Lecture 5 - Trace Elements in Seawater

Trace Elements – Those elements that do not contribute to the salinity. All elements are present in concentrations less than 1mg kg^{-1}

Many of these elements are present at very low concentrations (as low as 10^{-21} M). 1 ppm is equivalent to 1oz of salt in 32 tons of potato chips! 1 ppb is like 1 drop of gin in 100,000 liters (back yard swimming pool) of tonic water. This presents analytical challenges to measure and avoid contamination.

Why study trace element distributions?
  1. Many are nutrients and required to sustain life (e.g. P, N, Fe, Cu)
  2. Others are toxic (e.g. Cu, Hg)
  3. Some are tracers for redox conditions (Cr, I, Mn, Re, Mo, V, U)
  4. Some form economic deposits such as manganese nodules (e.g. Cu, Co, Ni, Cd)
  5. Some are tracers of pollution (e.g. Pb, Pu, Ag)

A classic paper written in 1975 by Boyle and Edmond (Nature, 253, 107-109) on trace metal chemistry of Cu represents a turning point in trace element analysis; most data prior to that are suspected to be wrong due to analytical and contamination problems. They suggest that data should be accepted only if it shows **Oceanographic Consistency.** Data must satisfy two criteria:
- Vertical profiles should be smooth.
- Correlations should exist with other elements that share the same controlling mechanisms.

Recycled Elements (also called Nutrient type or Biological)
As the name suggests the distribution of these elements is controlled by biological cycling. Typical profiles show depletion in the surface waters and increases with depth. Most of the marine "life" and certainly all the photosynthesizing organisms are confined to the upper 100 meters or so of the ocean (the photic zone). These phytoplankton uptake dissolved carbon and other nutrients in order to grow and produce organic matter and hard body parts. Therefore, such nutrients as phosphate, nitrate, dissolved silica and trace metals that are either needed for metabolic pathways or taken "by mistake" (e.g. Cd, Zn,) are deplete from surface water. 90% of the organic matter produced is recycled in the photic zone but the remaining 10% (of dead organisms and fecal matter) sinks into the deeper ocean, gets remineralized (bacterial oxidation or dissolution) and returns to the water column as dissolved inorganic compounds. The result is depletion of the dissolved "recycled elements" in surface waters and enrichment at depth. Note the depth profiles for elements related to the organic (soft parts, e.g. phosphate and nitrate) and those concentrated in hard parts (shells, e.g. silica) are different. This depends on the depth of highest remineralization (shallower for organic matter and deeper for the skeletal remains). The elements whose concentrations in surface waters drop down to zero are considered **bio-limiting,** as they have the potential to limit biological productivity. Others, like C, Sr, Ba and Ca are only partially depleted and are considered **bio-intermediate**. Many other elements follow these types of curves because they adsorb or react with the organic or skeletal particles are recycled with them. Several of the most important elements in living organisms (O, H, S and also C) are not limiting in the ocean.

Macronutrients

There are many elements required for life, but in oceanography, we speak of the main *macronutrients* as those major elements that are believed to be limiting to plant growth in the surface ocean. They have typical concentrations in the range of micromoles kg^{-1}. Phosphorus, nitrate and silica are the important macronutrients. The figures below for phosphate and silica show the different depth distributions. P and NO_3 have maximum concentrations shallower than silica because maximum degradation of organic debris happens shallow in the thermocline. SiO_2 increases with depth because of the dissolution of siliceous tests of diatoms, which dissolve deeper in the water column and on the sea floor.

