The Oceanic Phosphorus Cycle and Ecological Stoichiometry
OUTLINE

• The marine P-cycle: general features
• Ecological (C-N-P) Stoichiometry
• Contemporary issues: North Pacific gyre
• Challenges/opportunities for the future
CONCLUSIONS

• P biogeochemistry and metabolism are time-variable, climate-sensitive, non steady-state processes that must be studied as such.
• Microbial community structure matters – variations thereof control P-cycle genomics/biodynamics in the sea.
• P-cycle should not be studied in “isolation” (C-N-P stoichiometry).
Discovery of phosphorus in 1669 by Henning Brand – unsuccessful merchant, amateur alchemist

Painting: *Alchemist in search of the Philosopher’s stone*, 1771, by Joseph Wright
DISCOVERY OF PHOSPHORUS 
(H. BRAND, 1669)

- Collect large volume of urine; store til putrid
- Boil urine to reduce it to thick syrup, then heat until a red oil distills up from it; remove the oil
- Cool residue until it separates into black spongy top and salty base; discard salt, mix spongy and oil, heat til white fumes evolve (phosphorus gas)
- Pass through cold water to solidify

5,500 L urine → 120 g phosphorus (or “P”)
MARINE P CYCLE

Particulate and dissolved organic-P
(C-O-P = ester and C-P = phosphonate)

no redox change except under extremely reducing conditions where
org-P → H₃P ↑ (phosphine)
Whole seawater sample

Measured pools:
SRP
TDP
PP

Derived pools:
Total P = TDP + PP
DOP = TDP - SRP

filter through glass fiber filter

dissolved fraction

12-MPA
spectrophotometer
[SRP]

oxidize
(UV, persulfate)

12-MPA
spectrophotometer
[TDP]

particulate fraction

combust at 500 C

extract in HCl

12-MPA
spectrophotometer
[PP]
PHOSPHORUS

- The staff of life: ATP, RNA, DNA
- Genome regulatory function
- Biome regulatory function
- Seasonal variations in major P pools
- Coastal region

Figure 4  Annual changes in various living and nonliving P pools and total inventories for the samples collected in the English Channel. The annual dominance of TDP (>80% of total P) is evident. The most notable seasonal change in the P inventory is the shift from Pi dominance in winter to DOP dominance in late spring–summer. Redrawn with permission from Harvey (1955).
Chapter 6

Dynamics of DOP

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Department of Oceanography
School of Ocean and Earth Science and Technology
University of Hawaii
Honolulu, Hawaii

1. Introduction
2. Terms, Definitions, and Concentration Units
3. The Early Years of Pelagic Marine P-cycle Research (1884–1955)
4. The Pelagic Marine P-cycle: Key Pools and Processes
5. Sampling, Incubation, Storage, and Analytical Considerations
   A. Sampling
   B. Use of Isotopic Tracers in P-cycle Research
   C. Sample Processing, Preservation, and Storage
   D. Detection of Pi and P-containing Compounds in Seawater
   E. Analytical Interferences in SRP and TDP Estimation
6. DOP in the Sea: Variations in Space
   A. Regional and Depth Variations in DOP
   B. DOP Concentrations in the Deep Sea
7. C:N:P Stoichiometry of Dissolved and Particulate Matter Pools
8. DOP in the Sea: Variations in Time
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9. DOP Pool Characterization
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   B. DOP Pool Characterization by Enzymatic Characterization
   C. DOP Pool Characterization by 31P NMR
   D. DOP Pool Characterization by Partial Photochemical Oxidation
   E. Direct Measurement of DOP Compounds
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10. DOP Production, Utilization, and Remineralization
    A. DOP Production and Remineralization

B. Direct Utilization of DOP
C. Enzymes as P-cycle Facilitators
D. DOP Interactions with Light and Suspended Minerals
X. Conclusions and Prospectus

References

Biogeochemistry of Marine Dissolved Organic Matter
Edited by
Dennis A. Hansell and Craig A. Carlson
• Near-surface SRP (PO$_4$) depletion
• Near-surface DOP enrichment
• HOT Sta. ALOHA
Global Open Ocean DOP

"GOOD" Data Set
• Near-surface SRP (PO₄⁻) depletion
• Near-surface DOP enrichment
• HOT Sta. ALOHA
• Deep water P (and C, N and all other bio-philic nutrients) increases from N. Atlantic to N. Pacific

• So does water mass age!
Yep! Inverse correlation between SRP and O₂ in oceanic deep waters
First, a few comments on the Carbon-Nitrogen-Phosphorus cycles of the sea
# THE ELEMENTS OF MICROBIAL LIFE

