Impact of global change on ocean biogeochemical cycles (N, P, C and trace elements)
Palma de Mallorca, 17 – 21 Oct 2011

I. Micro-nutrients in the oceans

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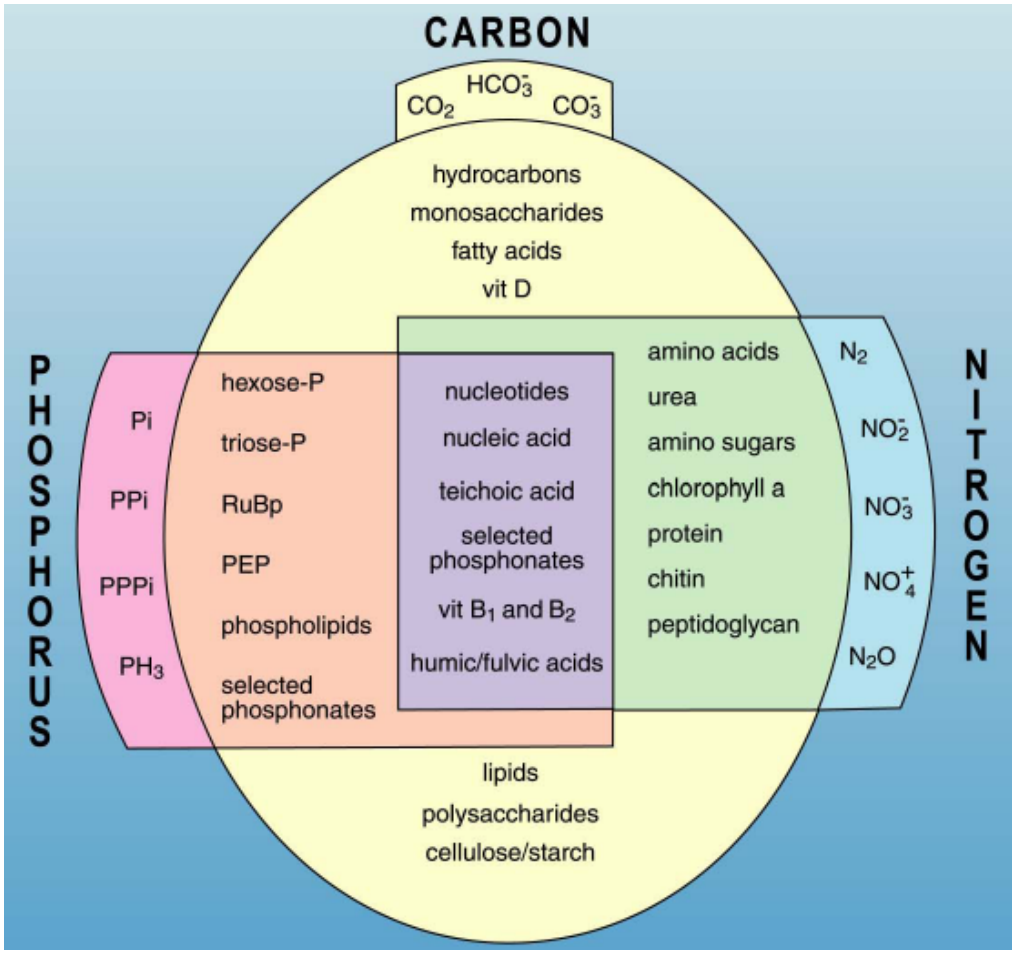
outline of this presentation

C, N P and Si reservoirs in the oceans



outline of this presentation

C, N P and Si reservoirs in the oceans

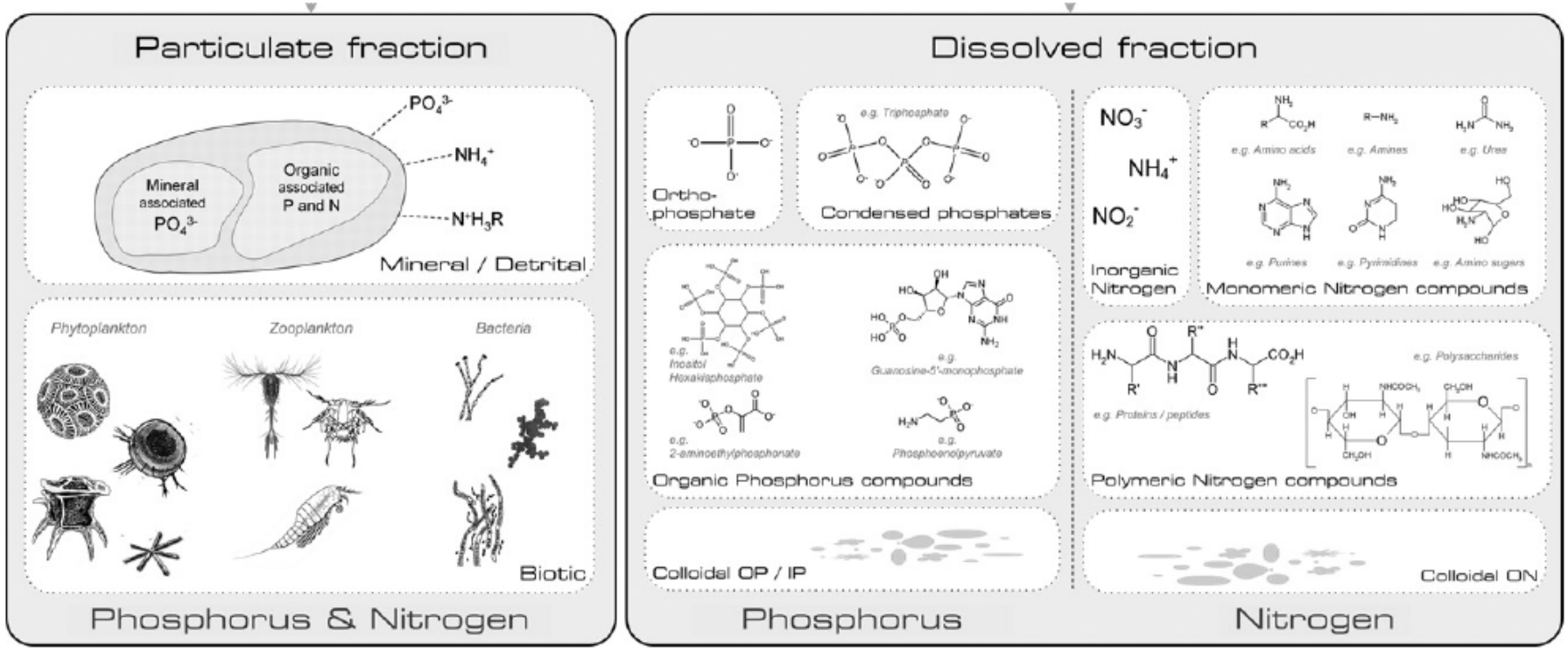


Fig. 2 – Representation of typical P and N components in the operationally defined dissolved and particulate fractions of a total sample.

