Coastal and Estuarine Processes
http://ecowin.org/aulas/mega/pce

Ocean chemistry

J. Gomes Ferreira
http://ecowin.org/

Universidade Nova de Lisboa

Lecture outline

- Light – the primary driver of life in the sea
- Dissolved oxygen – a key limiting factor
- Natural ‘pollution’ – the Black Sea
- Carbon in the ocean – the cycle, the consequences
- Shellfish and the carbon economy
- Nutrients – nitrogen and phosphorus
- The Redfield ratio, distributions, and models

Coastal and Estuarine Processes
http://ecowin.org/aulas/mega/pce

Light, dissolved oxygen

J. Gomes Ferreira
http://ecowin.org/

Universidade Nova de Lisboa

Radiation units

Illumination, energy, power density...

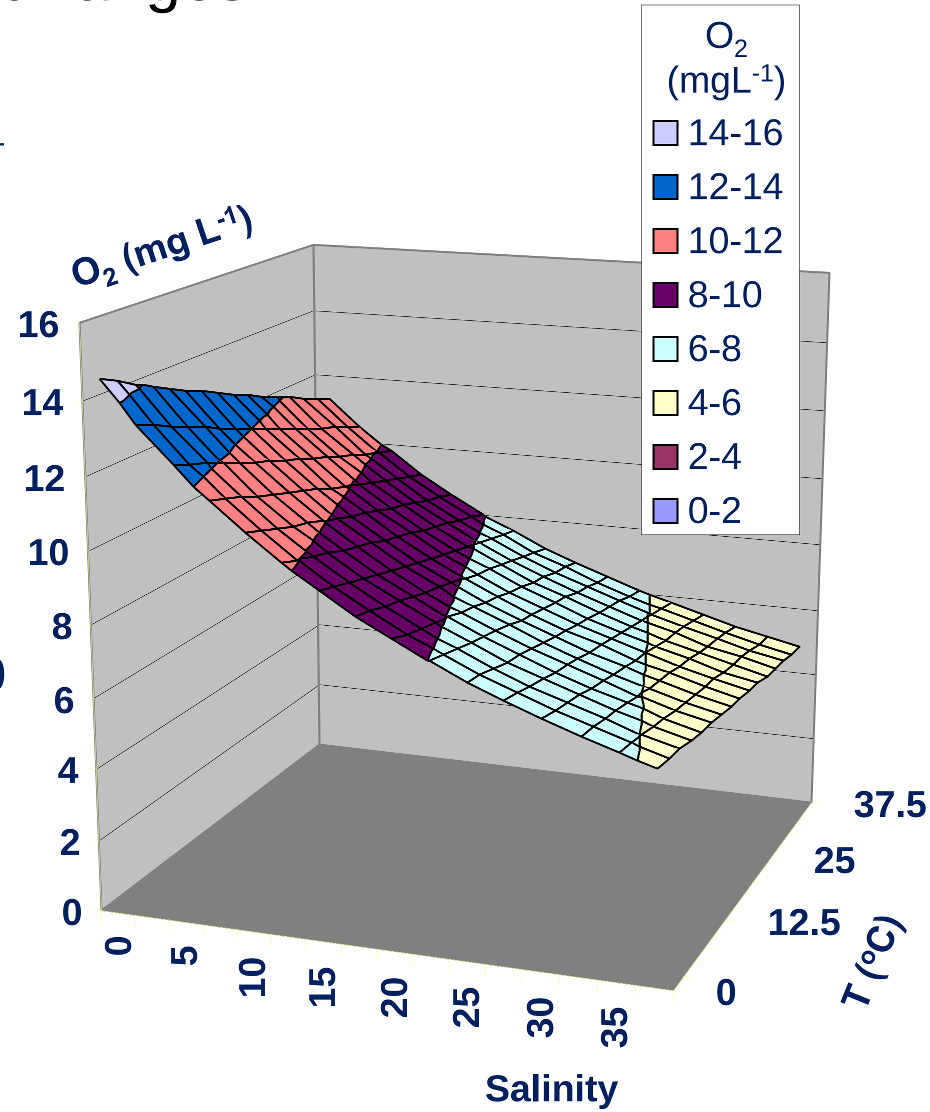
Unit	Conversion to	Type	Meaning/comments
lux (lx)	6 X 10^{-6} ly min-1		Light at sea surface
lux (lx)	1 IC m-2		Flux (illumination/time)
international candle (IC)			Illumination
langley	1 gcal cm-2	Energy/area	
Einstein (1 mol)	6.02 X 10^{23} quanta	Energy	
Einstein	52000 gcal		For λ=550 nm
gcal	4.185 Joule	Energy	
μE m-2 s-1		Power density	500-1500 at sea surface
W m-2	1 J s-1 m-2	Power density	200-600 at sea surface

Adapted from: Parsons, Takahashi & Hargrave, 1984. Biological Oceanographic Processes 3rd. Ed. & Jërlov - Light in the Sea

Dissolved oxygen in seawater

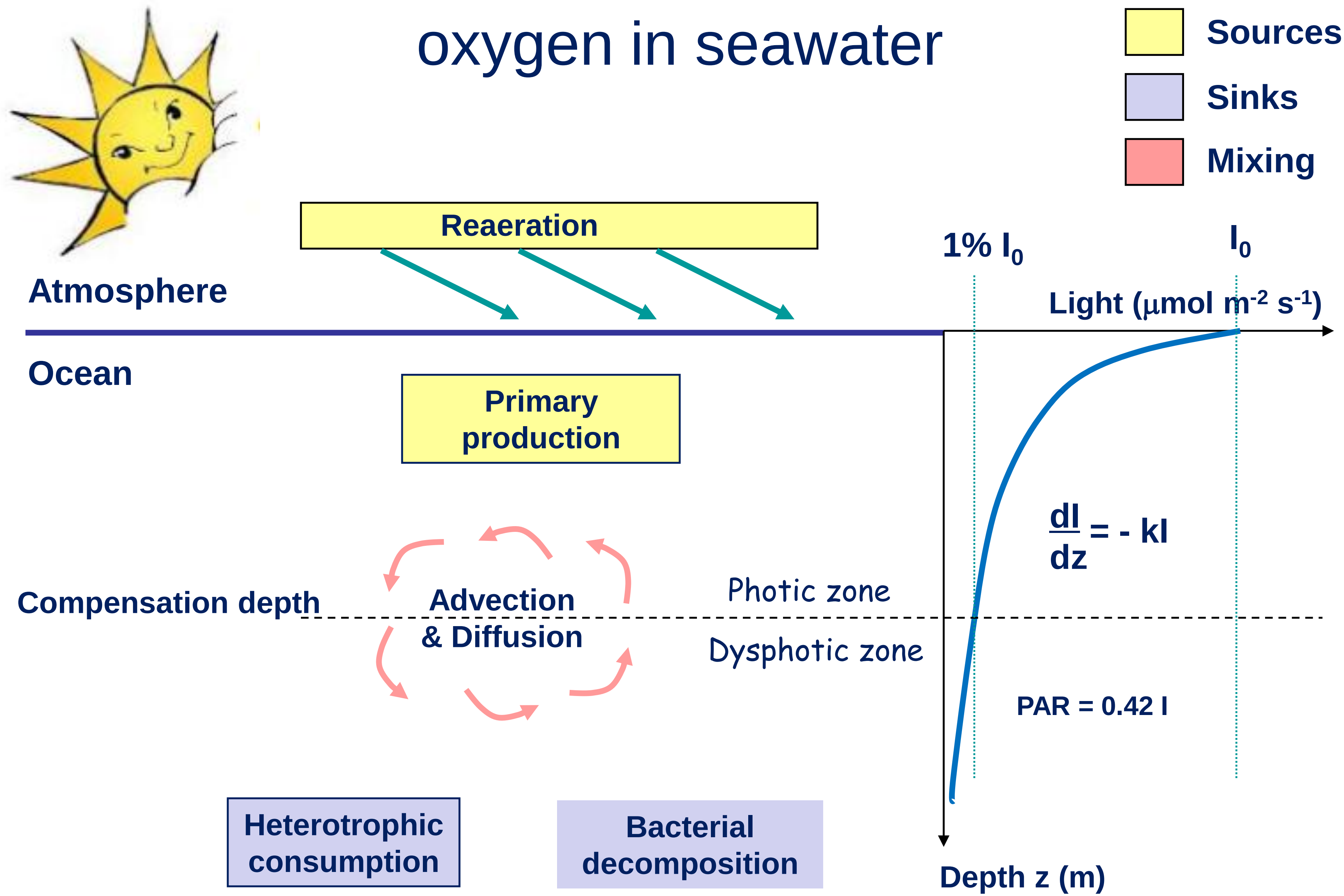
Units and ranges

- O_2 is usually measured in mg L^{-1} or ml L^{-1}
- Dissolved oxygen in seawater ranges from 0-10 mg L^{-1}
- The atomic mass of O_2 (32g) corresponds to 22.4 litres at STP, so 5 ml L^{-1} = 5 X 32/22.4 i.e. about 7 mg L^{-1}
- The maximum oxygen concentration in seawater (~ 7 ml L^{-1}) is therefore about 30 times lower than in air (200/7)
- The solubility of oxygen depends on the salinity and temperature of the water.



Dissolved oxygen is a critical limiting factor for life in seawater.

Sources and sinks of dissolved oxygen in seawater

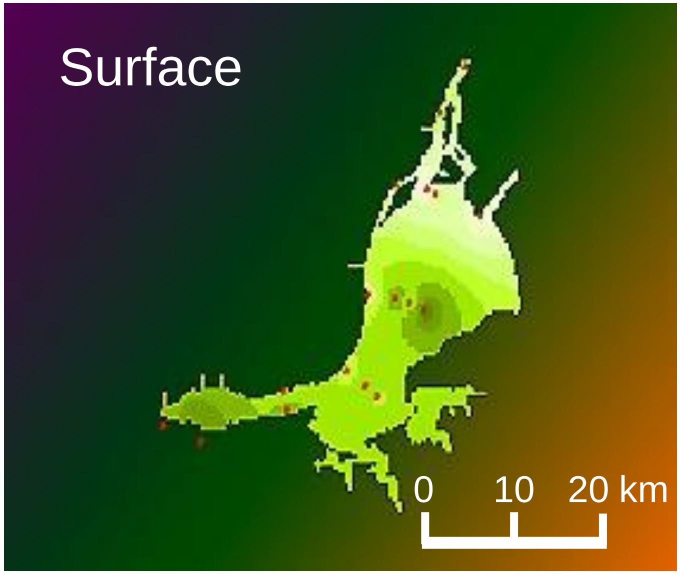


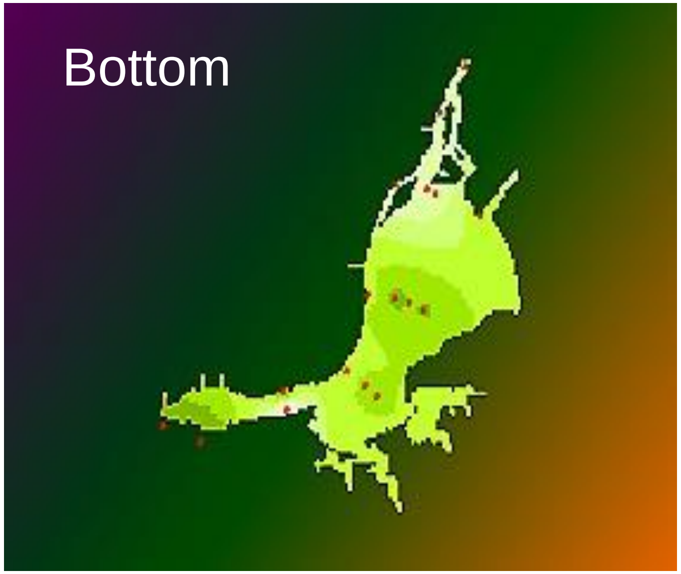
Oxygen is supplied in the mixed layer, deeper water is a net oxygen sink.

GIS – dissolved oxygen

Tagus Estuary

Summer





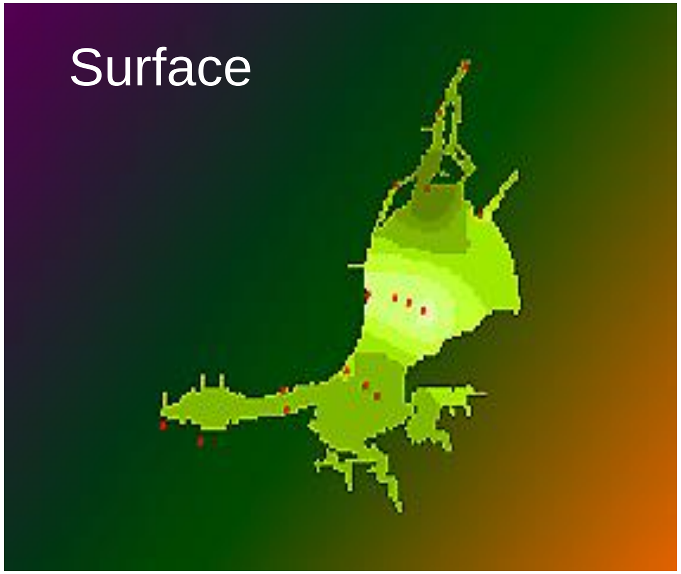
Summer D.O. (mg/l)

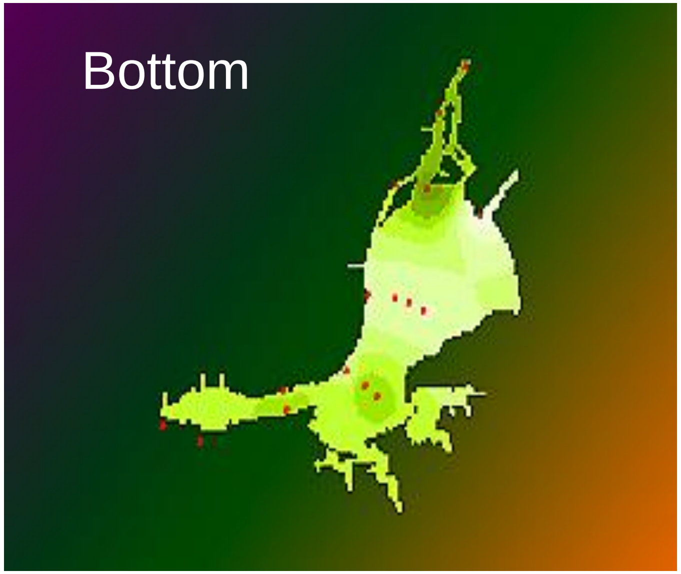
- 4.5 - 5
- 5 - 5.5
- 5.5 - 6
- 6 - 6.5
- 6.5 - 7
- 7 - 7.5
- 7.5 - 8
- 8 - 8.5
- 8.5 - 9
- No Data

Winter D.O. (mg/l)

- 5.5 - 6
- 6 - 6.5
- 6.5 - 7
- 7 - 7.5
- 7.5 - 8
- 8 - 8.5
- 8.5 - 9.5
- 9.5 - 10.5
- 10.5 - 14
- No Data

Winter

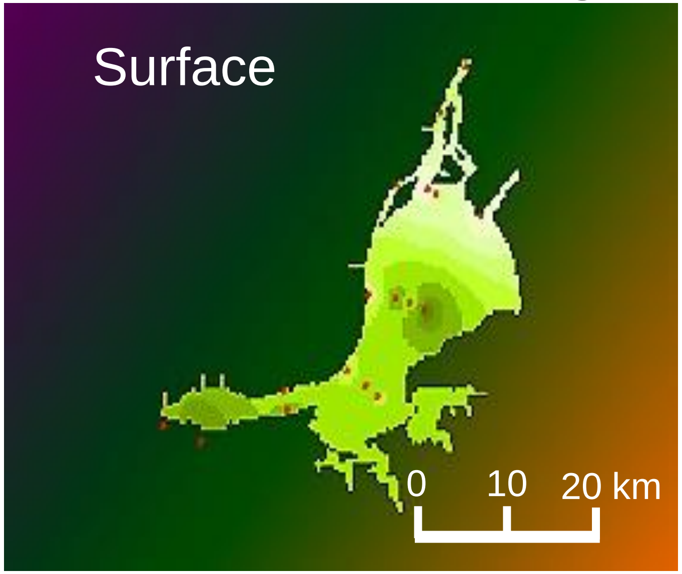


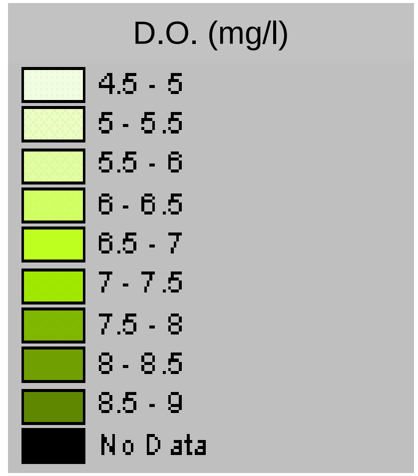


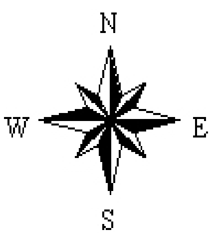
The estuary does not show significant oxygen problems.

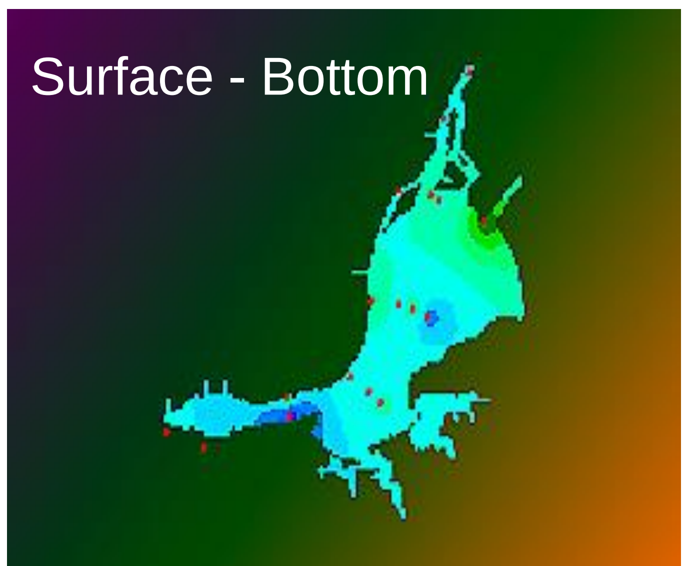
GIS – dissolved oxygen

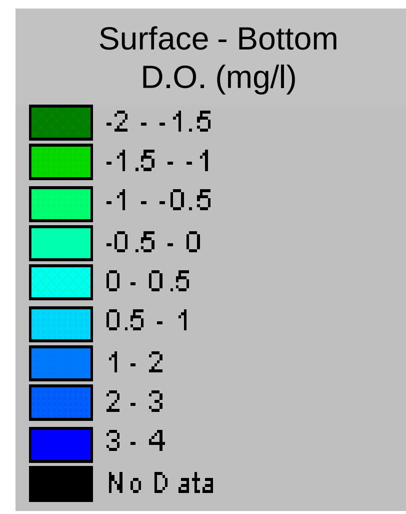
Tagus Estuary - summer







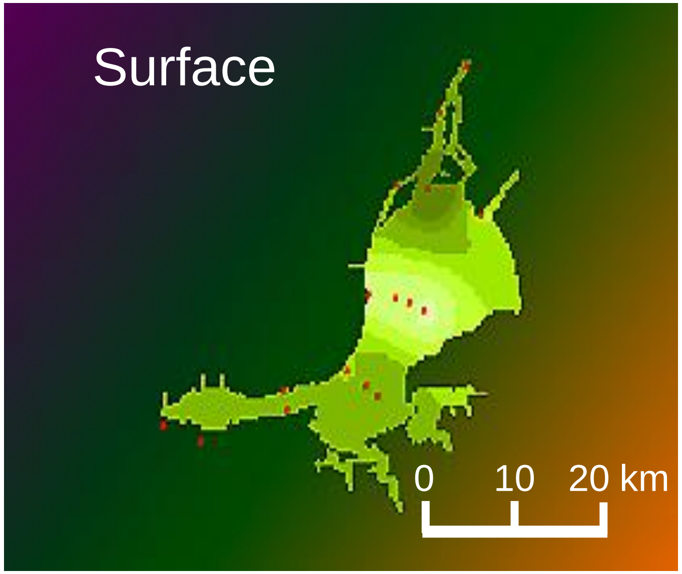




In summer, the estuary does not show vertical stratification.

