

**Ocean Colour Remote Sensing Course
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TOPIC 14: NUTRIENTS

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Phosphorus Cycle

Phosphorus in sea water is present (Fig. 1):

- as dissolved inorganic phosphorus (DIP)
- as dissolved organic phosphorus (DOP)
- as particulate phosphorus (PP) (including living & dead organisms/POP and inorganic particles)

[PP] >	[DOP] >	[DIP]
% 60-70	% 20-30	% 5-12 (in lake water)
	[DOP] <	[DIP] (in sea water)
	[DOP] >	[DIP] (in sea water when the cells are more abundant)

In eutrophic environments [DIP] is % 90 of the dissolved phosphorus.

Gain terms for DIP:

- 1- Excretion by bacteria (autolysis). Microbial hydrolysis of esters of DOP (This process is very rapid and limits the persistence of DOP to a few hours).
- 2- Abiotic hydrolysis (This is a slow process).
- 3- Decay of PP (mainly particle org.-P) and regeneration by animals.

The amount of DIP produced by 1 and 2 < 3

Slow processes for the gain of DIP:

- ➔ The weathering of the rocks (geological process).
- ➔ River runoff and wind transport.
- ➔ Artificial input: Fertilizers used on land and transported to the sea.

➤ Guano birds feed on marine animals and P is transported from the sea to the land.

➤ The processes that provide (regeneration) and remove (uptake) DIP are rather fast: The residence time for DIP in for example oligotrophic waters (Eastern Mediterranean, Sargasso Sea) is just few minutes due to the rapid uptake by algae and bacteria.

➤ That is why P in sea water is found principally incorporated in living particles. And low phosphate concentration in the surface waters is caused by uptake of primary producers and bacteria.

Or [DIP] < [PP] > [DOP]

(algal uptake)	(decay)
0.67	0.08
DIP (0.35 μM) →→ PP (3 μM) →→ DOP (0.6 μM)	
←←	←←
(excretion & dead)	(bacterial uptake)
0.41	2

(Exchange rates: → μM/day)

Relationship between DIP, PP and DOP in coastal waters of Nova Scotia (Adapted from Watt and Hayes, 1963).

POP

Gain terms:

Dead, shedding, moulting of
Organisms (both phyto- and zoo-)

Adsorption of phosphate
On to particles produces POP

Loss terms:

Decay of particles
(as release of DIP)

Settlement onto sediment
(Further degradation of org-p
to DIP in the sediment and further adsorption of
DIP on particles and precipitation)

Phosphorus Dynamics:

Phosphate conc. is low in surface waters ($< 1\mu\text{M}$) due to uptake. During (spring) bloom periods phosphate conc. reduces sharply but particulate phosphorus conc. increases. DOP may increase due to algal activity (Fig. 2).

K_s (Half saturation) conc. for phytoplankton uptake = $0.6-1.7\ \mu\text{M}$ (which is comparable to ambient conc.).

K_s (Half saturation) conc. for bacterial uptake = $6.7-11.3\ \mu\text{M}$ (which is \gg phosphate conc. in sea water).

➤ In the open ocean phosphate (PO_4) conc. increases below the surface waters to a peak value near the permanent thermocline. If the water column is deep enough PO_4 conc. is more or less uniform below the thermocline (maintained by vertical mixing) (Fig. 3).

Peak PO_4 conc. are associated with the layer of O_2 min and CO_2 max where microbial and zooplankton activity regenerates DIP and CO_2 .

➤ DIP is regenerated by zooplankton in substantial amount in the water column.

For example: In *Calanus*:

- 17 % of ingested P is used for growth
- 23 % of ingested P is egested as fecal pellets
- 60 % of ingested P is excreted as dissolved-P which can be uptaken by phytoplankton.

➤ Most of the organic matter (including faecal pallets) that leaves the euphotic zone is degraded within the water column.

For example:

68-87% of the P used in the production is regenerated in the above 75m,
91-95% is regenerated above 700m (Coastal California waters).

87% is regenerated in the above 75m,
99% is regenerated down to 1000m (Pacific ocean).

➤ The rate at which zooplankton regenerate phosphate is not constant.

When algae is abundant: Larger amount of P is converted to eggs and stored as Phospholipids.

When algae is less: The stored lipids are used as energy source and P is excreted and relatively more phosphate is regenerated.