Worsfold et al., Anal. Chim. Acta, 2008

outline of this presentation

dissolved inorganic compounds in the oceans

- dissolved inorganic nitrogen in the oceans
- dissolved inorganic phosphorus in the oceans
- dissolved silicon in the oceans

inorganic micro-nutrients in the oceans

dissolved inorganic compounds in the oceans

$$TA = [Na^+] + 2\cdot[Mg^{2+}] + 2\cdot[Ca^{2+}] + [K^+] + 2\cdot[Sr^{2+}] + \ldots$$

$$\ldots - [Cl^-] - 2\cdot[SO_4^{2-}] - [Br^-] - [F^-] - \ldots$$

Concentrations, $[c_i]$ (mmol kg-1), and charge concentrations, $[q_i] = z_i \cdot [c_i]$ (mmol kg-1), of conservative ions in seawater at S = 35.

Cations	$[c_i]$	$[q_i]$		Anions	$[c_i]$	$[q_i]$
Na^+	467.8	467.8		Cl^-	545.5	545.5
Mg^{2+}	53.3	106.5		SO_4^{2-}	28.2	56.4
Ca^{2+}	10.3	20.6		Br^-	0.8	0.8
K^+	9.9	9.9		F^-	0.1	0.1
Sr^{2+}	0.1	0.2			·	
Total	·	605.0		Total	·	602.8

Figure by MIT OCW.

the concept of alkalinity

Zeebe and Wolf-Gladrow (2001)

inorganic micro-nutrients in the oceans

dissolved inorganic compounds in the oceans

$$TA = [HCO_3^-] + 2\times[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [BASES] - [H^+]$$

$$[OH^-] = [OH^-] + [Mg(OH)^+]$$

$$[H^+] = [H^+] + [HSO_4^{2-}] + [HF]$$

$$[H^+] = [HCO_3^-] + 2\times[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [BASES]$$

pHsws = 4.25

the concept of alkalinity

inorganic micro-nutrients in the oceans

dissolved inorganic compounds in the oceans

$$CO_2 + H_2O \underset{}{\overset{K_1}{\Leftrightarrow}} HCO_3^- + H^+$$

$$HCO_3^- \overset{K_2}{\Leftrightarrow} CO_3^{2-} + H^+$$

$$H_3BO_3 + H_2O \overset{K_B}{\Leftrightarrow} B(OH)_4^- + H^+$$

	pKa	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
HCO_3^-/CO_2	6.04	0,000	-1,000	-1,000
CO_3^{2-}/HCO_3^-	9.23	0,000	-2,000	-2,000
$B(OH)_4^-/H_3BO_3$	8.74	0,000	-0,213	-0,213

STANDARD SEAWATER

(pHsws = 8.0; $\sum CO_2$ = 2100 µmol·kg^{-1})

$K_1(35, 15) = 10^{-6.04}$ $[CO_2]$ = 13.8 µmol·kg^{-1} (0.7%)

$K_2(35,15) = 10^{-9.23}$ $[HCO_3^-]$ = 1916.5 µmol·kg^{-1} (91.3%)

$\alpha_S(35,15) = 10^{-1.43}$ $[CO_3^{2-}]$ = 169.6 µmol·kg^{-1} (8.0%)

$K_B(35, 15) = 10^{-8.74}$ $[B(OH)_4^-]$ = 88.7 µmol·kg^{-1} (21.3%)

$[H_3BO_3]$ = 327.7 µmol·kg^{-1} (78.7%)

$A_C = [HCO_3^-] + 2\cdot[CO_3^{2-}] = 2256$ µmol·kg^{-1}

$$A_B = \left[B(OH)_4^-\right] = 0.213\cdot[B]_T = 0.213\cdot\left(416\cdot\frac{S}{35}\right) = 88.7 \text{ µmol kg}^{-1}$$

the concept of alkalinity

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)

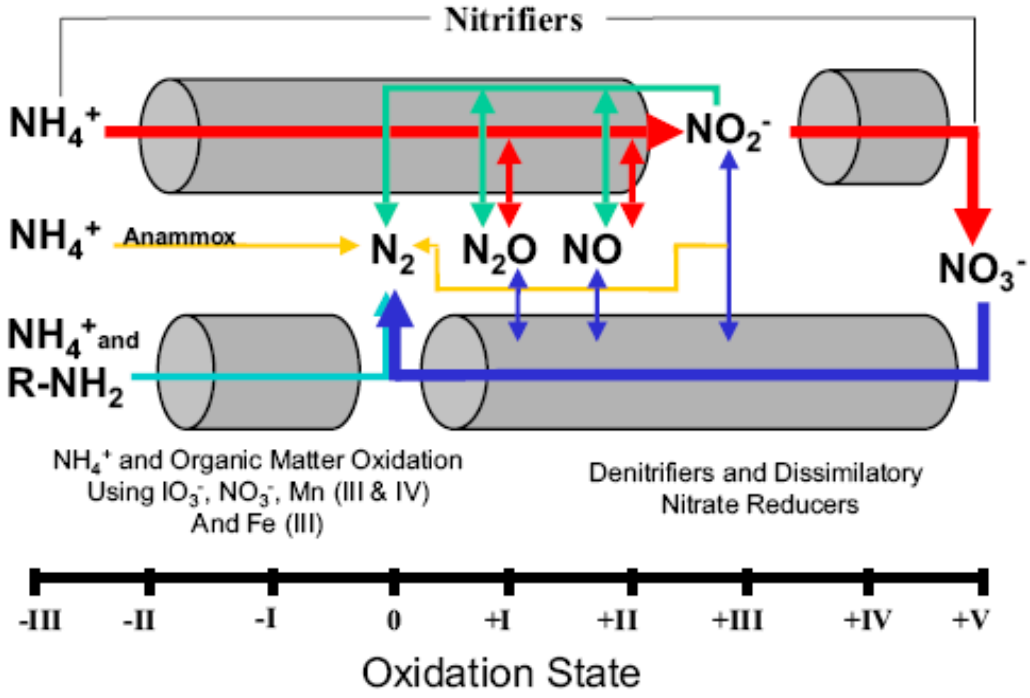


Fig. 1. This figure is re-drawn and updated from Codispoti et al. (2005). The suite of reactions supporting canonical denitrification are shown by the red (nitrification) and dark blue (canonical denitrification) arrows. The green arrows indicate a denitrification process that is associated with nitrification. This process produces N_2O and might also produce N_2. During these three processes, the intermediates, N_2O, NO, and NO_2^- can leave the cell and be changed between nitrifiers and denitrifiers. The NO_2^- produced can also support the anammox pathway (yellow arrows) in which NH_4^+ is oxidized to N_2 and NO_2^- is reduced to N_2. A review of the literature also suggests that oxidation of organic-N or NH_4^+ by NO_3^-, iodate (IO_3^-), oxidized metals such as Mn (III&IV), Fe (III) and various oxidized trace metals can also produce N_2 (light blue arrow). Not shown is the possibility that the oxidation of Mn (II) by NO_3^- may also produce N_2 (Luther et al., 1997). Intermediate chemicals involved in the anammox reaction (e.g. hydrazine) are omitted for simplicity.

dissolved inorganic nitrogen species

Codispoti, Biogeosciences, 2007

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)

$$K_{NO3}$$

$$NO_3H \longrightarrow NO_3^- + H^+$$

$$K_{NO2}$$

$$NO_2H \Leftrightarrow NO_2^- + H^+$$

$$(K_{NH4})^{-1}$$

$$NH_3(aq) + H^+ \Leftrightarrow NH_4^+$$

	pKa	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
HNO_3/NO_3^-	-1,4	-1,000	-1,000	0,000
HNO_2/NO_2^-	3,25	–0,909	–1,000	–0,091
NH_4^+/NH_3	9,23	+1,000	+0,915	-0,085

contribution of dissolved inorganic nitrogen to alkalinity

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)

