Sampling and analytical tools in the Ocean chemistry

Need for chemical observations in the ocean

Chemical composition of the seawater modifies by

Atmospheric processes – Dust composition, lightening, UV radiation, rainfall etc.

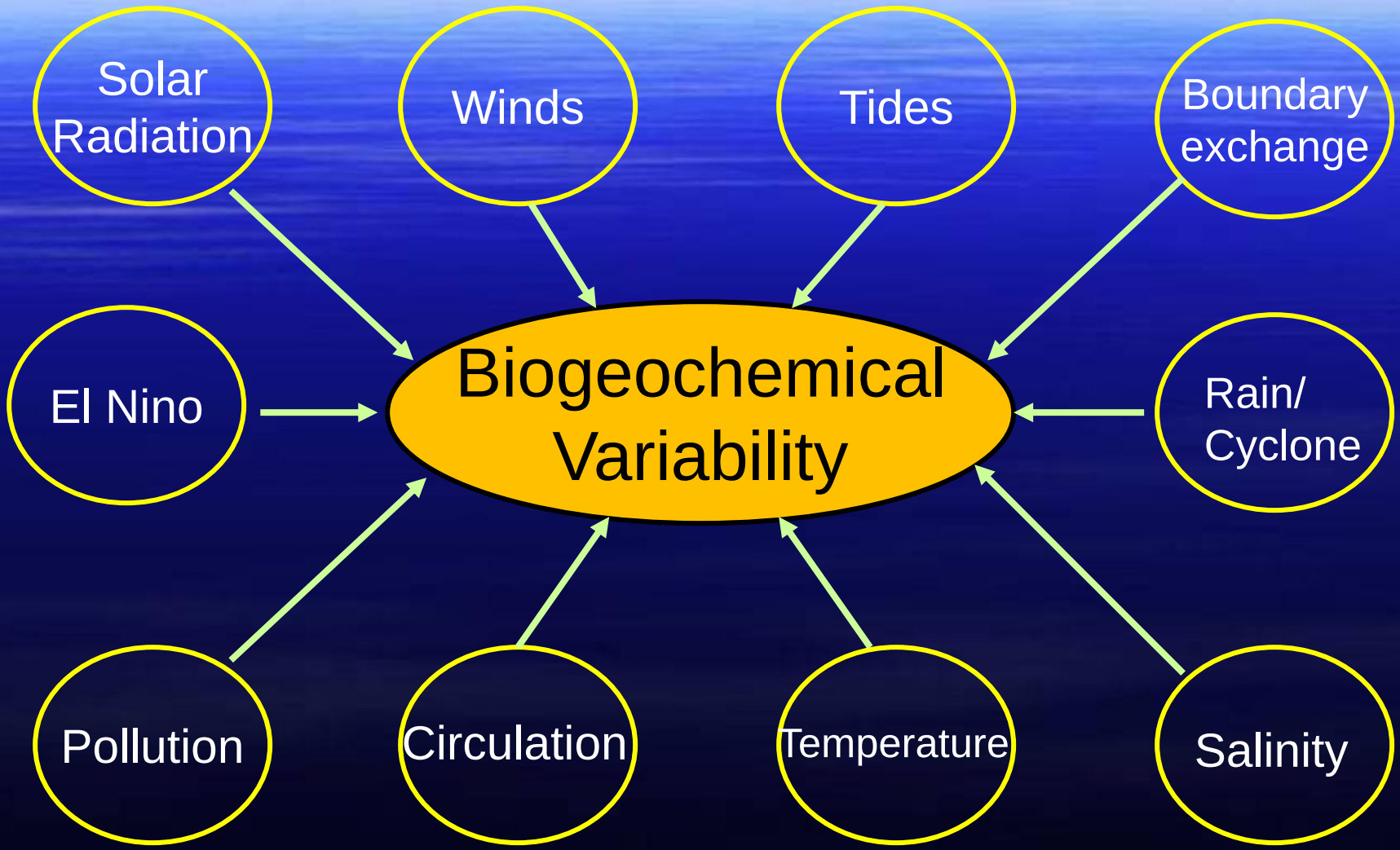
Physical processes – Evaporation, ice formation/melting, currents, mixing diffusion, freshwater (river) discharge, etc.

Chemical processes – chemical interaction, nutrients, organic and inorganic carbon, ligand formation, pH, speciation etc.

Biological processes – osmotic regulations, plankton composition, biological uptake, decomposition of organic matter, food web etc.

Geological processes – removal from water column, Sedimentation etc.

Various influencing factors



Variability at different time-scales

Nutrients…

Diurnal variations - changes in solar radiation, uptake by phytoplankton tides …etc.

Daily variations - changes in winds, mixing, phytoplankton production atmospheric inputs …etc

Seasonal variations - changes in wind direction/speed, precipitation, Land-Ocean exchanges, vertical mixing..etc.

Inter-annual variations – Atmospheric extreme events such as Indian Ocean Dipole, El Nino etc.

Decadal variations – shifts in atmospheric pressure systems, plankton community shifts, climate change impacts, anthropognic forcings…etc.

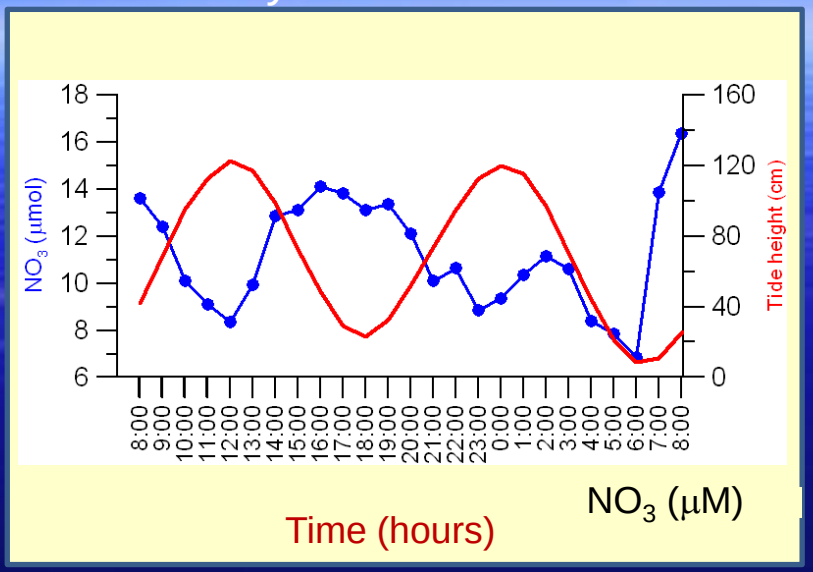
Experimental approaches

Chemical composition of seawater is modified by natural, and Anthropogenic processes and will have significant impact on ecosystem functioning. Hence it is important to understand the variations in chemical composition of seawater with reference to:

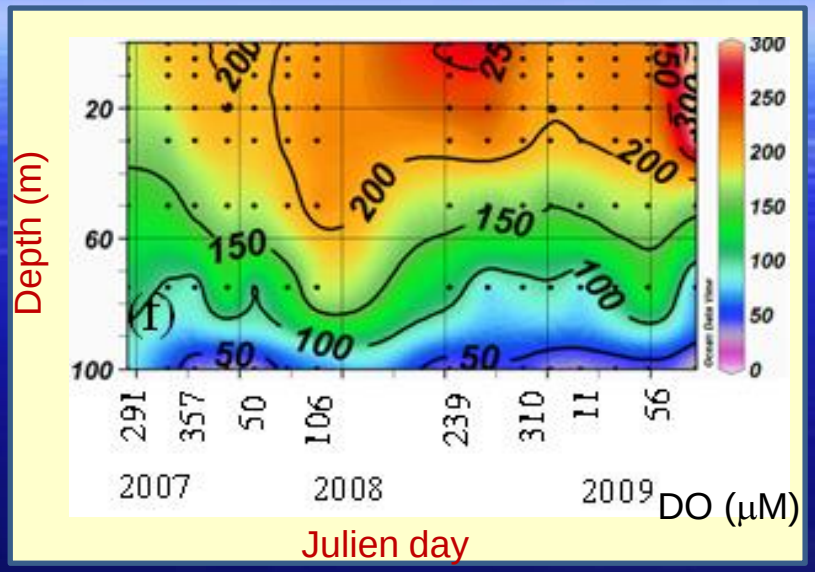
Spatial, and temporal variations
Variable sources and sinks
Cycling of materials in the sea
Modification through physical and biological processes
Impact of anthropogenic processes
Influence of climate change

Time-series observations at fixed location

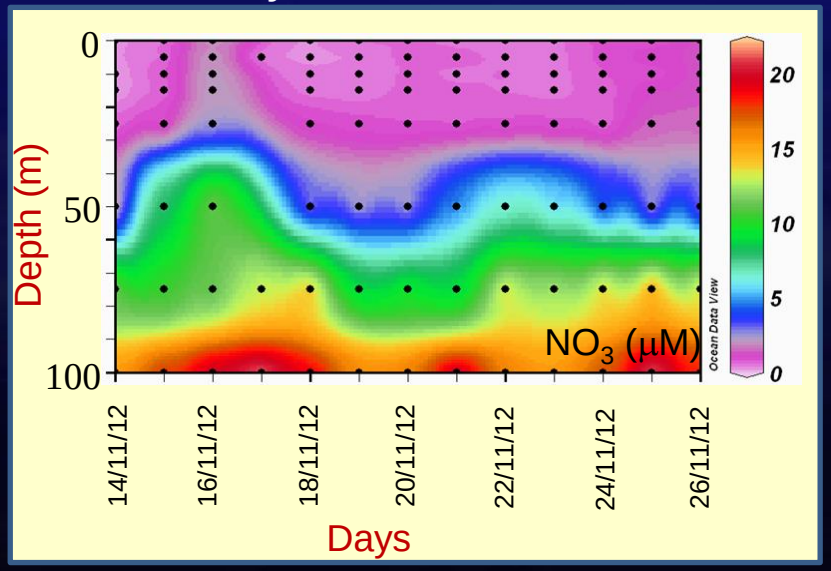
Hourly time-series



Monthly time-series

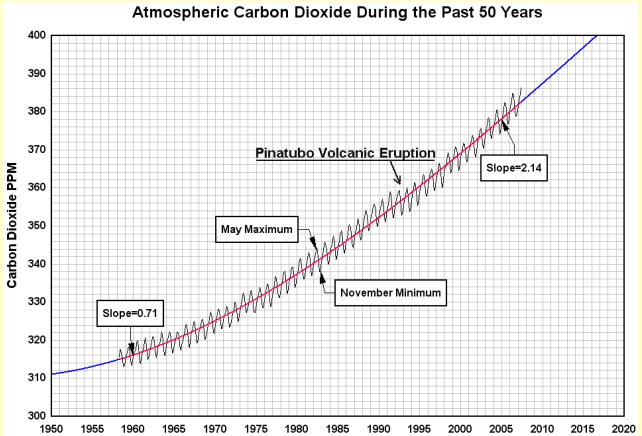


Daily time-series

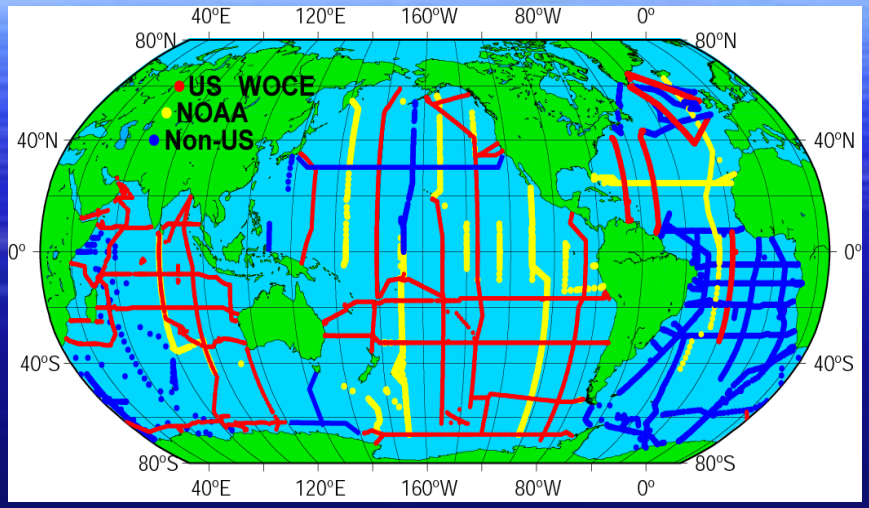


Long-term time-series

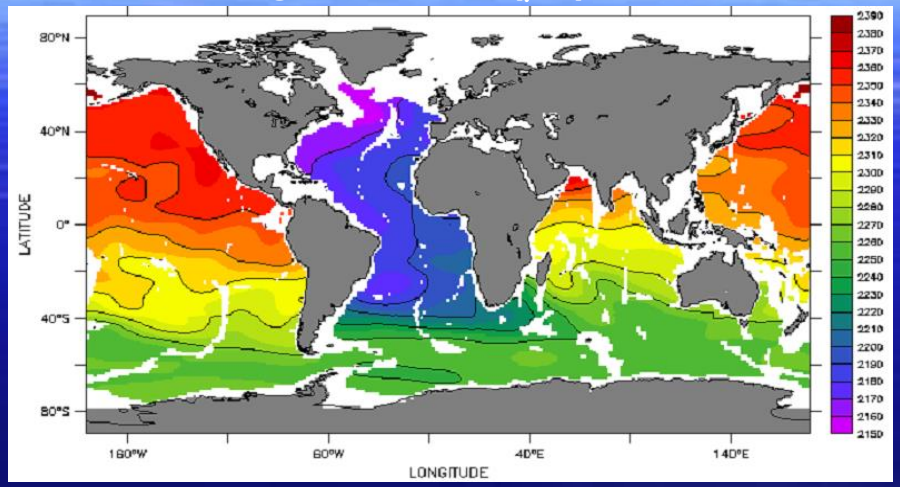
CO_2 (µatm)