PO4 (umol/kg)

Si (umol/kg)

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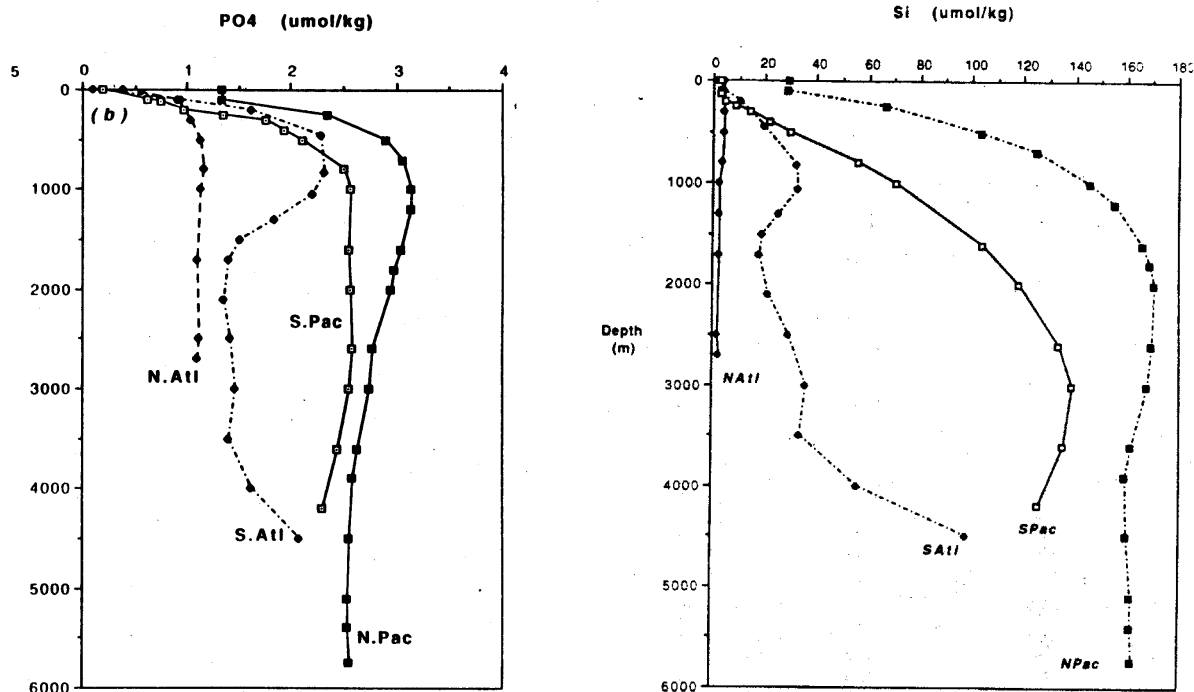
Bio-limiting Elements

