



¿Que es un metal traza (o metal pesado)?

1. Químicamente corresponden a los elementos de transición, pero también se incluyen elementos no metálicos i.e., Al (III); Pb(IV); As(V), Se(VI)
2. Tienen con una densidad $> 5 \text{ g/cm}^3$
3. Su concentración en sedimentos es muy baja ($< 0,1\%$)
4. Son esenciales y tóxicos



Table 9.1 *Analysis of trace metals in seawater: The state of the art in 1970*

<i>Metal</i>	<i>Concentrations ($\mu\text{g kg}^{-1}$)</i>			<i>Present estimates of the "true" values</i>
Cadmium				
Lab A ^(a)	0.03			
Lab B	2.1	0.5	0.7	0.0001–0.12
Cesium				
Lab A	0.29	0.29	0.28	
Lab B	0.332	0.305	0.310	
Lab C	0.18	0.2	0.17	0.29
Cobalt				
Lab A	0.014	0.014	0.013	
Lab B	0.037	0.036	0.037	
Lab C	0.510	0.448	0.427	
Lab D	0.037	0.040	0.038	0.0006–0.006
Copper				
Lab A	1.35	1.55	1.42	
Lab B	7.5	6.3	6.3	
Lab C	27.4	2.21	2.81	
Lab D	0.9	0.8	1.0	
Lab E	15.0	15.0	14.4	0.06–0.4

^(a)The laboratory coding is different for each element. Most analysts would not participate unless the identifications of results with analysts were kept confidential.

An extract of some data from the results of a trace element intercalibration study, reported by Brewer and Spencer 1970.



The Problem of Metals

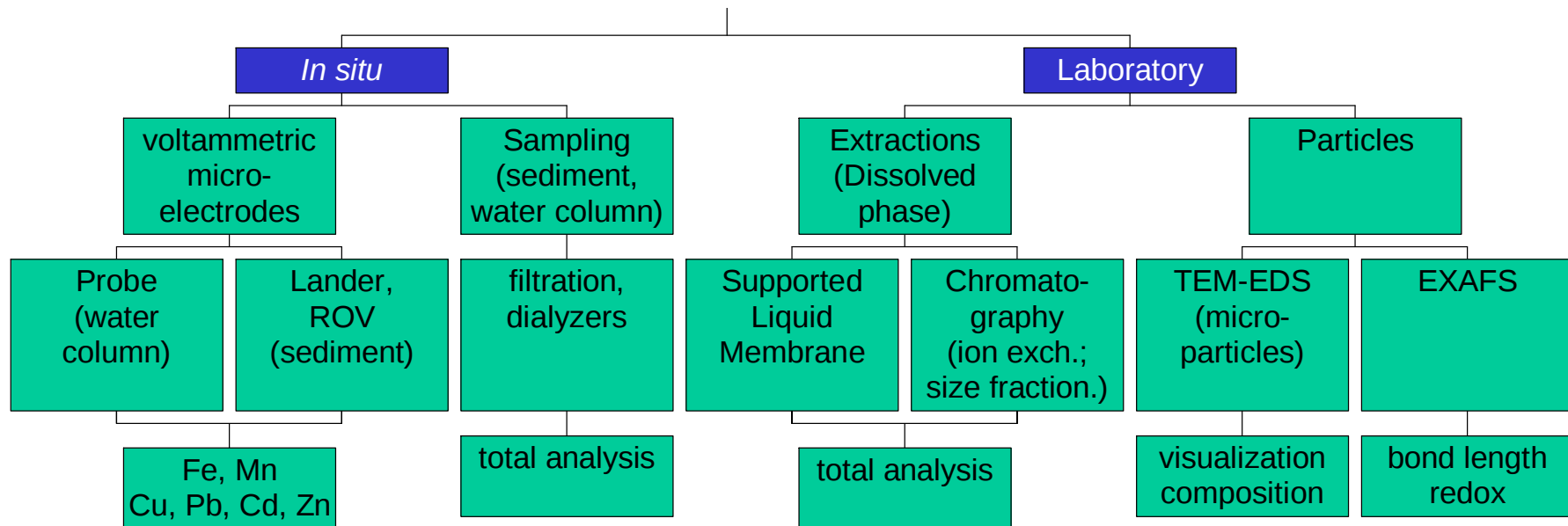
- Metals are potentially dangerous because they can affect enzymatic functions and the nervous system
- Anthropogenic activities contribute to their accumulation in the environment
- Metals are not biodegradable

=> What is the toxic species and how much?

=> What is the residence time?



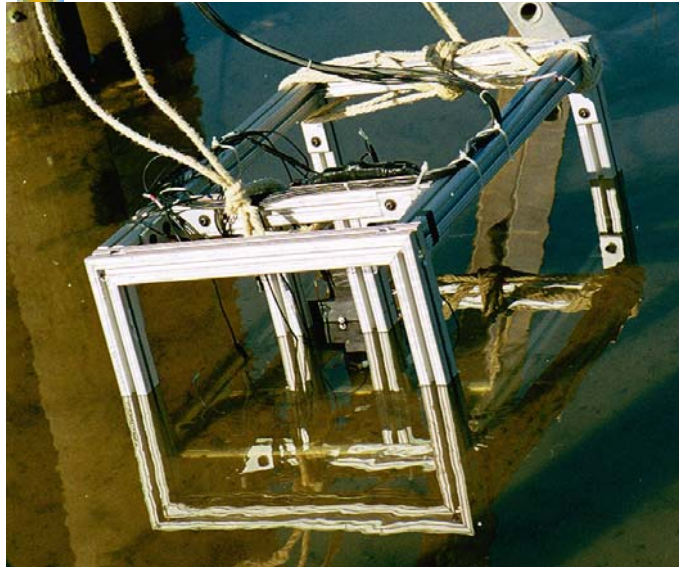
Analytical Speciation (multi-techniques)



- few techniques available
- speciation is operationally defined
- artifacts due to sampling and handling



In Situ Voltammetric Measurements



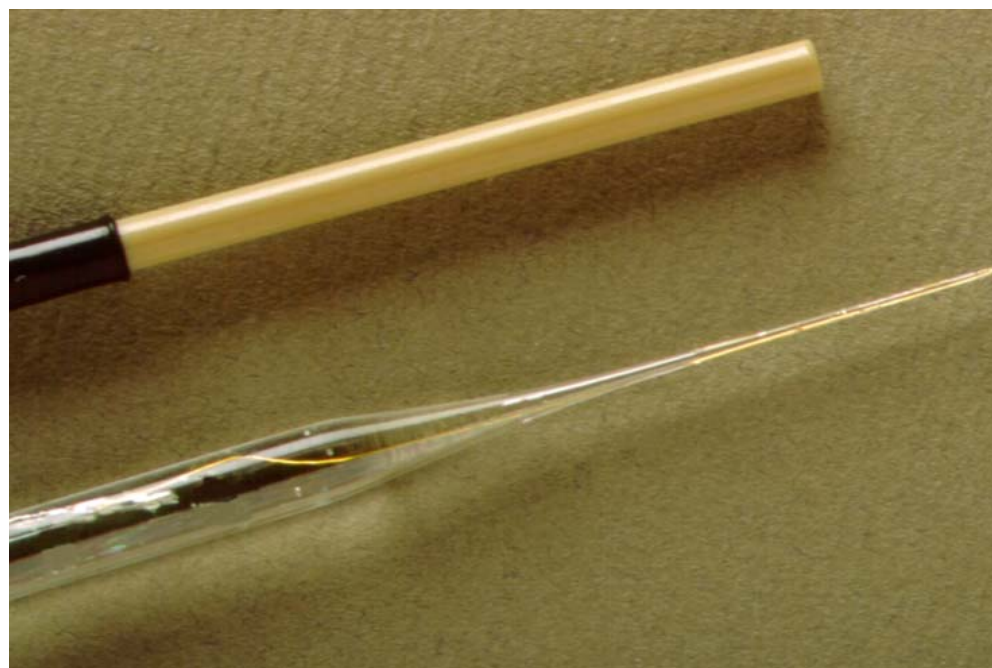
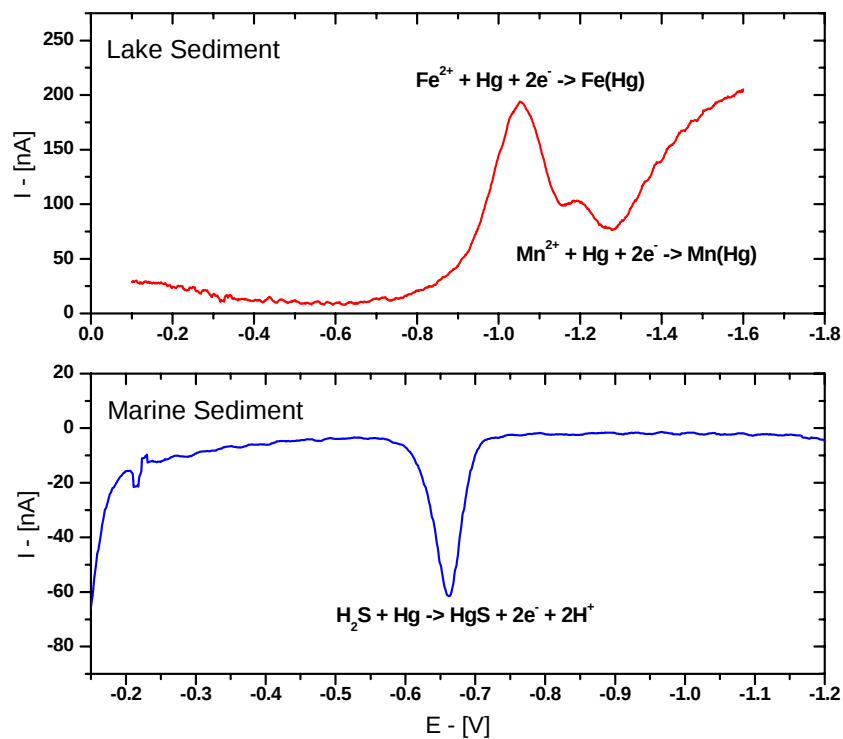
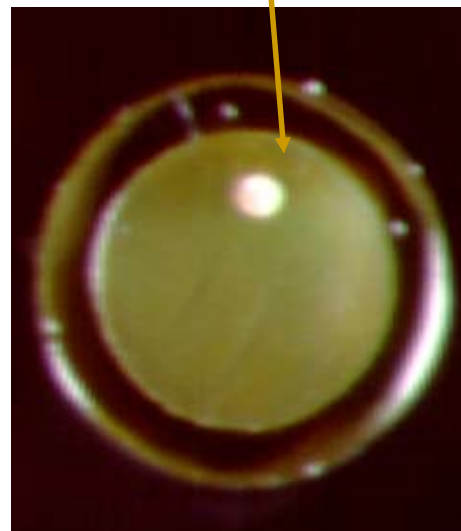


Design of *in situ* sensors

100 μm diameter Au

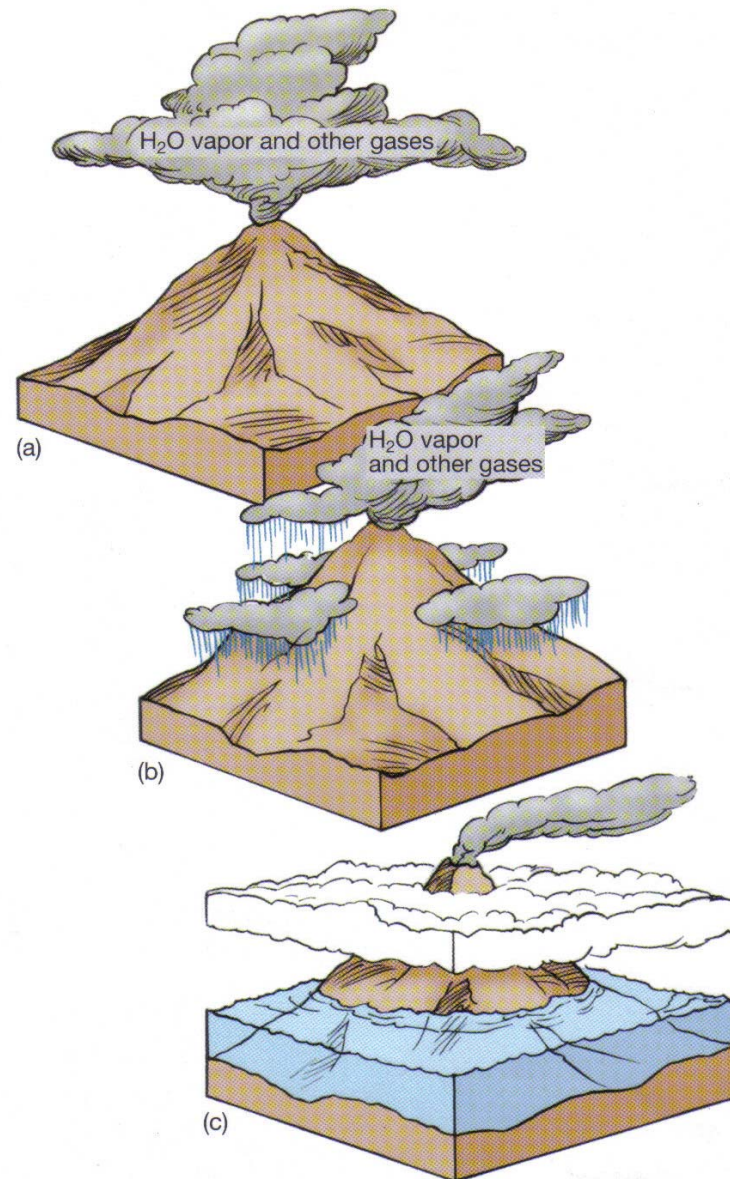


- Reliable, automatic measurements
- Simple, compact, low-cost
- Minimization of artifacts
- Multi-element analysis
- High sensitivity (1 pM to 100 nM)
- Speciation capabilities
- Microsensors





