8 Water Chemistry

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8.1 Introduction

During the second leg of the excursion water samples could be taken at three stations. At each station water samples were taken at two depths, one sample above and one below the thermocline. The hope was to find significant differences in chemical properties because a thermocline and the corresponding jump in density commonly indicates a separation between two different water masses. The samples were taken with the water sample rosette attached to the CTD at the stations 18-1, 22-1 and 29-1. Station 18 and 29 both were located in the Tiefe Rinne south south west from Helgoland. The Tiefe Rinne is a canyon in the sea floor where the water is about 60 meters deep. At most locations the North Sea is only 20-30 meters deep. The samples from the Tiefe Rinne were taken at different moments during the tidal cycle. The first one approx. 2 hours after low tide and the second one approximately in between high and low tide. [Tidal Calendar]

Water samples could only be taken when a CTD profile was taken anyways. The aim was to determine the alkalinity of the seawater, the dissolved inorganic carbon content (DIC), the chlorophyll content and the nutrient content of the different water samples. However the titration system for the determination of the total alkalinity was broken and could not be repaired. The other measurements were only prepared to be done in the lab back on land, however were not analyzed. Thus in this report first the theoretical background of some parameters of interest will be introduced. Then the analytic methods to obtain them will be explained. Last it will be discussed what values or trends would have been expected.

Table (8.1) gives information about the different stops were samples were taken, figure 8.1 sketches were the stations were.

Station	Day and Time (UTC)	Location	Total water depth	Sample depth
HE398/018-1	4/15/13, 10:36 am	$54°8,68N$ $7°52,32E$	58.9 m	3.6 m, 54.1 m
HE398/022-1	4/16/13, 8:43 am	$54°9,05N$ $7°59,66E$	33.6 m	12.2 m, 31.3 m
HE398/029-1	4/17/13, 6:05 am	$54°8,70N$ $7°52,11E$	57.8 m	5.4 m, 52.8 m

Table 8.1: Table of the sample locations

Figure 8.1: Sketch of the sample locations, in the east the left pin belongs to station 29, the right to station 18.

8.2 Theoretical background

8.2.1 DIC

The dissolved inorganic carbon is the sum of the concentrations of dissolved Carbon Dioxide and its reaction products in water.

$CO_{2(aq)} + H_20 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$

Which of the species is actually dominant depends on mainly pH dependent equilibria. This is also the basic process leading to ocean acidification. Increasing carbon dioxide concentrations in the atmosphere lead to a higher concentration of carbonic acid in the seawater. Carbonic acid then releases protons when dissociating to bicarbonate or carbonate ions and produces acidity. The

DIC content is then:

$$DIC = \sum CO2 = [HCO_3^-] + [CO_3^{2-}] + [CO_{2(aq)}] + [H_2CO_3]$$

Under normal seawater pH conditions bicarbonate is with approx. 90 percent the most abundant species followed by carbonate (slightly less then 10 percent) and dissolved carbon dioxide (less than 1 percent). This can be read from the Bjerrum plot (figure 8.2) that shows the species composition in dependence of the pH. [Notes]

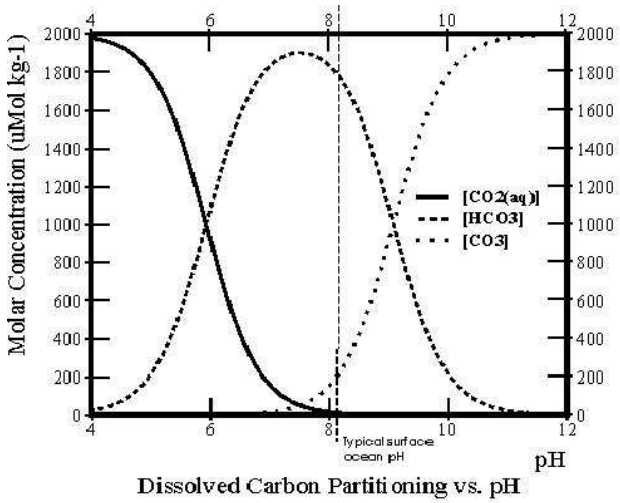

Figure 8.2: Bjerrum Plot [Bjerrum Plot].

