NUTRIENT EFFECTS ON AQUATIC ECOLOGY, RECREATION AND DRINKING WATER SUPPLY: NUTRIENT AND KEY RESPONSE INDICATORS

MJ Paul, Tetra Tech, Inc.

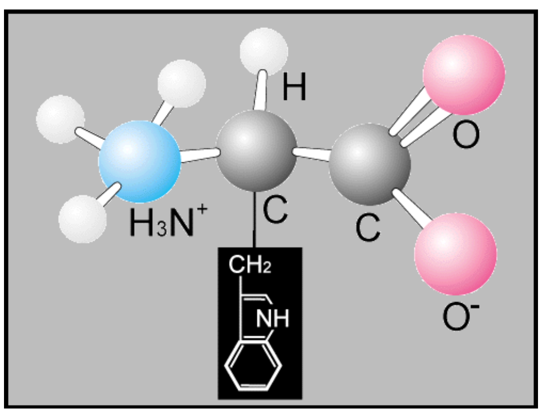
What are nutrients?

- Elements required for growth
- C, H, O, N, P, S – The Big Six Macronutrients
- 20 Other Micronutrients: B, F, Na, Mg, Si, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Sn, I

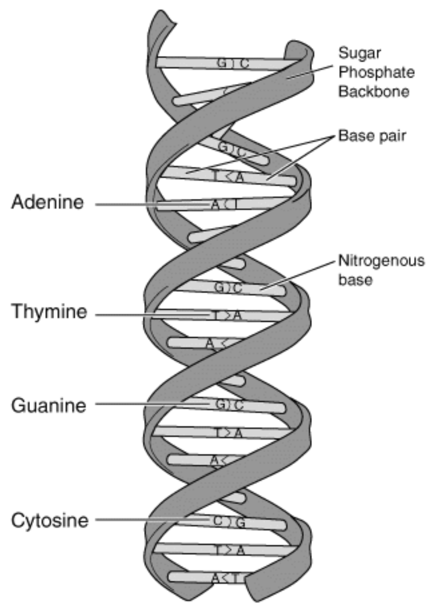
- Of the big six, C, H, O, and S are generally readily available and rarely limit growth
- Not so for N and P

Nitrogen and Phosphorus

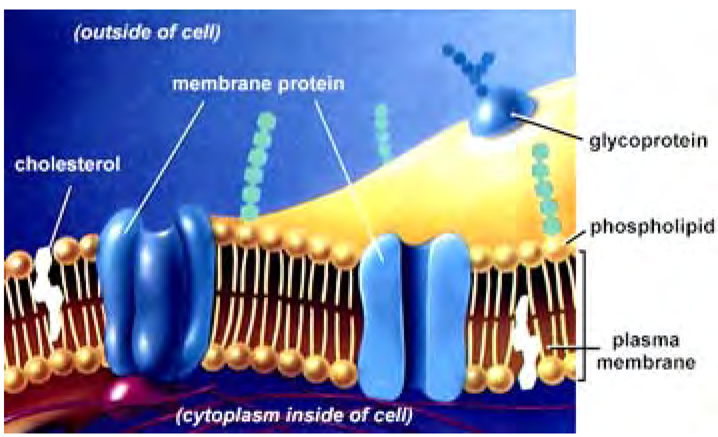
- Essential elements
  - Nitrogen: e.g., amino acids (all proteins), nucleic acids (DNA, RNA)
  - Phosphorus: e.g., nucleic acids, organelle walls (P-lipids), energy molecules (ADP/ATP/NADP)



A. Acid (Tryptophan)



DNA



Phospholipid Bilayer

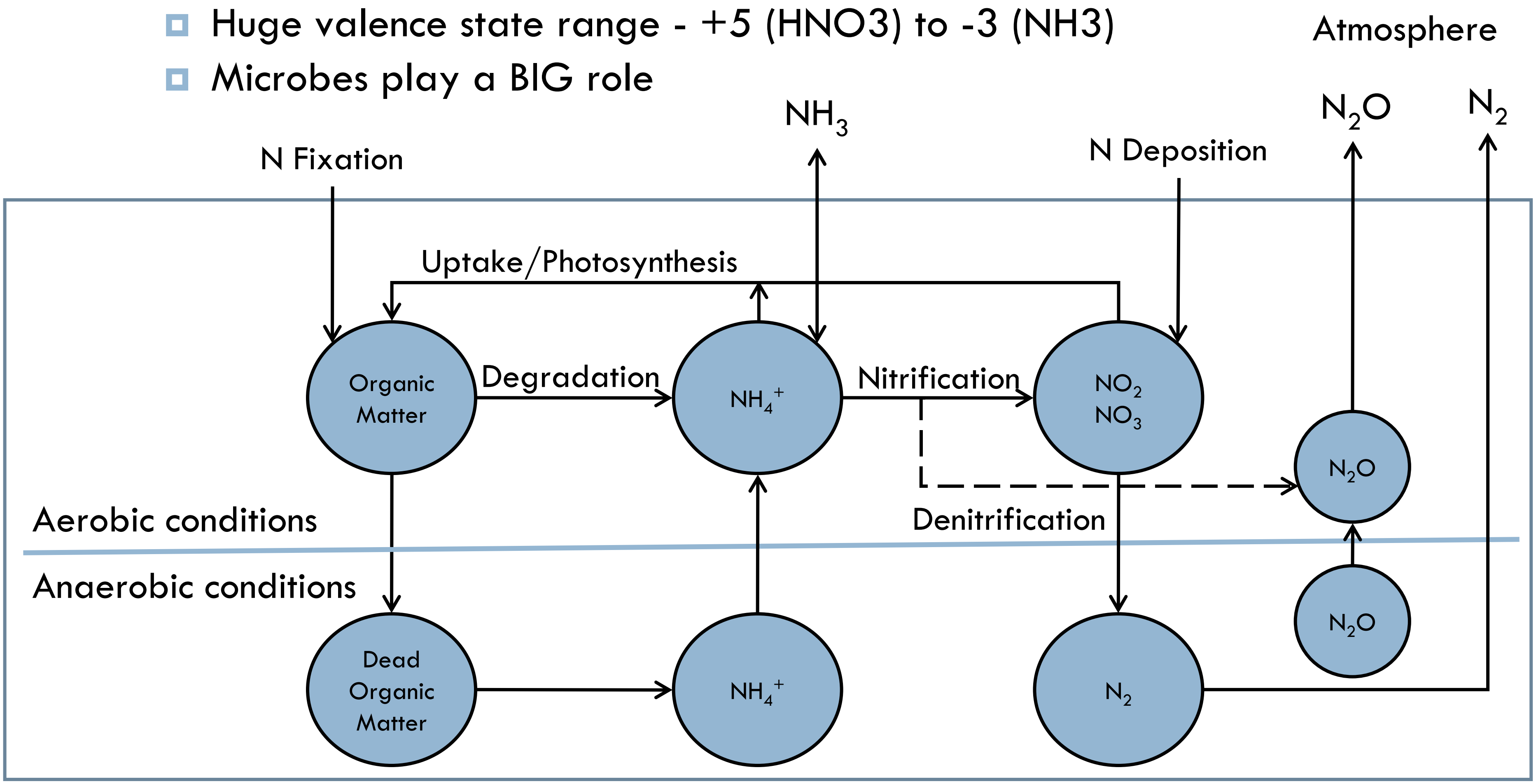
Limitation

- Organisms contain nutrients in specific ratios
  - Redfield Ratio: 106:16:1 (C:N:P molar) of phytoplankton; pretty plastic
  - *Daphnia* C:P is 80:1; not so plastic
- Liebig's Law: Growth is controlled by the scarcest resource

- So, in order to build more organisms, you need to get over the limiting nutrient
  - Frequently these nutrients are N and P

Nitrogen, why so limiting?

