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Detection of Nutrients and Major Ions at Al Muthanna Storage Site Soil

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Abstract:

In the early 90s military operations and United Nations Special Commission "UNSCOM" teams have been destroyed the past Iraqi chemical program. Both operations led an extensive number of scattered remnants of contaminated areas. The quantities of hazardous materials, incomplete destructed materials, and toxic chemicals were sealed in two bunkers. Deficiency of appropriate destruction technology led to spreading the contamination around the storage site. This paper aims to introduce the environmental detection of the contamination in the storage site area using geospatial analysis technique. The environmental contamination level of nutrients and major ions such as sulphate (SO_4), potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), chlorine (Cl), phosphate (PO_4) and nitrate (NO_3) were detected and analyzed. The grid soil samples on the site and surrounding areas have been investigated, analyzed, and compared to the background points. The storage area grid was divided into 30 major sectors and all samples were evaluated from acquires 10 samples from each sector. The detection results have indicated that SO_4 level was exceeded the permitted level by 25 times, K level also exceeded the permitted level but by 460, Na ions were 85 times greater the permitted level. Mg level was 180 times higher than that of permitted content. Activity level of Ca in the soil samples of the study area has also exhibited variability with nine times over the permitted level near the bunkers. However, very high contamination spot activity of Cl was found in destruction zone about which 44 times over the background level was found while PO_4 level exceeded the permitted level by 35 times over the permitted level and there was no activity detected for the nitrate in the storage area site.

Key words: Al Muthanna Storage Site, Geospatial Techniques, Ions, Iraqi Chemical Program, Nutrients.

Introduction:

Al Muthanna State Establishment has been used as the key facility for the production of chemical weapons in Iraq last century. It is located 90 km northwest of Baghdad as shown in Fig. 1 and 2. According to the Security Council Resolution 678 (1991))1). Iraq accepted to declare and destroy its weapon of mass destruction (WMD) program. Al Muthanna State Establishment (MSE) production facilities were converted to destroy the chemical agents and the precursors under the supervision united nation special commission (UNSCOM). Due to the high-risk and the lack of appropriate destruction technology, the UNSCOM selected two bunkers to secure and isolate the remnants resulted from the destruction process from the population.

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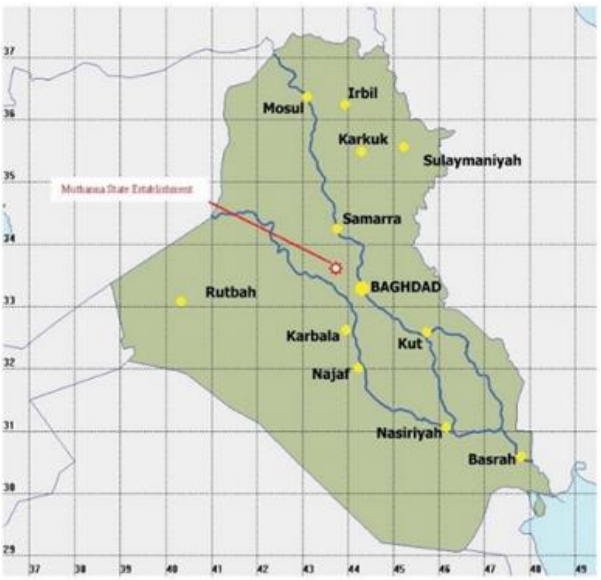

Figure 1. Al-Muthanna location

Iraq declared the contents of two bunkers according to the Chemical Weapons Convention

(CWC) in June 2009 and committed to submit the destruction plan to the Technical Secretariat. (2)

These serious problems led to increased problems in the environment, including water contamination, air pollution and ecosystem degradation. These activities may create different sources of contamination. Pollutants that are deposit in the aquatic environment may accumulate in the food chain and cause ecological damage while also posing a risk to human health. (3). The abnormal conditions created in the environment by these activities, certain effect in biological system, due to the change in the environment, shortage in supply and security lead to unbalanced satiation in nature. (4)

The contaminated area was investigated and analyzed by using the integration of Geospatial Information Systems and statistical software.

