

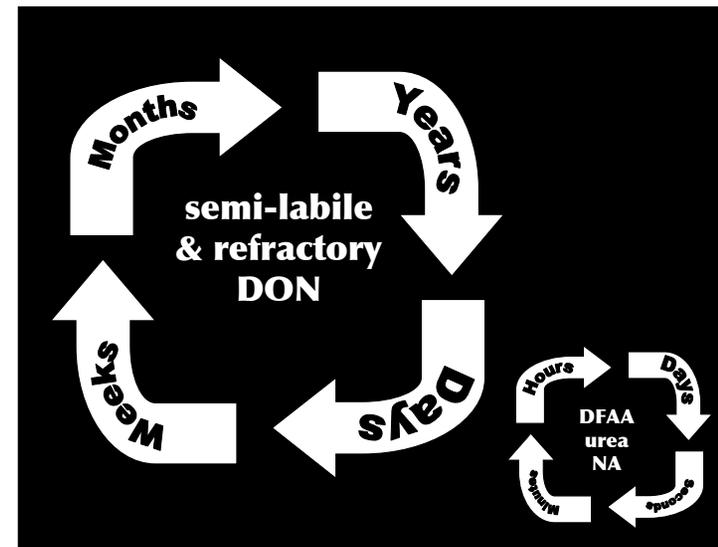
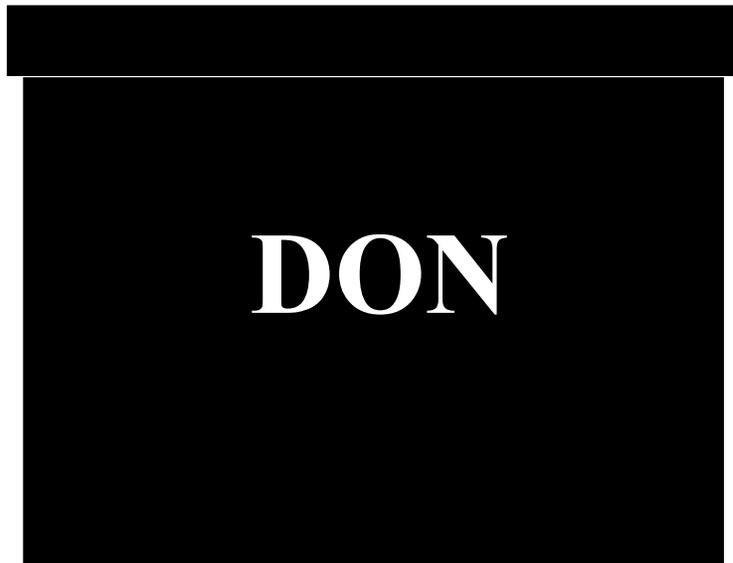
DON sources: methods and processes

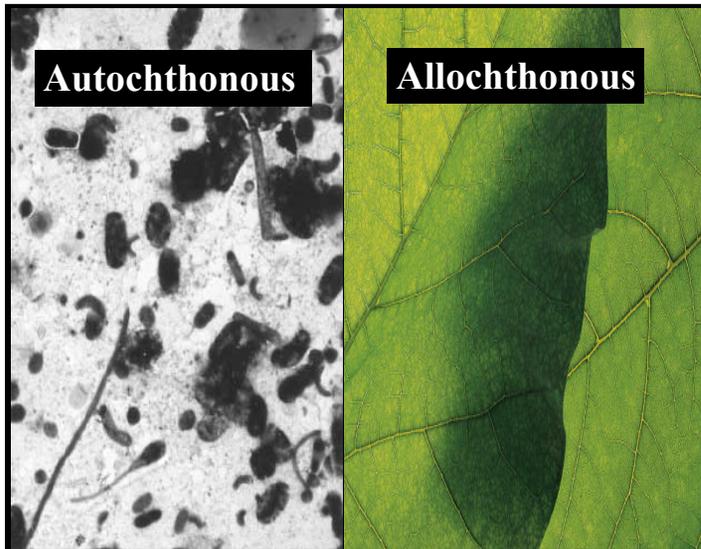
Deborah A. Bronk
Department of Physical Sciences



What is DON?

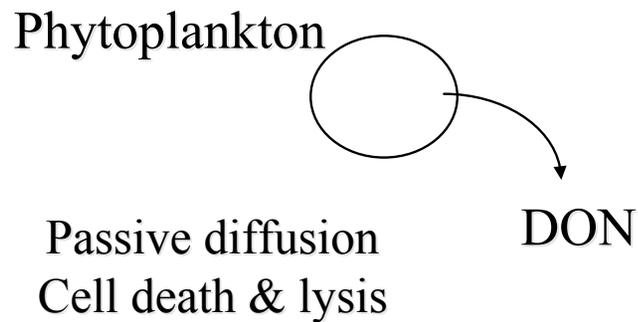
Labile	Semi-labile	Refractory
DFAA urea nucleic acids methylamines	proteins DCAA amino polysaccharides (chitins & peptidoglycans)	humic acids fulvic acids porphorins amides



