DON sources: methods and processes

Deborah A. Bronk
Department of Physical Sciences

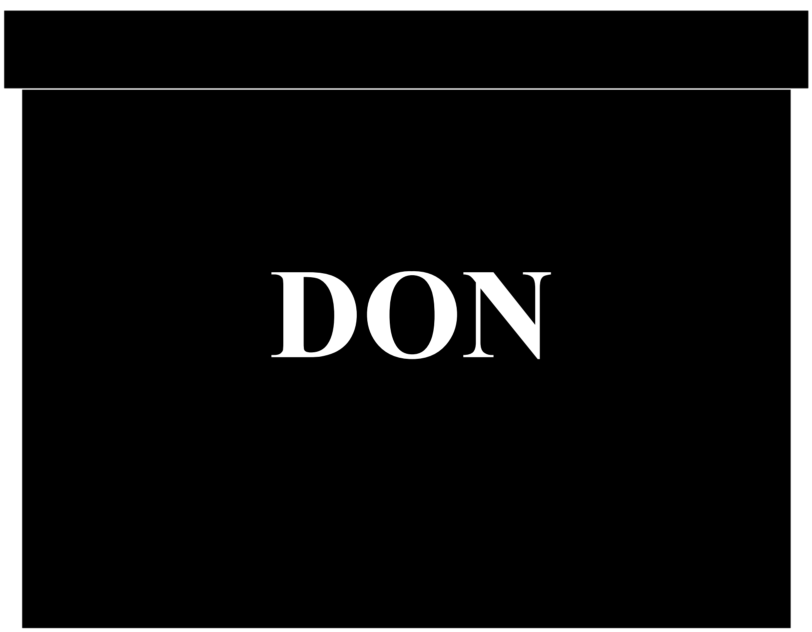
WILLIAM & MARY
VIMS
VIRGINIA INSTITUTE OF MARINE SCIENCE
SCHOOL OF MARINE SCIENCE

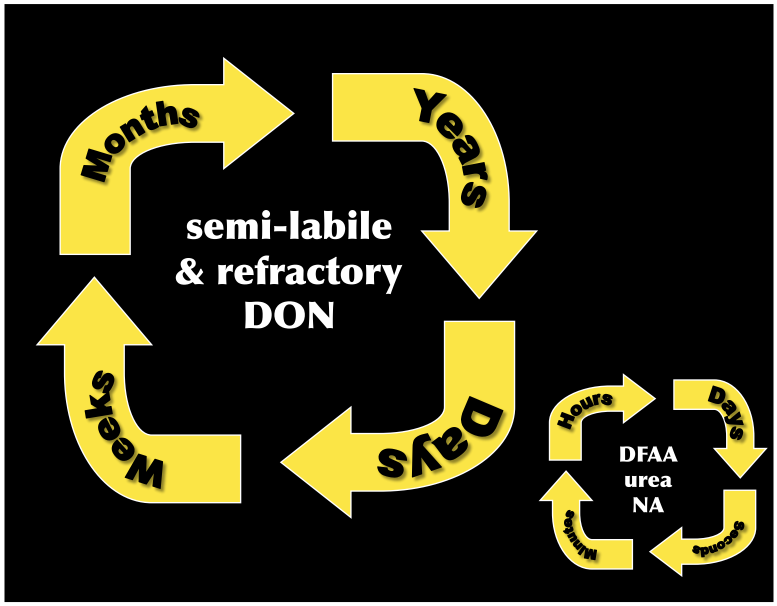
Outline:

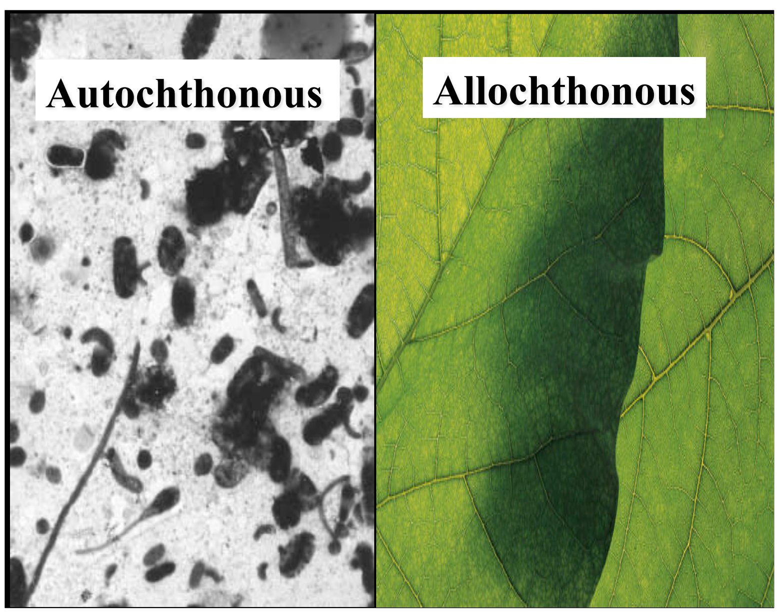
- What is DON?
- Methods to study release
- Autochthonous sources
- Allochthonous sources
- DON as a mode of N delivery

What is DON?

Labile	Semi-labile	Refractory
DFAA	proteins	humic acids
urea	DCAA	fulvic acids
nucleic acids	amino	porphorins
methylamines	polysaccharides (chitins & peptidoglycans)	amides




Months
Years
semi-labile
& refractory
DON
Days
Weeks
Hours
Days
DFAA
urea
NA
Seconds
Minutes


Autochthonous
Allochthonous

What is DON?

Labile	Semi-labile	Refractory
DFAA	proteins	humic acids
urea	DCAA	fulvic acids
nucleic acids	amino	porphorins
methylamines	polysaccharides (chitins & peptidoglycans)	amides

Autochthonous (Labile and Semi-labile) — Allochthonous (Semi-labile and Refractory)

Methods for studying release:

1. Bioassays
2. Radioactive tracers
3. Stable isotope tracers
   a. Direct measures
   b. Isotope dilution

Bioassays & Radiotracers (^{3}H, ^{14}C, ^{32}P)

Absolute amounts

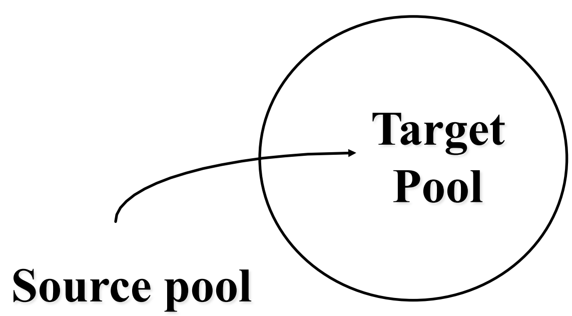
~ Net rates

Stable isotope tracers (^{15}N, ^{13}C)

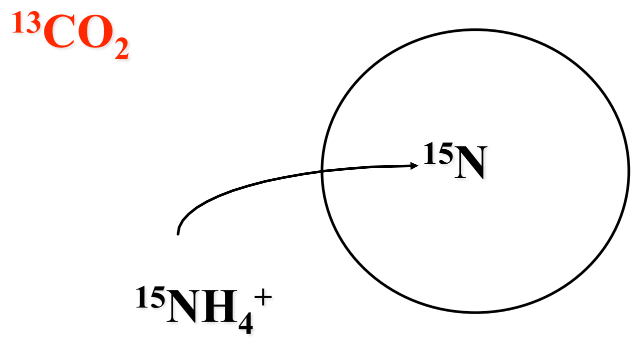
Ratios ($^{15}N/^{14}N$ or $^{13}C/^{12}C$)