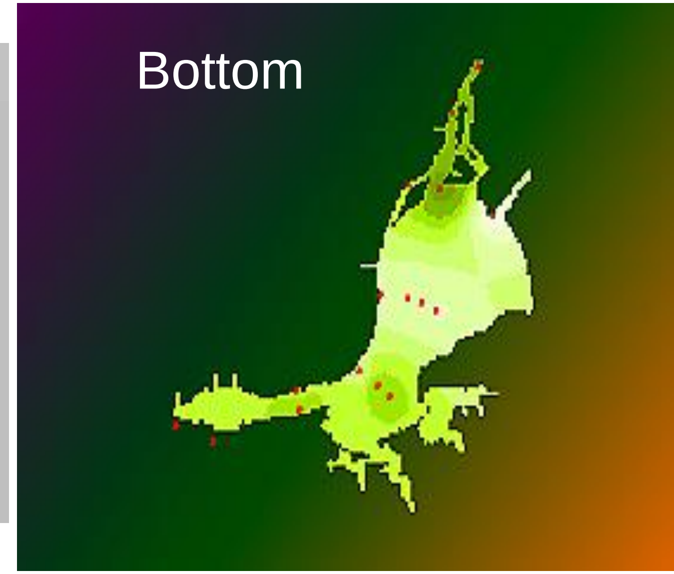
GIS – dissolved oxygen

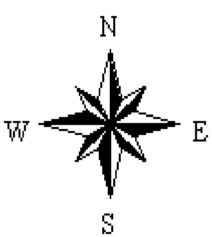
Tagus Estuary - winter

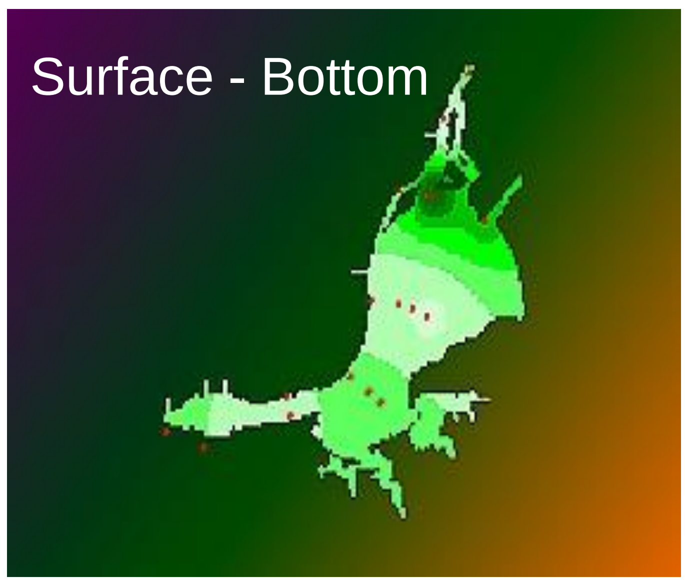


D.O. (mg/l)

- 5.5 - 6
- 6 - 6.5
- 6.5 - 7
- 7 - 7.5
- 7.5 - 8
- 8 - 8.5
- 8.5 - 9.5
- 9.5 - 10.5
- 10.5 - 14
- No Data







Surface - Bottom D.O. (mg/l)

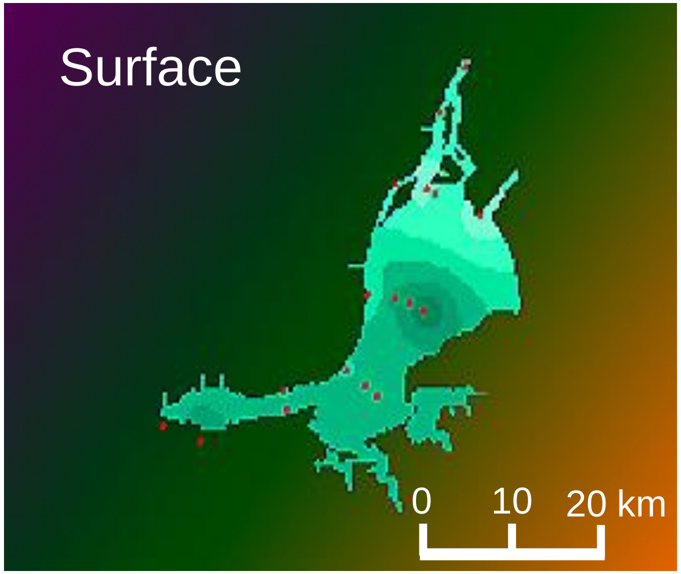
- 0 - 0.25
- 0.25 - 0.5
- 0.5 - 1
- 1 - 1.5
- 1.5 - 2
- 2 - 2.5
- 2.5 - 3
- 3 - 3.5
- 3.5 - 4
- No Data

In winter, vertical stratification is more evident, with lower bottom water D.O.

GIS – oxygen saturation

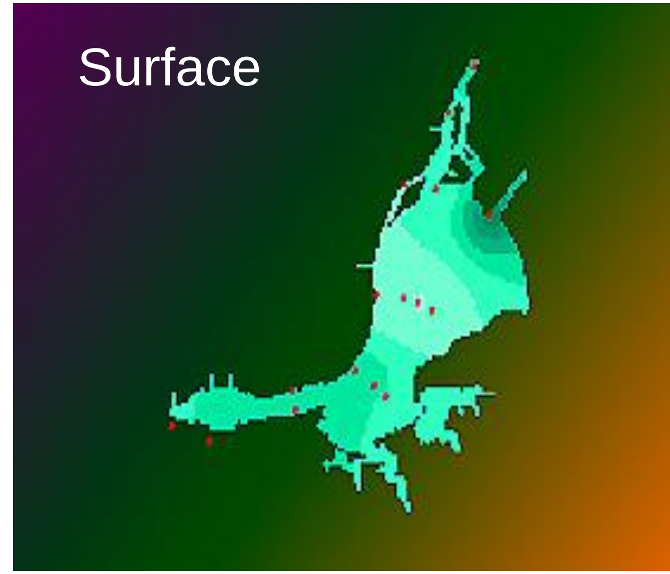
Tagus Estuary

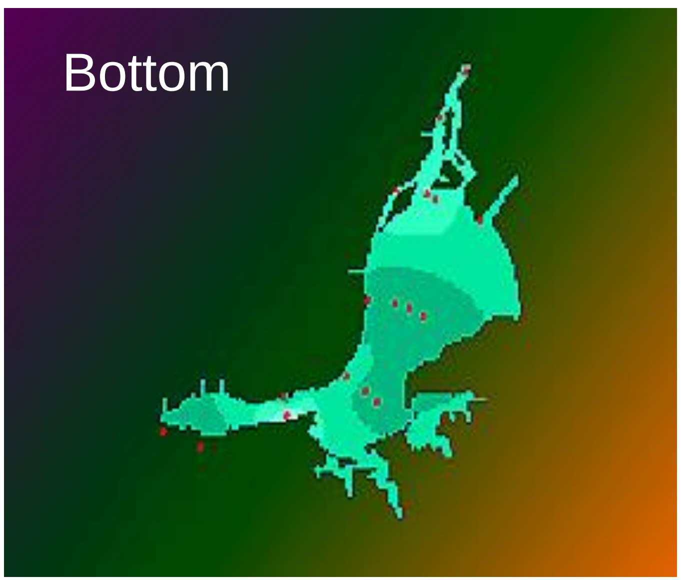
Summer | **Winter**



Summer Oxygen Sat (%)

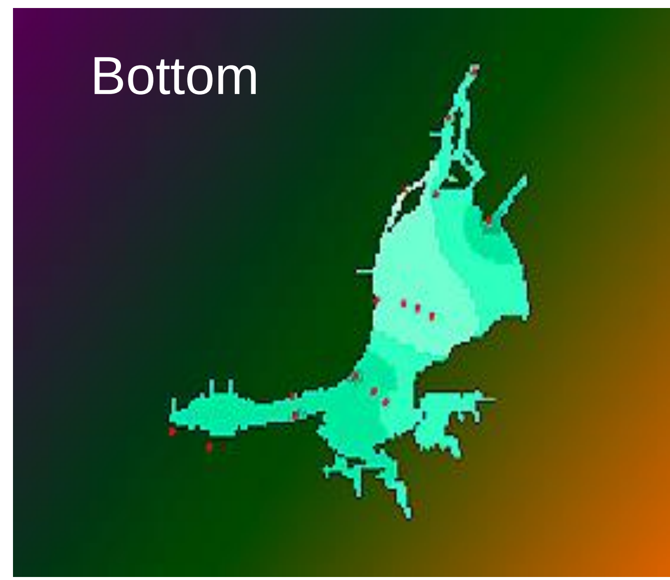
- 0 - 50
- 50 - 60
- 60 - 70
- 70 - 80
- 80 - 90
- 90 - 100
- 100 - 110
- 110 - 120
- 120 - 130
- No Data





Winter Oxygen Sat (%)

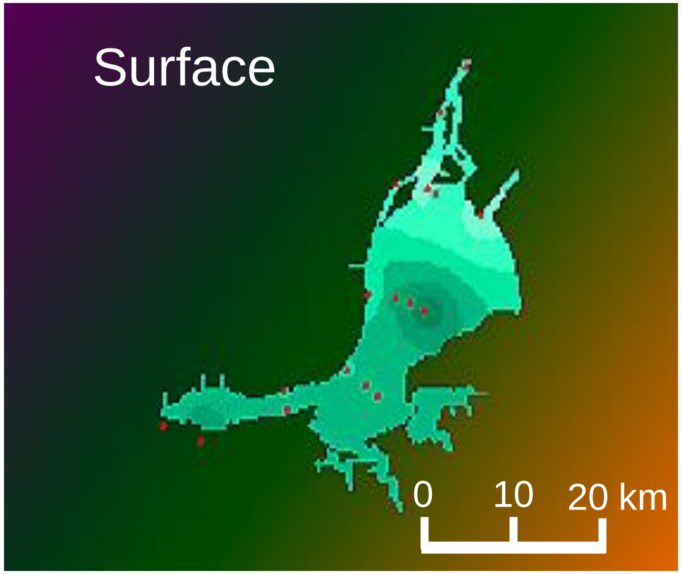
- 0 - 50
- 50 - 60
- 60 - 70
- 70 - 80
- 80 - 90
- 90 - 100
- 100 - 110
- 110 - 120
- 120 - 130
- No Data



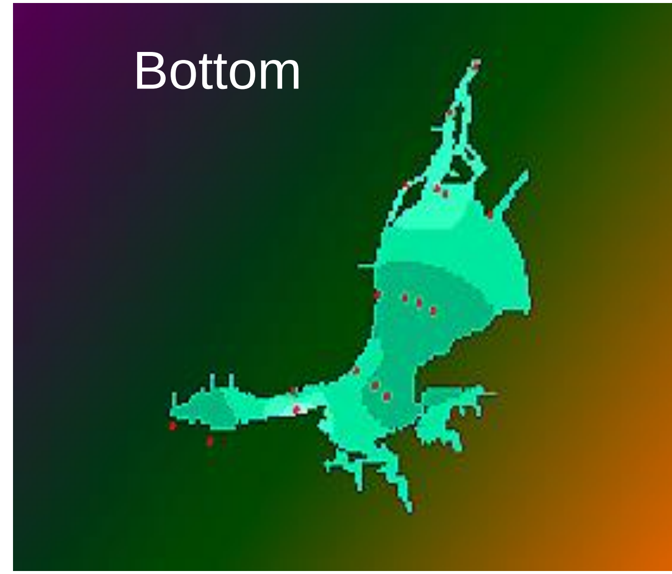
Oxygen saturation in the estuary is generally above 70%.

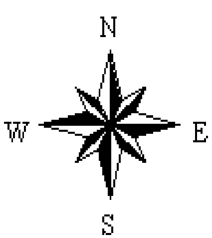
GIS – dissolved oxygen

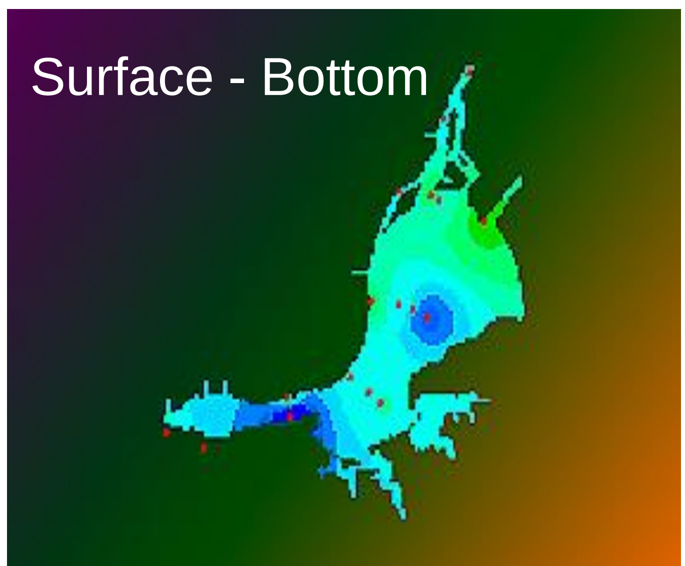
Tagus Estuary - summer



Oxygen Sat (%)
0 - 50
50 - 60
60 - 70
70 - 80
80 - 90
90 - 100
100 - 110
110 - 120
120 - 130
No Data



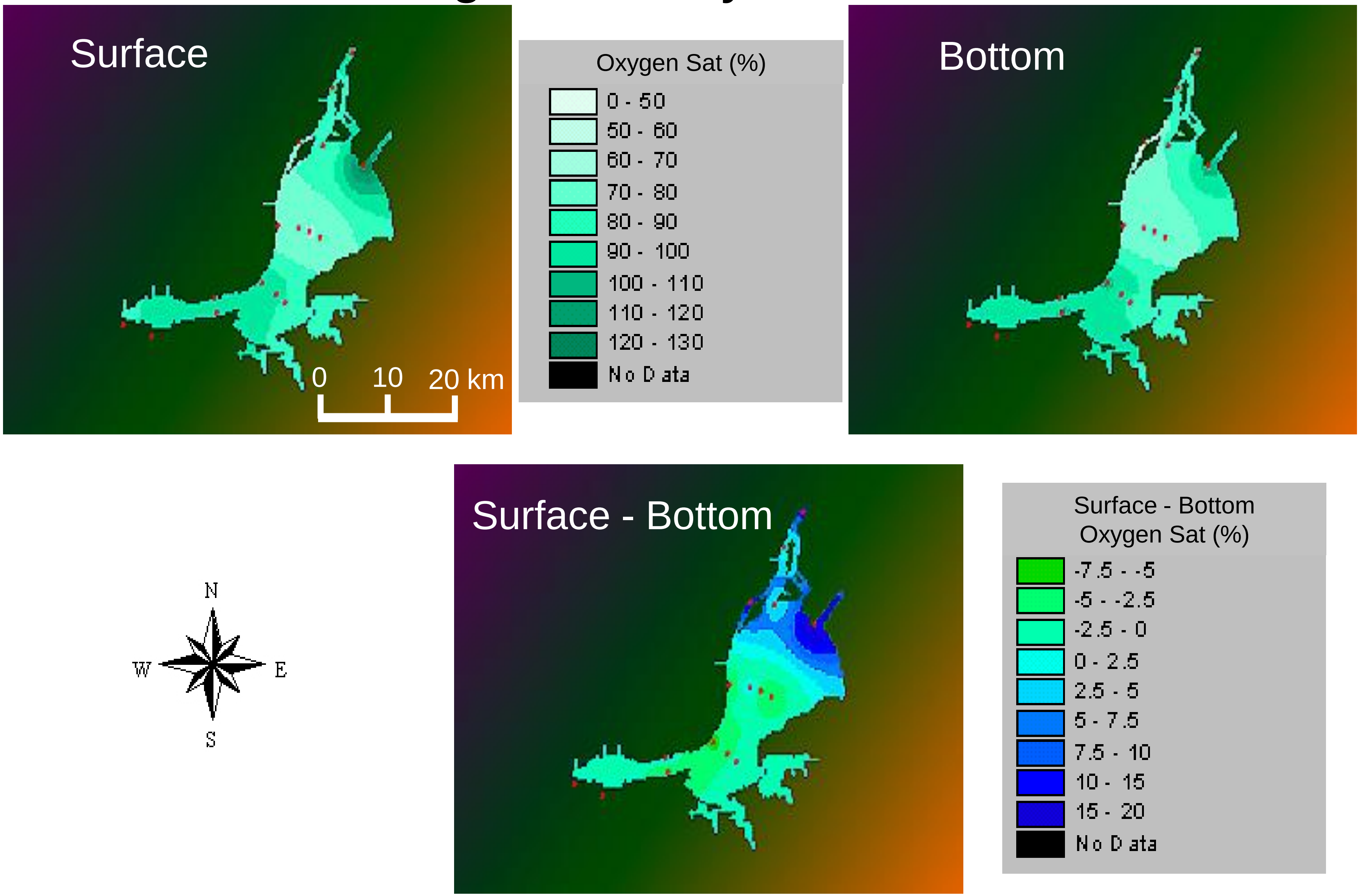




Surface - Bottom Oxygen Sat (%)
-25 - -15
-15 - -5
-5 - 0
0 - 5
5 - 10
10 - 15
15 - 20
20 - 30
30 - 45
No Data

There is no difference in oxygen saturation except in hotspots like the Sorraia.

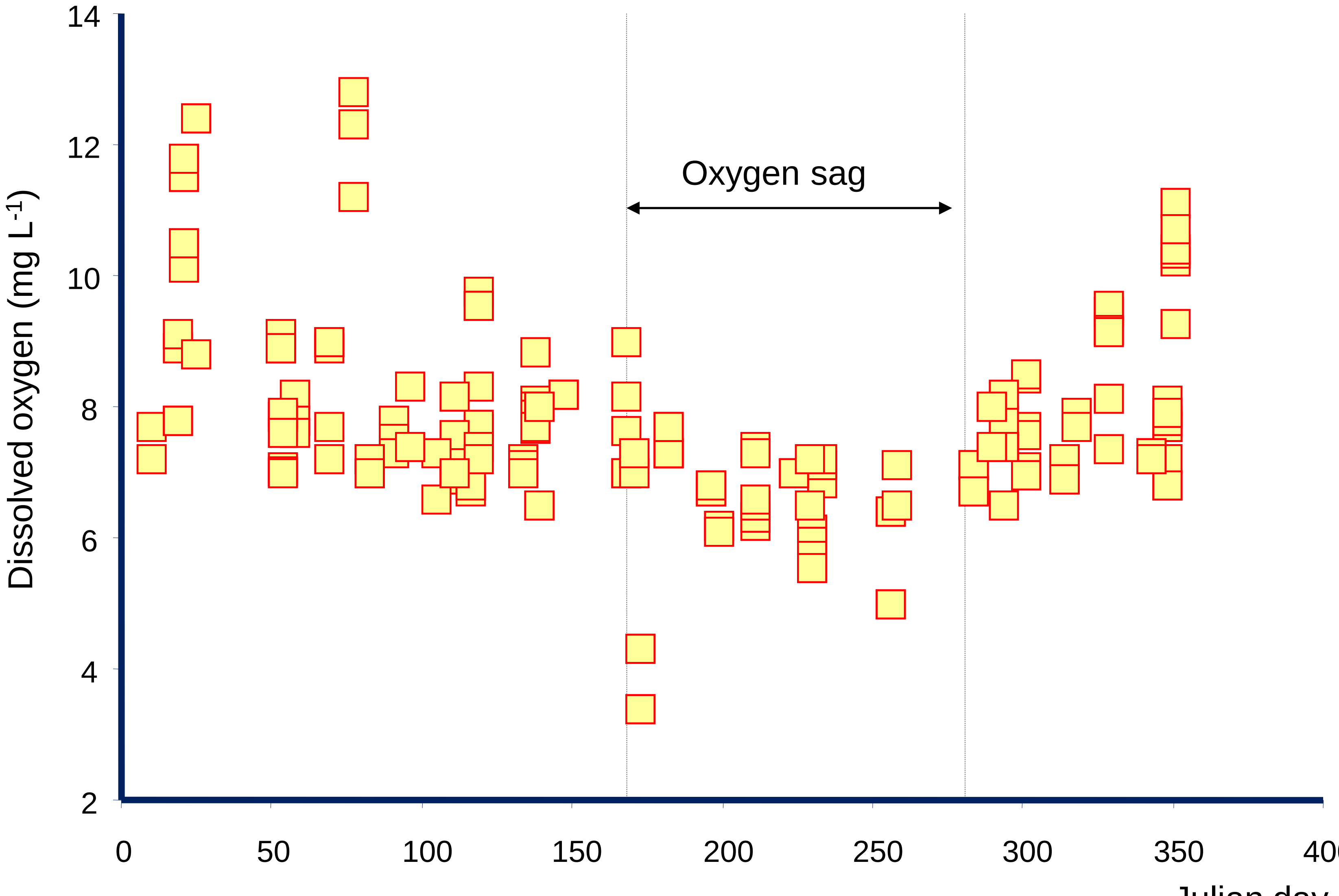
GIS – dissolved oxygen
Tagus Estuary - winter



The upper part of the estuary shows significant differences in winter.