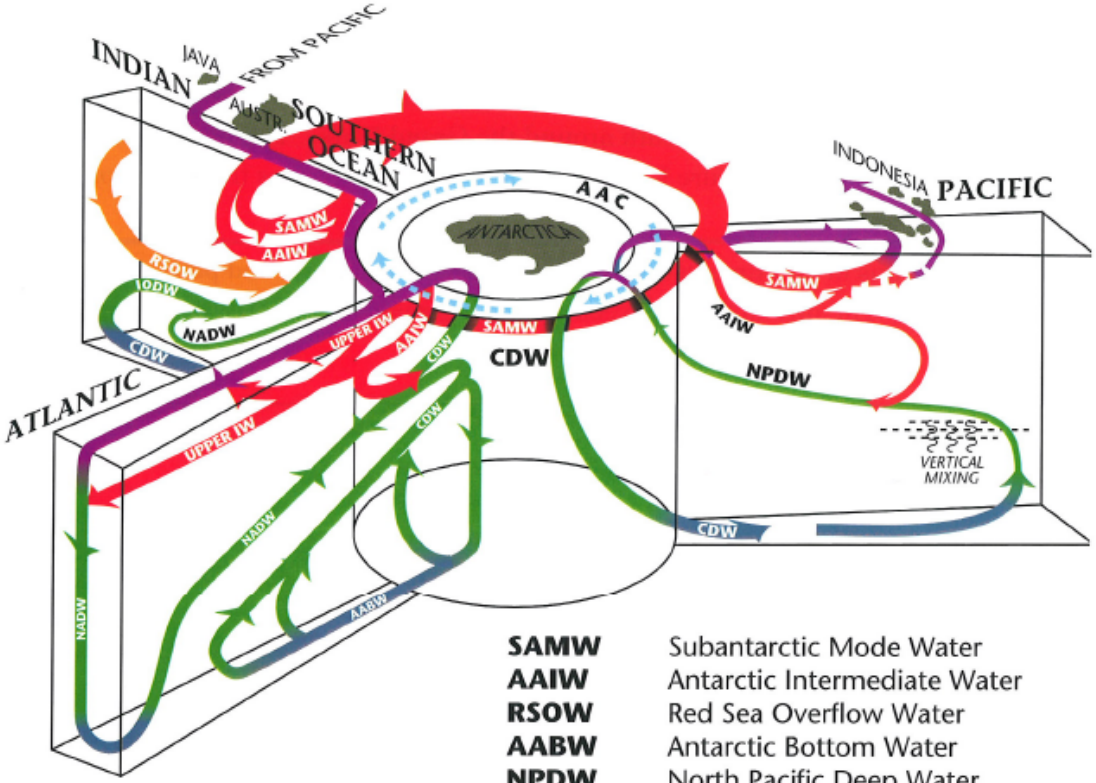
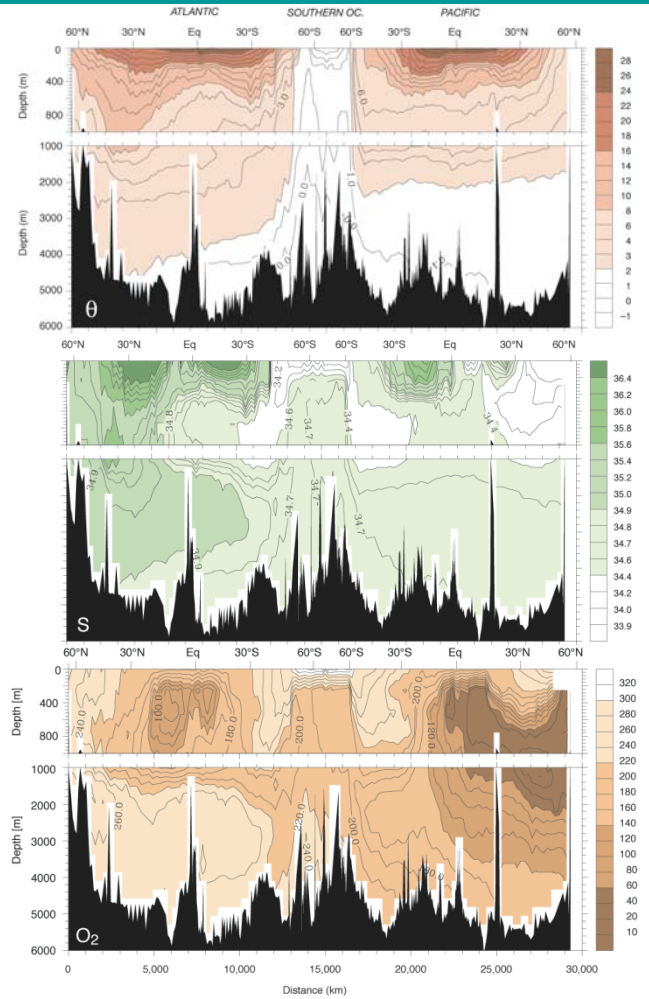


Figure I-91: A new version of Figure I-90 with schematic meridional sections of interbasin flow for each ocean with their global linkages.

SAMW	Subantarctic Mode Water
AAIW	Antarctic Intermediate Water
RSOW	Red Sea Overflow Water
AABW	Antarctic Bottom Water
NPDW	North Pacific Deep Water
AAC	Antarctic Circumpolar Current
CDW	Circumpolar Deep Water
NADW	North Atlantic Deep Water
UPPER IW	$26.8 \leq \sigma_\theta \leq 27.25$
IODW	Indian Ocean Deep Water