T-14 Fig. 1-14 Formation of Earth's oceans





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Area: 361,100,000 square kilometers (139,400,000 square miles)

Volume: 1,370,000,000 cubic kilometers (329,000,000 cubic miles)

Average depth: 3,796 meters (12,451 feet)

Average temperature: 3.9°C (39.0°F)

Average salinity: 34,482 grams per kilogram (0.56 ounce per pound), 3.4%

Average land elevation: 840 meters (2,772 feet)

Most abundant elements (by mass):

Oxygen	(86%)
Hydrogen	(11%)
Chlorine	(1.9%)
Sodium	(1.1%)
Magnesium	(0.1%)

Age: About 4 billion years

Future: Uncertain

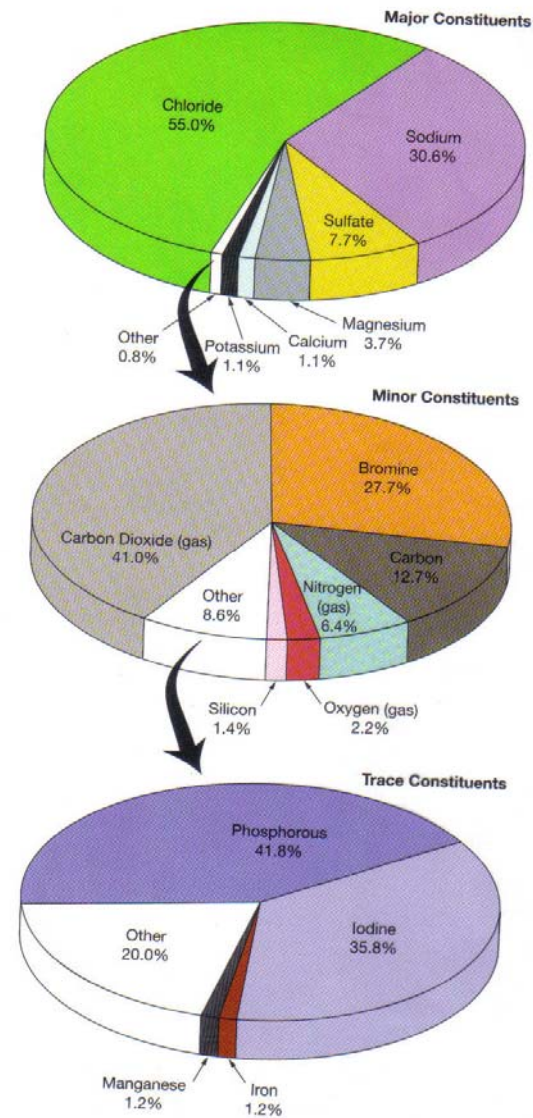
Characteristics of the ocean world

**TABLE 7-1** Composition of seawater.

Ion	% (by weight)	g/1000 g seawater (%)
Na ⁺	30.66	10.77
Mg ²⁺	3.65	1.29
Ca ²⁺	1.17	0.41
K ⁺	1.13	0.40
Sr ²⁺	0.023	0.008
Cl ⁻	55.02	19.35
SO ₄ ²⁻	7.71	2.71
HCO ₃ ⁻	0.30	0.12
Br ⁻	0.19	0.067
CO ₃ ²⁻	0.046	0.016
B(OH) ₄ ⁻	0.023	0.008
F ⁻	0.004	0.0014
OH ⁻	0.0004	0.0001
B(OH) ₃	0.055	0.019
Trace components	0.02	0.007
Total	100	35.0