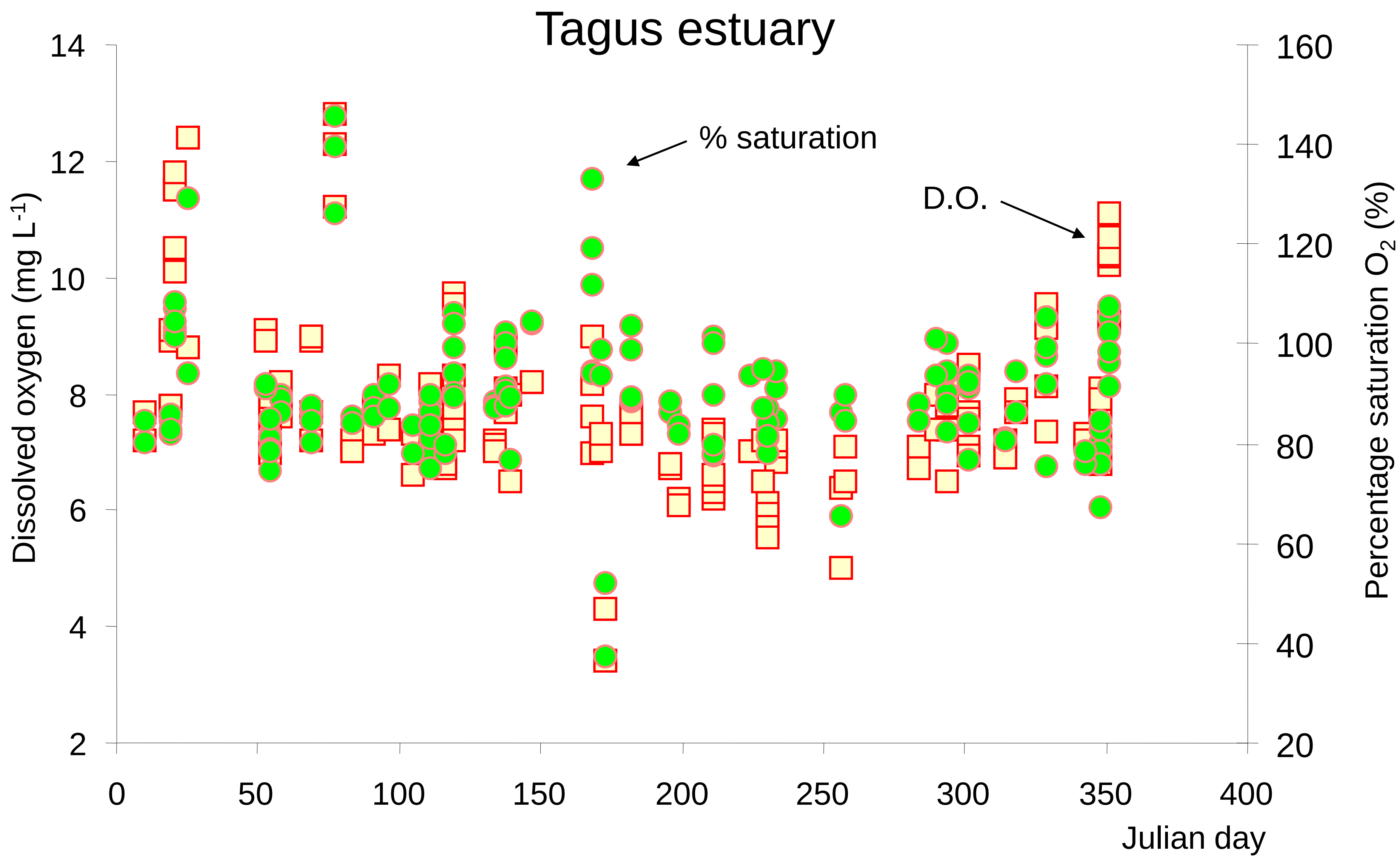
Dissolved oxygen in the maximum turbidity zone

Tagus estuary



There appears to be a clear sag in summer dissolved oxygen – is this pollution?

Dissolved oxygen and percentage saturation in the maximum turbidity zone



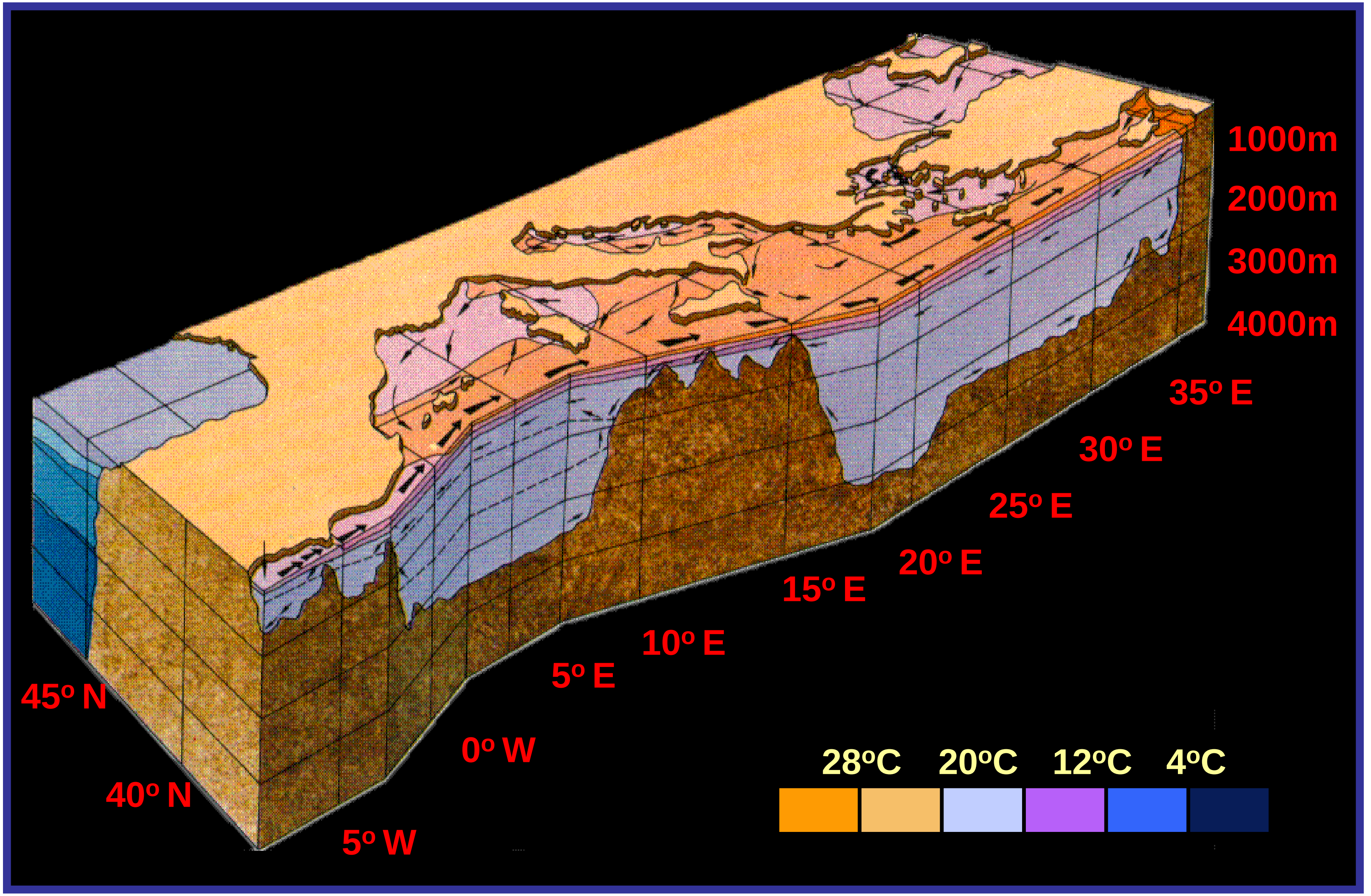
The effect of pollution seems to have disappeared.

Case study- natural "pollution"

Hypoxia in the Black Sea

http://www.ancientrade.com/

Mediterranean Sea- Circulation



Two major deep basins, increasingly saline and oligotrophic.

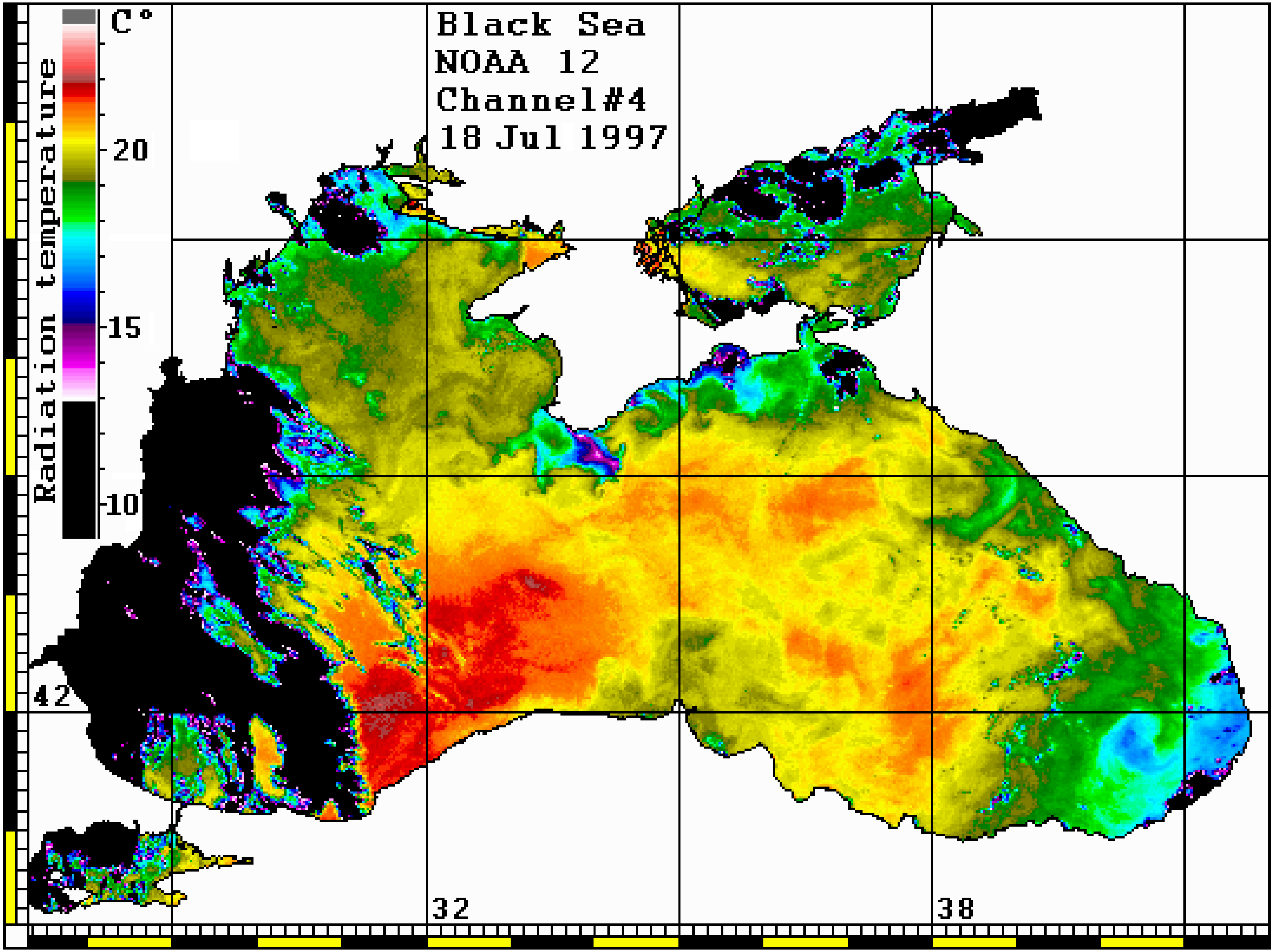
Black Sea – Circulation
Freshwater input from the NW coast

Name	Catchment area km^2	Length km	Total runoff $km^3\ y^{-1}$	Total runoff $m^3\ s^{-1}$	Sediment discharge $10^6\ t\ y^{-1}$
Danube	817000	2860	208	6596	51.7
Dnieper	505810	2285	51.2	1624	2.12
Dniester	71990	1328	10.2	323	2.5
Southern Bug	68000	857	3	95	0.53
Chorokh	22000	500	8.69	276	15.13
Rioni	13300	228	12.8	406	7.08
Inguri	4060	221	4.63	147	2.78
Kodori	2030	84	4.08	129	1.01
Bzyb	1410	-	3.07	97	0.6
Yesilrmak	-	416	4.93	156	18
Kizilrmak	-	1151	5.02	159	16
Sakarya	-	790	6.38	202	-
Total	1505600	8363	306	9693	83

http://www.grid.unep.ch/

Three major rivers, including the largest European river (runoff: 15X Tagus).

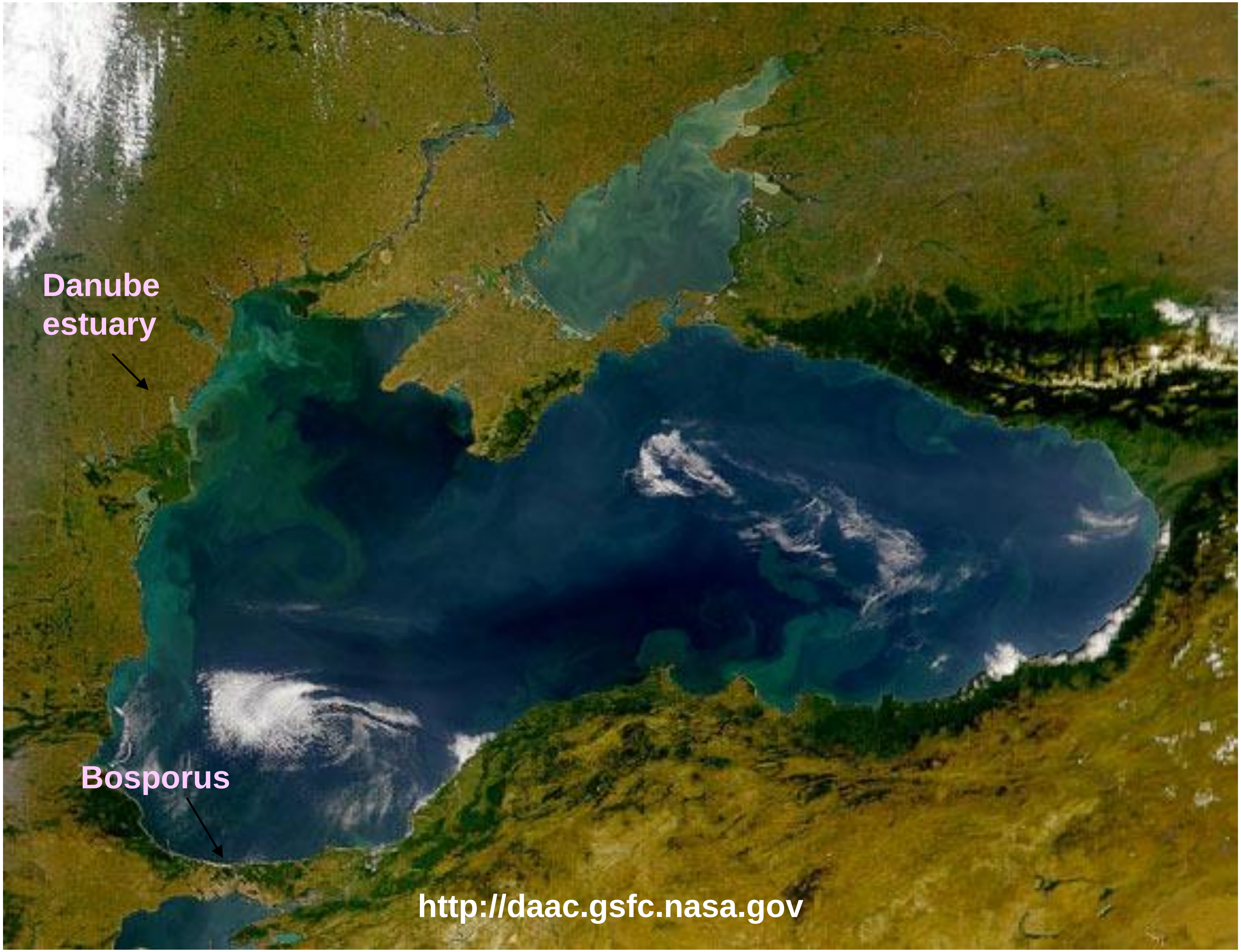
Black Sea – surface temperatures



http://www.grid.unep.ch/

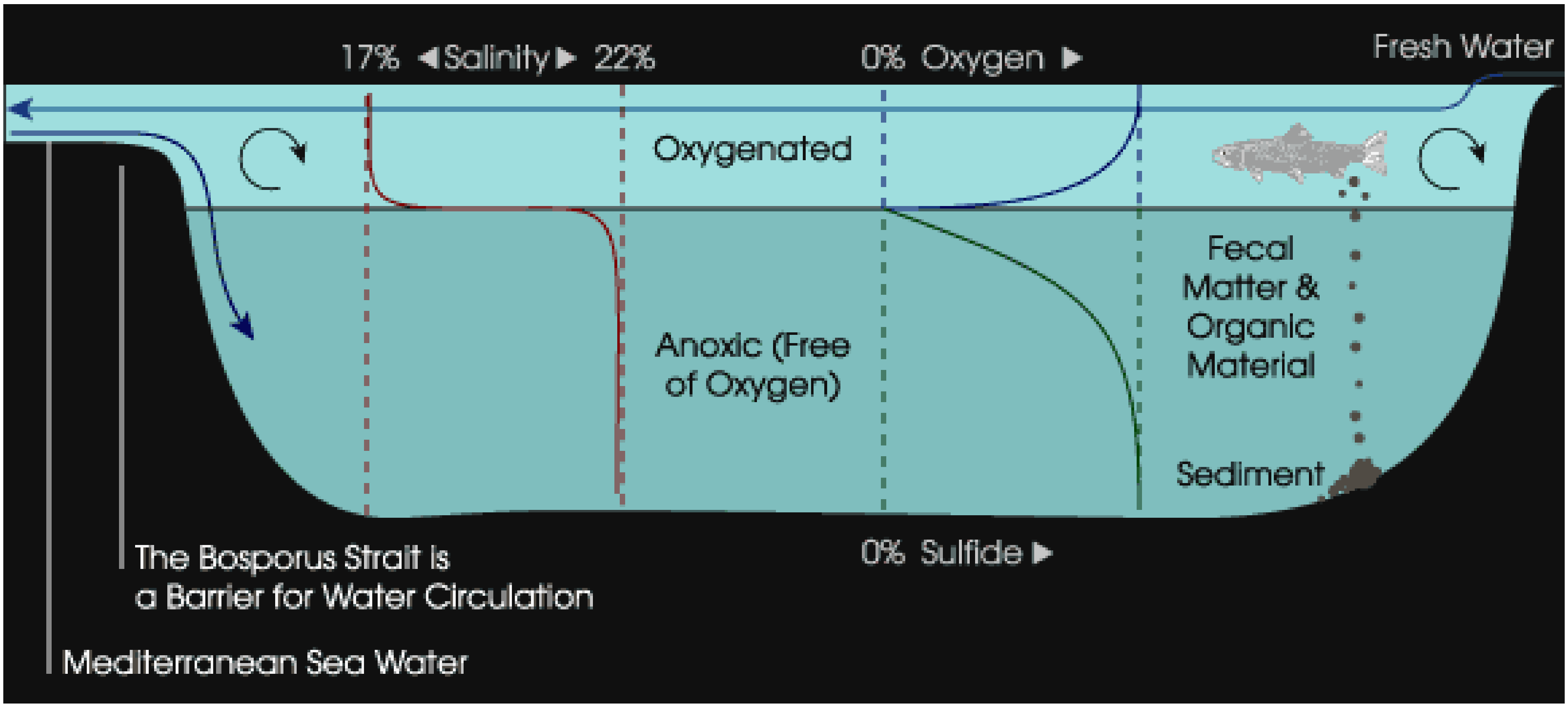
High temperatures in the summer limit the oxygen concentration of the surface layer.