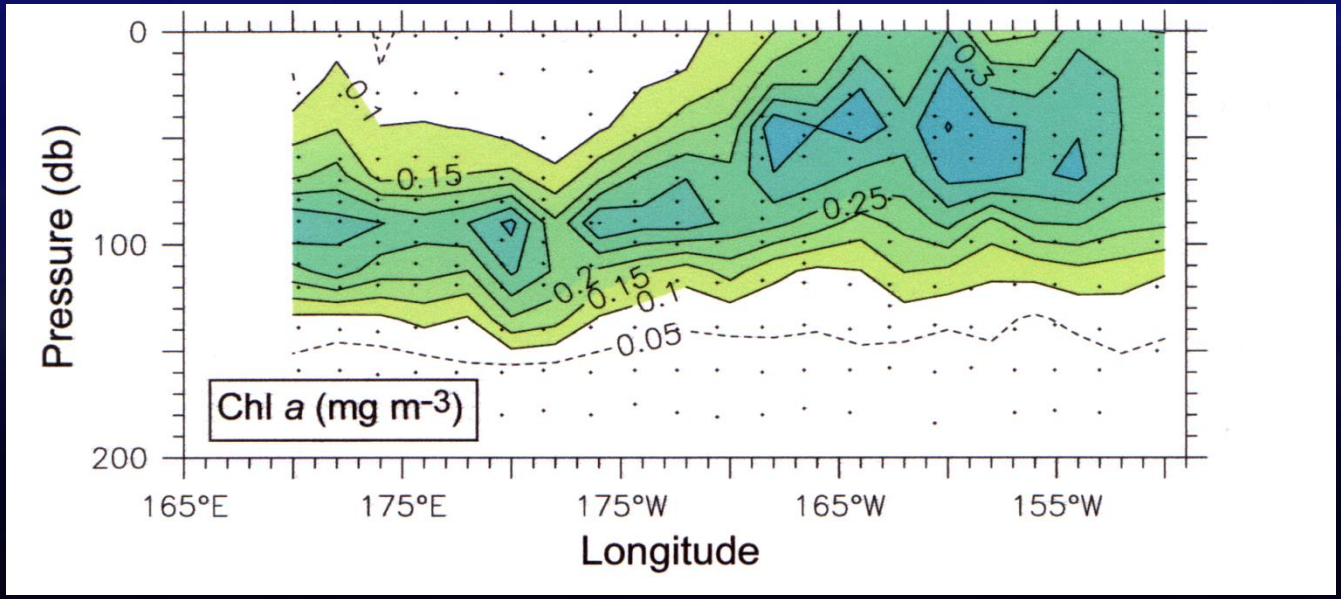


Spatial Variations in properties



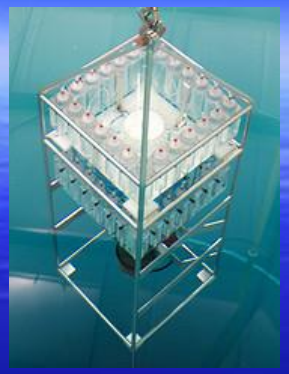
Dissolved inorganic carbon (μM)





Gadgets for time-series observations

Shipboard sampling



Automated sampling

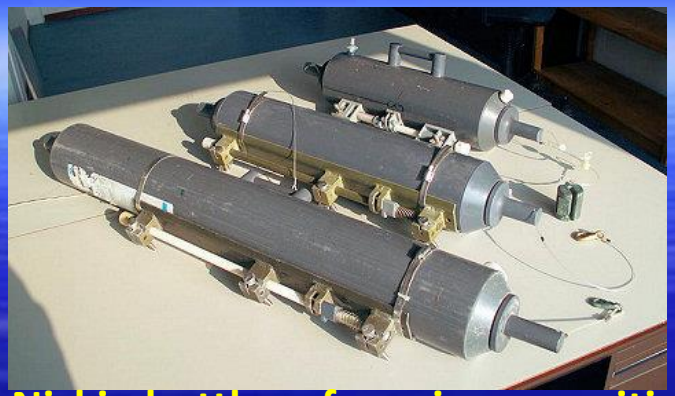
Sensor based at
Fixed location
At surface

Sensor based at
Fixed location
at variable depths

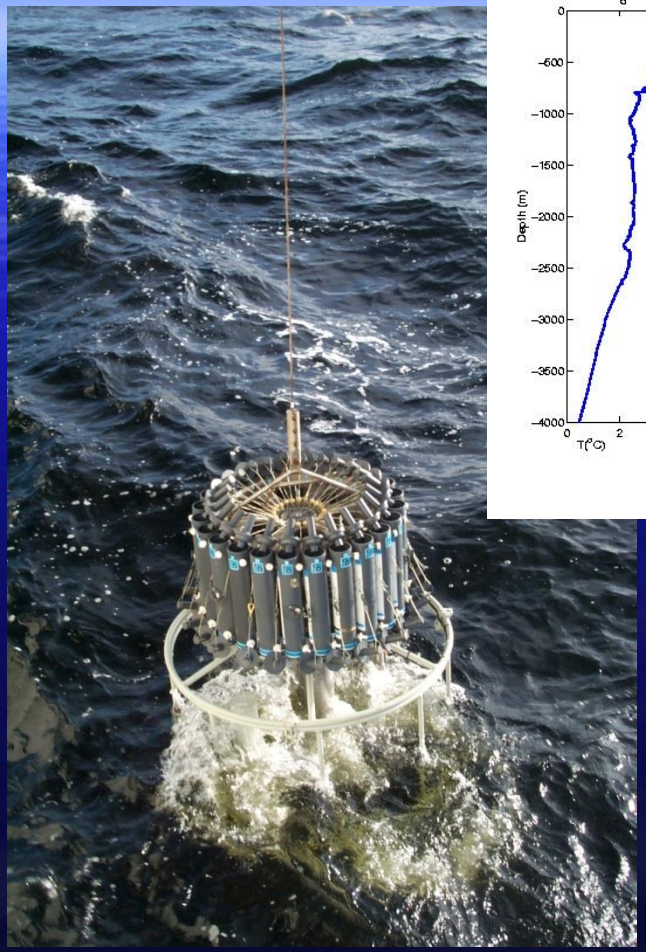
Sensor based
Covering part of Basin

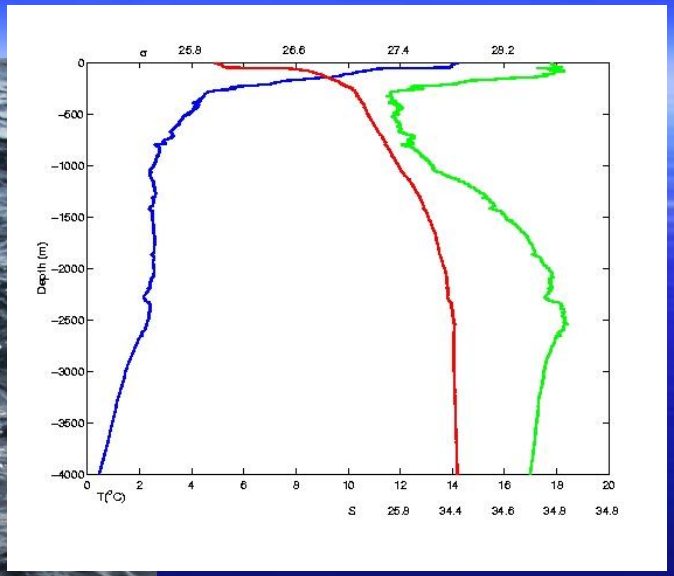
Repetition of sections
In the basin/global ocean

Water sampling system



Niskin bottles of varying capacities





Hydrocast using a Niskin bottle and portable CTD

CTD-rosette system to measure temperature, Salinity, depth continuously.