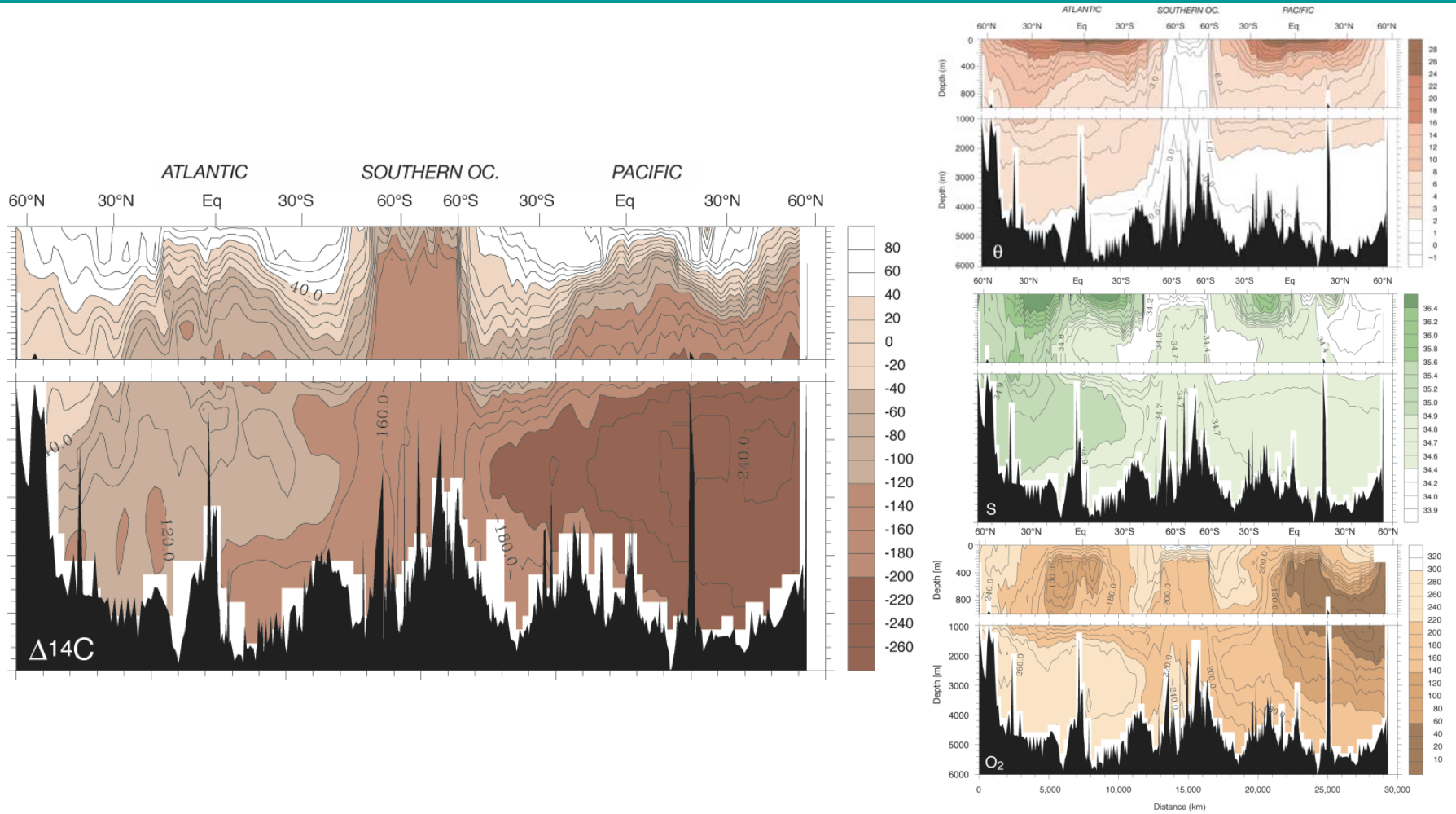


distribution of NO_3^- in the oceans

Schmitz, WHOI, 1995 Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)

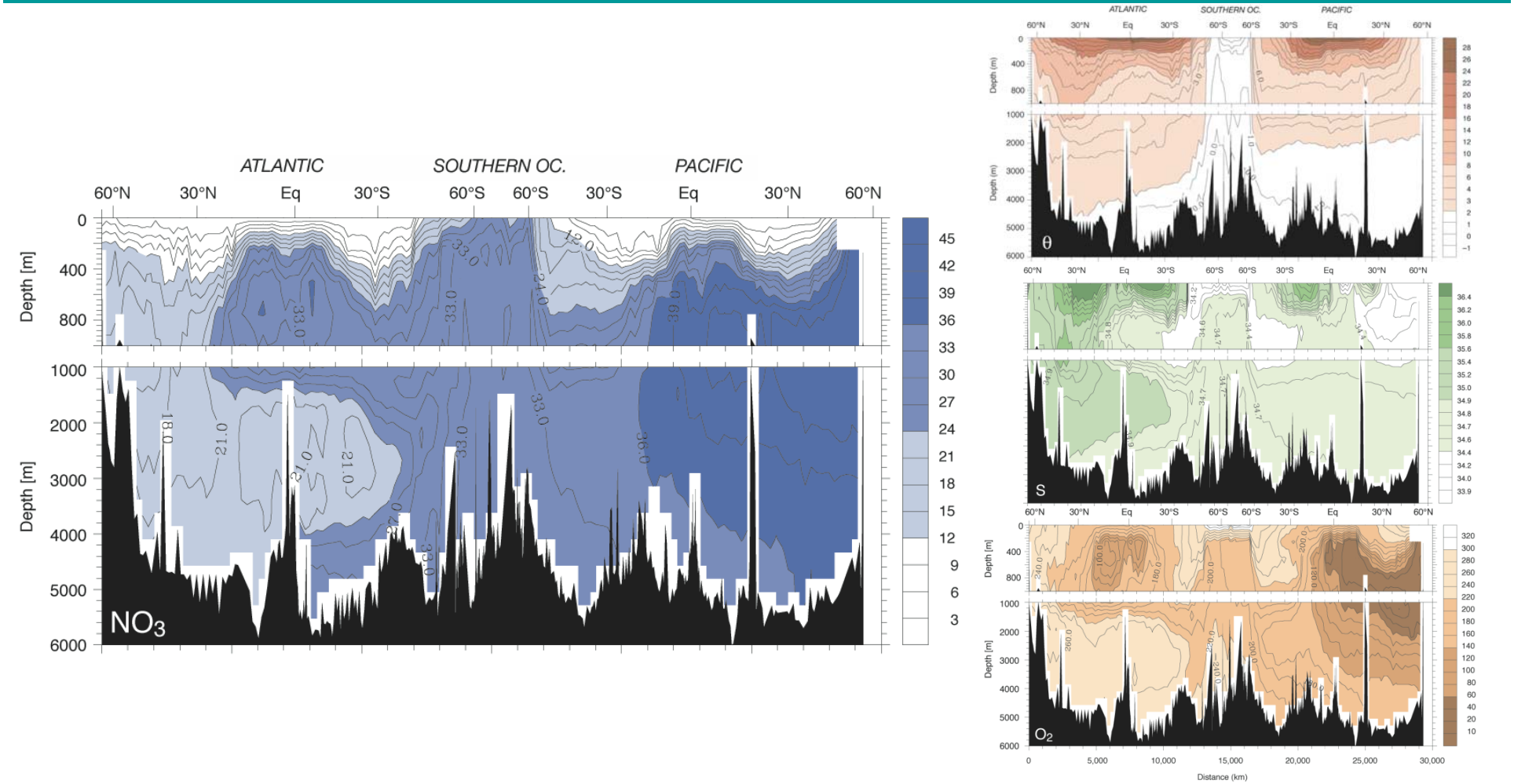


distribution of NO_3^- in the oceans

Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)