Black Sea – Coccolith blooms (SeaWifs)



These turquoise-coloured blooms can account for 90% of the phytoplankton biomass.

Black Sea – circulation and stratification



http://daac.gsfc.nasa.gov/

High concentrations of sulphide in the anoxic bottom waters.

Consequences

- Brackish, oxygenated mixed layer
- Saline, hypoxic deep water (same occurs in fjords)
- Elevated concentrations of sulphide in deep water
- Overturn events deplete dissolve oxygen from mixed layer and cause fish kills
- Dead animals increase organic decomposition and depletion of dissolved oxygen, a positive feedback cycle of pollution
- This is an example of natural “pollution”

Understand more about simulating dissolved oxygen using an online model:
http://insightmaker.com/insight/9381

Coastal and Estuarine Processes
http://ecowin.org/aulas/mega/pce

Carbon

J. Gomes Ferreira
http://ecowin.org/

Universidade Nova de Lisboa

Distribution of carbon on the planet

Reservoir	gC X 10^{20}
Atmosphere (1973)	0.00675
Ocean	
Inorganic carbon	0.38
Organic carbon (live)	0.01
Detritus	0.0129
Land	
Organisms	0.0164
Organic C (sedimentary rock)	68.2
Calcareous rock	183

Ocean holds 60X more carbon than the atmosphere.
Most carbon is only mobile on a geological (not ecological) time scale.

Carbon transport to the ocean

Source	gC y^{-1} X 10^{14}	%
Primary prod. (phytoplankton)	200 - 360	98.9
Rivers and streams	3 - 3.2	1.1
Groundwater	0.8	0.3
Aerosols, volatile compounds	1.5 - 4	0.6
From plants		
Hydrocarbons (oil)	0.046	0.017

After Handa (1977), Duce & Duursma (1977) & Farrington (1980)
In Valiela, I., Marine Ecological Processes

Phytoplankton is the elephant in the room.

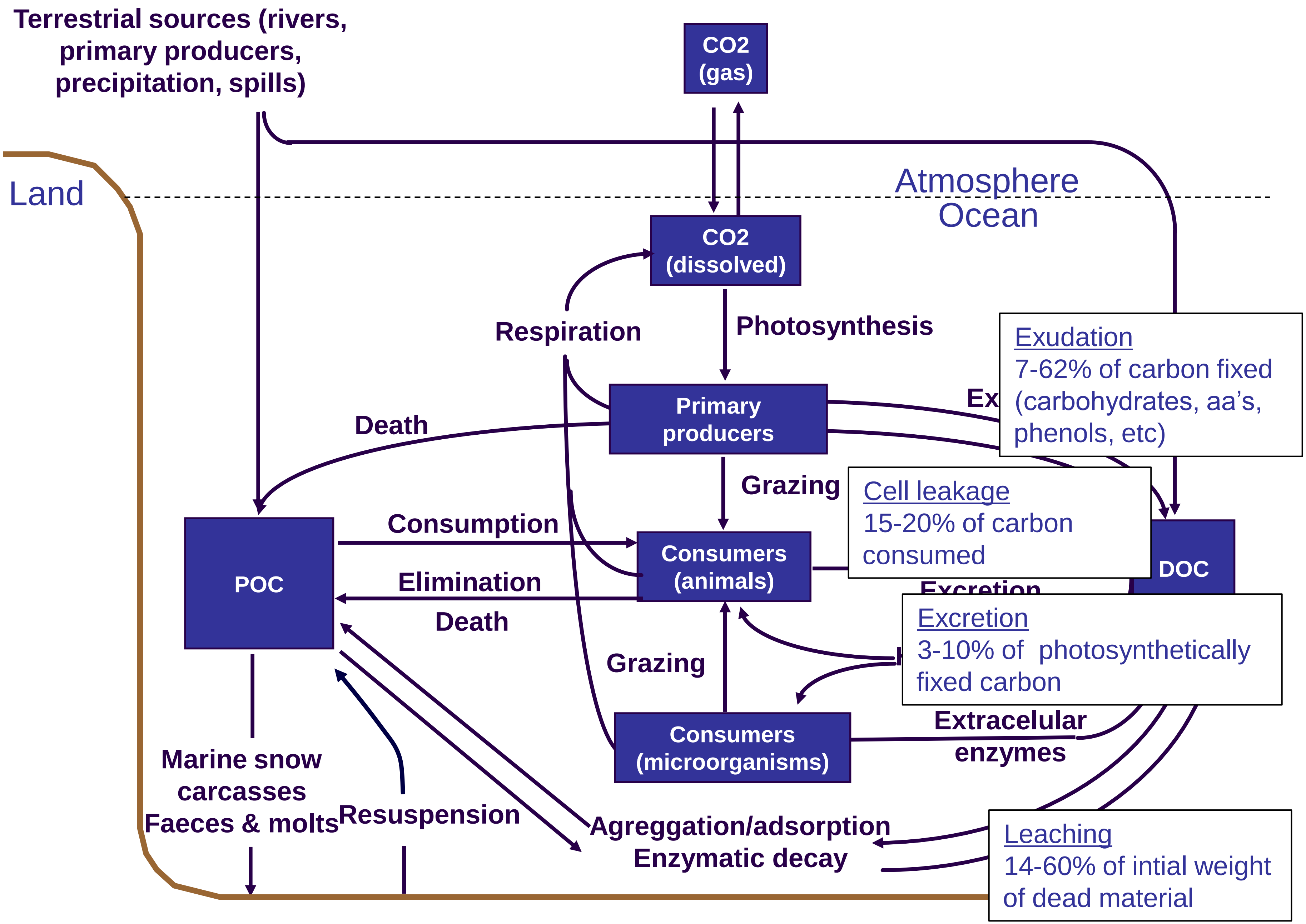
Distribution of Particulate Organic Matter

Data from various authors, in Valiela, Marine Ecological Processes

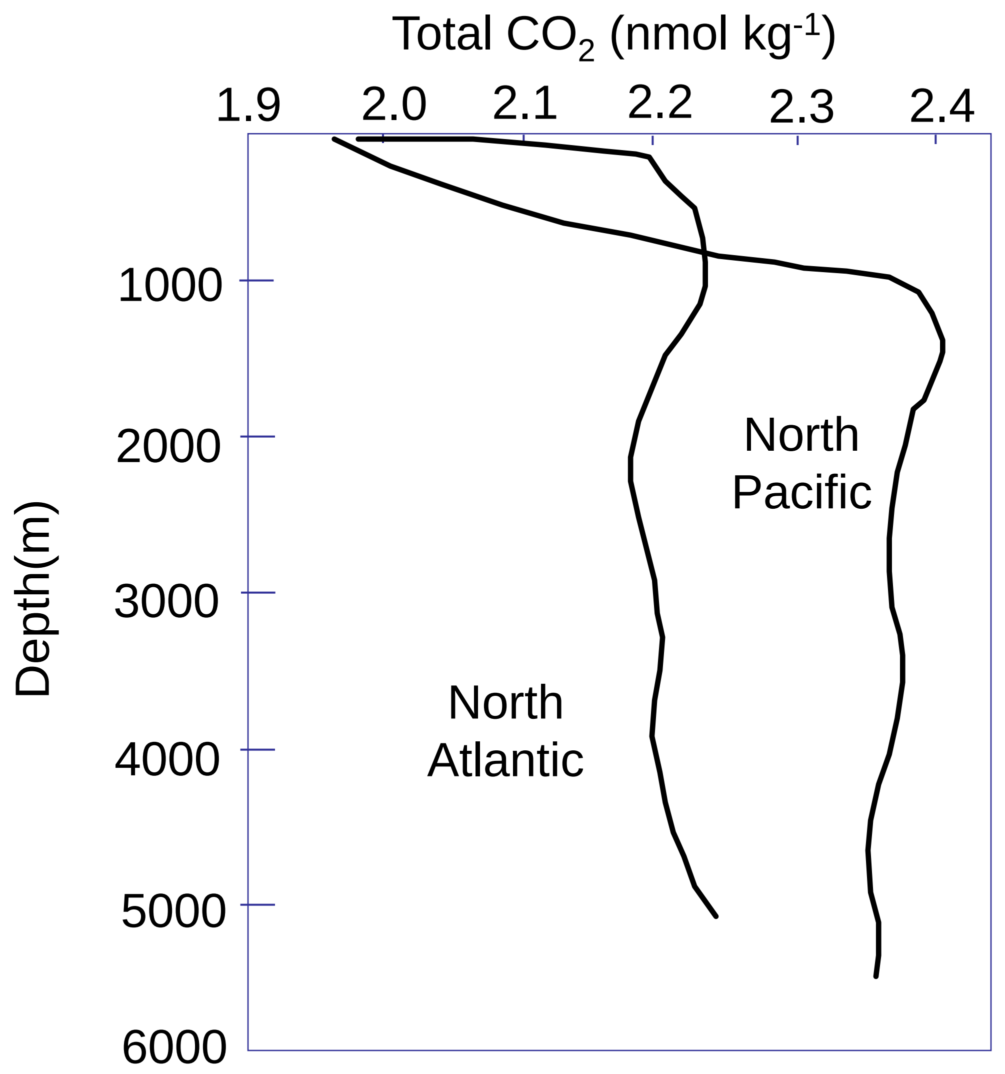
	Particulate organic matter ($\mu gC\ l^{-1}$)	% total POM			
		Phytoplankton	Zooplankton	Bacteria	Detritus
Sea of Azov	750-1500	5-10	3-10	0.3-7	80-92
Arabian Sea	100-250	1-31			
Black Sea	200-250	0.2-1	5-20	0.4	78-95
Tropical Atlantic					
15o meridian	450-600	0.5-1.3	0.6		98-99
16o parallel	100-250	0.6-1.3	0.7		98-99
Upwelling (South Africa)	70-900	30-43	4-14		9-14
Hudson estuary	660-2250	2-72			40-93
New York Bight	200-840	12-51			38-90
Baltic (western)	492-505	23-27	33-35		41-43
Chesapeake Bay	11.5-84	23			77
English Channel	950-2500	15-17			
Aberdeen Bay	200-3400	8-10			
Wadden Sea	1000-4000	10-25			
Akeshi Bay		9.7	1.7		

Much of the POM in the ocean is detritus, and we don’t know much about bacteria.

Carbon cycle in the marine environment



Carbon cycle in the marine environment



Adapted from GEOSECS atlas - vols. 2 & 4

The biological carbon pump transports CO_2 to the deep ocean. Higher concentrations in the Pacific reflect longer water residence time.

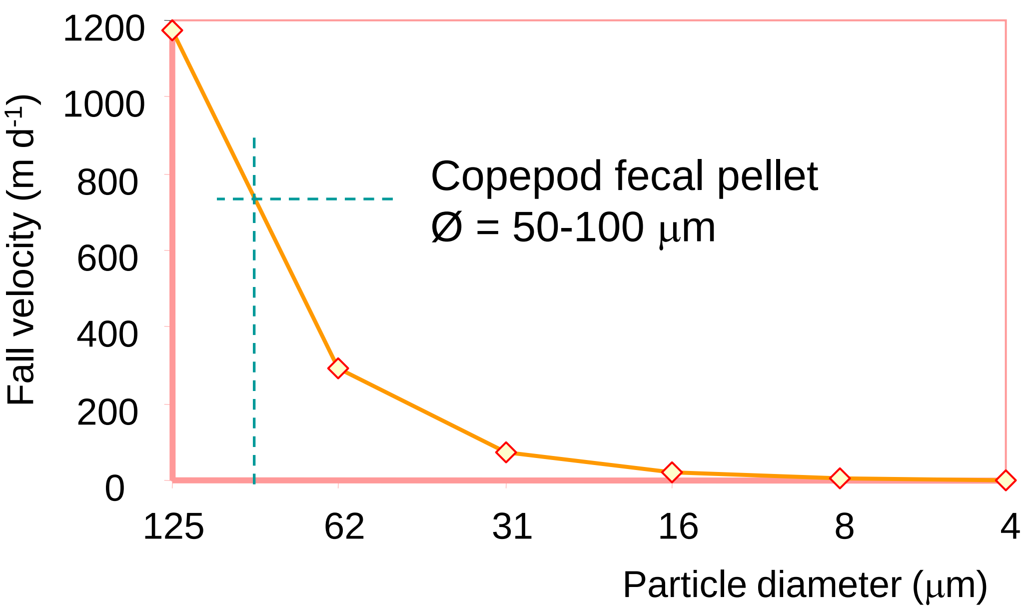
Sediment traps
Different designs, same idea

http://jpac.whoi.edu/atsea/instrument.html

Sediment traps

- Capture larger particles (faecal pellets, etc) which fall at a rate of hundreds of metres per day
- Should not be placed too near the bottom (resuspension) or too

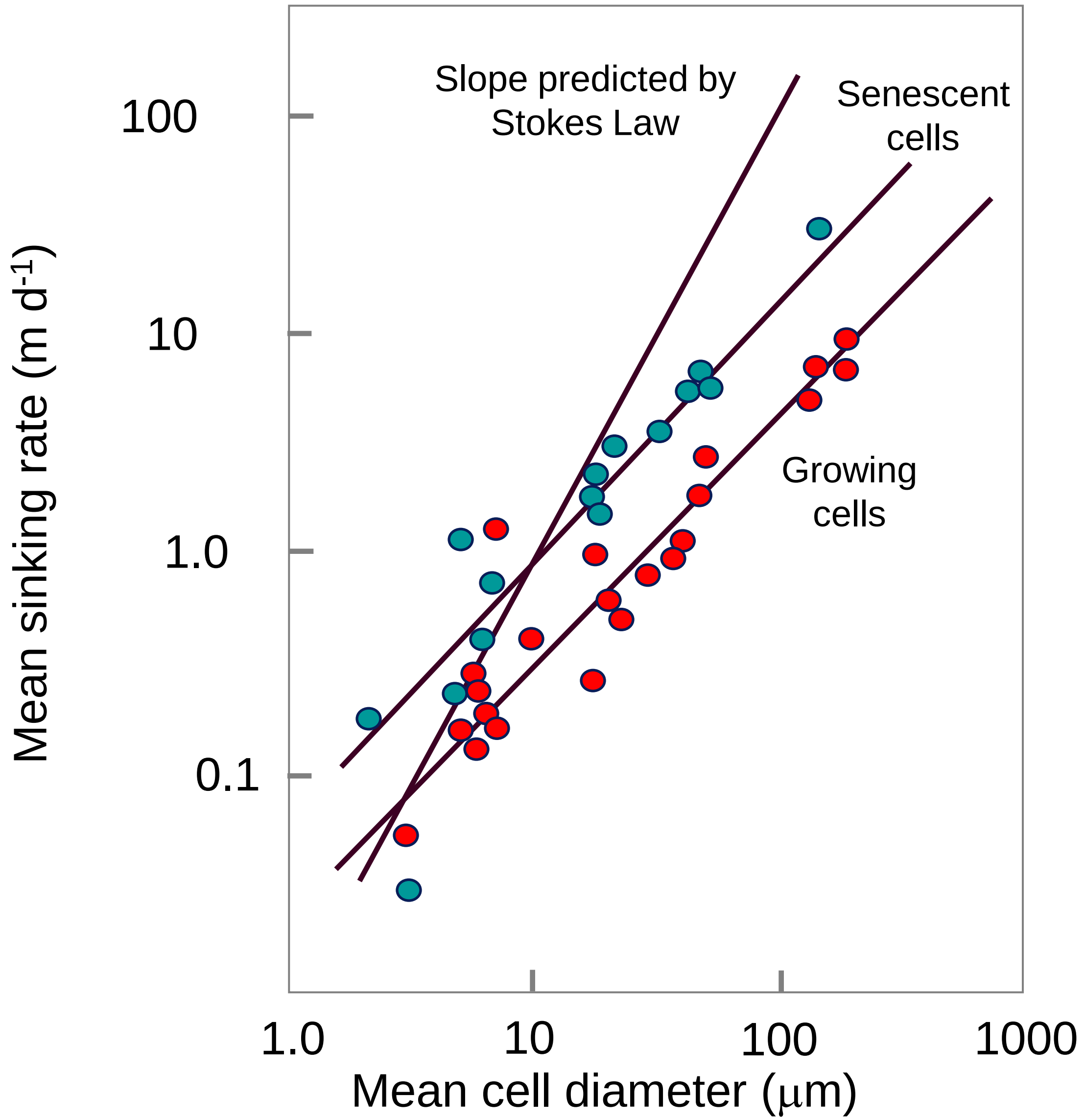
near the surface (mixing)
- May be scavenged by deep-sea organisms
- "Inhibitors" may be added to reduce this effect



- Isotopic markers may be used to identify particle sources, using fallout tracers and other approaches

Marine snow is the mechanism which accounts for rapid transport of organic material to the deep sea and benthos.