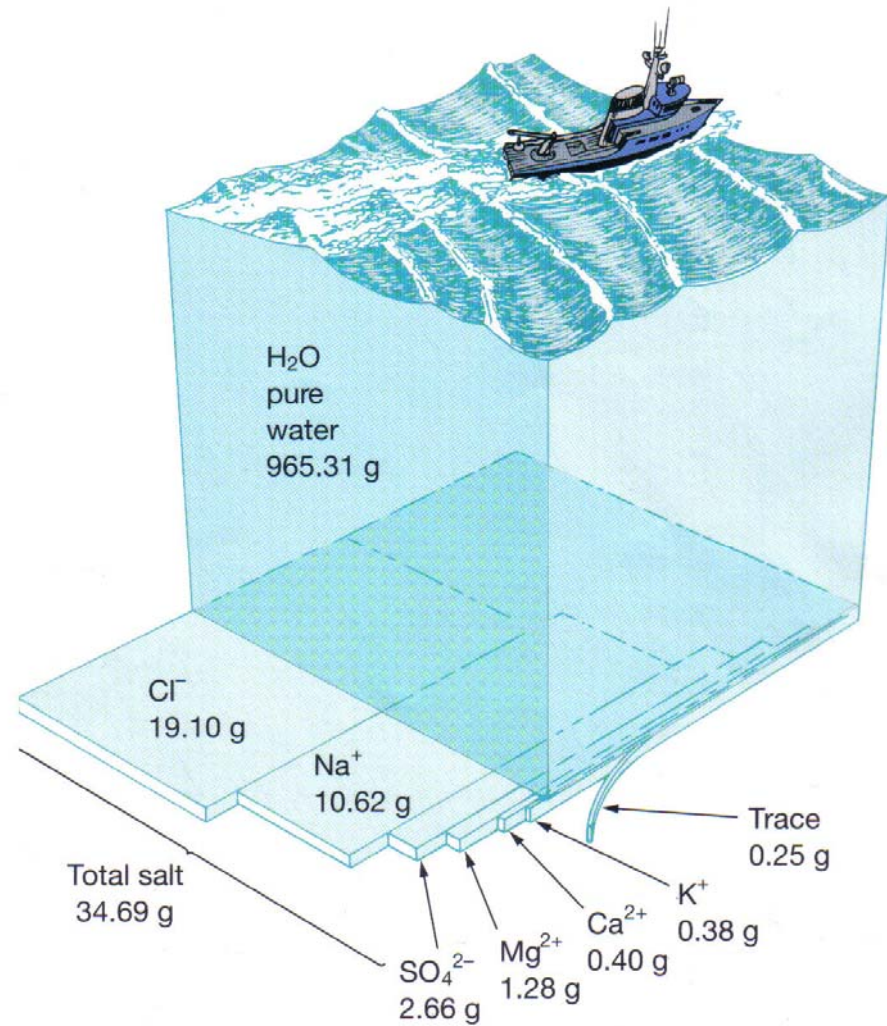


T-104 Fig. 5-14 Major dissolved materials in seawater



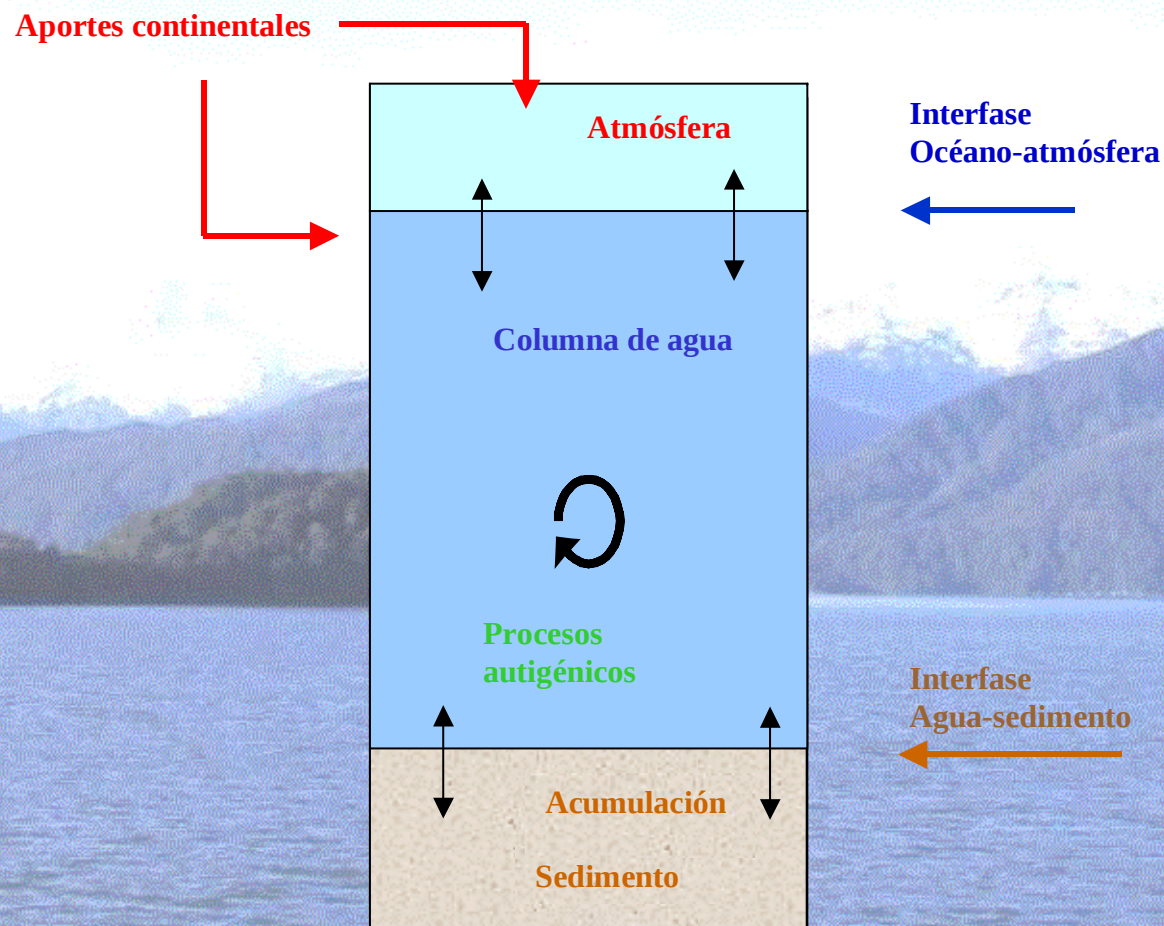


T-103 Fig. 5-13 Constituents of ocean salinity



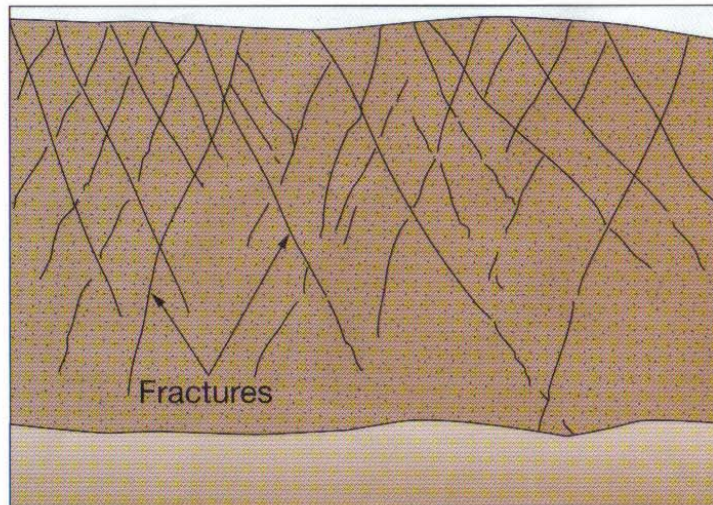


SISTEMA MARINO COMO AMBIENTE



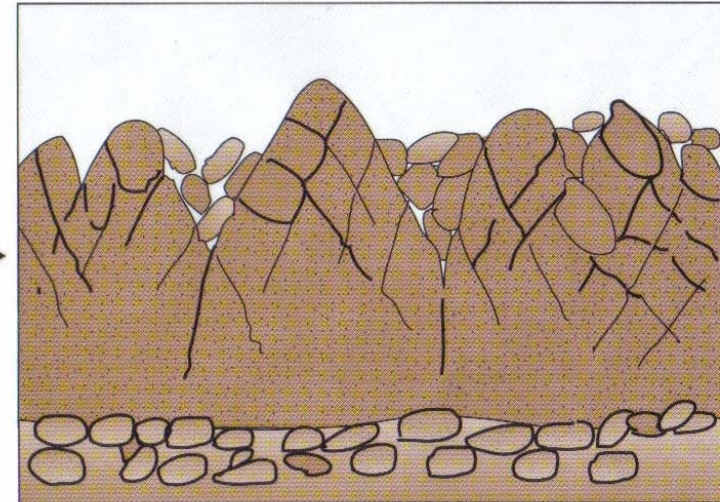




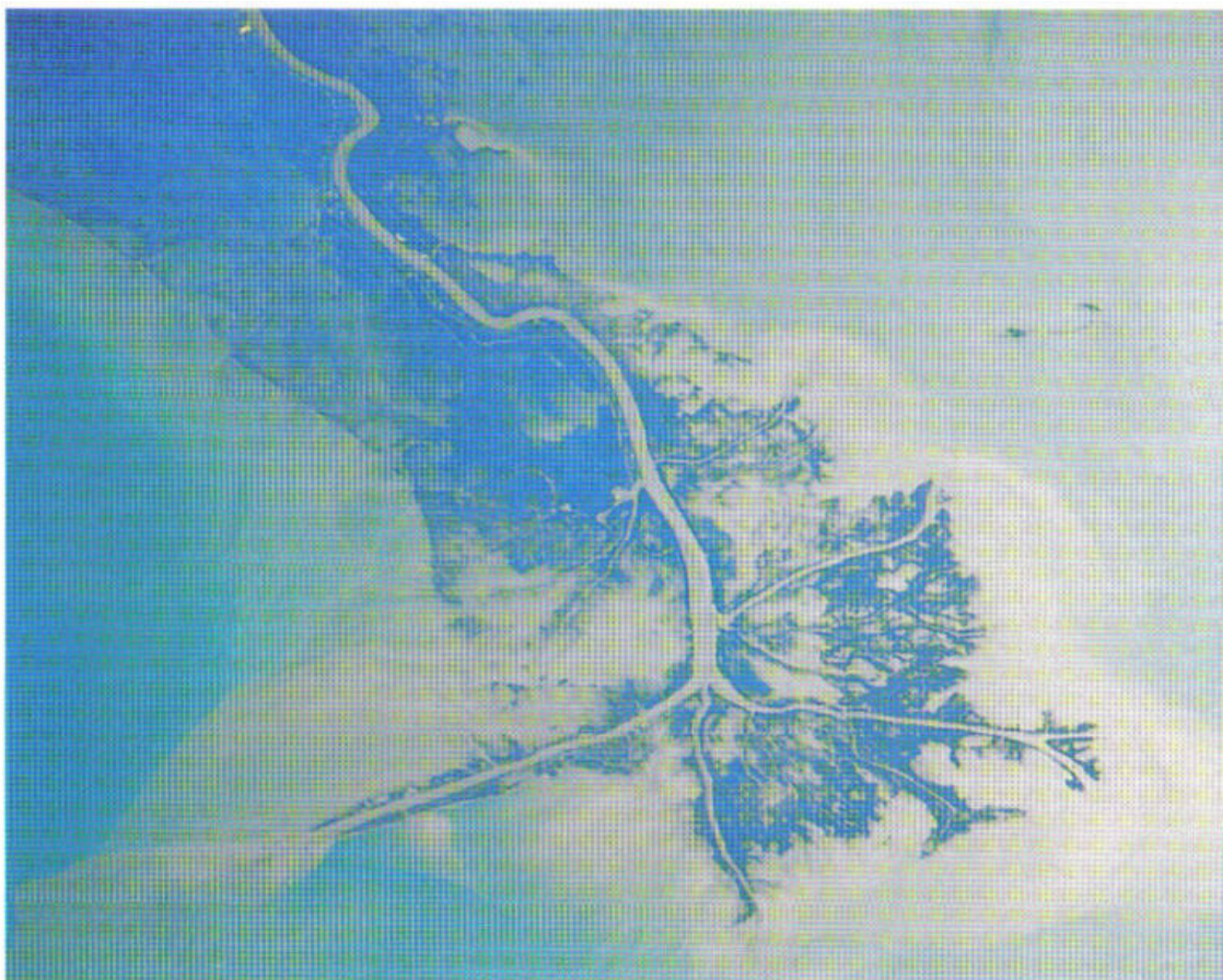


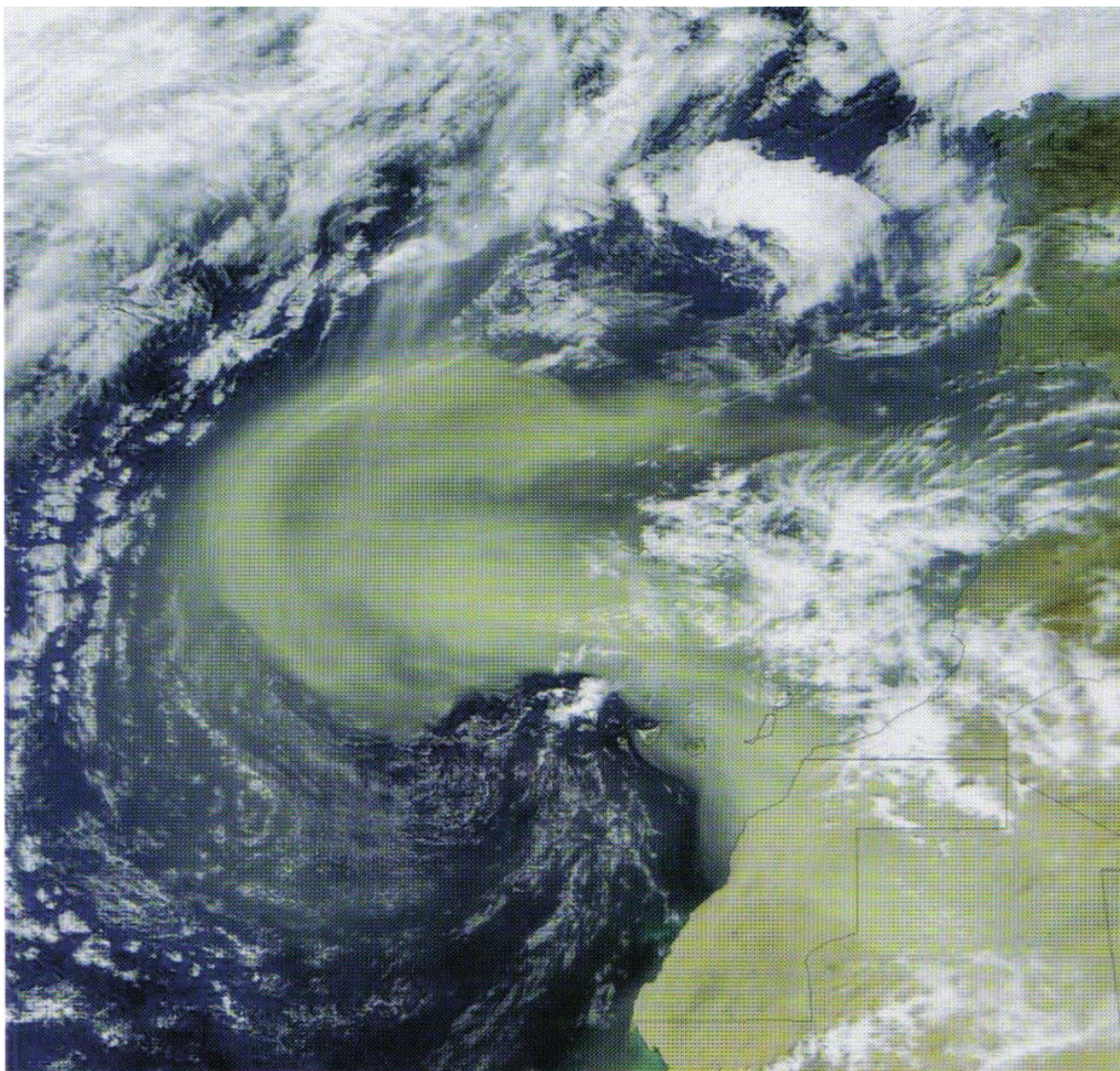
(a)

over
time
→

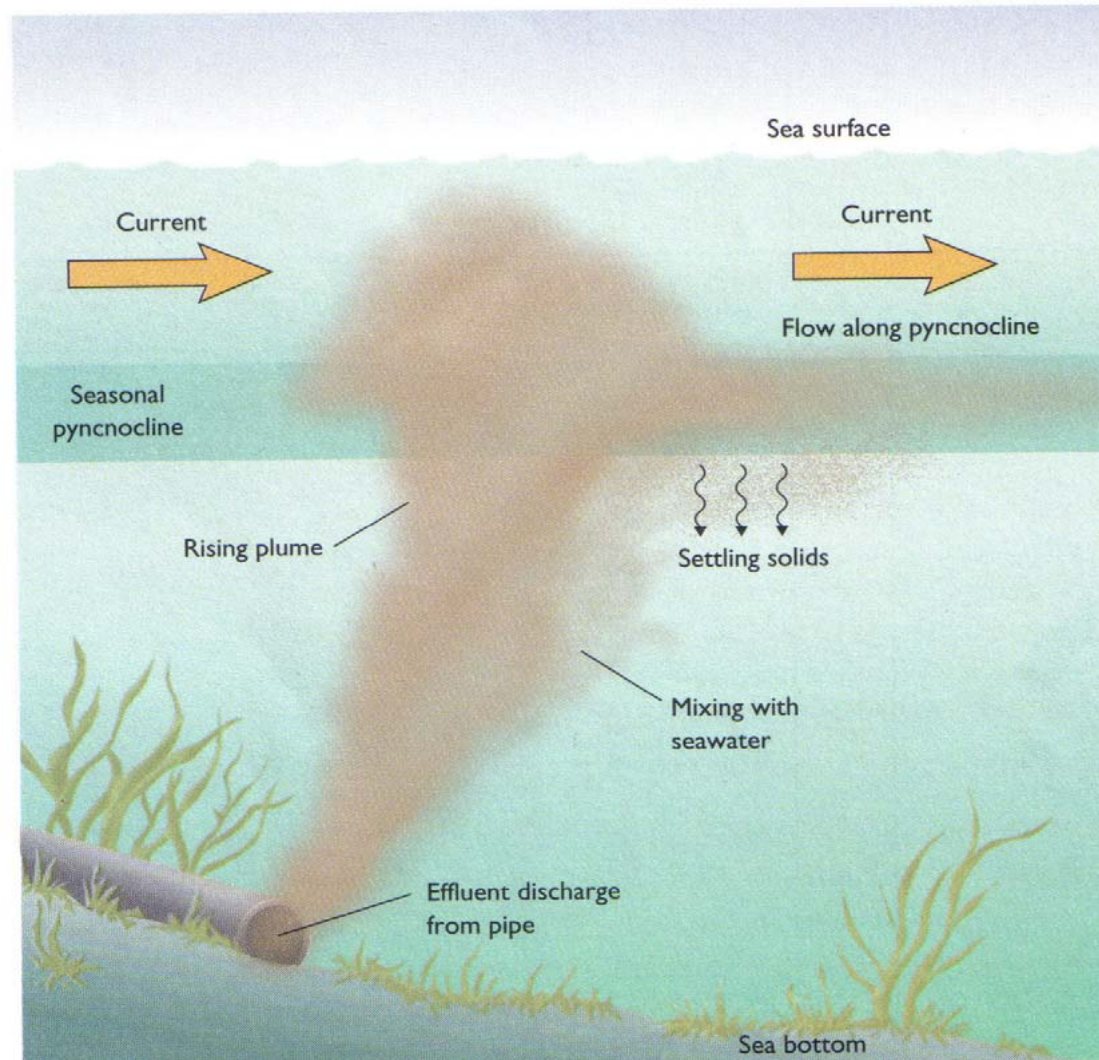


(b)