- Nitrogen Cycle
  - Abundant in the atmosphere – but very tough to break…
  - Huge valence state range - +5 (HNO3) to -3 (NH3)
  - Microbes play a BIG role

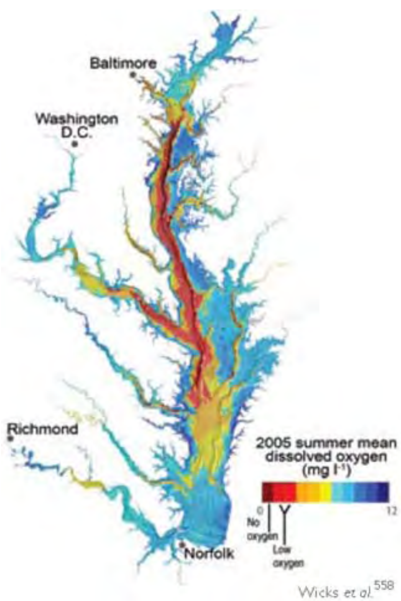


Anthropogenic Impact

- Nitrogen Cycle
  - Humans have increased N fixation by 2-3 times natural
    - Haber-Bosch: N2 to NH3 (fertilizer to biosphere) using methane
    - N-fixing crops
    - More reactive N in biosphere as a result
  - Humans have also increased N inputs to the atmosphere
    - Fossil fuels (NOx)
    - Increased denitrification from increased N fixation (N_2, N_2O)
    - N in atmosphere increasing as a result

Anthropogenic Impact

- Nitrogen Cycle
  - And, of course, increasing the availability of a limiting nutrient is affecting ecosystems as well
  - More reactive N floating around means more productivity



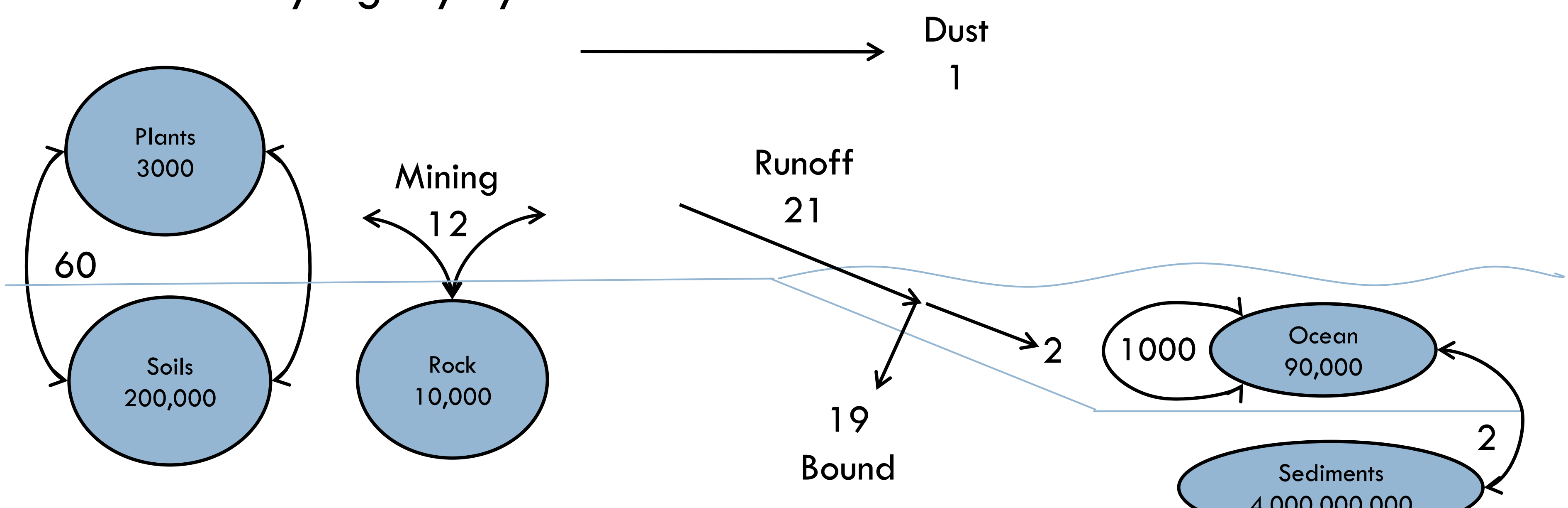

Issues in Ecology
Published by the Ecological Society of America
Number 1, Spring 1997
Human Alteration of the Global Nitrogen Cycle: Causes and Consequences

Nitrogen – What is measured

- Dissolved Forms (filtered – 0.45 μm)
  - NH_3-N (ammonia) and NH_4^+-N (ammonium)
  - NO_3/NO_2-N (nitrate/nitrite)
  - DIN = ammonia + nitrate/nitrite
  - Total Kjeldahl Nitrogen (TKN = DON-N + NH_3-N)
  - DON = TKN – (NH_3-N)
  - Total (TN) = TKN + NO_3/NO_2 (persulfate digestion)
- Total forms (unfiltered)
  - Same species as above including particulate forms
  - Particulate by subtraction

Phosphorus, why so limiting?

- Phosphorus Cycle
  - No gaseous phase
  - No valence changes – PO_4 is basically it
  - Apatite is the primary source and not much of that
  - Very tightly cycled



Units - 10^{12} g P/yr

Phosphorus, why so limiting?

- Phosphorus Cycle
  - PO_4 is bound tightly to biota and Al and Fe-oxides
    - In the ocean, SO_4 can bind to reduced Fe – increase P availability

Plenty of light
But not much P "available"
Bound P deposited
Released in decomposition and solubilized

Plenty of Light
Soluble P mixed to the top
KA-BLOOM!