Gross and net rates

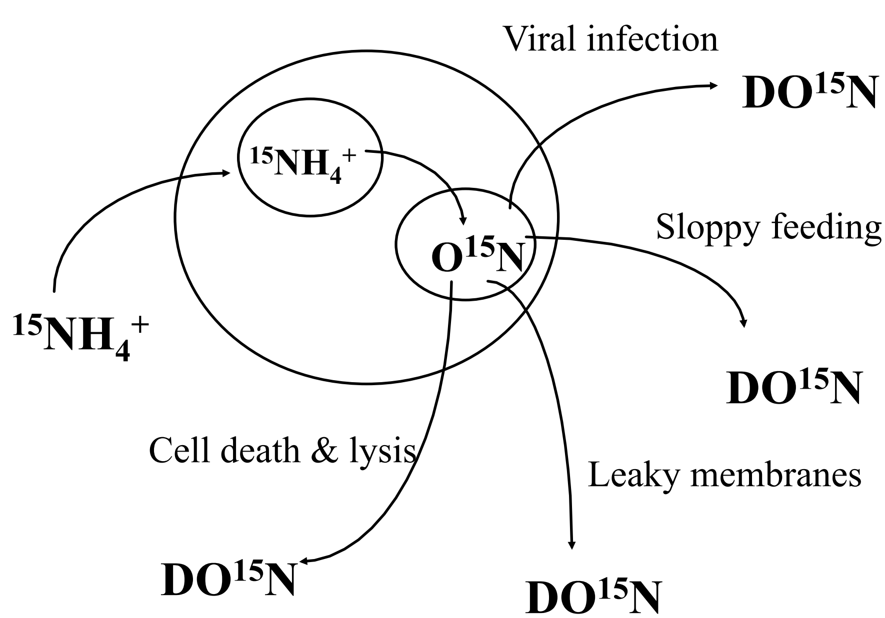
Uptake and regeneration simultaneously



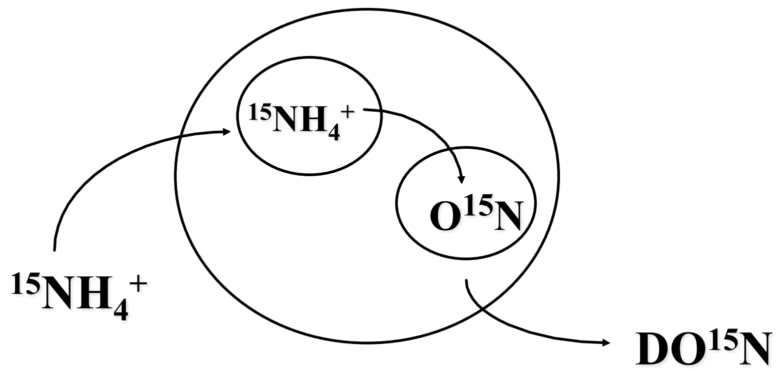
$$\text{Rate} = \frac{\text{atom \% of target}}{\text{atom \% of source} \times \text{Time}} \times [\text{target}]$$



$$\text{Net Uptake Rate} = \frac{\text{atom\% PN}}{\text{atom \% } NH_4^+ \times \text{Time}} \times [PN]$$



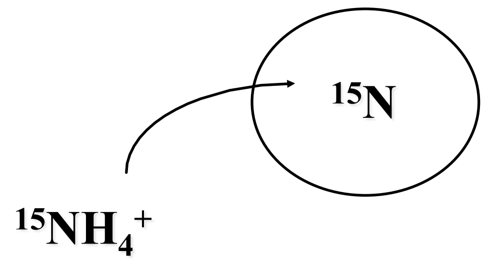
Bronk 1999 JPR



$$\text{Gross Uptake Rate} = \frac{{}^{15}\text{N in PN \& DON}}{\text{atom \% } NH_4^+ \times \text{Time}} \times [\text{PN}]$$

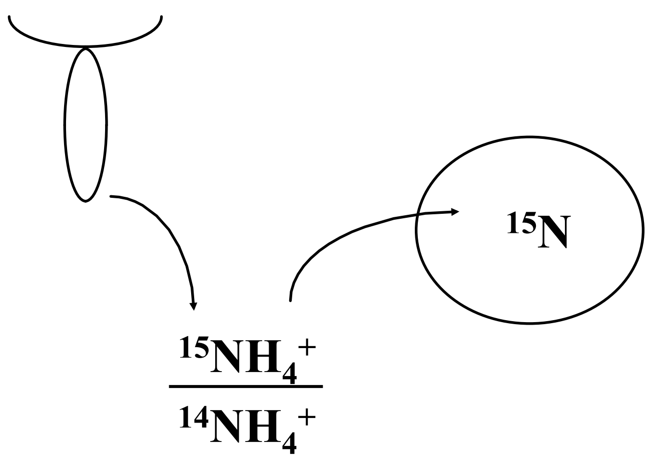
Bronk et al. 1994 Science

Gross Uptake - Net Uptake = DON Release



$$\text{Net Uptake Rate} = \frac{^{15}N \text{ in PN}}{\text{atom \% } NH_4^+ \times \text{Time}} \times [PN]$$

Isotope dilution



$$\text{Net Uptake Rate} = \frac{^{15}N \text{ in PN}}{\text{atom \% } NH_4^+ \times \text{Time}} \times [PN]$$

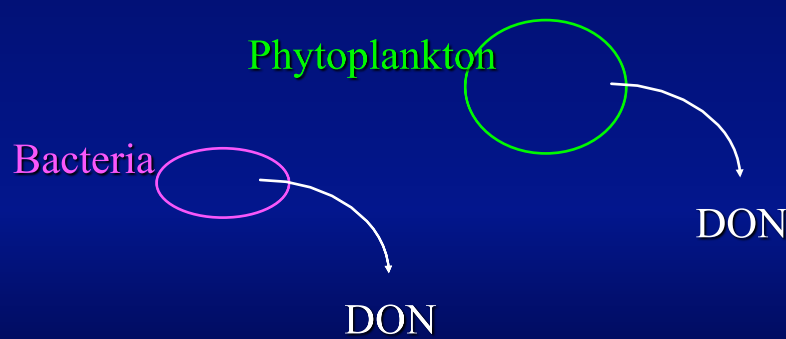
$$P_t = P_0 + (d - u)t$$

$$\ln(R_t - R_a) = \ln(R_0 - R_a) - [d/(d - u)][\ln P_t/P_0]$$

P_t and P_0 = ambient NH_4^+ conc at end and start of incubation
R_t and R_0 = atom % of the NH_4^+ pool at end and start of incub.
u = absolute uptake rate
d = regeneration rate

Glibert et al. 1982 L&O

Autochthonous sources of DON



Direct release - Passive diffusion
Cell death and lysis (autolysis)
Bacterial exoenzyme release

Excretion of organic matter by phytoplankton: Do healthy cells do it?

