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# Chemical Oceanography: An Insight into An Ocean

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**ABSTRACT:** Chemical Oceanography is the study of ocean chemistry; the behavior of the chemical elements within the earth ocean. The chemistry of the ocean is closely tied to ocean circulation, climate, plant and animals that live in the ocean. Now it is necessary to take care of our ocean as it covers 71% of the land on the earth by chemical oceanography. It also studies the chemical oceanography at different oceans around the world. Climate-induced forcing of upwelling trends can alter the zooplankton community in this highly productive region with potential consequences for the ecosystem food web. It studies biogeochemistry, a systems science closely related to systems ecology.

**KEYWORDS:** Ocean, Chemistry, Elements, Ecology, Biology, Manned field work, Autonomous systems, Phytoplankton, Zooplankton, Biogeochemistry.

### I. INTRODUCTION

Chemical oceanographers study the chemical composition of the ocean and the processes responsible for controlling it. The ocean has been compared to a factory in which the chemical elements are input (via rivers or the atmosphere, for example), processed and removed. Virtually all the elements of the periodic table are present in the oceans. Oceanographers sample the oceanic water column to characterize its density structure, chemical composition, biota and other aspects of the marine food web (including the rates of primary and secondary production). Chemical oceanographic studies in the North Indian Ocean have revealed several interesting and unique features. Higher nutrients and lower oxygen concentrations occur in the bottom layer as compared to the overlying water column in deep waters of the Bay of Bengal and Arabian Sea, suggesting that considerable quantities of organic matter reach the deep-sea floor, probably as fecal pellets, and get oxidized in the bottom layer. Among the more than 100 sea water samples from all oceans and seas used as the basis for this equation, only a few were from the Baltic Sea, and it has been found that in waters with a salinity below 20‰ the deviations from the relationship may exceed 0.02%. The proportions of the conservative elements in sea water are usually expressed relative to chlorinate, and anomalies are defined relative to the proportions of these elements in ocean water. Dissolved oxygen (DO) content of the marine environment is a crucial parameter for life and water quality as well as playing an important role in biogeochemical processes, and respiration of plants and animals, and decomposition of organic matter by bacteria is the primary processes that consume dissolved oxygen content of water and pore-water in sediments. If the oxygen concentration of water falls below about 2 mg/l,

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living organisms become stressed and the consequent conditions lead to hypoxia. Marine particles play a critical biogeochemical role in determining the distribution and concentration of carbon, nutrients, and many trace elements and isotopes (TEI's) throughout the oceans. Physical and chemical characteristics of the Adriatic Sea during 2001 are analyzed to better understand the influence of an exceptional flooding of the Po River (the largest river flowing into the Adriatic Sea) occurred in October 2000. River plumes play an important role in the processing of nutrients discharged from the land into the sea. The global oceans have absorbed about 30% of anthropogenic CO<sub>2</sub> emitted since the start of the Industrial. In the light of climate change and associated worldwide changing oceanographic regimes, the study of phytoplankton as primary producers within the marine realm is crucial. In the light of climate change and associated worldwide changing oceanographic regimes, the study of phytoplankton as primary producers within the marine realm is crucial. Phytoplankton (photosynthetic microalgae) are responsible for 50% of the global annual net primary production and link the atmospheric and the oceanic carbon cycle via the biological carbon pump. Zooplankton are considered to be a suitable indicator for assessing the impact of climate change-related environmental variability on the structure and functioning of global marine ecosystems (Roemmich and McGowan, 1995; Mackas et al., 2007; Chiba et al., 2015). This is because zooplankton populations and communities respond rapidly to the environmental variables affected by climatic changes (Richardson, 2008). Optical oxygen sensors based on fluorescence were introduced to oceanography by Thomson et al. (1988). These sensors utilize molecular oxygen's ability to quench the fluorescence of certain lumiphores. The rivers carry appreciable amounts of organic N which is more or less refractive. The concentration of CO<sub>2</sub> in the atmosphere is well measured and the variations sufficiently well-known on a global scale. Our knowledge of the role of S (and Se) in marine biochemistry is not sufficient. The methods to separate and determine optical isomers are being advanced particularly by the great interest of the pharmaceutical industry.

## II. LITERATURE REVIEW

### 2.1 Chemical Oceanography of Indian Ocean:

Chemical oceanographic studies in the North Indian Ocean have revealed several interesting and unique features. These are caused by the diverse conditions prevailing in the area which include immense river runoff in the northeast (Bay of Bengal) and a large excess of evaporation over precipitation and runoff in the northwest (Arabian Sea, Persian Gulf and Red Sea), resulting in the formation of several low- and high-salinity water masses. The occurrence of coastal upwelling seasonally makes the region highly fertile, and the existence of the Asian landmass, forming the northern boundary, prevents quick renewal of subsurface layers. Consequently, dissolved oxygen gets severely depleted below the thermocline and reducing conditions prevail at intermediate depths (ca. 150-1200m) resulting in the reduction of nitrate (denitrification). The North Indian Ocean may contribute up to 10% of the global marine DE nitrification. The "denitrified" nitrogen, when combined with the rate of photosynthetic production reaching below the euphotic zone, gives the average residence time of water between 75 and 1200m as 43-51 years. The inorganic nutrient concentrations in the subsurface layers are very high in close proximity of the euphotic zone. The two-layered circulation leads to an active recycling of nutrients. The presence of organic fractions of nitrogen and phosphorus in significant concentrations in the deep water suggest that oxidation of organic matter is incomplete even at great depths. The relationships between the apparent oxygen utilization (AOU) and nutrients and the stoichiometric composition of organic matter, deduced from the oxidative ratios and by analysis of plankton, are not very different from other oceanic areas. Higher nutrients and lower oxygen concentrations occur in the bottom layer as compared to the overlying water column in deep waters of the Bay of Bengal and Arabian Sea, suggesting that considerable quantities of organic matter reach the deep-sea floor, probably as fecal pellets, and get oxidized in the bottom layer. Very high silicate concentrations occur in the bottom water, especially in the Arabian Sea, decreasing steadily southward, indicating the solution of diatomaceous sediments from the sea floor. The silicate-rich waters appear to move southward over the north-bound, silicate-poor bottom water, resulting in the occurrence of a deep silicate maximum. The calcium:chlorinity ratio in the North Indian Ocean is appreciably higher than the oceanic averages. This is probably due to: (1) a high rate of river runoff in a relatively small area; and (2) excessive stripping of calcium at the surface associated with high biological productivity and its subsequent addition and regeneration in the bottom waters. The upward flux of calcium appears to be higher than in other oceanic areas. Other major constituents investigated (fluoride and magnesium) do not show any anomaly.