Stratified Lake

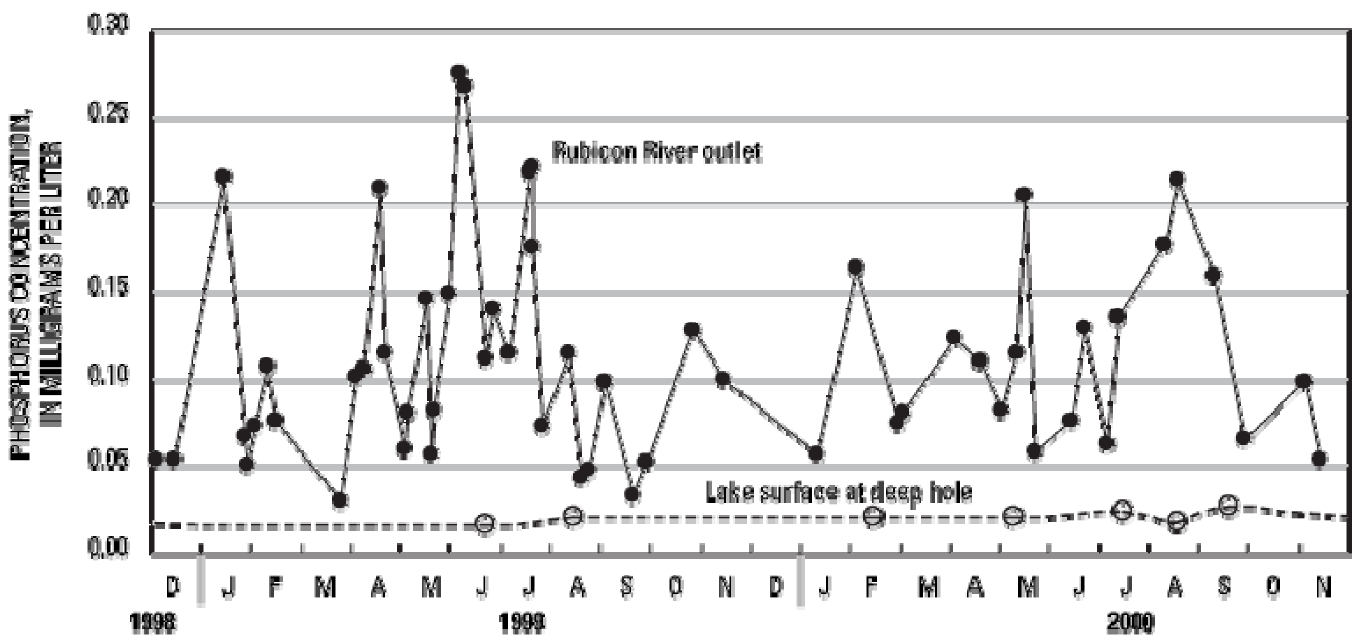
Non-Stratified Lake

Phosphorus – what is measured

- Orthophosphate (PO_4-P) – form measured (as P)
  - Dissolved Forms (filtered – 0.45 μm)
  - Dissolved or Soluble Reactive P (SRP)
  - Dissolved Acid hydrolyzable P (condensed and some organic)
  - Total dissolved phosphorus (TP) – acid digestion
- Total forms (unfiltered) (particulate by difference)
  - Total reactive P
  - Total acid hydrolyzable P
  - Total P (TP)

Nutrient Dynamics

- N and P vary, through time and space
- Lot of this is a function of climate and supply
- Frequently independent – so limiting nutrient often changes

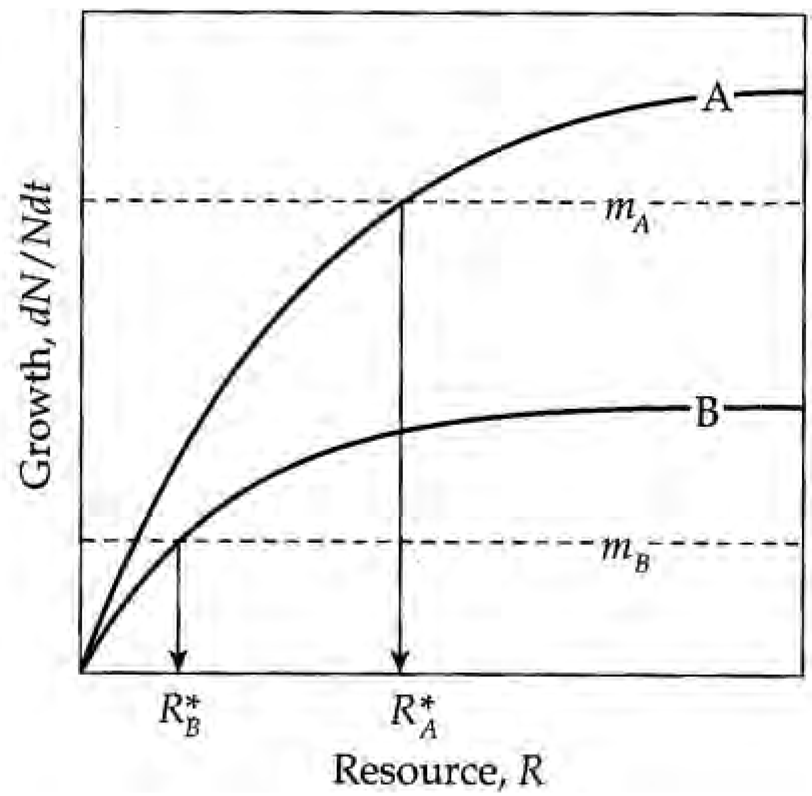


Nutrient Competition

- Species vary in their competitive abilities for nutrients as well
- This means species abundances are affected by nutrient concentration