By definition, bio-limiting elements are those necessary to sustain life and which may exist in low concentrations. These include the macronutrients; however, several trace elements can also be limiting, these are called **micronutrients** most notably is iron. Other metals like Cd, Zn, Ni, Cu, Se are depleted in surface waters and progressively enriched in deep waters. Concentrations of these metals correlate with those of the macronutrients. Some of these metals have biological functions, however others have no known biological function (e.g. Cd)
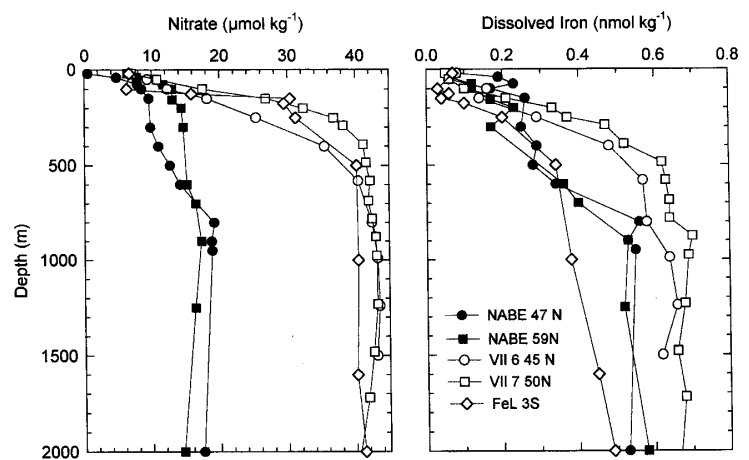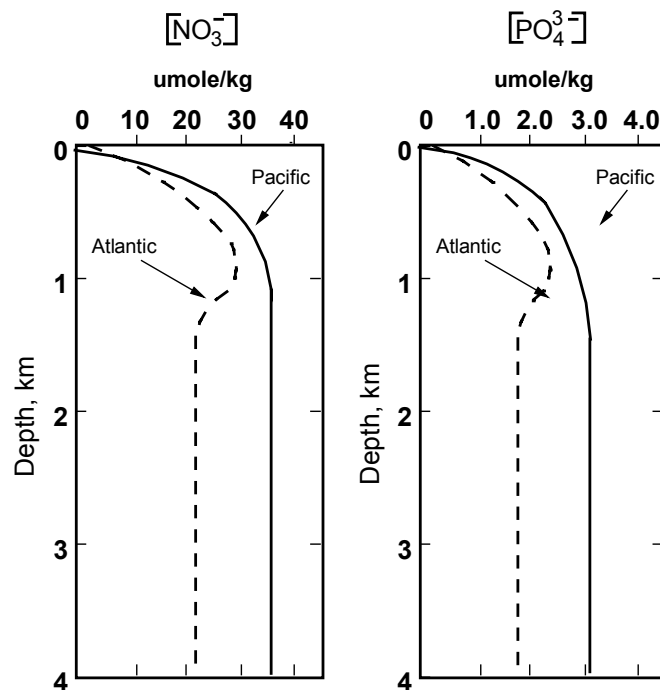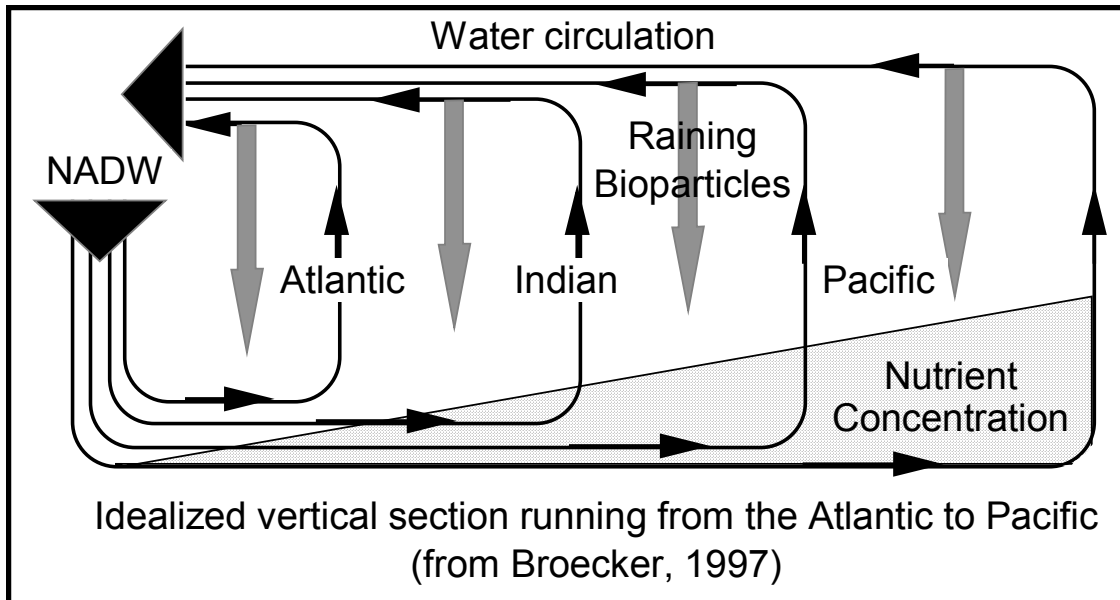
Fig. 9. Nitrate (a) and dissolved iron (b) versus depth at the same stations used in Fig. 8.