Al Muthanna Site Description

Al Muthanna storage site is located near Tigris river arm between Samara and Fallujah. The geographical coordinates are shown in Table1 and Fig. 2. The site was Iraq's main chemical weapons research, development, and production facility. It is located in Salhaldin province. This facility covers an area 1 km², the site was operate continuously from 1983 to 1991 and produced thousands of tons of precursors Chemical agents but from 1994 until now, it is used to store securely the remnants of the last project. The site was heavily bombed during First Gulf War. From 1992 to 1994, the UNSCOM Group has operated at this site to eliminate remaining precursor materials, equipment's, and destroy production plants or burn remaining chemical agents. (5, 6)

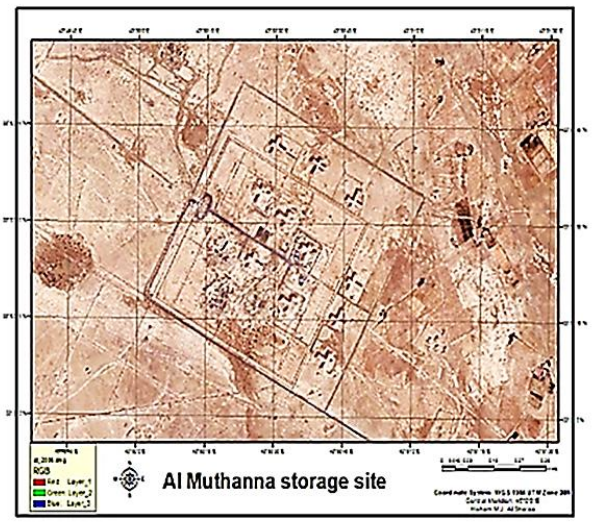

Figure 2. Al-Muthanna storage site area

The storages were semi-underground structures covered with protective layers of concrete. They resembled a truncated pyramid.

Table 1. Al-Muthanna Site Location.

Latitude	N 33° 52' 52"
Longitude	E 43° 50' 53"
Bunkers area	1 km^2

Materials and Methods:

In this paper, 300 soil samples were analyzed by using GC mass spectrometer procedure. The soil samples data used in this paper were collected in 2015. The bunkers area (850 m *1000 m) was divided as grid into 30 sectors (196 m* 163 m) as major sectors then each sector was divided into ten minor sectors the sampling method depending on two levels of soil samples, surface soil samples and samples from 50 cm depth were averaged, the minor sub-grid also averaged. Finally, each grid represented by one sample point for final statistical analysis. The background level was defined from samples located within about 1 km north and south from storages site. The contamination level of the main chemical ionic compounds was detected and evaluated (Sulphate SO_4, Potassium K, Sodium Na, Magnesium Mg, Calcium Ca and Chlorine Cl), from the soil samples of the site, surrounding areas were investigated and compared to the reference selected points. The average results for the two depth layers were combined to give major perspicacity for soil contamination in Al Muthanna storage site. The output digital map layer, which includes contours for Al Muthanna Storage zone maps, was created by additive interpolation method of the geographical information system using the integration between ArcGIS 10.4 and golden surfer. With ArcMap and Surfer spatial analysis extension and, DATA of subareas values can be imported to Geospatial through grid cells. (7) These grid cells, which have been classified in various ways and different colours, were chosen for each class; where the colors represent the progression of values for specified data (8). Class were achieved after the raster themes converted into a shape file, which includes contaminations concentrations and information that represents sub grade characteristics. 3D mountain range plot and 2D contour created a result for the evaluation stage. (9) Data were interpolated by kriging method to introduce a continuous surface as a visual display by using spatial interpolation which is the process of using points with known values to estimate values at other unknown points. (10) In the geospatial statistical analysis, spatial interpolation of these points can be applied to create a raster

surface with estimations made for all raster cells. (11, 12)

Results and Discussion:

