losses into groundwater and streams

Traditional views of factors affecting cyanobacteria blooms (Kravchuk, 2006)

- Temperature (affected by global warming)
- Phosphorus concentration
- N:P ratio
- Hydraulic conditions
- Light
- Grazing by zooplankton
- Controlling N is inefficient because N fixing blue greens (e.g., *Anabaena)* are also present that provide enough nitrogen

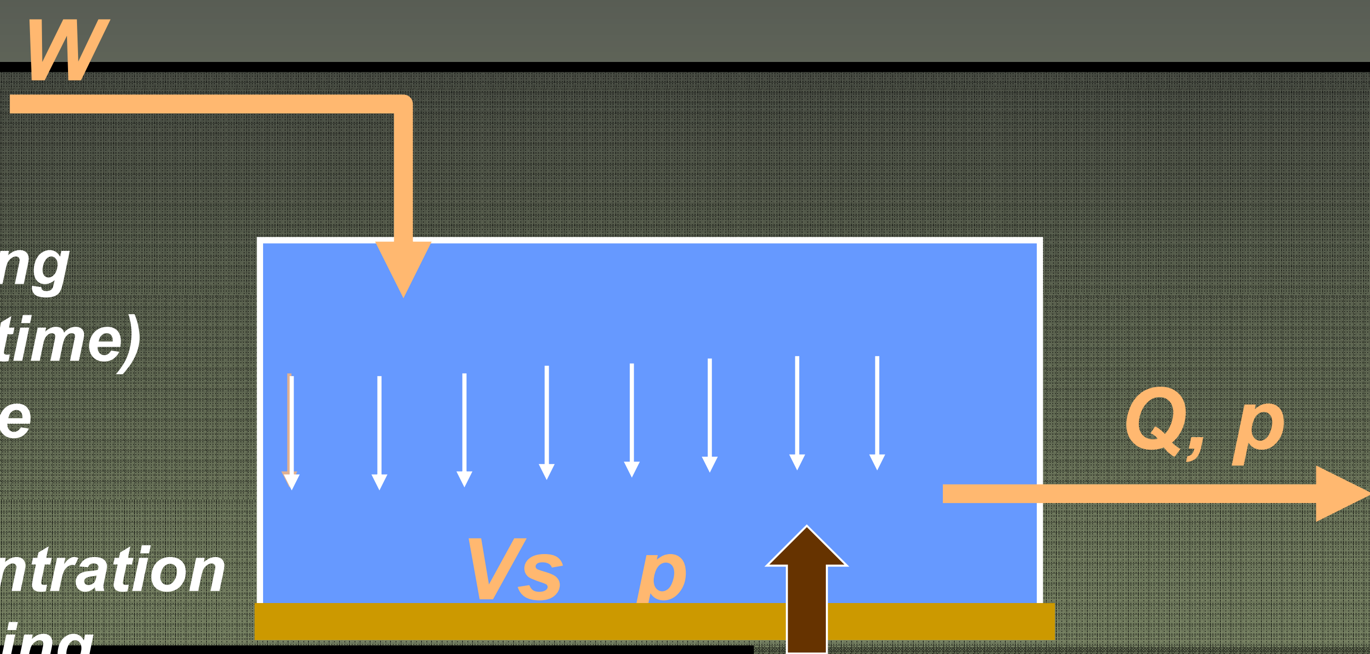
Cyano-HABs may occur suddenly even after nutrient controls have been implemented (Lake Delavan (WI), Charles River(MA)). **Once they occur they are extremely difficult and costly to control.**

Research on Taihu changed the control hypothesis (Paerl et al. 2010)

- N fixing cyanobacteria rarely provide enough N, less than 50% is fixed from N_2
- In N limited hypertrophic water bodies the succession from N_2-fixing to non-N_2-fixing taxa has not occurred and N:P stochiometry does not apply to hypereutrophic lakes
- Excess inputs of both N & P combined with internal cycling overwhelm the ability of a single nutrient to control eutrophication process

Both N & P inputs need to be reduced (including recycled N and P from sediments)

VOLLENWEIDER's COMPLETELY MIXED LAKE SCHEMATIC



W= loading (Mass/time)
V=volume
Q=flow
p=concentration
V_s = settling velocity
A_s= surface area

$$V\frac{dp}{dt} = W - V_s A_s p - Qp$$

σ_y=(annual mass of P deposited into sediment)/(mass of P in impoundment)

