

# Studying the Effect of Recovered Free Sulfur from Baniyas Oil Refinery- Syria on Sulfate Concentration in Marine water

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## ABSTRACT

Baniyas oil refinery contains a unit for recovering Sulfur compounds to a free Sulfur, which being collected and stored in exposed areas. This free sulfur may be affected by wind, and moves into atmosphere until it deposits through wet deposition or dry deposition. This research studies the effect of free Sulfur emission from Baniyas oil refinery on Sulfate concentrations in marine water in the area corresponding to the refinery. The emitted free sulfur were estimated using an equation as it shown in references, and Sulfate ions were determined in marine water by a turbidity measurement method. The results showed an increase in concentrations of Sulfate in marine water at all sites when compared with the reference site, while Pearson correlation coefficient between Sulfate concentrations and pH shows a strong relation, as it recorded a value of 0.54. Results also shows higher sulfate concentrations in the spring when compared to summer, this could be because of emitted free sulfur which recorded higher value in the spring. This indicates to the role that emitted free sulfur may play. Based on these findings it is suggested that free sulfur should not be stored in open areas and should be transported directly to the plants which are using it as raw materials in their industries.

**KEY WORDS:** Free sulfur, Wet deposition, Dry deposition, Turbidity.

## 1. INTRODUCTION

Industrial development has led to an increase in environmental pollution. Some pollutants from industrial plants and various human activities transport into atmosphere, which is an important pathway for pollutants before it deposit later in terrestrial ecosystems and water bodies. (Lohcha, 2018; Duce, 1991). Elemental Sulfur is one of the less toxic forms of sulfur, but due to oxidation and reduction processes, it turns into dangerous compounds to the environment and organisms. When this compounds move into atmosphere it can cause significant damage to the environment (Energy Economics Applied Optimization, 2011). Therefore, most refineries are recovering sulfur compounds from crude oil, gaseous emissions and acidic water in the refinery to a free sulfur (Huang, 2015).

In previous years, several scientific researches were made to determine the pollution levels by sulfur compounds. (Kuklinska, 2013) summed up knowledge about free sulfur toxicity and its bioavailability, results showed that protein cells help with its hydrophobic ends to surround hydrophobic free sulfur, and prevent forming crystallized sulfur S<sub>8</sub>. While hydrophilic ends react with aqueous medium in the cell. Elemental Sulfur can also exhibit strong toxic effects in some organisms like fungi, where toxicity is associated with crystallization form. Elemental Sulfur can affects the radiation process of some luminous bacteria, thus, it can affect the results of toxicological tests. In case of Wild organisms, large amounts of elemental sulfur can lead to kidney destruction, weight loss, irritation of the eyes and respiratory system, allergies and asthma.

Marine waters contain various forms of dissolved salts that may affect the results during determination of certain sulfur forms such as sulfate. Therefore, the accuracy and efficiency of methods used for analysis in the prevailing conditions within the marine environment must be tested. (Yang, 2013) developed a method that allows to determine sulfate in the conditions of high chloride concentrations based on ion chromatography.

Some researchers also studied the behavior of sulfur bacteria and the conditions for its work. Activity of sulfur bacteria was studied according to pH and carbon dioxide (PCO<sub>2</sub>) molecular pressure (Bayraktarov, 2013), through the incubation experiments that targeted the activity of sulfur bacteria in the sediments of the shallow zone of Milos-Greece, the results in the study showed that sulfur bacteria is able to cope with temperature and pH changes, while there is a sharp decline in Activity of the sulfur bacteria when CO<sub>2</sub> pressure increased from 2 to 3 bar.

In other studies, emission of industrial particles in open areas has been estimated. The amount of emitted particles is related to their smoothness and emission factor, as well as to the area of the surface that is exposed to wind. The estimated amount of emission can be calculated through the following equation (Asaad, 2000):

$$P=S \cdot Wc \cdot g \text{ (Equation -1)}$$

Where, P: The amount of emitted particles kg/second; S: The area surface that is exposed to wind m<sup>2</sup>; Wc: Emission factor (kg/ m<sup>2</sup>. Second); g ≈ 1: Smoothness factor.