An Oceanographer sub-sampling sea water from Niskin bottles

Chemical parameters of Oceanographic interest:

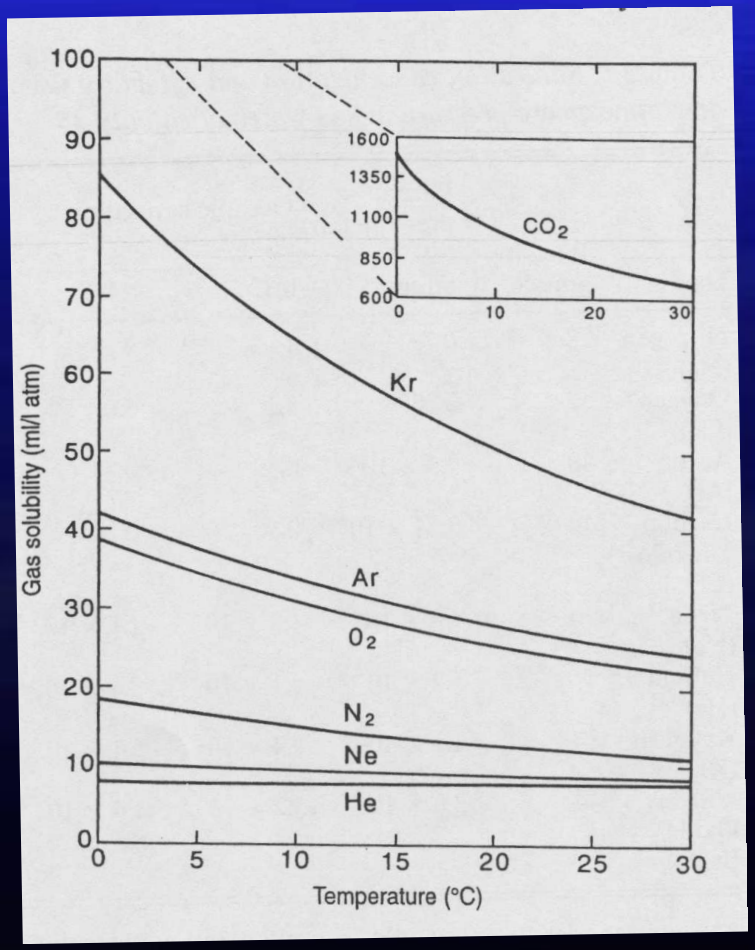
Gases: Dissolved oxygen (DO), Nitrous oxide (N_2O), Methane (CH_4), Carbon dioxide (CO_2) & Dimethylsulphide (DMS).

Nutrients: Nitrate (NO_3), Nitrite (NO_2), Ammonium (NH_4), Phosphate (PO_4) and Silicate (SiO_4)

Others: pH, dissolved and particulate organic carbon, dissolved and particulate trace metals, etc

Order of sampling

1. Dissolved oxygen
2. Dissolved gases (N2O, CH4, CO2, DMS….)
3. pH
4. DIC
5. Total Alkalinity
6. DOC
7. Nutrients
8. Pigments
9. Biological sampling …..



Sampling bottles

1. Dissolved oxygen - Glass
2. Dissolved gases (N_2O, CH_4, CO_2, DMS….) - Glass
3. pH – Glass
4. DIC - Glass
5. Total Alkalinity – Glass
6. DOC - Glass
7. Nutrients - Plastic
8. Pigments – Plastic (dark)
9. Biological sampling …..

Care to be taken while sub-sampling

Use glass tube that is connected to sampling bottle (Niskin) using flexible transparent rubber tube for sub-sampling.

Remove air bubbles in the sub-sampling tube before start sampling

1. Fill the bottle from the bottom slowly
2. Avoid turbulence in the bottle
3. Avoid generation of bubbles
4. Overflow at least three times of the bottle volume
5. Add preservative and tighten the cap immediately

For DOC sampling, avoid contact at mouth of the bottle and also use of sub-sampling tube

Sample preservation

1. Dissolved oxygen – Fix O_2 using Winkler reagents
2. Dissolved gases – Saturated $HgCl_2$
3. pH – Saturated $HgCl_2$
4. DIC – Saturated $HgCl_2$
5. Nutrients – Freeze samples at -4^{o}C
6. DOC – 5% H_3PO_4

Instrumentation

Dissolved oxygen (DO)

Required for survival of all life forms in the sea

Winkler's titration method:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$

$$2Mn(OH)_2 + {}^1/_2O_2 + H_2O \rightarrow 2MnO(OH)_2$$

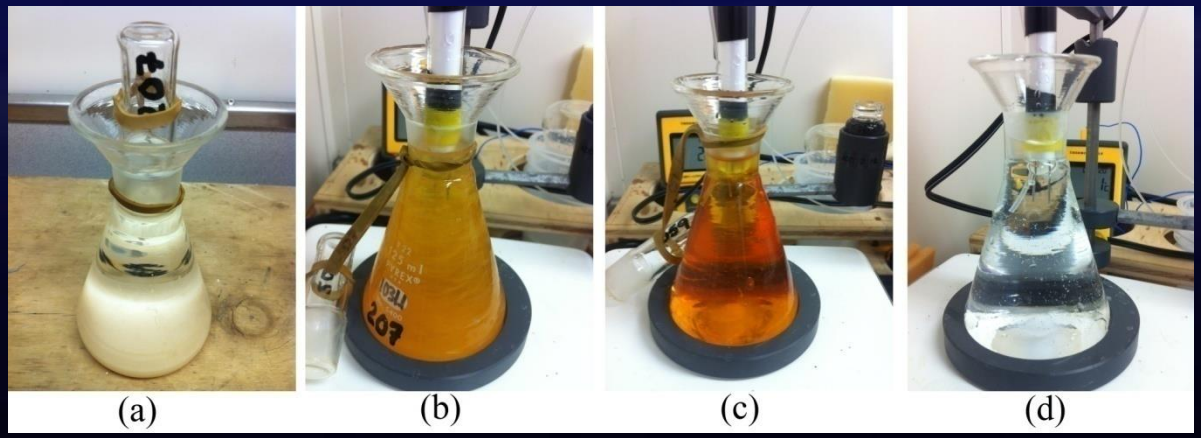
$$2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 6H_2O$$

$$I_2 + I^- \leftrightarrow I_3^-$$

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$

Reagents:

Winkler A (MnCl2 or MnSO4) and Winkler B (KI + NaOH)



(a) (b) (c) (d)

Nutrients (NO_3, NO_2, NH_4, PO_4 & SiO_2)

Colourimetry: "technique used to determine the concentration of colored compounds in solution"

Nitrite (NO_2): pink azo dye (543 nm)

Nitrate (NO_3): reduction to NO2 using Cu-Cd/Hg-Cd column, then same as above (543 nm)

Ammonium (NH_4): Indo phenol blue (630 nm)

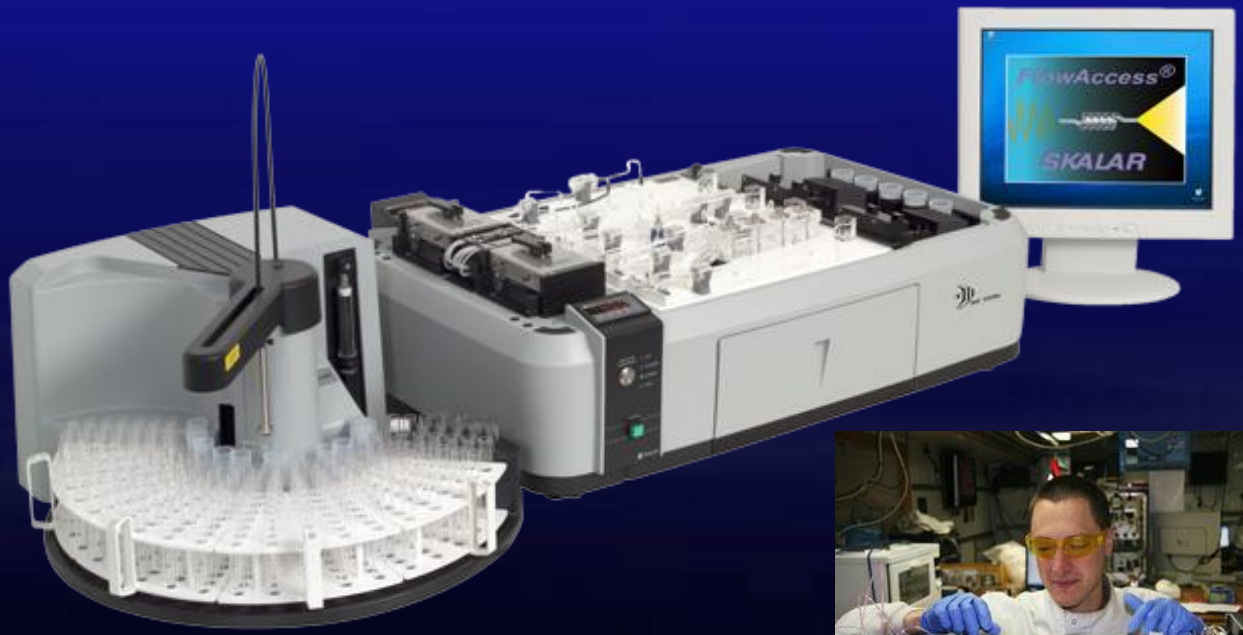
Phosphate (PO_4): Phosphomolybdenum blue (880 nm)

Silicate (SiO_2): Silicomolybdenum blue (810 nm)

NIO

Nutrients analysis by Autoanalyzer

Segmented flow analysis



pH measurements

Seawater scale

NBS Scale

Free-ion Scale

Total ion Scale

pH in total ion scale

Indicator: Bromo Cresol Purple

Once add BCP into water, it dissociate into unprotonated and protonated forms [I^{2-} and HI^{-}] each of them have different Spectral signatures.

$$\frac{[I^{2-}]}{[HI^{-}]} = \frac{A_1 / A_2 - \varepsilon_1(HI^{-})/\varepsilon_2(HI^{-})}{\varepsilon_1(I^{2-})/\varepsilon_2(HI^{-}) - (A_1 / A_2)\,\varepsilon_2(I^{2-})/\varepsilon_2(HI^{-})} \qquad (6)$$

where the numbers 1 and 2 refer to the wavelengths chosen. For the best sensitivity, the wavelengths corresponding to the absorbance maxima of the base (I^{2-}) and acid (HI^{-}) forms, respectively, are used. The various terms ε are the extinction coefficients of the specified species at wavelengths 1 and 2, respectively.

Preparation of m-cresol purple solution

The concentrated dye solution (2 mmol) of known pH adjusted in the range of seawater (7.9) is required. This implies that the ratios of A_1/A_2=1.6
i.e., 578 and 434 nm

Measure absorbance of the cell + Seawater

Take the samples in 10 m long path length cylindrical cell and place it in the thermostat compartment. Add 50 micro liters of dye to the sample. Measure the absorbance with at 730, 578 and 434 nm corresponding to background, maxima of the base (I^{2-}) and acid (HI^{-}) forms of the dye respectively.

Calculation of the pH

8.2 Calculation of the pH of the sea water + dye

The pH of the sea water and dye in the cell is computed from

$$\mathrm{pH} = \mathrm{p}K_2 + \log_{10}\left(\frac{A_1/A_2 - \varepsilon_1(\mathrm{HI}^-)/\varepsilon_2(\mathrm{HI}^-)}{\varepsilon_1(\mathrm{I}^{2-})/\varepsilon_2(\mathrm{HI}^-) - (A_1/A_2)\varepsilon_2(\mathrm{I}^{2-})/\varepsilon_2(\mathrm{HI}^-)}\right) \qquad (7)$$

where $\mathrm{p}K_2$ is the acid dissociation constant for the species HI^- (expressed on the total hydrogen ion concentration scale in mol kg-soln^{-1}), and A_1 and A_2 are the corrected absorbances measured at the wavelengths corresponding to the absorbance maxima of the base and acid forms, respectively. The various extinction coefficient terms ε correspond to values measured for the specified species at wavelengths 1 and 2, respectively (Table 1).

CDOM measurements

- The CDOM also refers to the sum total of all organic compounds in water that are both dissolved and absorb blue light. These compounds are produced by the natural metabolic processes of both plants and animals and are thus ubiquitous in aquatic systems.
- CDOM a heterogeneous mixture derived primarily from the decomposition products of plant material, bacteria and algae.

Sample collection and measurements

Sample should be collected in pre-cleaned amber borosilicate glass tubes / bottles and must be filtered as soon as possible. Keep it under low temperature until filtration. Filter on to 0.2µ membrane filter paper of 47mm diameter at low light to avoid degradation of organic matter.