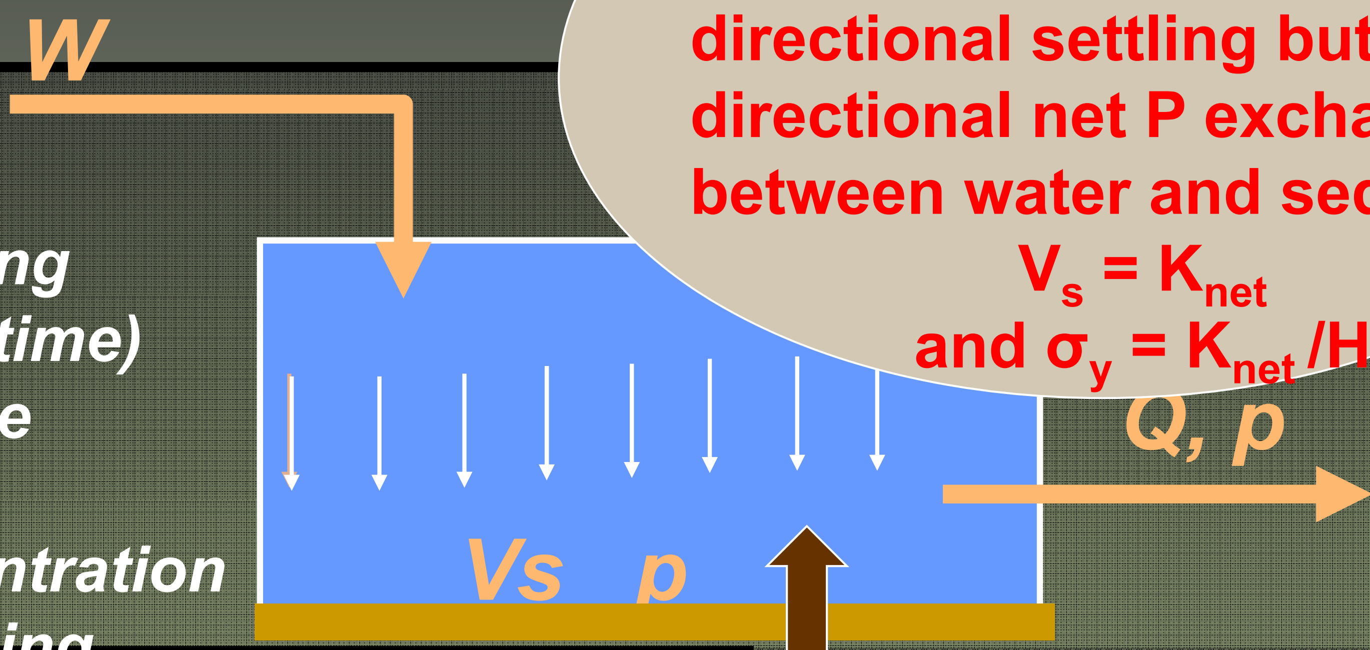
VOLLENWEIDER's CO
LAKE SCHEMATIC

PROBLEM!!

In hypereutrophic water bodies V_s is not one-directional settling but two directional net P exchange between water and sediment

$V_s = K_{net}$

and $\sigma_y = K_{net}/H$



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SIMPLE STEADY STATE SOLUTION MAY NOT WORK

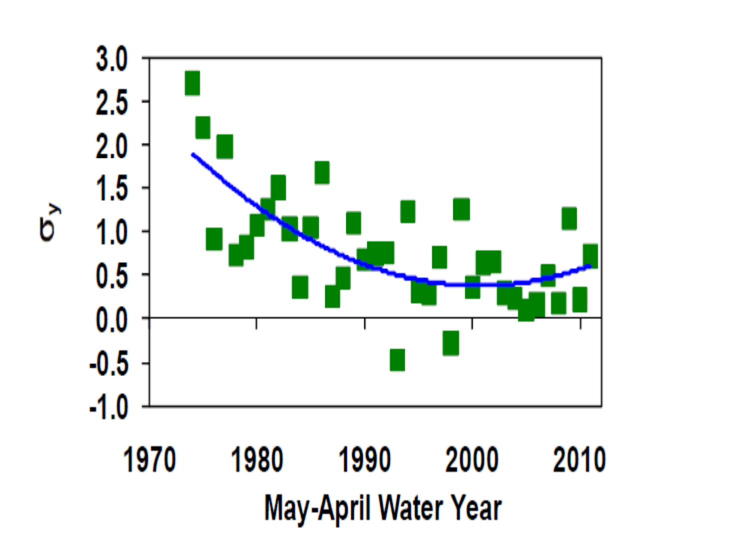
$$p = \frac{W'}{q_s + K_{net}}$$

From Reckow (1979)
$K_{net} = 11.6 + 0.2\, q_s$

Hence, min K_{net} ~ 12m/year

$W' = W/A_s$ = Loading of pollutant (phosphorus) per unit area (g/m^2-year)
$q_s = 1/\rho = Q/V$ = specific overflow rate (m/year)
ρ = flushing rate

Achilles heels of Models



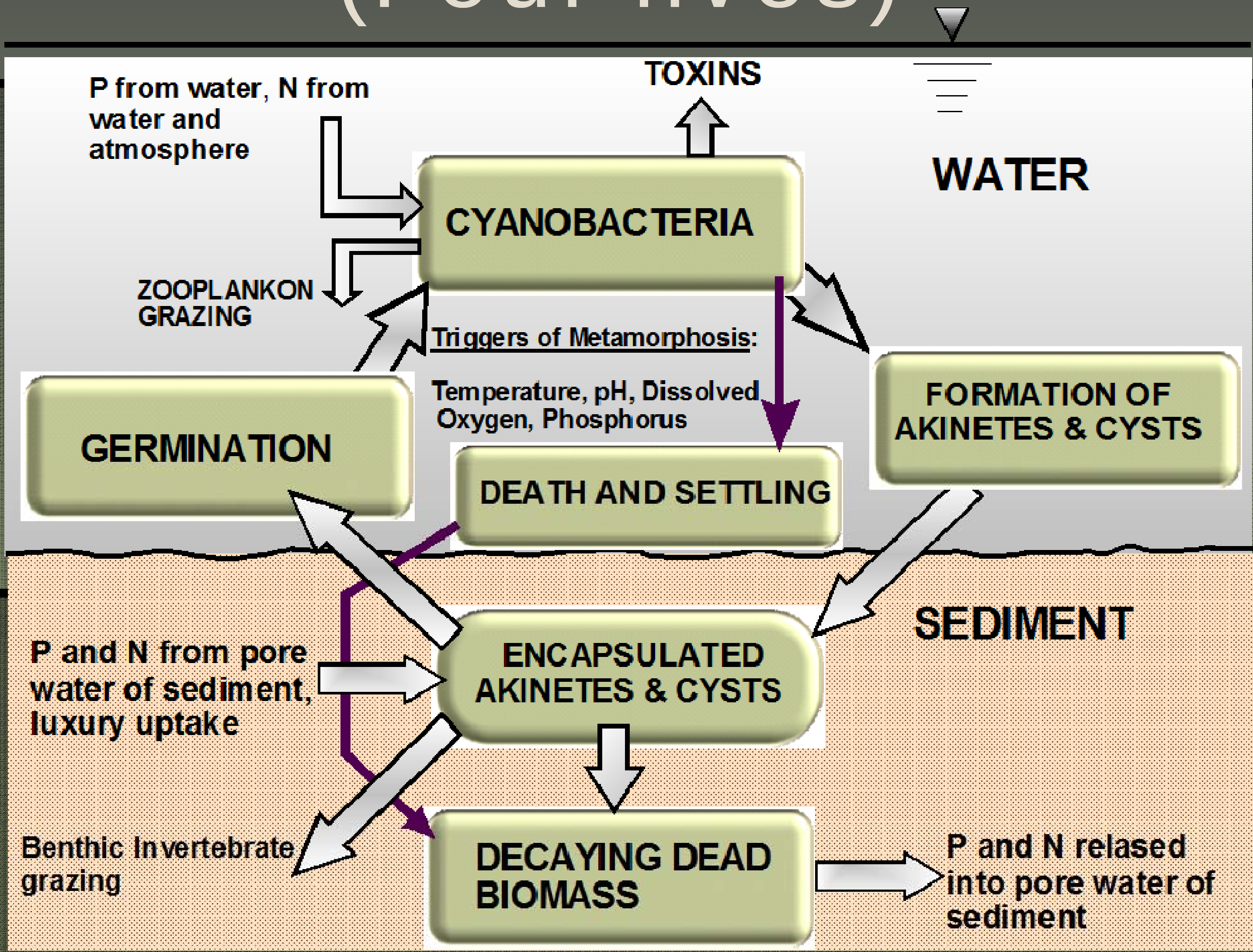
- K_{net} represents the net exchange of phosphorus between the water column and the sediment
  - σ_y for Lake Okeechobee. For average depth of H=2.7m K_{net} would range between -1.5 to 7.5 m/year
  - Sediments have a limited capacity to accept large loads of P
  - Chapra and Canale (1991) suggested $K_{net} = v_s - v_t$ where v_t is recycle mass rate of P from the sediment expected to be related to the oxic status of the water column above the sediment.

