

## Study the different phases of sulphur in the soil around the gas refinery and their relationship with other soil characteristics, an example from the NE Iran

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### 1-Introduction

Sulfur is found in the soil in the organic forms like ester sulfates, carbon bonded to sulfur, and inorganic compositions such as sulfates and sulfites (Havlin et al., 2004; Karimizarchi and Aminuddin, 2015). Elemental sulfur is one byproduct in gas processing, which is removed as H<sub>2</sub>S in the refining process of natural gas that includes sulfur compositions, and after transforming to elemental sulfur, it is stored in large block forms. With passing the time, due to erosion and physical tracking in these blocks, sulfur spreads out to adjacent areas (Maynard et al., 1986). Also, some pollutant gases discharge to the atmosphere that SO<sub>2</sub> is the most important of them, which may penetrate the human nutrition cycle and also affects ecosystems that constitute a significant concern (Chavoshi et al., 2012). This research aims to study and measure different sulfur phases in the soil inside and out of the Shahid Hashemi Nezhad gas refinery, located in 35 km Sarakhs city.

### 2-Methodology

Twenty-two soil samples were collected from surface soil in Shahid Hashemi Nezhad gas refinery and nearby areas, to study of sulfate accumulation in soil. The pH of soil samples was measured in equilibrium with pure water at 1: 2.5 ratio soil to water (Pawels et al., 1992). Different phases of sulfate were extracted in three stages to measure the content of water-soluble sulfate, absorbed sulfate and occluded with carbonates sulfate (Morche, 2008). First, the soil sample after 30 min shaking with deionized water at 1:10 (w/v) ratio was centrifuged, and the extract was separated from the mixture by what man paper No.42. In the next stage, the rest of the soil after 30 min shaking with 0.032 M NaH<sub>2</sub>PO<sub>4</sub> at 1: 10 (w/v) ratio, was centrifuged, then the extract was separated. In the final stage, 1M HCl was added to the rest of the soil at 1:20 (w/v) ratio, and it was centrifuged after 60 min shaking, and the extract was separated like previous stages. Also, the total content of sulfate was determined via a complete digestion method by the mixture of some different acids, including concentrated hydrofluoric acid, hydrochloric acid, and concentrated nitric acid (Morche, 2008). A mixture of 2 ml concentrated hydrofluoric acid, 5 ml hydrochloric acid and 8 ml concentrated nitric acid was added to 0.5 gr sieved soil in a digestion vessel, then was heated for 60 min at 170 °C, to measure the total content of sulfate. After cooling, the digest was evaporated to dryness at 130 °C. Then, the digest was dissolved in 2 ml nitric and 2 ml hydrochloric acid mixture and filled up with deionized water up to 25 ml. The sulfate content in the extracts was measured in an analytical chemistry laboratory of faculty of sciences in the Ferdowsi University of Mashhad by the gravimetric method. Having three different phases of sulfate and total sulfate and using the following equation, the organic sulfate content was calculated as the fourth phase:

$$SO_{4org} = SO_{4Tot} - (SO_4H_2O + SO_4NaH_2PO_4 + SO_4HCl)$$

The organic matter content was measured via titration method by 1 N Fe(SO<sub>4</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub> in 1 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution and concentrated sulfuric acid (Walkley and Black, 1934). The amount of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> anions was

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determined via soil extract titration by 0.01 N sulfuric acid in the presence of phenolphthalein and methyl orange reagents (Jaefari Haghighi, 2003).

### 3- Results and discussion

Among four measured phases of sulfate (one organic phase + three inorganic phases) in the soil samples, the maximum concentrations relate to organic sulfate, occluded with carbonates sulfate, water-soluble sulfate and absorbed sulfate respectively. Sulfate concentration in four phases in the samples nearby sulfur blocking site (TS5, TS6, and TS7) is more than the other samples (Fig. 1).