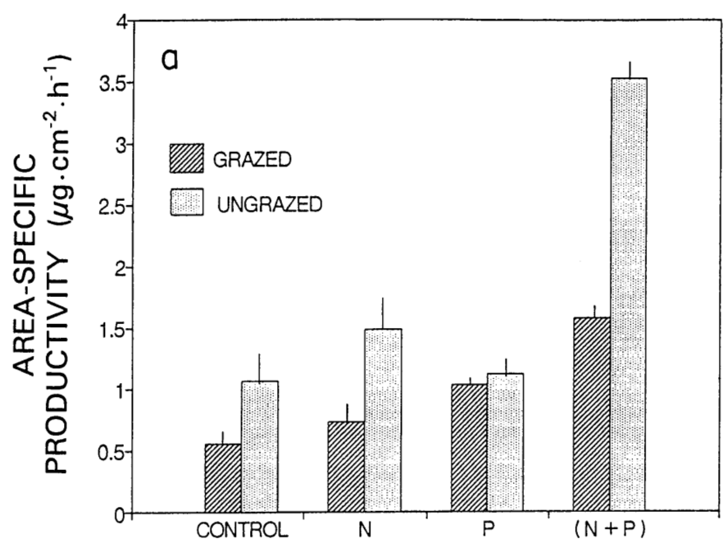
Species A vs Species B

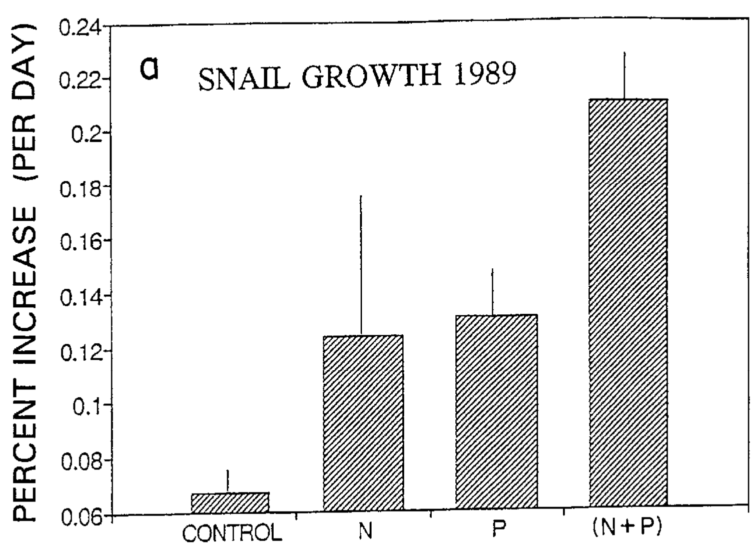
The *m* is mortality rate
When growth> *m*, population increases
R* is the minimum resource needed for population to be maintained
B will drive the nutrients down below R^*_B
Adding nutrients above R^*_A will favor species A



Nutrient Limitation

- Releasing species from nutrient limitation means not only changes in species, but increases in biomass.
- This can flow up a food web too.





A little aside – productivity, production and biomass

- Photosynthesis = primary productivity (mg $C/m^2/d$)
  - Gross PP = total amount fixed
  - Net PP = GPP – Respiration (algae respire too!)
  - Limited by concentration – determines growth rate
- Productivity over time = production (g C/m^2)
  - Likely limited by concentration and load
  - More N and P over time, will mean more accumulated production
- Biomass is standing stock = what is present at any one time (g C/m^2 or g Chl *a*/m^2)
  - Chlorophyll used as a surrogate of biomass – variable
    - Chl a/cell varies!
  - Biomass is related to productivity and production
  - Limited by both concentration and load

Chlorophyll

- Chlorophyll is not one molecule
  - *a*, *b*, and *c* common in freshwater; *d* also in marine;
  - Xanthophylls, carotenoids, phycobiliproteins, etc.
  - Chl *a* is the principal molecule in all plants
- Many methods exist
  - Filtering – glass fiber typical
  - Extracting – acetone typical
  - Measuring – spectrophotometer typical
- Measuring from the cosmos…

Direct toxicity

ELSEVIER

Chemosphere 58 (2005) 1255–1267

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

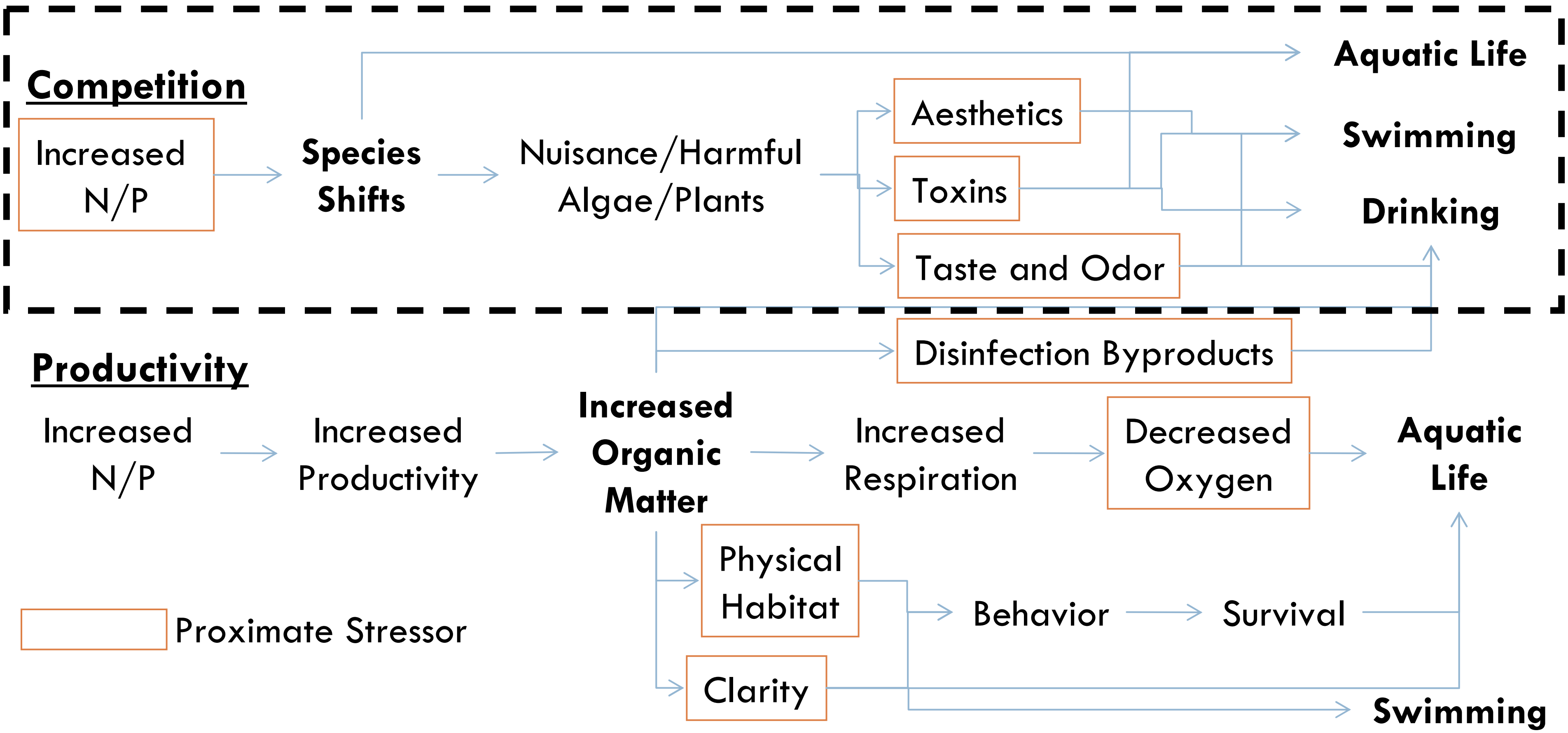
Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates