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The partial pressure of carbon dioxide in surface waters of the North Indian Ocean is higher than that in the atmosphere which results in a net flux of carbon dioxide from the sea to the atmosphere. Stagnation of intermediate layers, coupled with high organic productivity at the surface, results in high total carbon dioxide content at these levels. An increase in carbonate ion concentration occurs with depth in deep waters varies from 1000m to 3000m, increasing progressively southward.

## 2.2 Chemical Oceanography of Bay of Biscay:

The International Symposium of the Bay of Biscay (ISOBAY) offers every two years a unique opportunity to re-examine and advance many observations and concepts of this important large marine ecosystem region of the North Atlantic, the Bay of Biscay. This special issue of Deep-Sea Research II presents the best contributions presented and discussed during the XIII edition of ISOBAY organized in Santander (11–13 April 2012) by IEO. The issue, as a whole, represents one of the best and most complete compilations of the Bay of Biscay regional oceanography up to date and thus an essential reading for any scientist first approaching this region. A major emphasis of the editors while preparing the issue has been to highlight the implications of the new findings of the region with respect to the present scenario of climate change and climate variability. This variability is thought to be related to the availability of nutrients from the previous winter, and probably has an effect on the subsequent zooplankton out-burst and thus on the food availability for early life fish stages (larvae) and for planktivorous fish adults in the region. With a similar aim, bridging the long term Climate and the Regional Oceanography, we have included in this special issue an introductory Review that presents to the reader additionally the physical oceanography that orientates the following papers. Over-all this Review by Pingree and Garcia-Soto (2014) and the subsequent manuscripts, summarized below, provide a new look at the oceanography of the Bay of Biscay.

## 2.3 Chemical Oceanography of Persian Gulf:

Measurements of basic hydrographic properties, nutrient elements, alkalinity and total carbon dioxide were made in the Persian Gulf in February and March 1977, on R.V. Atlantis H Cruise 93. The outcomes demonstrate plainly the entrance into the Gulf of surface Indian Ocean water, at first of 36.5% saltness which is conveyed northwards along the Iranian Coast, slowly expanding in saltness to over 40%. The inflowing surface water is high in phosphate (1.0-0.5 micromoles kg<sup>-1</sup>) because of upwelling incited by the north-east storm. However, nitrate levels are at, or below, the detection limit and nitrogenous nutrients appear to be limiting. The seawater carbonate system is greatly perturbed by the precipitation of large quantities of calcium carbonate. The alkalinity-salinity relationship shows that the greatest carbonate loss occurs in the shallow waters of the Trucial Coast, where up to 125 moles kg<sup>-1</sup> of CaCO<sub>3</sub> have been lost from the water. Dense, saline low specific alkalinity water formed in the shallows appears to migrate down slope to augment the outflowing waters in the deeper part of the Gulf. The outflow of the Tigris, Euphrates and Karun rivers to the north provides an intense, but low capacity signal, of low salinity, high specific alkalinity, and waters. Large amounts of CO<sub>2</sub> are also fixed by photosynthetic processes. The classical Mediterranean type of circulation is plainly revealed. The residence time of water within the Persian Gulf is approximately 2.5 year.

## 2.4 Chemical Oceanography of the Chilean Patagonia:

Chilean Patagonia is one of the most extended fjord regions in the world that covers nearly 240,000km<sup>2</sup> with an extremely complex coastline and topography in one of the least densely populated areas of the country (1–8 inhabitantsevery10km<sup>2</sup>). In recent years, the area has been undergoing somewhat intense pressure since several commercial projects in hydroelectricity, tourism, and commercial salmon and mytilid cultures have been developed, or are in progress. Concomitantly, several large research programs have been devised to study the physical, chemical, and biological environment of Patagonia, such as the CIMAR FIORDO, and recently COPAS Sur-Austral based at Universidad de Concepcion, that attempts to close the bridge between oceanographic knowledge and its use by society. Fjords are high latitude estuaries that are usually longer than they are wide, with relatively deep water column sand presenting steep walls. They were formed by erosion due to the advancement and retreat of glaciers during the last ice

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age, and filled with seawater during high sea level in the inter glacial. Fjords undergo estuarine circulation due to the occurrence of a river discharging at their most upstream point. The irregular bottom topography and the presence of several sills enhances deposition of sinking particles and may slow down circulation. Even though low oxygen concentration has been detected (ca.100 mM), in the Chilean fjords, no anoxic basins have been found. That contrasts with some fjords in the Oslo fjord and the Framvaren in Norway, and in Saanich Inlet in British Columbia. The Chilean Patagonia is also characterized by the presence of five large Ice Fields (Northern Patagonian, Southern Patagonian, Muñoz-Gamero Peninsula, Santa Inés Island, Darwin Mountain), considered valuable fresh water reservoirs of worldwide importance (for instance, the Southern Ice Field provides ca.3000 m<sup>3</sup> water s<sub>-1</sub> to the ocean, and it is world's third most important reserve of fresh water after Antarctica and Greenland). These ice fields are unique at these latitudes (46–48oS) and are conserved due to atmospheric and oceanic circulation patterns.

## 2.5 Anomalies in the Composition of Baltic Sea Water:

The Baltic Sea was found to be the early studies of the chemical composition of sea water. However, the time was not ripe for a systematic study of the relationships between the different components of the Baltic Sea water, especially the so-called major constituents, Cl, SO<sub>4</sub>, Br, B, F, Na, Mg, Ca, K and Sr. Information was needed on the constant relation between the chloride concentration, or more exactly, the total amount of halides excluding fluoride expressed as chlorides, and the total salt content of the different sea waters. Knudsen (1903) established a relationship between salinity and chlorinity in sea water, viz.:  $S\% = 1.805 Cl\% + 0.0300$ , this equation being based on 13 different samples, only 8 of which were taken from the Baltic Sea and the transition area. The constant term takes into account the mean anomalies of the Baltic Sea water which derive from the dilution of ocean water with river water. More recently, salinity has been redefined on the basis of the relative conductivity of sea water (Cox et al., 1962), and the relation between salinity and chlorinity has been internationally defined by the expression (Wooster et al., 1969):

$$S\% = 1.80655 Cl\% *$$

Among the more than 100 sea water samples from all oceans and seas used as the basis for this equation, only a few were from the Baltic Sea, and it has been found that in waters with a salinity below 20 ‰ the deviations from the relationship may exceed 0.02‰ \*. The proportions of the conservative elements in sea water are usually expressed relative to chlorinity, and anomalies are defined relative to the proportions of these elements in ocean water. Because of the unusual hydrographical features of the Baltic Sea, it might be expected that these elements would show significant anomalies. More than 200 rivers annually discharge about 450 km<sup>3</sup> of fresh water from drainage areas in different geological environments. In addition, the water added to the Baltic Sea by precipitation (about 200 km<sup>3</sup> a<sup>-1</sup>; cf., Chapter 2) has a chemical composition which differs significantly from that of distilled water. The situation is further complicated by the presence of dissolved organic substances having considerable complexing properties, e.g., humic substances, and by variations in the redox conditions. When these factors are considered, it is surprising that the relative proportions of the major elements in Baltic Sea water are so similar, to those in ocean water. An extensive discussion on the anomalies of the constituents of the Baltic Sea water has recently been published by Grasshoff (1975). This discussion is summarized here with some additional comments.