The analysis of contamination activity levels of the main chemical ionic compounds were detected and evaluated (Sulphate SO_4, Potassium K, Sodium Na, Magnesium Mg, Calcium Ca, Chlorine Cl, Phosphate PO_4 and Nitrate NO_3) in the soils from different locations of the site, indicating a relatively asymmetrical distribution tailing slightly towards higher concentration. However, the activity level of SO_4 in the soil samples exhibited higher variability and ranged around 2170- 6079 ppm with an average value of 5199 ppm. Similarly, it was observed that the activity level of Ca in the soil samples of the study area also exhibited large variability and ranged between 1824- 3259 ppm with average values of 2750.9 ppm and for the Cl high concentration spot around 442 ppm can be seen with zone average 165.89 ppm. Whereas, the concentration level for the elements in the soil samples was above the reference background levels taken about 1 Km away from the study site as shown in Table 2. The obtained values of sulphate level exceeded the permitted level by 25 times; potassium level exceeded the permitted level by 460, Sodium exceeded by 85 times over the permitted level. Magnesium level exceeded the permitted over 180 times, Activity level of calcium in the soil samples of the study area also exhibited variability with 9 times over the permitted level near the bunkers. Very high contamination spot activity of chlorine was found in destruction zone about 44 times over the background level. However, the activity of phosphate distribution showed that there were three hotspots near storage bunker zone with concentration above 620 ppm that exceeded permitted level by 130 times over the background level. For nitrate, no activity was detected in the storage area site as shown in Fig. 3, 4, 5, 6, 7, 8, 9 as contour and mountain range plots. This approach was used as an upper limit contaminant and overall distribution, particularly higher concentrations due to hot spots being important parameters for demonstrating that the cleanup is very necessary to precisely achieve. The sulphate, chlorine and sodium spots level have given an indication for spoiling some chemicals in the area and destruction activates for the past program in the site. Thus, it is necessary to have an overall understanding for contaminant distribution to make this determination on hot spots acceptability. Many difficulties can be faced in this approach one of them is the large numbers of samples required to adequately characterize the upper tail of the distribution.

Table 2. Statistical summary for soil samples

	Po4 ppm	No_3 ppm	So_4 ppm	K ppm	Na ppm	Mg ppm	Ca ppm	Cl ppm
Avg.	255.0667	**0**	5199.033	144.86	33.93333	421.0333	2750.867	165.8667
Max.	623	**0**	6075	764	61	800	3259	442
Min.	59	**0**	2170	18	16	121	1824	50
Reference	264	0	4800	130	32.5	280	2970	300