Julio A. Camargo *, Alvaro Alonso, Annabella Salamanca

- Nitrate and methemoglobinemia in humans
  - Some evidence for toxicity in aquatic organisms, but generally at higher concentrations, except some sensitive species and life stages
  - Generally above nutrient enrichment concentrations, but we're learning more
- Ammonia toxicity
  - More toxic at higher pH and temperatures
  - Can be at concentrations below eutrophic levels
- Phosphate is not toxic

Nutrient Enrichment

- Competition and productivity explain how nutrients alter aquatic ecosystems and designated use



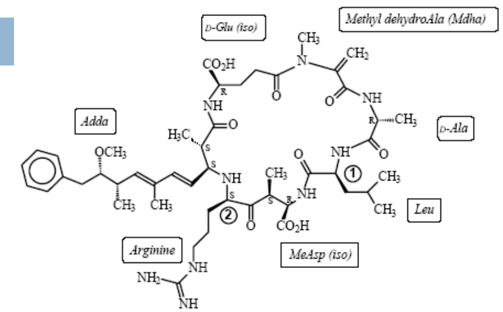
Nuisance Algae and Swimming

- Nuisance Algae/Plants
  - Many are poor competitors for low nutrients
  - In blooms, they look (and smell) bad
  - Decomposition and chemicals produced by senescing algae

Increased N/P → Species Shifts → Nuisance/Harmful Algae/Plants → Aesthetics → **Swimming**

Aesthetics → Taste and Odor → **Swimming**

Nuisance Algae and Swimming/Drinking



- Many produce toxins
  - Cyanotoxins (70 kinds):
    - Hepatotoxins: Microcystins, Nodularin
      - Liver damage; tumor promotion
      - *Microcystis, Anabaena, Oscillatoria, Nostoc, Anabaenopsis*
    - Neurotoxins: Anatoxins, saxitoxins
      - Block neurotransmission - paralysis
      - *Anabaena, Aphanizomenon, Microcystis, Oscillatoria,*
    - Cylindrospermopsin
      - Blocks protein synthesis –liver and kidney damage
      - *Cylindrospermopsis*
    - Lyngbyatoxin, debromoaplysiatoxin
      - Dermatitis
      - *Lyngbya*

Increased N/P → Species Shifts → Nuisance/Harmful Algae → Toxins → **Swimming** / **Drinking**

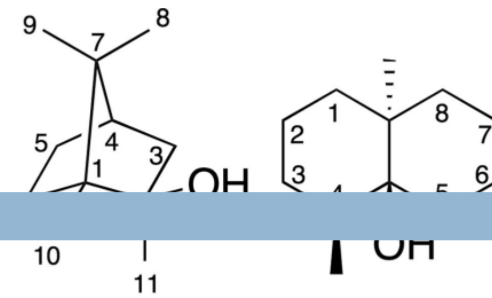
Nuisance Algae and Swimming/Drinking

- Cyanotoxins
  - Commonly detected, infrequently above threat levels
  - Most treatment facilities (US) remove from potable supply
  - Health risk to livestock, pets, and, potentially, swimmers
  - What controls toxicity? Still developing
    - Temperature
    - Light intensity
    - Nutrients
    - pH

Nuisance Algae and Swimming

- Marine nuisance algae – harmful algae/red tides
  - Several species
    - *Karenia brevis, Pfiesteria piscicida, Pseudonitzchia, Protoperidinium crassipes, Gambierdiscus toxicus, Dinophysis, Prorocentrum, Alexandrium, Pyrodinium, Gymnodinium, Lyngbya*
  - Evidence suggests linkage to nutrient inputs to bloom frequencies of many species
  - Still an area of much research

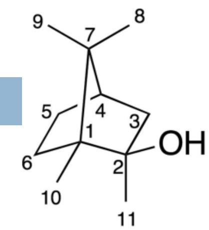
Nuisance Algae and Drinking

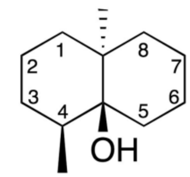


- Taste and Odor
  - Several nuisance taxa can produce chemicals that create taste and odor issues for drinking water and in fish tissue – at very low concentrations
  - 2-Methylisoborneol (MIB) and geosmin
    - Produced by actinomycete fungi (*Streptomyces*) and filamentous cyanobacteria (*Oscillatoria*, *Phormidium*, *Anabaena*, *Pseudanabaena*, *Lyngbya*, *Aphanizomenon*, *Planktothrix*, etc.)
    - Wines, cheese, beets, forest etc. – earthy/musty smell

Increased N/P → Species Shifts → Nuisance/Harmful Algae → Taste and Odor → **Drinking**

Nuisance Algae and Drinking





- Taste and Odor
  - 2-Methylisoborneol (MIB) and geosmin
  - Predictors of MIB and geosmin formation include chl a, TN, and TP
    - Cyanobacteria linked to taste and odor
      - Annie and Fannie are big players
    - Infrequent in oligotrophic waters

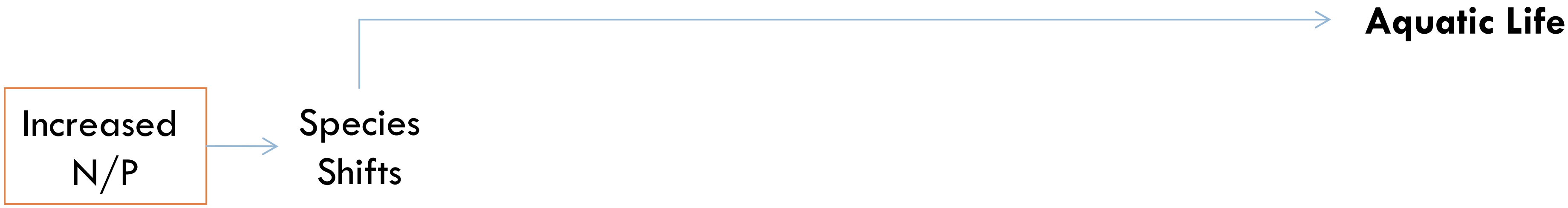
Increased N/P → Species Shifts → Nuisance/Harmful Algae → Taste and Odor → **Drinking**

Nuisance Algae and Aquatic Life

- ## Harmful Algae
  - Several nuisance species described above can also kill aquatic life or present a threat to fisheries (shellfish)
  - Marine harmful algae
    - Shellfish poisoning - *Karenia brevis, Pseudonitzchia, Protoperidinium crassipes, Gambierdiscus toxicus, Dinophysis, Prorocentrum, Alexandrium, Pyrodinium, Gymnodinium*
    - Fish mortality - *Pfiesteria piscicida*
  - Freshwater
    - Fish mortality - *Prymnesium parvum, Chrysochromulina polyepis, Peridinium polonicum*
  - Again, linkage to nutrients anecdotal/suspected/stronger, but an active research area