Baniyas oil refinery is one of Syrian oil refineries located on the Syrian coast, which contains a unit to recover various forms of sulfur into free sulfur, which collected in exposed areas and may be affected by wind. Studies indicate that the percentage of wind that may contribute to the transfer of free sulfur particles towards the marine environment is about 29.25% of the total wind types over the Syrian coast throughout the year, (Fig.1) (Ibraheem, 2008).

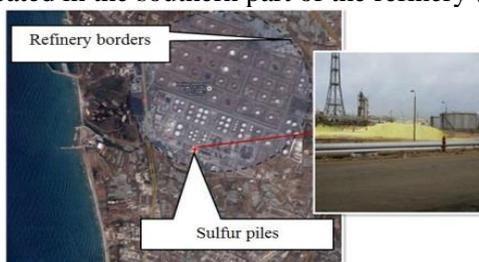


**Figure.1. Percentage of wind moving from land to marine environment in the study area throughout the year**

When wind is weak (not fast), Land breeze could be an important factor in the transfer of pollutants to marine environment. This research studies the effect of free Sulfur emission from Baniyas oil refinery on Sulfate concentrations in marine waters in the area corresponding to the refinery.

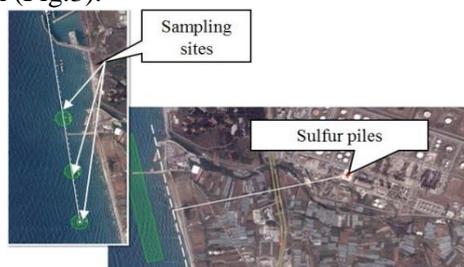
## 2. MATERIALS AND METHODS

Baniyas oil refinery is located on Syrian coast in Tartous city and extends to approximately 2.02 km<sup>2</sup> along the sea, while free sulfur piles are located in the southern part of the refinery (Fig.2)



**Figure.2. Location of free sulfur piles**

**Sampling :**Sea water samples were taken in spring and summer from the area corresponding to the refinery, while distance between each site was 500 m (Fig.3).



**Figure.3. Shows the distance between sulfur piles and the sea, and shows sampling sites**

The emitted free sulfur were estimated using an equation as it shown in references (Asaad, 2000) :

$$P=S \cdot Wc.g \text{ (Equation -1)}$$

Emission factor (mg/cm<sup>2</sup>. Second) is affected by wind speed and it is equal to 1 mg/cm<sup>2</sup>.Second, when wind speed is less than 1.5 meters/sec, while its value is 9 mg/cm<sup>2</sup>.Second, when wind speed ranges from 1.5 to 8.5 meters/sec. If sulfur piles are three months old or longer, the values vary and become 0.6 mg/cm<sup>2</sup>.Second at wind speed less than 1.5 meters/sec, and it is 7 mg/cm<sup>2</sup>.Second, when wind speed is between 1.5 and 8.5 meters/sec.

**Determination of sulfate SO<sub>4</sub><sup>-2</sup> in sea water:** Sulfate SO<sub>4</sub><sup>-2</sup> was determined in sea water by a turbidity measurement method, due to its accuracy, ease and its low cost, which depends on adding Barium chloride solution to the studied samples and measuring level of turbidity resulting from the formation of barium sulfate (Tabatabai, 1974).

**Correlation coefficient:** Between amounts of emitted free sulfur and SO<sub>4</sub><sup>-2</sup> concentrations in marine waters was determined by Pearson's equation.

## 3. RESULTS AND DISCUSSION

- Coordinates of each site, pH, salinity, temperature, wind direction and SO<sub>4</sub><sup>-2</sup> concentrations were measured in two seasons, and results were as follows:
- First sea voyage was in the spring on 17/4/2017, the wind was northwesterly, and the estimated surface area of exposed free sulfur piles was 2126 m<sup>2</sup>. Wind speed was 6.3 m/s, and estimated value of emitted free sulfur was 0.01913 kg/sec. Sea temperature was 22.1<sup>0</sup>C, while lowest pH value was 7.75 at ST2-1, and its highest value was 7.81 at both ST3-4 and ST4 sites, with an average of 7.78. Salinity had the lowest value of 36.8 and highest value of 37.4 with an average of 37.2 as shown in Table.1.

