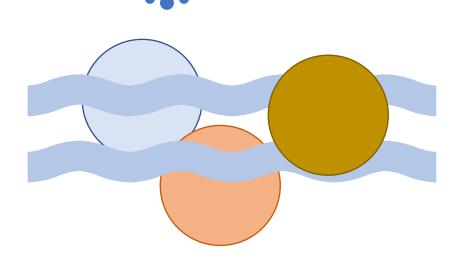
Surface Water Quality Modeling



C. D. Guzman, PhD Week 10 Wednesday, Mar 25, 2020



1. Reflection: "Open" How are you managing the days/weeks?

2. Workshop

- **3. Eutrophication Pb & Nutrients**
- 4. Plant Stoichiometry
- **5. Nitrogen & Phosphorus**
- 6. Example

HW 5 (Due April 3)

28.1, 28.3, (28.4) 29.1 (29.2) 36.1, 36.2 (36.3)

March 25th -27th: Discussion

April 8th: Rough Draft

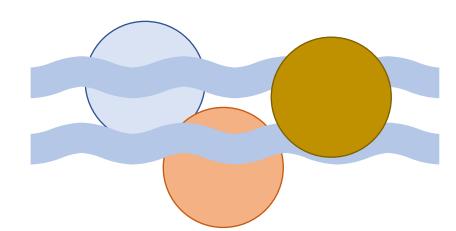
April 15th: Peer Review

April 22nd : Submission & Presentations

Workshop

The Eutrophication Prb & Nutrients







Eutrophication Prb & Nutrients

Too much of a good thing

"overfertilization" phenomenon is generally referred to as eutrophication. This terminology was originally coined to describe the natural aging process whereby a lake is transformed from a lake to a marsh and meadow. The accelerated process is sometimes called *cultural eutrophication*.

Water bodies are classified in their trophic state:

- -Oligotrophic (poorly nourished)
- -Mesotrophic (moderately nourished)
- -Eutrophic (well-nourished)
- -Hypertrophic (overnourished)

Eutrophication Prb

Several deleterious effects can happen:

Quantity: Profuse growth of floating plants decrease water quality, and can lead to overgrowth which can hinder navigation and recreation.

Chemistry: Plant growth and respiration can affect the system's water chemistry

Biology: Eutrophication can alter the species composition of an ecosystem.

Nutrients

Inorganic nutrients provide chemical building blocks for life in aquatic systems.

Macronutrients: required in large quantities for cell development, carbon, oxygen, nitrogen, phosphorus, sulfur, silica, and iron.

Micronutrients: necessary nutrients required in smaller quantities, manganese, copper, and zinc.

Water-quality modeling has focused on four macronutrients: Phosphorus, nitrogen, carbon, silica

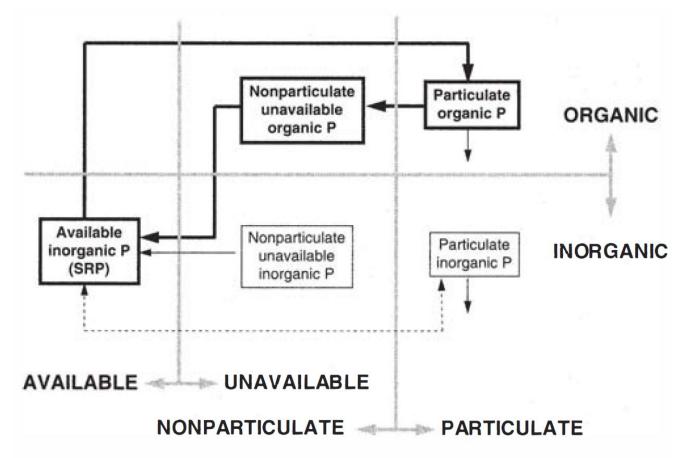


FIGURE 28.1

Forms of phosphorus found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Phosphorus is in short supply relative to other macronutrients.

