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MEASUREMENT AND CALIBRATION OF THE ACIDITY OF THE COAST WATER OPPOSITE THE ZAWIYA OIL REFINERY – LIBYA

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Abstract— **High levels of carbon dioxide (CO_2) in the atmosphere from fossil fuel combustion and deforestation, companied with reduce of farming practices and de-vegetation for architectural development. Which cause increases in levels of inorganic carbon CO_2 in seawater. This increase led to a drop in pH, which was accompanied by chemical changes in the waters of the seas and oceans. This study focused on field inspection represented in sampling random points on the coast of the Zawiya oil refinery to determine the impact of emissions on the water near the coast. The pH, electrical conductivity and temperature of samples taken from the surface were measured because the sea surface is usually most affected by carbon melt from the atmosphere and is less affected with the depth. The measurements of these samples were different from the theory we developed about the impact of coastal water on industrial wastewater resulting from separation and cooling operations from the Zawiya refinery, where the measurements came to a pH rate between 7.6 and 8.9. This study ended with a set of important recommendations, the most prominent of which was the focus on the use of clean energy and further research on marine life and its impact on Mediterranean acidity.**

Keywords— **Carbon Dioxide, Ocean Acidity, Ph, Electrical Conductivity.**

I. INTRODUCTION

For more than 200 years since the Industrial Revolution, the concentration of carbon dioxide (CO2) in the atmosphere has increased due to the burning of fossil fuels and land-use change. The ocean absorbs about 30 percent of the CO2 released into the atmosphere, and as atmospheric CO2 levels increase, levels in the ocean increase. Like global warming, this phenomenon is known as ocean acidification, and it is a direct result of increased levels of carbon dioxide (CO2) in the Earth's atmosphere. (The National Ocean Service).

Before industry, the concentration of carbon dioxide in the atmosphere was 280 ppm (ppm). With the increase in fossil fuel use, this figure is now approaching 400 ppm and the growth rate is accelerating. Scientists calculate that the ocean currently absorbs about a quarter of the carbon dioxide emitted by humans. When carbon dioxide combines with seawater, chemical reactions occur that reduce the pH of seawater, hence the term ocean acidification. Further, the average pH in the ocean was about 8.2. Today the average pH of the ocean is 8.1. This means that the oceans today are about 30 percent more acidic than they were in pre-industrial times. By 2100, the ocean's pH could drop to about 7.8, making the ocean 150 percent more acidic and affecting half of marine life, according to the Intergovernmental Panel on Climate Change (IPCC) Sixth Assessment Report.

The Mediterranean Sea, a semi-enclosed sea, already suffers from signs of acidification and other stressors, including high temperatures, overfishing and pollution. It is a complex body of water that supports an estimated 400 million people and an additional 175 million visitors annually. Scientific information is necessary to determine the short- and long-term effects of acidification and how this phenomenon will affect important sectors such as tourism and fisheries. This work has already begun: Mediterranean acidification in climate change (MedSeA) is a project that aims to understand how key biogeochemical and ecosystem processes are affected by increased acidification. (Frontiers In Marine Science.2023)

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II. GENERAL DISCERPTION OF THE AREA:

The study was carried out on the coast opposite the Zawiya oil refinery. The Zawiya refinery started operating in 1974 and its production capacity was 60,000 barrels per day, and in 1971 its capacity increased to 108,000 barrels per day, and by May 2019 its production capacity reached 140,000 barrels per day. Zawiya refinery is one of the oil refineries that performs only basic work and does not have conversion units, which limited its work to the production of gasoline only. The refinery produces approximately 25% of fuel oil, 40% of medium distillate and 35% of light distillate.