- The hypothesis of constant K_s or σ_y is simplistic and coincidental; other factors such as P and sulfate loads into sediments are more important (Hupper and Levandowski, 2008)
- During blooms most of P in water is associated with biomass either inside the cells or adsorbed on organic cellular C.

Traditional eutrophication model do not represent hypereutrophic conditions

- Most models treat algal biomass as a chemical constituent (mg/L or mg Ch/L)
- In reality the cyanobacteria exist in several stages, are highly vertically mobile and can move up and down, including into sediment, in search of the best conditions for their nourishment and survival.

Life cycles of cyanobacteria (Four lives)



Internal loads of P (and N) from sediments are significant

- In Lake Okeechobee (FL) the average annual external load is about 500 tons/year during 2007-2011 period. The P content in the upper 10 cm of sediment is about 30,000 tons.
- A great portion of P in the upper sediments is in the living (cyanobacteria) and decomposing biomass.
  - In Brno reservoir in the Czech Republic the concentration of cyanobacteria in the sediment was greater than in the water column (10^6 cells/ml).
- Mineral P (PO_4^{3-}) in sediments is held in insoluble Fe(III) and Al (IV) complexes, or adsorbed on clay and organic C.

P and N redox holding in the sediment and wet soils

WATER	**Oxygen Reduction Zone**	*AEROBIC RESPIRATION*
WATER LOGGED SOIL OR SEDIMENT	**Oxygen Reduction Zone** *Eh =≥ 300 mV*	$DOC + O_2 \rightarrow CO_2 + H_2O$ $TKN + O_2 \rightarrow NO_3^-$
	Nitrate Reduction Zone **Mn^{4+} Reduction Zone** *Eh =100 to 300 mV*	*FACULTATIVE ANOXIC RESPIRATION* $DOC \rightarrow CH_3\,COOH + H_2 + CO_2$ $2NO_3^- + CH_3COOH + H_2 \rightarrow 2H_2O + N_2\uparrow + 2\,(HCO_3)^-$
DEPTH	**Fe^{3+} Reduction Zone** *Eh = - 100 to 100 mV*	$Mn^{4+} + 2e \rightarrow Mn^{2+}$ $Fe^{3+} + e \rightarrow Fe^{2+}$ $FePO_4 + e \rightarrow (Fe^{2+})_3(PO_4^{3-})_2$
	Sulfate Reduction Zone *Eh = - 200 to -100 mV*	$SO_4^{2-} + CH_3COOH \rightarrow HS^- + 2HCO_3^- + H_2$ $HS^- + Me^{2+} \rightarrow MeS + H^+$
	Methanogenesis (Methane Formation Zone) *Eh ≤ -200 mV*	*ANAEROBIC* ZONE $DOC \rightarrow CH_3COOH + H_2 + CO_2$ $CH_3COOH \rightarrow CH_4 + CO_2$ $4H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$

Effects of key parameters

- **Dissolved Oxygen and Nitrate**
  - Hypolimnetic DO has little effect on P release from the sediment controlled by mobile P in pore water
  - In the interstitial sediment-water layer sediment oxygen demand (SOD) is created by oxidation of dissolved methane and nitrification of ammonium emanating from the anaerobic sediment.
  - Nitrate is formed from ammonium in the top oxic layer of the sediment and transferred by diffusion into anoxic nitrate layer below the oxic layer
  - The oxygenated top sediment layer is thin (few mm) and the aerobic decomposition of organic matter in the top oxic layer is negligible when compared to anoxic/anaerobic processes and denitrification in the sediment below.