**Sodium:** Kremling (1969) has found an average Na/Cl ratio of 0.5547 –I 0.0021, which value is not significantly different from that of 0.5555 (Culkin, 1965) for open ocean water. Indeed, no marked differences would be expected as the Na/Cl ratio for river water is of the same order of magnitude.

**Potassium:** The K/Cl ratio is not quite constant in the samples collected from different parts of the Baltic Sea (Kremling, 1969). The lowest values have been found in the southern Baltic Sea, while the highest have been recorded in the Aland Sea and in the Gulf of Bothnia. However, the mean value of 0.0206 is the same as that reported for oceans (Cox and Culkin, 1966).

**Calcium:** It has been proved by numerous workers (Von Brandt, 1936; Gripenberg, 1937; Wittig, 1940; Rohde, 1966; Kremling, 1970) that of all the major elements calcium is the one whose ratio to chlorinity in the Baltic Sea water most markedly exceeds the ratio in ocean water. This is the result of the high Ca/Cl ratio of the river water discharged into

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the Baltic Sea. The Ca/Cl ratio recorded near the mouths of several rivers shows marked elevation compared with that for oceans, i.e., 0.02125 (Cox and Culkin, 1966). Also in the open sea areas both the slope and constant term in the regression equation for Ca and Cl vary notably in surface water with a chlorinity below 4.5‰. This results partly from regional differences, partly from scattering of the analytical results.

**Bromide:** Kremling (1969, 1970) has found a slight negative anomaly for the Br/Cl ratio, which is evidently caused by the low ratio in the river water component of the Baltic Sea water.

**Magnesium:** In contrast to calcium, magnesium does not show marked regional variations in its relation to chlorinity. This was first shown in 1957 by Voipio, who obtained a ratio of 0.06695, which is rather similar to that found in oceans, i.e., 0.06680 (Cox and Culkin, 1966). However, more recent analyses indicate that the Baltic Sea value evidently slightly exceeds the oceanic Mg/Cl ratio (Nehring and Rohde, 1966; Rohde, 1967; Kremling, 1969, 1970 i.e., 0.0672).

**Sulphate:** The available data suggest that the Baltic Sea waters with a salinity higher than 8‰ do not show sulphate anomalies (Kremling, 1970). However, the relatively large standard deviations indicate local deviations from the oceanic SO<sub>4</sub>/Cl ratio, i.e., 0.1400 (Morris and Riley, 1966). The results obtained by Kremling for chlorinities 4.5‰ were 0.1410 and 0.1405 for 12 and 15 samples collected in 1967 and 1968, respectively.

## 2.6 Evaluation of marine pH sensors:

Contestants' sensors were deployed in a series of trials designed to test their accuracy, repeatability, and stability in laboratory, coastal, and open-ocean settings. This report details the validation efforts behind the competition, which included designing the sensor evaluation trials, providing the conventional true pH values against which sensors were judged, and quantifying measurement uncertainty. Expanded uncertainty (coverage factor k52, corresponding to 95% confidence) of validation measurements throughout the competition was approximately 0.01 pH units. The global oceans have absorbed about 30% of anthropogenic CO<sub>2</sub> emitted since the start of the Industrial Revolution (Sabine et al. 2004; Le Quere et al. 2015), resulting in an approximately 28% increase in [H<sup>+</sup>], corresponding to a 0.11 decrease in pH (Gattuso et al. 2015). The rate of this decline in pH, termed ocean acidification (OA), is faster than at any other time in the geologic record (Zeebe 2012). Ocean acidification is expected to have deleterious effects on many marine taxa and ecosystems, including reduced growth in marine calcifiers and impaired sensory function in fishes (Nilsson et al. 2012). The effects of ocean acidification on foundational species like coral, phytoplankton, and shellfish will have cascading effects on community structure, food webs, biogeochemical cycling, and commercial fisheries (Hofmann and Schellnhuber 2009; Narita et al. 2012; Kroeker et al. 2013; Punt et al. 2014; Ekstrom et al. 2015; Mathis et al. 2015). Despite the documented effects of altered seawater carbonate chemistry on many ecosystems, ocean acidification data are limited in both coverage and quality (Borges et al. 2009). Global ocean climate datasets like the World Ocean Climate Experiment (WOCE), Hawaii Ocean Time-series (HOT), and Bermuda Atlantic Time-series (BATS) have included carbon variables only since the late 1980s. These large-scale sampling efforts and long-term time series have mostly concentrated on the open ocean. Coastal areas experience more variability in CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) and represent 10–20% of the oceanic CO<sub>2</sub> sink (Chen and Borges 2009; Doney et al. 2009; Takahashi et al. 2009), yet most pCO<sub>2</sub> time-series in coastal waters are less than a decade old (Borges et al. 2009; Feely and Dickson 2009). This relative paucity of data can be attributed to both economic and technological limitations. Recent developments in floats, profilers, and automated underwater vehicles are increasing scientists' capacity to measure ocean conditions across time and space by increasing the number of observations and decreasing the cost of obtaining them (Byrne 2014). Equally important to the development of these new sensing platforms are high quality, cost-effective autonomous sensors that perform comparably to established laboratory methods and that have effective in situ quality control. Furthermore, sensors need to be capable of long deployments, which requires in situ calibration, anti-biofouling materials, and low power consumption. As platforms add more sensing packages, the capacity for sensors to integrate with others and communicate both bi-directionally and remotely with users becomes more important. Newer autonomous pH-sensing technologies, namely potentiometry with ion sensitive field effect transistors (ISFETs) and spectrophotometry with pH-sensitive indicator dyes, have the potential to meet the GOA-ON "climate" standard.

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ISFETs were initially tested for seawater applications and have been commercialized in the last 7 years. Spectrophotometric methods for pH, regularly used in oceanography, were developed 15 year earlier.