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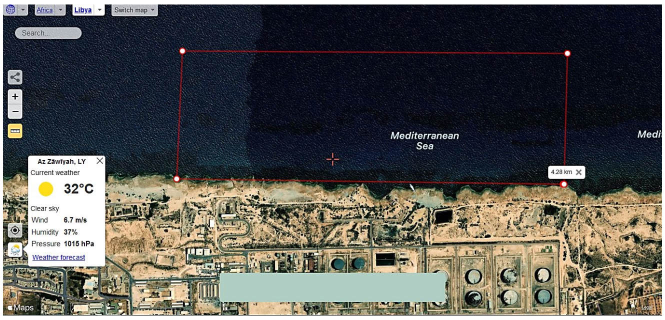

Fig.1 Showing the location of study's area

B. Procedures and method of work:–

The practical side of the study included a field visit to the Zawiya refinery, which is located in the northwestern part of the center of Zawiya city. The physical inspection of the coast was carried out, seawater samples were taken from 7 different points (as shown in the figure) and the geographical location(s) of each point were taken for future comparison.

Fig 2 shows the sampling areas of the coast of the Zawiya refinery

Table (1) shows the points coordinates of the sampling areas for the coastal waters

Longitude	Latitude	Location Number
12°42'36.68"E	32°47'35.50"N	**1**
12°42'9.49"E	32°47'36.22"N	**2**
12°41'47.85"E	32°47'34.73"N	**3**
12°42'25.23"E	32°47'43.65"N	**4**
12°42'12.40"E	32°47'50.36"N	**5**
12°41'55.09"E	32°47'50.35"N	**6**
12°41'35.86"E	32°47'43.65"N	**7**

III. . RESULTS AND DATA ANALYSIS:

Since pH is the measurement of a particular ion (i.e., hydrogen). In contrast, conductivity is an indefinite measurement of the concentration of positively and negatively charged ions in a sample. In short, the relationship between pH and specific conductivity is that the presence of hydrogen ions affects the pH of the sample, and the presence of these ions may affect electrical conductivity. However, hydrogen ions account for only a small fraction of the ion concentrations measured by conductivity meters.

Therefore, the importance of the relationship will depend on the presence of hydrogen compared to other concentrations of non-pH ions. The pH and conductivity of seawater samples from the coast opposite the Zawiya refinery were measured and the following table shows these values for each measurement point.

Table (2) shows the measurement results for sample analysis

Conductivity (mS/mm)	pH	T (C°)	Sample #
45.6	8.6	27.2	**1**
45.9	8.8	26.8	**2**
45.92	8.9	26.6	**3**
45.3	7.6	29	**4**
45.36	7.67	28.8	**5**
45.4	7.9	28.78	**6**
45.48	8.2	28.76	**7**
45.56	**8.23**	**27.99**	**AVG**

Usually, the electrical conductivity of seawater ranges from 44 to 58 millimeters / cm (or milliseconds / cm) with an average of about 50 millimeters / cm. Of course, conductivity and salinity are closely and positively related. A multiplier of 0.64 can be used to convert conductivity to salinity for practical purposes. The pH of seawater ranges from 7.6 to 8.4. The average pH in the oceans is said to be 8.1, but the average pH of seawater slowly but surely decreases as the concentration of carbon dioxide in the atmosphere increases, resulting in a higher concentration of dissolved carbon dioxide in the sea. Carbon dioxide is acidic and forces the pH to descend. Looking at the results obtained, we find that the average pH of the refinery coast water is estimated at 8.23 at an average temperature of 27.9 Co, and the electrical conductivity is an average of 45.56 mess/mm.