- Regeneration of phosphate is “temperature” dependent.
- Regeneration process is so active in the coastal waters and only small portion of P is lost permanently to the sediment by burial.
- PO_4 is to a very large extent determined by biological activity. As a result, O_2 uptake by organisms is well correlated to P and N conc. (Stumm and Morgan, 1981), since nutrients are released during aerobic respiration of organic matter.
- The cycles of individual nutrient are never isolated, the biological transformations link P, N, S and all elements present in organic matter.
- During the oxidation of organic matter, the reduction reactions involved are also important. Such reactions change redox potential and alkalinity. Alkalinity has important consequences for chemical reactions.

PO_4 conc. is variable in the sediment (Fig. 4).

- In anaerobic sediments there is a peak at relatively shallow depth, where reduced conditions combine to make PO_4 salts to dissolve and PO_4 is released.
- Above the max there is a decrease of PO_4 due to the release of PO_4 to overlying waters via diffusion. This is the source of PO_4 at the bottom waters.

This diffusion provides about 5% of the total P content of the overlying waters per week which is quite significant.

- Regeneration from the sediment:

15-50 $\mu\text{M}/\text{m}^2/\text{h}$ (Max in spring-summer due to the high temperature).

For example 50% of the water column productivity is provided by released phosphate from the sediment in Narragansett Bay. An additional 20% comes from DOP which is also released by the sediments. In general this ratio is about 30%.

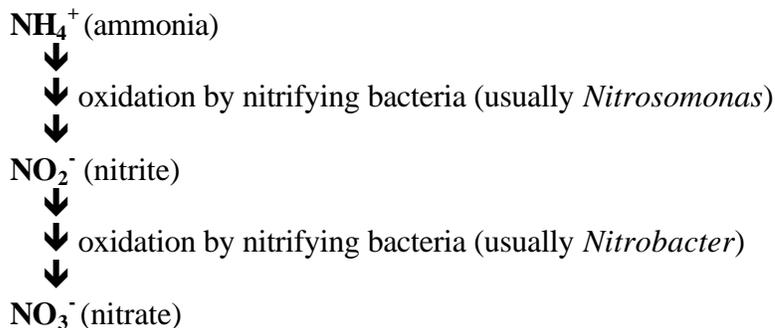
NITROGEN

Reference: Valiela, 1995

Transformations of Nitrogen:

(Fig. 5)

- NO_3^- is the **most oxidized form of nitrogen** and it is uptaken by phytoplankton, bacteria, and plants in aerobic environments.
- NO_3^- is reduced by assimilation processes involving several enzymes (e.g. nitrate reductase) to $-\text{NH}_2$ (amine) form. Amine is used in metabolic processes.
- NO_3^- is also used as a terminal e^- acceptor (or as oxygen source) and it is reduced to N_2 (via NO_2^- , NO and N_2O). This process -the dissimilative reduction of nitrate- is called as **DENITRIFICATION** and requires a supply of **organic matter and anaerobic conditions** and it is temperature dependent.
- Denitrifiers may reduce NO_3^- to NH_4^+ (via NH_2OH , hydroxylamine) intermediate but this is not as important as the decay of **Org-N**.
- NH_4^+ is also taken up by plants, algae and bacteria.
- Large amount of Org-N are released after the dead of animals. The org.-N is decomposed by heterotrophs to NH_4^+ .
- Excretion by zooplankton also produces NH_4^+ and DON (amino acids and urea).
- **NITRIFICATION** process is driven by bacteria and both of the following reactions require O_2 and they yield energy. They are autotrophic bacteria and they use the yielded energy to fix carbon. Nitrification can proceed at low level of O_2 but the rate is limited by the supply of O_2 .



N_2 -Fixation:

- Molecular N_2 is the most abundant N specie. It is stable, inert and most of the organisms can not utilize it for their growth.
- Biological N_2 fixation plays an important role in the conversion of N_2 to other nitrogenous compounds in the marine environment.

➤ N₂ fixing capacity is restricted to two groups of organisms:

1-Non-symbiotic N₂ fixing organisms:

Heterotrophic bacteria (*Azobacter*, *Klebsiella*, *Clostridium*)

Blue green algae (*Nostoc*, *Anabaena*, *Trichodesmium*)

2-Symbiotic N₂ fixers: (*Rhizobium*)

They are symbiotic with primary producers/animals/sea urchins.