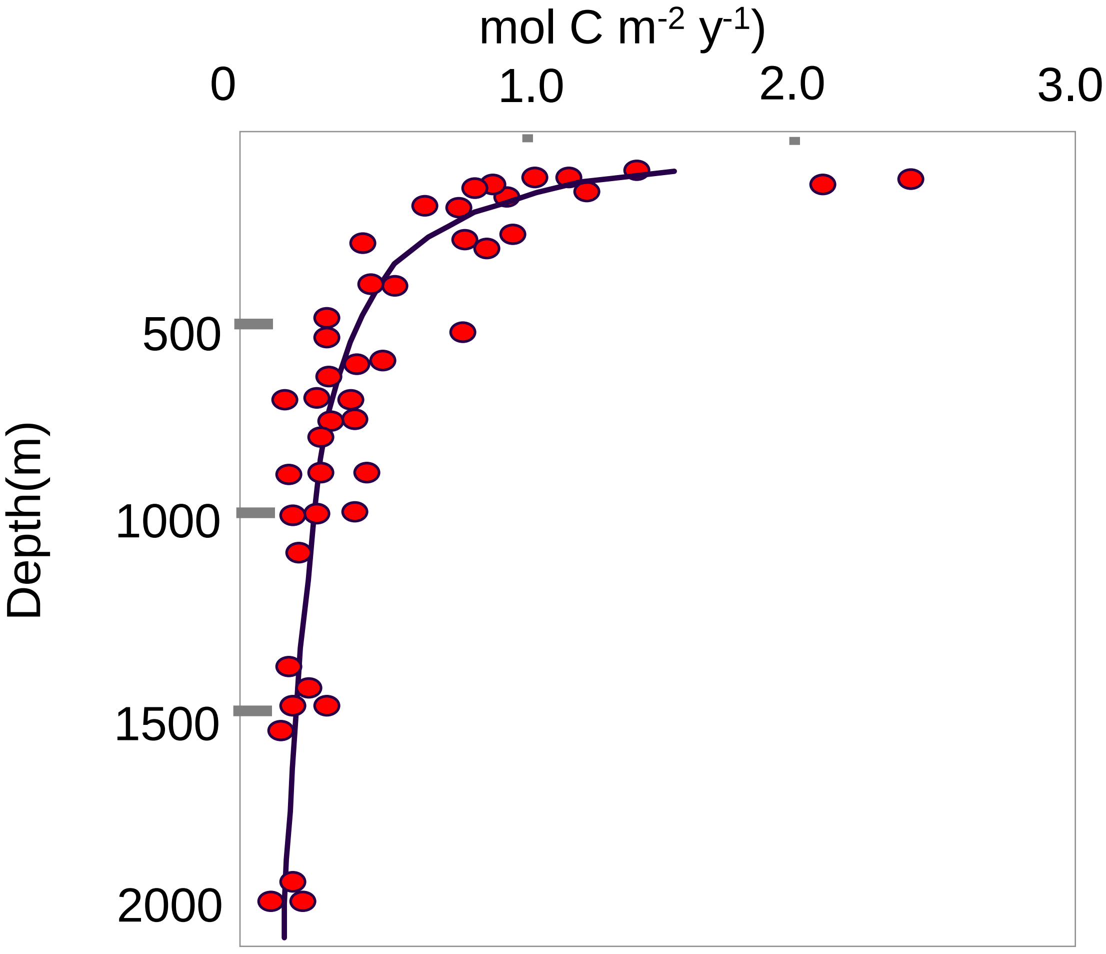
Relationship between cell diameter and sinking rate



Smayda, T.J., 1970 - Oceanogr. Mar. Biol. Ann. Rev. 8, 353-414

Living cells sink slower than dead ones.

Vertical carbon flux in the northeast Pacific



Results from 6 stations, obtained through sediment traps.
Martin et al., 1987, Deep Sea Res. 34, 267-285

Flux is highest in the mixed layer, where organic production occurs.

Sedimentation of POC

Ecosystem	POC flux from surface waters (mgC m^{-2} d^{-1})	% primary production (%)	% benthic respiration (%)
Low productivity			
Equatorial Atlantic	6.8	0.8 (5000 m)	133-667
NW Atlantic	5.5-16.5	4-6 (~3000 m)	-
Oligotrophic gyres	1.6	6.2	-
High productivity			
Peru upwelling	533	10 (50m)	-
New York Bight	299	59	-
Coastal waters	37-168	30-46	-

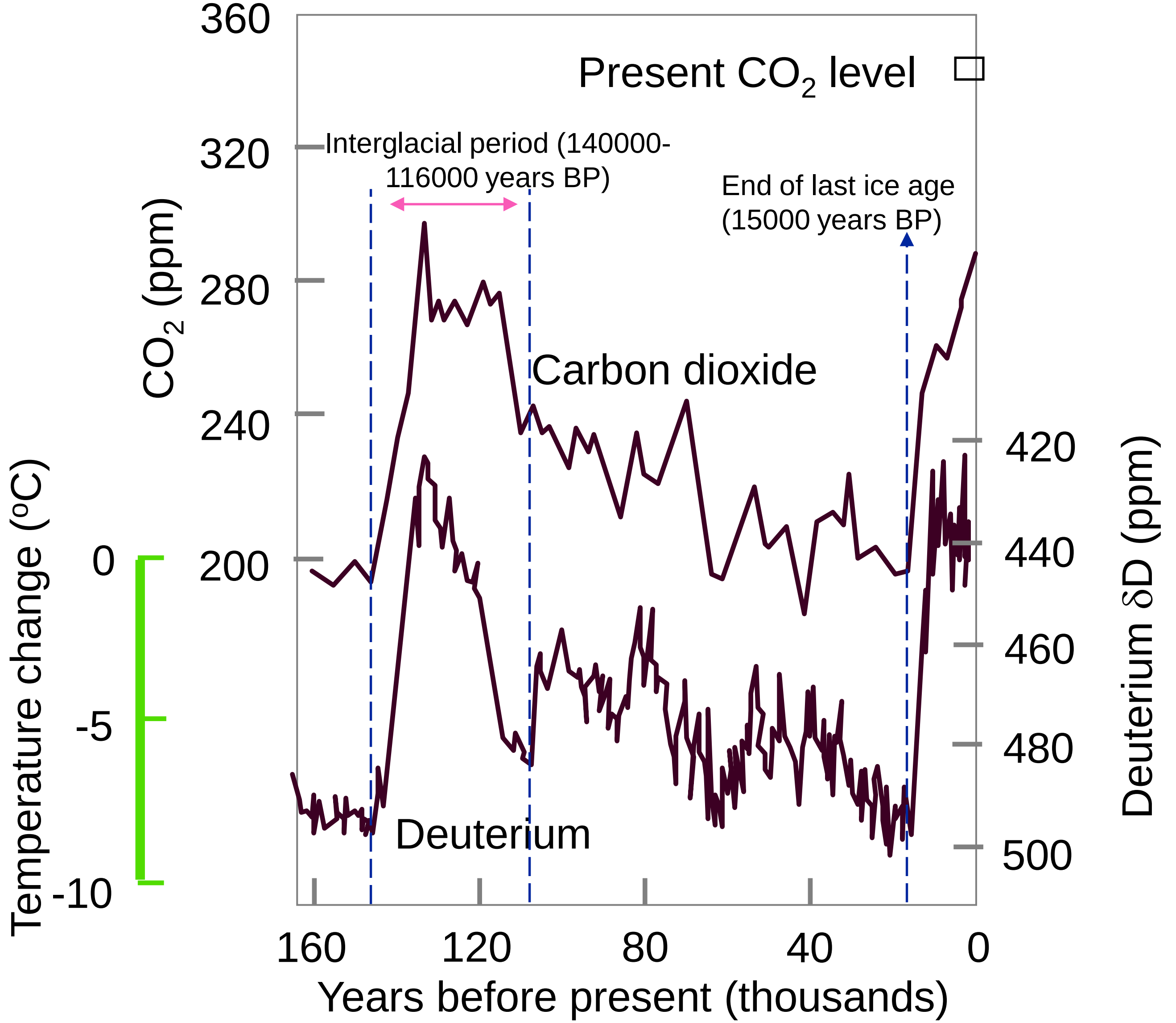
Various authors, In Valiela, I., Marine Ecological Processes, 1984 - Springer-Verlag

Aquatic photosynthesis and sedimentation of organic carbon

Region	Area (km^2)	Net primary production ($x10^{12}$ kgC yr^{-1})	Sediment organic carbon sink ($x10^{12}$ kgC yr^{-1})
Open ocean	3.1×10^8	18.6	0.19
Continental shelf	2.7×10^7	5.40	0
Continental slope	3.2×10^7	2.24	0.50
Fresh water marshes	1.6×10^6	1.51	0.15
Estuaries and deltas	1.4×10^6	0.92	0.20
Salt marshes	3.5×10^5	0.49	0.05
Rivers and lakes	2.0×10^6	0.40	0.13
Coral reefs	1.1×10^5	0.30	0.01
Seaweed beds	2.0×10^4	0.03	0
Total	3.75×10^8	29.89 (C input)	1.23 (C output)

Walsh & Dieterle, 1988 - *In* Scales and Global Change, Wiley, New York

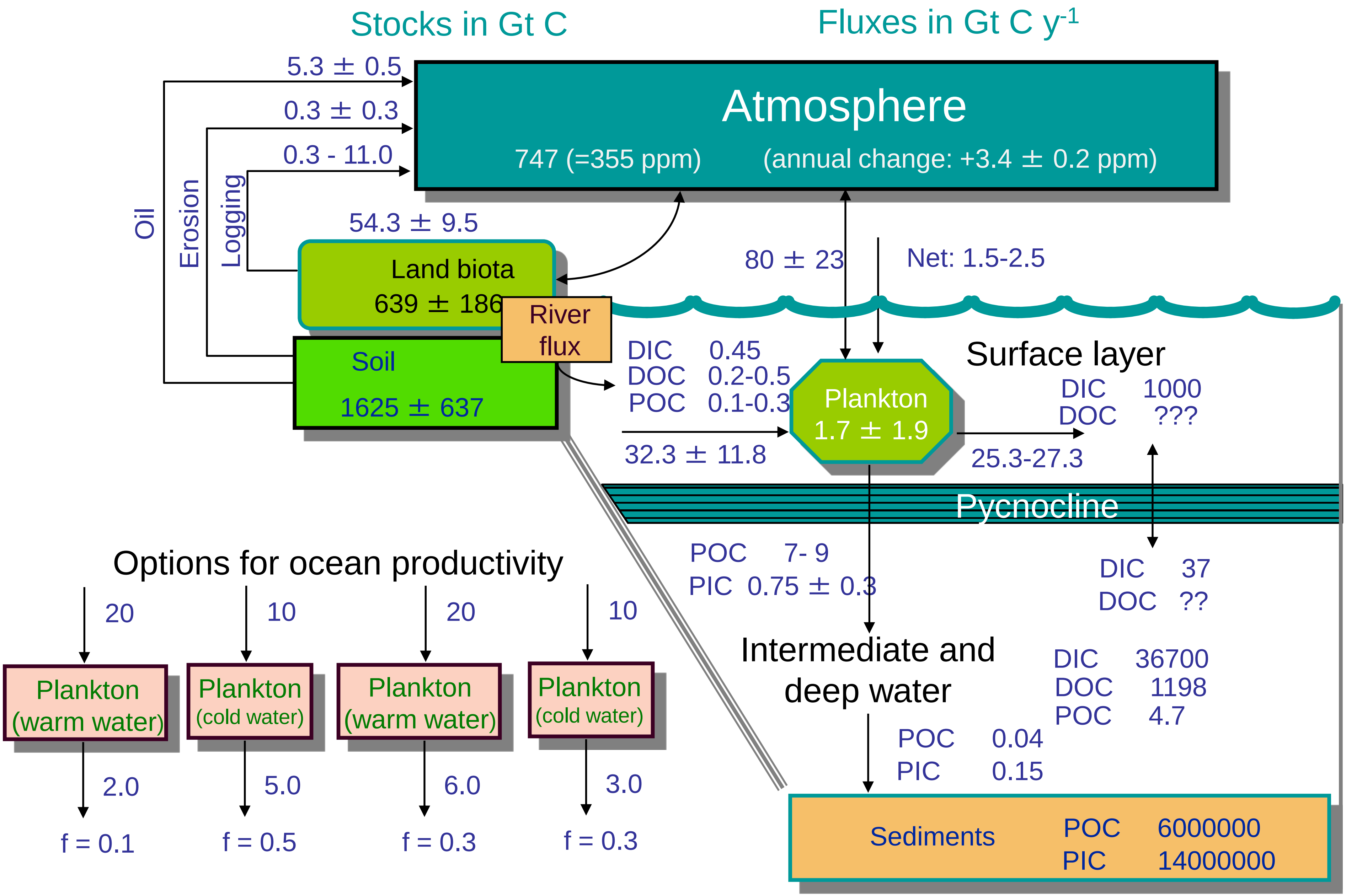
CO_2 content and δD in Vostok ice core
2200m deep - 160000 years before present (BP)



Barnola *et al.*, 1987. Nature, 329:408-412

Ice for forensic analysis of CO_2. Deuterium is a good temperature proxy.

Vertical carbon flux in the northeast Pacific



Models of this kind are useful but have great uncertainties.

Sequestration of carbon by shellfish

Effect on greenhouse gases

What is the role of shellfish?

- The carbon removed by consumption of algae and detritus is an effective carbon sink, since the organic material removed is not mineralised in the water
- The carbon used for building the calcium carbonate ($CaCO_3$) shell is not a net sink
- Formation of $CaCO_3$ removes CO_2 but also removes calcium, thereby changing the alkalinity of seawater removal: $Ca^{2+} + HCO_3^- \Rightarrow CaCO_3 + H^+$
- As a consequence, the pH buffer system in seawater increases the dissociation of bicarbonate: $H^+ + HCO_3^- \Rightarrow CO_2 + H_2O$
- The net effect is zero change in marine CO_2 as a result of shell building, so there is no drawdown from the atmosphere

Shell formation in bivalves is not a carbon sequestration mechanism.

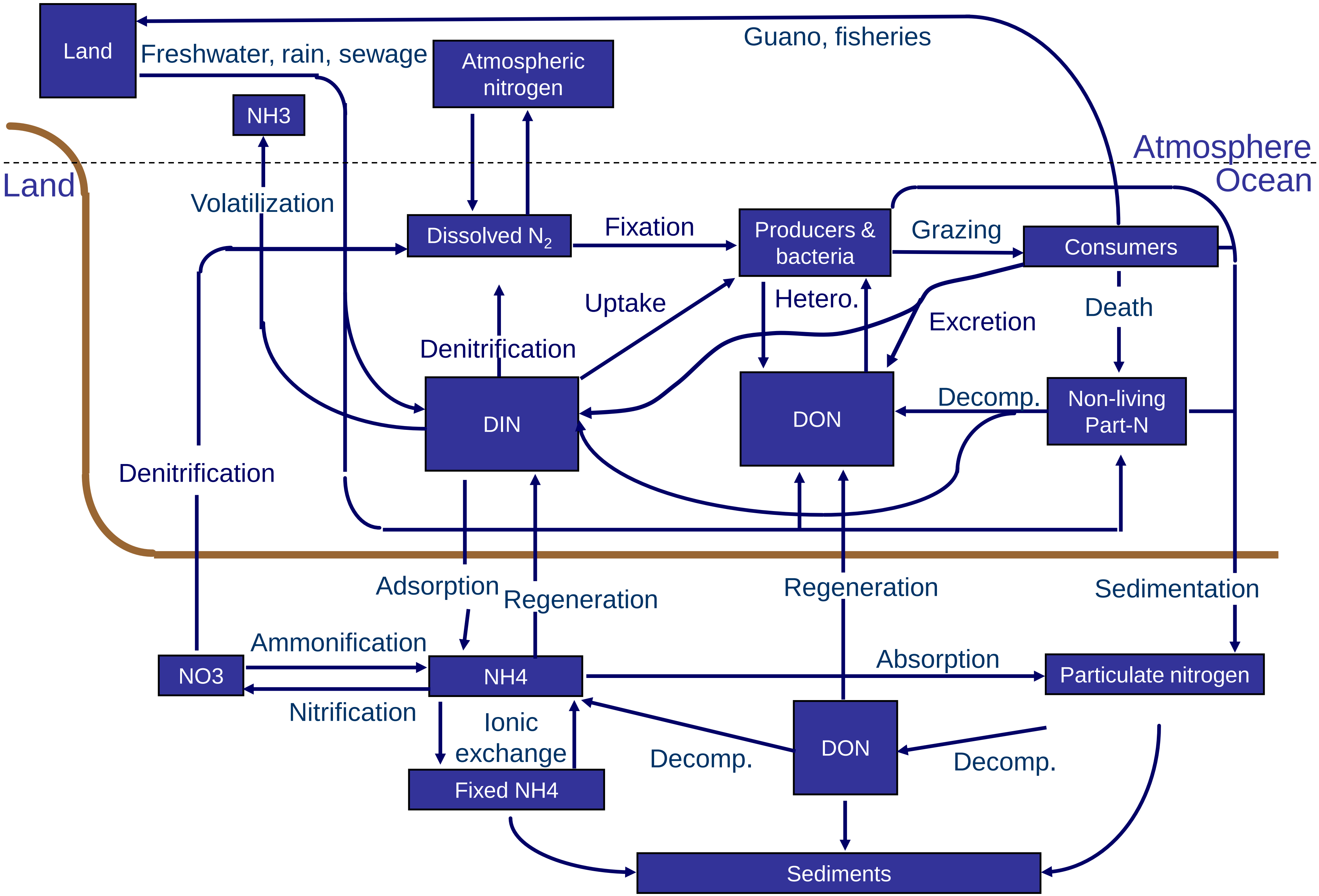
Coastal and Estuarine Processes
http://ecowin.org/aulas/mega/pce

