Assessment of Heavy Metal Contamination in the Soil of Al-Muthanna Storage Site using Geospatial techniques

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Abstract. During the early 90s, military operations and United Nations Special Commission “UNSCOM” teams have destroyed the Iraqi past chemical program. Both operations led to a large number of scattered remnants of contaminated areas. The quantities of hazardous materials, incompletely destructed materials and toxic chemicals were sealed in two bunkers. Lack of appropriate destruction technology led to the spread of contamination around the storage area. This paper aims to introduce the environmental assessment of the hazard contamination in the storage site area using Geomatics analysis technique. The environmental assessment for contamination level of eight main chemical compounds (Chromium Cr, Phosphate PO₄, Nitrate NO₃, Cadmium Cd, Copper Cu, Nickel Ni, Zinc Zn and Lead Pb) have been assessed and analyzed. Soil samples taken from the grid on the site and its surrounding areas have been investigated and analyzed compared to the reference points. The storage area grid was divided into 30 major sectors. 10 samples from each sector were acquired and evaluated. The assessment results indicated that Cr level exceeded the permitted level by (180) times, PO₄ level exceeded the permitted level by (35) times, Cu by (1050) times over the permitted level and Ni level exceeds the permitted level over by (50) times. Activity level of Zn in the soil samples of the study area also exhibits large variability with (16000) times over the permitted level on the surrounding isolation protection on the north-west Wall. Very high Contamination spot activity of Pb was found in Destruction zone, about (1350) times over the background level. There is no activity detected for the Cadmium and Nitrate in the storage area site.

1. Introduction

Over a period of thirty years, Al-Muthanna has been used as the key facility for production of chemical weapons in Iraq last century. It is located 90 km northwest of Baghdad as shown in Figures 1 and 2. Al-Muthanna State Enterprise was the basis of the Al-Muthanna State Establishment created in 1985 [1]. At the time of the Gulf War, according to the Security Council Resolution 678 in 1991, Iraq accepted to declare and destroy its Weapon of Mass Destruction (WMD) program. At the time of the Gulf War, Al-Muthanna State Establishment was the nucleus of Iraq’s entire chemical ammunition program. It was a large complex spread over approximately 170 square kilometres [2]. It consisted of the main site, which US forces called Al-Muthanna [3].

Al-Muthanna State Establishment (MSE) production facilities were converted to destroy the chemical agents and the precursors under the supervision of United Nation Special Commission (UNSCOM). UNSCOM inspectors conducted their first chemical inspection of Al-Muthanna during
early June 1991. The site was very dangerous because of multi military operations that damaged chemical ammunition and unexploded ordnance due to the high-risk and the lack of appropriate destruction technology, the UNSCOM has select two to secure and isolate the remnants resulted from the destruction process from the population [1,2].

Contaminated area was investigated and analysed for this unique case to assess the contamination across soil of the storage site of Al-Muthanna using the integration of Geospatial Information Systems and statistical software.

These serious problems led to increasing problems in the environment including water contamination, air pollution and ecosystem degradation. These activities may create different sources of contamination. Pollutants that are deposited 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 a 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.

2. Al-Muthanna storage site description
Al Muthanna storage site, located 90 km North West of Baghdad on Tigris River arm between Samara and Fallujah. The geographical coordinates are shown in Table 1 and Figure 2. Al Muthanna Was Iraq's main chemical weapons research, development, and a production facility. Located in Saladin Governorate, this facility covers an area of 1 km². The site operated continuously from 1983 to 1991, producing thousands of tons of Chemical agents including mustard gas, sarin, tabun, and VX. The site was heavily bombed during the Gulf War. From 1992 to 1994 the UNSCOM Chemical Destruction Group operated at this site to eliminate remaining precursor materials, destroy production plants and equipment, and hydrolyse or burn remaining chemical warfare agents [5, 6, 7].

The storage areas were semi-underground structures covered with a protective layer of sandy clay. They resembled a truncated pyramid.

| Table 1-1 Al-Muthanna Site Location |
|------------------------------------|
| Latitude                           |
| N 33 52 522                        |
| Longitude                          |
| E 43 50 538                        |
| Bunkers area                       |
| 1 km²                              |