## 2.7 Continuous Flow Analysis in Chemical Oceanography:

Most continuous flow analyzers consist of a sample dispenser and a pump and tubing for the sample and reagents, which are mixed sequentially along a flow path leading to some kind of detector for the analytic species of interest. The fundamental problem, which until 1957 frustrated all attempts to use this kind of approach, is the considerable mixing of the sample along the tube which, without modifications in the flow system, would cause excessive dispersion (dilution) of the detectable analytic species and "tailing" of one sample into another over long time periods. The first successful attempt to limit the dispersion problem was made in the course of work on clinical analyzers by Skeggs (1957) who introduced a regular flow of small air bubbles into the sample stream immediately after the pump. He chose a peristaltic pump to meter the sample, air and reagent flows. The air bubbles segmented the liquid stream throughout the analytical manifold and were removed just before the detector. The air segments maintained a sharp concentration profile in the system and reduced tailing effects caused, in the laminar flow conditions employed, by the slower liquid flow along the tube walls. They also promoted mixing within the liquid segments. A commercially manufactured instrument utilizing segmented flow analysis (SFA) was quickly developed by the Technicon Corporation as the Auto Analyzer (see Fig. 1). A measure of the success of this instrument during its first 10 years of development are the very large number of literature citations to it: more than 1500 during the same period (Foreman and Stockwell, 1975). The Auto Analyzer, now modified to incorporate technological advances and new materials, is still the most popular integrated automatic analytical system. A large variety of commercially manufactured SFA instruments are now available. An entirely different approach to limiting sample dispersion was introduced by Hansen (1975) and Beecher et al. (1975). In this technique, termed flow injection analysis (FIA), a plug of sample is injected into a laminar reagent stream in a narrow-bore tube. As the sample plug travels along the tubing towards the detector it disperses and mixes with the adjacent reagent and, under suitable analytical conditions, will produce a sharp peak of the detectable analyte species. Sample injection is usually achieved using a rotary valve with a sample loop of the type designed for high performance liquid chromatography. An alternative system was designed by Johnson and Petty (1982) for seawater analysis, in which a reagent plug is injected into a sample stream. These authors termed this variant as "Reverse flow injection analysis (RFIA)". Of course, there are other possible approaches to the automatic analysis of seawater. Various instruments are marketed in which small discrete batch samples are sequentially mechanically processed reagents may be added, the sample stirred or heated and automatically transferred to the detector. Apparatus, such as the Auto lab or the Du Pont "aca", both fully described by Foreman and Stockwell (1975), can analyze large numbers of samples at a high throughput, but lack the versatility of SFA or FIA systems and are very expensive, and thus have had limited application in marine chemistry. There is a further central problem in continuous flow analysis. Many reactions have relatively slow kinetics and in order to reach a steady state, long flow paths would be required, though these are often inconvenient from the point of view of sample dispersion. However, if the handling of each sample is identical, a true steady-state need not be reached in order to assay a sample successfully. This principle was employed in the first generation of commercial SFA instruments (Auto Analyzer-I). It was found however, that very small variations in the bubble flow pattern, which are often a result of their compressibility, could significantly alter the analytical precision of the instrument (Hansen, 1981). A new generation of slightly slower SFA instruments (Auto Analyzer-II) was thus developed in which steady-state reactions were utilized and precision was increased. Two chemical phenomena help to achieve a steady state: the reaction kinetics tends to be faster in narrow tubes, probably due to wall effects (Hansen and Grasshoff, 1983), and many of these reactions can be accelerated by heating or by the judicious use of suitable catalysts. Most of the auto analytical techniques published since about 1972 use the steady-state principle. In the case of FIA, the use of a constant and virtually incompressible liquid flow leads to such highly reproducible conditions that non-steady-state chemistry is totally acceptable (Hansen, 1981). This considerably reduces the length of the reaction tube and the consequent analytic dispersion and thus leads to high sample throughput rates. Simple FIA systems can analyze samples at 5--10 times the rate of corresponding steady-state SFA instruments.

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## 2.8 Mapping of Oceanographic Properties:

The Palagruza Sill, a 170-m deep ridge separating the 1200-m deep South Adriatic Pit (SAP) from the 275-m deep Jabuka Pit has been recognized as an important location for tracking Adriatic-wide processes and dynamics (Zore, 1956). All Adriatic water masses are interchanged in this area (Zore-Armanda, 1963). North Adriatic Dense Water (NADDW), the densest Mediterranean water mass, which is characterized by very low temperature, moderate salinity and high dissolved oxygen content, is generated at the northern Adriatic shelf and flows as dense bottom current over the western and central parts of the sill (Vilibić and Supić, 2005). Middle Adriatic Deep Water (MADDW), which carries old waters from the deep Jabuka Pit toward the SAP, is characterized by higher nitrate and nitrite values (Grilli et al., 2013). Adriatic Deep Water (AdDW) is generated at the central SAP through deep convection processes (Vilibić and Orlić, 2001). It then flows toward the Ionian Sea but also enters the middle Adriatic. Finally, Levantine Intermediate Water (LIW), which is characterized by high salinity, high temperature and low dissolved oxygen values, is generated in the Eastern Mediterranean and enters the middle Adriatic Sea over the eastern and central parts of the sill, especially during ingression years (Buljan, 1953). The flow is driven by cyclonic circulation in the northern Ionian Sea. All of these water masses exhibit low levels of orthophosphates (Grilli et al., 2013), which are generally low in the Eastern Mediterranean (Krom et al., 1991). For these reasons, regular monitoring activities along the sill were initiated in the early 1950s (Buljan and Zore-Armanda, 1966) and continuously executed over the last 60 years, providing a long-term dataset of different physical, chemical and biological parameters. This dataset has been used to assess different oceanographic properties and processes in the area. Inter annual salinity variations were detected in the early 1950s (Buljan, 1953) and were used for the first definition of the Adriatic water masses (Zore-Armanda, 1963), which were then widely used to describe Adriatic oceanography (e.g., Buljan and Zore-Armanda, 1976; Orlić et al., 1992; Artegiani et al., 1997; Vilibić and Orlić, 2002). Mediterranean-wide processes, such as the Eastern Mediterranean Transient (Klein et al., 1999) and Bimodal Adriatic-Ionian Oscillation have also been detected by the series. Monitoring has led to the discovery of new findings and updates to existing theories, such as the strong inflow of intermediate Western Mediterranean waters to the Adriatic. In addition, SOM has been widely used in the global oceanographic community (Liu et al., 2006; Liu and Weisberg, 2011). It has been successfully applied to a variety of problems in which a reduction of dimensionality (Murtagh and Hernandez Pajares, 1995), extraction of patterns (Kopp et al., 2010) or detecting outliers (Munoz and Murazabal, 1998) was performed. Although the method prefers large datasets, which are provided via remote sensing techniques (e.g., satellites, Richardson et al., 2003) or climate studies (e.g., Morioka et al., 2010), SOM has been successfully applied to limited datasets, such as in situ oceanographic data, from which patterns have been extracted and connected to driving processes and forces (e.g., Fendereski et al., 2014). The motivation for this research is to assess the applicability of the SOM method to extract characteristic oceanographic profiles from a limited in situ oceanographic dataset. Physical and chemical parameters that were measured along the transect spanning the northern part of the Palagruza Sill, from coastal waters along the eastern Adriatic coastline (characterized by a large freshwater load) toward the deepest parts of the sill, were used in the analyses. The study period spanned from 1998 to 2011, when the transect was regularly surveyed on a monthly or seasonal basis. Section 2 introduces the data and SOM method. A seasonal analysis and extraction of SOM-based characteristic patterns are presented.