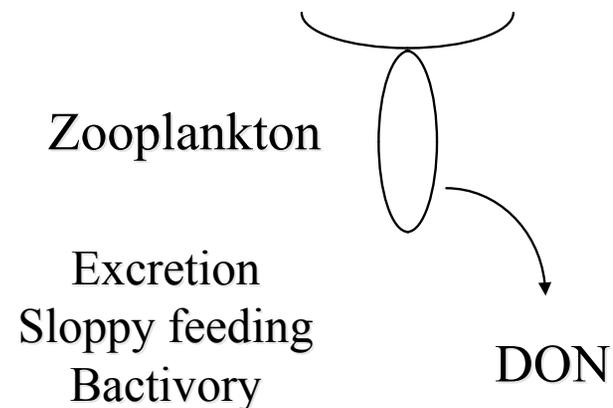


- Autochthonous sources
- Methods to study release
- Allochthonous sources
- DON as a mode of N delivery

Autochthonous sources of DON



Autochthonous sources of DON



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

Stable isotope tracers
(¹⁵N, ¹³C)

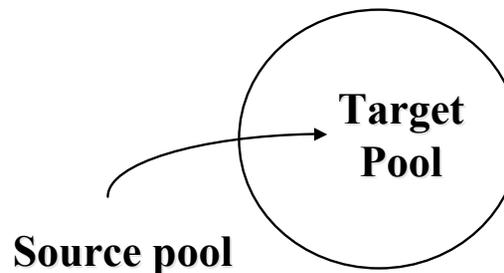
Absolute amounts

Ratios
(¹⁵N/¹⁴N or ¹³C/¹²C)

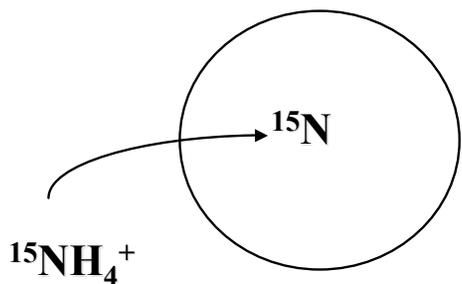
Net rates

Gross rates

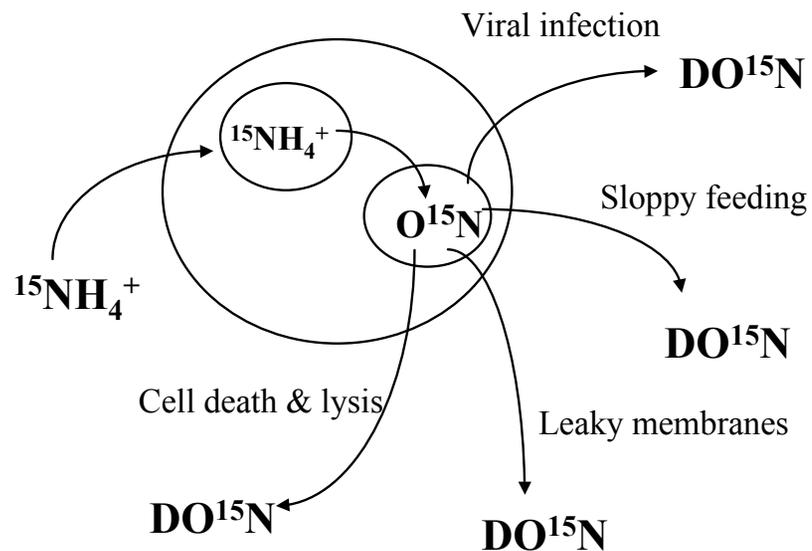
Uptake and regeneration
simultaneously

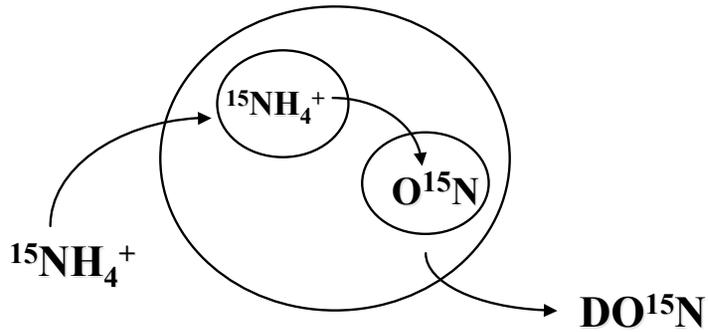


$$\text{Rate} = \frac{\text{atom \% of target}}{\text{atom \% of source} \times \text{Time}} \times [\text{target}]$$



$$\frac{\text{Net Uptake Rate}}{\text{atom \% NH}_4^+ \times \text{Time}} = \frac{\text{atom\% PN}}{\text{atom \% NH}_4^+ \times \text{Time}} \times [\text{PN}]$$