➤ The process of nitrogen fixation requires a supply of energy (provided by DOC) and a reductant. The e⁻ transport system differs among various kinds of N₂ fixing organisms.

➤ Presence of NH₄⁺ in the water inhibits the N₂ fixation. Since assimilative reduction of N₂ is an energy demanding process.

➤ Anaerobic conditions are required by fixers because the enzymes involved in fixation are sensitive to O₂. (*Azobacter* reduces surrounding oxygen pressure at the nitrogen fixing site by active respiratory consumption of O₂. Many N₂-fixing blue green algae contain specialized cells that lack oxygen evolving system of photosynthesis).

➤ Light energy stimulates N₂-fixation since fixation by blue-green algae stops in the dark.

➤ Large amount of Fe is required for growth of cyanobacteria with N₂ rather than NH₄⁺ and NO₃⁻. Fe deficiency may limit N₂ fixation.

Distribution of N-species:

Water Column:

➤ NO₃⁻ is most abundant in winter (which is provided by vertical mixing and when it is not used by primary producers). It disappears from the euphotic zone during algal blooms. NO₃⁻ is greater at depth (Fig. 6).

➤ NO₂⁻ conc. is low in the water column.

➤ NH₄⁺ is abundant in shallow productive regions due to large amount of Org. matter and its decay. When temperature is high, microbial degradation is high and the ammonia production is high.

➤ [DON] >> [DIN]

Amino acids and urea comprise only a small component of the DON and the remainder part is resistant to decomposition. Therefore most of the DON is not nutritionally suitable for phytoplankton.

Sediments:

➤ The concentrations of N-compounds in interstitial waters of sediments are much higher than in water due to degradation of large concentration of organic matter.

➤ The redox state determines the relative abundance of inorganic nitrogen compounds and their vertical distribution (Fig. 7).

In aerobic sediments Org. matter accumulates near the surface. This leads to active decay of organic matter, most NH₄⁺ is released near the sediment surface. Benthic fauna are more abundant near

the surface and their excretion also contributes to ammonia concentration. Nitrification process also takes place in the upper sediment layer.

In anaerobic sediments NH_4^+ conc. is far more higher than in aerobic conditions due to the stoichiometry of anaerobic decay. NO_3^- is seldom abundant since denitrification and less importantly ammonification remove nitrate.

Nitrogen Cycle: (Fig. 8)

Sources of new nitrogen

- N_2 Fixation
- Vertical mixing
- Horizontal transport
- Precipitation

N_2 Fixation: Incorporation of nitrogen from gas form into Org.-N form which is a source of new nitrogen for marine ecosystems.

$\text{N}_2(\text{g}) \ll \text{N}_2(\text{aq}) \approx \text{Org.-N}$

- It is in equilibrium with the atmosphere except in special circumstances where exchange is restricted (Fjords, Black Sea deep waters, interstitial waters of sediments).
- N_2 fixation rate is measured using ^{15}N tracer technique (Hauck and Bremner, 1976).
- Cyanobacteria are the principal organisms that fix nitrogen in aquatic environments.
- Blue green algae make up 50 % of the planktonic biomass in fresh waters and this leads to relatively high rates of N_2 -fixation. In such regions P in general is limiting nutrient.
- N_2 -fixation rates (and abundance of blue green algae) in marine waters are generally lower than fresh waters.

The reason for this:

- 1- N_2 -fixation by marine blue-greens is limited by the availability of Mo, an element that is part of the enzymes involved in the fixation process.
 - 2- The abundant SO_4^{2-} in sea water interferes with the uptake of Mo, this reduces the N_2 -fixation. SO_4^{2-} may inhibit fixation rates by 1-5% in fresh water, 15-20% in sea water and 70% in highly saline waters.
- In marine systems, water column is more turbulent, reduces anoxia in general and mixes blue-green algae below critical depths (to dimmed light); this process reduces the N_2 -fixation.
 - N_2 -fixation rates are also reduced by insufficient supply of Fe and by appropriate organic sources of energy.
 - In more eutrophic waters N_2 -fixation rates are higher.
 - High NH_4^+ concentration inhibits the N_2 -fixation.

Vertical Mixing:

- Second source of new nitrogen for the euphotic zone is the vertical mixing of nitrate rich deep waters. This is the major source for most pelagic systems and has a major influence on seasonal patterns (McCarthy and Carpenter, 1984).
- Two opposing processes, mixing and stratification regulate the structure of the euphotic zone and the magnitude of the biological activity within it.