3. Materials and methods
300 soil samples were evaluated and analysed. The data samples used in this paper were collected in 2015. The samples were collected from inner and outer perimeters of Muthanna storage area. The site zone was divided into 30 sectors on two levels. Soil samples from the soil surface and samples from 50 cm depth were collected. Background level is defined from samples collected within about 1 km north and west from storages site. Contamination level of eight main heavy metal chemical compounds was detected and evaluated (Chromium Cr, Phosphate PO₄, Nitrate NO₃, Cadmium Cd, Copper Cu, Nickel Ni, Zinc Zn and Lead Pb) from the soil samples of the site surrounding areas were investigated and compared to the reference points selected. The average results for the two depth layers were combined to give us major perspicacity for soil contamination in the site. The output digital map layer which includes contours for AL Muthanna Storage 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 colors, are chosen for each class; the colors represent the progression of values for specified data. [8] It was achieved after the raster themes are converted into a shapefile, which includes contaminations concentrations and information that represents subgrade characteristics. 3D mountain range plot and 2D contour have been creating a result for the evaluation stage. [9] Data are 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, 13]

4. Results and discussions

Environmental assessment of contamination activity for Chromium Cr, Phosphate PO$_4$, Nitrate NO$_3$, Cadmium Cd, Copper Cu, Nickel Ni, Zinc Zn and Lead Pb in the soil samples indicates relatively asymmetrical distribution tailing slightly towards higher concentration for some elements. However, the activity level of Chromium in the soil samples exhibits higher variability and is ranged between 4.6-47 ppm with an average value of 22.3 ppm. Which exceeds the background level by (180) times. Similarly, Phosphate distribution shows there are three hotspots near the storage bunker zone with a concentration above 620 ppm that exceeds permitted level by (130) times over the background level. For Nitrate and Cadmium, no activity was detected in the storage area site. However, the activity level of Copper in the soil samples exhibits higher variability and is ranged between 3-42 ppm with an average value of 6.08 ppm that exceeds the permitted level by (1050) times. For Nickel we can see one hotspot above 50 ppm with (95) times over permitted level. The activity level of Zinc in the soil samples of the study area also exhibits large variability and is ranged between 0.4-407 ppm with average values of 36.46 ppm, with (16000) times over the permitted level on the surrounding isolation protection on the north-west Wall. Mountain graph for Lead shows high concentration spot around 34 ppm with zone average of 6.63 ppm. Very high Contamination spot activity of lead was found in destruction zone about (1350) times in the soil samples which was above the reference background levels taken about 1 km away from the study site as shown in table 1. 2D contour and 3D mountain range plots are shown in Figures 3 to 8.

This approach may be thought of as an upper limit, recognizing that both the Contaminant mean and overall distribution, particularly the higher concentrations due to hotspots are important parameters for demonstrating if the cleanup has achieved the release criteria. Thus, it is necessary to have an overall understanding of the contaminant distribution to make this determination on hot spot acceptability.

One difficulty in this approach is that a large number of samples are required to adequately characterize the upper tail of the distribution. That is, with relatively few data, the uncertainty in the upper percentiles of distributions is great.

| Table 1. Statistical summary for heavy metals soil samples |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cu ppm | Zn ppm | Cr ppm | PO4 ppm | Ni ppm | Pb ppm |
| **Avg.** | 6.08 | 36.46333 | 22.26667 | 255.0667 | 24.82333 | 6.653333 |
| **Max.** | 42 | 407 | 47 | 623 | 49 | 34 |
| **Min.** | 3 | 4.2 | 4.6 | 59 | 13 | 1.3 |
| **Reference point** | 3.15 | 2.4 | 16.5 | 264 | 24.5 | 2.25 |
Figure 3. Chromium contamination 2D contour and 3D ‘mountain range’ plot

Figure 4. Phosphate contamination 2D contour and 3D ‘mountain range’ plot

Figure 5. Copper contamination 2D contour and 3D ‘mountain range’ plot
Figure 6. Nickel contamination 2D contour and 3D ‘mountain range’ plot

Figure 7. Zinc contamination 2D contour and 3D ‘mountain range’ plot

Figure 8. Lead contamination 2D contour and 3D ‘mountain range’ plot
5. Conclusions
The environmental assessment for contamination level of eight main chemical compounds (Chromium Cr, Phosphate PO$_4$, Nitrate NO$_3$, Cadmium Cd, Copper Cu, Nickel Ni, Zinc Zn and Lead Pb) have been assessed and analyzed. The assessment results indicated that Cr level exceeds the permitted level by (180) times, for PO$_4$ level exceeds the permitted level by (35), and for Cu by (1050) times over the permitted level was found near bunker 41 and bunker 13 storage areas. For Ni level exceeds the permitted level over (50) times. Activity level of Zn in the soil samples of the study area also exhibits large variability with (16000) times over the permitted level on the surrounding isolation protection on the north-west Wall. Very high Contamination spot activity of Pb was found in Destruction zone about (1350) times over the background level and there is no activity detected for the Cadmium and Nitrate in the storage area site. More research on the effect of this site should be done because that contamination could not be the result of a single source. Ongoing monitoring of the health status of visitors and workers in this site should also be done.

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