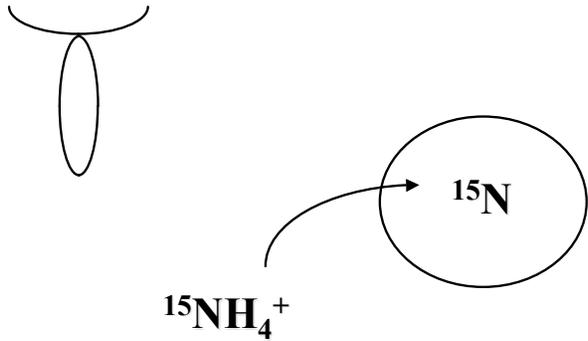




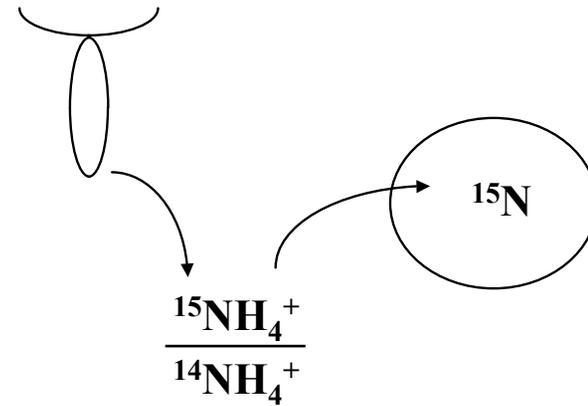
$$\text{Gross Uptake} - \text{Net Uptake} = \text{DON Release}$$

$$\text{Gross Uptake Rate} = \frac{^{15}\text{N in PN \& DON}}{\text{atom \% NH}_4^+ \times \text{Time}} \times [\text{PN}]$$

Bronk et al. 1994 Science



$$\text{Net Uptake Rate} = \frac{\text{atom \% PN}}{\text{atom \% NH}_4^+ \times \text{Time}} \times [\text{PN}]$$



Isotope dilution

$$\text{Net Uptake Rate} = \frac{^{15}\text{N in PN}}{\text{atom \% NH}_4^+ \times \text{Time}} \times [\text{PN}]$$

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

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

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

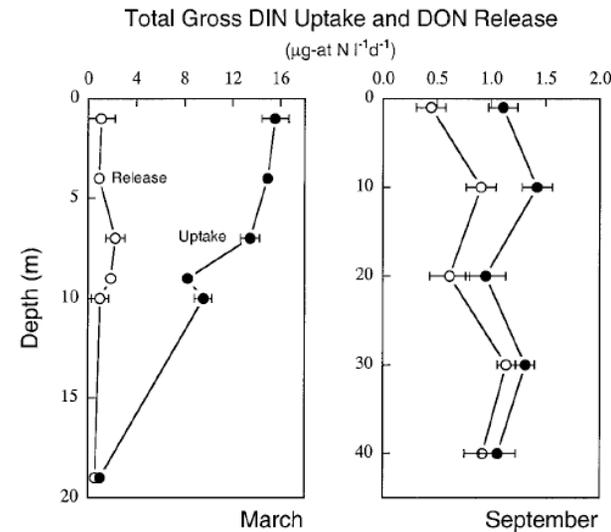
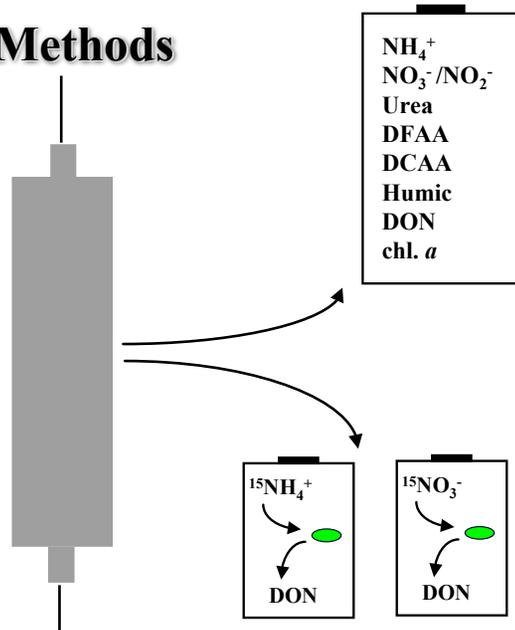
Glibert et al. 1982 L&O