In the open sea the stratification of the sea is set mainly by temperature and the homogeneous mixed layer of varying depth is formed by the balance of mixing and stabilizing forces (e.g. the air-sea temp. difference, short-wave radiation from sun light, heat balance, wind stress etc.).

The two layer system is observed in the Black Sea where the upper layer is less saline due to fresh water input and the lower part is occupied with Mediterranean origin salty and dense waters. This is a permanent stratification which prevents the vertical mixing and transport of substances.

Molecular diffusion is the only way substances move in the absence of turbulent mixing (or in the presence of stratification). In turbulent mixing, small parcels of water masses with many molecules are moved.

Turbulent diffusion is X 1000 of Molecular diffusion

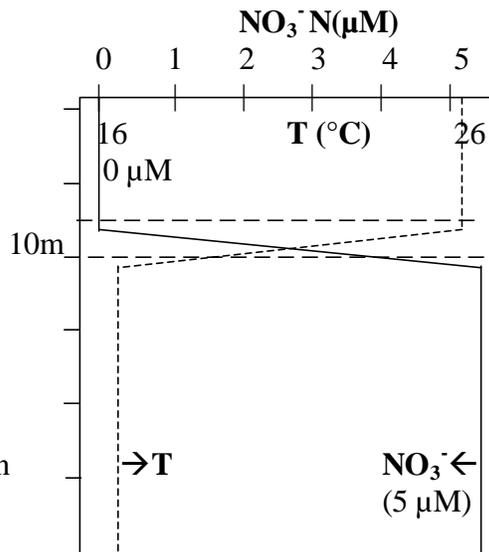
Example:

Assume an upper mixed layer with no NO_3^- , at the base of which there is a 10 m thick pycnocline with $5 \mu\text{M}$ NO_3^- underneath (e.g. Sargasso Sea). Thus $dC/dz = 5 \mu\text{M}/10\text{m}$
Or = 0.5 mM m^{-4}

In the presence of turbulent mixing the NO_3^- flux into the surface layer is

$$K_v dC/dz$$

where K_v is the vertical eddy diffusion coefficient ($=0.6 \times 10^{-4} \text{ m}^2 \text{ sec}^{-1}$ for Sargasso Sea).



$$\text{Nitrate flux} = 0.6 \times 10^{-4} \text{ m}^2 \text{ sec}^{-1} \times 0.5 \text{ mM m}^{-4} = 0.2 \text{ mmole m}^{-2} \text{ day}^{-1}$$

Equivalent to the levels of nitrate uptake measured in the Sargasso Sea.

In the absence of turbulent mixing at the base of the mixed layer, the nitrate flux would be 10^3 times lower which is not enough to sustain observed levels of biological activity.

Structure and evaluation of the mixed layer:

Photosynthesis depletes the nutrients from the mixed layer when it is shallower than (I) or coincident (II) with the euphotic zone (EZ = photosynthetically active zone). When the mixed layer is deeper than the EZ (III) phytoplankton are mixed into the darkness (biomass is present), but there is no net growth or uptake (carbon production is absent) and no nutrient depletion (Fig. 9).

The mixed layer depth varies over three important time scales:

- 1- diurnal scale
- 2- seasonal scale
- 3- synoptic scale (the scale of passage of atmospheric frontal systems).

Horizontal transportation: (Tables 1-3)

- The river outflow is important for phytoplankton production in the coastal waters. Much of the nitrogen (and other nutrients) transported by the rivers originates from fertilization.
- While river transport is an obvious source of nutrients, intertidal and subtidal flux of ground water carrying nutrients from land to coastal waters contributes the nutrient input.
- The disposal of sewage can also convey large amounts of nitrogen.

In the near coastal waters of New York city (western end of Long Island)	NH_4^+ 45-100 μM	NO_3^- 8-20 μM
Away from the city (open waters)	0-5 μM	0.5-8 μM

- Another example: Runoff, rivers and sewage provide 99.5 % of N and 99.7 of P in Narragansett Bay (Rhode Island).
- The N-budgets of salt marshes (and many marine systems) are dominated by physical transport processes.

Precipitation:

- The amount of N transported to the marine environment by rain, snow and dry deposition is usually relative to other.