**Table.1. The coordinates of sites from which samples were taken, values of pH and salinity in each location in spring on 17/4/2017**

Site		Coordinates		pH	Salinity
		East	North		
ST1	ST1-1	35.949897°	35.212986°	7.77	36.9
	ST1-2	35.949565°	35.212405°	7.76	37.2
	ST1-3	35.949407°	35.212856°	7.77	37.3
	ST1-4	35.949341°	35.213339°	7.76	37.3
	ST1-5	35.948868°	35.212691°	7.77	37.4
ST2	ST2-1	35.951238°	35.208627°	7.75	37.4
	ST2-2	35.950786°	35.208011°	7.76	37.3
	ST2-3	35.950620°	35.208500°	7.78	37.3
	ST2-4	35.950467°	35.209032°	7.8	37.4
	ST2-5	35.950076°	35.208410°	7.79	37.4
ST3	ST3-1	35.952438°	35.204040°	7.78	37.1
	ST3-2	35.951912°	35.203586°	7.79	37.3
	ST3-3	35.951883°	35.204035°	7.8	37.4
	ST3-4	35.951851°	35.204487°	7.81	37.4
	ST3-5	35.951341°	35.204035°	7.79	37.4
St1-4	ST4	35.952553°	35.199120°	7.81	36.8

Sulfate ( $\text{SO}_4^{2-}$ ) concentrations ranged between 0.103 g/L at ST2-1 and 0.224 g/L at ST3-3, with an average of 0.148 g/L. Concentrations of all sites were high when compared to reference site (ST4) sample, which was 0.097236 g/L as shown in Table.2. The reason for this difference is likely to be due to the deferent distance between sampling areas and free Sulfur piles, where ST4 was the farther site from piles location. All ST3 samples showed an increase in Sulfate ( $\text{SO}_4^{2-}$ ) concentrations when compared to ST1 and ST2 samples. This may be due to the proximity of this station to a wastewater disposal area, which may contribute to the seawater near it with sulfate ions  $\text{SO}_4^{2-}$ , causing this increase in its concentrations.

According to a study conducted on Egyptian marine waters near the estuary of the Nile (Nessim, 2015) showed that the average sulfur concentrations in Spring 2008 was 0.219 g/l in the western part of Egyptian coastal waters with an average of 0.261 g/l in the eastern part of the Egyptian coastal waters. The concentration rates in this study was very close to the concentrations of Sulfate obtained in third station samples (ST3) in this research, which was 0.212 g/l.

The increase in ST3 Sulfate concentrations when compared to ST1 and ST2 concentrations may be due to the decrease in the activity of sulfur bacteria in ST3, and this low activity of sulfur bacteria may be due to the increase of pH in ST3 samples. Studies indicate that the value of the Hydrogen number (pH) affects the activity of Sulfur bacteria, this activity is higher within pH range 6-7. These conditions help to reduce sulfate to less oxidized forms, and in anaerobic conditions,  $\text{H}_2\text{S}$  results as a reduction product.

**Table.2. Shows the values of  $\text{SO}_4^{2-}$  concentration in marine water samples in spring on 17/4/2017**

Site		Sulfate concentration g/l
ST1	ST1-1	0.121212
	ST1-2	0.105228
	ST1-3	0.103896
	ST1-4	0.107892
	ST1-5	0.109224
ST2	ST2-1	0.102564
	ST2-2	0.103896
	ST2-3	0.20979
	ST2-4	0.10323
	ST2-5	0.10656
ST3	ST3-1	0.1998
	ST3-2	0.218448
	ST3-3	0.224442
	ST3-4	0.214452
	ST3-5	0.20646
ST4	ST4	0.097236

In second sea voyage in the summer on 12/8/2017, the wind was southwesterly. The estimated surface area of the exposed free sulfur piles was 2330 m<sup>2</sup>, and wind speed was 4.8 m/s. The estimated value of emitted free sulfur was 0.01631 kg/sec, Additional samples were taken from the Estuary of Gober river (ST5) which passes near the refinery. Temperature of seawater was 30°C.