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleus (DNA)</td>
<td>C-N-P</td>
</tr>
<tr>
<td>Ribosome (RNA)</td>
<td>C-N-P</td>
</tr>
<tr>
<td>Membranes</td>
<td>C-P</td>
</tr>
<tr>
<td>Cell wall</td>
<td>C-N</td>
</tr>
<tr>
<td>Proteins/enzymes/ flagellum</td>
<td>C-N</td>
</tr>
<tr>
<td>Storage bodies:</td>
<td></td>
</tr>
<tr>
<td>• PHB</td>
<td>C</td>
</tr>
<tr>
<td>• Poly-P</td>
<td>P</td>
</tr>
</tbody>
</table>
THE REDFIELD OCEAN

• Redfield ratio concept
  — Uniform biochemical stoichiometry (N:P = 16)
  — Biological control of nutrient elements in the sea
• N₂ fixation or denitrification can alter the N:P ratio, but rates are believed to be balanced over long time scales
• Under P-limitation, N:P ratio in organisms increases due to P-sparing effect (N:P > 20)
• Under N-limitation, N:P in organisms decreases due to P-storage (N:P < 10)
• Ultimately P must control biogeochemical fluxes (due to N₂ fixation)
“THE RATIO”

  N:P = 20
- Cooper (1937/1938) in JMB, UK
  N:P ratio redefinition based on salt correction of 1.35x for P analyses!
- Today N:P = 15-16
REDFIELD STOICHIOMETRY OF LIFE

$C_{106}:N_{16}:P_1$

Carbon

Nitrogen

Phosphorus

C:N = 6.6 / C:P = 106 / N:P = 16
Fe-normalized Stoichiometry

C_{50,000} : N_{7,550} : P_{472} : Fe_{1}

Vitamin B_{12}-normalized Stoichiometry

C_{1,120,000,000} : N_{169,000,000} : P_{10,566,000} : vit B_{12}
Experimental Variation of the C:N:P Ratios (by Atoms) in Cultures of the Freshwater Alga, *Chlorella pyrenoidosa* (Ketchum and Redfield, 1949)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>C</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal cells</td>
<td>47</td>
<td>5.6</td>
<td>1</td>
</tr>
<tr>
<td>Phosphorus deficient cells</td>
<td>231</td>
<td>30.9</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen deficient cells</td>
<td>75</td>
<td>2.9</td>
<td>1</td>
</tr>
</tbody>
</table>
Laws & Bannister (1980)
L&O 25: 457-473

- N:C ratios were linearly correlated with dilution rate under both light or nutrient limitation - but with opposite signs

- N:C approaches Redfield ratio at $\mu_{\text{max}}$
Experimental Designs: Lab vs. Field

N vs. P
NUTRIENT SUPPLY

(N:P = 16)
Redfield reference point

Global Marine Range
TN:TP

N-limited lab cultures
1

8

32

P-limited lab cultures
500
Prochlorococcus C-N-P
Bertilsson et al. (2002)

- N:P/C:P much higher than "Redfield"
- P quota for P-L
cells = $0.34 \times 10^{-15}$ g
  $\sim 2 \times$ DNA requirement
  (1.66 Mb genome)
Sulfolipids dramatically decrease phosphorus demand by picocyanobacteria in oligotrophic marine environments

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PNAS 6 June 2006 issue

• *Prochlorococcus* substitutes S for P in membrane lipids
• Biochemical adaptation for life under P-stress
• Other strategies may also exist!
R. Geider and J. La Roche (2002)
Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis
_Eur. J. Phycol._ 37: 1-17

- C:N:P is plastic, not fixed
- N → P limitation transition much higher than 16:1

*General conclusion:* “Our analysis suggests caution in application of the Redfield Ratio in theoretical biogeochemical analyses and as a conversion factor in field studies.”
CASE STUDY: N$_2$-Fe-P Syntrophy

- N$_2$ fixation impact on ecosystem processes
- Controls and consequences
Long-term changes in plankton community structure and productivity in the North Pacific Subtropical Gyre: The domain shift hypothesis

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Data availability:
http://hahana.soest.hawaii.edu

Contact:
D. Karl (dkarl@soest.hawaii.edu)
Collaborators in HOT P-Cycle Research

OSU-based

UH-based
NUTRIENT DYNAMICS IN THE NORTH PACIFIC SUBTROPICAL GYRE
ENSO/PDO

INCREASED STRATIFICATION

Selects for
*Trichodesmium* & other N₂ fixers

- N₂-fixation
- P limitation
- DOM accumulation
- N₂O

Selects for
*Prochlorococcus*

- Alters food web structure
- Decreases fishery yield
- Decreases export production
The control of new and export production in the oligotrophic regions of the North Pacific Ocean oscillates, on decadal time scales, between N and P.

The alternation of N-P control is the result of changes in both habitat and populations.

Major habitat changes, resulting from large scale atmosphere-ocean interactions, select for or against N$_2$-fixing microorganisms and their activities (or lack thereof) ultimately establish N or P control.