For example, precipitation provides 12% of the nitrogen entering the mixed layers of the Black Sea (surrounded by industrialized land) (Sen Gupta, 1973). In Narragansett Bay, precipitation contributes 0.5 % of the N entering the area (surrounding area is less urbanized).

Precipitation is important for the open waters, stratified water bodies such as subtropical gyres where there are few other external sources of N (e.g. there is significant correlation between the amount of rainfall and NH_4 concentration in the surface waters of Sargasso Sea).

Uptake of Nitrogen:

- Most marine algae (including phytoplankton) preferentially uptake NH_4^+ over NO_3^- . The reason for this is the energy required to reduce NO_3^- to the $-\text{NH}_2$ form which is easily incorporated into proteins.
- Some producers (especially estuarine and coastal species) may use organic sources of N (e.g. methylamine, amino acids, urea), but this uptake may only amount to a fraction of nitrogen used by primary producers (Mc Carthy, 1980).

➤ Particulate-N is consumed by animals, sinks to the sediment, decays and is regenerated as DON.

Regeneration of Nitrogen:

➤ Regeneration and release make organically bound-N newly available. This is a key process, since inputs of new-N are not sufficient to support the requirements of primary production.

Regeneration in the water column:

Regenerative production is supported by the flux of NH_4^+ and urea, the products of animal and bacterial metabolism.

➤ Most organisms in the water column contribute to the regeneration of nitrogen. Smaller organisms (such as protozoans) release more nutrients than larger species (Glibert, 1982).

In coastal California waters, 90% of the mineralization of NH_4^+ is accomplished by organisms $<35 \mu\text{m}$ and 40% of was done by cells $<1 \mu\text{m}$ (Harrison, 1978).

➤ The abundance of small and large particles vary so much, however, bacteria do not always release more NH_4^+ than the larger zooplankton.

➤ Nitrogen regeneration rate, **E**, is related to metabolic properties of the organisms, including the **C/N** ratios of the consumer **biomass (b)** and **the food** (org. matter)(s), and the gross growth efficiency (**GGE**) of consumer:

$$E = C \times [(1:C/N_s) - (GCE:C/N_b)]$$

Where C is carbon consumption.

Example:

If bacteria has $C/N_b = 4$, $GGE = 50\%$

If phytoplankton has $C/N_s = 8$

$1:C/N_s = 1:8 = 0.5/4$ and $GCE:C/N_b = 0.5/4$ then, **E = 0!**

Therefore when $C/N_s < 8$, $E > 0$ and bacteria regenerates NH_4^+ .

When $C/N_s > 8$, the bacteria do not release ammonia but they need to consume ammonia in order to utilize all the carbon in the food.

➤ Bacteria, can either produce or consume NH_4^+ .

➤ **DOM** has $C/N_s = 10$ so bacteria tend to be net consumers of NH_4^+ if it is available.

➤ Protozoans have C/N_b of 5-6, whereas phytoplankton have $C/N_s > 6$. Unless GGE is very high they are the net excretors of NH_4^+ .

➤ Flagellates and even larger animals may be important generators of nitrogen. Gelatinous zooplankton also regenerate nitrogen.

➤ Nitrogen is regenerated by heterotrophs mainly as NH_4^+ , the form of nitrogen which is preferentially taken up by phytoplankton. Even when NO_3^- conc. is very high in Antarctic waters (17-31 μM) the

phytoplankton still use very substantial amounts of NH_4^+ although the conc. of NH_4^+ is only 0.1-2.5 μM (Glibert et al., 1982).

➤ Regeneration of nitrogen (and phosphorus) by zooplankton increases as more food is available.

For example:

Calanus excretes 2.6 % of its body-N/day in winter when there is not much phytoplankton but this is 4.6 % for the spring bloom period.

➤ It has been calculated that :

In the coastal waters: **54-70 %**,

In the open ocean: **82-87 %** of the production is supported by regeneration,

where the remaining portion is new production.

➤ In productive regions of the oceans, phytoplankton depend on large inputs of new nitrogen while phytoplankton in oligotrophic waters make do with recycled nitrogen (Dugdale and Wilkerson, 1992).

➤ The export of POM from the euphotic zone to deeper waters, on average, has to be equivalent to new production.

Regeneration in the Benthos:

➤ Organic-N remineralized (converted to inorganic form, usually as NH_4^+) in sediment as well. The inorganic-N in interstitial waters can then be released to the overlying water. This is a major pathway by which regenerated N is made available to the overlying plankton (Aerobic decay in the sediment).