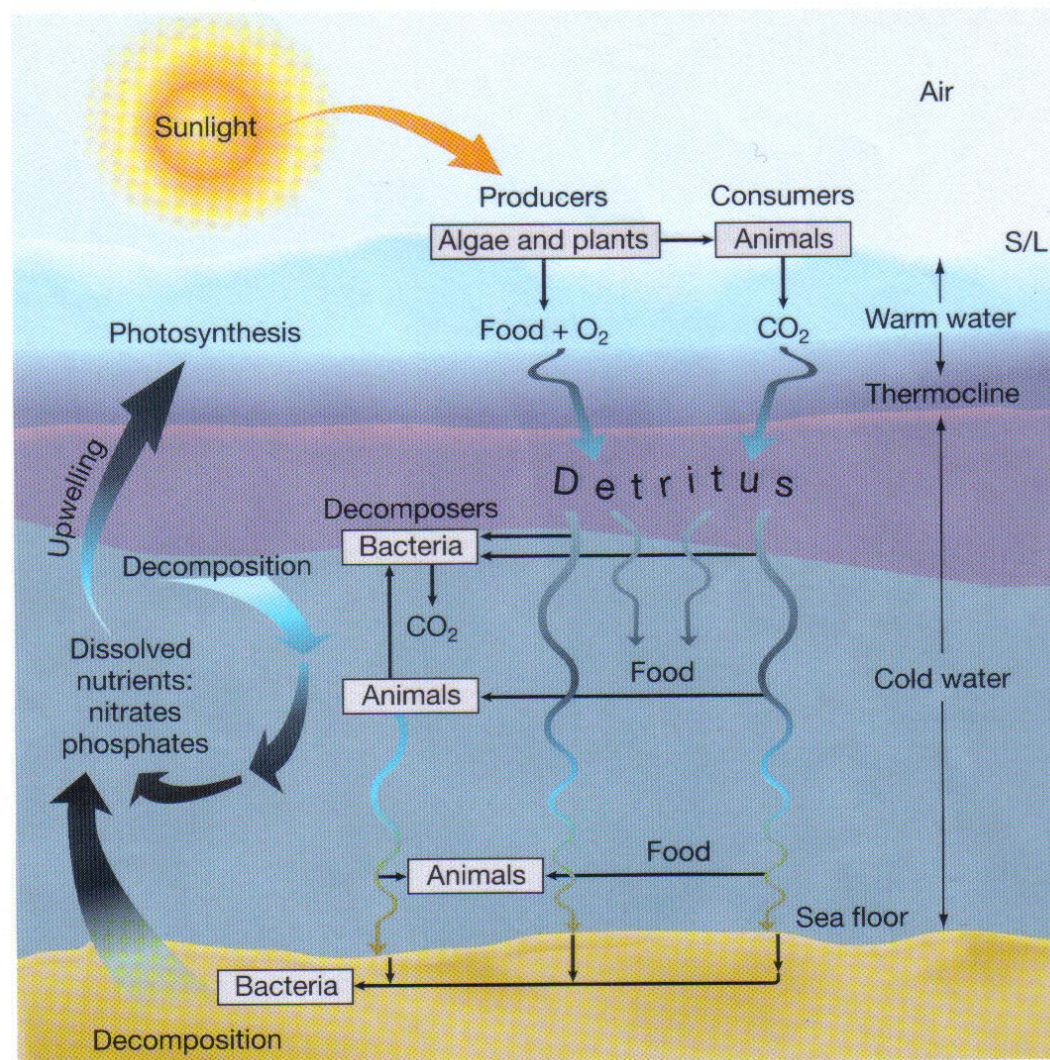






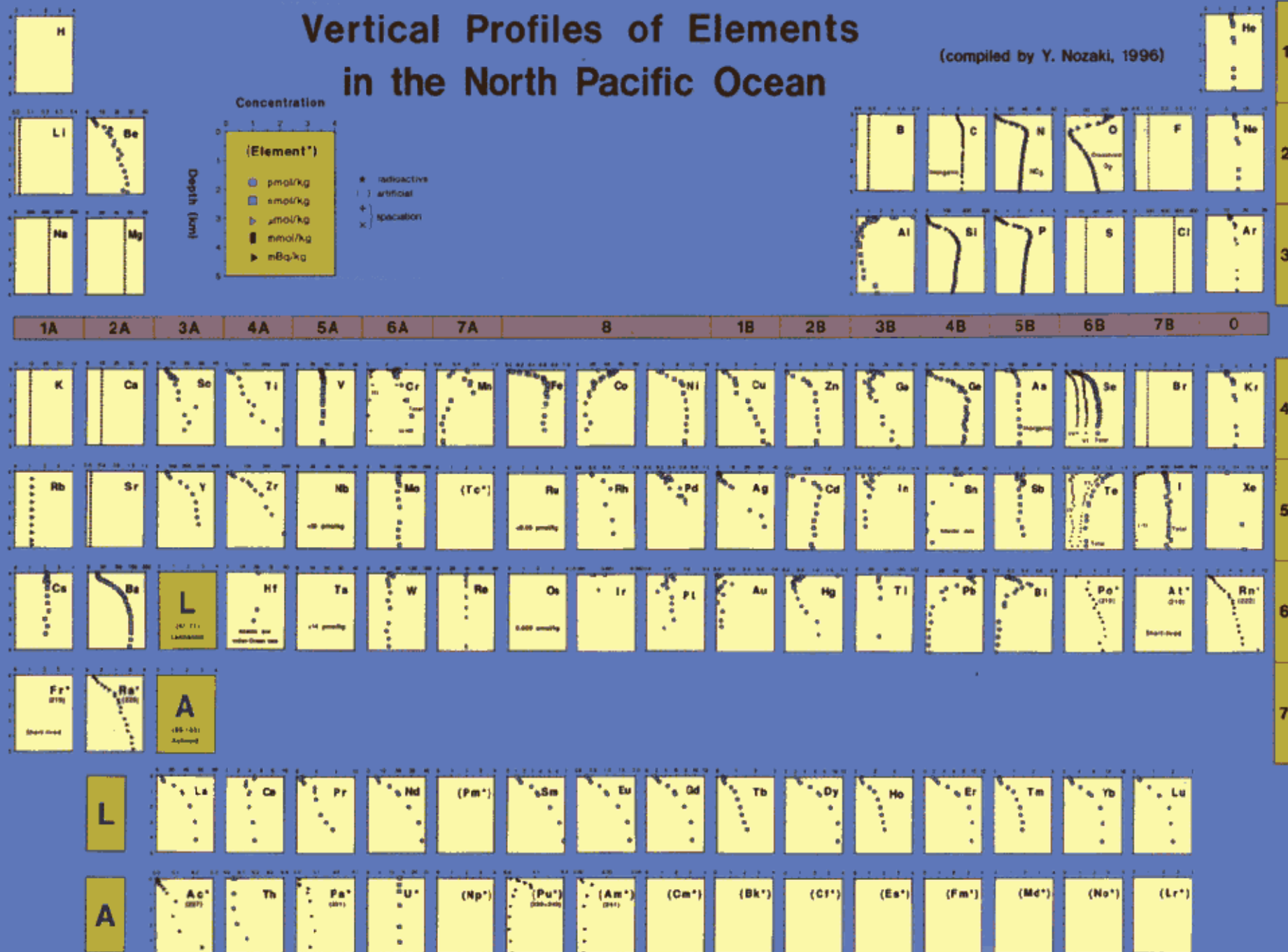


T-284 Fig. 13-16 Biogeochemical cycling of matter



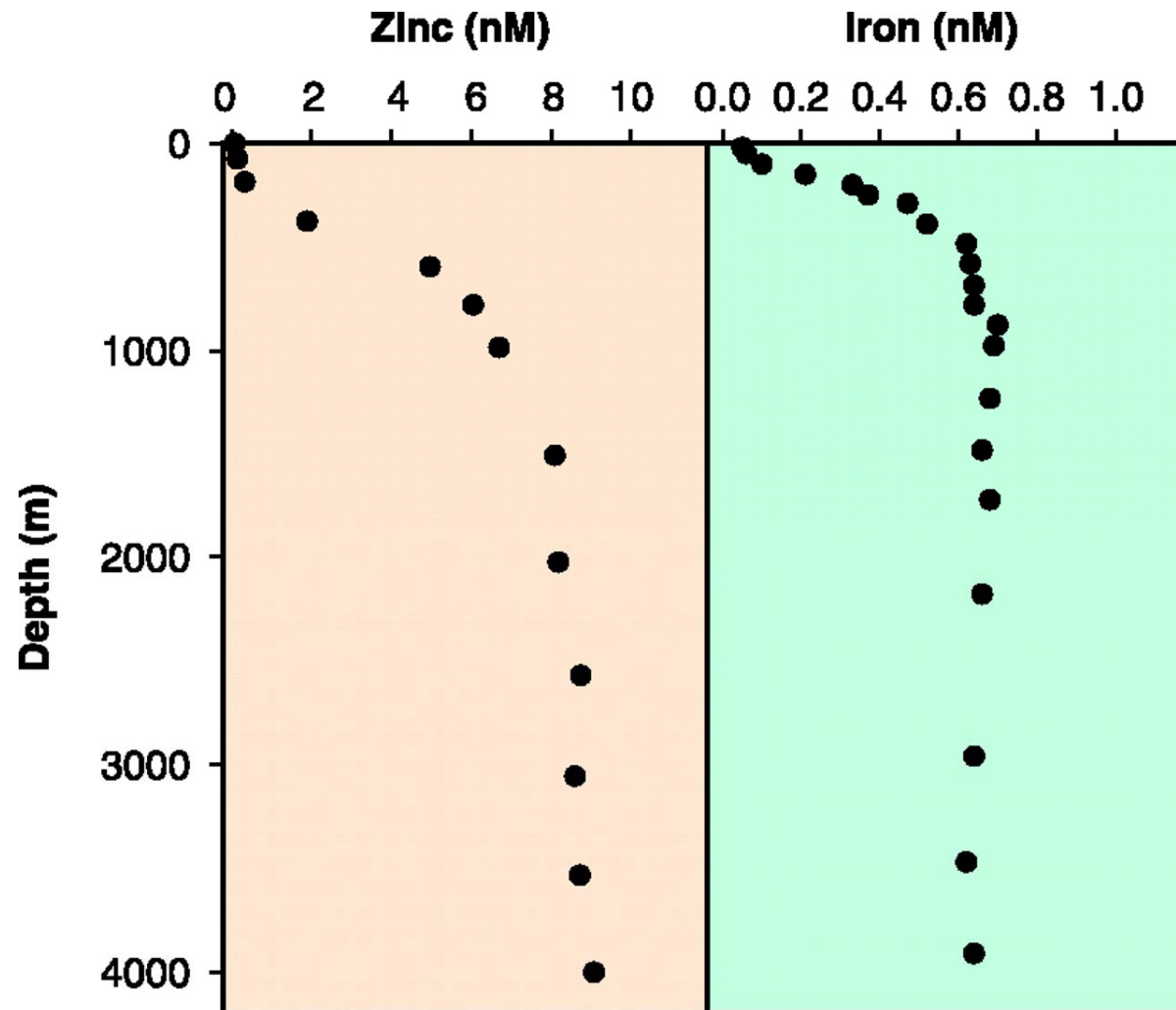
Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 1996)





Vertical profiles of dissolved zinc (43) and iron (44) concentrations in the north Pacific Ocean





Trace Metals and Other Minor Elements

2 Concentrations of the minor constituents in seawater, except the gases and some radioactive, but including uranium

Element		Concentration (units per kg)		Type of Distribution
Symbol	Name	Approx. Mean	Range	
Li	Lithium	25 μ mol	—	Conservative
Be	Beryllium	20 pmol	4–30	Nutrient; scavenged
N	Nitrogen (NO ₃)	30 μ mol	<0.1–45	Nutrient
Al	Aluminum	10 nmol	0.1–40	Mid-depth minima
Si	Silicon	100 μ mol	<1–200	Nutrient
P	Phosphorus	2.3 μ mol	<0.1–3.5	Nutrient
Sc	Scandium	15 pmol	8–20	Surface depletion
Ti	Titanium	200 pmol	4–300	Surface depletion
V	Vanadium	30 nmol	20–35	Sl. surface depletion
Cr	Chromium	4 nmol	2–5	Nutrient
Mn	Manganese	0.5 nmol	0.2–3	Depletion at depth
Fe	Iron	1 nmol	0.1–2.5	Depl. at surf. & depth
Co	Cobalt	20 pmol	10–100	Depl. at surf. & depth
Ni	Nickel	8 nmol	2–12	Nutrient
Cu	Copper	4 nmol	0.5–6	Nutrient; scavenged
Zn	Zinc	6 nmol	0.05–9	Nutrient
Ga	Gallium	20 pmol	2–50	Complex, scavenged
Ge	Germanium	70 pmol	<7–115	Nutrient
As	Arsenic	23 nmol	15–25	Nutrient
Se	Selenium	1.7 nmol	0.5–2.3	Nutrient
Rb	Rubidium	1.4 μ mol	—	Conservative
Y	Yttrium	250 pmol	80–300	?
Zr	Zirconium	200 pmol	12–300	Nutrient; scavenged
Nb	Niobium	(<50 pmol)	?	?
Mo	Molybdenum	100 nmol	92–105	Conservative
Ru	Ruthenium	(20 fmol)	?	?
Rh	Rhodium	0.8 pmol	0.3–1.0	Scavenged, nutrient ?
Pd	Palladium	0.6 pmol	0.2–0.6	Surface depletion
Ag	Silver	25 pmol	0.5–45	Nutrient, complex
Cd	Cadmium	0.7 nmol	0.001–1.1	Nutrient
In	Indium	(0.1 pmol)	0.05–0.15	Scavenged ?
Tl	Tin	(4 pmol)	(1–12)	Depl. at depth ?
Sb	Antimony	(1.2 nmol)	?	?
Te	Tellurium	0.6 pmol	0.4–1.7	Scavenged
I	Iodine	0.4 μ mol	0.2–0.5	Nutrient
Cs	Cesium	2.2 nmol	—	Conservative
Ba	Barium	100 nmol	32–150	Nutrient
La	Lanthanum	30 pmol	8–57	Surface depletion
Ce	Cerium	20 pmol	16–26	Surface depletion
Pr	Praeseodymium	5 pmol	1–8	Surface depletion
Nd	Neodymium	25 pmol	5–40	Surface depletion
Sm	Samarium	4 pmol	1–6	Surface depletion
Eu	Europium	1 pmol	0.3–1.7	Surface depletion
Gd	Gadolinium	6 pmol	2–9	Surface depletion
Tb	Terbium	1 pmol	0.2–1.5	Surface depletion
Dy	Dysprosium	8 pmol	2–12	Surface depletion





Table 9.2 Continued

Num.	Element		Concentration (units per kg)		Type of Distribution
	Symbol	Name	Approx. Mean	Range	
67	Ho	Holmium	2.5 pmol	0.5–3	Surface depletion
68	Er	Erbium	8 pmol	2–10	Surface depletion
69	Tm	Thulium	1 pmol	0.3–1.5	Surface depletion
70	Yb	Ytterbium	7 pmol	1.5–11	Surface depletion
71	Lu	Lutetium	1 pmol	0.2–1.8	Surface depletion
72	Hf	Hafnium	(20 pmol)	?	Surface depletion
73	Ta	Tantalum	(<14 pmol)	?	?
74	W	Tungsten	56 pmol	45–67	Conservative
75	Re	Rhenium	40 pmol	—	Conservative
76	Os	Osmium	(9 fmol)	?	?
77	Ir	Iridium	(0.7 fmol)	0.5–0.9	?
78	Pt	Platinum	1 pmol	0.54–1.64	Surface depletion
79	Au	Gold	50 fmol	20–200	variable
80	Hg	Mercury	2 pmol	0.5–12	Complex, scavenged
81	Tl	Thallium	60 pmol	—	Conservative
82	Pb	Lead	10 pmol	5–175	High in surface water
83	Bi	Bismuth	(0.1 pmol)	(<0.015–0.24)	Depletion at depth
92	U	Uranium	13.6 nmol	± ~ 1–2%	Conservative

Name	Abbrev.	Fraction	Number of chemical units
mole	= mol	= 1 mol	= 6×10^{23} atoms or molecules ^(a)
millimole	= mmol	= 10^{-3} mol	= 6×10^{20} atoms or molecules
micromole	= μ mol	= 10^{-6} mol	= 6×10^{17} atoms or molecules
nannomole	= nmol	= 10^{-9} mol	= 6×10^{14} atoms or molecules
picomole	= pmol	= 10^{-12} mol	= 6×10^{11} atoms or molecules
femtomole	= fmol	= 10^{-15} mol	= 6×10^8 atoms or molecules.



TABLE 11.1
Oceanic Inputs of Some Trace Metals in 10^9 g/y

<i>Element</i>	<i>Mining</i>	<i>Continental and Volcanic Dust Flux</i>	<i>Industrial and Fossil Fuel Emissions</i>	<i>Atmospheric Rainout</i>	<i>Stream Load</i>	<i>Industrial and Fossil Fuel Emissions Atmospheric Rainout</i>
Cd	170	3	55	510	1,200	0.1
As	460	28	780	2,900	3,000	0.3
Hg	89	0.4	110	410	50	0.3
Se	12	7	120	200	180	0.6
Co	260	70	44	62	3,500	0.7
Ni	6,600	280	980	1,200	13,000	0.8
Zn	58,000	360	8,400	10,000	25,000	0.8
Cu	71,000	190	2,600	2,600	11,000	1.0
Sb	690	10	380	340	1,000	1.1
V	190	650	2,100	1,900	24,000	1.1
Mn	92,000	6,100	3,200	3,000	160,000	1.1
Cr	23,000	580	940	720	17,000	1.3
Mo	830	11	510	310	700	1.7
Ti	10,000	35,000	5,200	2,700	840,000	1.9
Fe	600,000	280,000	110,000	49,000	9,900,000	2.2
Al	120,000	490,000	72,000	33,000	17,000,000	2.2
Pb	35,000	59	20,000	5,700	4,700	3.5
Sm		41	12	3	900	4.0
Ag	92	0.6	50	10	130	5.0
Sn	2,400	52	430		2,900	

Source: From F. T. Mackenzie, R. J. Lahtzy, and V. Paterson, reprinted with permission from *Mathematical Sedimentology*, vol. 11, p. 101, copyright © 1979 by Plenum Press, New York.