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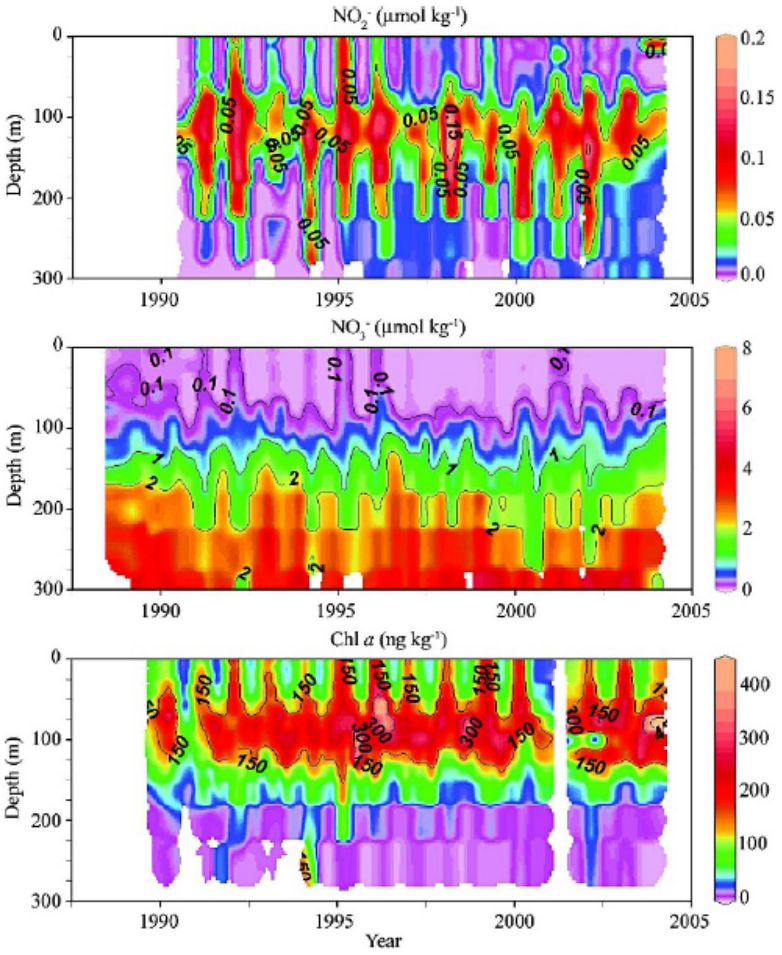
Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)



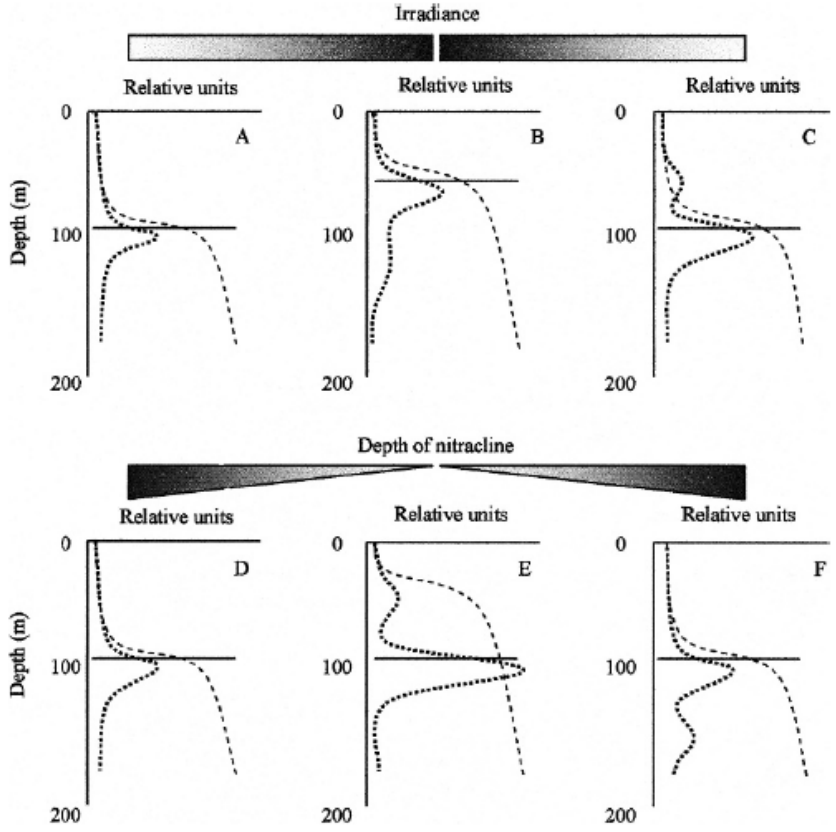


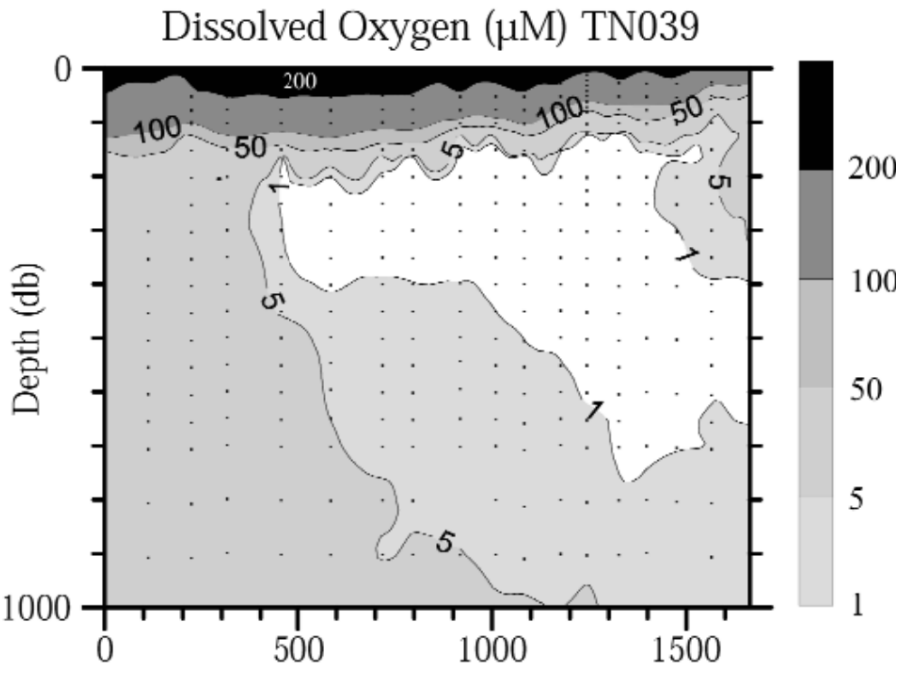
Fig. 3. Conceptual models of relative changes in the depth of 1% PAR (mean 93 m based on Siegel et al. 1997; solid line), nitracline (dashed line), and the primary nitrite maximum (dotted line) under the scenarios described in the text. Panels A–C represent a transition from periods of high to lower incident PAR (A→B) and back again (B→C). Panels D–F represent the vertical uplifting of the nitracline (due to an internal wave or eddy heaving; D→E) and subsequent relaxation (E→F). These models are described further in the text.