Nutrients

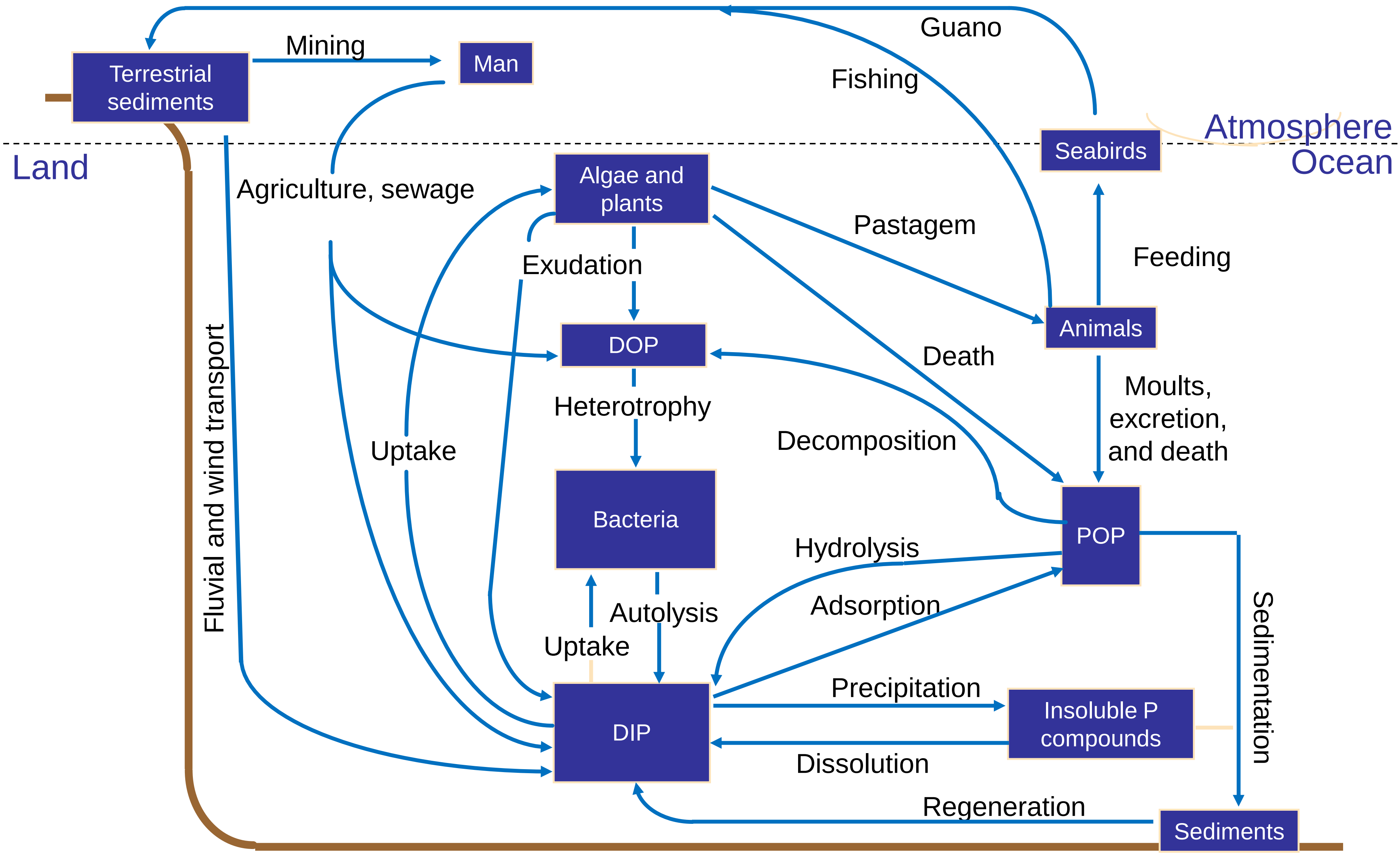
J. Gomes Ferreira
http://ecowin.org/

Universidade Nova de Lisboa

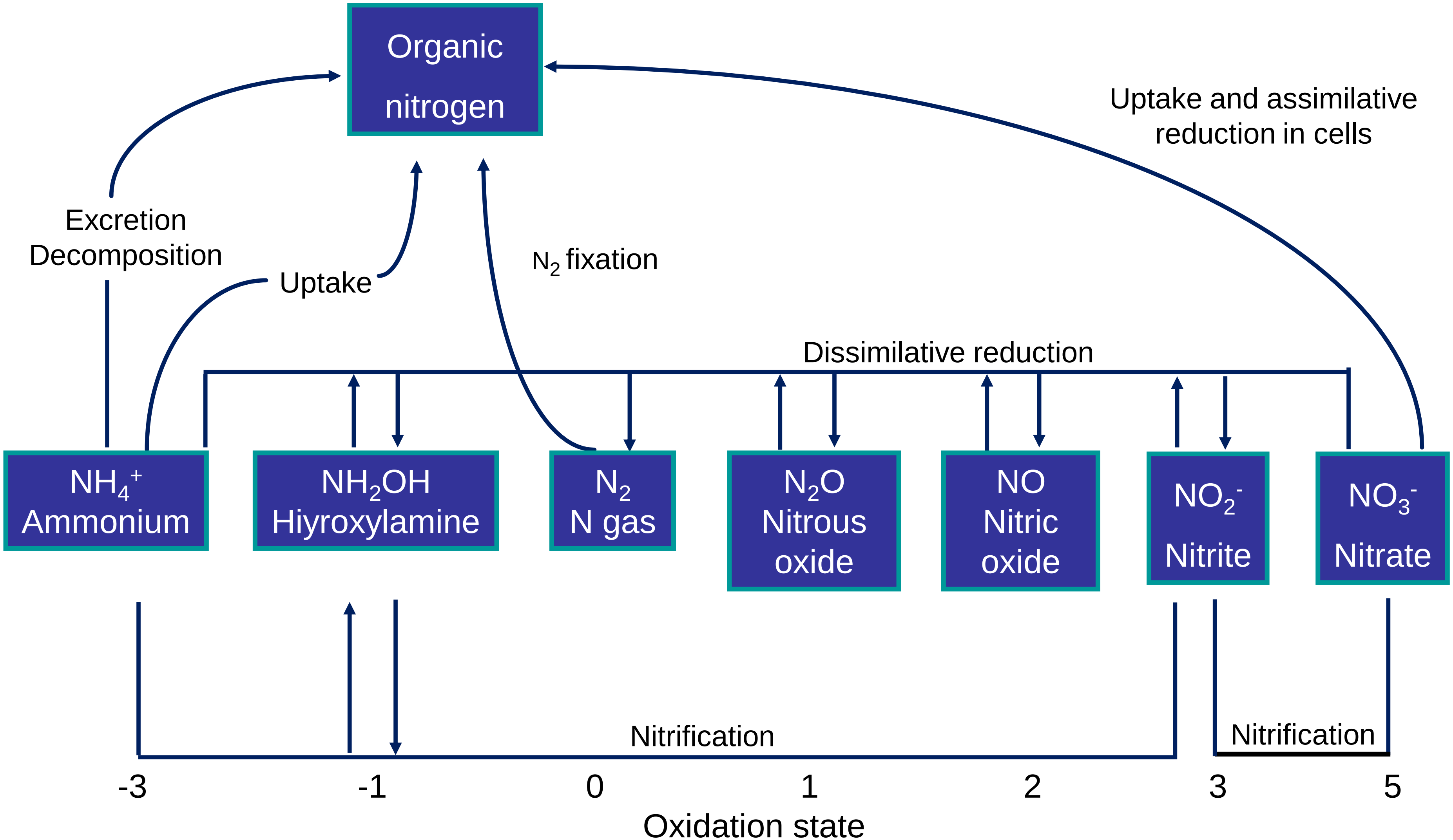
Nitrogen cycle in the marine environment



Phosphorus cycle in the marine environment

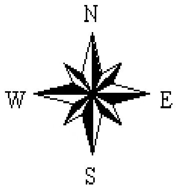


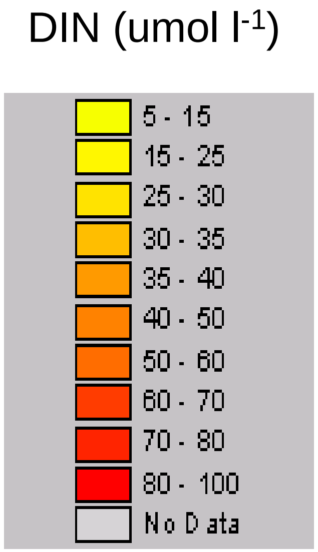
Transformations of nitrogen

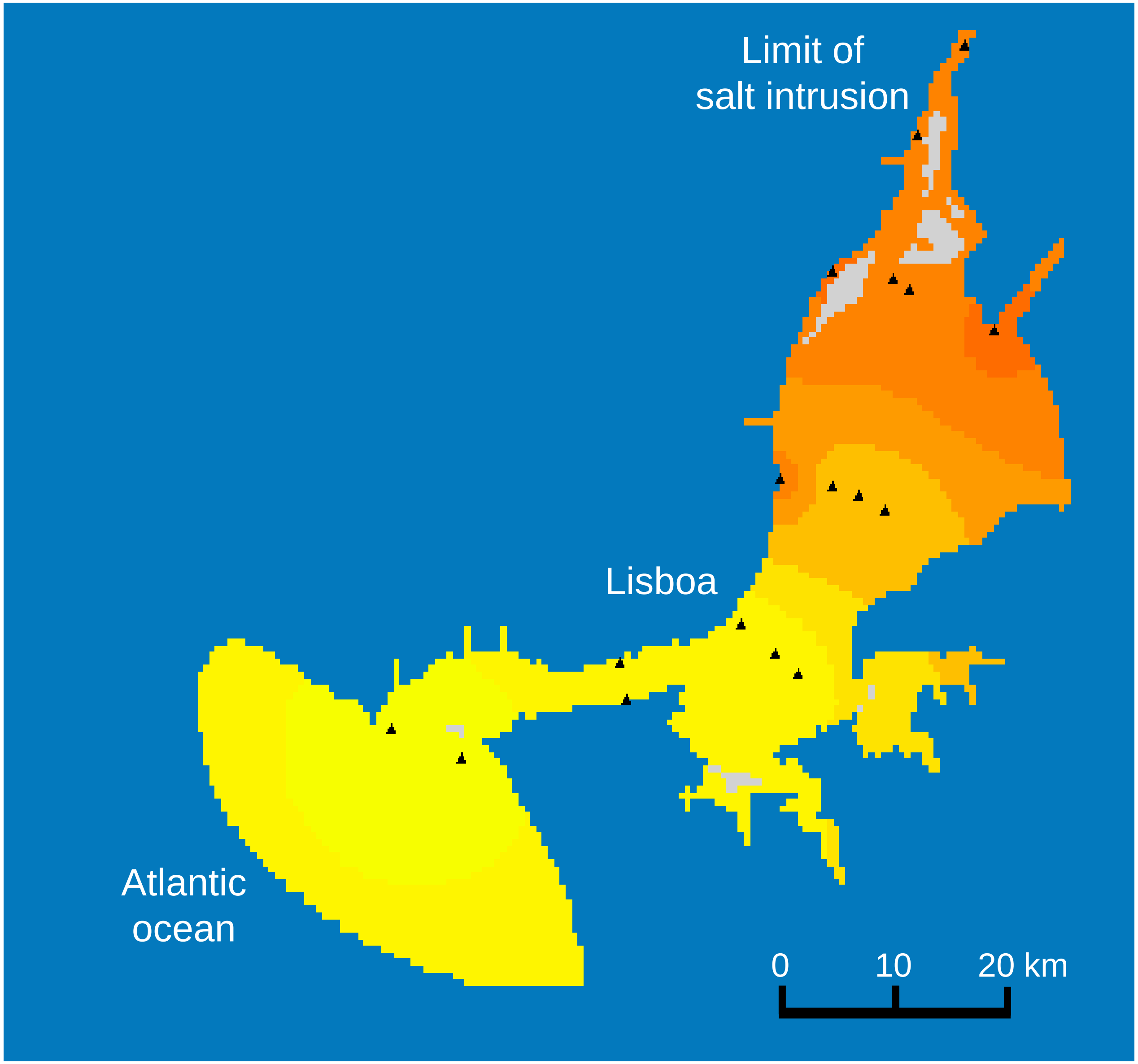


Fenchel & Blackburn, 1979. Bacteria and mineral cycling. Academic Press.

GIS – annual mean DIN in the Tagus Estuary

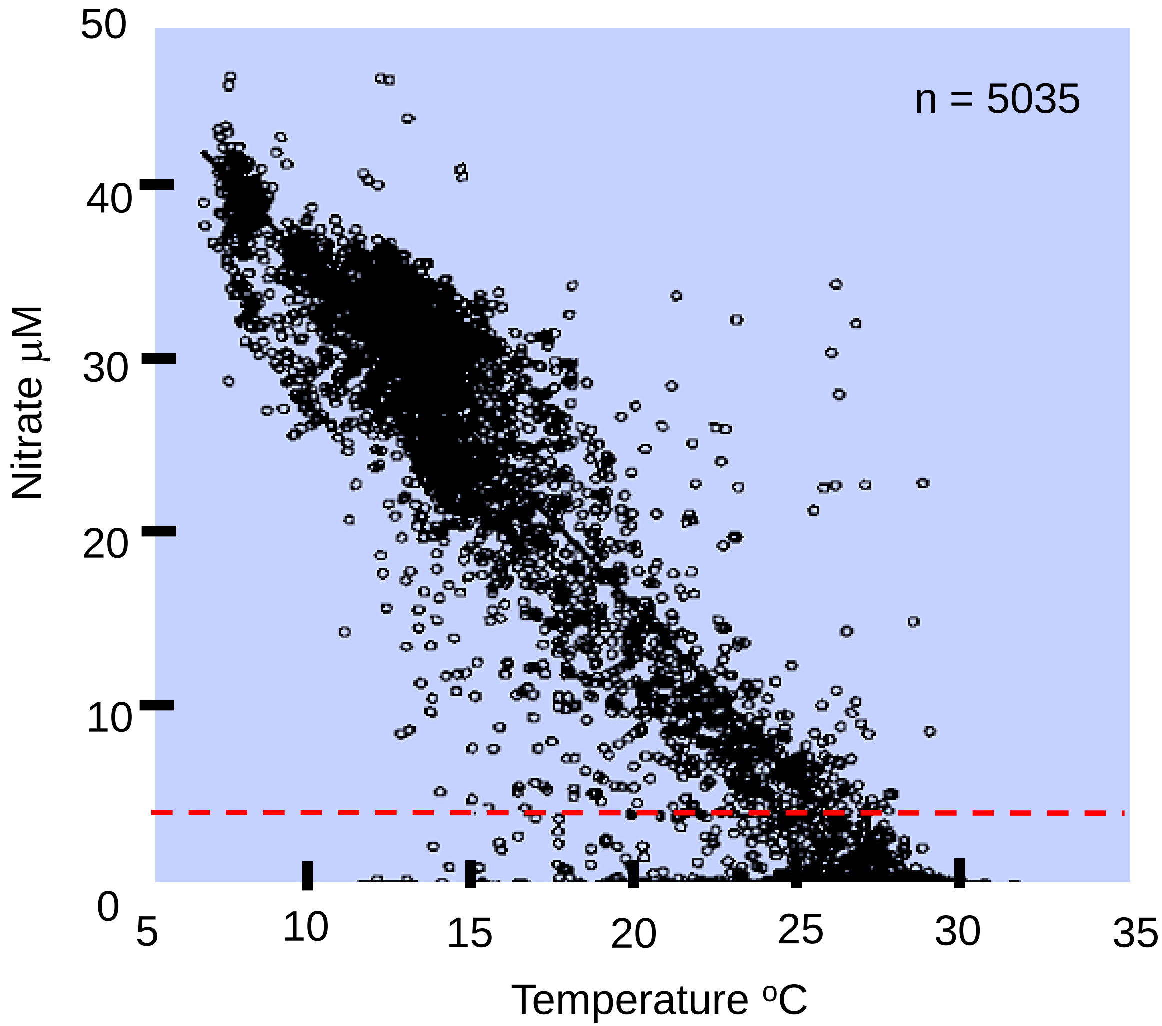






There is a clear gradient in the dissolved inorganic nitrogen concentration.

NO_3-Temperature relationship for the eastern tropical Pacific (Aug.-Nov. 86-88)



Fiedler *et al*., 1991 - Limnol. & Oceanog. 36, p. 1834-50

Nitrate concentration increases with depth.

Redfield Ratio

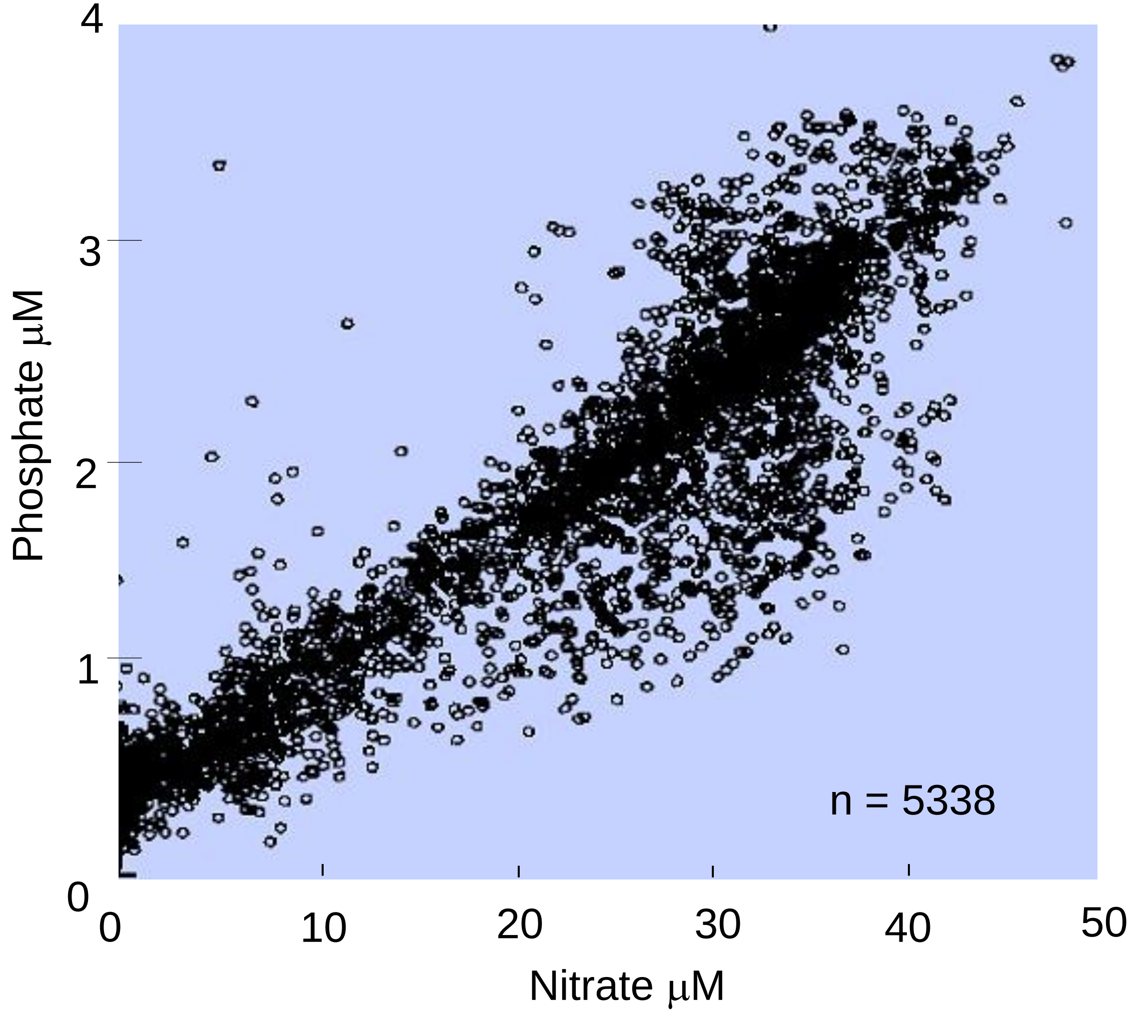
Definitions

- “Standard” ratio of C:N:P
- May be expressed in atoms or mass
- Derives from the constancy of composition of biota
- C:N:P 106:16:1 (in atoms)
- C:N:P 45:7:1 (in mass)
- Oxygen may also be included, considering that for every carbon atom fixed two oxygen atoms are produced

$$CO_2 + 2H_2A \xrightarrow[\text{Pigments}]{\text{Light}} CH_2O + 2A + H_2O$$

O:C:N:P 212:106:16:1

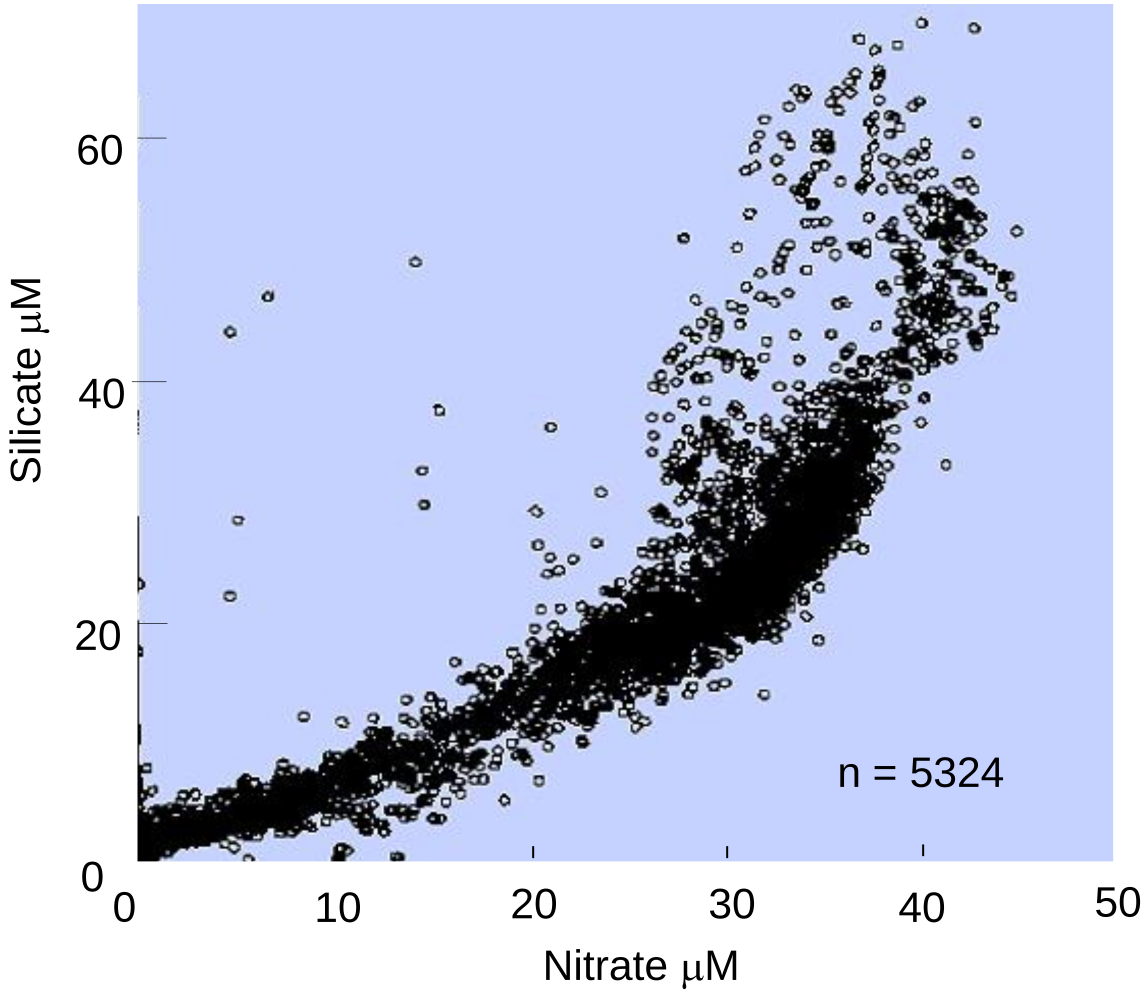
PO_4 - NO_3 relationship for the eastern tropical Pacific (Aug.-Nov. 1986-88)



Fiedler *et al*., 1991 - Limnol. & Oceanog. 36, p. 1834-50

Redfield ratio of about 15:1 (N:P).