TABLE 11.4
Enrichment Factors for Metals in
the Tissues of Phytoplankton and
Brown Algae

<i>Element</i>	<i>Plankton</i>	<i>Brown Algae</i>
Al	25,000	1550
Cd	910	890
Co	4600	650
Cr	17,000	6500
Cu	17,000	920
Fe	87,000	17,000
I	1200	6200
Mg	0.59	0.96
Mn	9400	6500
Mo	25	11
N	19,000	7500
Na	0.14	0.78
Ni	1700	140
P	15,000	10,000
Pb	41,000	70,000
S	1.7	3.4
Si	17,000	120
Sn	2900	92
V	620	250
Zn	65,000	3400

Source: From *The Handbook of Environmental Chemistry*, P. J. Craig (ed.: O. Hut-zinger), copyright © 1980 by Springer-Verlag, Heidelberg, p. 210. After *Trace Elements in Biochemistry*, H. J. M. Bowen, copyright © 1966 by Academic Press, Orlando, FL, pp. 87–88. Reprinted by permission.



A

Cu

CuY

Cu

CuZ

sid

+ Fe(III)

$\rightleftharpoons$ Fesid

L

+ Co

$\rightleftharpoons$ CoL

Cd

CdX

X = $(\gamma\text{EC})_2\text{G}$
 Y = QC & RC
 Z = unknown
 sid = alterobactin A
 L = unknown

B

Fe(III)

Fe(II)

O_2

$h\nu$

Fe(II)L

Fe(III)O_x

Mn(II)

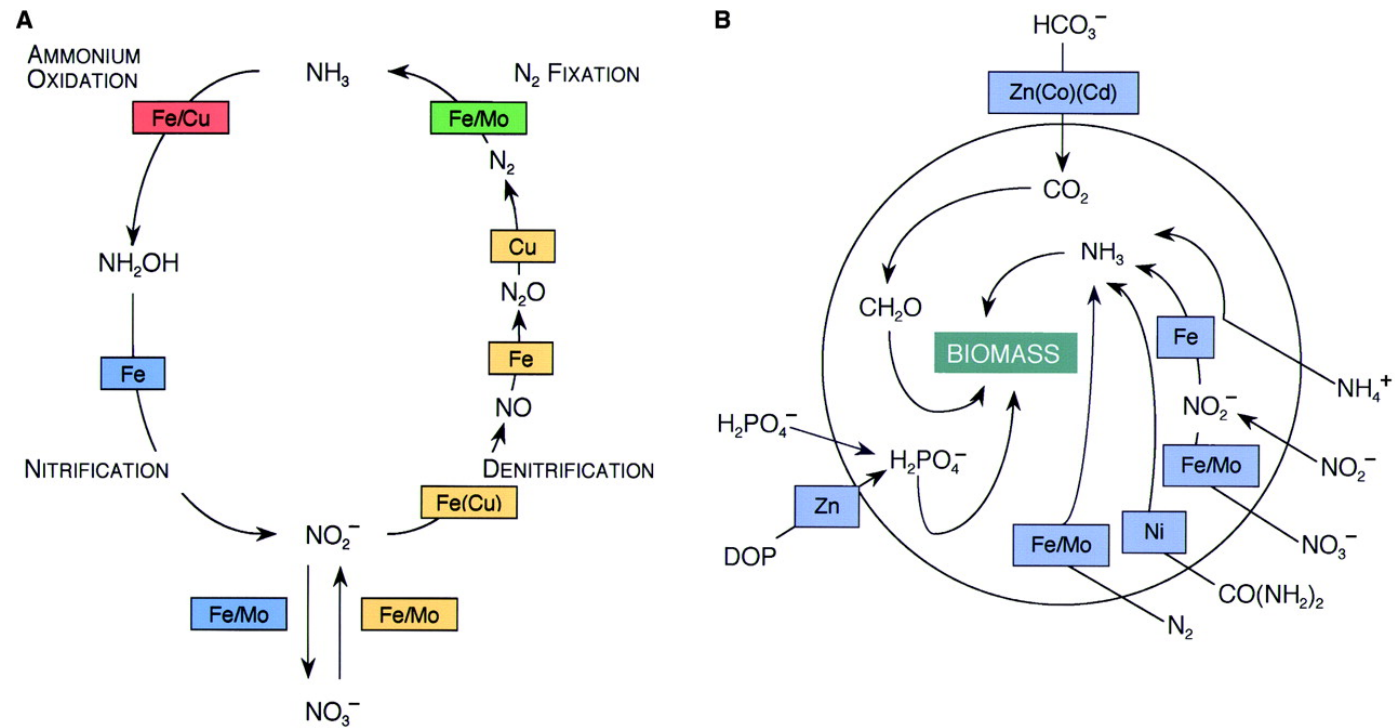
MnO_2

$h\nu$

Mn(IV)O_x



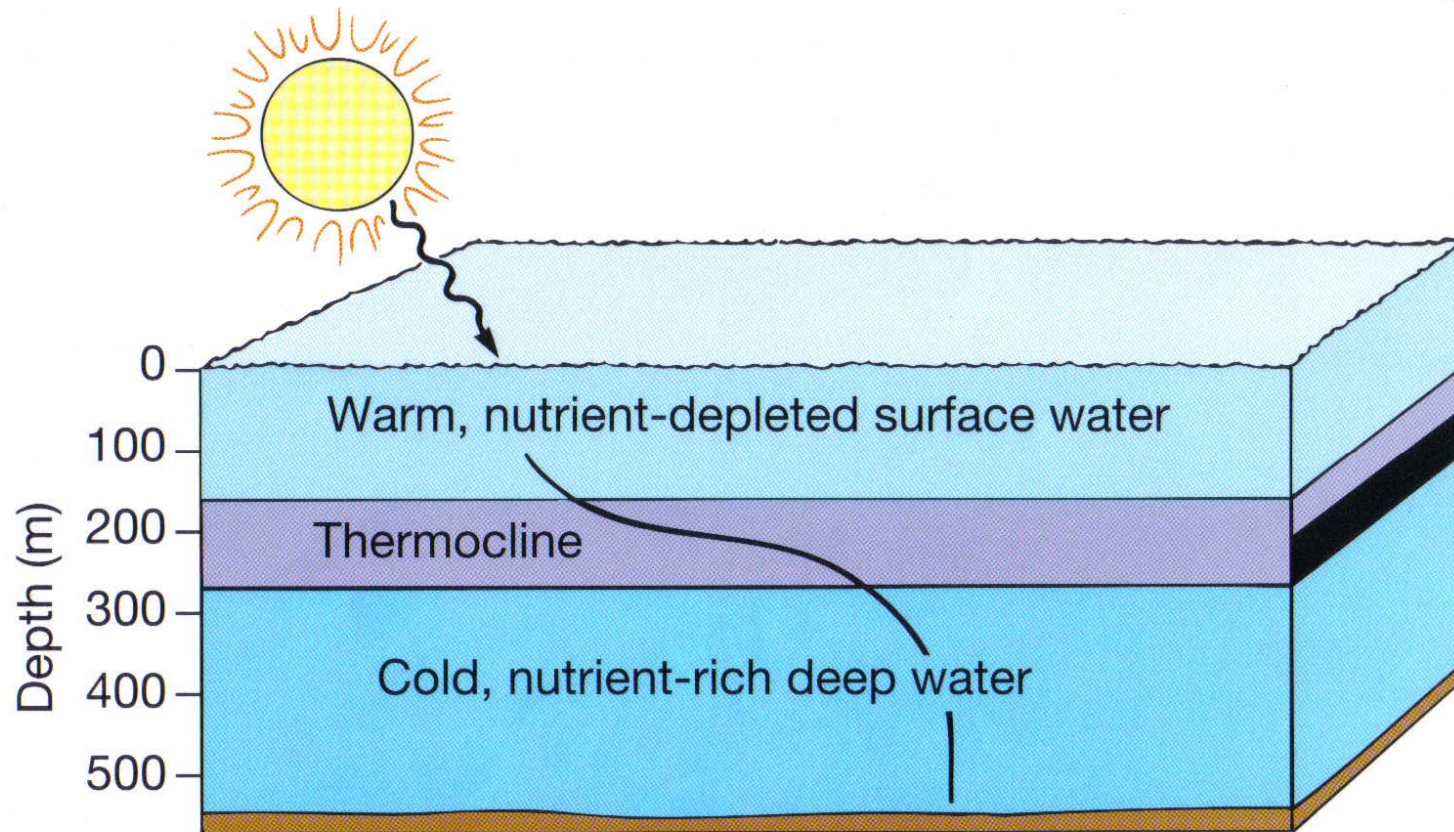
Fig. 3. (A) A diagram of the nitrogen cycle, illustrating the metal cofactors in each enzymatically catalyzed step