Species Shifts and Aquatic Life

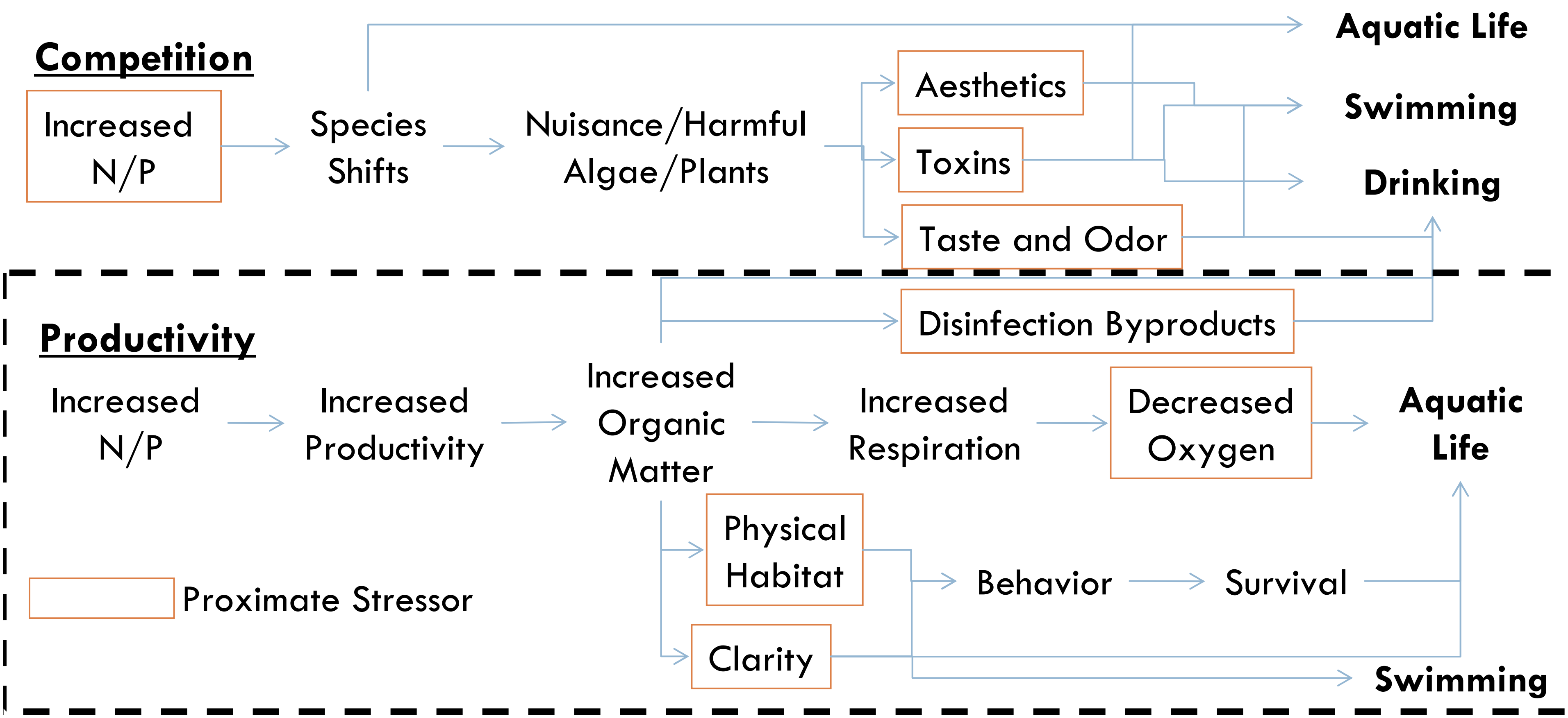
- “Balanced flora and fauna”
- “Alteration of wildlife”



- Changes in invertebrates and fish are used as indicators of altered aquatic life use
- Are algae/plants so different?
- Algae contribute to loss of native macrophytes/seagrasses
- Also, changes in species from palatable to unpalatable forms will affect consumers

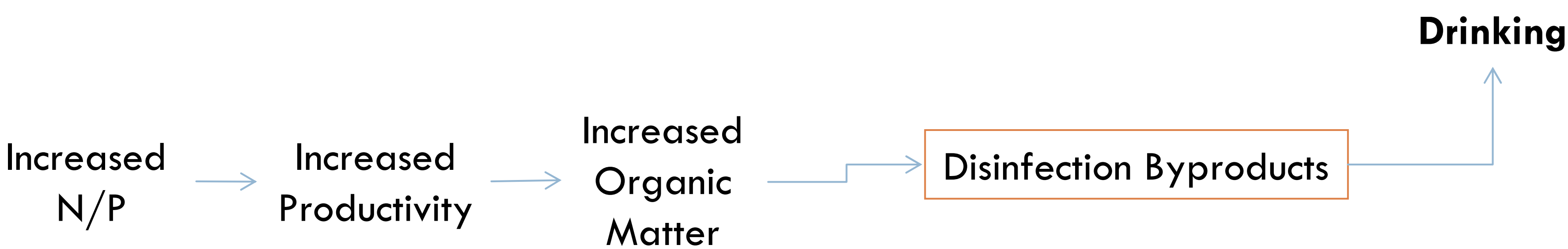
Nutrient Enrichment

- Competition and productivity explain how nutrients alter aquatic ecosystems and designated use



Organic Matter and Drinking

- Disinfection By-products
  - Algae are "leaky" and also release DOC when the die
  - Natural DOC reacts with halides to form a variety of DBPs
    - Halides used in water treatment/disinfection stage (mostly Cl and Br)
    - Trihalomethanes, haloacetic acids, bromate, chlorites
  - Carcinogenic and teratogenic (reproduction/development)