Sharp 1977 L&O

Active release outflow model

Fogg 1966 OMBAR

Passive diffusion model

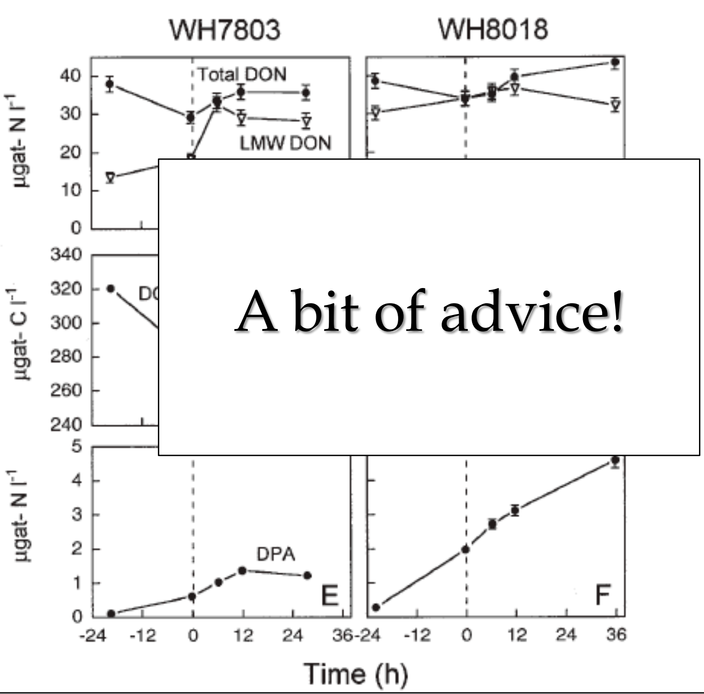
Fogg 1966 OMBAR

Reduction of viruses

Murray 1995 JPR

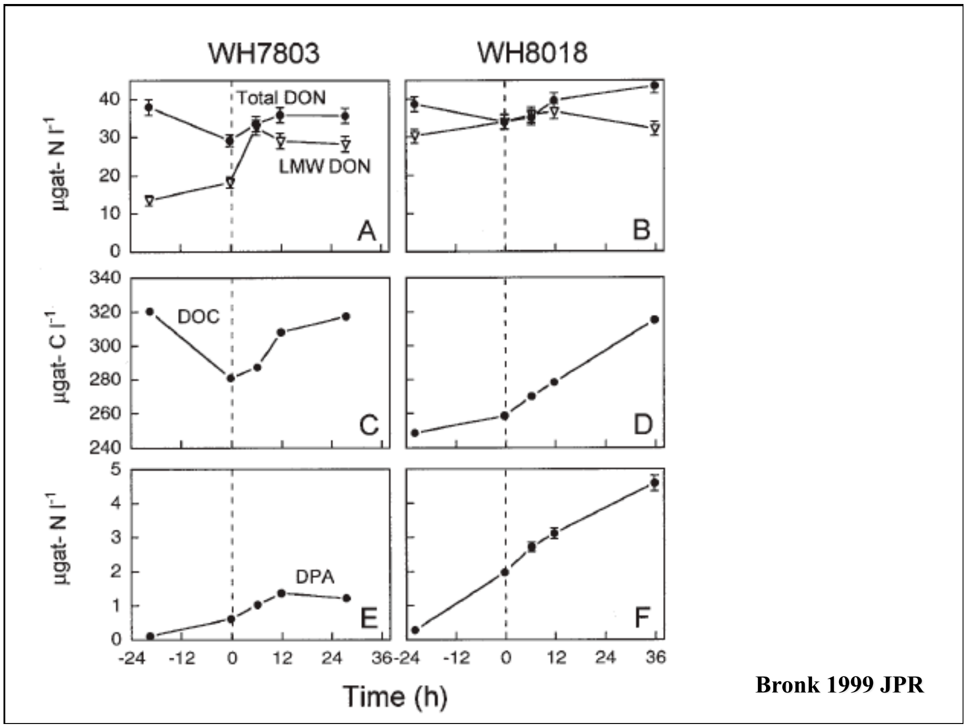
Bacteria as ectoparasites

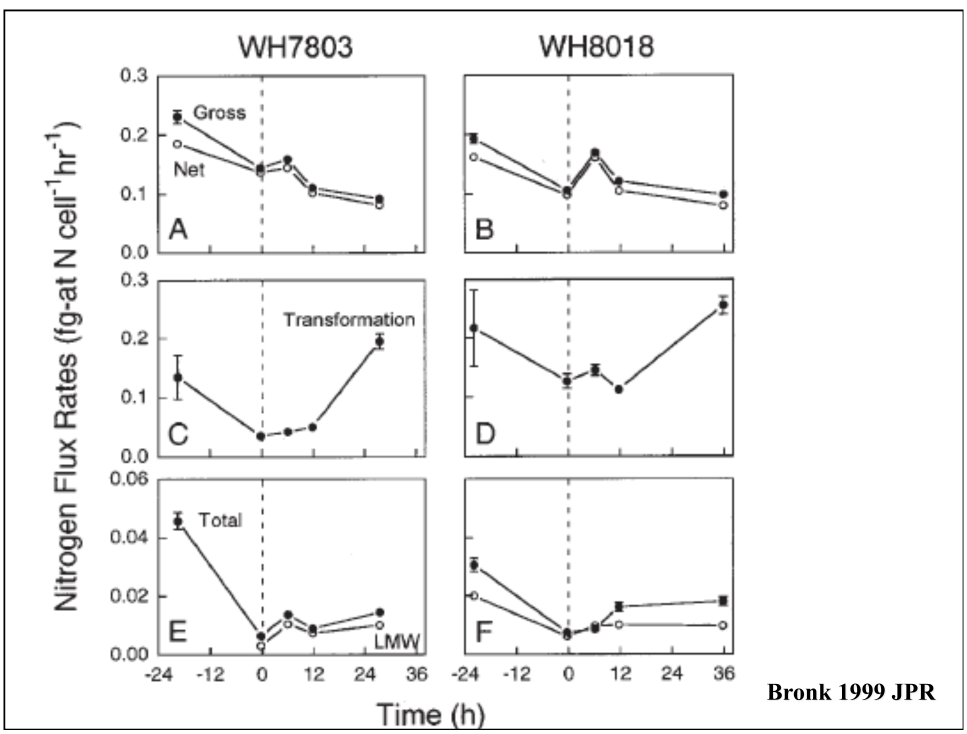
Bjørnsen 1988 L&O

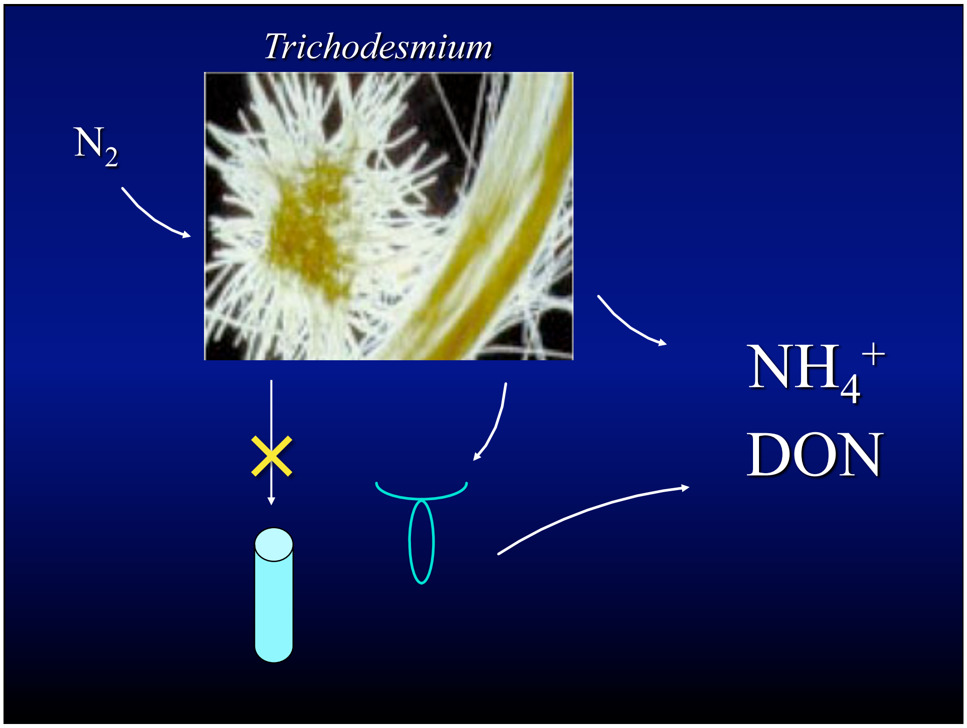


A bit of advice!