CDOM free water should be prepared. Filtered rainwater is an excellent blank. Obtain spectra between 200 and 800 nm and examine for low or no peaks in absorbance for blank.

Fill both reference and sample cells of 10 cm path length with blank water and autozero the instrument.

Place the filtered sample in the sample compartment and scan again between 200 and 800 nm

$$a_{CDOM}(\lambda) = a_{CDOM}(440) \exp[-s(\lambda - 440)] \quad [m^{-1}]$$

[a_{CDOM} (440): absorption at 440 nm, s: slope of the curve resulted by plotting logarithm of a_{CDOM} against wavelength (λ)]

↓

Correct the absorption coefficients for backscattering of small particles and colloids

$$a_{CDOM\_corr}(\lambda) = a_{CDOM}(\lambda) - a_{CDOM}(700) * (a\lambda/a700) \quad [m^{-1}]$$

Sensors and automated sampling system

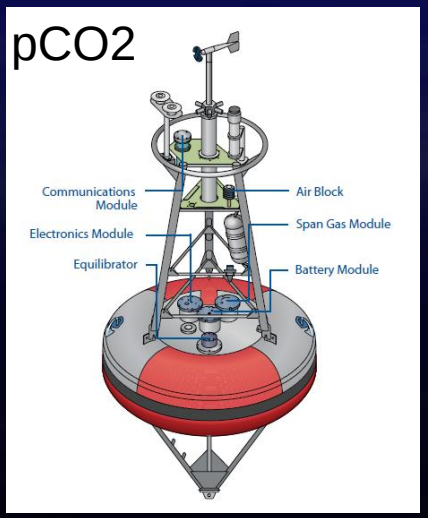
DO

Chl-a

Nitrate

Video Plankton Recorder

pCO2

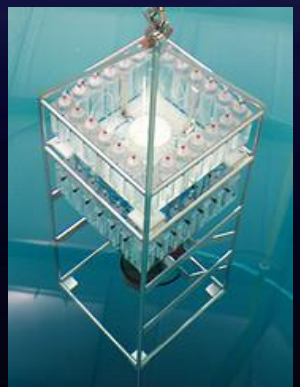


Transmissometer

Gas Tension Device

In situ filtration system

Remote access sampler



PAR

pH

Sediment trap

FRRF

Calibration
and
standardization of method

Preparation of standard

Advisable to prepare nutrient standards in the nutrient-free seawater to avoid matrix effects. Collect seawater from the offshore (blue waters) where nutrients are low and age them over a period of time (several months).

Filter them through 0.22 um filter to remove particulate and biological cells.

Autoclave the water to remove left over life

Store them in the container for further use

Standard for long-term use

Prepare one low and high concentration standard with nutrient-free seawater and store them in the glass ampoules/plastic bottle.

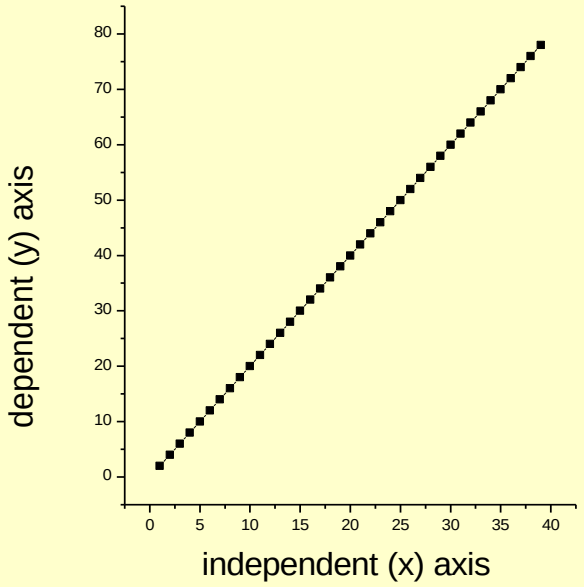
Use the same standard every time you run samples and values must be consistent.

You may send these samples to other laboratories to check consistency.

Calibration must be prepared during every time when samples are analyzed. Do not use same factor for several months!

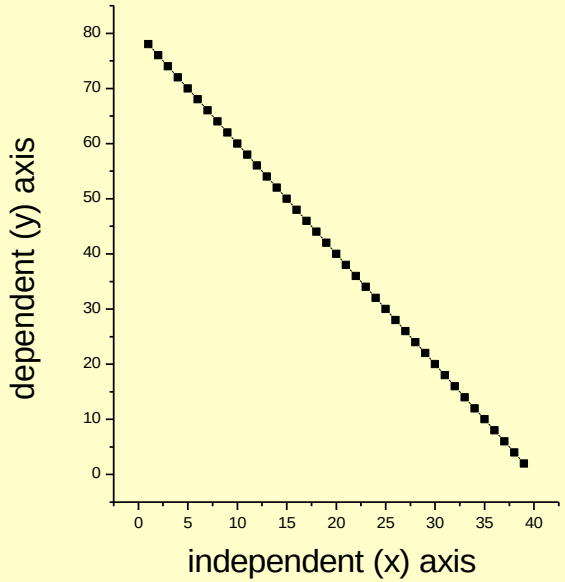
Data analysis

Graphical Representations-2D



DIRECT

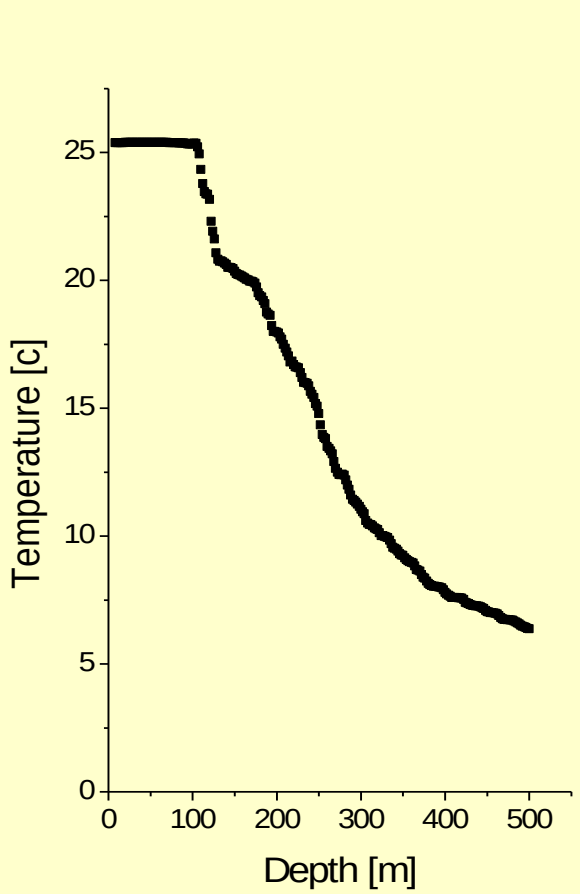
Example: Increased water temperature results in increase in the growth rate of plankton.