T-279 Fig. 13-11

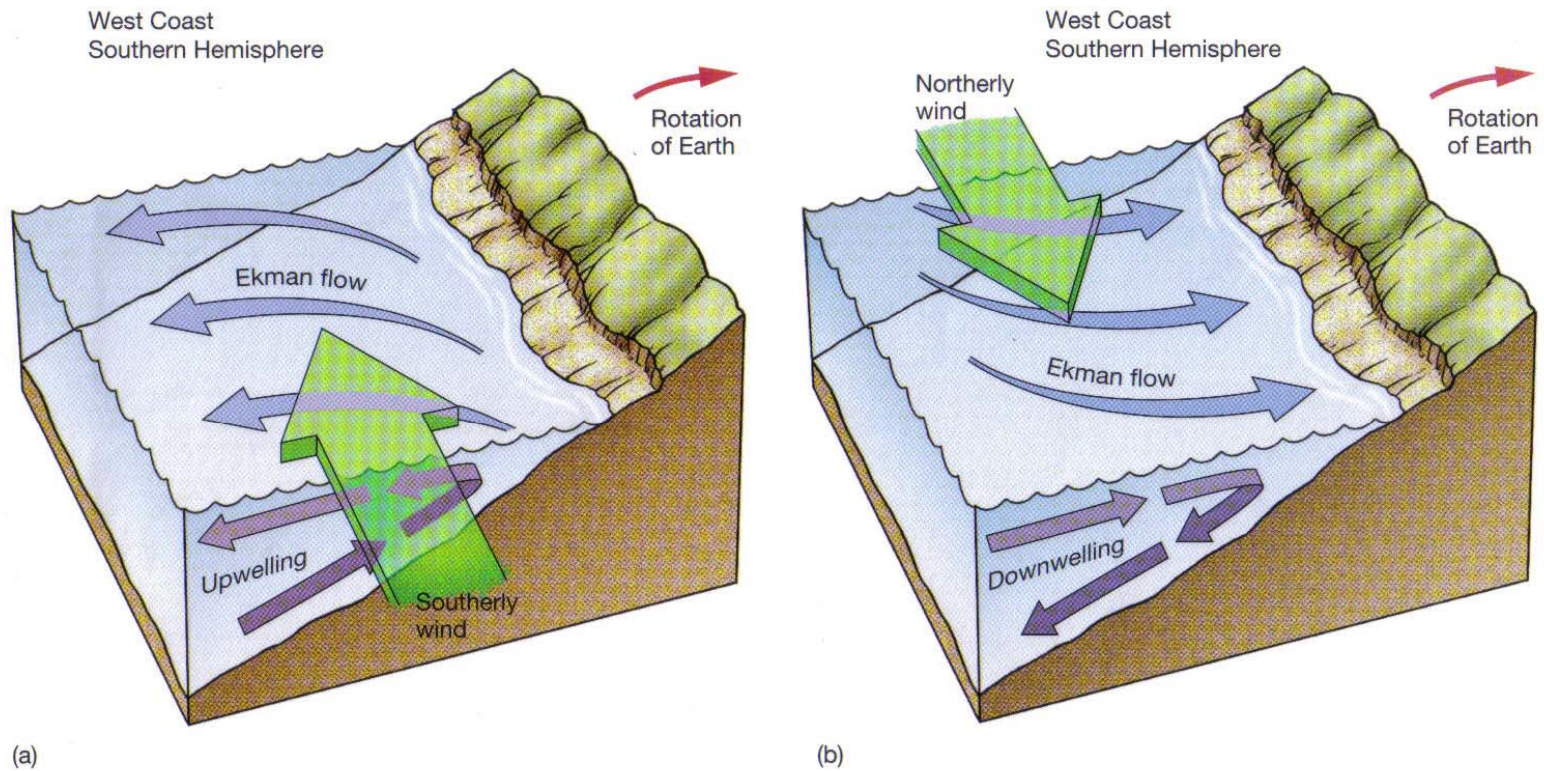
Productivity in tropical oceans





T-155 Fig. 7-11

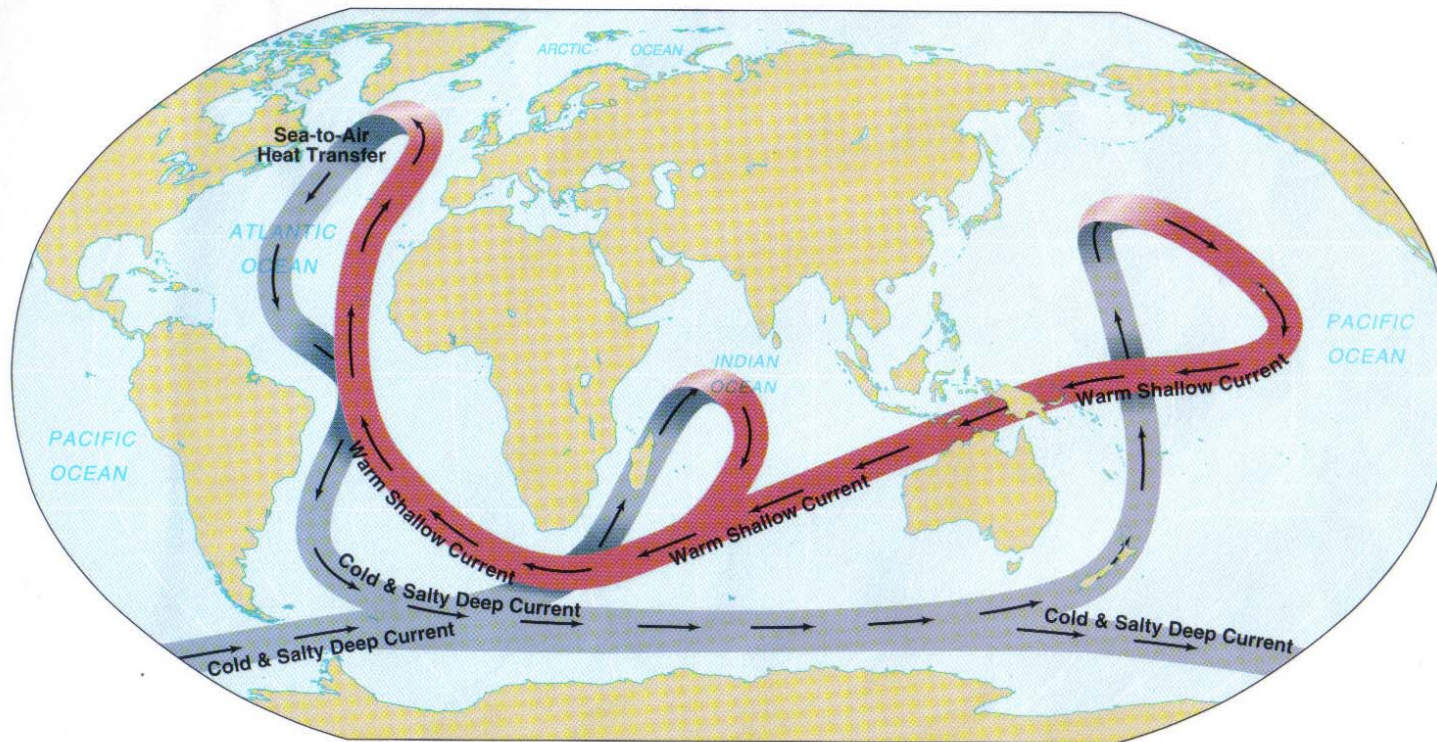
Coastal upwelling and downwelling





T-168 Fig. 7-27

Conveyer-belt circulation



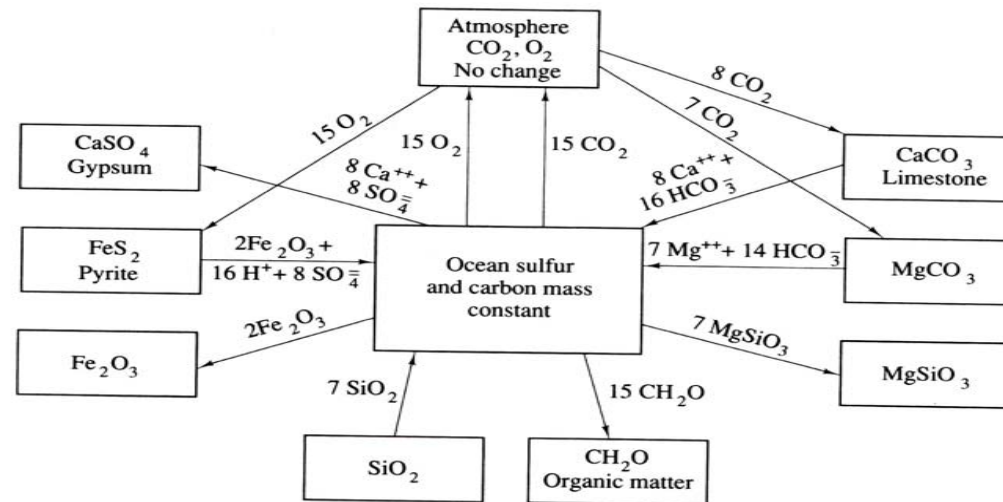
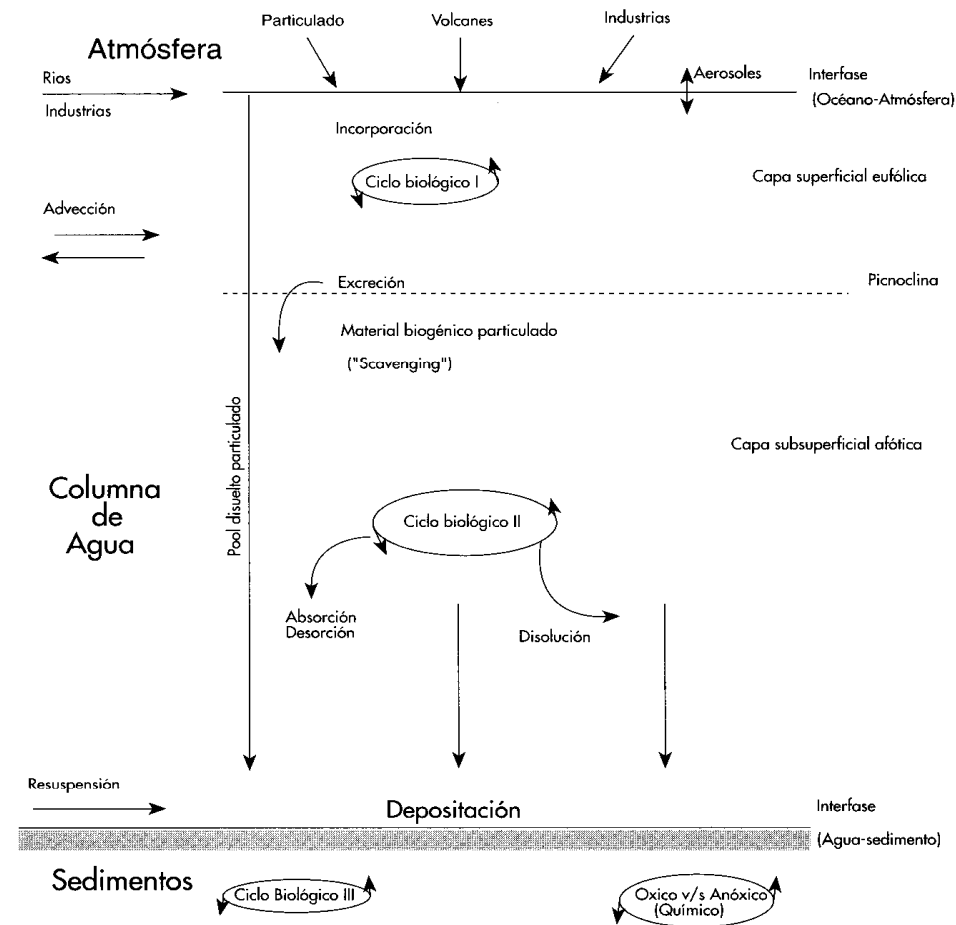


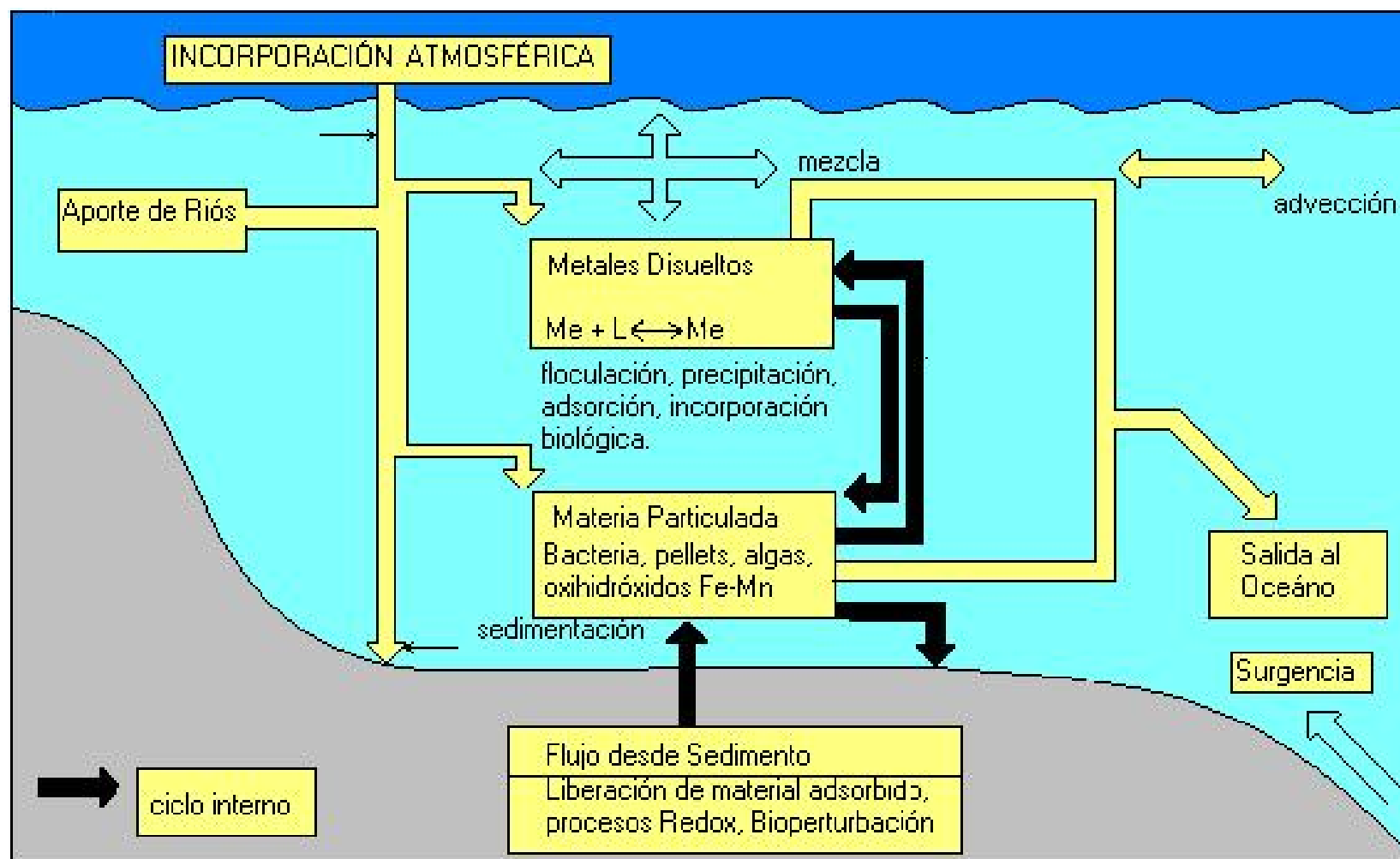
Figure 1.1 A model of major sedimentary reservoirs and the transfers between them that are associated with an increase in the mass of the biosphere by 15 moles. From Garrels and Lerman (1981).