Bronk 1999 JPR


WH7803
WH8018
Total DON
LMW DON
DOC
DPA
µgat- N l⁻¹
µgat- C l⁻¹
µgat- N l⁻¹
A
B
C
D
E
F
Time (h)
Bronk 1999 JPR


WH7803
WH8018
Gross
Net
Transformation
Total
LMW
Nitrogen Flux Rates (fg-at N cell⁻¹ hr⁻¹)
A
B
C
D
E
F
Time (h)
Bronk 1999 JPR



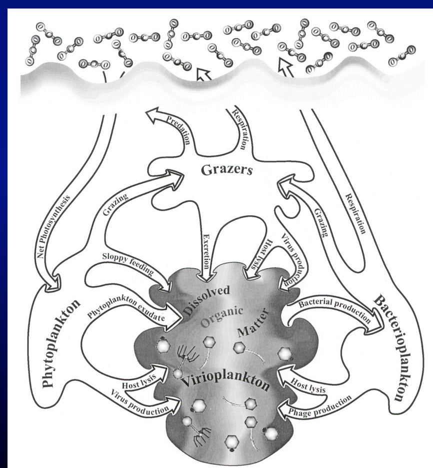
Autochthonous sources of DON

Viral lysis

Phytopl.

Bact.

DON and NH_4^+



Viruses are unique in that they are “part” of the DOM pool (~<2%).

Wommack and Colwell 2000 Microbiol. Mol. Bio. Rev.

Photochemical Ammonification

UV radiation

Humic or fulvic acids
Proteins
Large organic moieties

NH_4^+
DPA
NO_2^-

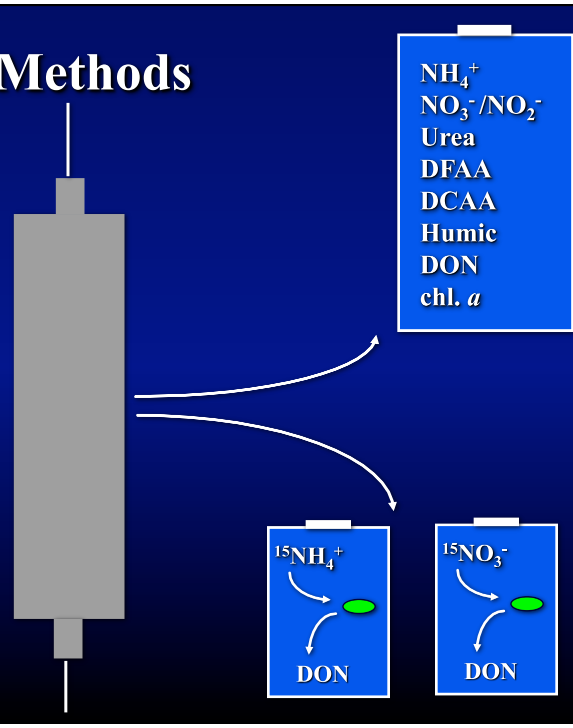
phytoplankton

?