## 2.9 Problems in Chemical Oceanography and Marine Chemistry:

### Organic N:

The rivers carry appreciable amounts of organic N which is more or less refractive. This N has to be characterized both chemically and biologically as a source of N nutrient. Its importance in the N cycle has to be elucidated. For high precision alkalinity titration, its acid-base properties should be known. It seems that humic substances that are formed in fertilized soils contain several percent of organic N.

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## Isomers:

The methods to separate and determine optical isomers (racemates, enantiomers, diastereomers) are being advanced particularly by the great interest of the pharmaceutical industry. Such methods (e.g. liquid chromatographic) should be of prime interest for marine chemists.

## S chemistry:

Our knowledge of the role of S (and Se) in marine biochemistry is not sufficient. The function of some S compounds (e.g. methionine) in living organisms is known, but in other cases (e.g. their metal-binding functions) the knowledge can be improved. The routes by which dimethylsulfide and carbonyl sulfide (COS, carbon oxydisulfide) are formed and decomposed should be further studied. A comparative study of CO<sub>2</sub> and COS might be fruitful. Our knowledge of the sulfide complexation of metal ions is not good, and certainly not sufficient for the evaluation of the chemical state of trace metals in sulfidic seawater.

## Fluxes:

For the understanding of the dynamics involved in the circulation of elements and compounds on a global scale it is vital to determine the fluxes. Thus it is not sufficient to measure a depth profile somewhere in the sea. Also, the steady state concept should be used carefully. We really do not know if we are at present in a transfer from one state to another. Hydrothermal activities and glaciation are two examples of global processes that vary. Chemical tracers encompass one way to measure fluxes and mixing processes, and new analytical techniques and probes would be most helpful.

## CO<sub>2</sub>:

The concentration of CO<sub>2</sub> in the atmosphere is well measured and the variations sufficiently well-known on a global scale. However, our knowledge of the variations of CO<sub>2</sub> in surface seawater should be improved. A suitable probe should be developed in order to monitor these variations. It is difficult to determine if one problem is more important than another. Because the fluxes are related to each other, there is a need for better knowledge in many areas of chemistry and oceanography.

## III. CHEMISTRY OF OCEAN

Ocean science, generally called sea life science, is affected by turbidity streams, sediment, pH levels, ecological constituents, transformative development, and nature. Natural techniques in the ocean are controlled by the science (supplement availability). Meanwhile natural techniques are a basic control on substance scatterings. The collaboration amongst science and science has prompted a radical new flourishing sub-teach called biogeochemistry. The field of concoction oceanography thinks about the science of marine conditions including the impacts of various factors.

### 3.1 Natural mixes in the seas:

Hued broke up natural issue is evaluated to extend 20-70% of carbon substance of the seas, being higher close stream outlets and lower in the untamed sea. Marine life is to a great extent comparable in natural chemistry to earthbound living beings, aside from that they occupy a saline situation. One outcome of their adjustment is that marine life forms are the most productive wellspring of halogenated natural mixes.

### 3.2 Compound environment of extremophiles:

The sea gives extraordinary marine situations occupied by extremophiles that flourish under surprising states of temperature, weight, and obscurity. Such conditions incorporate dark smokers and cool leaks on the sea floor, with whole biological systems of living beings that have an advantageous association with microorganisms and hydrocarbon intensifies that gave vitality through a procedure called chemosynthesis.



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## 3.3 Environmental change:

Expanded carbon dioxide levels, coming about because of anthropogenic elements or something else, can possibly affect sea science. A dangerous atmospheric deviation and changes in saltiness have huge ramifications for biology of marine conditions. One proposition recommends dumping monstrous measures of lime, a base, to switch the fermentation and "increment the ocean's capacity to retain carbon dioxide from the air".

## IV. BIOGEOCHEMISTRY

Biogeochemistry is the logical teach that includes the investigation of the compound, physical, geographical and organic procedures and responses that oversee the structure of the regular habitat. Specifically, biogeochemistry is the investigation of the cycles of concoction components, for example, carbon and nitrogen, and their communications with and fuse into living things transported through earth scale natural frameworks in space through time. Biogeochemistry is a frameworks science firmly identified with frameworks environment. The field centers on compound cycles which are either determined by or impact natural action. Specific accentuation is set on the investigation of carbon, nitrogen, sulfur, and phosphorus cycles. There are biogeochemistry explore bunches in numerous colleges around the globe. Since this is a profoundly between disciplinary field, these are arranged inside an extensive variety of host disciplines including: barometrical sciences, science, biology, geo microbiology, ecological science, topography, and oceanography and soil science. These are regularly sectioned into bigger trains, for example, earth science and ecological science.

Numerous analysts research the biogeochemical cycles of substance components, for example, carbon, oxygen, nitrogen, phosphorus and sulfur, and their steady isotopes. The cycles of follow components, for example, the follow metals and the radionuclides are additionally considered. This examination has clear applications in the investigation for mineral stores and oil, and in remediation of ecological contamination.

### Some important research fields for biogeochemistry include:

- Modelling of natural systems
- Soil and water acidification recovery processes
- Eutrophication of surface waters
- Carbon sequestration
- Soil remediation
- Global change
- Climate change
- Biogeochemical prospecting for ore deposits

## V. EXPERIMENTAL APPROACH

### 5.1 Manned Field Work:

In this field work the physical and chemical properties of the ocean is determined by using chemical oceanography equipment's such as carousel, spectrophotometer and winch on lab scale as well as in ship board analysis.

### 5.2 Autonomous System:

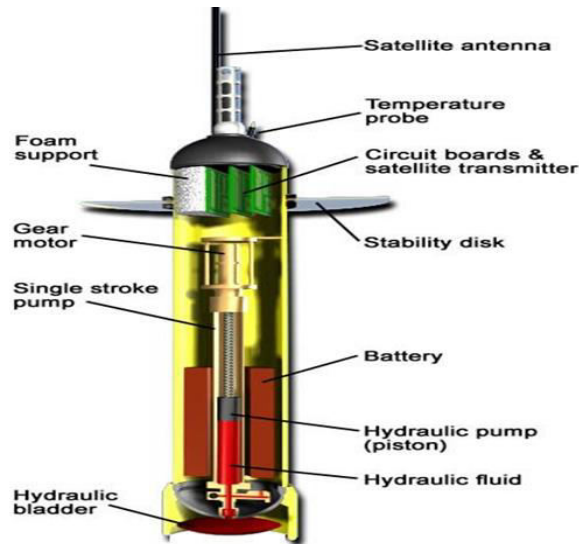
To reduce the amount of time highly trained personnel dedicate to supervising automated system. The autonomous sampling devices such as Sea Gliders and Argo floats are used.