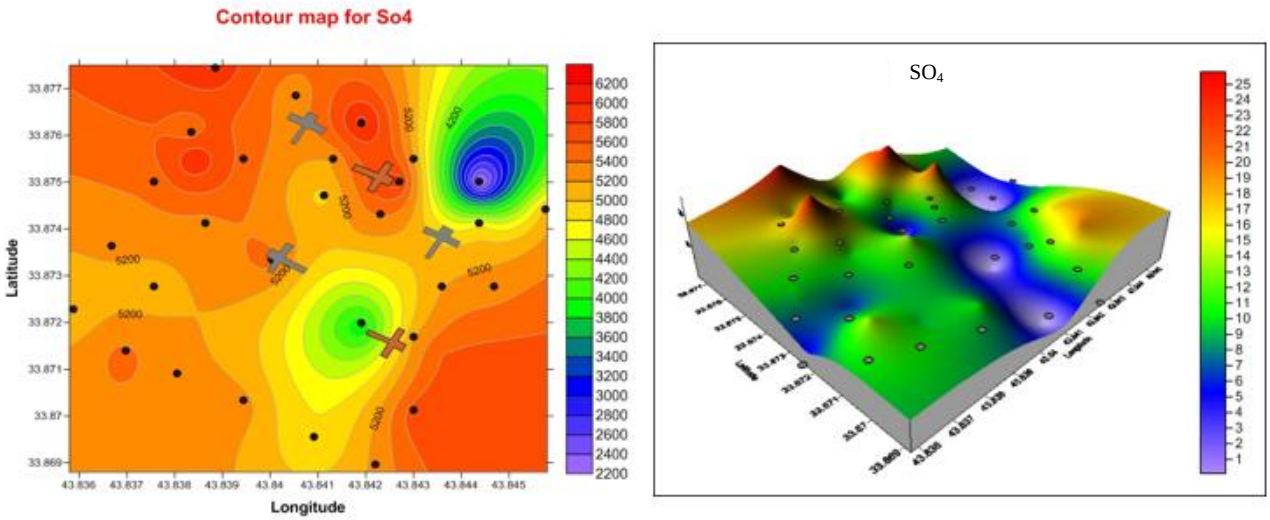

Figure 3. Sulphate contamination contour and 'mountain range' 3D plot

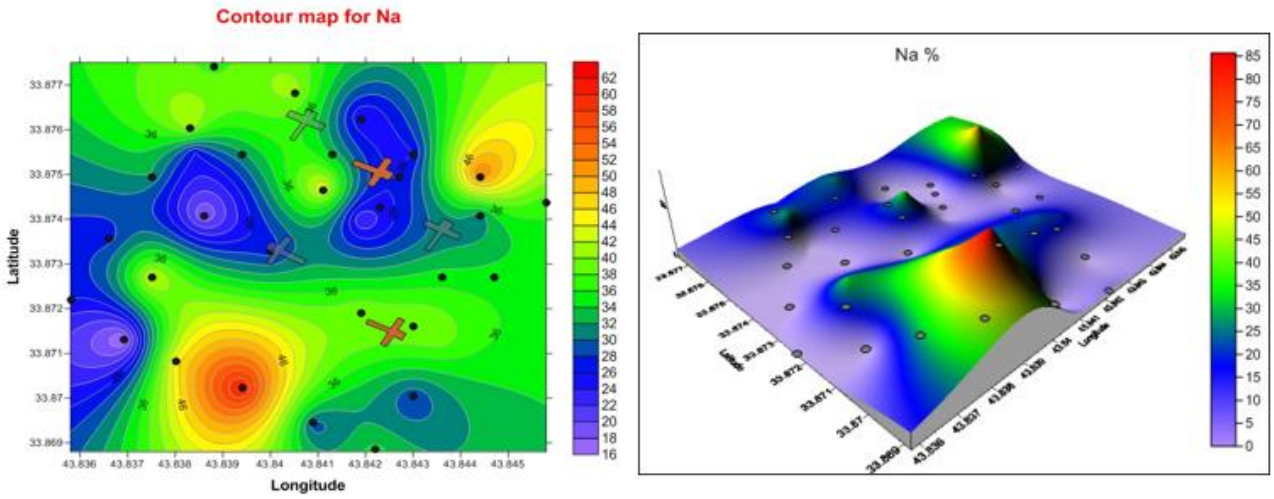

Figure 4. Sodium contamination contour and 'mountain range' 3D plot

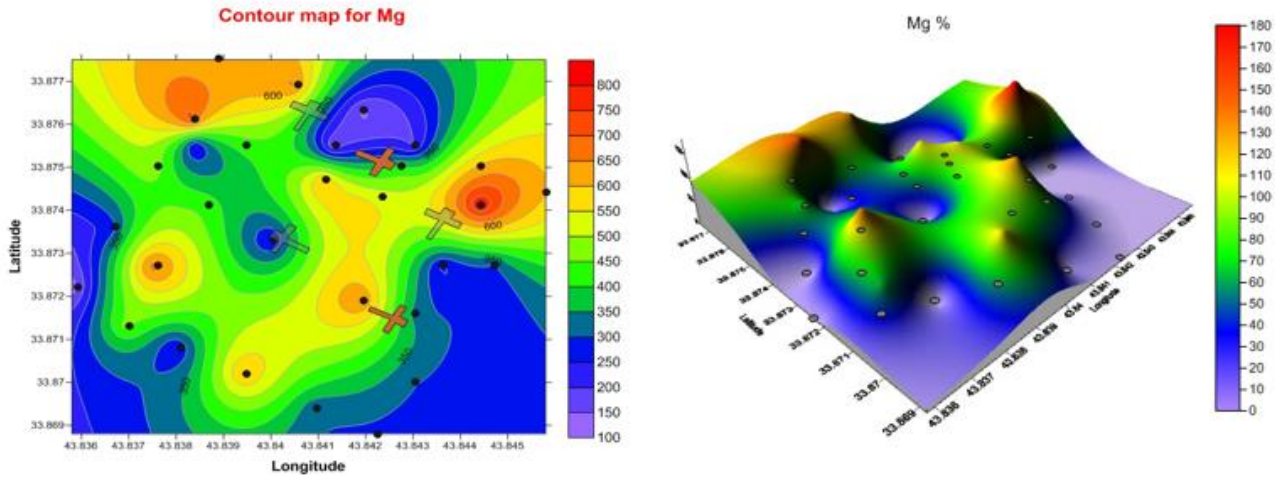