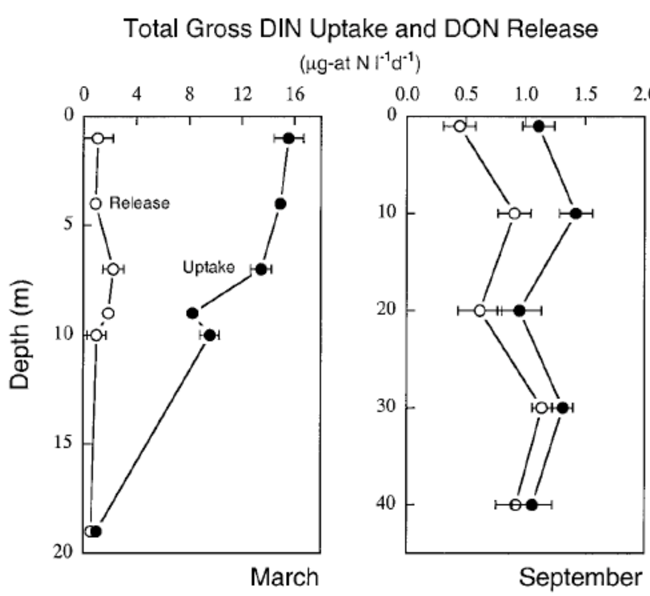
bacteria

Bushaw et al. 1996 Nature

Field Methods

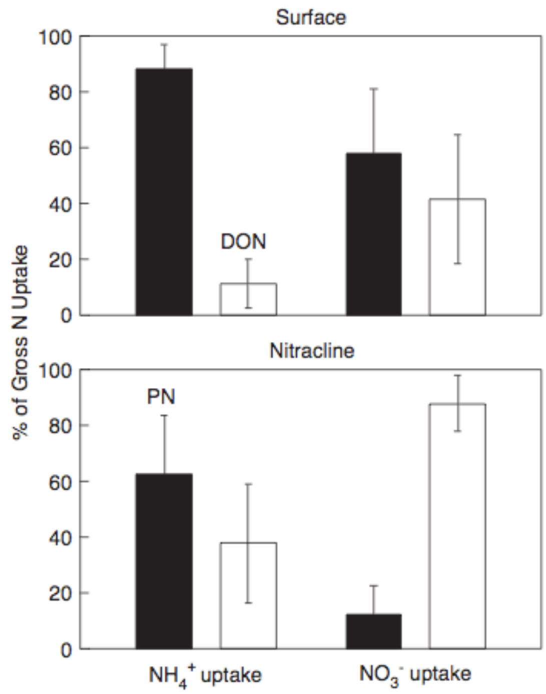


Monterey Bay

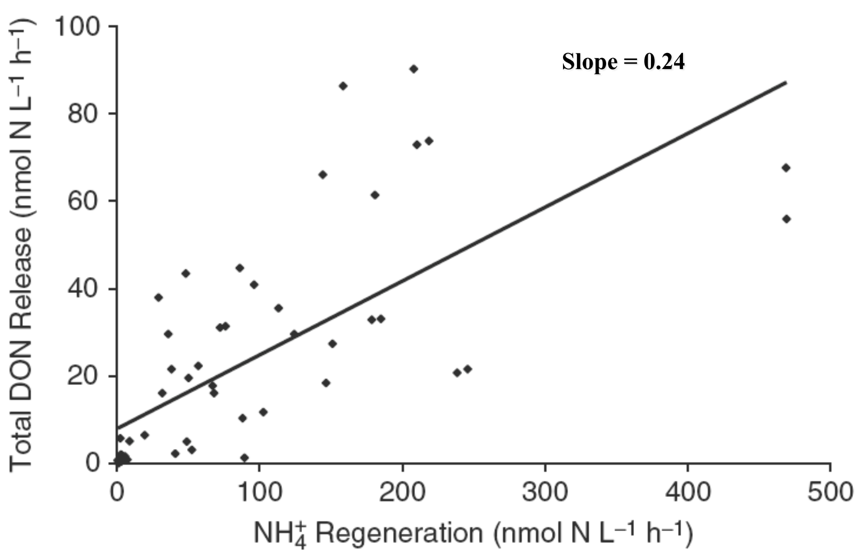


Bronk & Ward 1999 L&O

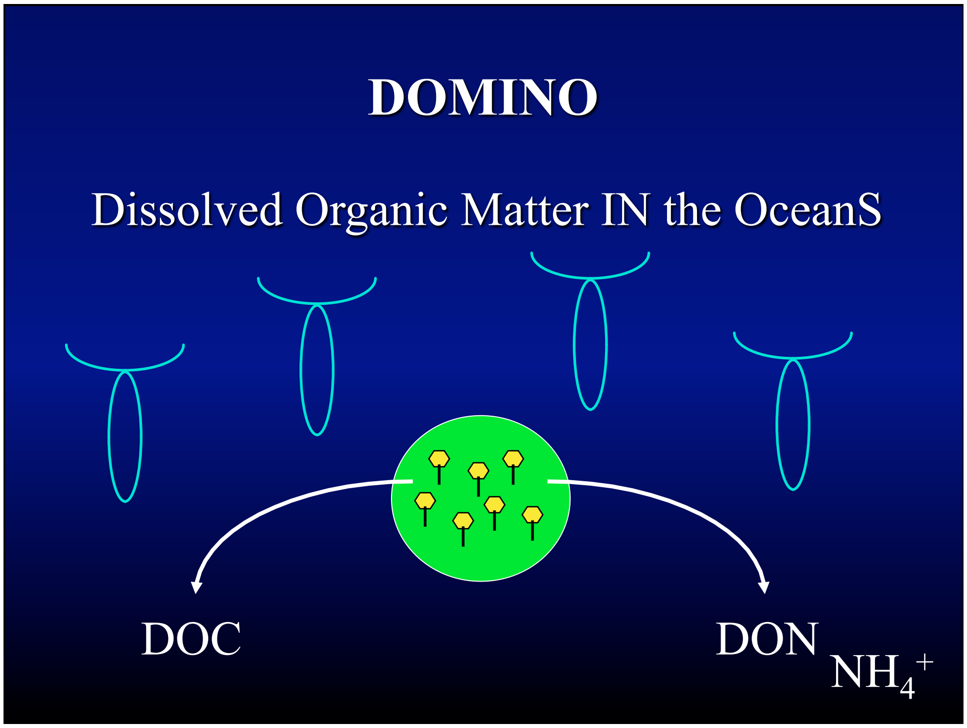
Southern California Bight

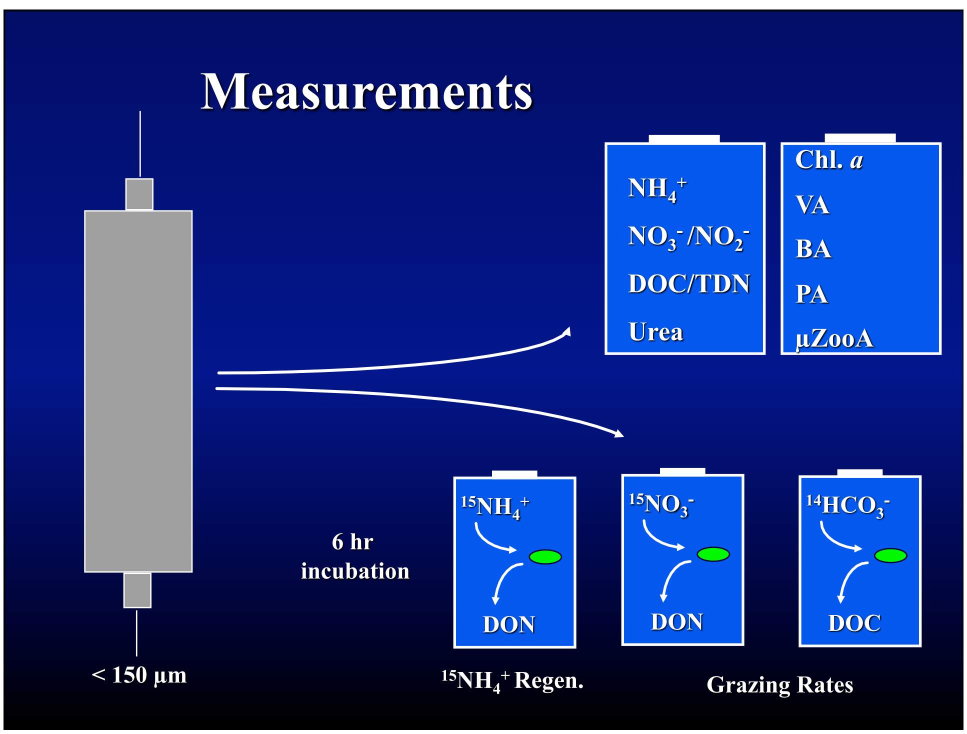


Bronk & Ward 2005 DSRI

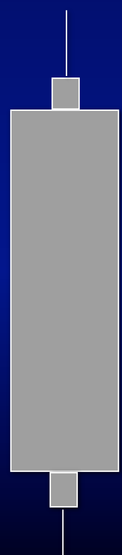


Bronk & Steinberg 2008 N Bible


DOMINO
Dissolved Organic Matter IN the OceanS
DOC
DON
NH_4^+


Measurements
NH_4^+
NO_3^-/NO_2^-
DOC/TDN
Urea
Chl. *a*
VA
BA
PA
µZooA
6 hr
incubation
$^{15}NH_4^+$
DON
$^{15}NO_3^-$
DON
$^{14}HCO_3^-$
DOC
< 150 µm
$^{15}NH_4^+$ Regen.
Grazing Rates

Ambient Conditions



NH_4^+ ~9 µM

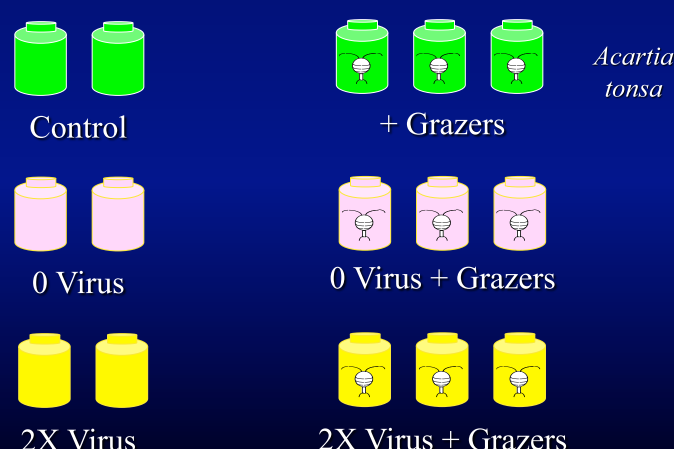
NO_3^- ~10 µM

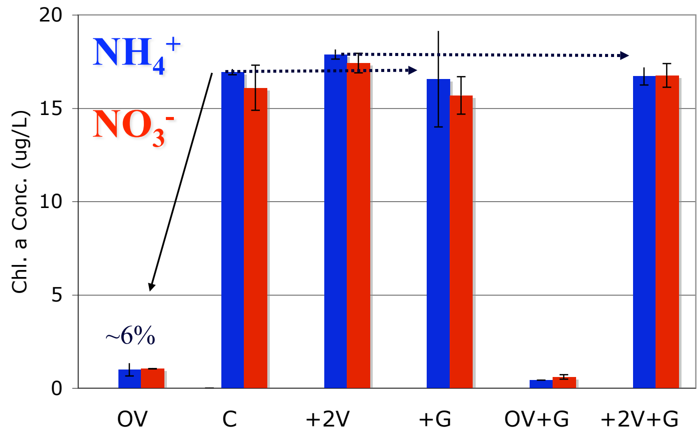
DOC ~185 µM

DON ~10 µM   (C:N 18)