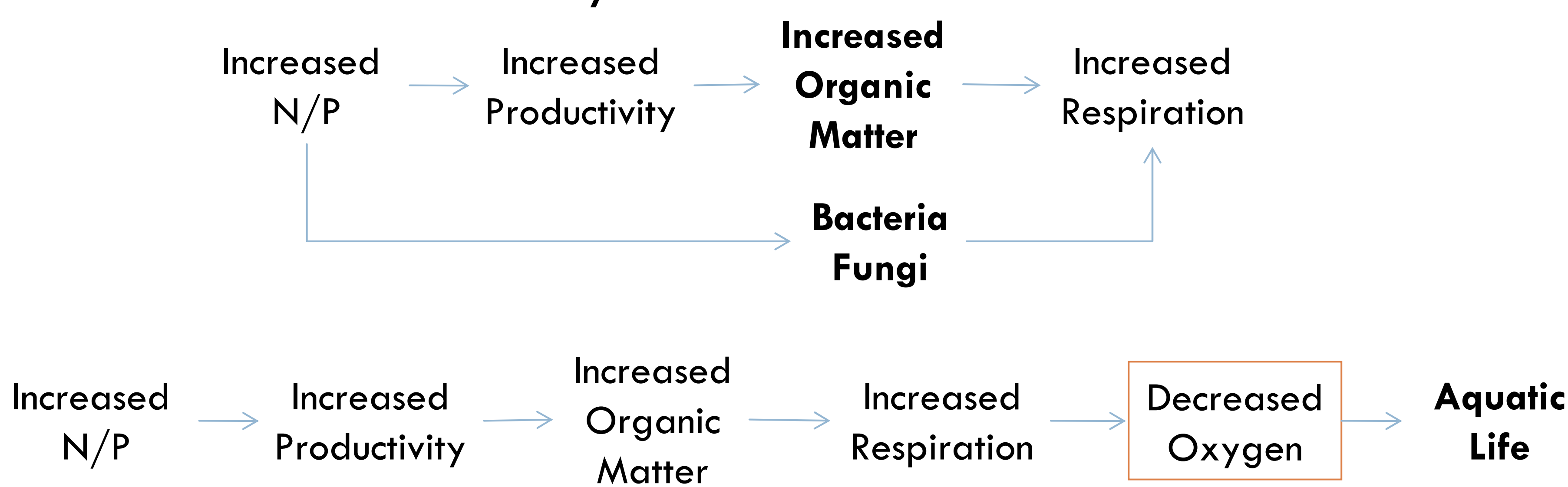
Organic Matter and Drinking

- Filtration costs
  - Excess organic matter in suspension or on intake structures can increase operating costs
  - Clog intake screens, Increase coagulant demand, Shorten filter runs, Increase filter backwash water requirements

Increased N/P → Increased Productivity → Increased Organic Matter → **Drinking**

Organic Matter and Aquatic Life

- Pretty straightforward and well understood effect
- Increased organic matter means increased respiration
  - Both plant (green) and microbial (brown) pathways stimulated by nutrients
  - A double whammy



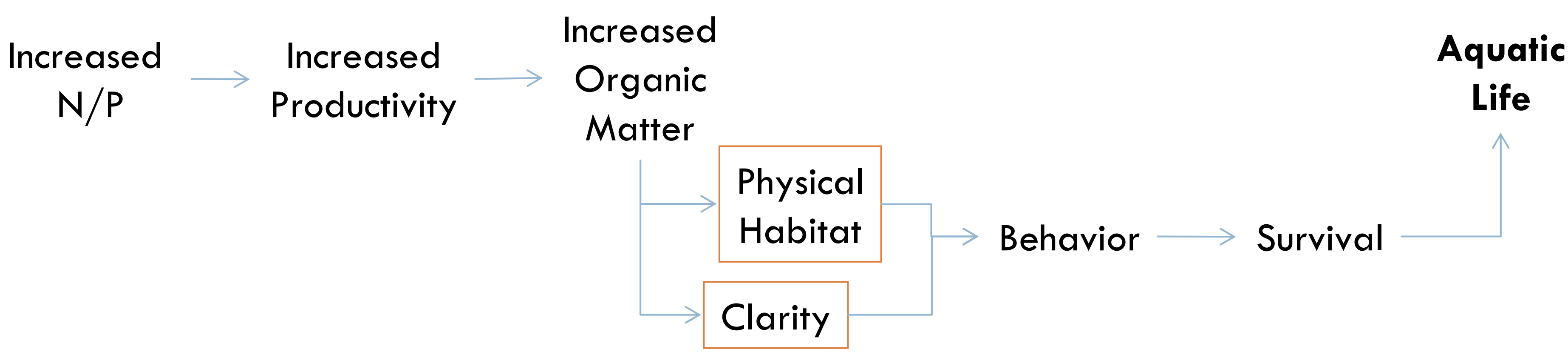
Organic Matter and Aquatic Life

- Respiration drives down dissolved oxygen
  - Hypoxia (<2 mg/L) and Anoxia (0 mg/L)
  - Organisms that need oxygen must either move, die, or both
  - Hypoxia/Anoxia can make other pollutants more "available" and this synergy may increase their toxicity

Increased N/P → Increased Productivity → Increased Organic Matter → Increased Respiration → Decreased Oxygen → **Aquatic Life**

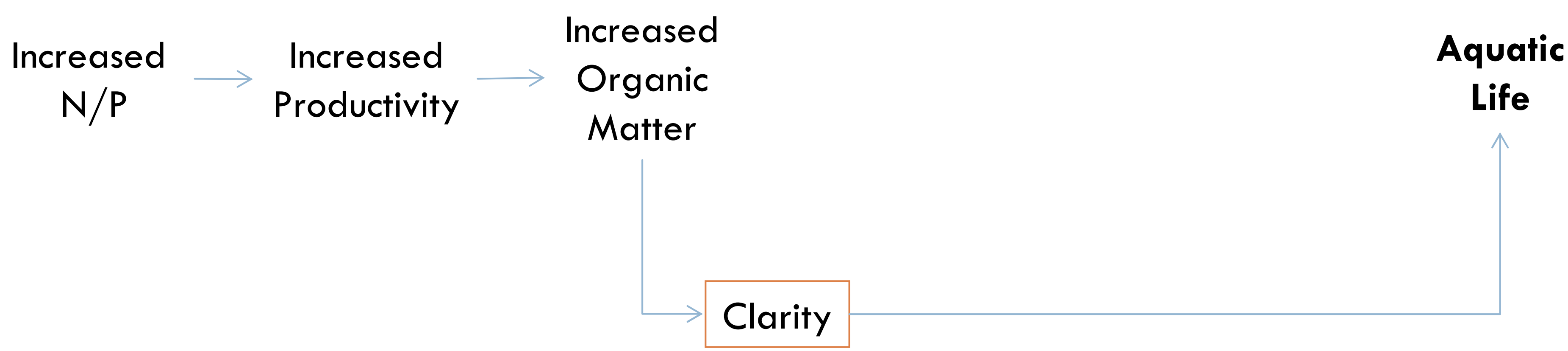
Organic Matter and Aquatic Life

- Habit change is another way eutrophication affects aquatic life
  - Feeding and reproductive habitats are altered by excess plant growth
  - This influences survival/growth and affects species survival



