POLLUTION OF MINING INDUSTRY SULFUR PURIFICATION PLANT AT AL MISHRAQ

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ABSTRACT

The Al Mishraq site has been the subject of many scientific studies for the period before and after the fire in 2003. Five visits to the site were conducted twice in 2003 for general fact-finding, twice in 2004, and once in 2005 for detailed sampling and monitoring.

Desk-based research and laboratory analysis of soil and water samples results indicate that surface water and groundwater pollution from Al Mishraq site was significant at the time of its operation. The primary pollution source was the superheated water injection process, while the principal receptor is the River Tigris. Now that the plant is idle, this source is absent.

Following the June 2003 sulphur fire, initial investigations indicate that short damage to vegetation was severe close to the plant but there is no evidence of widespread or significant long-term damage. Rainwater and drainage ponds and gullies close to the sulphur processing and acid contain hazardous levels of acid. Runoff from these areas may be affecting local water quality. There is regional moderate groundwater contamination by sulphate and hydrogen sulphide, but much of this may be naturally sourced.

The site in its current state represents a low risk to human health and the environment principally due to the acidic surface water ponds, but in the absence of corrective action, the hazard levels may be elevated after some decades.

الخلاصة:

كان موقع المشراق عنوانا لكثير من البحوث العلمية التي اجريت للفترة قبل وبعد حرب العراق في ٢٠٠٣. فقد تم اجراء خمسة زيارات الى موقع كبريت المشراق اثنتان في ٢٠٠٣، كزيارة استطلاعية واثنتان في ٢٠٠٤، وواحدة في ٢٠٠٥ لسحب عينات الفحص والتحري الدقيق.

بينت الدراسة المكتبية ونتائج التحاليل المختبرية على نماذج التربة والمياه السطحية والجوفية في الموقع ان التلوث ملحوض في المنطقة اثناء اشتغال المعمل وان المصدر الاساس للتلوث كان من حقن المياه الساخنة في باطن الارض وان المستلم الاساسي (principal receptor) هو نهر دجلة، وبتوقف المعمل يغيب مصدر التلوث.

بينت التحريات الابتدائية التي اعقبت الحريق الهائل الذي شب في الموقع في حزيران ٢٠٠٣ حدوث تدهور للغطاء النباتي لمنطقة محدودة محيطة بالمعمل ولايوجد اثر لانتشار التدهور للغطاء النباتي على مساحات ابعد او تدهور مستمر (long-term damage). ان انسياب وجريان مياه الامطار والمياه المتجمعة في الاحواض وقنوات المياه القريبة من مناطق تكدس الكبريت وانتاج الحامض وما تحتويه من نسب عالية وخطرة من مستوى الحامضية تكون ذات تاثير على نوعية المياه المحلية . وكما تبين الدراسة هناك تلوث في المياه الجوفية بالكبريتات وكبريتيد الهيدروجين ، ولكن معظم هذا التلوث يعزى الى مصادر طبيعية لها علاقة بطبيعة المنطقة. واخير ان كان لابد من الحكم على الموقع فان الموقع يمثل مستوى واطئ من الخطورة حاليا بسبب تواجد المياه الحامضية في البرك والاحواض ولكن بغياب الاجراءات التصحيحية قد يتفاقم الخطر الى مستويات عالية بعد بضعة عقود

Keywords: Sulphur, Sulphate, Al Mishraq site, Sulphur fire, Hydrogen sulphide, AL-control Geochem. Laboratories

INTRODUCTION

Broader industrial development began in the 1970s when the Iraqi government started a development programme largely funded from oil export revenues; the focus was on medium technology industries such as textiles, food production, construction materials and heavy industry including iron, steel and basic petrochemicals(Iraq Country Analysis, 2005). Higher technology goods were, and still are, largely imported.

The minerals industry grew gradually with a focus on sulphur, phosphate and potash, including post-processing of ores to produce sulphuric acid, alum and fertilizers. At its peak in the 1980s, Iraq was one of the world's largest producers of fertilizer (Mobbs, 2000).