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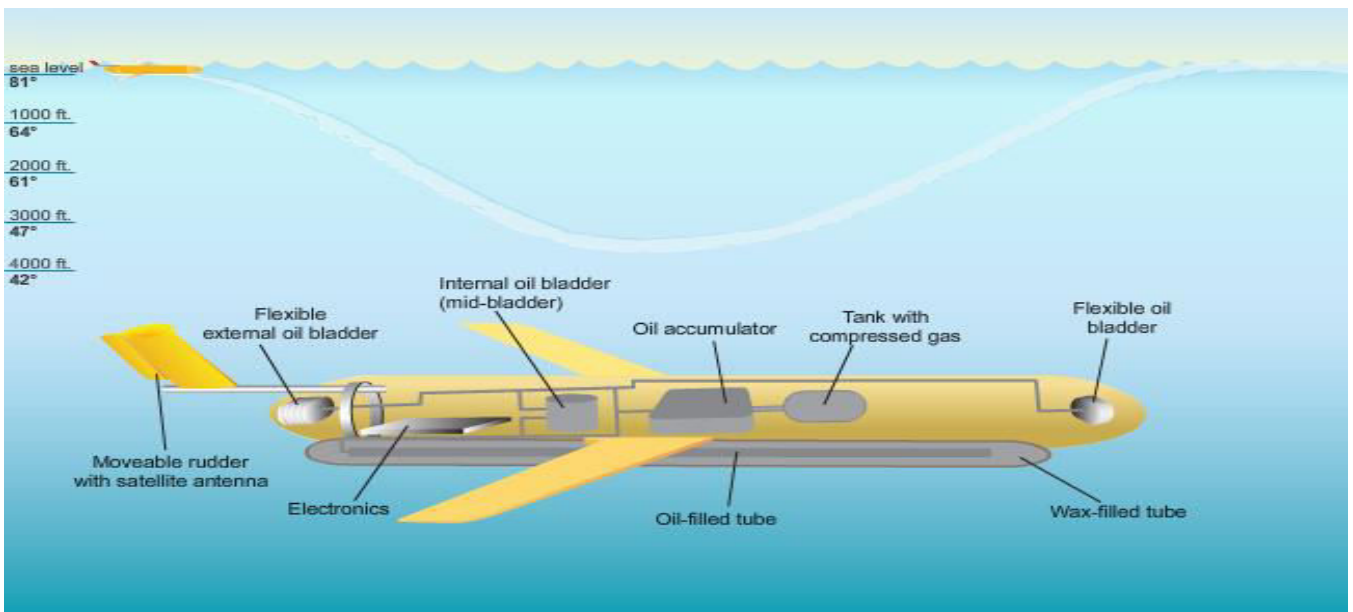
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**Fig 5.2a: ARGO FLOAT**

**Argo Float:** Argo floats are used to determine physical properties of ocean and depth of the ocean. These floats are autonomous and are operated automatically which provides less manpower.



**Fig 5.2b: SEA GLIDER**

**Sea Glider:** The system's pitch and roll are controlled using adjustable ballast (the vehicle battery). Sea gliders are used to measure depth of ocean, temperature, salinity depth average current.

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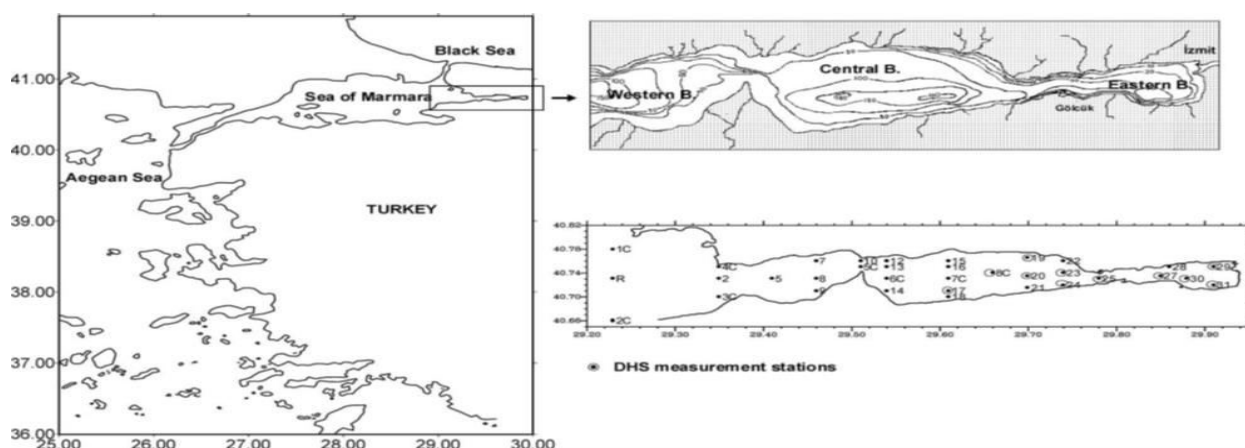
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### VI. VARIOUS METHODS AND SELECTION WITH APPLICATIONS

#### 6.1 Method to determine Dissolved Oxygen (DO) and Measurement of Dissolved hydrogen sulfide (DHS):

The sampling period includes August 1999, immediately after the Earthquake and continued monthly in 1999 and in February, May and August during 2000.



**Fig 6.1.:** The location (left) and bathymetry (above) of the study area. The location of sampling station in Izmit Bay (below).

Samples for DO determinations were drawn first from the Niskin bottles of Rosette to prevent any biological activity and gas exchanges with the atmosphere. DO determination was carried out by the Winkler method (Greenberg et al., 1985) on board from all the stations (Fig. 6.1). The precision of method was estimated at 1.9%. Dissolved hydrogen sulfide (DHS) was measured only at stations where DO concentrations are lower than the detection limit of the method (0.03/mgl), in all the sampling periods, except August and September 1999. DHS contents were measured by an iodometric titration method (Strickland and Parsons, 1972). PH values measured along the water column at all stations with a WTW 526 pH-meter equipped with a temperature-compensation adjustment on board.

#### 6.2 Continuous Plankton Recorder (CPR) and Torque Meter Method:

The adaptation of the new model in relation to the traditional Continuous Plankton Recorder CPR involved the proposal of a more modern concept, with a facilitated manufacturing process and lower cost due to the use of alternative materials (fiberglass composite). Based on the same mechanical principles as the CPR, the layout of the vehicle was based on the Undulating towed vehicle described by Hays et al. (1998), Reid et al. (2003) and Mair and Fernandes (2004), but with changes to its structure and compartmentalization (multi parameter cassette and probe). Produced completely in fiberglass composite, the resulting equipment is resistant, lightweight, easy to handle, and low-cost, making it ideal for various types of ship of opportunity. To reduce the amount of work on board, the new cassette (plankton collector) does not use the fuse wire traction mechanism used in the traditional CPR (Fig 6.2a), which is a device consisting of a steel wire that directly pulls a cone-shaped spool, which gathers in the silk containing the collected organisms, and compensates for the increase in diameter, due to the accumulation of mesh with each turn of the collection spool.