Anaerobic decay also regenerates NH_4^+ in large amounts and this process is temperature dependent as well.

➤ In coastal waters there is consistent depletion of N compared to phosphorus during regeneration. This loss may be the result of denitrification. The N-limitation commonly found in the coastal waters may be due to the remineralization of 25-50 % of the org.-matter in the sediments where the regenerated nitrogen may subsequently be lost by denitrification.

In the sediment some NH_4^+ (released from org.-matter) is nitrified to NO_3^- and then denitrification converts substantial amount of N to N_2 .

➤ Large gradient (100-1000 fold difference) in N-concentration between overlying waters and interstitial waters lead to movement of N out of sediment.

Losses of Nitrogen:

➔ By burial in sediment

➔ Transport by water

➔ Denitrification (The most important process)

➤ Denitrification depends on the supply of NO_3^- by external sources:

➔ Water overlying sediment

➔ Local nitrification of NH_4^+ released by the decay of org.-matter (Coupled nitrification/denitrification process).

➤ Denitrification occurs primarily where there is a contact of oxic and anoxic conditions (Black Sea example).

➔ Because denitrifiers (bacteria) are anaerobic.

➔ Nitrification requires O_2 .

Higher rates therefore found at the sediment interface and in the sub-oxic zone in the Black Sea.

➤ Denitrification ($NO_3^- \rightarrow N_2$) makes biologically active DIN unavailable. Because of N-availability is important to many marine processes this kind of microbial respiration is quite important since nitrogen is lost by this process.

➤ Denitrification and nitrification processes produce N_2O (nitrous oxide, a biogenic gas and it is an intermediate product) and that is currently increasing in the atmosphere (Greenhouse effect).

➤ Denitrification is quantitatively important in N-budgets for the entire ecosystem.

Denitrification rate depends on

➔ NO_3^- Concentration

➔ DOC Concentration

➔ Temperature

THE SILICON CYCLE

➤ Silicon in the marine environment exists in only one oxidation state and it is involved in the regulation of the ocean pH on a long-term basis.

➤ The major processes of the silicon (Si) biogeochemical cycle are as follows:

(1): Weathering of igneous rock leads to the removal of silicon in the form of clays (inactive pool),

(2): Transportation of dissolved silica via rivers (active pool),

(3a and 3b): Interaction occurs and silicon is present in the ocean as reconstituted clays or as dissolved silicon respectively,

(4a and 4b): Further processes of interaction can occur; suspended Si in rivers release dissolved silicate or take up dissolved silicate from silica enriched sea water respectively,

(5a): Dissolved silicon is used by lower organisms in primary productivity,

(5b): These organisms die and release silica,

(6): The primary organisms are ingested by higher organisms,

(7): The organisms release silicon either upon excretion and death,

(8): Particulate silicon (as clays, dead organisms) sinks to the ocean bottom,

(9): Ultimately, the sediment and sea water are entrapped and converted to igneous rocks.

➤ Dissolved Silicon: Dissolved form exists largely as,

Ortho-silicic acid: Si(OH)_4

In sea water Silicon exists as monomeric Si(OH)_4 rather than as colloidal form and only small fraction (about 5% at pH 8.1) exists as dissolved form.

➤ The formation of siliceous hard parts (cell walls and skeletons) is the most important mechanism by which dissolved silicon is removed from sea water. Because of vertical segregation, dissolved silicon concentrations tend to increase with depth and range from 1 to 100 μM .

➤ Abiogenic precipitation is important only in locations such as pore waters and estuaries where dissolved silicon concentrations are high. Both biogenic and abiogenic precipitation produce an amorphous solid, called “**opaline silica**” or “**opal**”.

➤ Silica also occurs in crystalline form , as **quartz**.

➤ Biogenic silica is produced by diatoms and silica-flagellates, which are phytoplankton, and by radiolaria, which are protozoans.

➤ Diatom productivity is limited by the availability of dissolved silicon. In locations where dissolved silicon is abundant, diatoms are the dominant phytoplankton as they assimilate nutrients faster than any other type of pelagic algae.

➤ Dissolved silicon concentrations are highest in the regions subject to wind driven upwelling.

References:

Valiela, I., 1995. Marine Ecological Processes, Springer-Verlag, New York Inc.

(The other references are cited in Valiela, 1995).