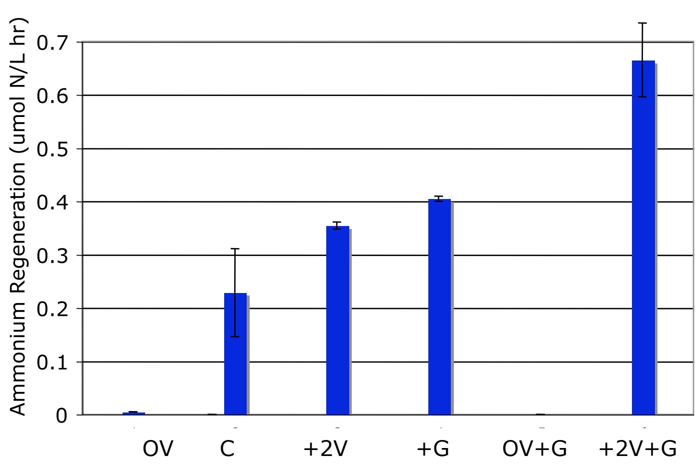
urea ~ 0.6 µM

Treatments

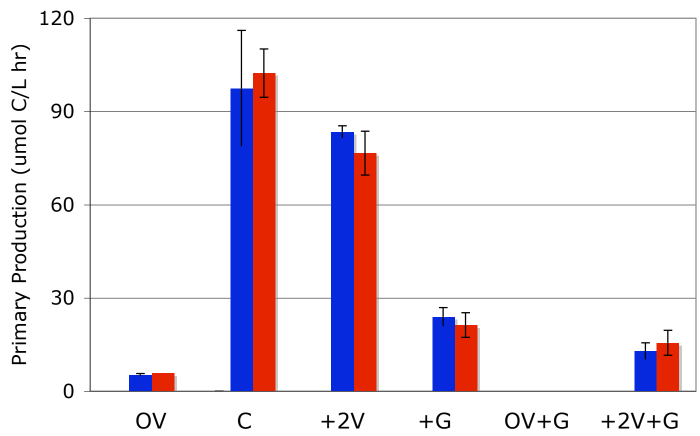




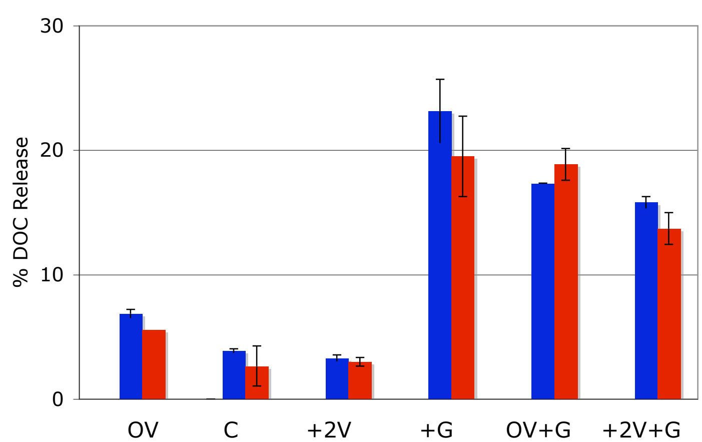
- **Slight decrease in Chl. a when grazers are added.**



- **Grazers and viruses increased the rate of NH_4^+ regeneration.**
- **Additive effect.**



- **Both grazers and viruses depressed primary production.**
- **Additive effect.**

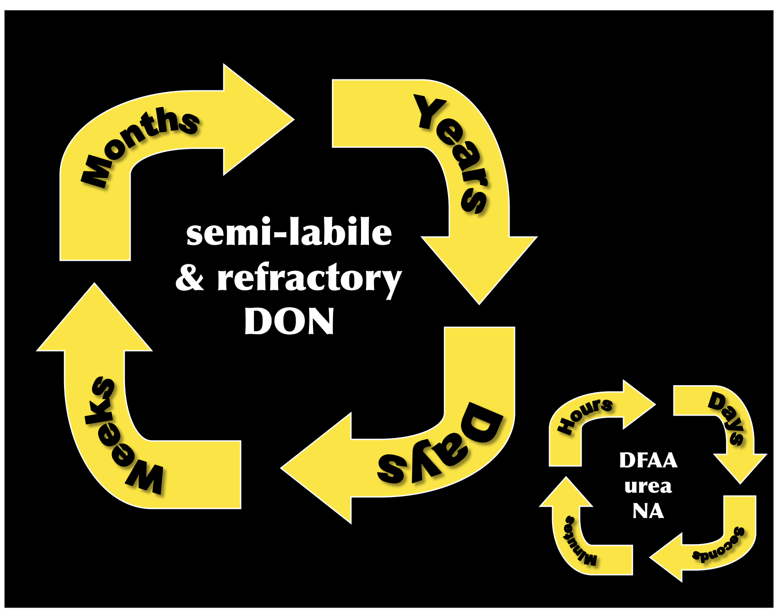


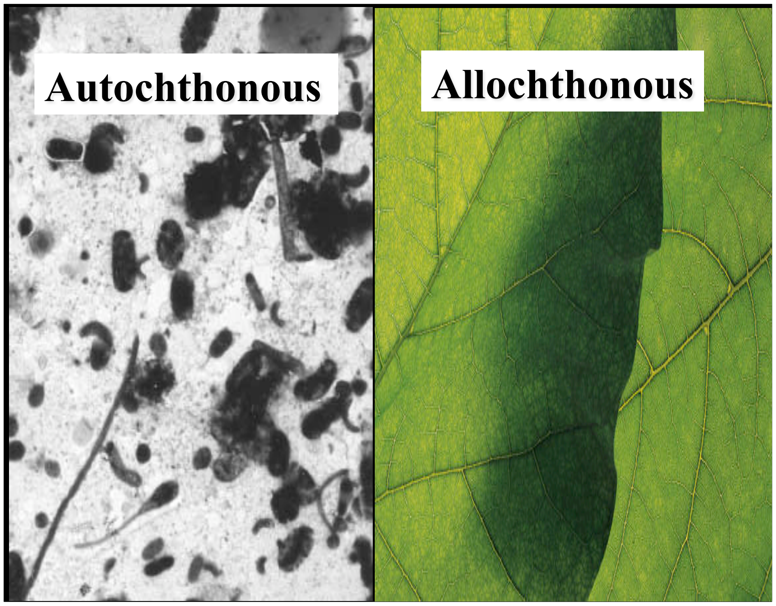
- **Grazers increased the % of primary production released as DOC.**
- **Viruses tended to decrease it.**

Turnover time = conc/rate

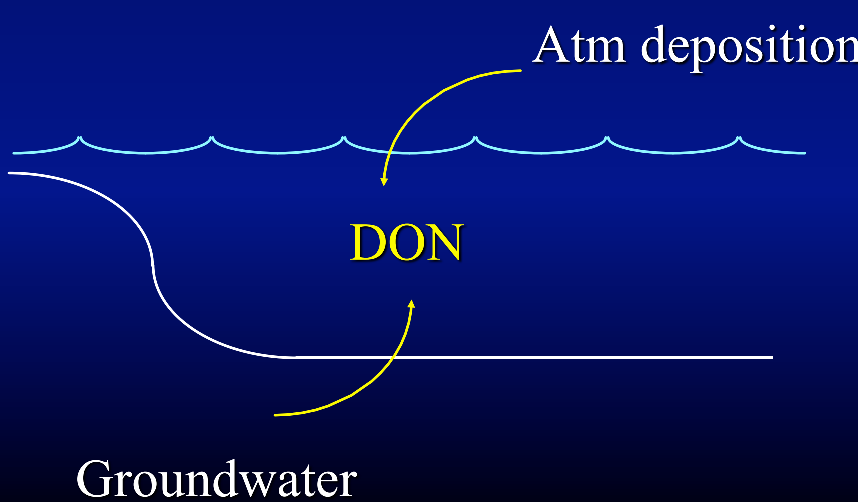
Location	Compound Considered	Turnover Time	Units
Oceanic			
Northeastern Pacific	DON	0.91	years
Equatorial Atlantic (15N-25N	DON	0.4 to 13.2[c]	years
Equatorial Atlantic (15S-15N)	DON	12.7 ± 26.1[c]	years
Equatorial Atlantic (35S-15S)	DON	2.1 to 300[c]	years
Caribbean Sea	DON	40.7 ± 10.4	days
Southern California Bight	DON	11 to 62	days
where?	HMW DON >1kD	~238[a]	days
Northern Sargasso Sea	Protein	0.38 to 3.42	days
Northern Sargasso Sea	Modified protein[d]	9.04 to 32.71	days
Northern Sargasso Sea	Modified protein[d]	9.04 to 32.71	days
Northern Sargasso Sea	DFAA	0.03 to 0.29	days
Central Arctic	DFAA	~2.72	days