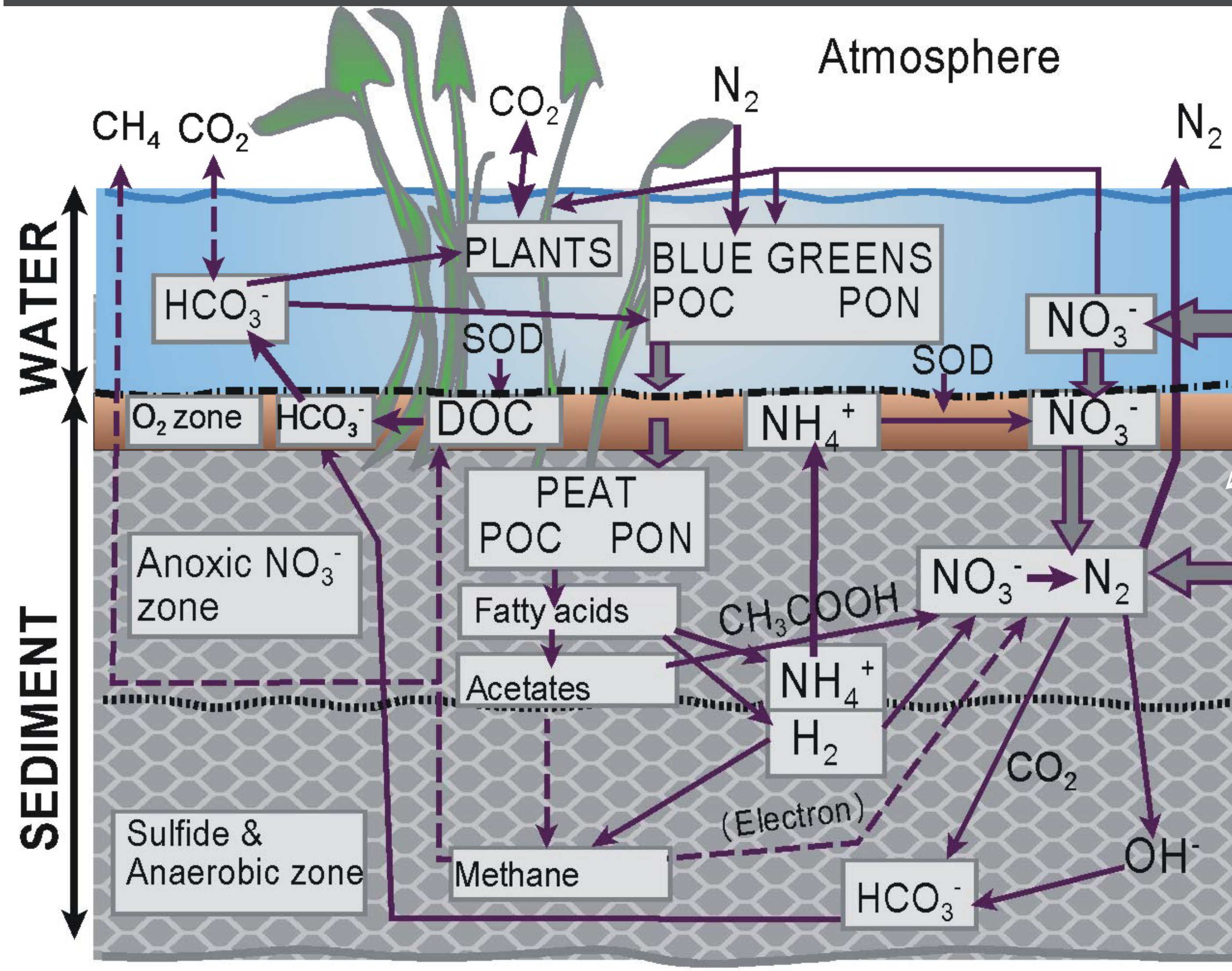
Nitrate effects

- Higher nitrate loads and concentrations are mostly anthropogenic
- If NO_3^- -N in the water column >1-2 mg/L, anoxic interstitial nitrate layer will form that will block reduction of Fe(III) to Fe(II) and prevents P release from the sediment (phosphate trapping)
- Studies have documented that if nitrate is present in the hypolimnion and nitrate layer is formed in the top sediment, water bodies with high N & P loads would not become hypereutrophic.

More on Nitrate Effects

- Nitrate suppresses methanogenesis in the anoxic sediments and wet soils
- Simultaneous nitrification and denitrification occurs if both oxic and anoxic nitrate layers are present. Nitrifying microorganisms are strict aerobes and reside mostly in the upper oxygenated sediment layer
- In the denitrification reaction in the anoxic nitrate zone, acetate is converted to alkalinity, and not reduced to CO_2 and methane, and hydrogen is oxidized to water

- **Mineralization (decomposition) of settled microorganisms**
  - Sediments containing dead algae and organic detritus are mostly anoxic and anaerobic .
  - Mineralization rate is fast and is affected by temperature.
  - Mineralization releases phosphates and ammonium into sediment pore water
  - The survival of akinetes and cysts is the sediment is not well known but they can reside in sediments for years and absorb nutrients as luxury uptake.
  - Anaerobic decomposition progresses in several phases
    - Formation of fatty acids acetates and hydrogen methanogenesis