The relationship between electrical conductivity and pH

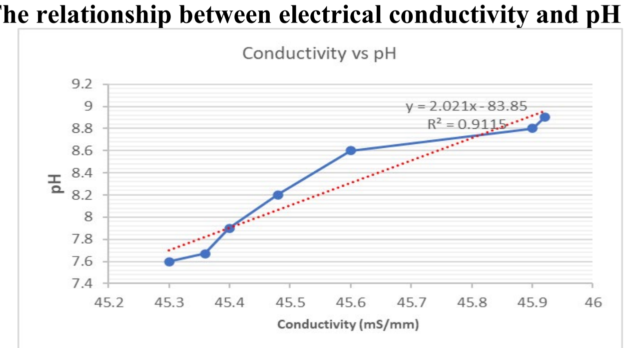

Fig 3 shows the relationship between electrical conductivity and pH

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Conductivity is directly proportional to temperature. While the pH is reversed. Relative. The pH value of water directly depends on the temperature. The pH decreases with increasing temperature. But this does not mean that water becomes more acidic at higher temperatures. A solution is considered acidic if there is an excess of hydrogen ions on hydroxide ions. In the case of pure water, there is always the same concentration of hydrogen ions and hydroxide ions, therefore, water remains neutral (even if the pH changes). However, in the case of seawater, the constant lack of pH affects organisms directly and indirectly, especially plankton and invertebrates.

The relationship between temperature and pH

As the temperature rises, molecular vibrations increase resulting in the ability of water to ionize and form more hydrogen ions. The dissociation of water into hydroxide and hydrogen ions can be represented as

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq) \quad (1)$$

The pH value of each sample changes through changes in temperature. Temperature affects the accuracy and speed of the pH electrode response.

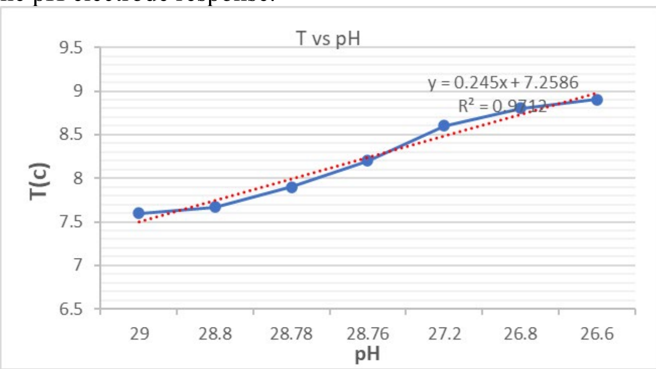

Fig 4 shows the relationship between temperature and pH

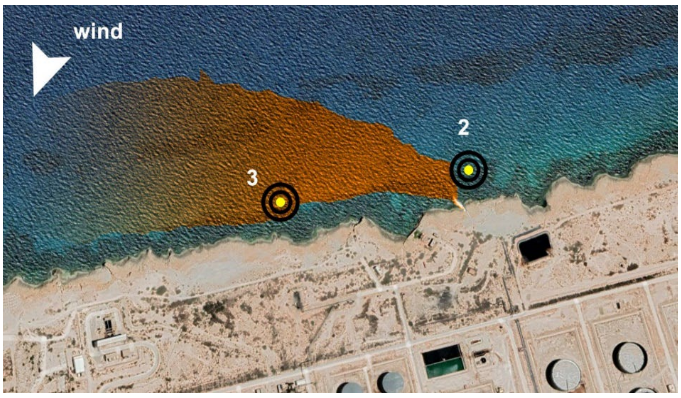

Fig 5 shows the locations of samples 2 and 3 and the location of the drain pipe

Samples No. 2, 3 taken near the drainage pipe for filtered water and used in separation and cooling processes and discharged after treatment. This water is usually of little salt or fresh salts, and we can see this on the analysis results of that sample. It is worth mentioning that the pH and conductivity measurements of coastal water samples are affected by wastewater coming out of the industrial processes of the refinery, and we notice this when taking samples and analyzing them for points farther from the drainage site. These results were compared with measurements made in Zuwara. We note that the values taken for samples from Zawiya refinery carry the lowest acidity values because they are affected by water coming out of industrial drainage operations, while the readings taken from the coast of Zuwara city are more acidic as a result of being affected by dissolved gases in seawater.