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

Brink 2002 Book chapter

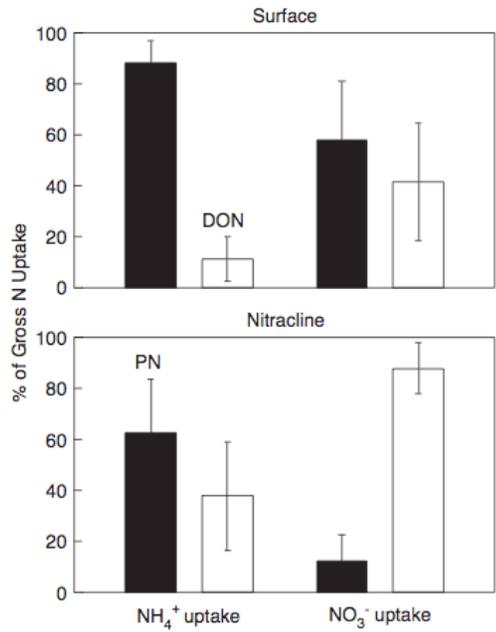
Field Methods



Monterey Bay

Brink & Ward 1999 L&O

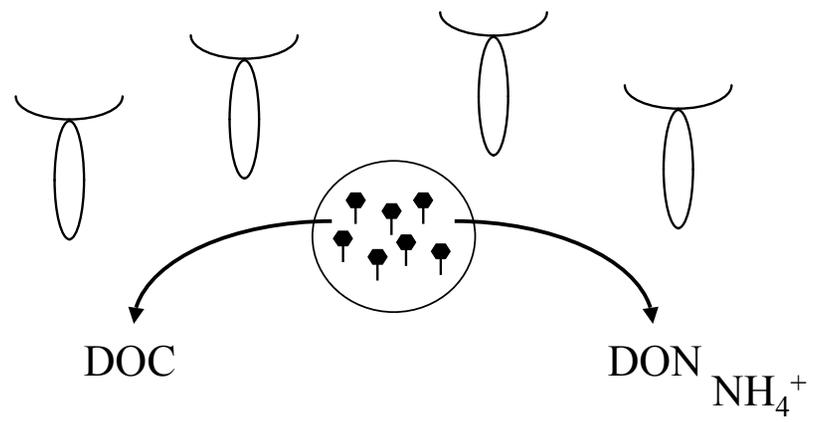
Southern California Bight



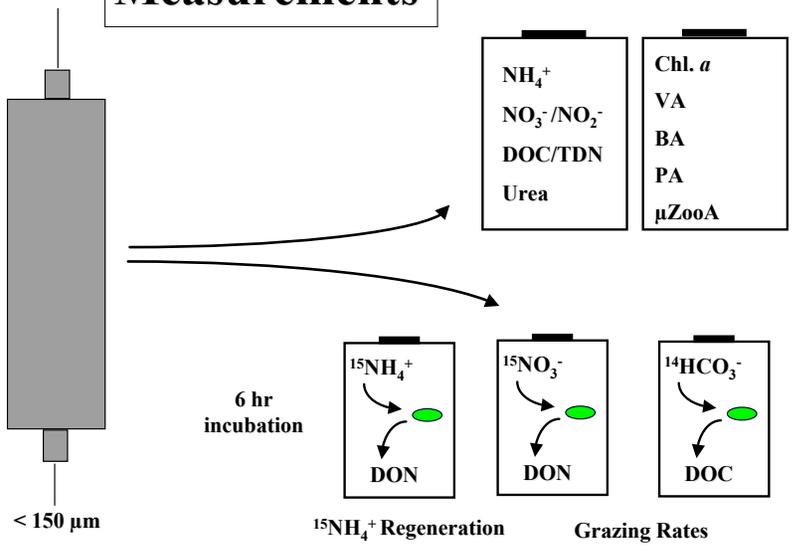
Bronk & Ward 2005 DSRI

DOMINO

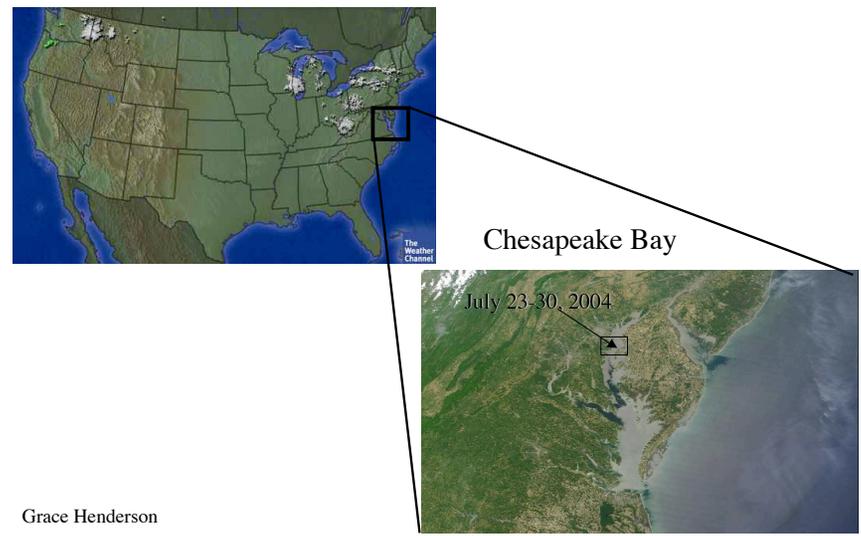
Dissolved Organic Matter IN the OceanS



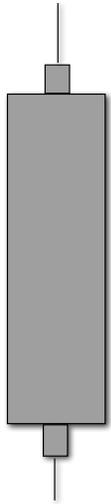
Measurements



Field Study Site