Horizontal distributions

Another characteristic of the distribution of the recycled elements is the higher concentration in the deep Pacific relative to the deep Atlantic. This is a result of the superposition of the vertical flux of biologically produced particles on the horizontal circulation of the ocean. The elements accumulate during progressive regeneration and dissolution as the water mass "ages" and make its way along the conveyor belt.

Water circulation

NADW

Raining
Bioparticles

Atlantic   Indian   Pacific

Nutrient
Concentration

Idealized vertical section running from the Atlantic to Pacific
(from Broecker, 1997)

$[NO_3^-]$

umole/kg

0   10   20   30   40

Pacific

Atlantic

Depth, km

$[PO_4^{3-}]$

umole/kg

0   1.0   2.0   3.0   4.0

Pacific

Atlantic

Depth, km

Biologically Required Elements
(H also needs to be included)

Scavenged Elements

These elements typically have depth profile that shows some decrease with depth. This is a result of adsorption of the ions or ionic complexes onto particle surfaces, such as clay minerals, organic matter, bacteria, fecal pellets etc. The concentration of particles is typically higher at the surface, resulting in effective adsorption of the scavenged elements. These elements are very reactive and do not like to stay in solution, they thus have relatively short residence time (<100 years). For example, ^{137}Cs, ^{95}Zr and other nuclides from the Chernobyl nuclear incident in 1986 were stripped out of the water column within a month of the explosion. As the residence time of these elements is shorter than the oceanic mixing time, it follows that their distribution reflects their source of origin. Accordingly, they display some variability in their profiles; following are some examples:

Surface enrichment and depletion with depth, this distribution is at least partly because of dust input from the atmosphere. The metal is relatively unaffected by biological uptake, but adsorbs onto particles as they sink in the ocean causing a decrease in concentration with depth. Metals with this behavior include Pb, Sn, Co. If an element is predominantly delivered via rivers or by release from shelf sediments, it can mix horizontally into surface waters leading to surface maxima in coastal areas – examples for such elements are Mn and ^{228}Ra.

Some elements display surface enrichments due to *in situ* production in the euphotic zone mediated by biological reduction processes coupled with redox equilibration throughout the water column (e.g. Cr^{3+}, As^{3+}, I^-).

Mid-depth minima, can result from a surface input coupled with regeneration near the sediment and scavenging throughout the water column (Cu).

Mid-depth maxima can result from hydrothermal activity input (Mn and ^3He).

Maxima or minima within sub-oxic or anoxic layers can occur because of reduction processes either in the water column or in the adjacent slope sediments (a) maxima occur if the reduced element is more soluble (Mn^{2+}) and minima if the reduced form is relatively insoluble or labile to become associated with solid phases (Cr^{3+}).