Figure 5. Magnesium contamination contour and 'mountain range' 3D plot

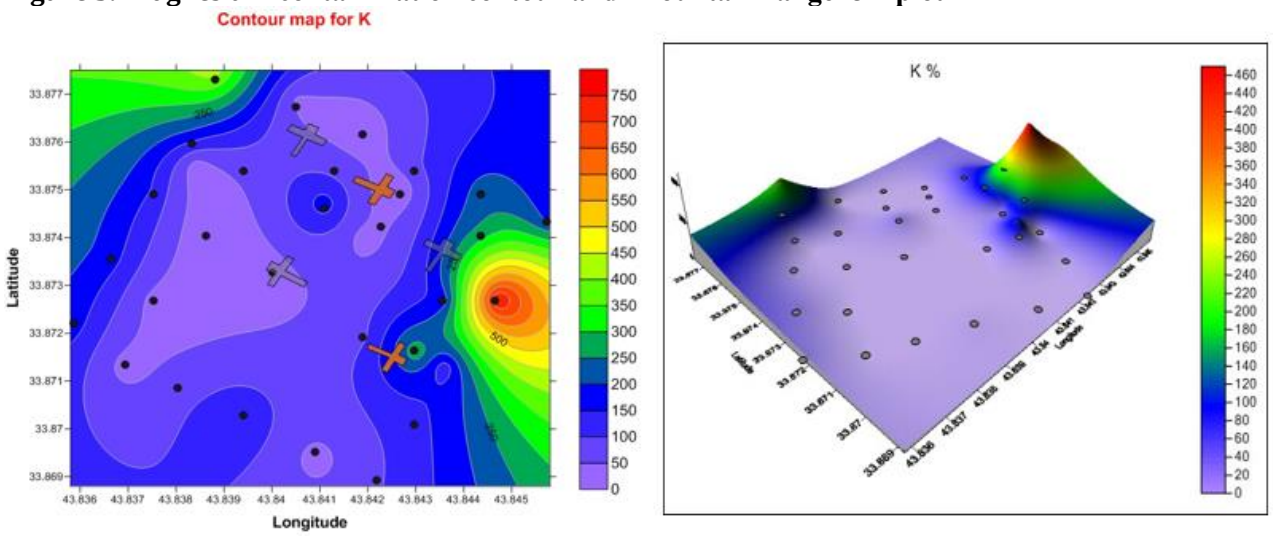

Figure 6. Potassium contamination contour and 'mountain range' 3D plot

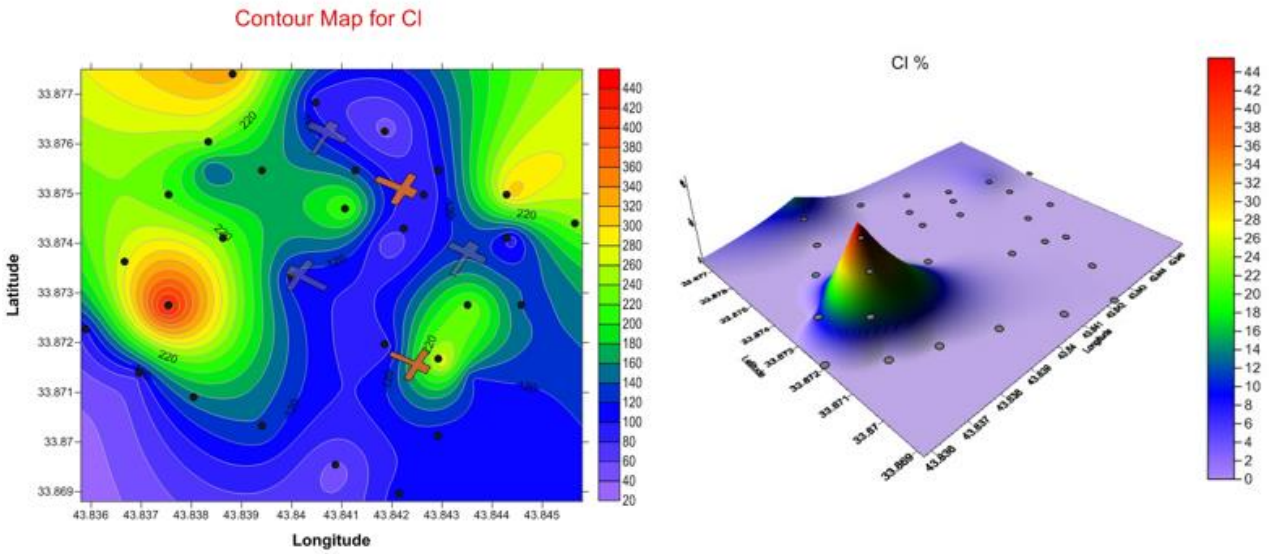

Figure 7. Chlorine contamination contour and 'mountain range' 3D plot