8.3 Analytic Methods

8.3.1 Dissolved Inorganic Carbon

To measure the DIC the water from the CTD rosette samples was first filled into a syringe. Approx. 5 millimeter of the water were then pressed through a filter (mesh size 0.2 micrometer) into a small, closable test glass. Here it was particularly important that the glass was completely filled with water and no air was included in the sample. This is crucial to prevent equilibrium reactions between the water and the sample. They could change the measured DIC in case Carbon Dioxide dissolves into the solution if the DIC of the sample is really low or in case Carbon Dioxide effervesces out of the sample in case its DIC is really high. The sample was then stored in the fridge to be analyzed in the lab.

In a lab one would mix the sample with sulphuric acid. All components of the DIC would then react to gaseous carbon dioxide. This gas would then be directed into a solution containing sodium hydroxide solution and phenolphthalein. The latter acts as a pH indicator and colors the basic solution pink. However when the Carbon Dioxide is injected it reacts to form carbonic acid and lowers the pH and the intensity of the color decreases. This change is measured by a photometer to detect the change of the pH. This can then be used to calculate the amount Carbon Dioxide that has dissolved in the basic solution. The DIC is then simply this amount divided by the volume of the sample. [Notes]

8.3.2 Chlorophyll

The first step in the preparation of the chlorophyll sample is to filter 250 milliliter through a Nucleopore filter membrane with a mesh size of 0.8 micrometer. To accelerate this process under pressure is applied below the filter sucking water trough it. This under pressure (200mbar) is generated by a pump. The pump can only be turned on after the filter was fixed on the Fritte by dropping one drop of water on it. The cone that holds the water is fixed with a clamp. The filter is then stored in a container and frozen.

In the lab this filter is put into a test class, silicon spheres, acetone and some solvent is added. It is then put into a device that vibrates the sample at high frequencies. The acetone disintegrates both the filter and the cell walls of potential microalgae. The vibration coupled with the silicon spheres further disintegrates and grinds the cells. Afterwards the sample is stored in a centrifuge, liquid is then extracted from the upper part. This liquid is then inserted into a photometer to measure the chlorophyll concentration. Several forms of chlorophyll are still abundant in the sample. Commonly one only refers to chlorophyll A. Chlorophyll A gets disintegrated by hydrochloric acid. Thus the acid is added and then the chlorophyll concentration is measured again in the photometer. The chlorophyll A concentration is then the difference of the two measured values.

The experimental set up of the filtration can be seen in figure 8.3. [Notes]

8.3.3 Nutrients

The water samples for the nutrient measurement were also filled in a syringe and pressed through the same filter that was used for the chlorophyll measurement. 10-12 milliliters were then filled into a test glass and stored in the

Figure 8.3: Set Up of Filtration, the filter is between the red cone and the 'Fritte'.

fridge.

The samples are mainly analyzed for phosphor and nitrogen species such as phosphate, nitrate, nitrite and ammonia since these dissolved are bioavailable. Phosphor and Nitrogen are the main macro-nutrients since there are needed in big amounts and are often bio limiting. Commonly one also analyzes for silicate since it is an important nutrient for siliceous organisms such as diatoms. Micronutrients such as iron are normally not investigated. For each nutrient species a specific color reagent is added to a subsample of the main sample. Then a photometer is used measures the absorption or extinction of the sample. This parameter can be related to the nutrient concentration with the Lambert-Beer Law.

$$A = \varepsilon \times l \times c$$

Where A is the absorbance, ε is a specific extinction coefficient, l is the length of the container that is used to store the liquid in the photometer and c is the concentration.