Yet the UN sanctions, which were in place from 1990 to 2003, the 1991 conflict and other problems either curtailed or prevented the export of minerals and finished materials. As a result, large stockpiles of unsold material built up at some mining and mineral processing sites. As an example, up to 500,000 tonnes of sulphur were stockpiled at the Al Mishraq mining complex pending export (Marr, 2004)

The mining sector in Iraq was completely state owned and is dominated by two large complexes; Akashat/Al Qaim and Al Mishraq (UNEP, 2005), both of which are currently shut down due to looting, lack of spare parts, power, security and other problems.

The Al Mishraq sulphur mine and associated chemical works supplied raw sulphur, sulphuric acid, and alum (aluminum sulphate). The mining operations commenced in the 1970s and by 1983 had reportedly resulted in pollution of the Tigris River. An incident at the site (looting or sabotage) in June 2003 caused a catastrophic sulphur fire.

The present work focused on the area of the 2003 fire, sulphur storage, waste areas, and groundwater wells outside the site.

In 2004, the alum plant operated intermittently using up existing stocks of raw materials before closing down. In July 2005, the entire site was shut down and secured. As a result of the looting and under-investment, the facility is semi-derelict

SITE DISCRIPTION

The Al Mishraq sulphur mining and processing complex is located 50 km south of Mosul, in northern Iraq close to the west bank of the River Tigris, and 1.5 km west of village of Al-Safinah . Figure 1 shows the site location and surrounding land uses. The complex is spread over a 17-km^2 area and consists of a sulphur mine, a sulphuric acid plant, an alum (aluminum sulphate) plant, and associated facilities for power generation, water treatment, injection, administration and engineering. The plant operated from 1972 to April 2003 and is currently idle and partly derelict (Center of Environmental Surveys and Pollution Control, 1998).

The complex is located in an undeveloped sparsely vegetated hilly area. The open sulphur storage and waste storage areas are located in the southern compound area and is surrounded on all sides by undeveloped land. The western outskirts of the small village of Al-Safinah is approximately 1,100m east of the waste piles (Mahmood and others, 2005).

Figure 1: Al-Mishraq site location and surrounding lands

The site appears to be as an area of undulating hills and shallowly incised valleys with moderate gradients on the western half of the complex area and flat gently falling plains on the eastern half. The general topography falls from 250m above sea level to the west of the complex area down to 200m on the banks of the Tigris to the east (Carn & Krueger, 2004).

GEOLOGY AND HYDROLOGY

The ore body (the area of commercial mineralization) is over 10 km^2 in area and located at a depth of 50 - 300m. It is composed of a mixture of sulphur, gypsum and bitumen contained within limestone bedrock and is below the groundwater table (Mobbs, 2000). Groundwater flows through the ore body from the hills to the north-west into the River Tigris. Natural hydrogen sulphide springs were observed in the river prior to the start of mining (Al-Bassam, , 1984).

Rainfall generally infiltrates into the unpaved soil, stockpiles, and waste piles, recharging groundwater. Rainfall -run off when generated discharges into natural channels and eventually into the River Tigris (Ma'ala, and others, 1989).

PROCESS DISCRIPTION

The sulphur was mined by the Frasch process, where superheated water, steam and compressed air are injected into a sulphur-bearing deposit where sulphur is stripped from the returned water. Sulphuric acid was used to clean bitumen and other minerals from the sulphur and the resultant waste solids and liquids were deposited on-site to form large mounds dispersed in an area of more than 1 km^2. The waste piles contained up to 70% sulphur in various mineral forms (Center of Environmental Surveys and Pollution Control, 1998)

The purified sulphur was stockpiled next to a rail yard for export. In March 2003, the stockpile volume was approximately 500,000 m^3. Production effectively ceased in March 2003 and the site was comprehensively looted over the period April to July 2003.

In June 2003, a fire started by looters destroyed a large volume of the purified stockpile and the adjacent waste piles.

The fire was started by arsonists on June 25th 2003 and burned continuously for a month, although it was largely under control by 8th July. Reports of the sulphur volumes burnt range from 300,000 to 400,000 tones (Mahmood and others .2005).

The fire was eventually contained by a combination of isolation by earth man-made embankments burial with earth and foam smothering. The state of the sulphur stockpile after the fire indicates an approximate 70% loss in area (GEOSURV. 2005).