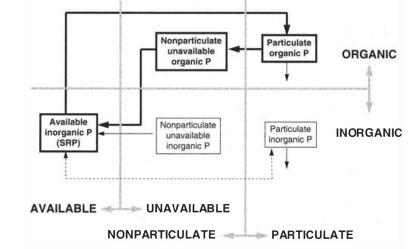


FIGURE 28.1

Forms of phosphorus found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

1. Not abundant in earth's crust, phosphate minerals are not very soluble

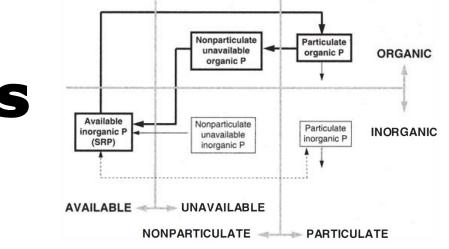
2. Does not exist in gaseous form (in contrast to carbon and nitrogen).

3. Phosphate tends to sorb strongly to fine-grained particles. Settling and sedimentation serves to remove phosphorus from the water

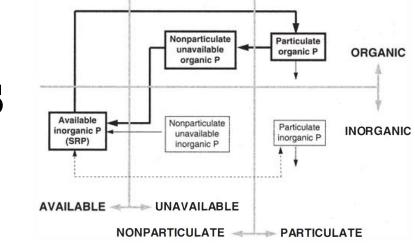
Human activities result in phosphorus discharge to

natural waters. Human and animal wastes both contain substantial amounts of phosphorus (also supplemented by detergent phosphorus). In addition, nonpoint sources from agricultural and urban land contribute excess phosphorus (fertilizer and P-containing chemicals).

Lastly, anthropogenic influences lead to soil erosion which also enhances phosphorus transport into waters.



Phosphorus in natural waters can be subdivided as:



The following is based on conventional measurement techniques and modeling necessity:

-Soluble reactive phosphorus (SRP): Also called orthophosphate or soluble inorganic P. This form is readily available to plants; $[H_2PO_4^{-7}]$, $[HPO_4^{-2-7}]$, and $[PO_4^{-3-7}]$

-Particulate organic P: living plants, animals, and bacteria and organic detritus.

-Nonparticulate organic P: dissolved or colloidal organic compounds containing phosphorus, from decomposition of particulate organic P.

-**Particulate inorganic P:** Phosphate minerals (apatite phosphorus), sorbed orthophosphate (on clays), and phosphate complexed with solid matter (calcium carbonate precipitates, iron hydroxides).

-Nonparticulate inorganic: condensed phosphates such as those found in detergents

Nutrients: Nitrogen

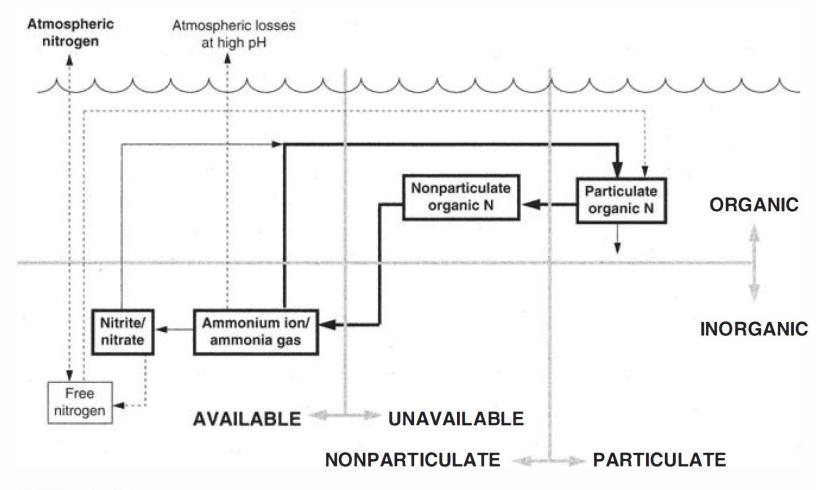


FIGURE 28.2

Forms of nitrogen found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Nutrients: Nitrogen

The nitrogen cycle described early included the primary forms:

- Free nitrogen (N₂)
- Ammonium (NH₄⁺)/ammonia (NH₃)
- Nitrite (NO₂⁻)/nitrate (NO₃⁻)
- Organic nitrogen