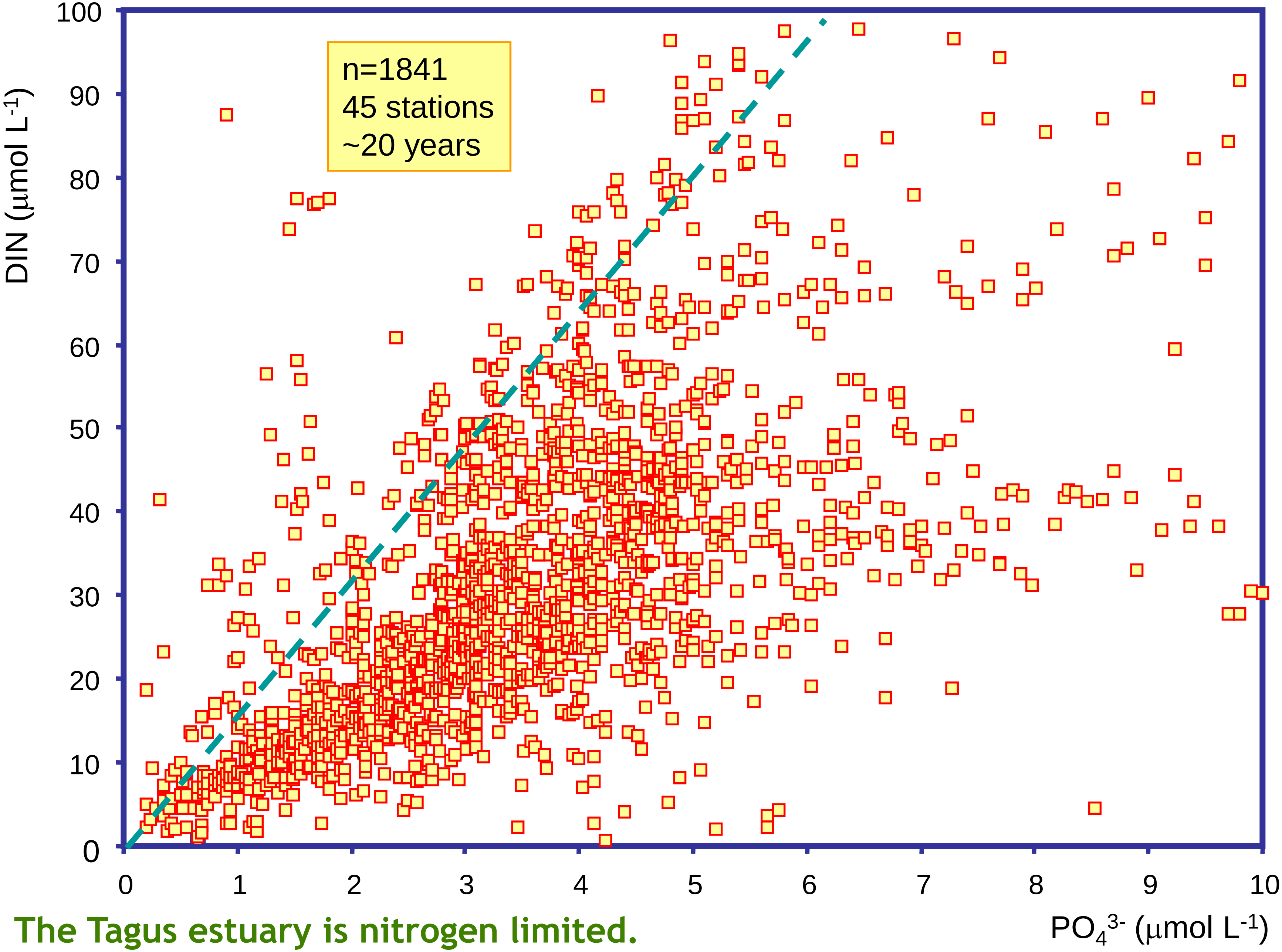
SiO_4 - NO_3 relationship for the eastern tropical Pacific (Aug.-Nov. 1986-88)



Fiedler *et al*., 1991 - Limnol. & Oceanog. 36, p. 1834-50

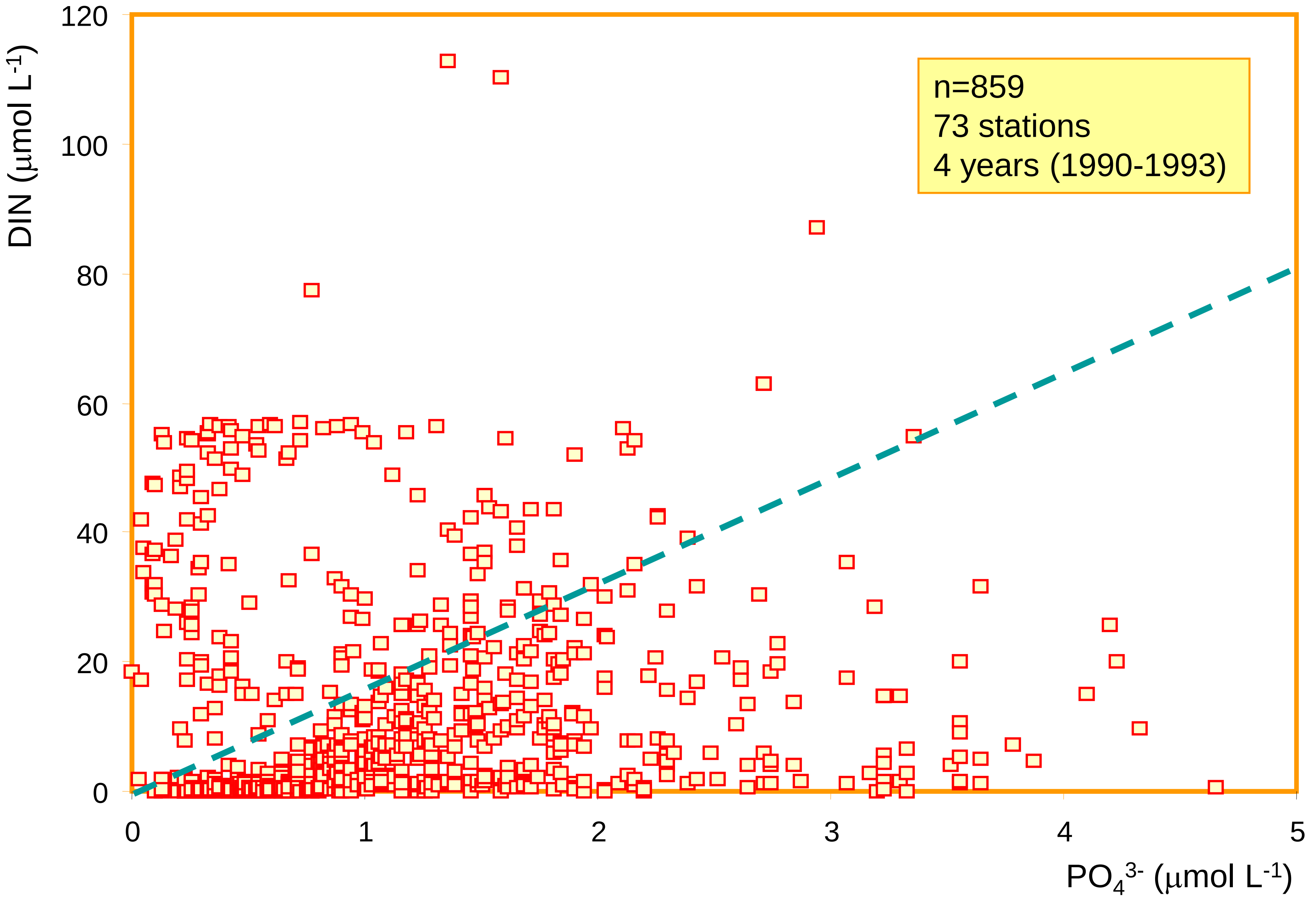
The ratio of silica to nitrate can vary substantially.

N:P ratio for the Tagus Estuary



The Tagus estuary is nitrogen limited.

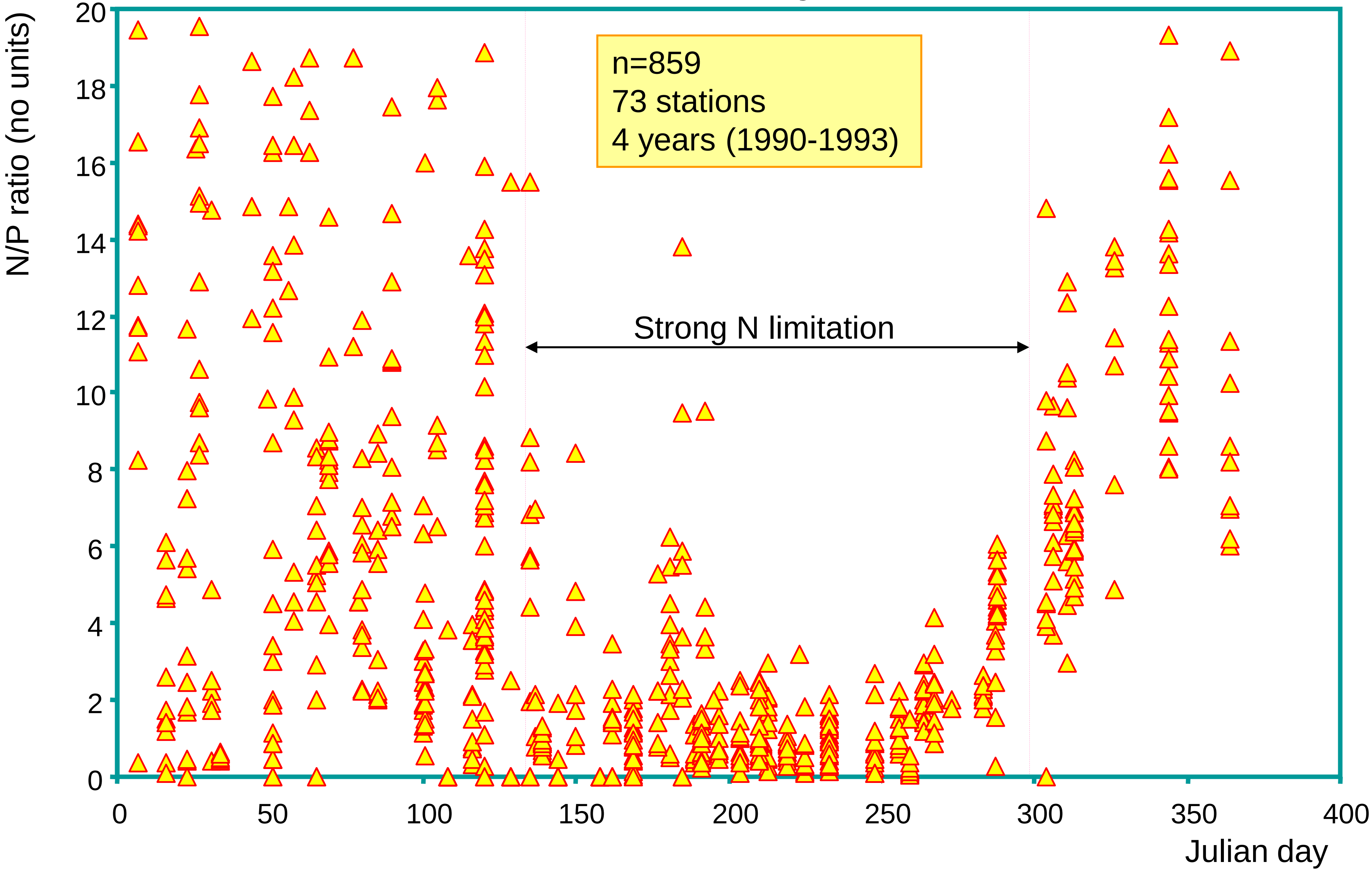
N:P ratio for Carlingford Lough, Ireland



Carlingford Lough does not seem to have a clear nutrient limitation pattern.

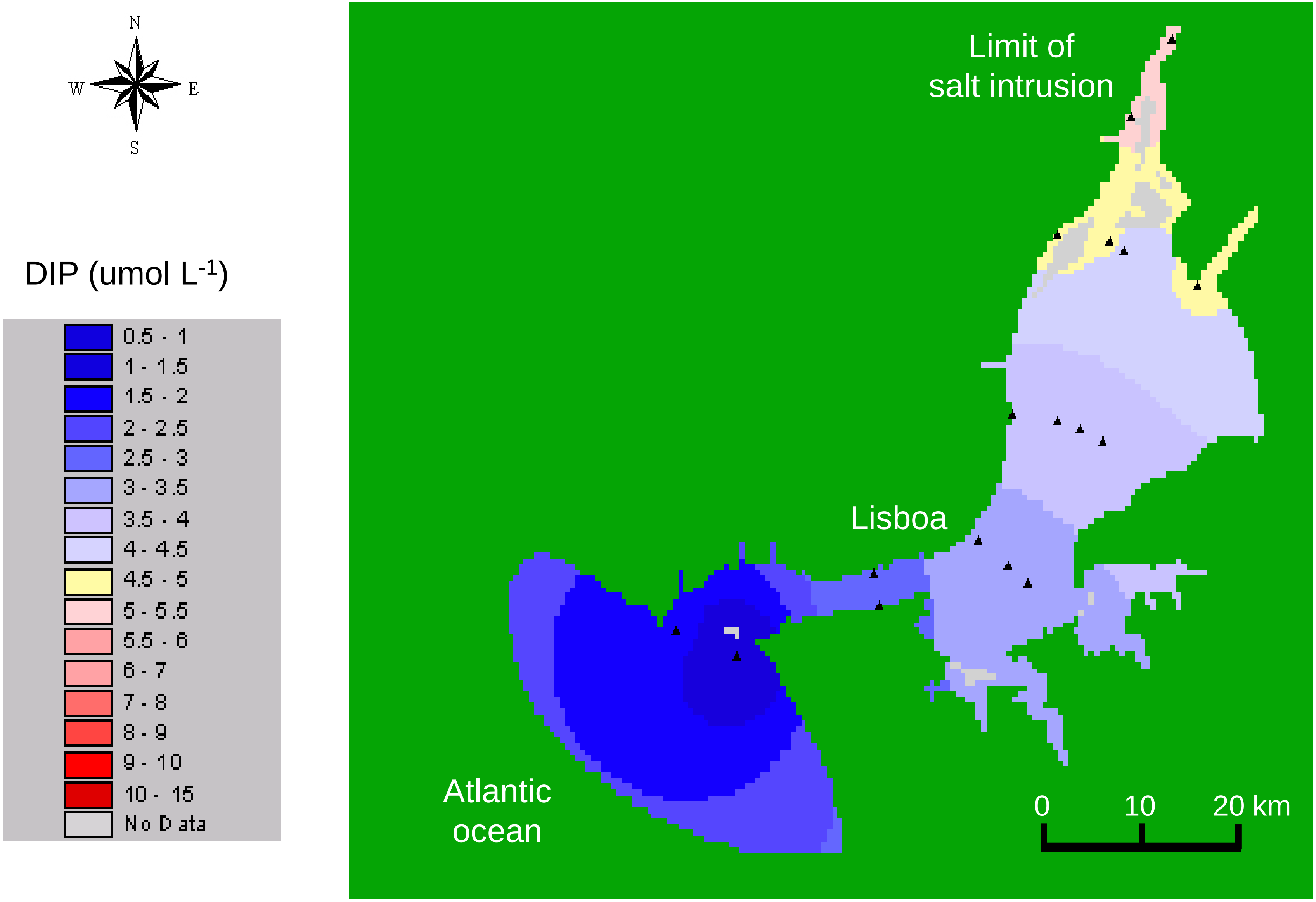
N:P ratio for Carlingford Lough, Ireland

seasonal analysis



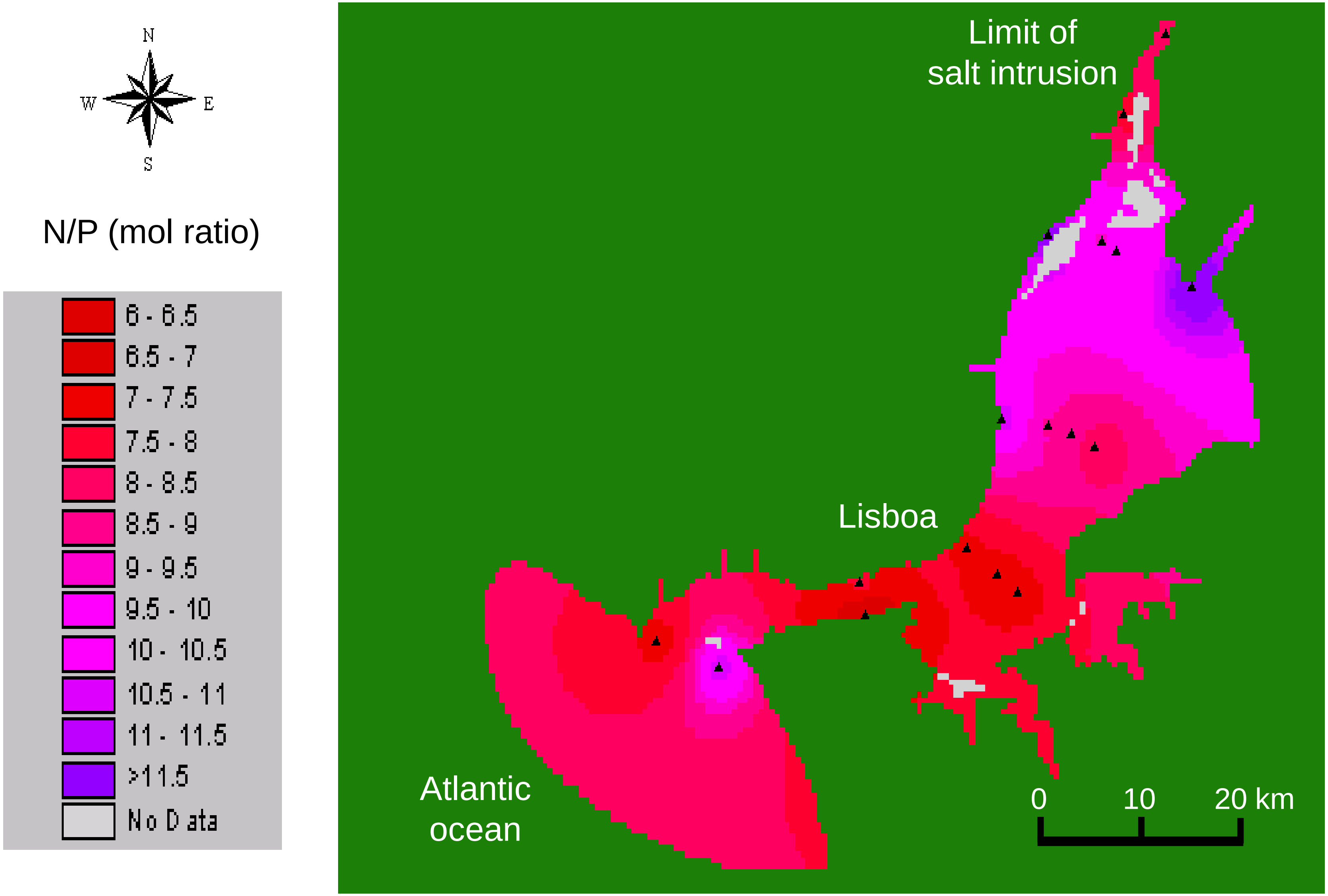
Carlingford Lough is P limited in winter and N limited in summer.