Anthropogenic nitrate load

Simultaneous nitrification/ denitrification

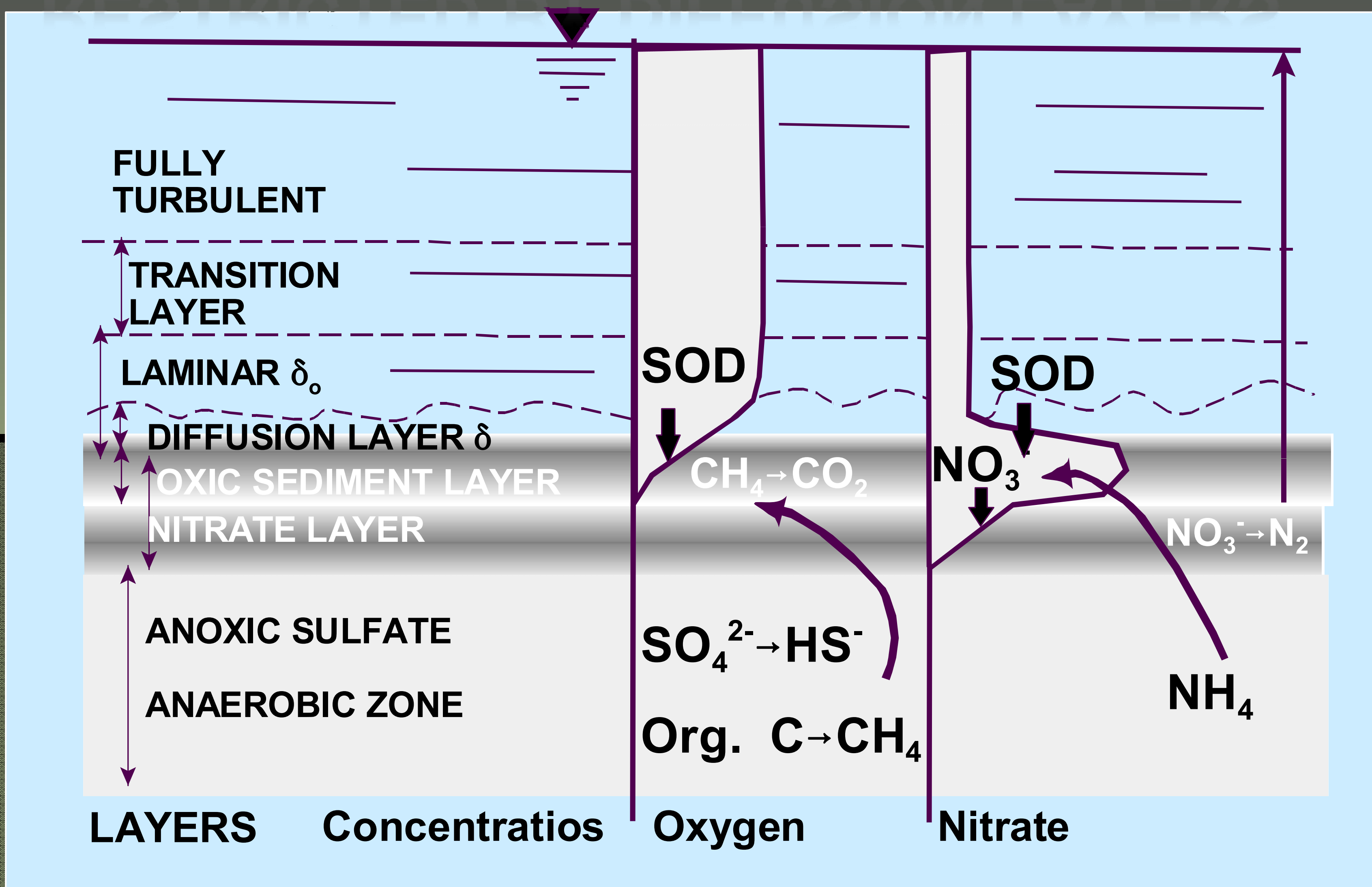
Phosphate bind to (trapped by) Fe(III) and Al (IV)

Phosphate is released by reducing Fe(III) to Fe(II) which does not occur if nitrate is present

$$2\ NO_3^- + CH_3COOH + H_2(g) \rightarrow N_2(g) + 2\ HCO_3^- + 2\ H_2O$$

- **Consequently and surprisingly wetlands and impoundments with higher nitrate loads sequester carbon and methane and retard hypertrophic conditions**