Mixed Behavior

Naturally, many metals exhibit behaviors that are a composite of the "nutrient-like" and "scavenging" categories, and some are difficult to understand. Two of these are aluminum and iron. The profile for *Aluminum* indicates surface enrichment from atmospheric input, and a decrease with depth and from the Atlantic to Pacific Ocean suggesting adsorption onto particles.
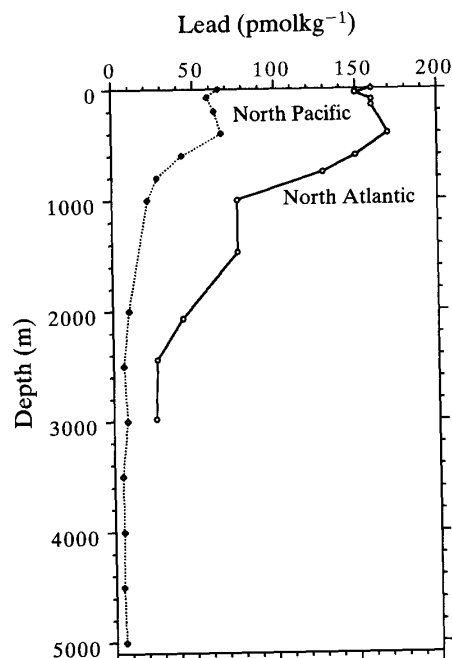
The increase with depth below 1000 m in the Atlantic may reflect a biological component that is overwhelmed in surface waters by the dust input or a source from the sediments.
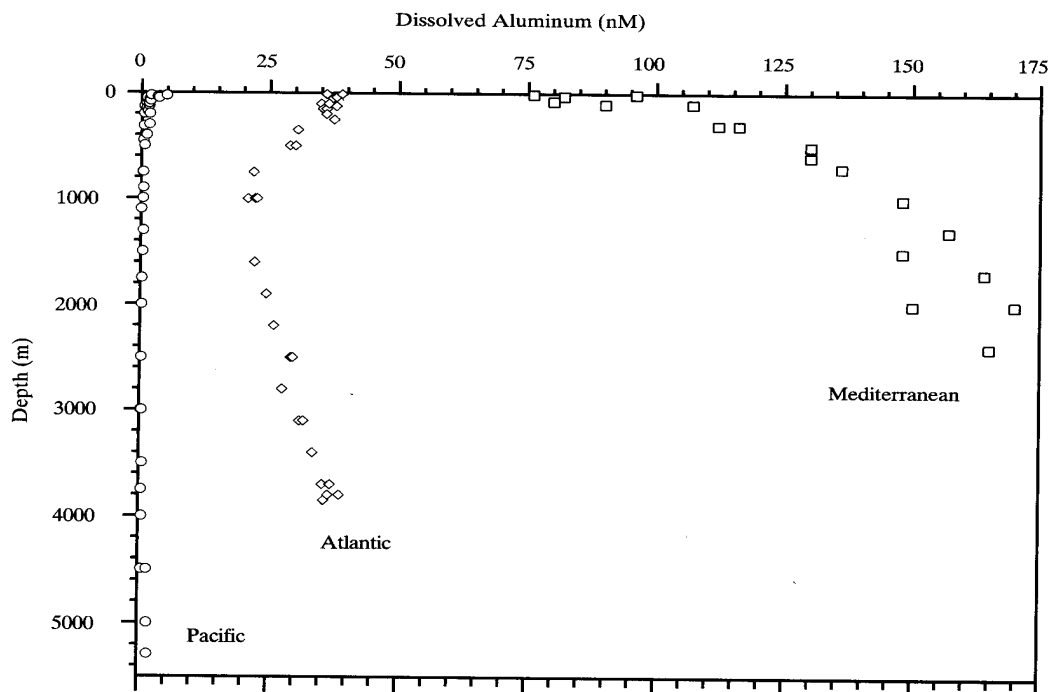
Other elements have more complicated profiles. Of course, these profiles could only be taken as being representative as, by definition, the concentrations and distribution of these scavenged elements would vary from place to place and in any one place with time.

The majority of the trace elements have residence times within the surface mixed layer (about 20 years) that are substantially shorter than the mean residence time of the water itself. Because of this, the distribution of the trace elements within the mixed layer is controlled by their input sources (e.g. upwelling, river, or atmospheric input). This results in lateral differences in distribution.

The distinction between conservative and non-conservative behavior depends on the extent to which an element participates in the biological or chemical reactions relative to its overall concentration (Mg and Cl participate but there is so much of them so the effect is negligible).

It is important to remember that just because an element has some type of profile it does not mean that it is not involved in other processes. For example there are elements with a recycled profile that are also scavenged (Ni, V, Cu, Zn, Fe), others with a scavenged profile are involved in metabolic reactions (Mn, Co) and the conservative Mg that is removed into carbonate shells. Rn that looks like recycled but has a bottom water source and decays as it diffuses up.