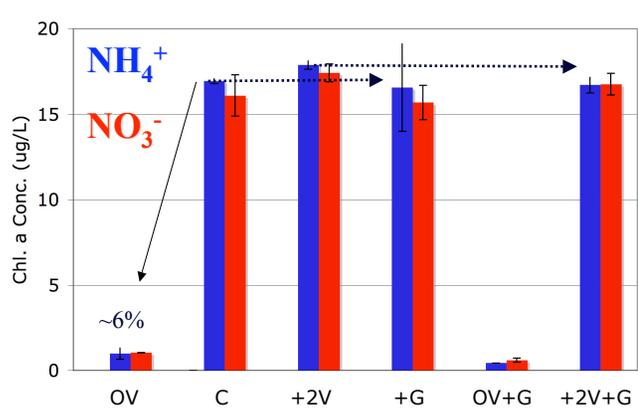
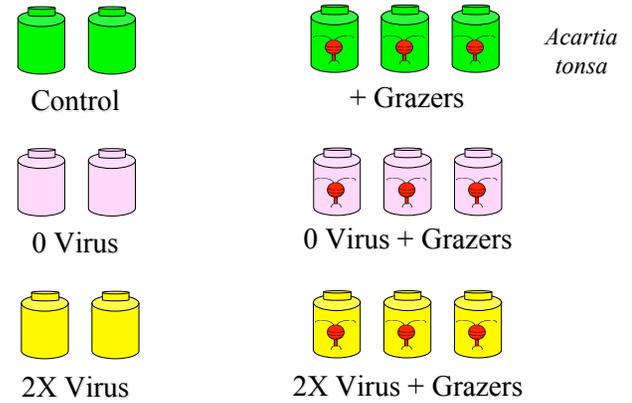
Grace Henderson



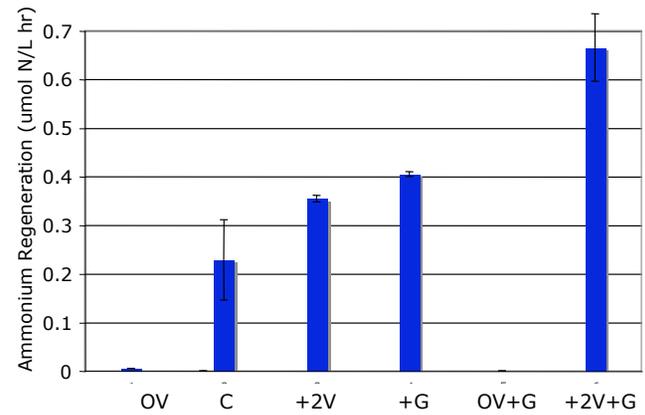
Ambient Conditions

$\text{NH}_4^+ \sim 9 \mu\text{M}$
 $\text{NO}_3^- \sim 10 \mu\text{M}$
 $\text{DOC} \sim 185 \mu\text{M}$
 $\text{DON} \sim 10 \mu\text{M}$ (C:N 18)
 $\text{urea} \sim 0.6 \mu\text{M}$

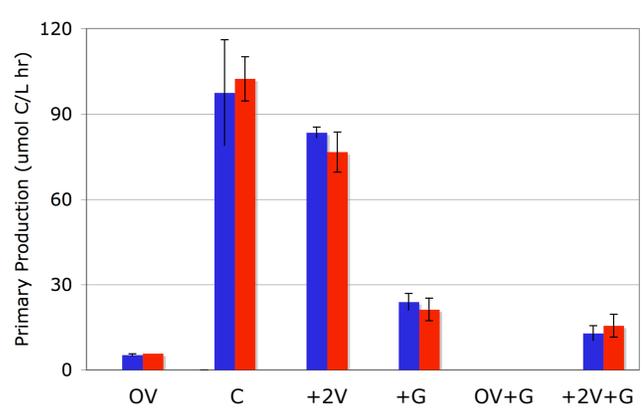
Treatments



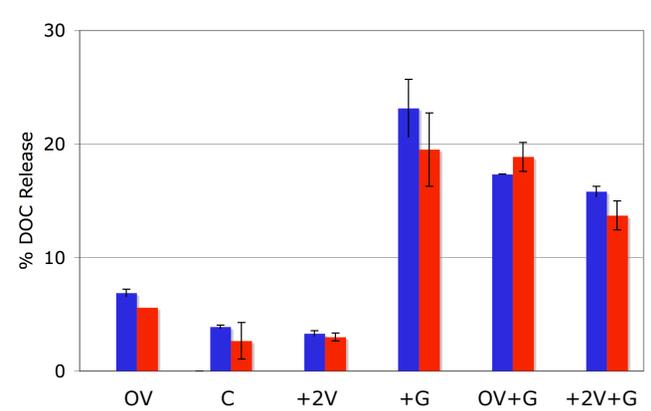
- Slight decrease in Chl. a when grazers are added.