Burning of pure sulphur produces corrosive and toxic sulphur dioxide gas and because of the high concentrations of that gas generated by the fire, it was present as an aerosol (white smoke/fumes), forming acid rain.

Satellite image tracking of the smoke plume showed the sulphur dioxide (SO_2) cloud dispersing generally to the southeast; however, on some days it was also dispersed northwards. Elevated SO_2 concentrations detected over 200 km distant (Mahmood and others 2005)

At the local level, 25 villages and 3 towns were badly affected, with many hospital reports of respiratory problems and at least two deaths. Media reports at the time of the fire indicate that extensive damage occurred to wheat crops near the fire. It is believed that this was a result of acute acid burns to the exposed plants, resulting in plant death and stunted growth (Riadh. et al, 1983).

During the mining operations, a portion of the superheated water mixture was not recovered and instead leaked laterally underground and into the river as sulphur springs, thereby polluting the river. In a 1983 report, the sulphur springs were reported as fountains springing from the riverbank and reaching a height of up to 50m, indicating very high flow rates and pollution loads. Later changes in mining methods and the installation of subsurface cut-off walls reduced but did not eliminate the flow of sulphurous water into the Tigris (Al-Bassam,, 1984).

SITE CHEMICALS

The most important chemicals and material present at the Al Mishraq complex are;

- Pure sulphur
- Aluminum sulphate
- Asphaltenes (bitumen)
- Sulphuric acid
- Hydrogen sulphide

Sulphur, aluminum sulphate and bitumen have relatively low toxicity to humans. Sulphur is present naturally in food and in low concentrations; it is an important element for human health. Aluminum sulphate is used in food preservatives, cooking and water clarification and purification (Ma'ala, and others, 1989). Bitumen, whilst toxic to ingest, is used universally in road construction (Center of Environmental Surveys and Pollution Control, 1998).

Sulphuric acid is of concern primarily due to its corrosive effects. The acid plant is expected to contain significant quantities of residual acid in pipes, tanks and basins. Acid may also be present in surface water drainage and leachate from the sulphur waste piles (Ma'ala, and others. 1989).

Hydrogen sulphide is a toxic gas, which is naturally present in the groundwater of Al Mishraq. Desk studies reported that at least four local village wells are no longer used due to elevated hydrogen sulphide levels (UNEP, 2005). Hydrogen sulphide may also be present in the waste sulphur piles if anaerobic conditions prevail (Ma'ala and others, 1989).

SAMPLING

Five visits to the site were conducted twice in 2003 for general fact-finding, twice in 2004, and once in 2005 for detailed sampling and monitoring.

The work focused on the area of the 2003 fire, sulphur storage and waste areas. Groundwater wells outside the site were sampled and monitored with a portable instrument.

a. Soil Sampling

The sampling techniques used generally involved the collection of surface soils and substances. A total of 22 soils were collected. Sampling depths recorded range from surface with no depth range specified (but assumed to be 0-0.3m), to a maximum depth of 3m below ground level. Five of the 22 samples were taken from depths of approximately 1m and more.A lithological description of the samples submitted to the laboratory is given in table ١.

b. Water Sampling

A single water sample was collected from water well on site. A further 9 water samples were collected including one from the river. A number of duplicate water samples were also submitted. Five samples from local village wells outside the site at a distance of 1-5 km from the site boundary. Four out of five wells were reported by the local population as unusable wells due to high sulphate or hydrogen sulphide levels. Table 2 summarizes ground water analyses activities.

LABORATORY ANALYSIS

Samples collected during the site investigations were put into separate containers and labeled with a unique sample number. Plastic tubs of 500 gm or 1kg capacity were used for the collection of soil and hazardous substance samples to be analyzed for metals and inorganic parameters. Wide neck glass jars of 250gm capacity were used for the storage of samples destined for the analysis of organic parameters.