GIS – annual mean DIP in the Tagus Estuary



There is a clear gradient in the phosphate concentration.

GIS – mean Redfield ratio in the Tagus Estuary



The Tagus estuary is nitrogen limited.

Redfield Ratio - Applications

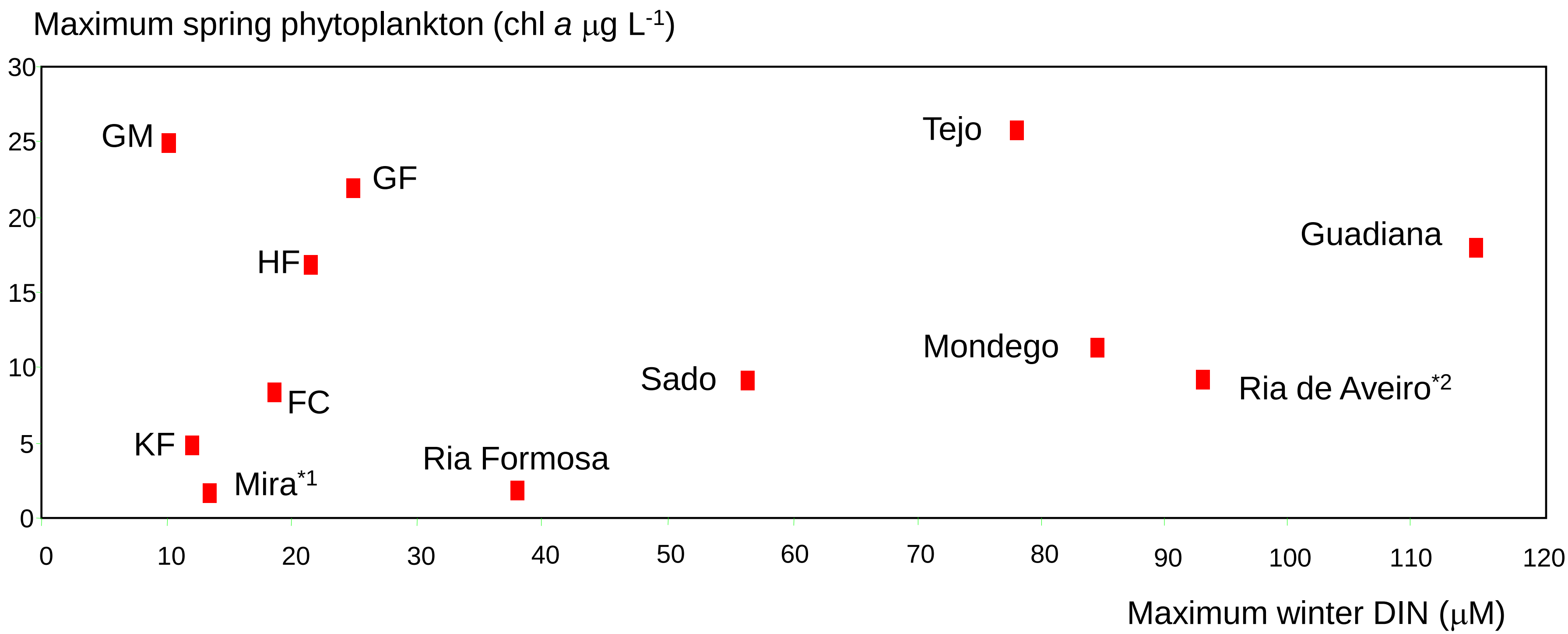
Caveat

A mean ratio, in some cases the variance will be large!

Applications

- Analysing the food chain (planktonic or detrital)
- Determining nutrient limitation
- Performing mass balances, i.e. understanding stocks and fluxes
- Management of input and uptake
- Understanding the role of autochtonous production, external inputs and export (outwelling)
- Ecological modelling (currency tables)

OAERRE data + TICOR data
Chlorophyll a and nutrients



Tett, P., Gilpin, L., Svendsen, H., Erlandsson, C.P., Larsson, U., Kratzer, S., Fouilland, E., Janzen, C., Lee, J., Grenz, C., Newton, A., Ferreira, J.G., Fernandes, T., Scory, S., 2002. Eutrophication and some European waters of restricted exchange. Continental Shelf Research, 23, 1635-1671, NEEA, and TICOR - Typology and Reference Conditions for Portuguese Transitional and Coastal Waters. INAG/IMAR, 2003.

*1 – Chlorophyll determined from graphical data

*2 – Nitrate, not DIN

No universal relationship emerges between chlorophyll and DIN.

Mass balance for loading and regeneration of nutrients in Narragansett Bay, U.S.A.

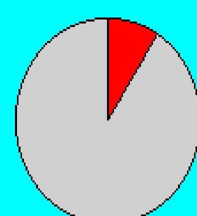
	Annual input (10^6 g-at y^{-1})	
	Nitrogen	Phosphorus
Inputs		
Fixation	0.2	-
Precipitation	2.8	0.19
Runoff	16.2	0.8
Rivers	235	17.3
Sewage	278	21.7
• Total	532	39.9
Regeneration		
Menhaden	0.8	0.1
Ctenophora	8.1	0.8
Zooplankton	98.5	-
Benthos	264	41.1
• Total	371	42

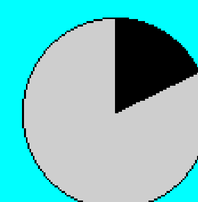
Nixon, 1981. Remineralization and nutrient cycling in coastal marine ecosystems. *In* Neilson & Cronin (Eds.) , Estuaries and Nutrients, Humana, p. 111-138.

Mass balance analysis helps to understand mass and energy flow in ecosystems.

Nitrogen mass balance for Sippewissett marsh, U.S.A. All values in kg N $^{y-1}$.

	Inputs	Outputs	Net exchange
Precipitation	380		380
Groundwater	6120		6120
N2 fixation	3280		3280
Tidal exchange	26200	31600	-5350
Denitrification		6940	-6940
Sedimentation		1295	-1295
Others	9	26	-17
• Total	35990	39860	-3870
% biotic exchange	9	18	
% physical exchange	91	82	





Valiela & Teal (1979). The nitrogen budget of a salt marsh ecosystem, Nature 280, 652-656.
Minus signs indicate export from the saltmarsh

Mass balance analysis highlights the importance of physical processes.

DIN mass balance for Cala do Norte (kg N y^{-1})

Advection-dispersion		Internal processes	
Inputs		Sources	
Upstream	817642	Phyto mortality	29740
Effluents	3109278	Zoo sloppy grazing	2819
Sub-total	3926920	Zoo metabolism	9632
		Zoo excretion	321
Outputs		Zoo mortality	1527
Downstream	-3607087	Sub-total	44039
Sub-total	-3607087		
		Sinks	
		Gross primary prod.	-363834
		Sub-total	-363834
Total	*319833*	*Total*	*-319795*

Total 38 kg y-1 (approx. zero) ΔN -0.113 μat g DIN L^{-1} y^{-1}

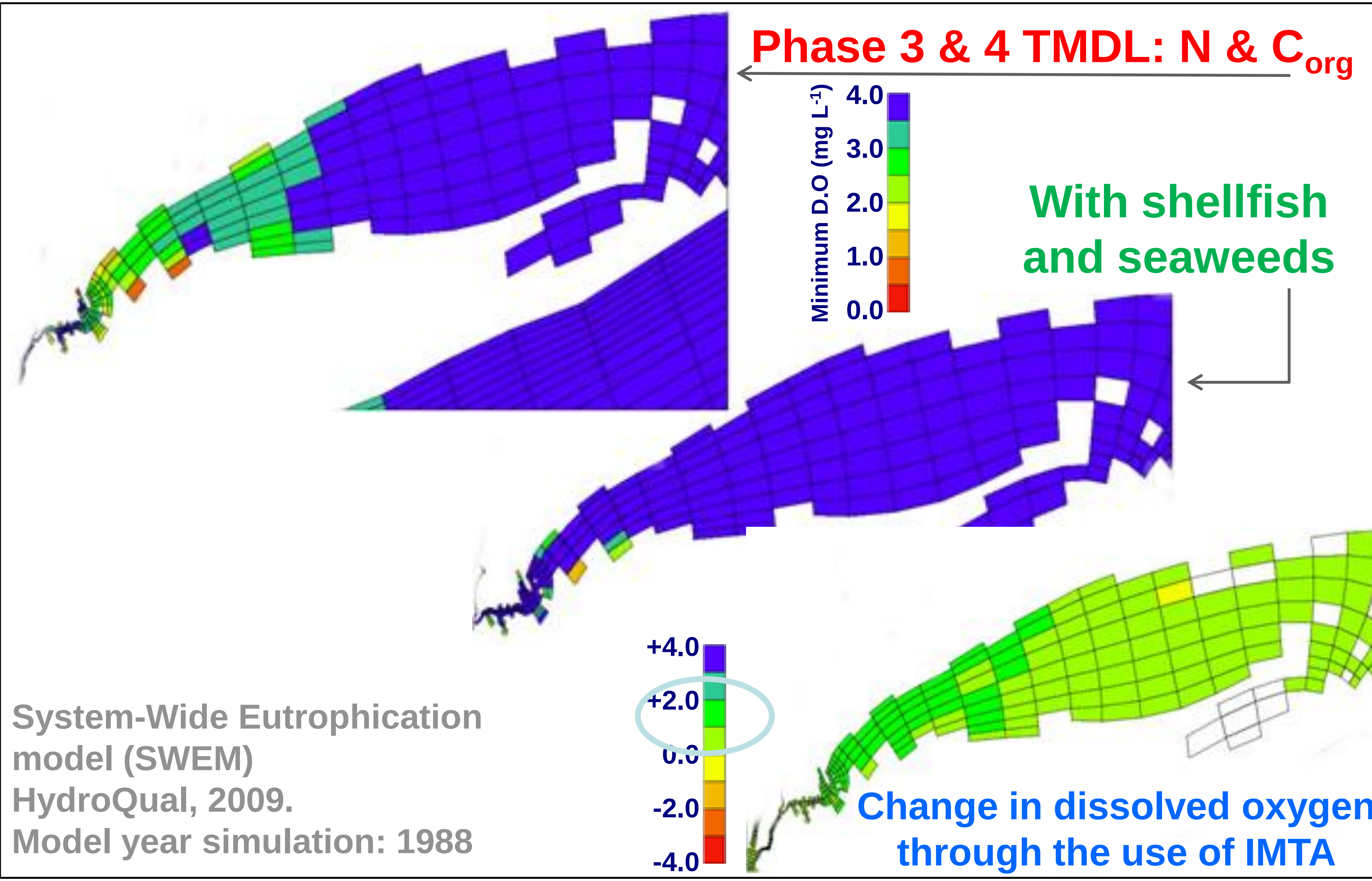
Primary production removes almost 10% of the nutrient input.

Phytoplankton N mass balance for Cala do Norte (gN m^{-2} y^{-1})

Advection-dispersion		Internal processes	
Inputs		Sources	
Upstream	11.88	Net primary prod.	20.53
Sub-total	11.88	Sub-total	20.53
Outputs		Sinks	
Downstream	- 28.24	Natural mortality	- 2.73
Sub-total	- 28.24	Grazing	- 1.44
		Sub-total	- 4.17
Total	- 16.36	*Total*	*16.36*
Total	0 g m^{-2} y^{-1}	Stock	0.150 gN m^{-2}

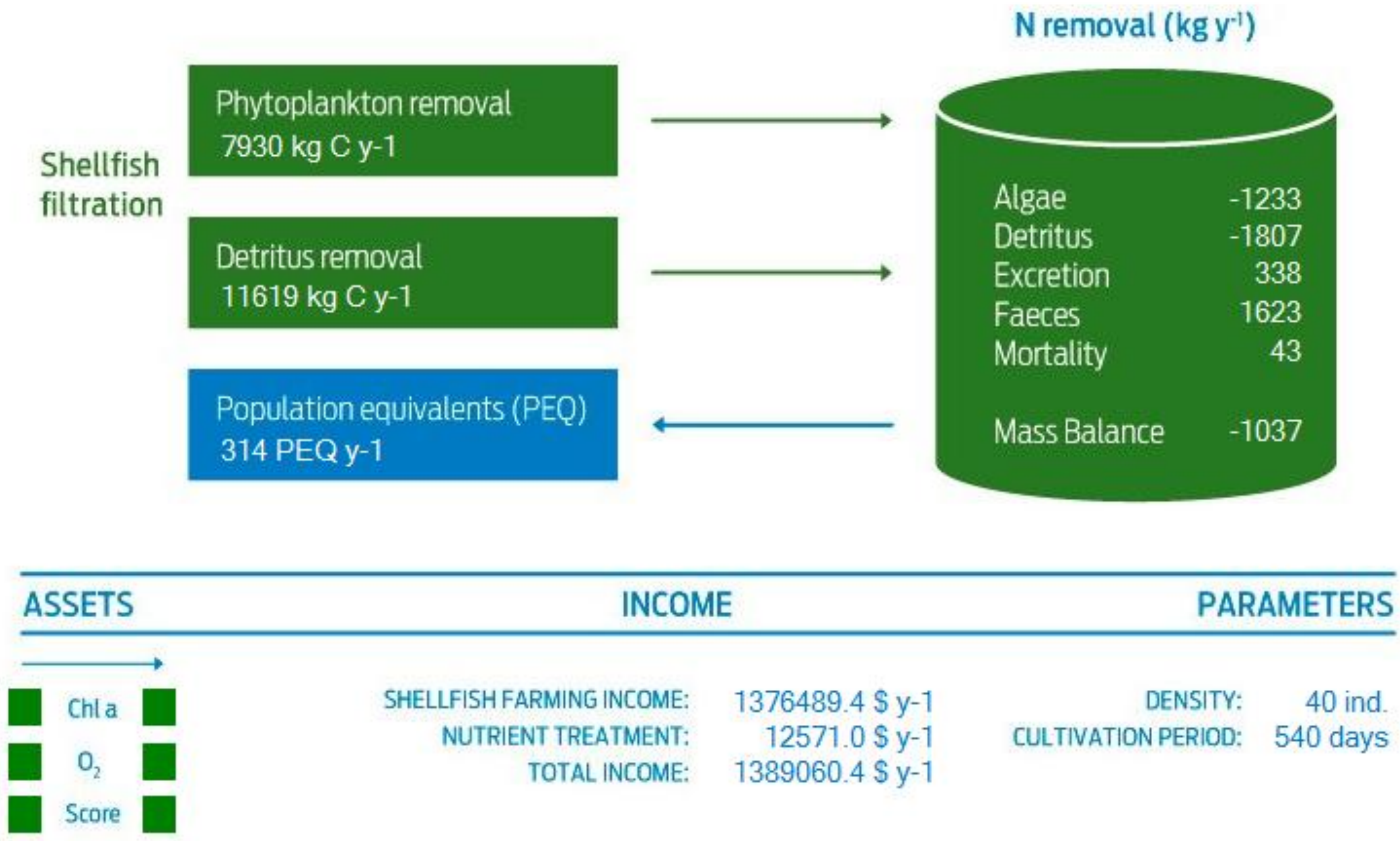
Normalization per unit area allows a comparison among ecosystems.

Simulation of dissolved oxygen with IMTA



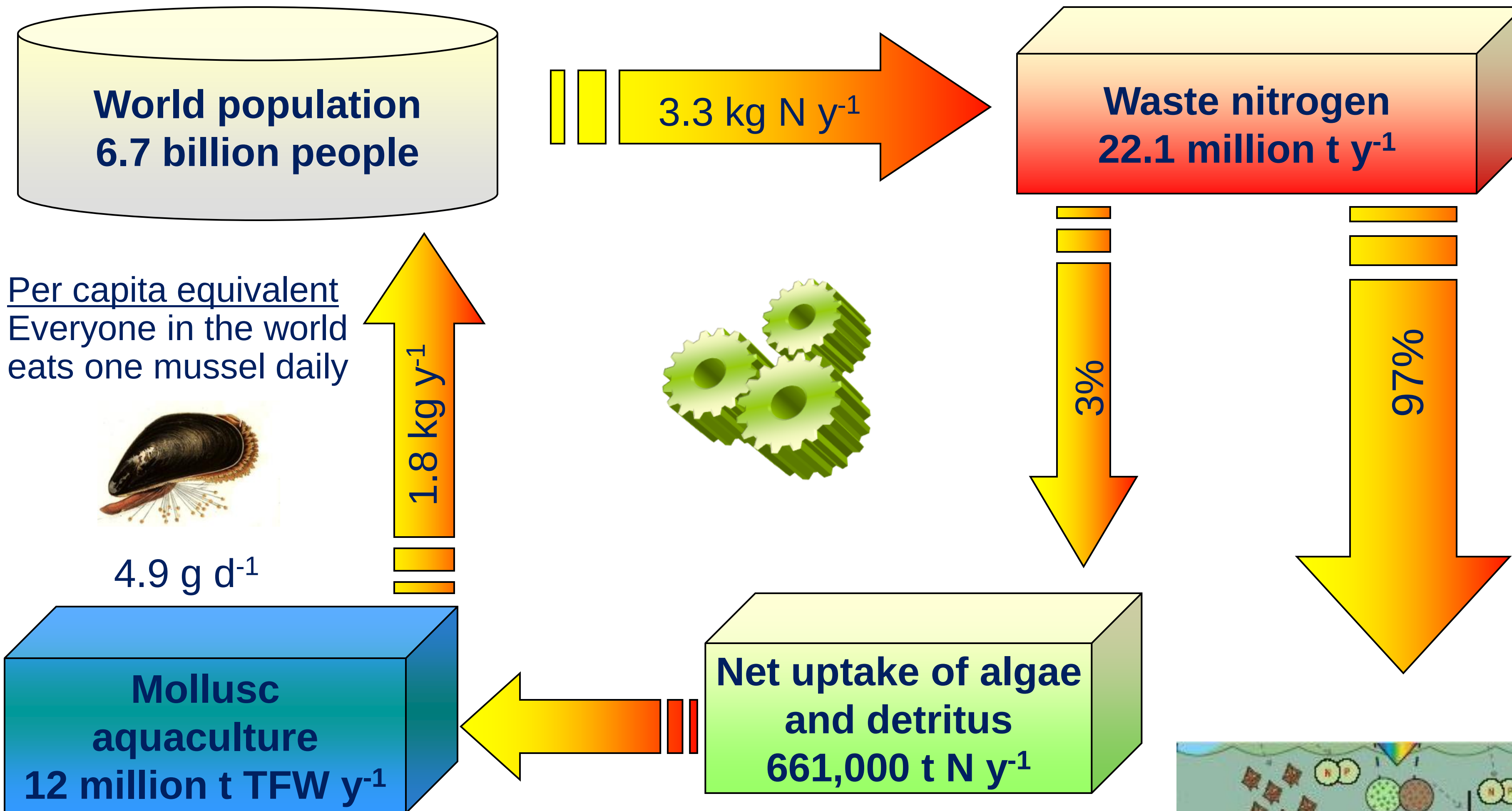
Top-down control of eutrophication symptoms short-circuits organic decomposition

Long Island Sound oyster farm
FARM model simulation for nutrient trading



Oyster cultivation in this 50 acre farm provides an ecosystem service equivalent to removal of nutrient discharge by over 300 people.

Shellfish aquaculture and the global nitrogen budget (upscaled from FARM results)



Substantial ecosystem services (53 billion € y^{-1}, 2% UK GDP)

Synthesis

- The availability of light and oxygen conditions the overall functioning of marine systems
- The sea is the most important reservoir of CO_2 on the planet, and plays a major part in climate regulation
- Organic cycles are an image of life. There are important differences between N and P cycles, particularly with respect to the sediment component
- Nutrient ratios and distributions are critical to understanding organic production and water management

All slides

http://ecowin.org/aulas/mega/pce