Trace Elements in Seawater
العناصر النزرة في مياه البحر

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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 1 oz of salt in 32 tons of potato chips! 1 ppb is like 1 drop of juice 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)

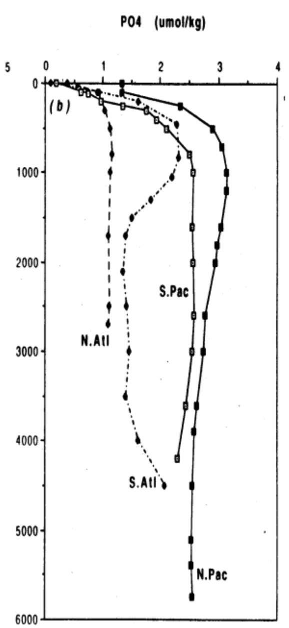
5- Some are tracers of pollution (e.g. Pb, Pu, Ag)

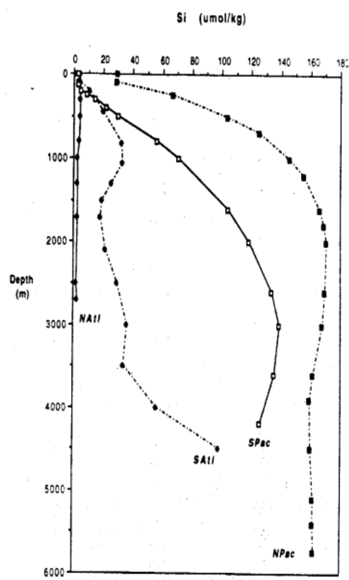
Recycled Elements (also called Nutrient type or Biological)

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. SiO2 increases with depth because of the dissolution of siliceous tests of diatoms, which dissolve deeper in the water column and on the sea floor.





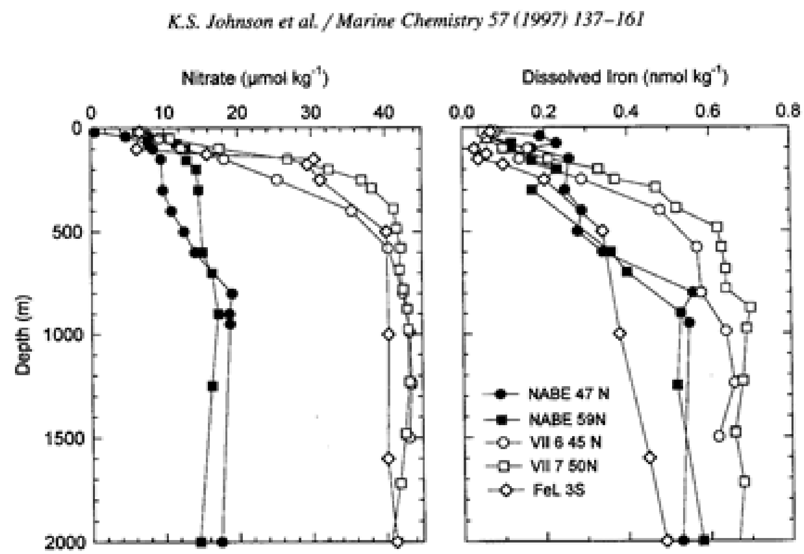


Fig. 9. Nitrate (a) and dissolved iron (b) versus depth at the same stations used in Fig. 8.

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)

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).

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:
1- Based on bulk compositional characteristics (e.g. elemental, isotopic, and spectral). Resulting data are broadly representative, but typically limited in information content.
2- By quantifying the amounts of different individual compounds, usually by chromatographic separation (GC, IC or HPLC) and detection.

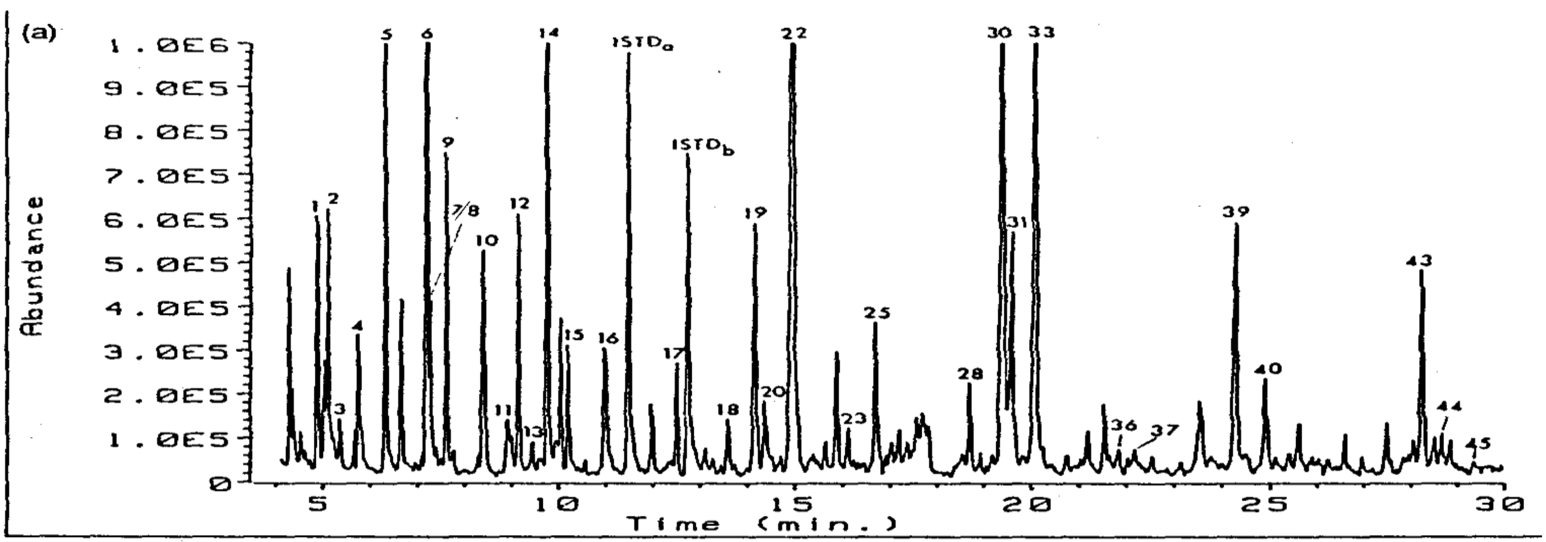
Resulting data are extremely detailed, but often not broadly representative of all the OM.

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.