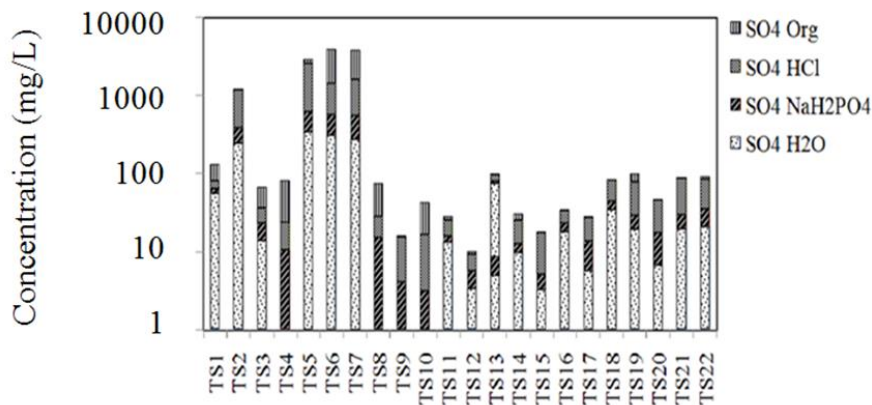


Fig. 1. The concentration of different sulfate phases in the soil samples.

The relation between the soluble sulfate phase and measured pH in the soil samples is shown in Fig.3. Based on this figure, by increasing of water-soluble sulfate concentration, pH decreases with high correlation ( $R^2= 0.735$ ); therefore, it can be stated the presence of this anion can make an acid condition in the soil (Fig. 2).

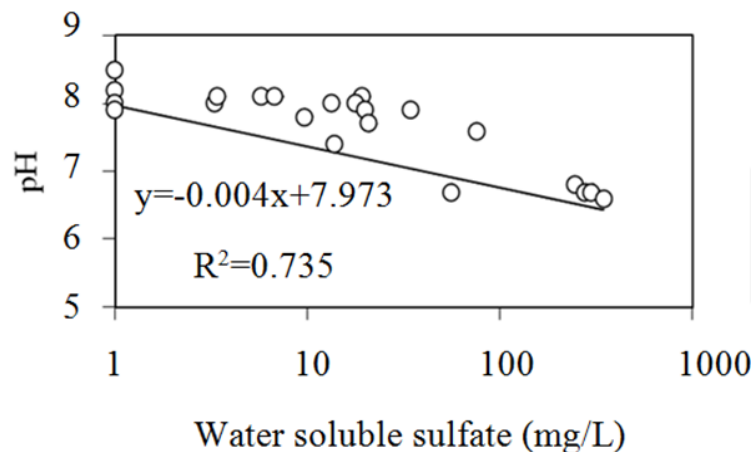


Fig. 2. The effect of water soluble sulfate phase on pH decrease of the soil samples.

The relation between the concentration of occluded with carbonates sulfate to  $CO_3^{2-}$  and  $HCO_3^-$  concentration is not significant, and it cannot be stated that by increasing  $CO_3^{2-}$  ( $R^2= 0.003$ ) and  $HCO_3^-$  content ( $R^2= 0.076$ ), accumulation of occluded with carbonates sulfate is augmented. Therefore, considering the formations containing gypsum and anhydrite in the study area, it can be said that such formations may be essential to provide this phase of sulfate. There is a direct relation between the increase in accumulation of absorbed sulfate phase and measured organic matter ( $R^2=0.8$ ) in these samples. Despite the low content of measured organic matter in the soil samples with an average of %1.06, organic sulfate content and organic matter show the linear

and direct relation with somewhat high correlation ( $R^2=0.63$ ), which indicates sulfur is accompanied with a considerable amount of measured organic matter in the soil samples.

#### 4-Conclusion

Based on obtained results, it can be concluded that the pollution, which is due to produced sulfur compounds in the Shahid Hashemi Nezhad gas refinery area, is observed in south zones, but pollution intensity is more significant in the inside samples than the others. Organic sulfate, occluded with carbonates, water-soluble, and absorbed sulfate, has the maximum concentration, respectively, that inside samples have higher amounts than the other samples. The reason is organic sulfate presence as an essential part of total sulfate in all soil and also lithology of the study area that includes gypsum and anhydrite formations -in addition to carbonate formations- which can have a considerable concentration of insoluble sulfate. Organic sulfate phase constitutes a significant portion of organic matter in the soil samples that were confirmed by a somewhat high correlation between this phase and organic matter. The accumulation of sulfate in the soil and  $SO_2$  gas in the atmosphere of the study area caused a considerable decrease in pH that is due to the biologic oxidation of sulfur and its compounds. Soil pH and organic matter are the most important factors which control the concentration of absorbed sulfate phase in the soil samples.

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