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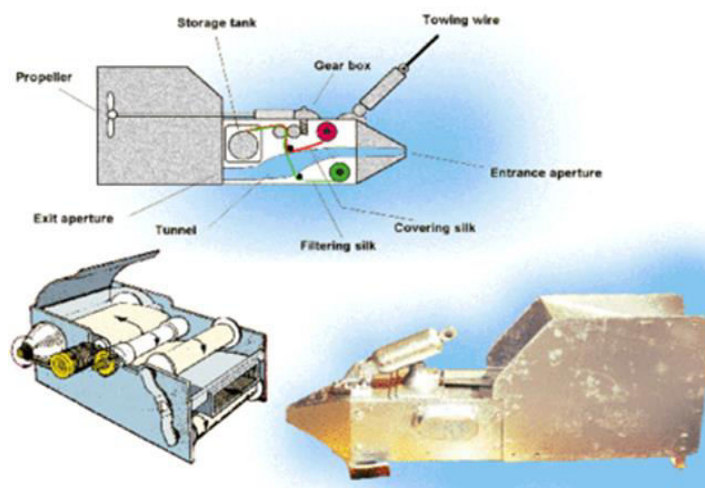


Fig 6.2a: Continuous Plankton Recorder (CPR)

**Uses:** CPR samples can also be used to estimate one of the most important properties of a community, the size of its constituent members.

**Advantages:** Easy to handle and the cost is low.

**Disadvantages:** Analysis of CPR data is difficult.

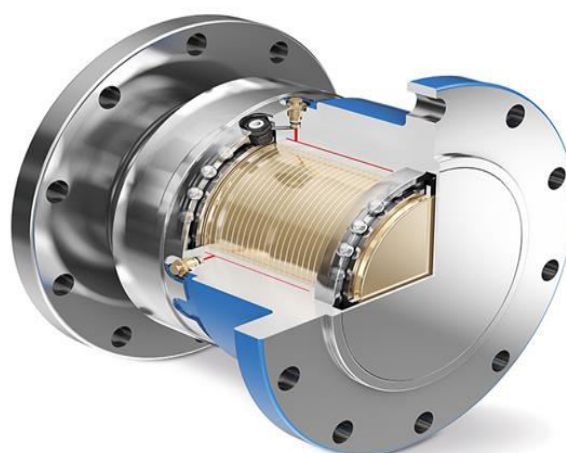


Fig 6.2b: Torque Meter

A torque meter system (Fig 6.2b) is responsible for gathering the mesh and compensating for the increased diameter of this latter spool due to the accumulation of the mesh over time. The use of the torque meter was aimed to minimize the work needed to deploy the VOR, as it does away with the need to rewind the steel wire on the spool. The most that needs to be done is to replace the plastic rod if it shows signs of wear.

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**Uses:** The use of the torque meter was aimed to minimize the work needed to deploy the VOR, as it does away with the need to rewind the steel wire on the spool. The most that needs to be done is to replace the plastic rod if it shows signs of wear.

**Advantages:** Works with most available couplings on the market with minor modifications, eliminating the need for coupling redesign. Less complicated coupling design. Temperature compensation of the unique “in-shaft” electronics reduces error in readings due to temperature variations and temperature gradients across the coupling; bonded strain gauge bridges provide reliable linear torque signals.

**Disadvantages:** Difficult to repeat and Low accuracy or high uncertainty

### 6.3 CTD Method to measure Salinity, Temperature, Depth and Concentration:

During the cruises, surface water samples were collected and analyzed for nutrient concentration and CTD casts were obtained for different depths. In situ temperature and salinity were measured by dual sensor CTD SBE 911-plus equipped with sensors measuring pressure, temperature, conductivity, fluorescence (Sea Tech Fluorimeter) and the Sea Bird Carousel water sampler (Rosette). The CTD sampling (Fig.5.3) frequencies were 24 Hz. Data were acquired and processed according to UNESCO (1988) guidelines and standards, to obtain pressure averaged data (0.5 db interval). Water was collected by the 121 Niskin bottles attached to a CTD-rosette system, which was triggered at pre-determined depths. During the three cruises 820 CTD casts and 328 seawater samples were collected. Dissolved oxygen was directly analyzed on board according to Winkler (1888), and samples were immediately fixed and stored in the dark and analyzed within 24 h using the potentiometric method (Furuya and Harada, 1995). Supplement water tests were sifted (Whatman GF/F, 0.7  $\mu$ m) and put away at  $-22^{\circ}\text{C}$  in polyethylene vials and dissected at the ISMAR-CNR Laboratory of Ancona. Supplements (ammonium –  $\text{NH}_4$ , nitrite –  $\text{NO}_2$ , nitrate –  $\text{NO}_3$ , orthophosphate –  $\text{PO}_4$  and orthosilicate –  $\text{Si}(\text{OH})_4$ ) were dissected with a Technicon Auto analyzer Traces 800 framework. Supplement fixations were resolved applying an alteration of techniques created by Strickland and Parsons (1972). Disintegrated Inorganic Nitrogen (DIN) was computed as the aggregate of the  $\text{NH}_4$ ,  $\text{NO}_2$  and  $\text{NO}_3$  focuses.



Fig 6.3: A CTD is brought into the dilute to gauge the saltiness, temperature, profundity and convergence of particles in the water section.

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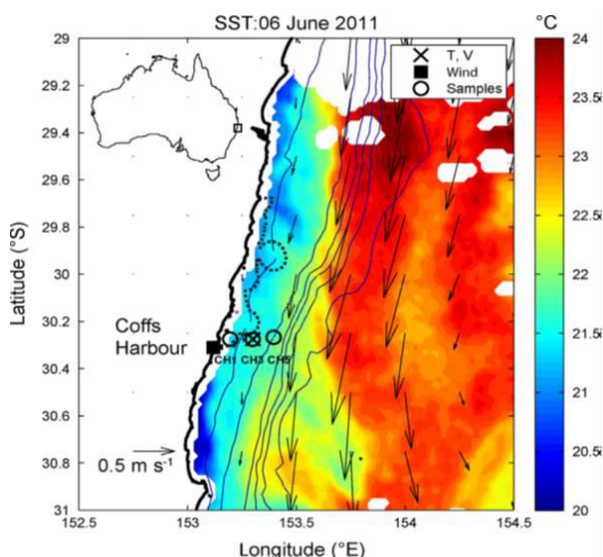
**Uses:** A CTD is an oceanography instrument used to measure the conductivity, temperature, and pressure of seawater (the D stands for "depth," which is closely related to pressure). The reason to measure conductivity is that it can be used to determine the salinity. The CTD may also be used for the calibration of sensors.