Group 1

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Scavenged Elements

Periodic table:

Group 1: 1 H 1.008; 3 Li 6.941; 11 Na 22.99; 19 K 39.10; 37 Rb 85.47; 55 Cs 132.9; 87 Fr (223)

Group 2: 4 Be 9.012; 12 Mg 24.30; 20 Ca 40.08; 38 Sr 87.62; 56 Ba 137.3; 88 Ra (226)

Transition Elements

3: 21 Sc 44.96; 39 Y 88.91; 57 La 138.9; 89 Ac (227)
4: 22 Ti 47.87; 40 Zr 91.22; 72 Hf 178.5; 104
5: 23 V 50.94; 41 Nb 92.91; 73 Ta 181.0; 105
6: 24 Cr 52.00; 42 Mo 95.94; 74 W 183.8; 106
7: 25 Mn 54.94; 43 Tc (99); 75 Re 183.2; 107
8: 26 Fe 55.85; 44 Ru 101.1; 76 Os 190.2
9: 27 Co 58.93; 45 Rh 102.9; 77 Ir 192.2
10: 28 Ni 58.69; 46 Pd 106.4; 78 Pt 195.1
11: 29 Cu 63.55; 47 Ag 107.9; 79 Au 197.0
12: 30 Zn 65.39; 48 Cd 112.4; 80 Hg 200.6

13: 5 B 10.81; 13 Al 26.98; 31 Ga 69.72; 49 In 114.8; 81 Tl 204.4
14: 6 C 12.01; 14 Si 28.09; 32 Ge 72.61; 50 Sn 118.7; 82 Pb 207.2
15: 7 N 14.01; 15 P 30.97; 33 As 74.92; 51 Sb 121.8; 83 Bi 209.0
16: 8 O 16.00; 16 S 32.07; 34 Se 78.96; 52 Te 127.6; 84 Po (210)
17: 9 F 19.00; 17 Cl 35.45; 35 Br 79.90; 53 I 126.9; 85 At (210)
18: 2 He 4.003; 10 Ne 20.18; 18 Ar 39.95; 36 Kr 83.80; 54 Xe 131.3; 86 Rn (222)

Lanthanides
58 Ce 140.1; 59 Pr 140.9; 60 Nd 144.2; 61 Pm (147); 62 Sm 150.4; 63 Eu 152.0; 64 Gd 157.3; 65 Tb 158.9; 66 Dy 162.5; 67 Ho 164.9; 68 Er 167.3; 69 Tm 168.9; 70 Yb 173.0; 71 Lu 175.0

Actinides
90 Th 232.0; 91 Pa 231.0; 92 U 238.0; 93 Np (237); 94 Pu (239); 95 Am (241); 96 Cm (244); 97 Bk (249); 98 Cf (252); 99 Es (252); 100 Fm (257); 101 Md (258); 102 No (259); 103 Lr (262)

Dissolved Organic Matter (DOM)

Organic **M**atter (**OM**) refers to any material with a backbone of carbon atoms joined to each other, and often to H, O, N and P.

We study organic matter in seawater because:

1. OM is the principle chemical form in which solar energy is made, stored, and used on Earth (source of fossil fuels).
2. About 80% of the total particulate carbon flux through the thermocline is in the form of organic matter.
3. About 20% of the total carbon buried in marine sediments is organic.
4. Over geological time scales OM burial in marine sediments is a major source of atmospheric O_2.

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$
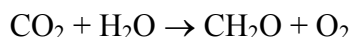
5. Organic compounds carry isotopic tags ($^{13}C/^{12}C$), nuclear clocks ($^{14}C/^{12}C$) and a wealth of structural information about their origins and reactions.

Total OM concentrations in natural samples are typically quantified based on the weight percent of organic carbon (%OC). This is done because:

1. OM is difficult to physically separate from inorganic matter (salt, minerals and ash) in seawater, suspended particles, and sediments.
2. OM in organisms and their remains is much too complex chemically to individually quantify all the molecule types present.
3. Carbon is a major element (~50 wt% of OM) whose inorganic forms can be quantitatively removed (by acidification) before organic forms are quantified (by combustion to CO_2).