The lowest pH value was 8.04 which was recorded at ST2-5, while highest value was 8.15 at ST1-3 with an average of 8.09. Salinity had the lowest value of 35.7 and the highest value of 38.6 with an average of 37.96 as shown in (Table.3). River samples (ST5) results show a decrease in pH and salinity values when compared to marine samples, where average pH was 7.47, and salinity value of 1.2.

**Table.3. The coordinates of sites from which samples were taken, values of pH and salinity in each location in summer on 12/8/2017**

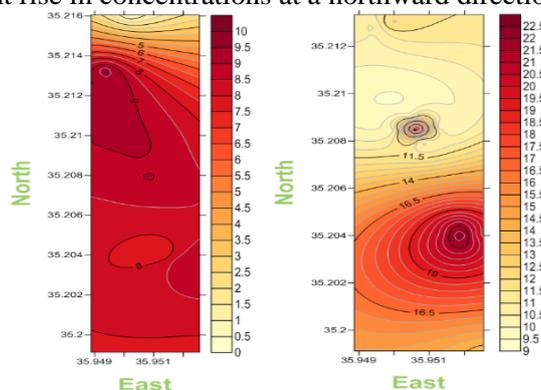
Site		Coordinates		pH	Salinity
		East	North		
ST1	ST1-1	35.949897°	35.212986°	8.13	37.6
	ST1-2	35.949565°	35.212405°	8.13	38.1
	ST1-3	35.949407°	35.212856°	8.15	37.8
	ST1-4	35.949341°	35.213339°	8.11	37.8
	ST1-5	35.948868°	35.212691°	8.08	38.1
ST2	ST2-1	35.951238°	35.208627°	8.09	37.9
	ST2-2	35.950786°	35.208011°	8.1	38.2
	ST2-3	35.950620°	35.208500°	8.13	38.3
	ST2-4	35.950467°	35.209032°	8.09	38.3
	ST2-5	35.950076°	35.208410°	8.04	38.5
ST3	ST3-1	35.952438°	35.204040°	8.12	37.9
	ST3-2	35.951912°	35.203586°	8.09	38.2
	ST3-3	35.951883°	35.204035°	8.1	38.2
	ST3-4	35.951851°	35.204487°	8.07	38.3
	ST3-5	35.951341°	35.204035°	8.1	38.6
ST4	ST4	35.952553°	35.199120°	8.04	35.7
ST5	ST5-1	35.950317°	35.216003°	7.4	1
	ST5-2	35.950199°	35.216013°	7.45	1.3
	ST5-3	35.950039°	35.216047°	7.58	1.3

Sulfate (SO<sub>4</sub><sup>2-</sup>) concentration in marine samples were higher than in river samples, lowest Sulfate (SO<sub>4</sub><sup>2-</sup>) value in marine samples was 0.07322 g/l at ST4, while the highest value was 0.0979 g/l at ST1-4 with an average concentration of 0.0977 g/l. Average river Sulfate concentrations was 0.00577 g/l as shown in Table.4.

**Table.4. Shows the values of SO<sub>4</sub><sup>2-</sup> concentrations in marine water samples in summer on 12/8/2017**