Bronk 2002 Book chapter





Allochthonous sources of DON



Galloway et al. 2008 Science

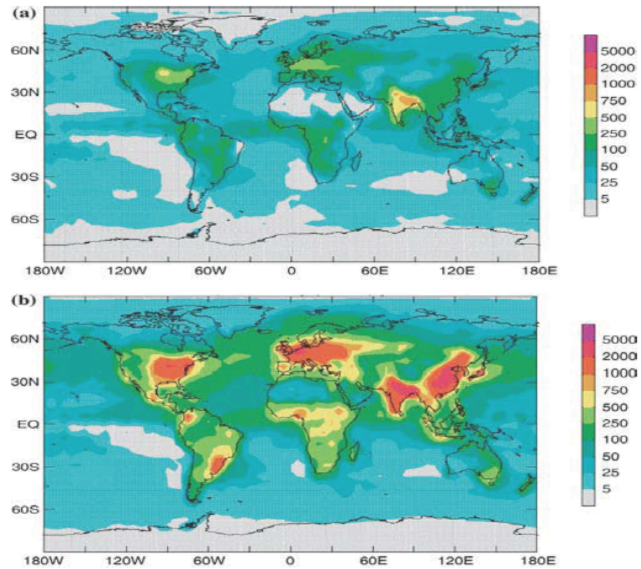


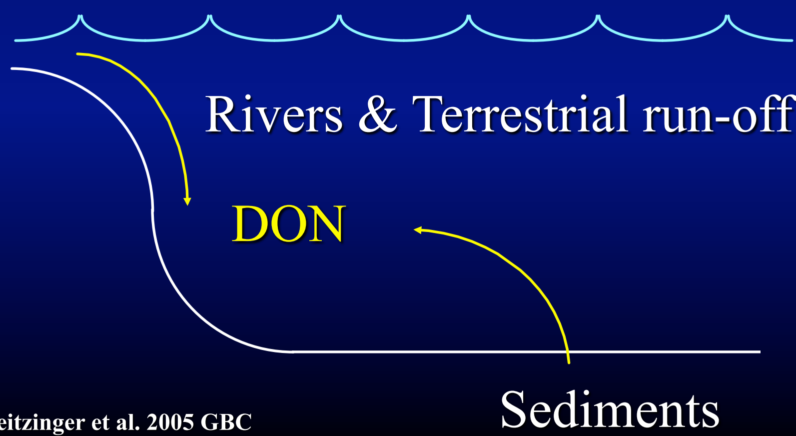
Figure 2: Spatial patterns of total inorganic nitrogen deposition in 1860 (top) and early 1990 (bottom) in units of kg nitrogen per square kilometer per year.

DON in atmospheric deposition Refractory??

Source/Location	% org N	Reference
Walker Branch, TN	34	Kelly and Meagher 1986
Coastal plain, FL	40–63	Riekert 1983
Cascade Mtns., OR	46–72	Fredriksen 1976
Coastal plain, SC	49	Richter et al. 1983
Philadelphia, PA*	19–52	This study
Chesapeake Bay	57	Smullen et al. 1982
Rhode River, MD	18–44	Jordan et al. 1995
New Brunswick, NJ*†	2–44	Seitzinger and Sanders unpubl. data
Narragansett, RI	19	Nixon et al. 1995
U.K.	21	Cornell et al. 1995
Czech Rep.	27	"
N. Carolina	21	"
Amazonia	22	"
Recife, Brazil	25	"
Bermuda	59	"
Tahiti	84	"
NE Atlantic	62	"
NE Atlantic	67	"
Cape Cod, MA	43	Valiela et al. 1997
Lewes, DE	23	Scudlark et al. 1998

Seitzinger & Sanders 1999 L&O

Allochthonous sources of DON



Seitzinger et al. 2005 GBC

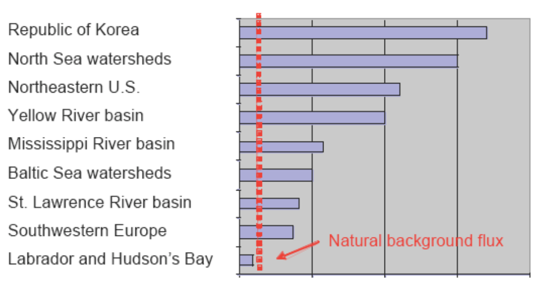


Figure 3: Flux of reactive nitrogen from the landscape to coastal oceans in rivers for key contrasting regions of the world in the temperate zone, in units of kg nitrogen per square kilometer of watershed area per year.

DON in rivers Refractory??

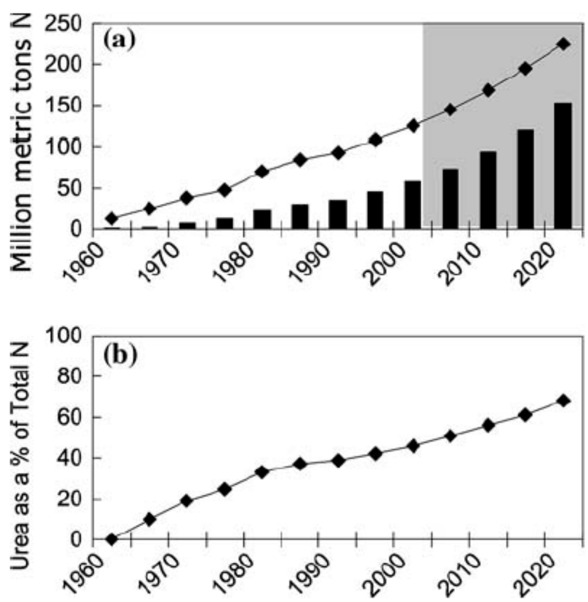
Table 5. Percent composition of inorganic and organic N in various rivers

River	% DIN	% DON	% PN	% ON	Reference
Mullica, NJ, USA	30	61	9	70	Durand (1988)
Mississippi, USA	53[a]			43	Turner & Rabalais (1991)
Amazon	25	29	46	75	Richey et al. (1991)
Mackenzie, Canada	10	15	75	90	Telang et al. (1991)
Unnamed stream, NH, USA	39	51	10	61	Likens (1985)
Blackstone, RI, USA	73	23	4	27	Nixon et al. (1995)
Pocono Mountain Stream, PA, USA	4			96	Seitzinger (unpubl.data)
Delaware, PA, USA	74	20	5	25	Culberson et al. (1987)
Rhode, MD, USA	30	14	56	70	Peterjohn & Correll (1984)
Como, CO, USA	10	90		90[b]	Meybeck (1982)
Lindaret, France	78	22		22[b]	Meybeck (1982)
Brevon, France	77	23		23[b]	Meybeck (1982)
Danube, Rumania	55	45		45[b]	Meybeck (1982)
Aare, Switzerland	73	27		27[b]	Meybeck (1982)
Reuss, Switzerland	56	44		44[b]	Meybeck (1982)
Rhine, Switzerland	74	26		26[b]	Meybeck (1982)
Rhône, Switzerland	56	44		44[b]	Meybeck (1982)
Ticino, Switzerland	57	43		43[b]	Meybeck (1982)
Missouri, USA	46	54		54[b]	Meybeck (1982)
Windrush, England	60			40	Heathwaite (1993)
Eastern Notec, Poland	29			71	Taylor et al. (1986)
Wda, Poland	70			30	Taylor et al. (1986)
Kullarna, Sweden	25			75	Lepistö et al. (1995)
Däntersta, Sweden	22			78	Lepistö et al. (1995)
Myllypuro, Finland	6			94	Lepistö et al. (1995)
Pahkaoja, Finland	21			79	Lepistö et al. (1995)
Avg world rivers	33			67	Meybeck (1982)