Water samples destined for metals and most inorganic analysis were collected in 250ml plastic bottles. Samples for organics analysis were collected in 500ml amber glass bottles. Where practicable each sample bottle was filled completely to the brim with no headspace in the field to minimize losses through volatilization from the sample (Iraq Digest - Mishraq fire, 2008)

On completion of the fieldwork, samples were shipped by courier to the project contract laboratory, ALcontrol Geochem Laboratories, Chester, England with the completed Analysis Request Form and Sample Custody Sheet.

In line with current best practice, all testing methods employed by the laboratory have a quality control component, which is dependent upon the type of analysis and any specifications as required by the client. The Quality Control protocols routinely employ blanks, sample spikes, and replicates within the analytical procedure.

Where possible, ice packs were added to the cool box before the courier collected the box for shipment.

. The analytical parameters determined and the numbers of samples analyzed by sample type were as follows:

Soils

A total of 22 soil samples from the site were analyzed as indicated in figures 2 through 4 for the following analysis:

-Metals (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc).

-Extractable Petroleum Hydrocarbons (EPH) (formerly known as Diesel Range Organics (DRO) carbon range: C10-C40)

-Gasoline Range Organics (GRO) carbon range C4-C10

-GRO carbon range C10-C12

- Volatile Organic Compounds (VOC): benzene, toluene, ethyl benzene, m & p xylene, oxylene & methyltert-butyl ether (MTBE)

-Total sulphur, and -Total sulphate

-pH, and conductivity

-Anions: carbonate, chloride, fluoride, nitrate, nitrite and phosphate.

-Cations; calcium, magnesium, potassium and sodium, as shown in figure 4(a) and 4(b)

Waters

A total of 10 water samples including 1 groundwater sample and 1 duplicate were analyzed as in figures 5 through 7 for the following analysis:

-Metals (antimony, arsenic, beryllium, cadmium, chromium, copper lead, mercury, nickel, selenium, silver, thallium and zinc)

-Extractable Petroleum Hydrocarbons (EPH) (formerly known as Diesel Range Organics (DRO) carbon range: C10-C40)

- -Gasoline Range Organics (GRO) carbon range C4-C10; - GRO carbon range C10-C12.

-Total sulphate, -Soluble sulphate, and -Free sulphur

-Volatile Organic Compounds (VOC): benzene, toluene, ethyl benzene, m & p xylene, o xylene & methyltert-butyl ether (MTBE)

-Hardness, total dissolved solids and total suspended solids.

-Anions: carbonate, chloride, fluoride, nitrate and nitrite

-pH and conductivity.

-Cations: calcium, magnesium, potassium and sodium.

RESULTS

No guidance values have been published in Iraq. Yet tier 1 process guidance values from Netherlands (Lenore and others, 1999) and from Australia (Spatial Planning and the Environment, 2000) have been used.

a. Soil

Criteria are not set for sulphate or total sulphur in either the Dutch or Australian systems. However, the Australian jurisdiction has set “Interim Urban” levels for sulphate and total sulphur intended for the protection of built structures. The Interim Urban sulphate level of 2,000mg/kg was exceeded on 21 of 22 soil samples. The total sulphur Interim Urban level of 600mg/kg was exceeded on all occasions (22/22).

The soil in the Al Mishraq area contains naturally high levels of native sulphur and sulphate, primarily gypsum. In the mine area, elevated concentrations of bituminous compounds are also found naturally. Accordingly, it would be wrong to conclude that the site is contaminated because of these compounds are present. Laboratory analysis of soil indicates levels of sulphate of up to 265800mg/kg (figure 4 a). This is thought to indicate that the soils or the waste contain a high percentage of gypsum. Concentrations detected have been compared against the two sets of example Tier I screening criteria (guidance values). Those contaminants of concern that exceeded the screening criteria are presented in Table 3. None of the Australian Tier 1 screening criteria were exceeded.

b. Waters

Laboratory analysis of surface water indicated high levels of sulphates and carbonates. Water contamination by sulphur compounds is also a natural process in the Al Mishraq area. Sulphur compounds known to exist naturally including sulphates and hydrogen sulphide. Much of what was analyzed could therefore have occurred naturally.