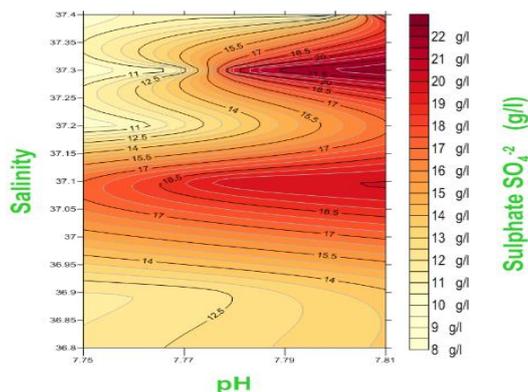
Site		Sulfate concentration g/l
ST1	ST1-1	0.091242
	ST1-2	0.093906
	ST1-3	0.094572
	ST1-4	0.097902
	ST1-5	0.089244
ST2	ST2-1	0.087246
	ST2-2	0.091242
	ST2-3	0.085914
	ST2-4	0.091908
	ST2-5	0.085914
ST3	ST3-1	0.088578
	ST3-2	0.08991
	ST3-3	0.083916
	ST3-4	0.081252
	ST3-5	0.07659
ST4	ST4	0.07326
ST5	ST5-1	0.005994
	ST5-2	0.005328
	ST5-3	0.005994

From the curve of iso concentration by coordinates, where concentration showed in mg/l. In the first Sea voyage in the spring (Fig.4-right curve), we observe higher concentrations as we move south, and decreasing concentrations when moving from the shore to the west, where the highest concentrations are located near third site samples (ST3). In the second Sea voyage in summer (Fig.4-left curve), the curve shows that the concentrations are convergent at all sites, with a slight rise in concentrations at a northward direction at first site samples.



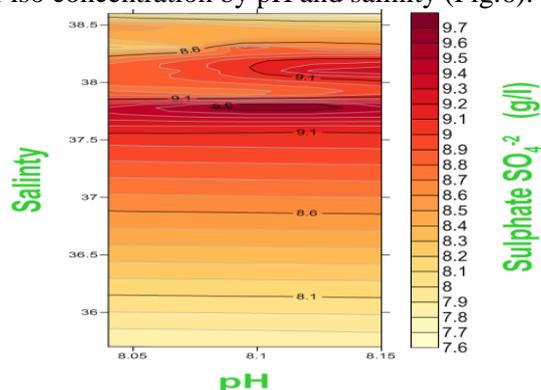
**Figure.4. Iso concentration by coordinates curve, right curve for first voyage results, while second voyage curve is shown to the left**

Pearson coefficient between sulfate concentrations and pH values was 0.55 in the spring, indicating to a strong correlation between sulfur concentrations and pH values. Higher Sulfate concentrations were observed at pH values above 7.8 and salinity between 37.28-37.32, as shown in the curve of iso concentration by pH and salinity (Fig.5).



**Figure.5. Iso concentration by pH and salinity curve- (Spring)**

Pearson coefficient between Sulfate concentrations and pH values in summer was almost identical to its value in spring, it recorded a value of 0.54, indicating to a strong correlation between sulfate concentrations and pH values. Higher sulfate concentrations were observed at pH values between 8.09-8.13, And a salinity range between 37.6-37.8 as shown in the curve of iso concentration by pH and salinity (Fig.6).



**Figure.6. Iso concentration by pH and salinity curve- (Summer)**

Results also show higher sulfate concentrations in the spring when compared to summer, this could be because of emitted free sulfur which recorded higher value in the spring. This indicates to the role that emitted free sulfur may play.

#### 4. CONCLUSIONS

Based on the previous results, it was found that there is an increase in Sulfate concentrations in the studied area when compared to reference sample or natural rates of Sulfate concentrations in marine waters of Mediterranean Sea. These concentrations were slightly higher in the areas closest to the refinery. Human activities play an important role in concentrations rates, such as exposed free Sulfur piles, which could be affected by wind, leading to the transport of free sulfur into marine waters. Sulfur bacteria also play an important role that affect sulfate concentrations. Under appropriate conditions, this bacteria can cause sulfate reduction to less oxidized forms.

**Recommendations:** pollution resulting because of human activities should be reduced, by transporting of recovered free sulfur periodically from the refinery to the plants that use it as raw material in its industries, or through designing a better place to collect these free sulfur, like covered and closed place as possible, this will help reducing of free sulfur emission into atmosphere. Wastewater must be treated before it reaches sea water, and the industrial waste of the refinery must be separated from the domestic sewage in the area surrounding the refinery.

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