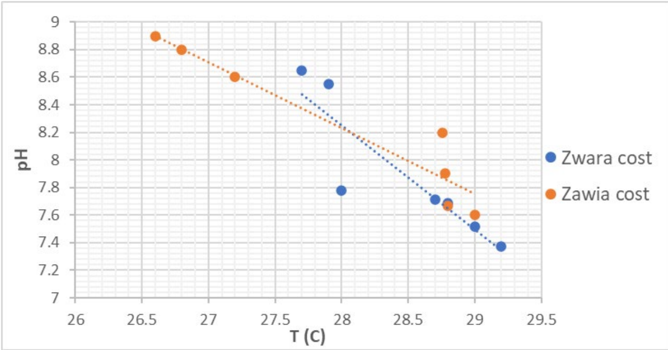

Fig. 6. shows the comparison between the measurement's samples for the Mediterranean coast in front of the Zawiya refinery versus measurement's samples from the Mediterranean coast opposite the city of Zuwara.

The pH measurements were also compared with a previous study by T. Lacoue-Labarthe, et al 2009 from a group of studies carried out by the International Atomic Energy Agency – Marine and Aquatic Solutions International, where the study was carried out on the European coasts of France and Spain, and they were as follows:

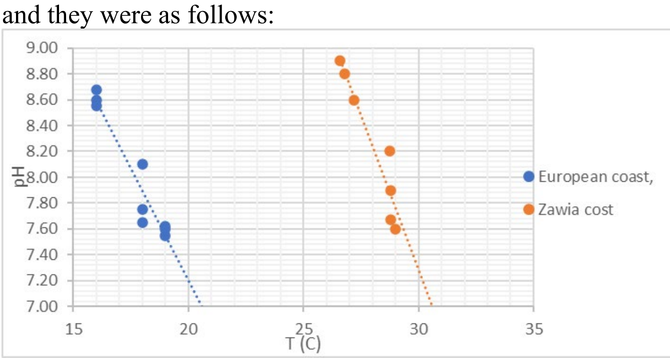

Fig 7 shows the comparison between the measurement's samples for the coast opposite the Zawiya refinery versus measurements samples from the coasts of France and Spain.

In fact, the results were close as the different in temperatures, also the European study focused on the effect of these concentrations on fish eggs and it was found that they have the opposite and harmful effect as they cause damage to fish eggs before the date of cutting them, and this is a dangerous harbinger of marine wealth in the Mediterranean basin.

IV.CONCLUSION

Although ocean acidification has only recently emerged as a scientific issue, it has quickly raised serious concerns about the short-term effects on marine organisms and the long-term health of the oceans and seas. Scientists estimate that over the next few thousand years, 90% of anthropogenic CO_2 emissions will be absorbed by the ocean. This may affect biological and geochemical processes such as photosynthesis and nutrient cycling that are vital to the marine ecosystems on which human society and many natural systems depend. The comparison we made is the biggest evidence of the increase in this phenomenon, as the measurements showed the large variation between natural measurements and others that were affected by industrial drainage, which contained high alkalinity. This water that was consumed in the oil industry was a catalyst for the acidity of seawater, and here we can say (perhaps harmful and beneficial). Also, what was observed from the civil inspection and satellite images is that the industrial wastewater was less saline, which helped the reproduction and spread of algae and marine plankton along the coast near the place of discharge, which requires a more comprehensive and specialized study to study the environmental and biological effects of wastewater on seawater. Scientific information must be accompanied by appropriate management at the national, regional and local levels. It is also critical to focus on the source of the problem and reduce carbon emissions by promoting low-carbon fuels and switching to alternative energy sources. This will be the most effective tool to solve the problem of acidification of the seas and oceans.

V. RECOMMENDATIONS:

1. Conducting a comprehensive study of the Libyan coast and making a comparison between the total measurements to compile a database for a future study.
2. Work on scientific cooperation between public and non-governmental organizations specialized in the environment with organizations concerned with wealth and marine biology to monitor the vulnerability to Mediterranean acidity.
3. Develop systematic plans to reduce the use of fossil fuels and use alternative methods of power generation and other industrial processes.
4. Exchange of experiences and knowledge between the countries bordering the Mediterranean Sea to monitor and develop radical solutions to the problem of acidification of the Mediterranean, where Spain and France were the first in this field.
5. Apply section No. 7 of Law 15 of 1992, which stipulates that oils and exhausts shall not be dumped into sea water. These exhausts and oils are hydrocarbons and volatile substances.

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