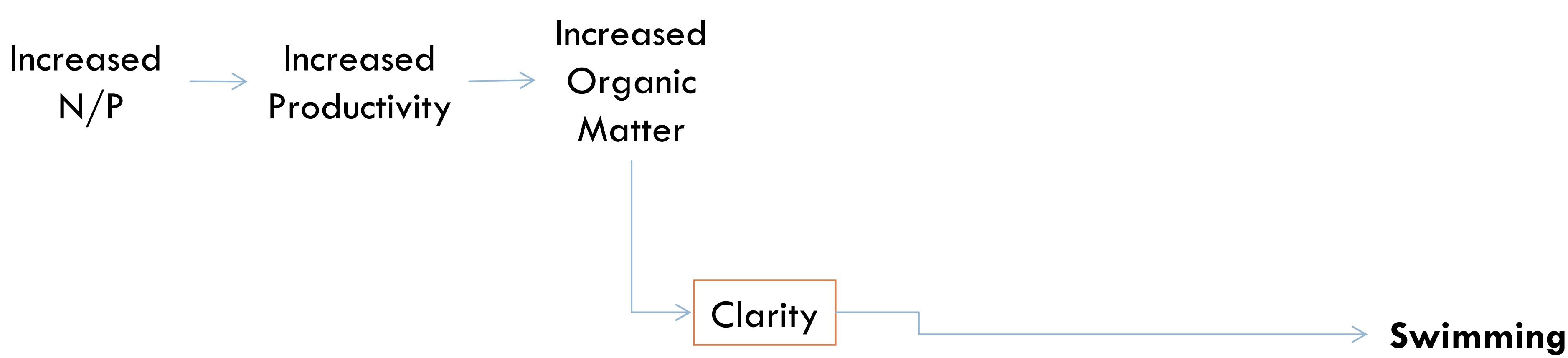
Organic Matter and Aquatic Life

- Reduced clarity caused by excess phytoplankton reduces light for other plants
  - Native macrophytes/seagrasses
  - Restoration of native macrophytes often includes nutrient reduction to improve clarity

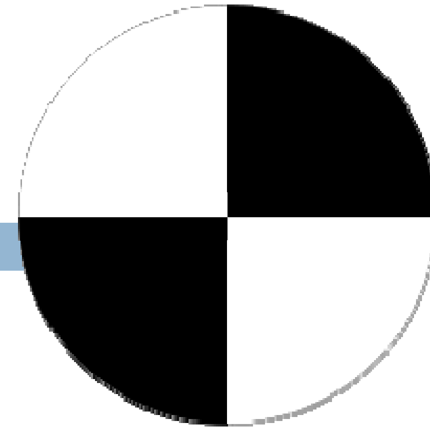


Organic Matter and Swimming

- Perhaps redundant with aesthetics
  - But safety is influenced by clarity when phytoplankton densities increase
  - BSA Safe Swim Defense: “Visibility: Underwater swimming and diving <u>are prohibited in turbid water</u>. Turbid water exists when a swimmer treading water cannot see his feet. Swimming at night is allowed only in areas with water clarity and lighting sufficient for good visibility both above and below the surface.”

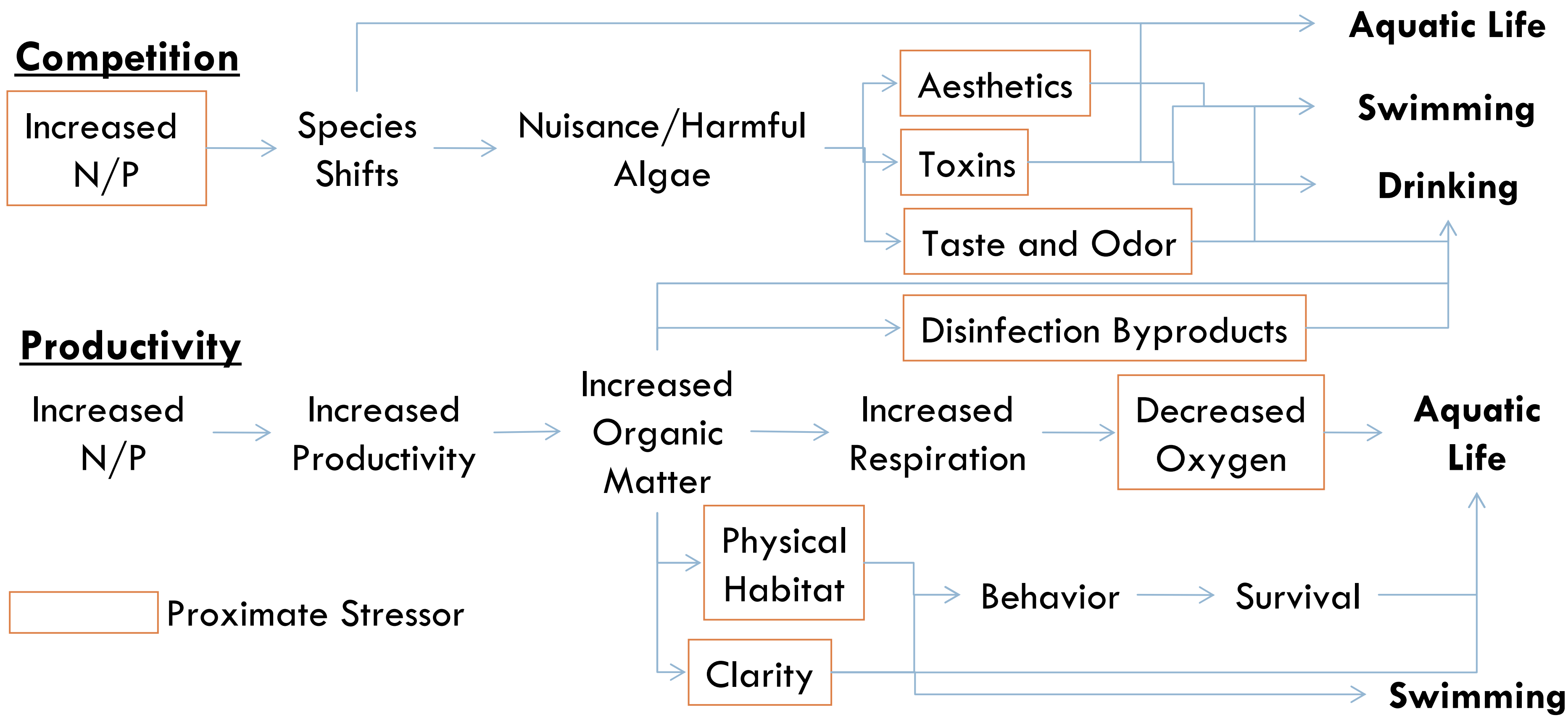


Clarity



- Secchi depth
  - Fr. Pietro Angelo Secchi (1818-1878)
    - Astronomer
    - Also oceanography, meteorology, and physics
    - Published 730 papers and several books
- Also measure photosynthetically active radiation and light attenuation
- Turbidity

Phew….



Competition
Increased N/P
Species Shifts
Nuisance/Harmful Algae
Aesthetics
Toxins
Taste and Odor
Aquatic Life
Swimming
Drinking
Disinfection Byproducts
Productivity
Increased N/P
Increased Productivity
Increased Organic Matter
Increased Respiration
Decreased Oxygen
Aquatic Life
Physical Habitat
Behavior
Survival
Clarity
Swimming
Proximate Stressor

What we covered

- Basic nutrients and nutrient cycles
- Principal ways nutrients affect designated uses
- Principal forms and measures of N, P, Chl, and Clarity
- Novel insights about nuisance algae

- Still a lot of science to be done