### Advantages and Disadvantages:

The advantage of CTD casts is the acquisition of high resolution data. The confinement of CTD testing is that lone a point in space (the inspecting site) can be examined at one time, and numerous throws, which are exorbitant and tedious, are expected to procure a wide photo of the marine condition of intrigue. From the data accumulated amid CTD throws, be that as it may, researchers can explore how physical parameters are connected, for instance, to the watched dissemination and variety of life forms that live in the sea, consequently developing our comprehension of the procedures that administer sea life.

### 6.4 Sampling Sites to Measure Wind Continental Shelf:

Sampling was undertaken at the 25, 70 and 100m isobaths in a cross-shelf transect off the east coast of Australia on 28May and 07 June, 2011. The most in shore located station (CH1) in (Fig.5.4) is located within the SIMP, whereas the other two stations (CH3 – mid-shelf and CH5 – offshore) are located in the adjacent Solitary Islands Marine Reserve. Station CH5, is most influenced by the intrusion of the EAC on to the shelf. This cross-shelf transect, henceforth identified as the CH-line, and extends about 26km off Coffs Harbour, Australia. Station CH3 is also the site of a long-term in-situ oceanographic mooring (CH070) which is part of the NSW Integrated Marine Observing System (IMOS). The mooring is instrumented with seven temperature loggers at 8m intervals through the water column from the bottom to within approximately 15m of the sea surface, while a bottom Acoustic Doppler Current Profiler (ADCP) measures the current velocity again at 8m intervals in the vertical). Data from this mooring as well as hourly land-based wind observations (Australian Bureau of Meteorology, BOM, was analyzed to describe the oceanographic context.



**Fig 6.4:** The location of the sampling sites (CH1,CH3 and CH5, circles), the BOM station (black square) measuring wind and the permanent IMOS mooring station (crossed circle) measuring temperature (T) and velocity(V) are shown.

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The wind stress was calculated from the 10m wind velocity and time series were low-pass filtered following Wood et al (2012). Both current and wind data are rotated to an along/across-shelf coordinate system, positive values being northward/eastward, respectively (Schaeffer et al., 2013)

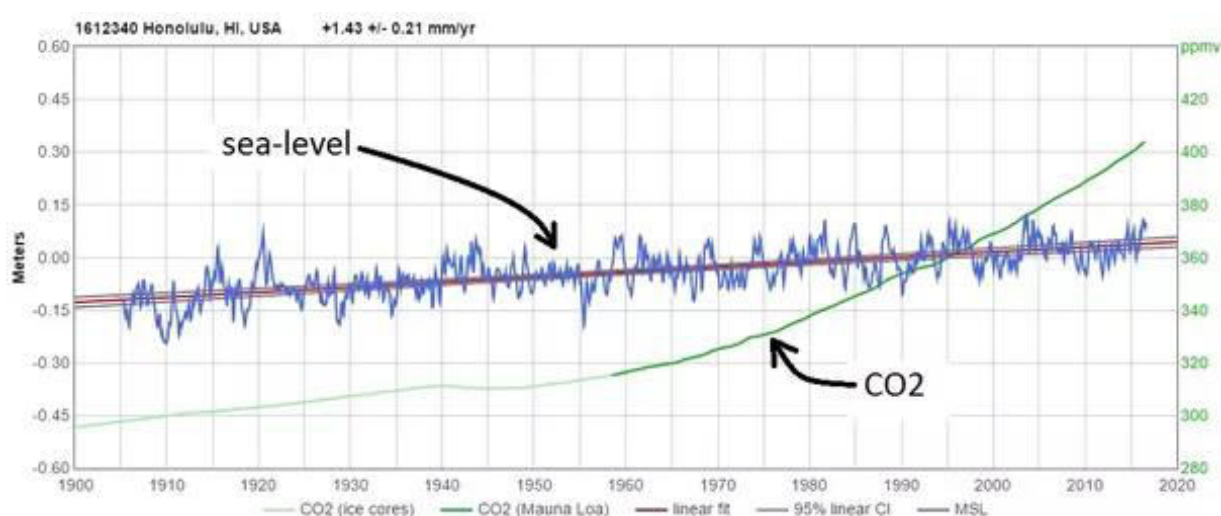
### 6.5 Continual Measurement Of Total Dissolved Inorganic Carbon:

An automated coulometric titration system has been developed for the accurate and continual measurement of total dissolved inorganic carbon (TCO<sub>2</sub>). The instrument achieves an analytical precision of +/- 0.5-1.0/tmol kg<sup>-1</sup> (0.025-0.05%). In a limited comparison with other coulometric-based titrators and with a manometric-based system, agreement was to 1 μmol kg. The capability for automatic continual analysis allows surface mapping of TCO<sub>2</sub>; a sample rate of 10 analyses gives a mapping resolution of 1-2 km. Provision for frequent standardization with a liquid substandard has been included in the development.

### 6.6 Strychnidine Method to determine Nitrate and Silicate Concentrations in Seawater:

Values of nitrate in deep seawater samples determined by a manual strychnidine method are higher than those determined either by an automated cadmium reduction method or by the strychnidine method with standard additions to each sample. The error increases with increasing concentration. High concentrations of nitrate determined by the two different techniques should not, ideally, be compared to assess long-term changes in the composition of deep water masses. Concentrations of silicate in seawater that were determined by the manual method were lower by a constant amount than those determined by the automated method. An incorrect reagent blank value had been subtracted from each sample absorbance. For all cruises, silicate data should be discarded if nitrate values in deep water were depleted, because silicates are too high in such examples.

## VII. FUTURE



**Fig 6.2: Role of CO<sub>2</sub> in atmosphere Year wise**

Since the ocean impacts the global climate and the overall health of our planet, oceanographers may find themselves investigating the ocean's impact on places far from the ocean. The CO<sub>2</sub> level is increasing year by year in atmosphere as compared to past years which affects the ocean causing problems to aquatic life. Most of the CO<sub>2</sub> released from the

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burning of fossil fuels and other human activities (e.g., cement manufacturing) is stored either in the atmosphere or in the oceans.

## VIII. CONCLUSION

Oceanographic parameters can be measured in situ, many measurements require laboratory processing and analysis. These require samples to be collected as described above, brought back to the laboratory and processed. Some measurements are made in laboratories on board the research vessel, and others require samples to be transported back to a shore-based laboratory for analysis. The major effects such as ocean acid level, global warming are due to the unbalanced chemical composition of ocean. The ocean is man's ultimate garbage can. Sooner or later, all of the civilization products find their way to this reservoir. Will our waste disposal methods lead to any significant changes in ocean chemistry? Hence chemical oceanography is necessary to save our prestigious natural resources.

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