[a]NO_3+NO_2 only. [b]Minimum estimates as based on DON only; no PN data

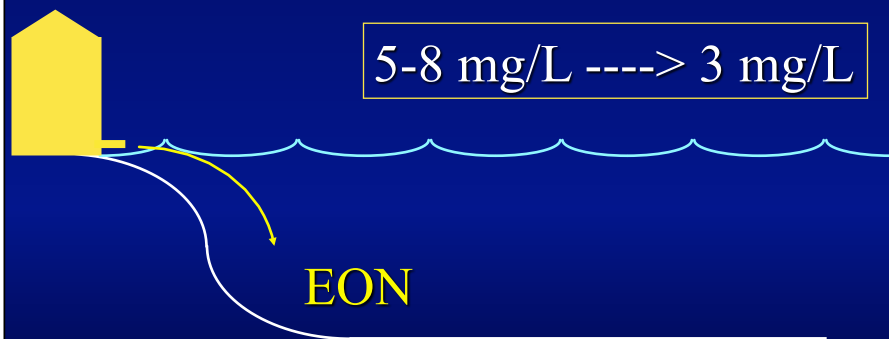
Seitzinger & Sanders 1997 MEPS

The rise of urea



Glibert et al. 2006 Biogeosciences

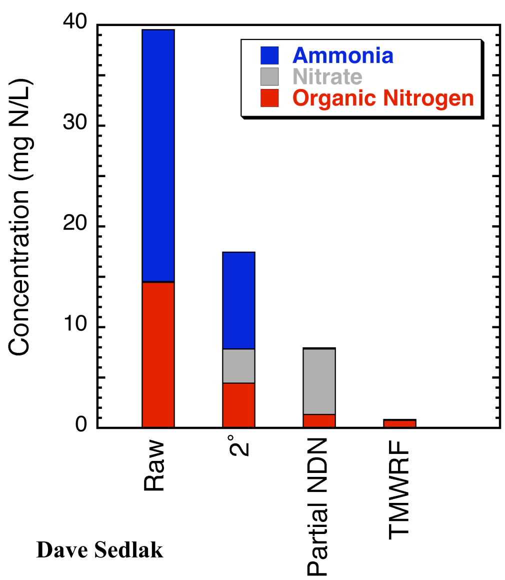
Allochthonous sources of DON



Effluent Organic Nitrogen

Mulholland et al. 2007 STAC

Nitrogen in Wastewater



Compounds poorly removed by treatment
- Humics in source
- Recalcitrant organics

Compounds formed during treatment

Dave Sedlak

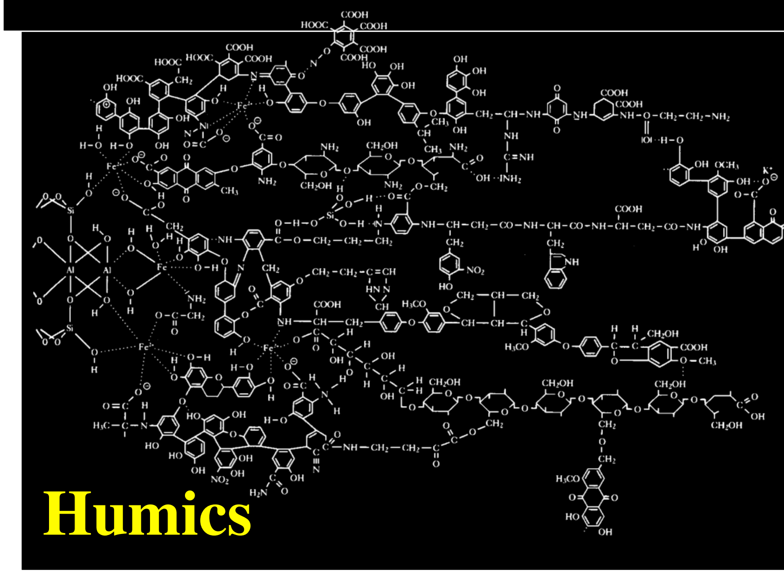
Composition of EON

TABLE 1. Total Amino Acid Concentrations in the Secondary Treated Wastewater Effluents (Scully et al., 1988b; Confer et al., 1995; Grohmann et al., 1998; Pehlivanoglu and Sedlak, in preparation)

	Wagott	Parkin	Elsässer	Hejzlar	Scully[a]	Scully	Confer	Pehlivanoglu
mg N/L	0.017	0.025	0.013	0.034	0.042–0.084	0.02	0.26	0.14–0.17
μM N	1.23	1.79	0.93	2.45	3–6	1.43	18.76	10–12

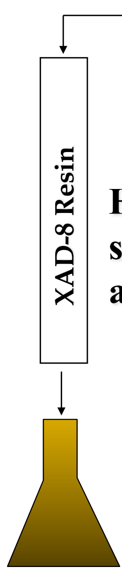
Note. Wagott, Parkin, Elsässer, Hejzlar, and Scully data are obtained from Grohmann et al. (1998).
[a]Primary effluent.

Organics as a mode of inorganic N delivery!



Humic Extraction Method

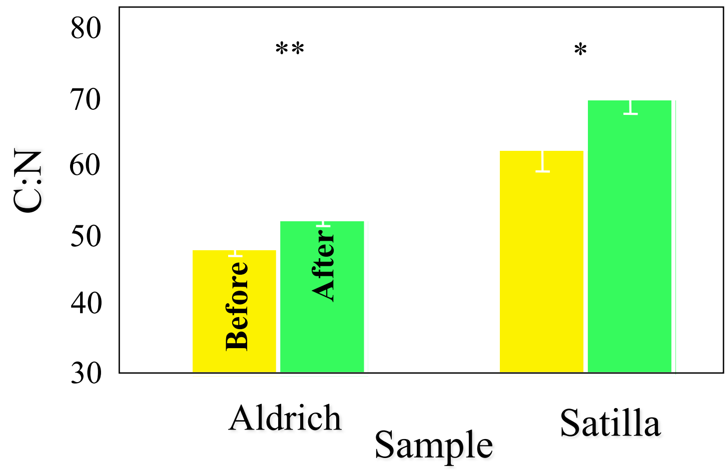
Acidified Sample (pH < 2)



Humic Substances
stick to the
acidified resin

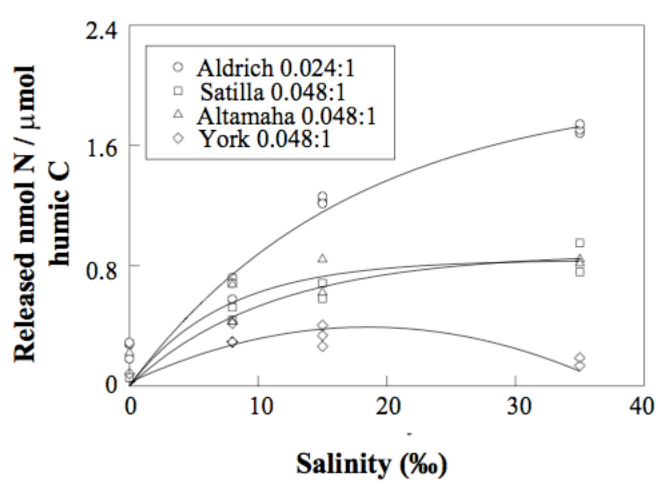
Humic fraction
elutes from column
with NaOH

C:N Ratio of Saturated Humics Before and After XAD Extraction



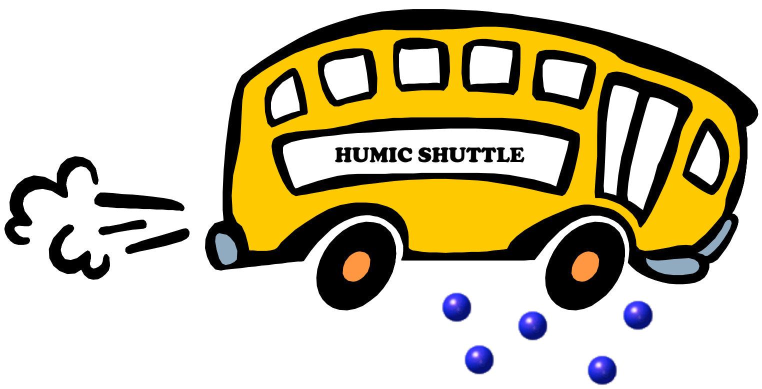
Samples Saturated at 4 µmol NH_4^+ (mg humic-C)$^{-1}$

See & Bronk 2005 Mar Chem



See 2003 Dissertation

When humics hit ~15 ‰ they dump NH_4^+



Outline:

- What is DON?
- Methods to study release
- Autochthonous sources
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- DON as a mode of N delivery