SEDIMENT –WATER MASS FLUXES ARE RESTRICTED BY DIFFUSION LAYERS

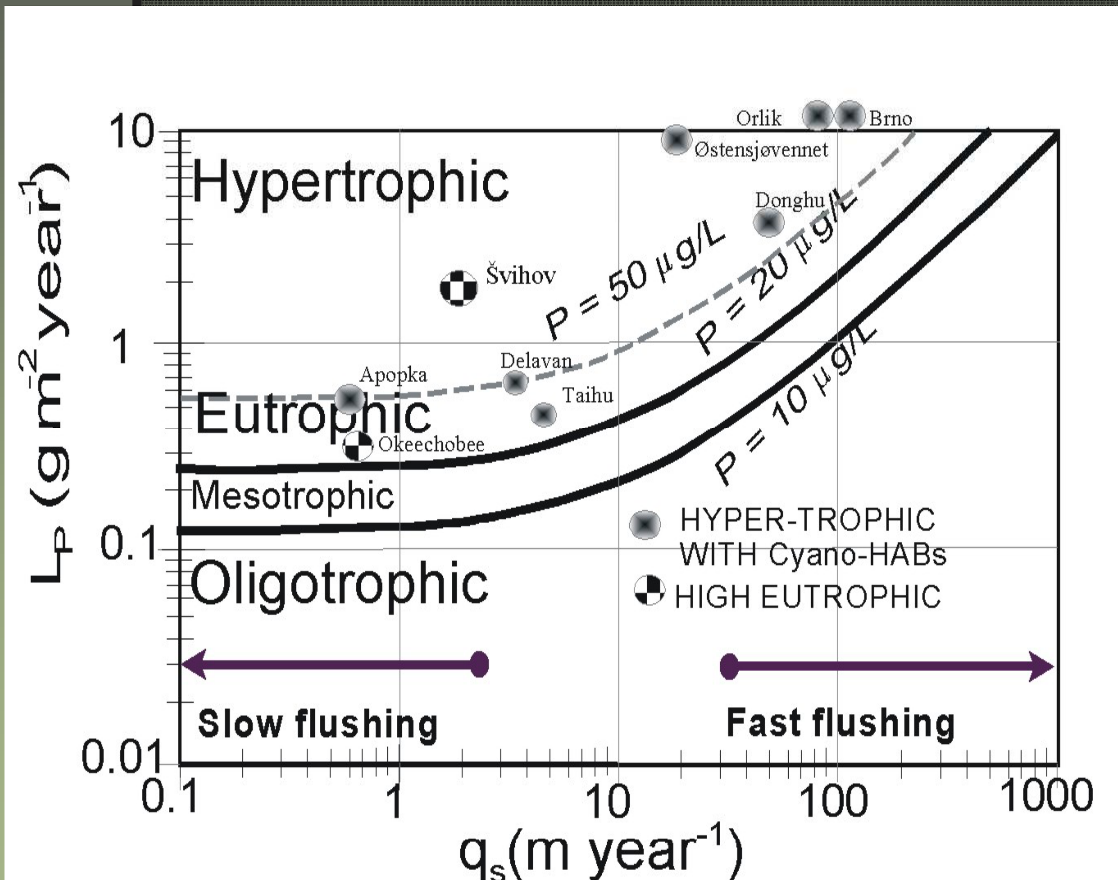


Švihov Reservoir (largest water supply reservoir in Czechia)

DAM

	%
Arable land	47.8
Meadows and pastures	12.3
Forests	29.0
Urban (built)	1.2
Other	9.7

High nitrate levels in the Švihov (CZ) and Okeechobee (FL) impoundments



- Both lakes have high phosphate loads.
- >90% of N in the Švihov reservoir is NO_3^- -N.
- In 2006 N>9 mg/L and P> 100 µg/L in all major tributaries
- In Lake Okeechobee NO_3^- load is about 50% of the total load.
- N in the other impound-ments in the figure is mostly TKN
- Lake Okeechobee and Taihu are completely mixed

Impoundment characteristics

Parameter	Taihu[1]	Donghu[2]	Švihov[3]	Orlik[4]	Brno[5]	Lake Apopka[6]	Lake Okeechobee[7]	Lake Delavan[8]	Østensj-øvannet[9]
Lake/reservoir surface area, km^2	2,338	28	14.3	27.33	2.59	124	1,740	7.23	0.34
Volume, 10^6 m^3	4,400	62	267	722	21	210	4,730	55.24	1.31
Average depth, m	2	2.2	18.6	27	8.2	1.7	2.7	7.62	3.9
Annual flow, 10^6 m^3/year	9 667	139.54	225.482	2 602	260.5 8	76	1244	27.6	6.62
Overflow rate q_s, m/year	4.13	4.98	15.77	95.2	100,5	0.61	0.71	3.81	19.5
Total nitrogen, tons/year g/m^2-year % NO_3^- - N	24,160 10.4 <10	- 53 <10	2,097 146.6 >90			342 2.75 ~0	5554 3.2 ~50	89.0 12.3 <20	
Total P load, tons/year g/m^2-year	1020 0.43	- 3.4	24 1.8	340 12	31 12	62.4 0.5	500 0.3	4.3 0.59	3.19 9.38
Trophic status	Hyper-trophic	Hype-trophic	Meso-trophic to Eutrophic	Hyper-trophic	Hyper-trophic	Hyper-trophic	Eutrophic	Hyper-trophic	Hyper-trophic

Characteristic values of $C_{90\%}$ in the monitoring profiles of the direct tributaries of the Švihov reservoir.

Data from the Vltava Watershed (Povodi) Agency by Hejzlar at al. (2006)

Parameter	Monitoring Profile			
	Želivka 42000	Martinicky p. 3000	Blažejovský p. 2100	Sedlický p. 0500
BOD_5, mg/L	3.7	3.1	[illegible]	4.0
Chloph[illegible]	[illegible]	23	28	38
pH	8.0	7.9	7.9	8.5
$N\text{-}NH_4^+$, mg/L	0.37	0.17	0.20	0.44
$N\text{-}NO_3^-$, mg/L	10.3	12.4	9.3	13.8
Total P, µg/L	170	180	180	140

Vulnerable - Hyper-eutrophication

Are high nitrate loads acceptable?