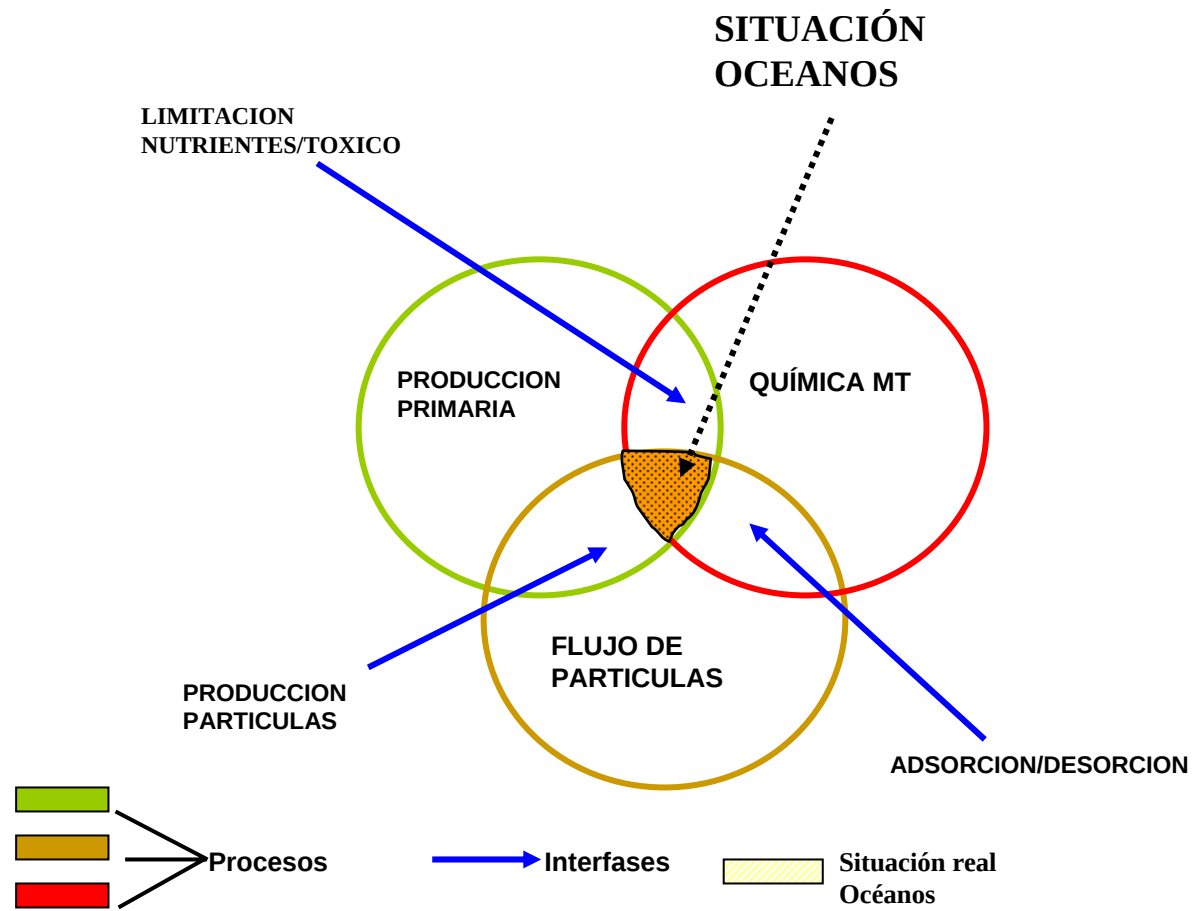


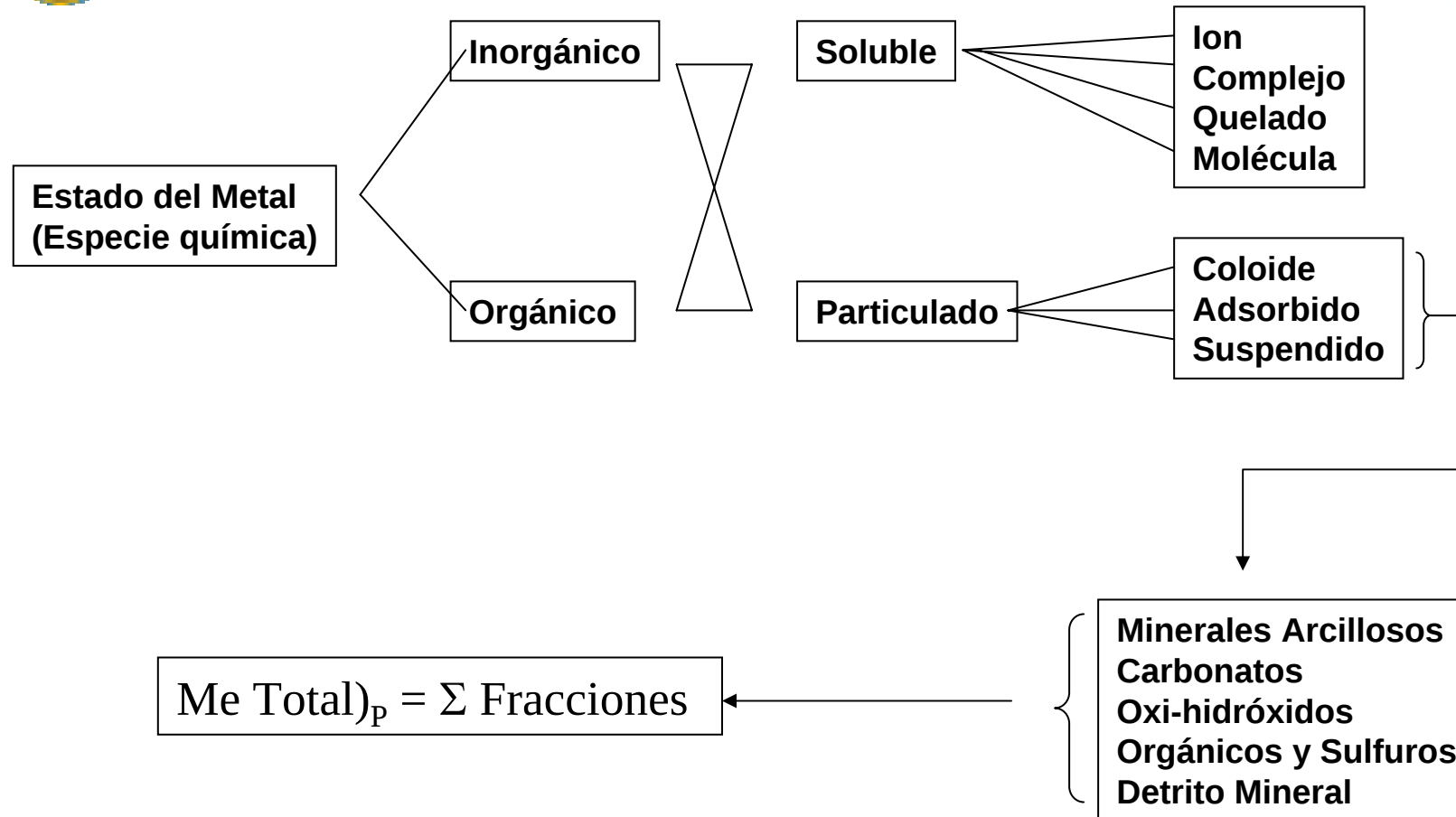
Ciclo Biológico I : Producción/Consumo (Incorporación/Excreción)
 Ciclo Biológico II : Degradación materia orgánica (Regeneración)
 Ciclo Biológico III : Bioperturbación (Incorporación)

Figura 3. Esquema de los principales procesos que determinan la abundancia de un metal partícula-reactivo marino costero.

Figure 3. Diagram of main processes that determine abundance of a metal particle-coastal marine reactive.







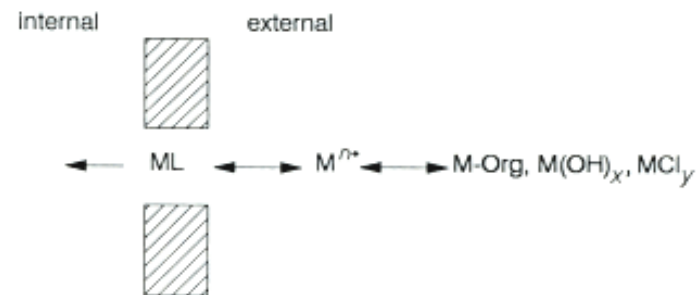


Uptake of Dissolved Metals

Uptake rate Membrane permeable M complex

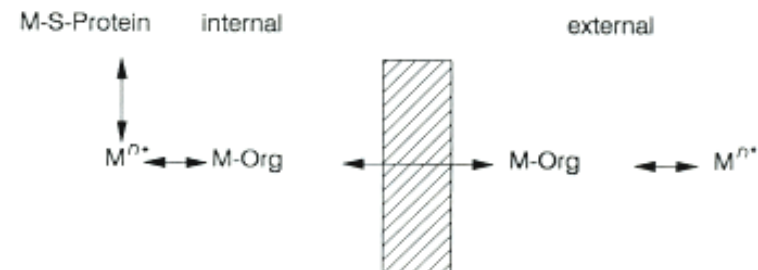
(a) Nutrient metal uptake systems

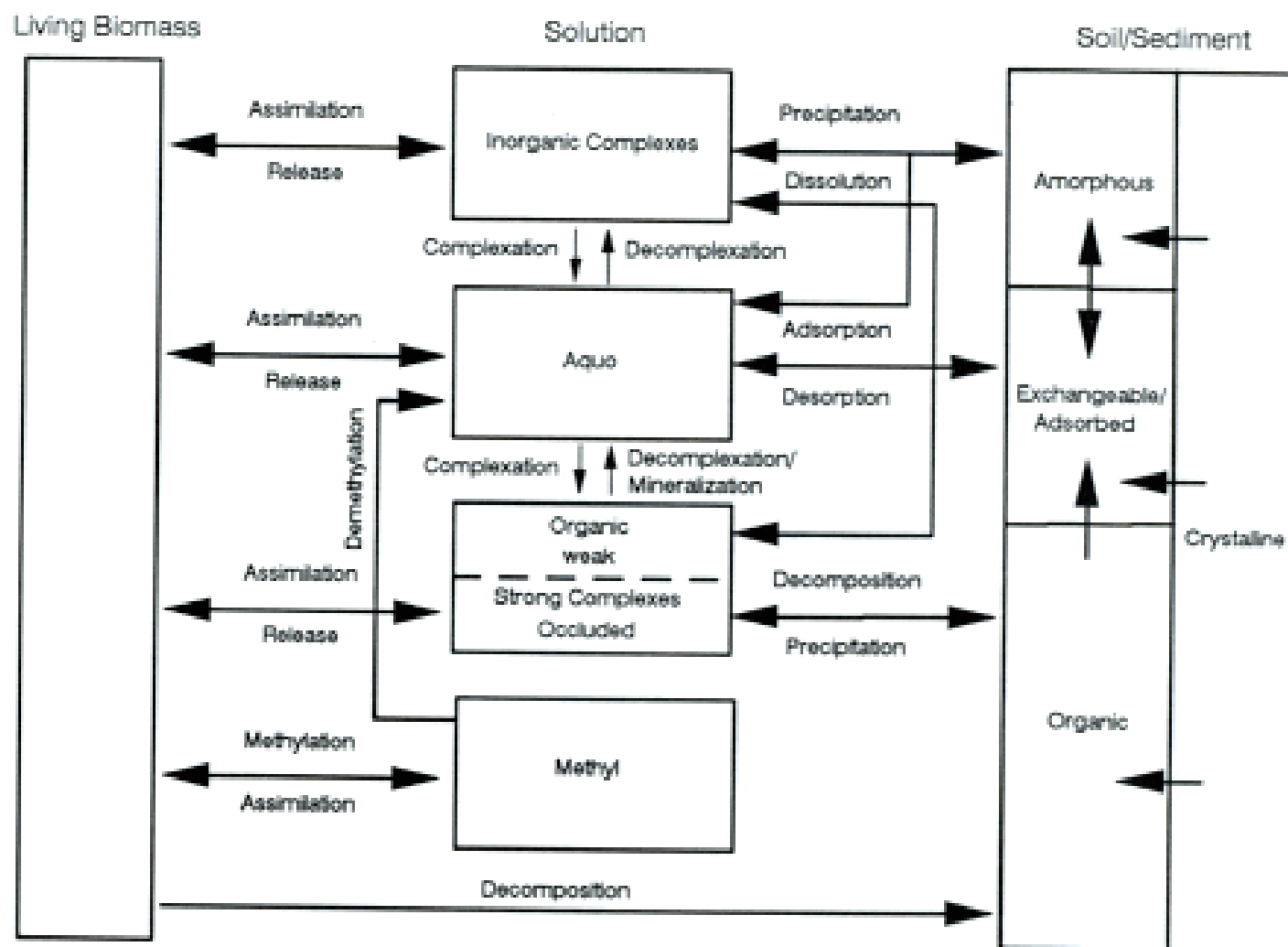
- Ligand associated with facilitated transport system (L), complexes metal for transport.
- M^{n+} can be "mistaken" for nutrient metals, e.g. Zn, Mn.



(b) Passive diffusion through membrane

- Membrane permeable species diffuse passively through plasma membrane.
- Neutral species (e.g. M-Org) may be most permeable.







LA FASE “TRANSPORTADORA”

Fases orgánicas : ácidos húmicos y fúlvicos

Material orgánico sólido

Fases carbonatadas

Fases Fe y Mn

Fases detríticas/no detríticas

Fases autigénicas/litogénica

Adsorción e intercambio iónico



MEDIO

ORGANISMO

EXPOSICIÓN

**AGUA O
SEDIMENTO**

INTERFASE

Organos y
Celulas

**DISPONIBILIDAD
AMBIENTAL**

**METABOLISMO
HOMEOSTASIS**

**BIODISPONIBILIDAD
AMBIENTAL**

**BIODISPONIBILIDAD
TOXICOLOGICA/
FARMACOLOGICA**

- Forma Química
- Concentración (Actividad)
- Compartimiento
- Tiempo Residencia

- Incorporación
- Tasa de Encuentro
- Eficiencia

Función al nivel
de Órganos o
Celular.



Distribución y acumulación de plomo en sedimentos de los fiordos de la XI región

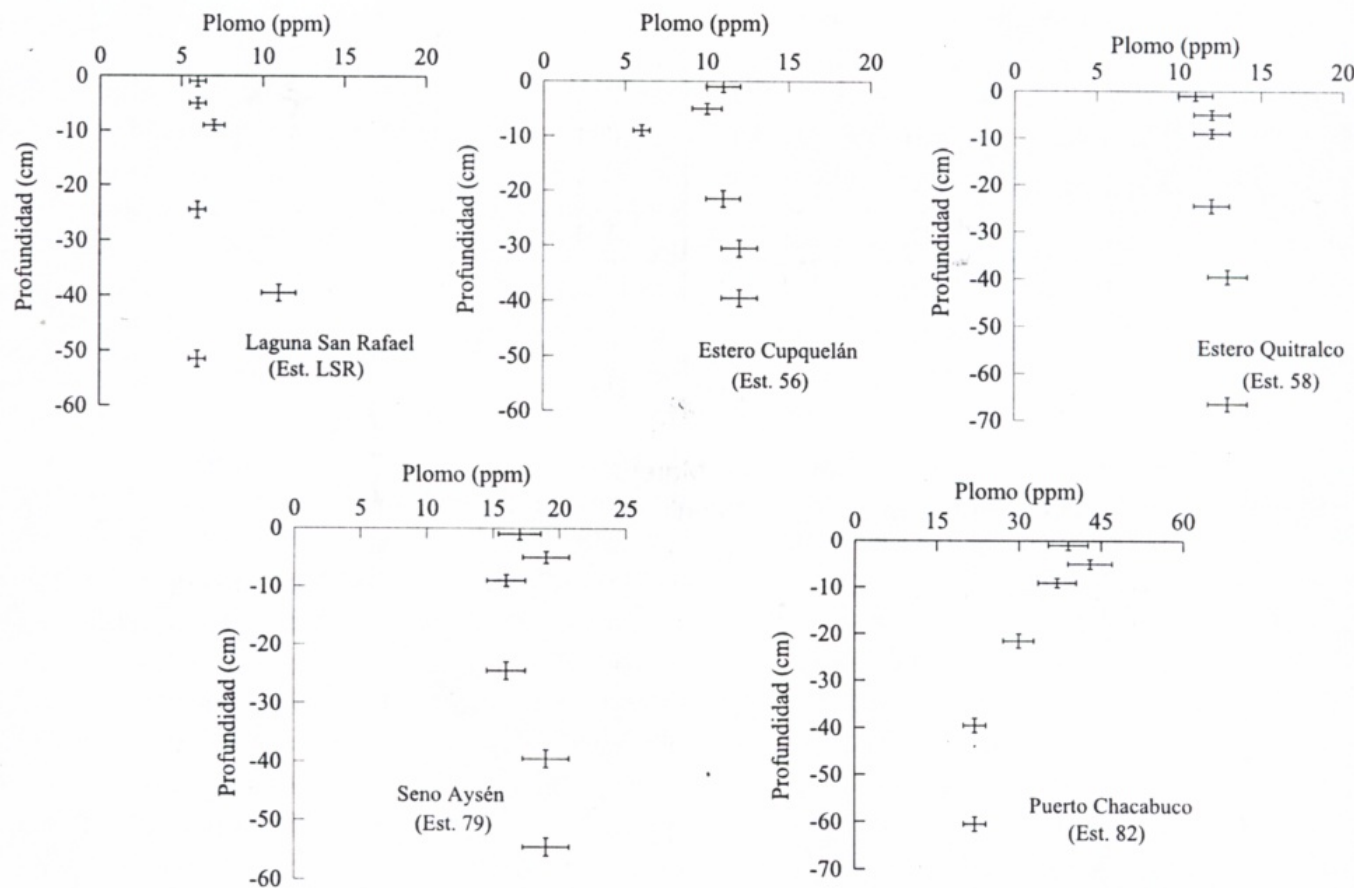


Fig. 3: Distribución vertical de Pb en los sedimentos de las localidades estudiadas.