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|---|
| DOC = dissolved organic carbon (<0.5 μm) |
| POC = particulate organic carbon (>0.5 μm) |
| TOC = total organic carbon (DOC+POC) |
| DOM = dissolved organic matter |
| NOM = nonliving organic matter |
| DON = dissolved organic nitrogen |
| DOP = dissolved organic phosphorus |

Two Fundamental Ways for Characterizing Organic Matter:
  A. Based on bulk compositional characteristics (e.g. elemental, isotopic, and spectral). Resulting data are broadly representative, but typically limited in information content.
  B. By quantifying the amounts of different individual compounds, usually by chromatographic separation (GC, IC or HPLC) and detection. Resulting data are extremely detailed, but often not broadly representative of all the OM.
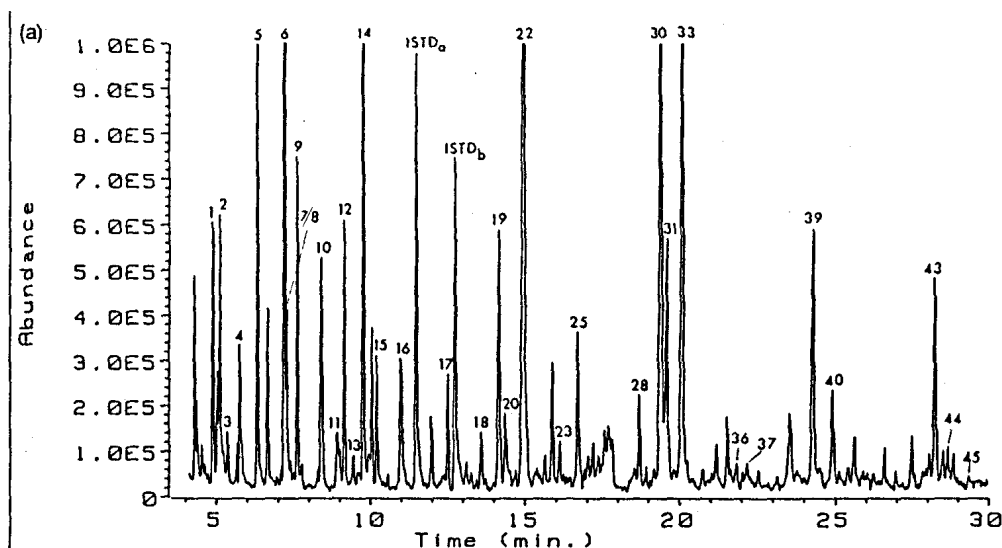
Gas chromatographic trace
  1. Each peak corresponds to a different compound type.
  2. Bigger molecules elute later (longer retention time).
  3. Peak area is proportional to compound amount.

DOC concentration in deep water ranges between 50μM-80μM (vs. 2300μM DIC, it is very dilute!); surface water concentrations are between 80-200μM. The DOM is composed of many substances which are mainly nonliving (excluding viruses and bacteria). It contains: dissolved free amino acids (with a major bacterial source), proteins, sugars, fatty acids, simple hydrocarbons, urea, vitamins etc. About 20-40% of the DOM is well characterized (identifiable) the rest in uncharacterized and is mostly humic substances. Humic acid includes compounds with molecular weights of 500-5000 Daltons; Fluvic acids, which also comprise this uncharacterized pool, consist of slightly lower molecular weights and are more hydrophilic. The organic matter in seawater can have a marine or terrigenous origin, terrigenous being more common close to shore. The terrigenous matter is more aromatic in character, having more benzene ring, which is typical to lignin; phenolic groups are the building blocks of lignin and they basically are benzene rings with an OH group attached. Organic acids are an important fraction of DOM, particularly carboxylic acid.