This can yield values that are even accurate in the micromole per liter range. [Notes]

8.4 Discussion and Expectation

Samples were taken above and below the thermocline. The spring bloom is over most organisms have died and sank to the bottom. Since the chlorophyll concentration is a proxy for the vegetable biomass it is expected that the concentration is the highest in lower water layers. Further up, were only low amounts of biomass were recently generated the chlorophyll concentration is probably rather low. These expectations were confirmed by the chlorophyll profiles that were gathered with the CTD. The factor that finally lead to the collapse of the spring bloom was the nutrient depletion of the upper water layers. When there are no more nutrients available the explosion of biomass can no longer prevail and the bloom stops. Considering that this is the current state of the ecosystem nutrient concentration in the upper water layers are probably extremely low. Dead biomass, as well as alive biomass not having active transport mechanisms in the end sinks down to the bottom. The further ones moves down the water column the more time the organisms there have already spent sinking. That also means that in this layers more and more respiration has already taken place. Respiration releases nutrients that were consumed to build up the biomass. Hence the nutrient concentrations at the bottom most likely exceed the concentrations in the top layer. The DIC is mainly replenished by dissolution of atmospheric carbon dioxide. The strong thermocline at all three locations indicates a strong separation of water masses. Hence the lower layers probably havent had contact with the atmosphere for a long time. Accordingly the DIC content should be lower at the bottom than at the top. However respiration in deeper layers releases some carbon dioxide again, thus with increasing depth the DIC will slightly rise again, however it will not exceed the values of the top layers. The expected profiles are depicted below in figure 8.4.

The aim of taking samples at the same location in different phases of the tidal cycle was to investigate weather some differences in the water chemistry can be seen. When sample 1 was taken the tidal cycle was in the transition from low to high tide, thus water was streaming into the North Sea area. This water was partly carried by longshore currents. In contrast when sample 3 was taken the cycle was in transition from high to low tide and water was streaming out of the North Sea. That also means, that the relative freshwater content from rivers was probably higher in sample 3. If one would sample data from the Weser and the Elbe and would know the average seawater composition one could make assumptions weather values at station 3 or 1 are higher.

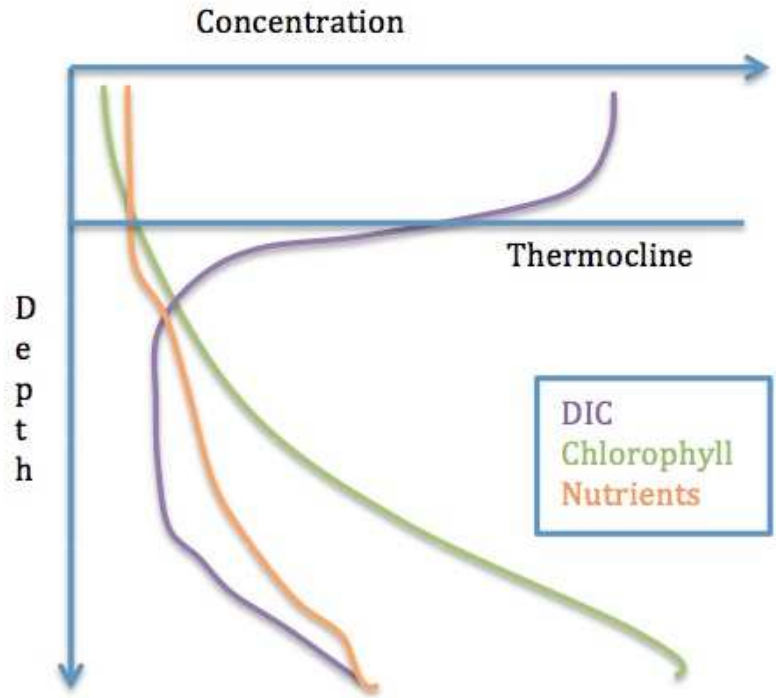

Figure 8.4: Sketch of the expected DIC, Nutrient and Chlorophyll profiles.