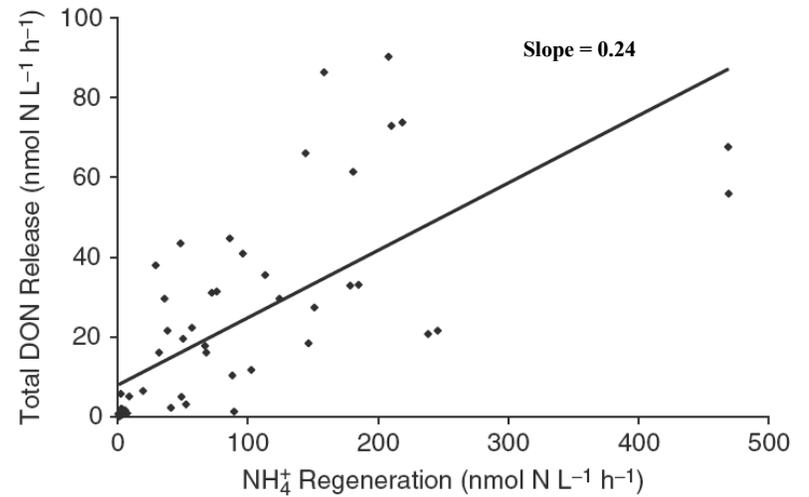
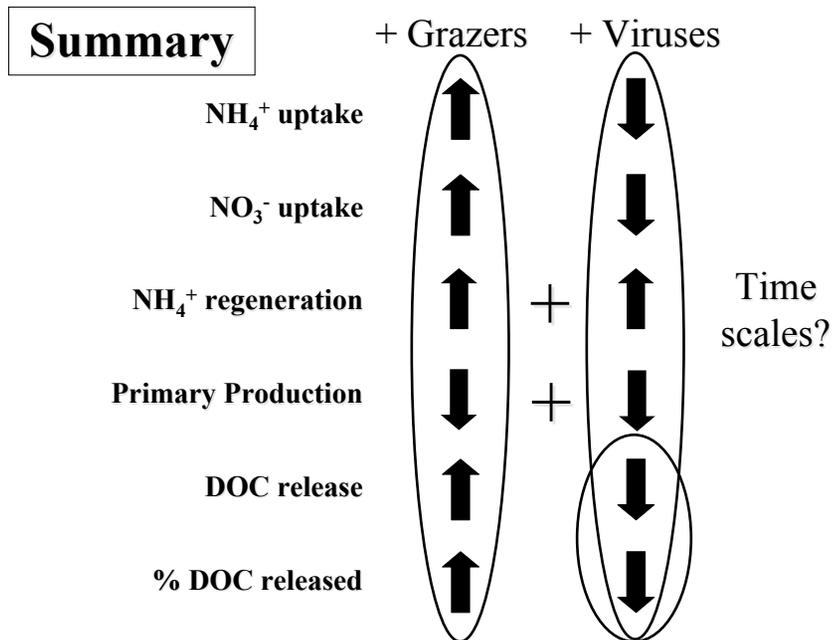
- Grazers and viruses increased the rate of NH_4^+ regeneration.
- Additive effect.



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



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



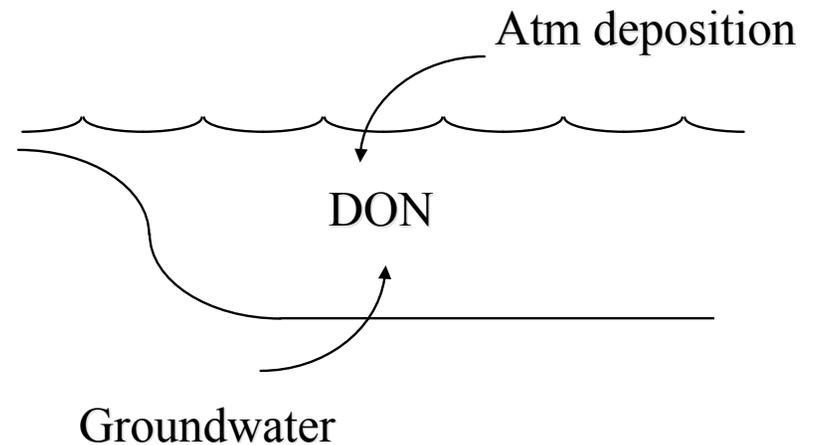
Allochthonous sources of DON

Rate 1	Rate 2	Depth	n	slope	r ²	p
Total DON release	NH ₄ ⁺ regeneration	euphotic zone	56 ^a	0.237	0.51	< 0.001
DON release (from NH ₄ ⁺)	Gross NH ₄ ⁺ uptake	upper euphotic	48 ^a	0.132	0.71	< 0.001
DON release (from NH ₄ ⁺)	Gross NH ₄ ⁺ uptake	lower euphotic	41 ^a	0.861	0.92	< 0.001
DON release (from NO ₃ ⁻)	Gross NO ₃ ⁻ uptake	upper euphotic	55 ^a	0.572	0.42	< 0.001
DON release (from NO ₃ ⁻)	Gross NO ₃ ⁻ uptake	lower euphotic	43 ^a	0.929	0.96	< 0.001

^a Rates from coastal and oceanic systems.

^b Rates from estuarine, coastal and oceanic systems.

Bronk & Steinberg In press N in the Mar Env.