The oligotrophic North Pacific ocean is currently in a “P-control” period.
ALTERNATING ECOSYSTEM STATES OF THE NORTH PACIFIC GYRE

1970's

<table>
<thead>
<tr>
<th>N/P = 16</th>
<th>N/P = 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/P = 16</td>
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</tr>
</tbody>
</table>

ENSO favorable and
Warm phase PDO (post-1980)

<table>
<thead>
<tr>
<th>N_2</th>
<th>N/P = 40</th>
<th>N/P = 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/P = 16</td>
<td>N/P = 25</td>
<td></td>
</tr>
</tbody>
</table>

SRP

1965 1980

1980 1995

N-limited
Low N_2 fixation

P-limited
High N_2 fixation

Time

SRP
EVIDENCE FOR N\textsubscript{2} FIXATION

• Inability to balance N-cycle
• Presence of putative N\textsubscript{2} fixing microbes
• Altered DOM/POM/export stoichiometry
• Direct field measurements of N\textsubscript{2} fixation
• Natural $^{15}$N isotope balance
• P pool drawdown over last decade
• DIC pool drawdown each summer
DIVERSITY OF N₂ FIXERS AT STA. ALOHA

<table>
<thead>
<tr>
<th>Picoplankton</th>
<th><em>Trichodesmium</em></th>
<th>Diatoms/Richelia</th>
</tr>
</thead>
<tbody>
<tr>
<td>- small (&lt;2 µm)</td>
<td>- large (&gt;20 µm)</td>
<td>- large (&gt;20 µm)</td>
</tr>
<tr>
<td>- “background” population</td>
<td>- bloom forming</td>
<td>- bloom forming</td>
</tr>
<tr>
<td>- dispersed</td>
<td>- floaters/migrants</td>
<td>- sinkers/migrants</td>
</tr>
<tr>
<td>- consumed by protozoans</td>
<td>- not readily consumed</td>
<td>- consumed by zooplankton</td>
</tr>
<tr>
<td>- high turnover / low export</td>
<td>- low turnover / low export</td>
<td>- variable turnover / high export</td>
</tr>
</tbody>
</table>
MICROBE-DUST CONNECTIONS

• Microbes require Fe for metabolism, especially N$_2$ fixation
• Fe delivery to the open ocean is via atmospheric dust deposition
• Dust deposition is a climate-sensitive parameter
Global estimate of N$_2$ fixation based on N-DIC drawdown in NO$_3$-depleted warm waters is equivalent to 0.8 ±0.3 Pg C yr$^{-1}$
STA. ALOHA

- EZ SRP has decreased by >80% over past 17 years
- How low can it go?
- N₂ fixation effect?
- Alternate “P capture” genes
**Stage I**

N → P

Low N:P ratio selects for N₂ fixation

<table>
<thead>
<tr>
<th>Low N:P</th>
<th>High N:P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
</tr>
</tbody>
</table>

Forced P-limitation

**Stage II**

Hi P → Low P

Intensification of P cycling

<table>
<thead>
<tr>
<th>Low SRP</th>
<th>Lower SRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low L/R-DOP</td>
<td>Lower L-DOP</td>
</tr>
<tr>
<td></td>
<td>Higher R-DOP (incl. C-P)</td>
</tr>
</tbody>
</table>

Selects for *Prochlorococcus*

**Stage III**

Hi P → Low P

Selection for alternative P “capture” mechanisms

1. Use of non-traditional R-DOP, including C-P.
2. Increased production of C-P (more stable).
3. “P”etered out.
4. Climate reversion back to N control?
Ecological Predictions

- Substrate selectivity and resource partitioning among competitors
- Changes in P-cycling and, perhaps, in productivity
- Genome and community selection for ability to use “unusual” substrates
Climate Variations (ENSO/PDO)

CAUSE

altered wind forcing and gyre circulation

decreased ML depth
enhanced oligotrophication

decreased N, P, Si flux

EFFECTS

selection for N$_2$-fixing Bacteria and Prochlorococcus

shift from N to P limitation
altered food web structure and function
non-Redfield CNP stoichiometry

REGIONAL IMPACTS

net carbon sequestration, DOC/DON pooling, microbial loop domination, altered export processes

other???
CONTEMPORARY CHALLENGES

• Temporal variations in P-pool inventories and fluxes: causes/ecological consequences
• DOP pool characterization and bioavailability
• Microbial C-N-P stoichiometry and plasticity
• C-N-P cycle decoupling by N₂ fixation
• Vitamin B₁₂ syntrophy
• P-cycle “genomics”
• Phosphonates (C-P): sources/sinks and connections to climate variability
P IS THE STAFF OF LIFE

“The plural of anecdote is data.”

Nelson Polsby

*We need additional observations, experimental data, and a comprehensive synthesis of extant knowledge on the marine P cycle, from genomes to biomes*