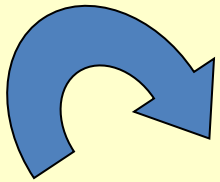


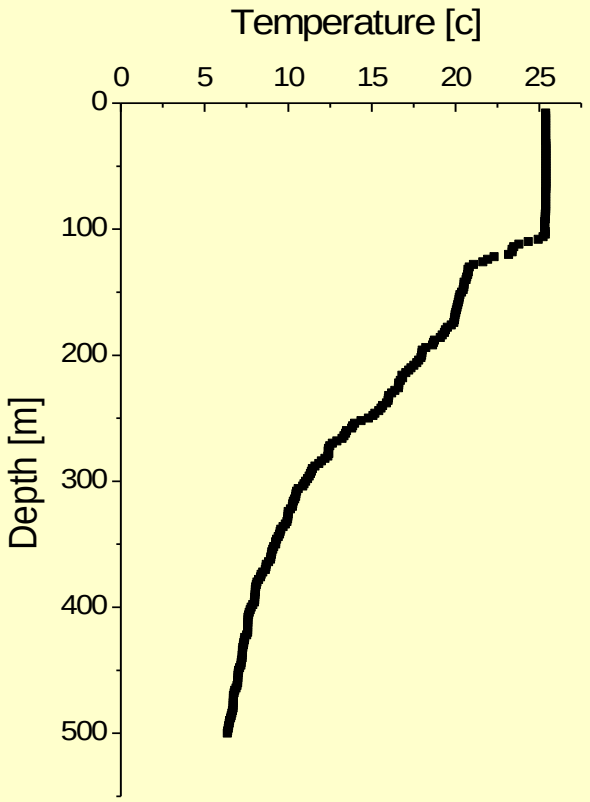
INVERSE

Example: Increase in wind-induced mixing of water column results in decrease in phytoplankton biomass.