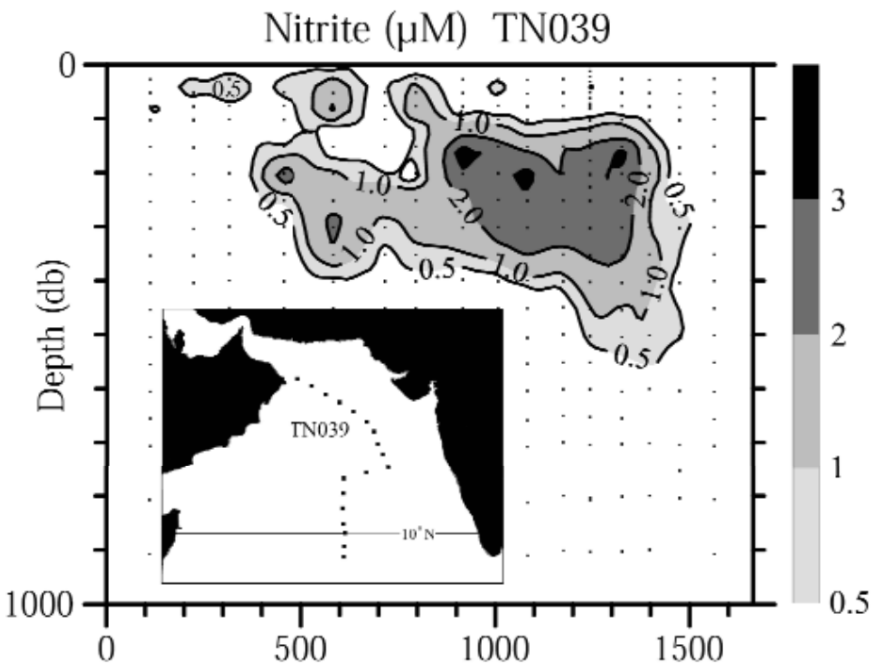
distribution of NO_2^- in the oceans: the primary maximum (< 1 µmol/kg)

Lomas & Lipschultz, Limnol. Oceanogr., 2006

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)





distribution of NO_2^- in the oceans: the secondary maximum (1-10 µmol/kg)

Codispoti et al., Sci. Mar., 2001

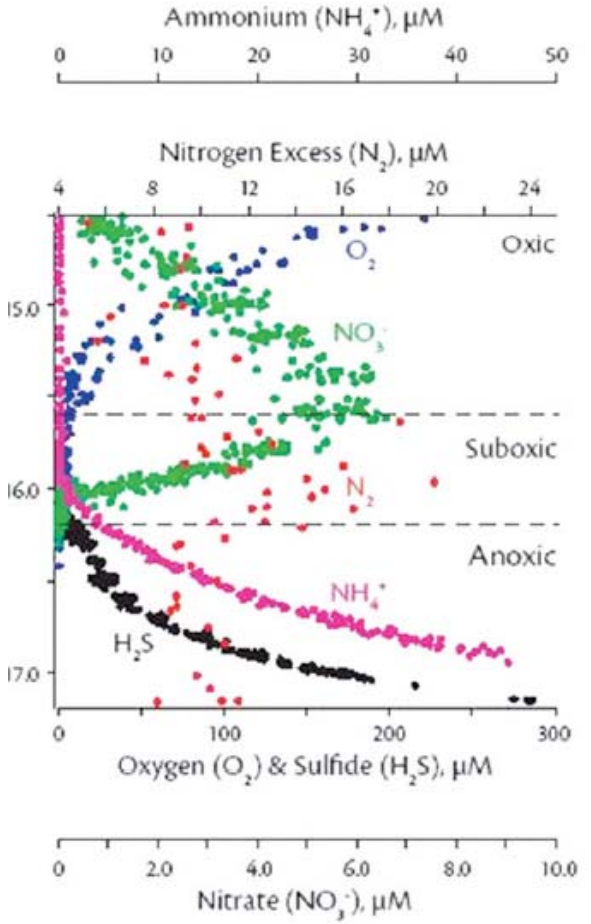
inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)

Se muestra seguidamente en cuatro ventanas las variables densidad, nitrógeno orgánico particulado, nitrato y amonio, a lo largo de una sección transversal de la Ría de Arousa.

En el centro de la imagen se incluye un indicador de las condiciones de afloramiento/hundimiento originadas por el arrastre del viento en plataforma. En condiciones de afloramiento una barra de color azul indicará la intensidad del mismo hasta valores de 3000 $m^3s^{-1}km^{-1}$ de costa. En condiciones de hundimiento una barra de color rojo se extiende hacia abajo hasta valores de 3000 $m^3s^{-1}km^{-1}$.

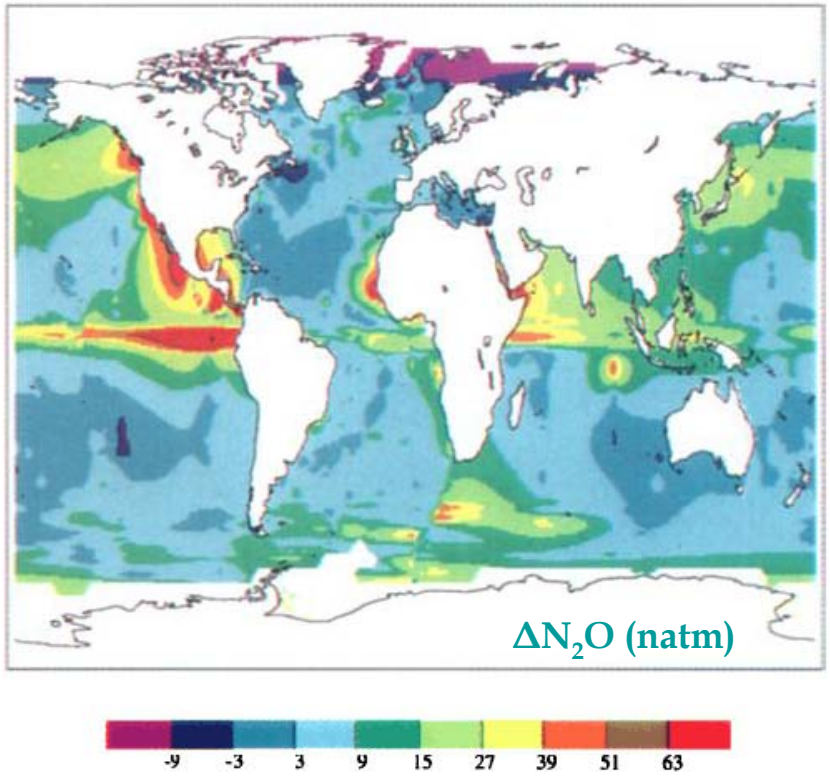
Las imágenes son resultado de la interpolación de datos reales obtenidos en muestreos realizados los lunes y los jueves de cada semana desde el 15 de mayo a 30 de octubre de 1989.

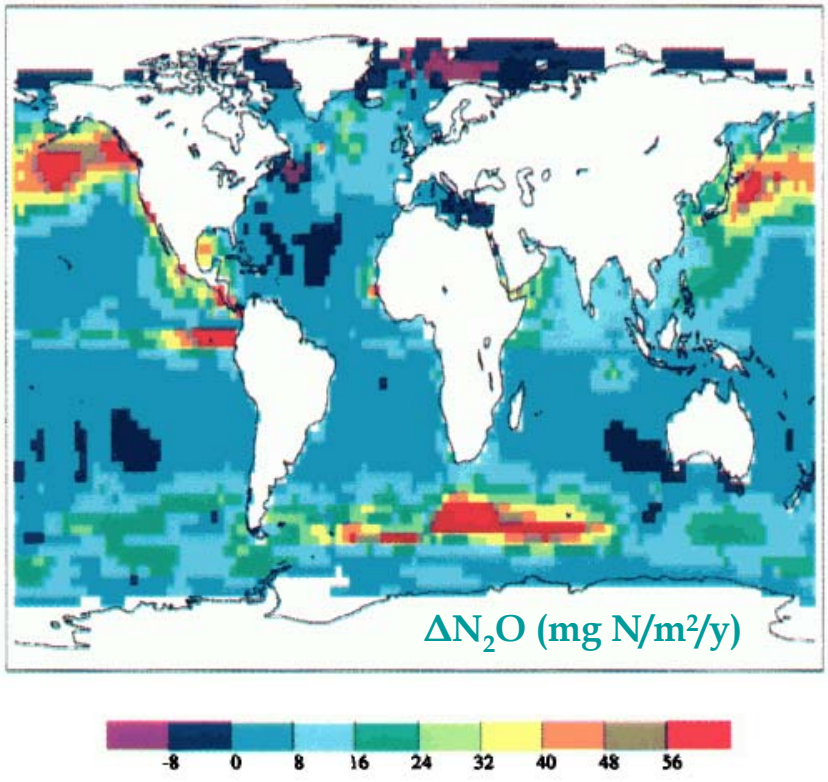


distribution of NH_4^+ in the oceans

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)