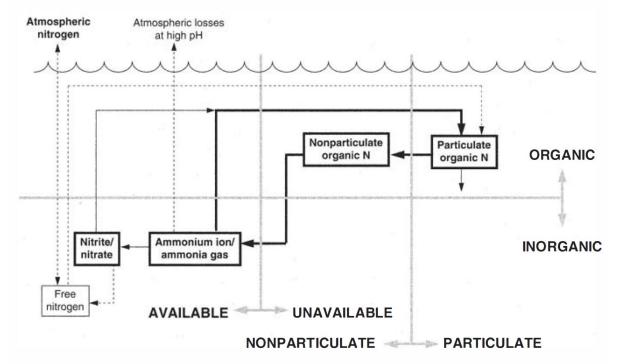


FIGURE 28.2

Forms of nitrogen found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Nutrients: Nitrogen

Organic nitrogen can be broken down into particulate and dissolved components, other major processes: Atmospheric losses

- -Ammonia and nitrate assimilation
- -Ammonification
- -Nitrification
- -Denitrification
- -Nitrogen fixation

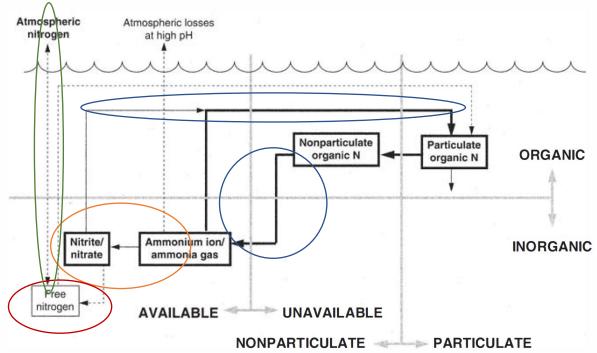


FIGURE 28.2

Forms of nitrogen found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Nutrients: Nitrogen/Phosphorus

Nitrogen and phosphorus differ in three ways:

1. Nitrogen has a gas phase

2. Inorganic forms of nitrogen do not sorb as strongly to particulate matter as does phosphorus

3. Denitrification represents a purging mechanism that does not occur phosphorus

Nutrients:

How fine scale should it be?

What are the system components you've seen/read about?

Nutrients: Carbon

Atmospheric carbon dioxide

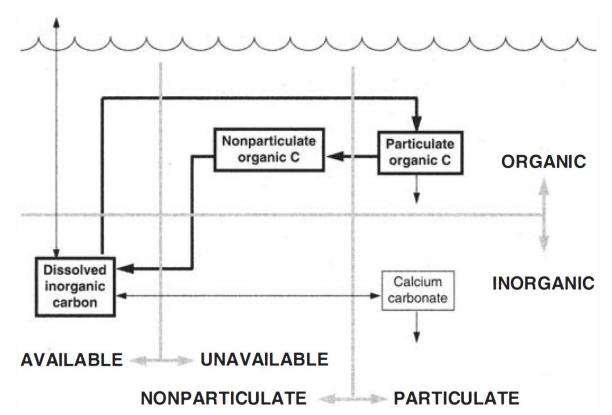


FIGURE 28.3

Forms of carbon found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Nutrients: Carbon

Carbon can play three roles in water quality modeling:

1. Nutrient

2. Biomass

3. Pollutant

Atmospheric carbon dioxide

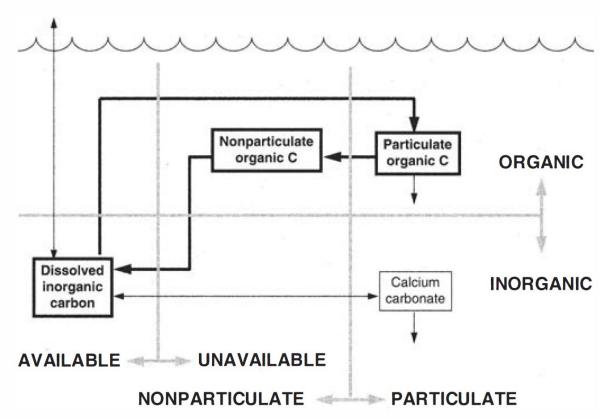


FIGURE 28.3

Forms of carbon found in natural waters. The principal forms involved in the production/decomposition life cycle are shown in bold.

Nutrients: Silicon

Although considered a minor nutrient, silicon has significance in the dynamics of phytoplankton because of its importance as a major structural element in the cells of an important plankton group- the diatoms.