NO

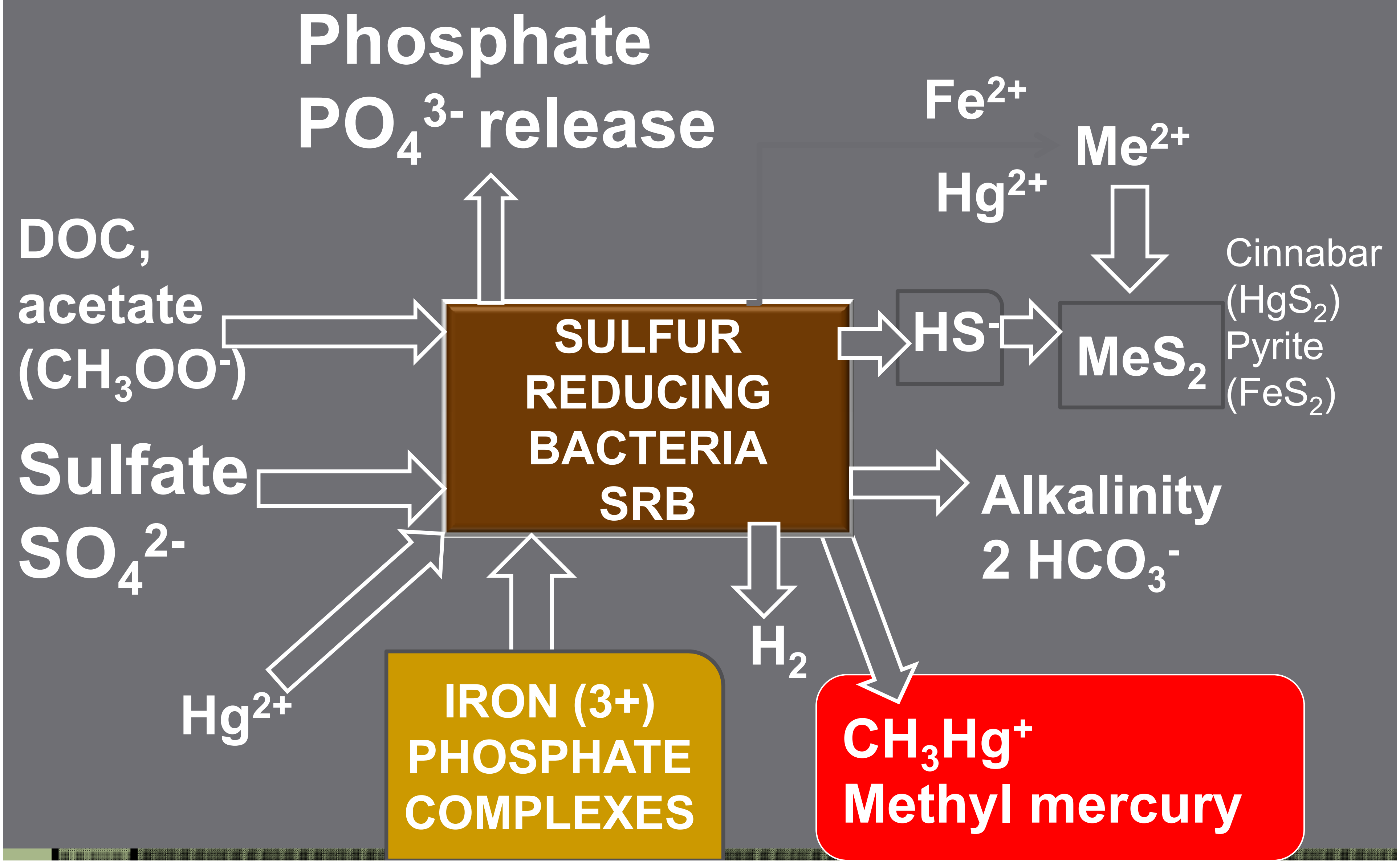
- The fact that Cyano-HABs are triggered by high N and P loads in water column has not changed and nitrate in the water column is a critical nutrient and its high concentration or addition could reduce only the P input from the sediment
- Relatively rapid denitrification in organic C rich sediments decreases the N/P ratio which shifts the development of HABs towards cyanobacteria dominated blooms
- The nitrate protective layer may be exhausted later in the year which could trigger Cyano-HAB

- Nitrate is a regulated pollutant both as a nutrient (nitrate directive in EU) and a water supply toxicant
- Nitrate content and nitrate layer in sediments are transient and unreliable as a control
- Relying on nitrates to prevent control hypertrophic conditions is playing Russian roulette with a time bomb

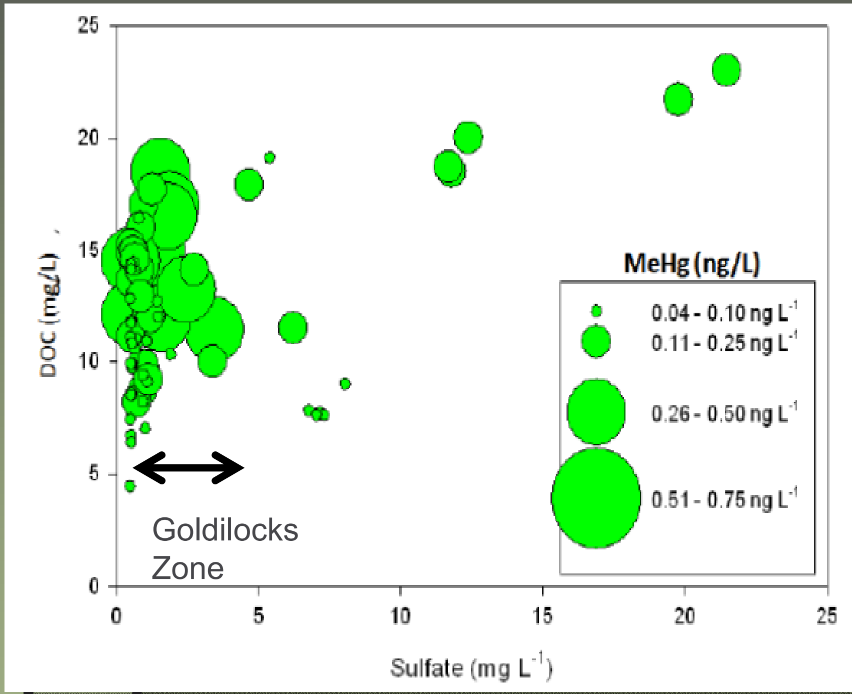
Role of sulfates

- The anthropogenic inputs of sulfates into surface water bodies have increased significantly over the last century
  - Mining – oxidation of pyrite
  - Drainage of wetlands (immobile sulfides oxidized to highly mobile sulfates)
  - Increased use of sulfuric acids by industries and agriculture (to acidify calcareous soils)
- Sulfates in water logged soils, sediments and wetlands are reduced to sulfides after oxygen is exhausted and nitrate is reduced to N_2 and ammonium

Sulfur reducing bacteria (SRBs) do more than just reducing sulfates



Methyl mercury formation in Everglades



- Boaccumulative MeHg is formed by SRBs
- Higher MeHg is formed only when sulfate is between 1-5 mg/L and DOC between 10 to 20 mg/L) (Goldilocks' effect)
- Higher sulfide concentrations are toxic and not result in MeHg. Hg may form cinnabar.
- Hg as low as in nanograms/L is sufficient to form MeHg

Picture credit US GS and South Florida Wat. Management District

Implications (pitfalls) for TMDLs

- The current mass balance models are inadequate and the traditional algae models do not represent the cyanobacteria
- The sediment processes, P accumulation and release are very important
- The biomass of cyanobacteria in sediments is alive and nourishing on nutrients
- Vertical movement of P in cyanobacteria in water is not settling
- Redox processes and nitrate and sulfate in sediments are very important
- Once Cyano-HABs develop their remediation is very complex and expensive. Reducing P to borderline concentrations (e.g., 50 to 100 µg/L) is not enough