Galloway et al. 2008 Science

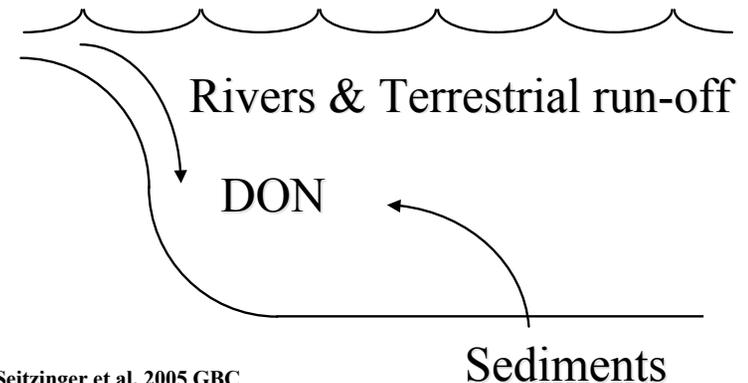
DON in atmospheric deposition

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

DON in rivers

Refractory??

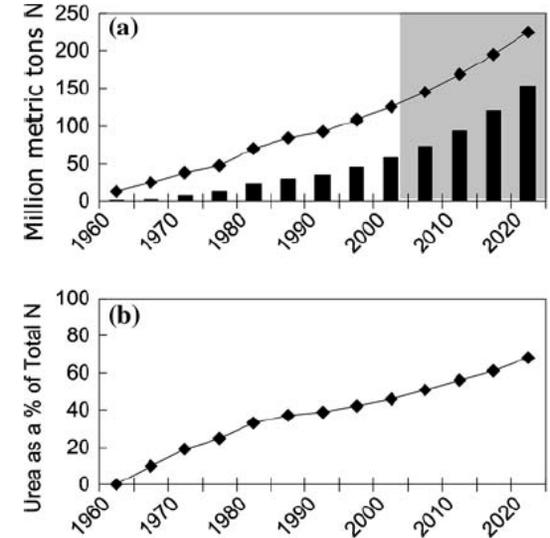
Table 5. Percent composition of inorganic and organic N in various rivers

River	% DIN	% DON	% PN	% ON	Reference
Mullica, NJ, USA	30	61	9	70	Durand (1988)
Mississippi, USA	53*			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	Culbertson et al. (1987)
Rhode, MD, USA	30	14		70	Peterjohn & Corneil (1984)
Camo, CO, USA	10	90		90*	Meybeck (1982)
Lindaret, France	78	22		22*	Meybeck (1982)
Brevon, France	77	23		23*	Meybeck (1982)
Danube, Rumania	55	45		45*	Meybeck (1982)
Aare, Switzerland	73	27		27*	Meybeck (1982)
Reuss, Switzerland	56	44		44*	Meybeck (1982)
Rhine, Switzerland	74	26		26*	Meybeck (1982)
Rhône, Switzerland	56	44		44*	Meybeck (1982)
Ticino, Switzerland	57	43		43*	Meybeck (1982)
Missouri, USA	46	54		54*	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)
Pahkkoja, Finland	21			79	Lepistö et al. (1995)
Avg world rivers	33			67	Meybeck (1982)