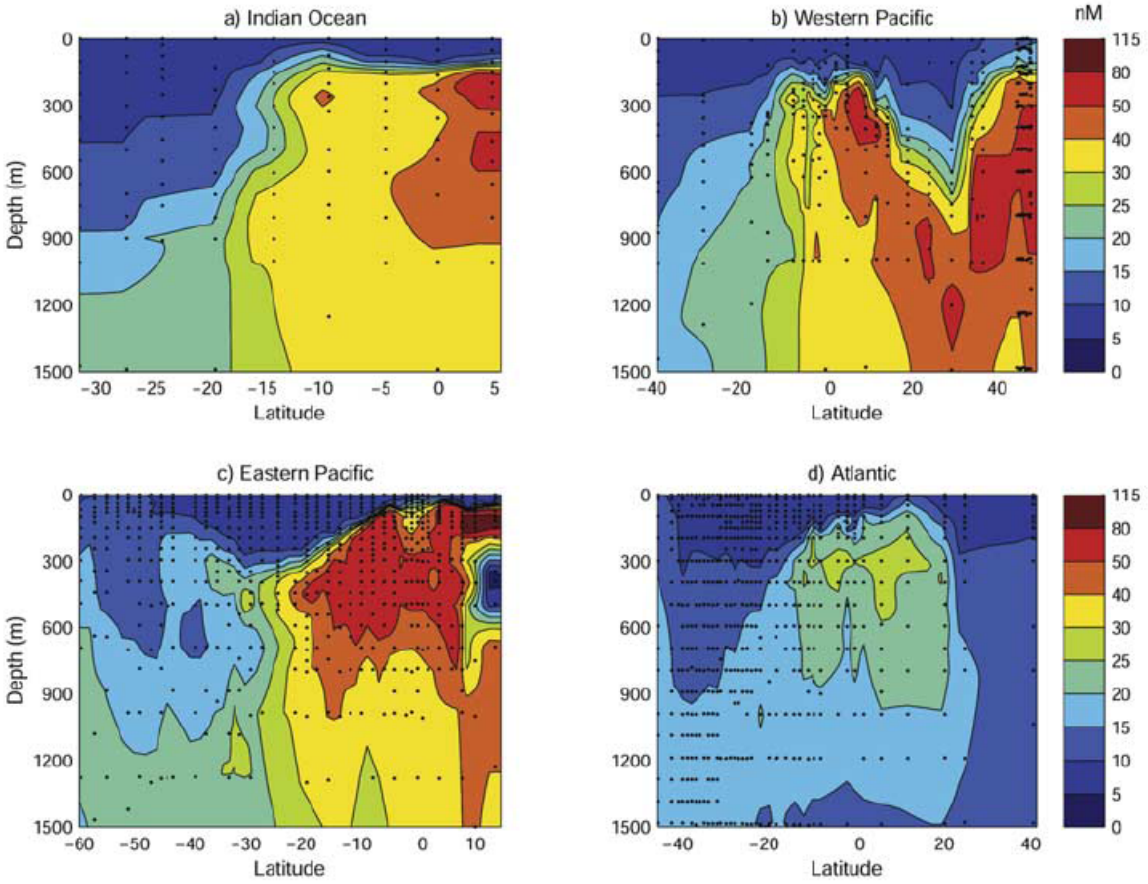


distribution of N_2O in the oceans

Nevison et al., Global Biogeochem. Cycles, 1995

inorganic micro-nutrients in the oceans

dissolved inorganic nitrogen (DIN)



distribution of N_2O in the oceans

Nevison et al., Global Biogeochem. Cycles, 2003

inorganic micro-nutrients in the oceans

dissolved inorganic phosphorus (DIP)

$$H_3PO_4 \overset{K_{1P}}{\Leftrightarrow} H_2PO_4^- + H^+$$

$$H_2PO_4^- \overset{K_{2P}}{\Leftrightarrow} HPO_4^{2-} + H^+$$

$$HPO_4^{2-} \overset{K_{3P}}{\Leftrightarrow} PO_4^{3-} + H^+$$

STANDARD SEAWATER

	pH_{SWS} = 8.0	pHsws= 4.25
H_3PO_4	0.0%	0.2%
$H_2PO_4^-$	0.8%	97.7%
HPO_4^{2-}	88.4%	2.2%
PO_4^{3-}	10.8%	0.0%

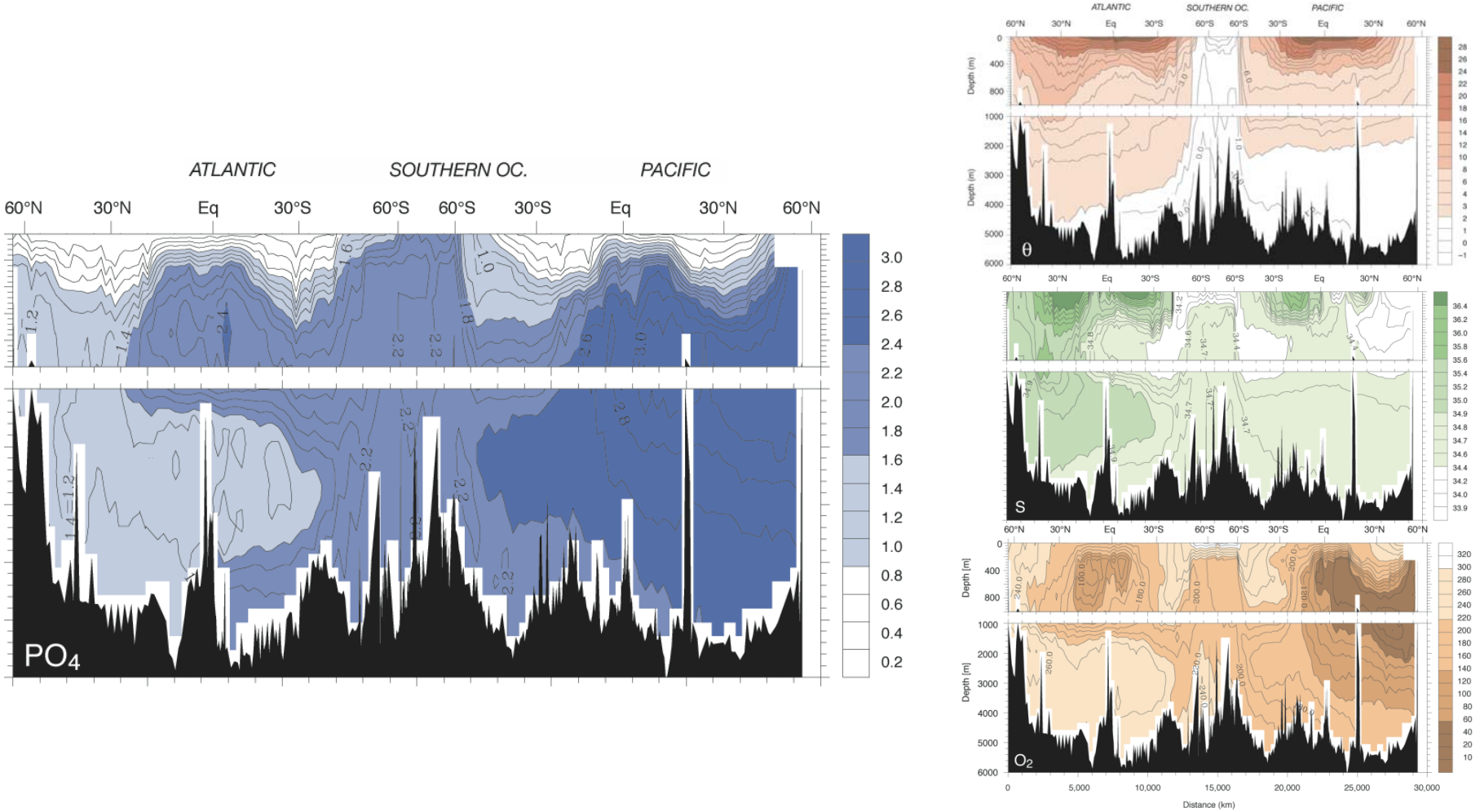
$$A_{PO4} = (3 \cdot [PO_4^{3-}] + 2 \cdot [HPO_4^{2-}] + [H_2PO_4^-])_{8.0} - (3 \cdot [PO_4^{3-}] + 2 \cdot [HPO_4^{2-}] + [H_2PO_4^-])_{4.25}$$