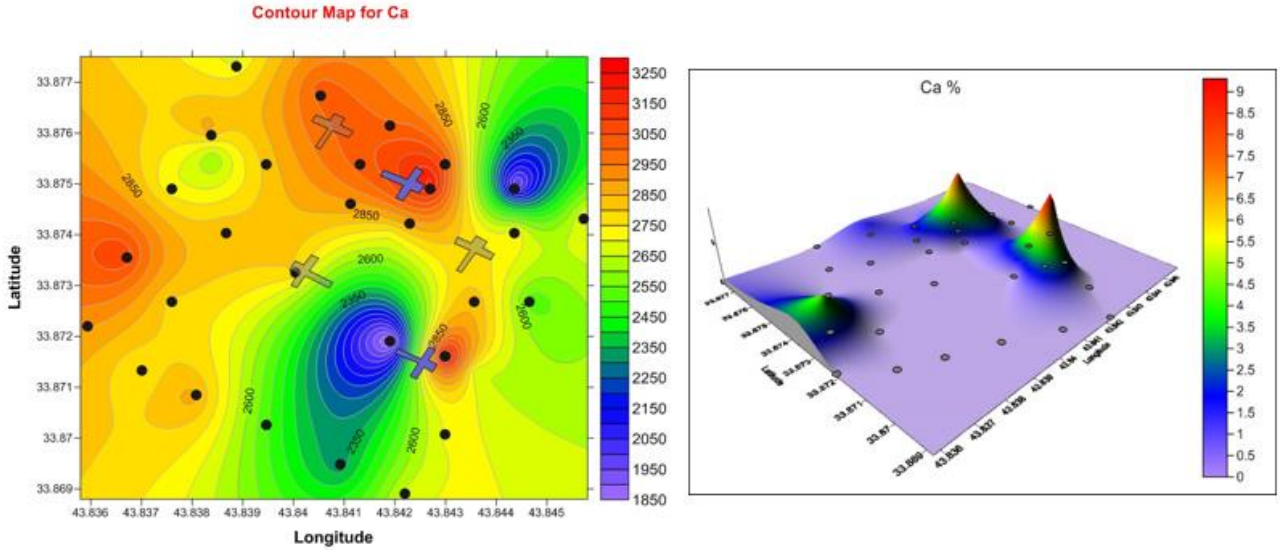

Figure 8. Calcium contamination contour and 'mountain range' 3D plot

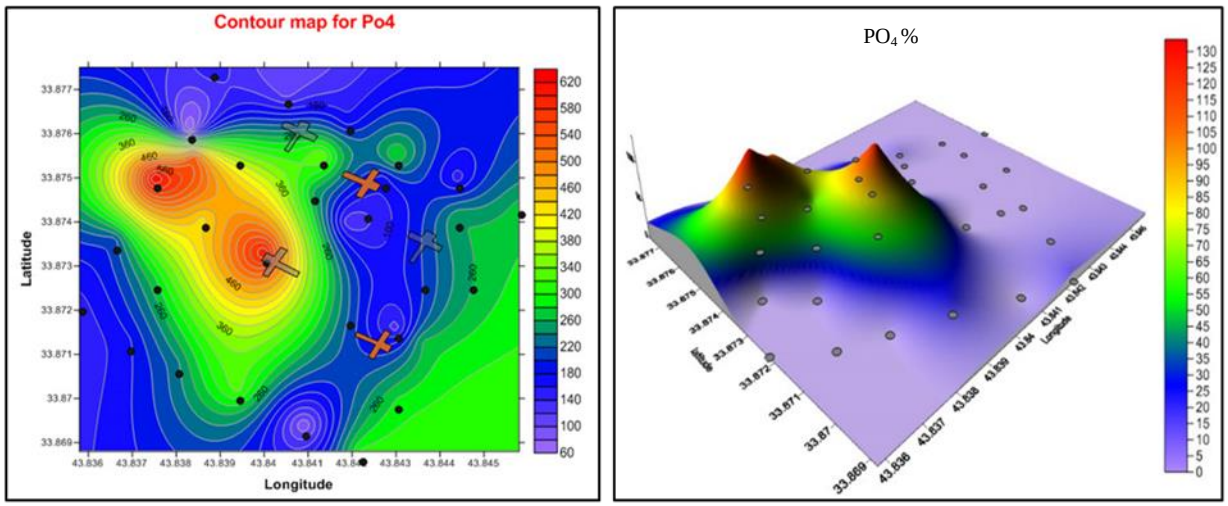

Figure 9. Phosphate contamination 2D contour and 3D 'mountain range' plot

Conclusions:

The current work has found that the concentrations of all examined chemical ionic compounds were found extremely higher than those of reference background and exceed the permitted levels in the soil samples. It is clear that this site has suffered from the contamination due to the past chemical weapons program activities and the

destruction of the chemicals and precursors related to this program. Severe contaminated hot spots were observed as follows:

- Sulphate hotspot near the storage bunkers exceed the reference values by 25%
- Potassium hot spot near the storage bunkers exceed the reference value by 460%
- Sodium hot spot near the storage bunkers exceed the reference value by 85%
- Magnesium hot spot near the storage bunkers exceed the reference value by 180%
- Calcium hot spot near the bunkers exceed the reference value by 9%
- Chlorine near the destruction area exceed the reference value by 44%
- Phosphate hotspot near the destruction area exceed the reference value by 35%
- There is no activity detected for Nitrate in the storage area site
- The Sulphate, Chlorine and Sodium spots level give an indication for spoiling some chemicals in the area and destruction activates for the past program in the site.

Due to these circumstances, it is essential to take the following action:

- Urgent action plan for decontamination
- Long term monitoring for the nearby water recourses.
- The agriculture activates should be moved out of the site by at least 1 km as recommended by the UN handover protocol.
- Medical examination for the nearby villages.
- More investigation and analysis for the other expected dangerous chemicals.

Conflicts of Interest: None.

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الكشف عن العناصر المغذيه والأيونات الرئيسية في موقع مخازن المثنى

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الخلاصة:

في أوائل التسعينيات من القرن الماضي، دمرت العمليات العسكرية وفرق لجنة الأمم المتحدة الخاصة "UNSCOM" البرنامج الكيميائي العراقي السابق. وادت كلتا العمليتين إلى اعداد كبيره من المخلفات المتناثرة في المناطق الملوثة. تم تجميع المواد الخطرة والمواد غير المكتملة التدميرية والمواد الكيميائية السامة في مخبأين. بسبب عدم وجود تكنولوجيا خاصه للتدمير مما ادى الى انتشار التلوث حول موقع المخازن. يهدف هذا البحث لكشف التلوث في الموقع باستخدام تقنية التحليل الجيومكاني. تم تقييم وتحليل الملوثات البيئية لمستوى تلوث المغذيات والأيونات الرئيسية (كبريتات SO_4، البوتاسيوم K ، الصوديوم Na ، المغنيسيوم Mg ، الكالسيوم Ca ، الكلور Cl ، الفوسفات PO_4 والنترات NO_3)، مأخوذة من عينات التربة في الموقع، والتحقق من المناطق المحيطة وتحليلها مقارنة بنقاط مرجعيه. تنقسم عينات منطقة التخزين إلى 30 قطاعًا رئيسيًا، حيث يتم تقييم جميع العينات من 10 عينات من كل قطاع. تشير نتائج الكشف إلى أن مستوى SO_4 يتجاوز المستوى المسموح به بمقدار (25) ضعفا ، مستوى K يتعدى المستوى المسموح به بمقدار (460) ضعف، أما Na فتتجاوز (85) مرة فوق المستوى المسموح به لمستوى Mg يزيد عن المسموح به (180) ضعف، ومستوى النشاط Ca في عينات التربة من منطقة الدراسة (9) مرات أكثر من المستوى المسموح به بالقرب من المخازن، تم العثور على بقعة ذات مستوى تلوث عالية جدا من Cl في منطقة التدمير حوالي (44) مرة مقارنه بالنقاط المرجعيه، مستوى PO_4 يتجاوز بمقدار (35) مرة فوق المستوى المسموح به، ولم يتم اكتشاف اثر للنترات في موقع منطقة المخازن.

الكلمات المفتاحية: العناصر المغذيه، الأيونات، البرنامج الكيميائي العراقي، التقنيات الجيومكانية، موقع تخزين المثنى.