Vertical Profiles of Elements in the North Pacific Ocean (compiled by Y. Nozaki, 1996)
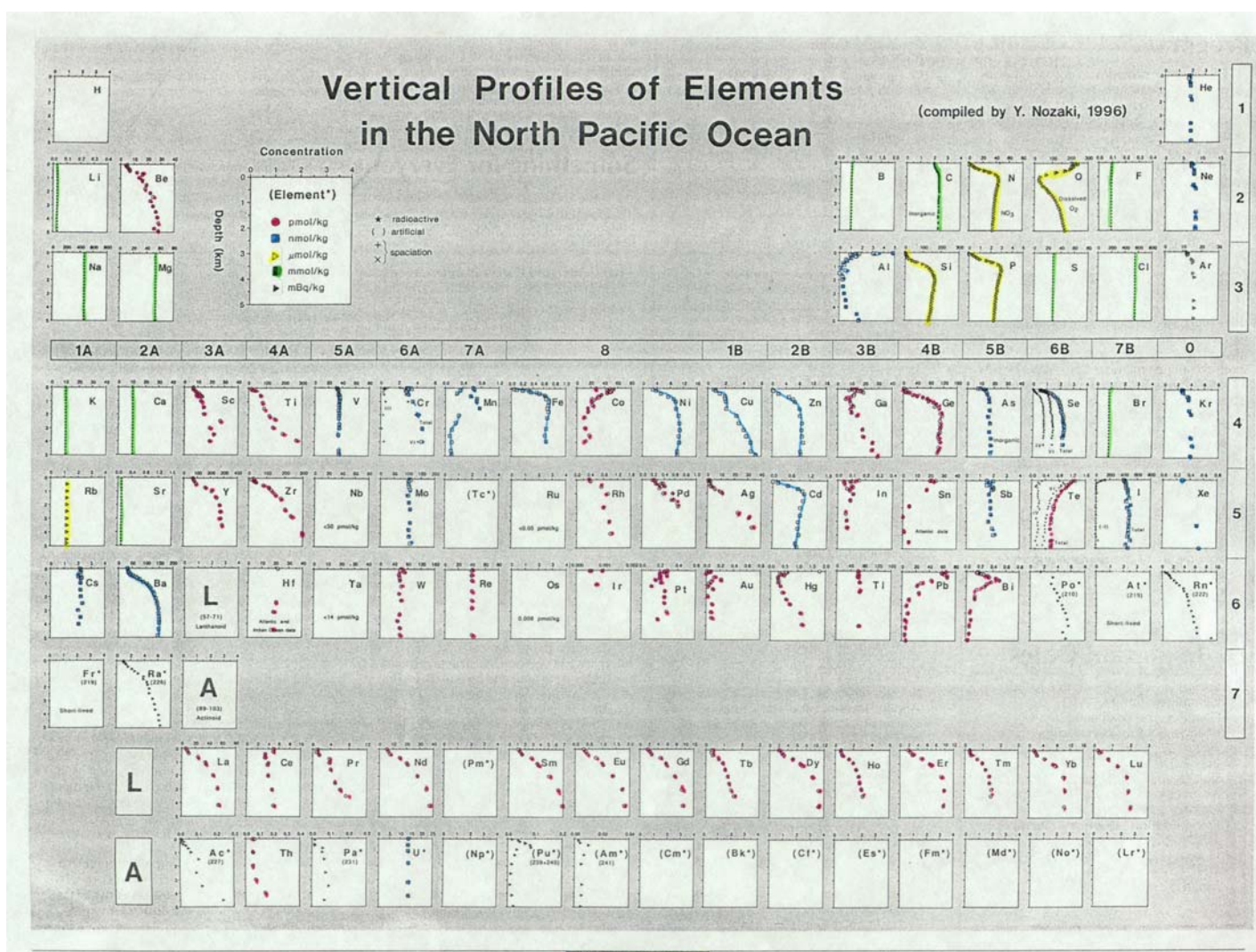
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