*NO₃+NO₂ only. *Minimum estimates as based on DON only; no PN data

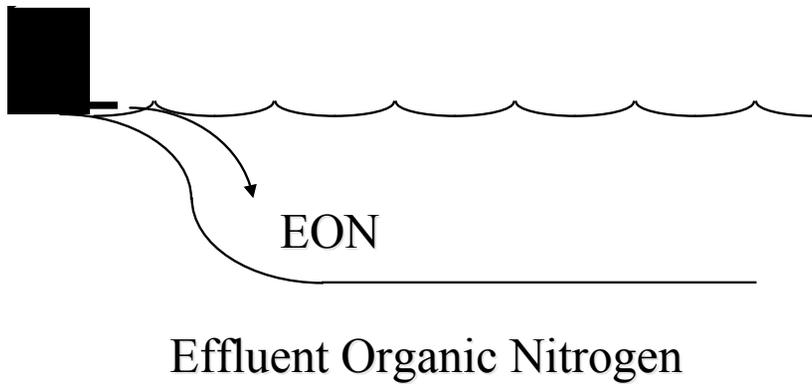
Seitzinger & Sanders 1997 MEPS

The rise of urea



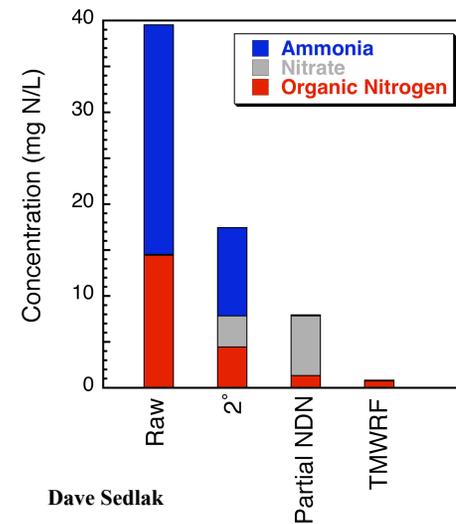
Glibert et al. 2006 Biogeosciences

Allochthonous sources of DON



Mulholland et al. 2007 STAC

Nitrogen in Wastewater



Dave Sedlak

Compounds poorly removed by treatment
 Humics in source
 Recalcitrant organics

Compounds formed during treatment

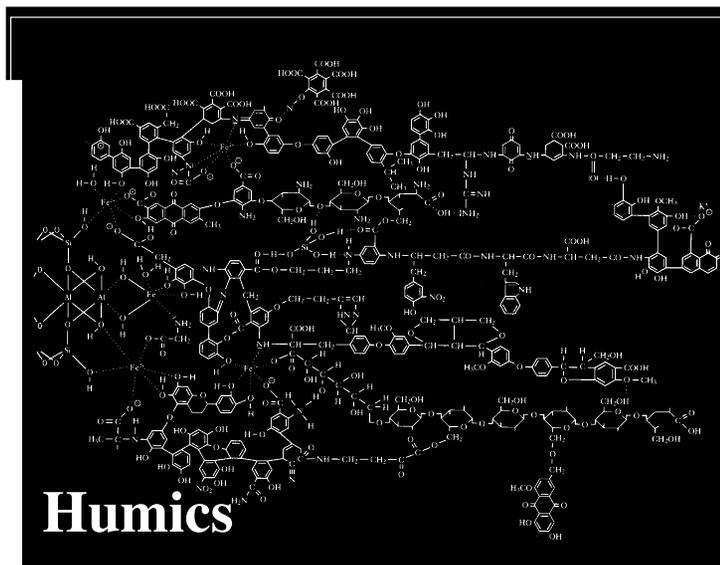
Composition of EON

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)

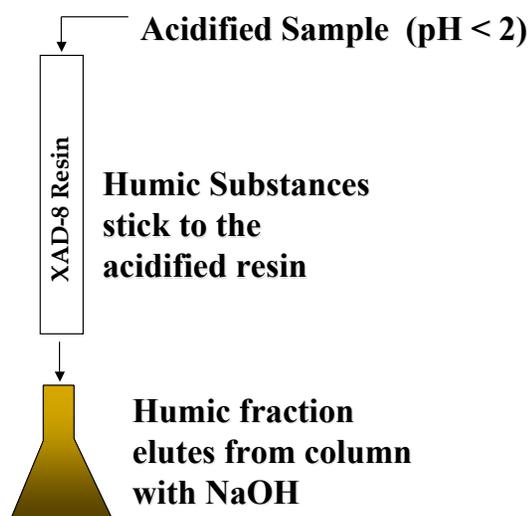
	Wagott	Parkin	Elsässer	Hejzlar	Scully ^a	Scully	Confer	Pehlivanoglu
mg N/L	0.017	0.025	0.013	0.034	0.042–0.084	0.02	0.26	0.14–0.17
$\mu\text{M N}$	1.23	1.79	0.93	2.45	3–6	1.43	18.76	10–12

Note. Wagott, Parkin, Elsässer, Hejzlar, and Scully data are obtained from Grohmann et al. (1998).

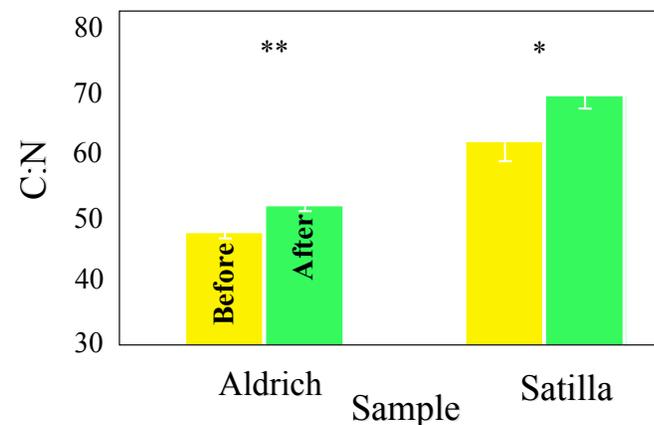
^aPrimary effluent.



Humic Extraction Method

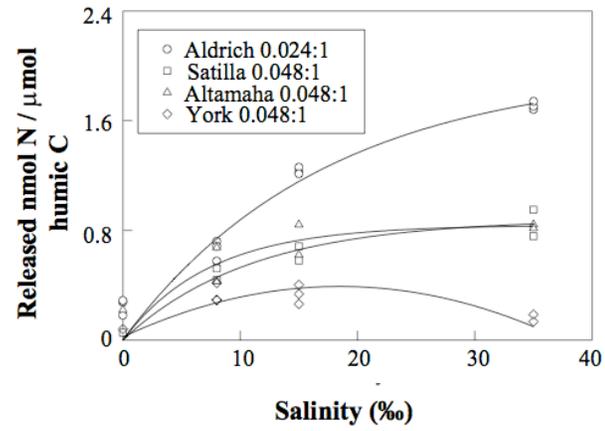


C:N Ratio of Saturated Humics Before and After XAD Extraction



Samples Saturated at $4 \mu\text{mol NH}_4^+$
(mg humic-C)⁻¹

See & Bronk 2005 Mar Chem



See 2003 Dissertation

When humics hit ~15 ‰ they
dump NH_4^+