Graphical Representations-2D



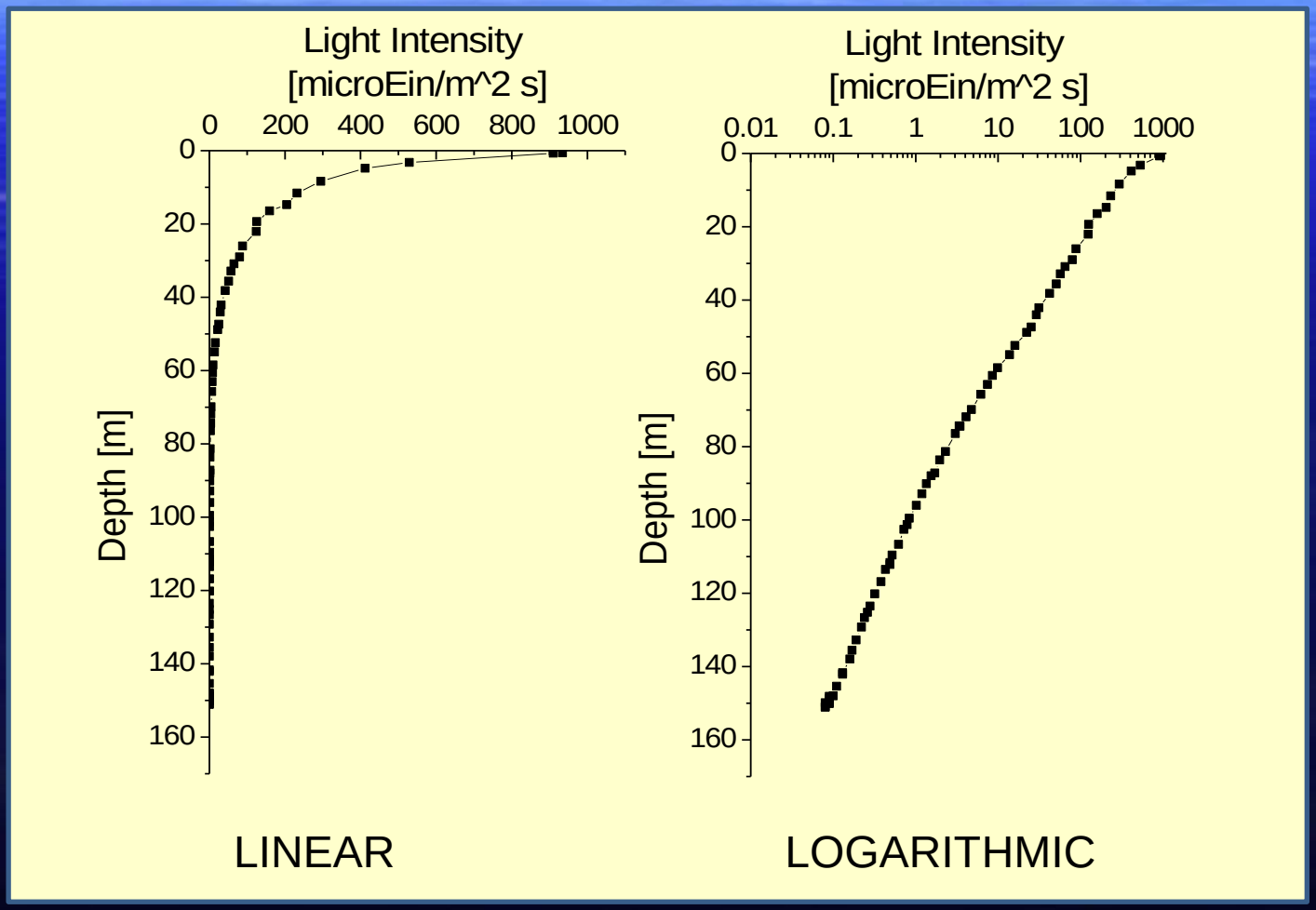




Typical 'x-y' graph

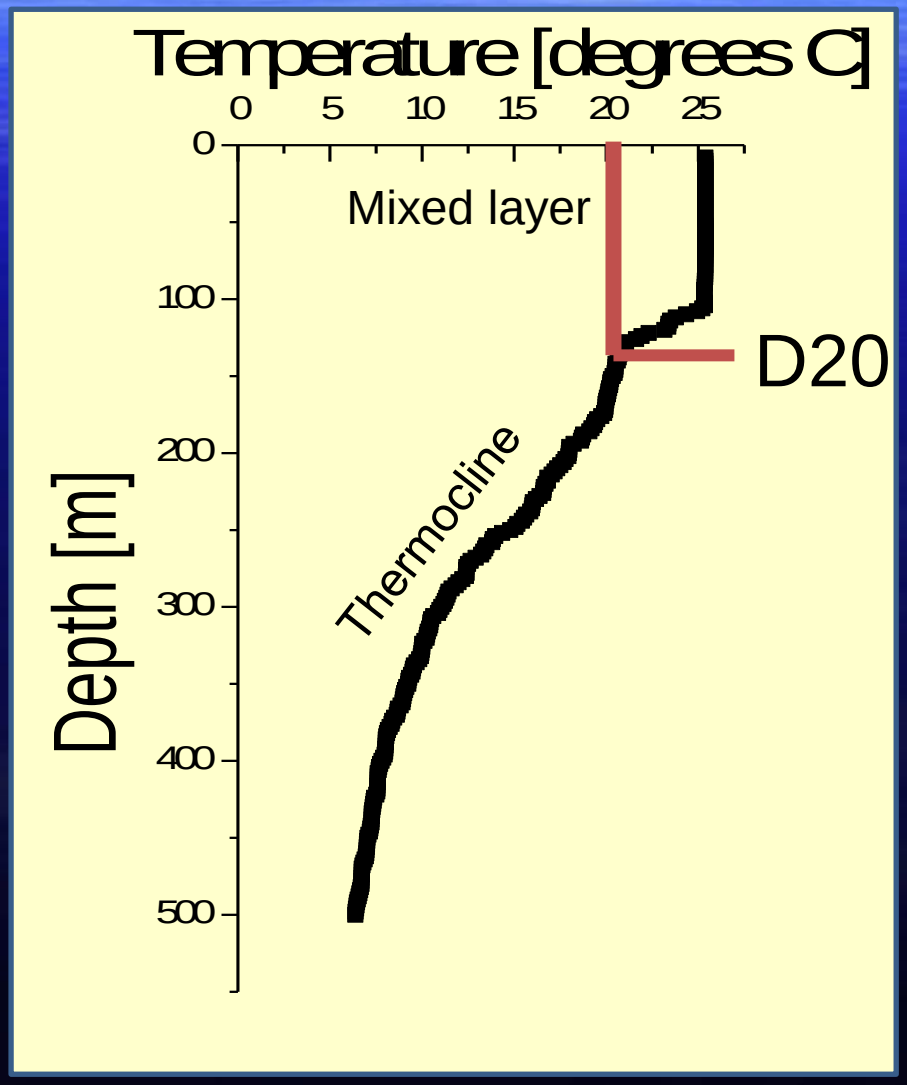
Oceanographic profile graph

Graphical Representations-2D

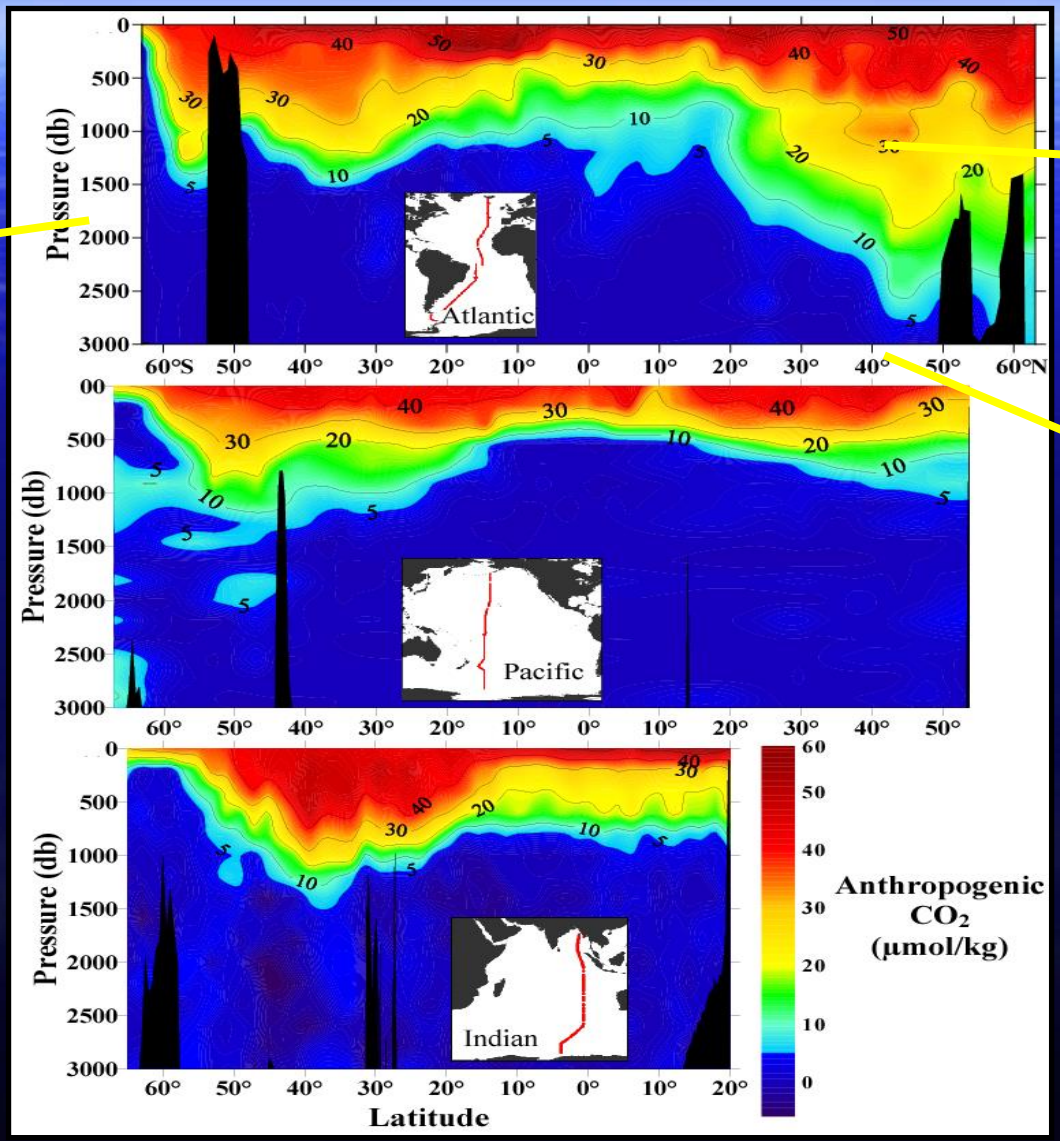


Graphical Representations-2D

Anatomy of a graph



Graphical Representations - 3D



Y-axis

Z-axis

X-axis

Random and systematic error

Random error: fluctuations (in either direction) of measured values due to precision limitations of the measurement device. Random error is quantified by the variance or standard deviation.

(PRECISION)

Systematic error (bias): offset, high or low, which cannot be determined through statistical methods used on the measurements themselves.

An oceanographic example:

Two or more technical groups measure the same parameters (e.g. temperature, nutrients or oxygen, etc). The mean values the groups obtain differ because of differences in methods, chemical standards, etc. Error can only be evaluated by comparison of the two sets of measurements with each other or with an absolute standard.

(ACCURACY)

Precision of the analysis can be obtain from repeated measurements of different aliquots of same sample several times and standard error gives precision of the property measured

The deviation of the measurement from that of Known samples (called standard) is called Accuracy of the property measured.

Standard deviation vs. standard error

Standard deviation is a measure of variability in the field that is measured.

Standard error is a measure of how well the field is sampled.

Standard deviation of the measurements: $\sigma = \sqrt{(x-x')/N}$

Standard error: $\sigma/\sqrt{N}$

Questions