Diatoms use dissolved reactive silicon $[Si(OH)_4]$ to build a frustule or "glass wall" that surrounds the cell.

The other key part of the eutrophication process is the food chain. The exchange between two components represents a cycle. Production converts inorganic nutrients into organic matter, whereas decomposition reverses the process.

An important factor in this process is the stoichiometric composition of organic matter (Stumm and Morgan, 1981):

 $106CO_2 + 16NH_4^+ + HPO_4^{2-} + 108H_2O \iff C_{106}H_{263}O_{110}N_{16}P_1 + 107O_2 + 14H^+$

This can be used to determine mass ratios of carbon to nitrogen to phosphorus:

$$C$$
: N : P 106×12 : 16×4 : 1×31 1272 : 224 : 31

It is also known that plant protoplasm is about 1% phosphorus on a dry-weight basis. Therefore we can normalize the ratios to the mass of phosphorus and express the results as percentages of dry weight.

Therefore 1 gram of dry weight organic matter would be 10 mg P. 72 mg N, 400 mg C.

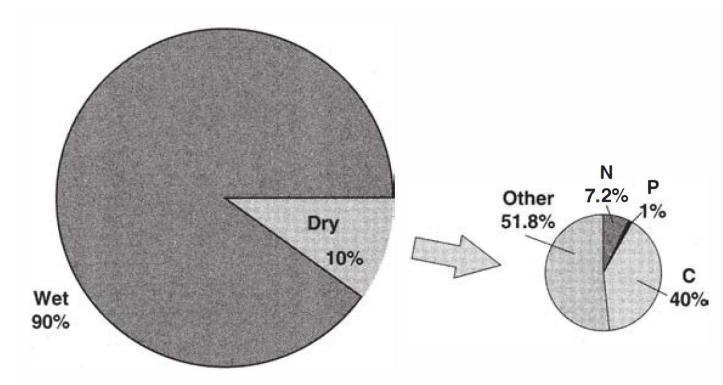


FIGURE 28.4

Pie diagram showing the percentages of nutrients and water constituting the average phytoplankton biomass.

EXAMPLE 28.1. PHYTOPLANKTON STOICHIOMETRY. Suppose that a lake has a volume of 1×10^6 m³ and a phytoplankton concentration of 10 µg L⁻¹ of chlorophyll *a*. If the carbon-to-chlorophyll ratio is 25 µgChl mgC⁻¹ and all the other stoichiometry follows Fig. 28.4: (*a*) Reexpress the phytoplankton concentration as organic carbon. (*b*) If the phytoplankton are decomposing at a rate of 0.1 d⁻¹, what is the resulting rate of oxygen demand in g m⁻³ d⁻¹? (*c*) What is the rate of release of nitrogen and phosphorus in g d⁻¹?

Diatoms are different from other forms of phytoplankton in that silicon makes up a large fraction of their biomass.

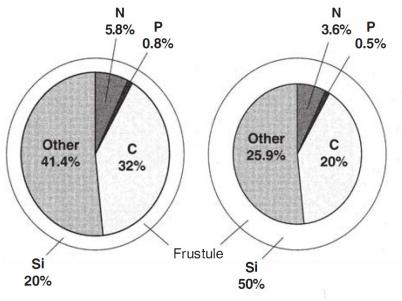


FIGURE 28.5

Pie diagram showing the percentages of nutrients on a dry-weight basis for diatoms with different silicon content in their "glass" cell walls or frustules.

Nitrogen and Phosphorus

Because they are the primary controllable nutrients, nitrogen and phosphorus have been the focus of efforts to control eutrophication.

Point sources of nitrogen and phosphorus are summarized in the table. The use of phosphate detergents has had a great impact on the amount of phosphorus in wastewater.