Surprising findings

- Denitrification of nitrates and reduction of sulfates in sediments of wetlands and impoundments sequester GHGs methane and CO_2
- Phosphorus “settling” into sediments is diminishing with time, and sediments can become a net source of P
- In some cases, nitrate can retard on-set of hypereutrophy
- Reducing sulfates to very small concentration can trigger formation of MeHg

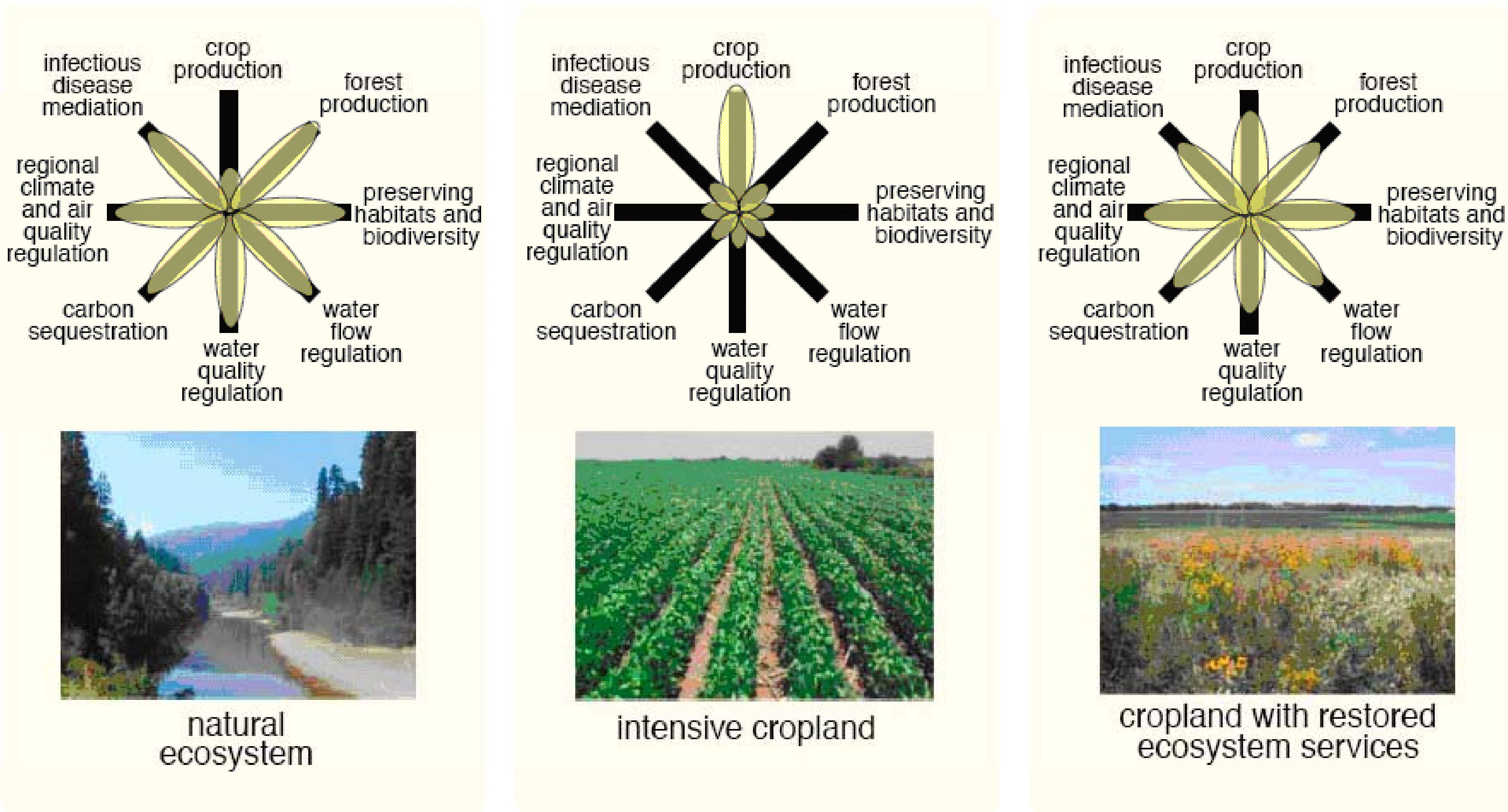
Alternatives to be developed for nutrient control in the water body

- Focusing on significant P controls and removal both in inlet water and sediment. Dredging sediment has been suggested and sometimes used.
- Oxidized iron and aluminum in sediments are important. Epilimnion aeration has been successfully used (Brno reservoir) but with a caution.
- Phosphorus precipitation by alum and iron salts has been used to temporarily precipitate P from water and form a buffer sediment surface zone.
- Fish management and manipulation have been used to increase algae grazing by zooplankton
- Restoring riparian wetlands to enhance N and P removals and by denitrification reduce GHGs.

Wetlands are natural sinks of nutrients and could sequester carbon

Buffers and soil erosion control

Developing watershed ecoregion to combat hypertrophy



Source: US EPA

Final Conclusions

- Prevention of hyper-trophic conditions in vulnerable impoundments requires a comprehensive watershed and water body management and protection
- Existing and increasing future occurrences of nuisance algal blooms of blue green algae (cyanobacteria are a major problem
- Significant reductions of N and P loads are needed.
- The current models are inadequate for modeling hyper-eutrophic conditions. Better models (e.g., agent based models) are being developed
- Landscape is an important part of the solution and should provide protective barriers and attenuation of nutrient loads
- Because of uncertainty and inadequacy of models and estimates, the planning process and watershed and water body management should be adaptive, recurrent and include common sense immediate actions and long term plans.


THANK YOU
TO BE CONTINUED