	pK_1	pK_2	pK_3	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
H_3PO_4	1,60	6,03	8,99	–1,016	–2,149	–1,133

dissolved inorganic phosphorus species

inorganic micro-nutrients in the oceans

dissolved inorganic phosphorus (DIP)



distribution of dissolved inorganic phsophorus in the oceans

Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)

inorganic micro-nutrients in the oceans

dissolved silicon (SiO_2)

$$H_4SiO_4 \overset{K_{si}}{\Leftrightarrow} Si(OH)_3O^- + H^+$$

STANDARD SEAWATER

$K_{Si}(35,15) = 10^{-9.52}$

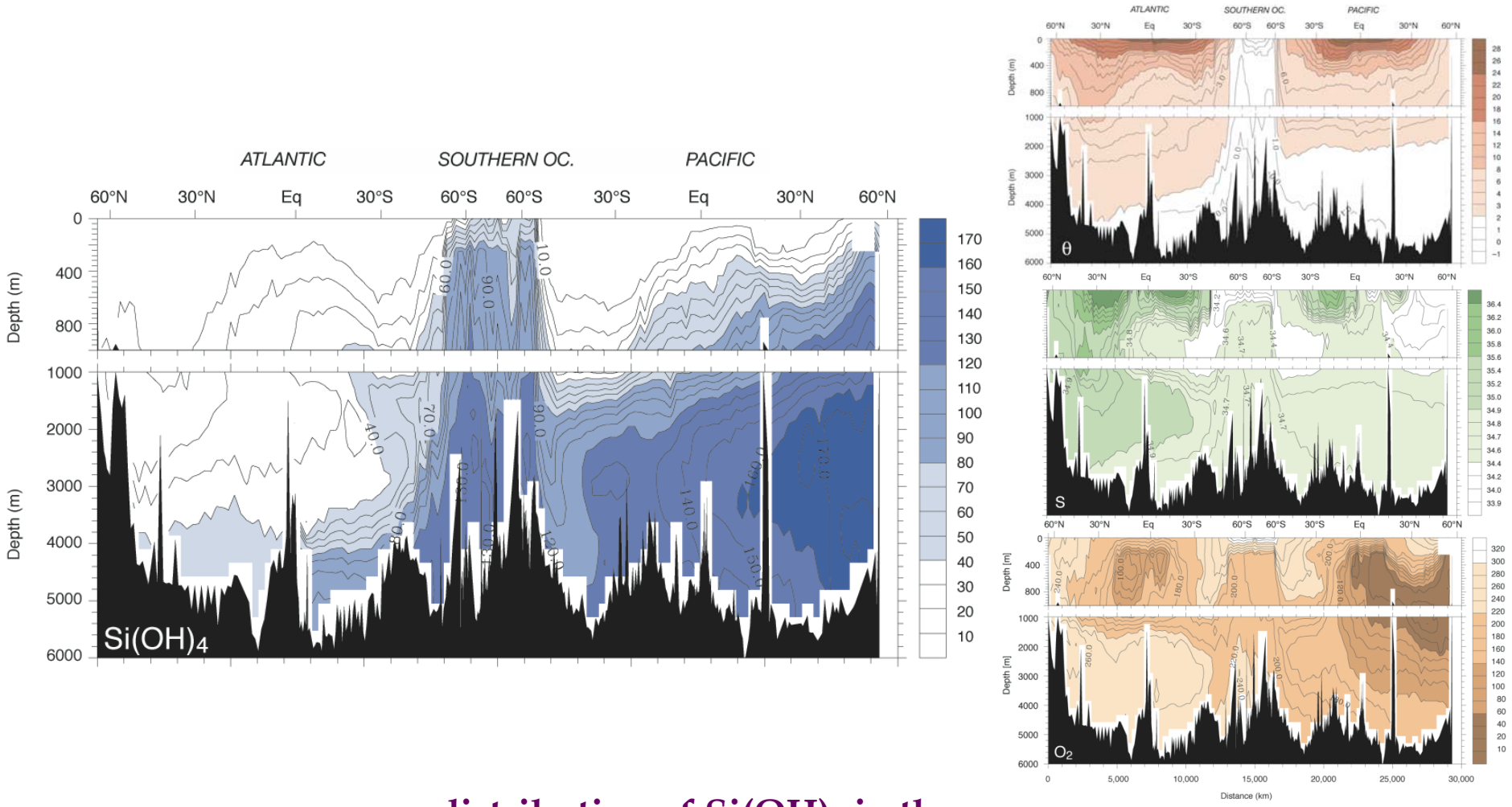
	pHsws = 8.0	**pHsws = 4.25**
H_4SiO_4	96.7%	100 %
$Si(OH)_3O^-$	4.2%	0.0%

	pKa	$\varepsilon_{4,25}$	$\varepsilon_{8,0}$	$\varepsilon_{8,0} - \varepsilon_{4,25}$
$SiO_4H_3^-/SiO_4H_4$	9,52	0,000	-0,042	-0,042

dissolved inorganic silicon species

inorganic micro-nutrients in the oceans

dissolved silicon (SiO_2)



distribution of $Si(OH)_4$ in the oceans

Sarmiento & Gruber, 2006 (http://www.up.ethz.ch/people/ngruber/publications/textbook)