TABLE 28.1

Amounts of nitrogen and phosphorus in untreated domestic sewage in the United States. Numbers in parentheses represent ranges (from Metcalf and Eddy 1991, Thomann and Mueller 1987)

Nutrient	$\begin{array}{c} \text{Concentration} \\ (\text{mg } L^{-1}) \end{array}$	Per-capita loading rate (g capita ⁻¹ d ⁻¹) ⁺	
Nitrogen	40	23	
	(20 - 85)		
Organic N	15	8.5	
	(8-35)		
Free ammonia	25	14.2	
	(12–50)		
Phosphorus (with detergents)	8	4.5	
	(4 - 15)		
Organic P	3	1.7	
	(1-5)		
Inorganic P	5	2.8	
	(3–10)		
Phosphorus (without detergents)	4	2.3	

^{*}Based on a per-capita flow rate of 0.57 m³ capita⁻¹ d⁻¹ (150 gal capita⁻¹ d⁻¹).

Nitrogen and Phosphorus

Some typical nonpoint sources are summarized this this table. Urban and agricultural use greatly increase the export of both nitrogen and phosphorus from the land.

TABLE 28.2

Nitrogen and phosphorus export rates (kg ha⁻¹ yr⁻¹) generated from various nonpoint sources in the United States (numbers in parentheses represent ranges)

Nutrient	Forest	Agricultural	Urban	Atmospheric
Nitrogen	3 (1.3–10.2)	5 (0.5–50)	5 (1–20)	24
Phosphorus	0.4 (0.01–0.9)	0.5 (0.1–5)	1 (0.1–10)	l (0.05–5)

N:P Ratio

As plants grow, they take up inorganic nutrients from the water in proportion to their stoichiometry.

A first cut at identifying this "limiting nutrient" is to compare the levels of the nutrients in the water with the cell stoichiometry.

A rough rule of thumb is the nitrogen-to-phosphorus ratio. Recall that in biomass this ratio is approximately 7.2. Hence an N:P ratio less than 7.2 suggests that nitrogen is the limiting nutrient. On the other hand, if it is higher than 7.2, this implies that phosphorus will limit plant growth. **EXAMPLE 28.2.** N:P RATIOS. Suppose that a batch reactor has an initial concentration of algae of 1 μ gChl L⁻¹. If the plants are growing according to first-order kinetics ($k_g = 1 \text{ d}^{-1}$), determine how both plant and nutrient concentrations evolve for initial nutrient levels of (a) $n_0 = 100 \mu$ gN L⁻¹ and $p_0 = 10 \mu$ gP L⁻¹, and (b) $n_0 = 72 \mu$ gN L⁻¹ and $p_0 = 36 \mu$ gP L⁻¹.

N:P Ratio

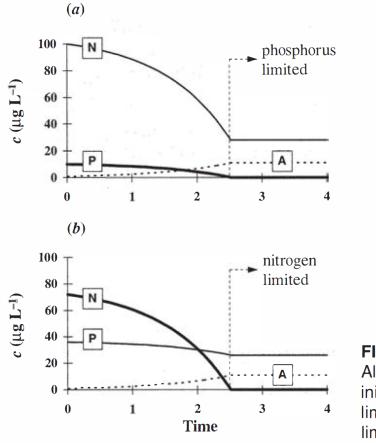


FIGURE 28.6

Algal growth in a batch reactor starting with initial N:P ratios that lead to (*a*) phosphorus limitation (initial N:P = 10) and (*b*) nitrogen limitation (initial N:P = 2).

N:P Ratio

Sewage is generally enriched in phosphorus. Therefore, water bodies dominated by wastewater effluents tend to be nitrogen limited.

Estuaries tend to be deficient in nitrogen and hence usually nitrogen-limited. Those systems subject to phosphorus removal and non-point source input are generally phosphorus limited.

TABLE 28.3

N:P ratios for point, nonpoint, and marine waters (data from Thomann and Mueller 1987, Omernik 1977, and Goldman et al. 1973)

Source type	TN/TP [†]	IN/IP [‡]	Limiting nutrient
Raw sewage	4	3.6	Nitrogen
Activated sludge	3.4	4.4	Nitrogen
Activated sludge plus nitrification	3.7	4.4	Nitrogen
Activated sludge plus phosphorus removal	27.0	22.0	Phosphorus
Activated sludge plus nitrogen removal	0.4	0.4	Nitrogen
Activated sludge plus nitrogen and phosphorus removal	3.0	2.0	Nitrogen
Nonpoint sources	28	25	Phosphorus
Marine waters		2	Nitrogen

 † TN/TP = total nitrogen/total phosphorus; ‡ IN/IP = inorganic nitrogen/inorganic phorphorus.