Fig. 3: Vertical distribution of Pb in the sediments of studied locations.

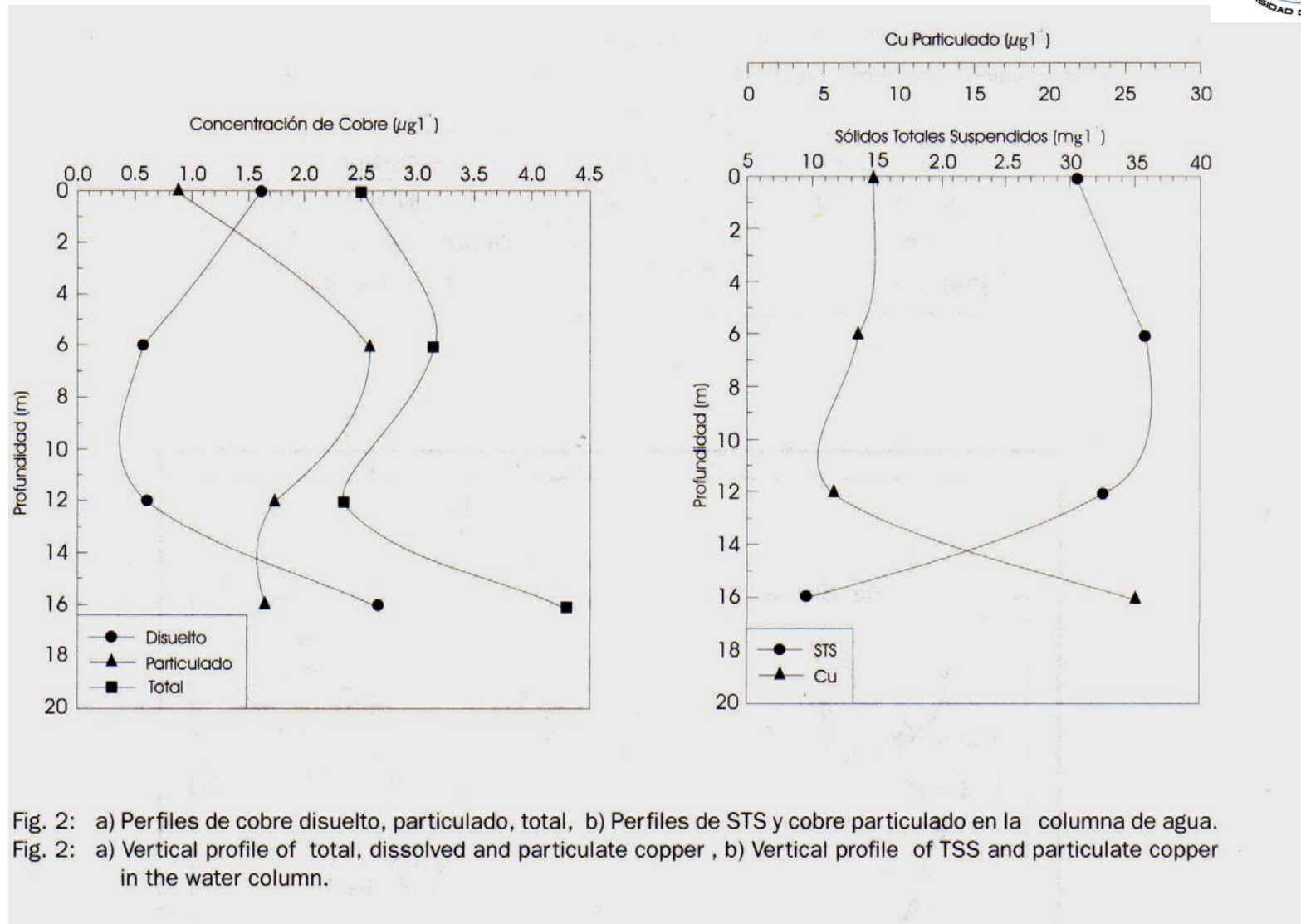


Fig. 2: a) Perfiles de cobre disuelto, particulado, total, b) Perfiles de STS y cobre particulado en la columna de agua.
 Fig. 2: a) Vertical profile of total, dissolved and particulate copper, b) Vertical profile of TSS and particulate copper in the water column.

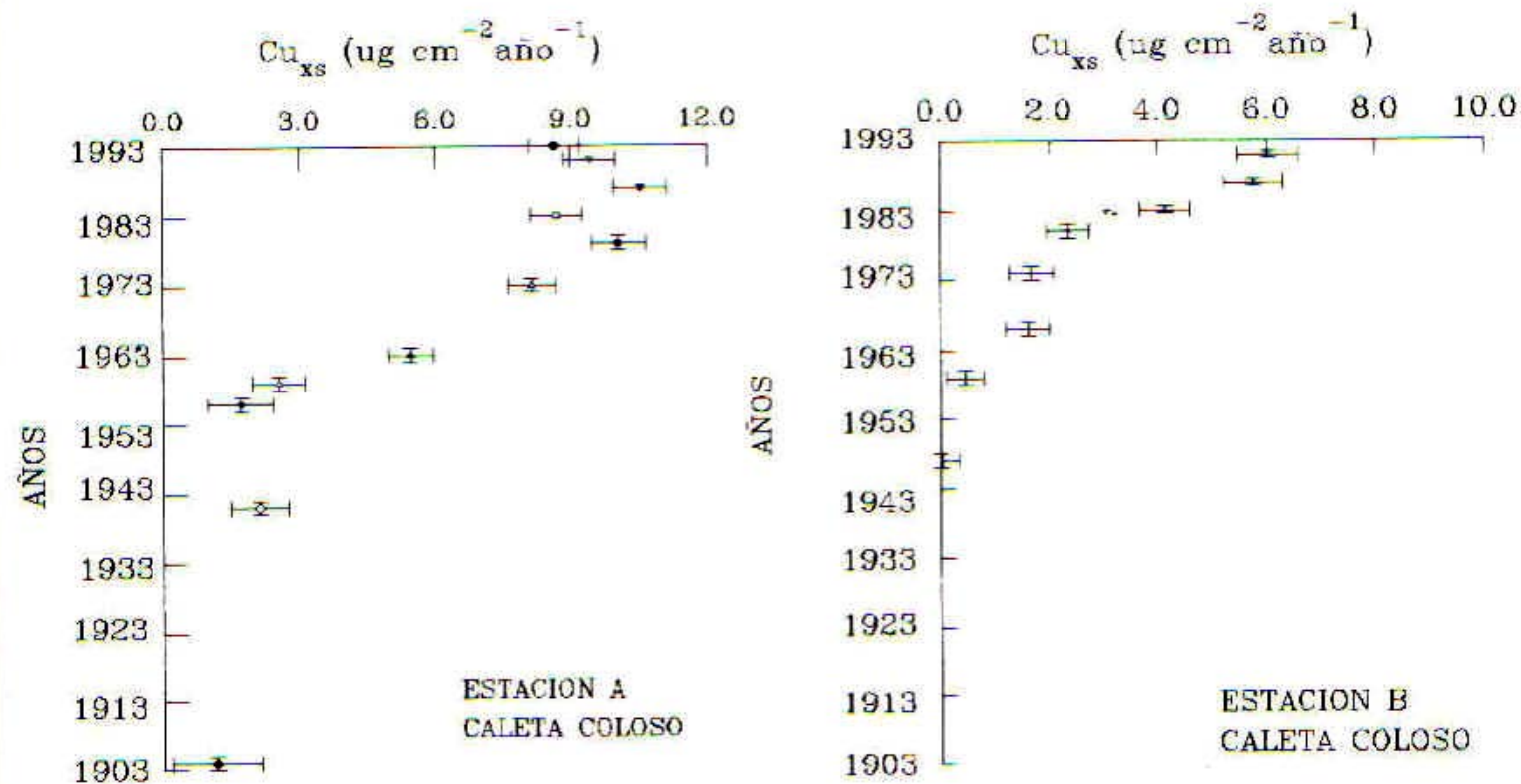
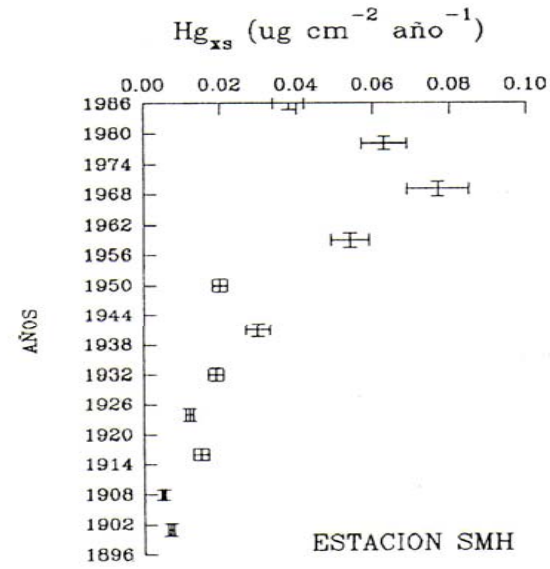
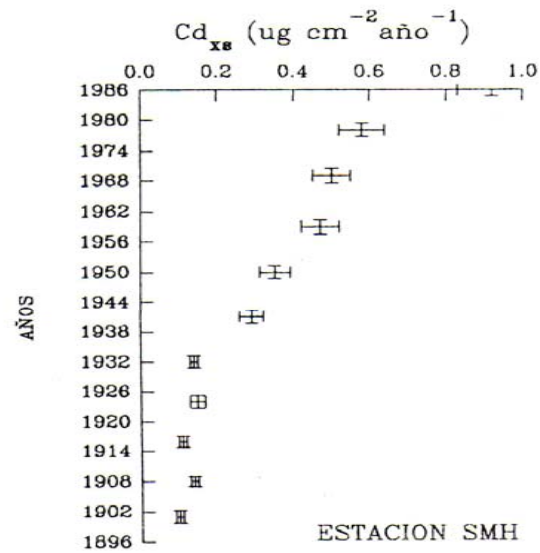
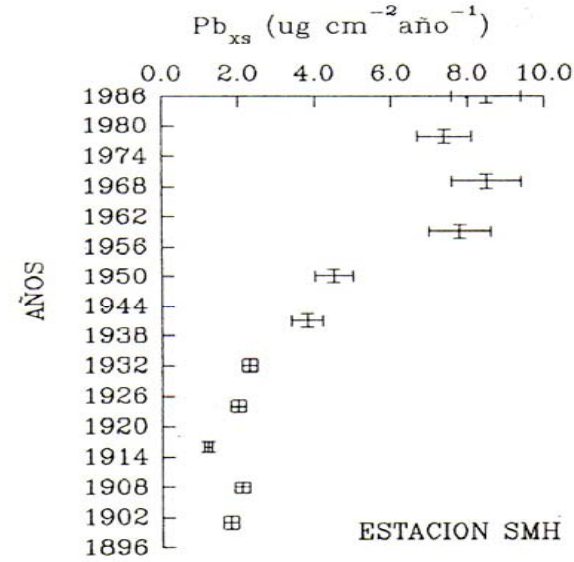
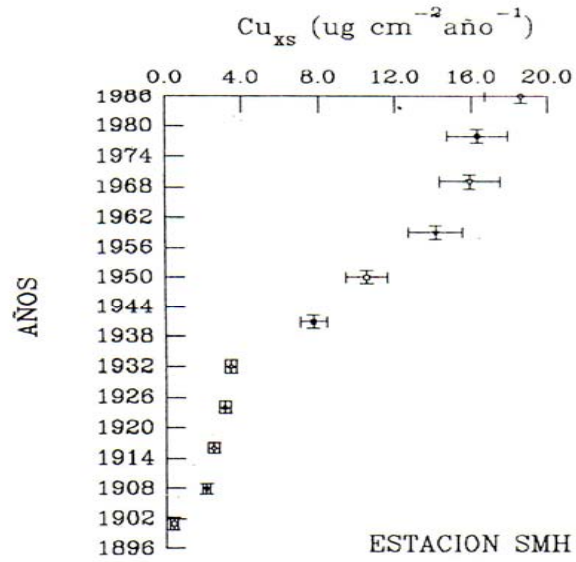


FIGURA 6. Flujo de exceso de Cu con respecto al tiempo en Caleta Coloso.





	Inventario (mg Cu cm ⁻²)	Inventario (mg Pb cm ⁻²)
Entradas		
Advección ⁽¹⁾	0,004	0,02
Transporte atmosférico ⁽²⁾	0,210	0,05
Aporte Antropogénico ⁽³⁾	0,410	0,09
	0,624	0,16
Salidas		
Acumulación en sedimentos	0,624	0,16

(1): Asume 100% de remoción de Cu y Pb desde columna de agua

(2): Estimado a partir del nivel pre-industrial

(3). Estimado por diferencia (ver texto)