The natural and induced contamination was differentiated on the basis of pH. What is not expected naturally is strongly acid water, i.e. pH 4 or below. The natural baseline for surface waters for the River Tigris was recorded as pH 8.4. In contrast, four surface water ponds and channels in the vicinity of the sulphuric acid plant and waste piles had pH values of 0.6, 0.7, 2.2 and 4.1 indicating highly acidic sources. The sample with a pH of 0.6 also had elevated levels of metals including copper, lead, arsenic, chromium and beryllium. This is to be expected in such an acidic sample as metals are liberated from soil minerals under acidic conditions.

The area of acidic surface water is located approximately 4 km from the River Tigris and is connected to the river by two steep sided gullies. The gullies appear to be mainly dry and the drainage rate during March 2005 visit was limited (less than 0.lm3/second). Significant short-term flows could however be expected during the rare rainy periods.

Sulphur and mineral deposits lining the drainage canal indicate water pollution has been ongoing for many years. As the plant had been shut down for two years, the surface water sample is not effluent from ongoing operations.

The acid is therefore either residual effluent mixed with rainwater or ongoing acid drainage due to sulphide decomposition. In either cases, the surface water in the vicinity of the sulphur treatment complex is unlikely to regain a balanced pH in the short to medium term.

Water samples analytic results have been compared against the two sets of example Tier 1 screening criteria (guidance values) for groundwater. The contaminants of concern that exceeded the screening criteria are presented in tables 4 and 5.

Conclusions

- Mineral extraction industries may recover partially, if at all. The work done in this study provide firm evidence that the damage to the environment from the Al Mishraq fire was not permanent and natural recovery is very well advanced after two years. The temporary nature of the damage is probably due to the soil buffering capacity, which can neutralize episodic acidic rain and surface water and thereby protect plant root systems from permanent damage.

Leaves and stems exposed to the acidic aerosols will have been damaged at the time of the fire, but plants survived and grew back whilst future crops planted or sown will be largely unaffected.

- The maximum detected concentration of chromium in one soil sample exceeded the screening criteria 3-fold implying that a pocket or pockets of moderately high contamination are present. The very limited

- High concentrations of minerals occur naturally in the Al Mishraq area and any assessment of chemical contamination and wastes disposed at the site needs to consider this.
- Only a very small numbers of soils (1 of 26 samples: sample No.6) exceeded the Dutch Tier 1 screening criteria for their respective chemical parameters. The criteria are only exceeded for 2 of 13 metals (chromium and nickel). None of the hydrocarbon criteria is exceeded. None of the analytical parameters determined in the soils exceeded the Australian Tier 1 screening criteria.
  nature of the site investigation does not enable the lateral or vertical dimensions of such contamination sources to be delineated.
- A small number of water samples (1 of 10: sample WI) exceeded the screening criteria for 6 to 8 metals (Australian and Dutch respectively). The concentrations of the metals nickel and lead exceeded their Dutch screening criteria concentrations by more than 150-fold and 10-fold respectively.

- Acid drainage into the Tigris may affect local water quality but the scale of the river flow compared to the drainage gullies indicates that the impacts would be localized due to dilution and the buffering capacity of the river water.

Acronym and abbreviations

bgl : Below Ground Level

BTEX: Benzene, Toluene, Methylbenzene, and Xylem

DRO: Diesel Range Organics

EPH: Extractable Petroleum Hydrocarbons

GCMs: Gas Chromatography Mass Spectrometer

GRO: Gasoline Range Organics

IR: Infra Red

ISO: International Standards

PCBs: Poly Chlorinated Biphenyls

PID: Photo Ionization Detector

SVOCs: Semi Volatile Organic Compounds

VOCs: Volatile Organic Compound

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence spectroscopy

Table 1 Description of Soil Samples

Sample no.	Depth m bgl	Description
1	0-0.2	Loose dry grey sandy clayey SILT with a little gravel up to 20mm size
2	1.0	Loose damp light yellow-brown sandy SILT with brown inclusions of clay-like consistency
3	2.2	Loose fine silty orange-brown sandy clayey SILT with occasional small angular stones
4	1.5	Dry medium-dark brown clayey sandy slightly cohesive SILT with occasional gravel up to 25mm size
5	0.15	Light to medium brown sandy SILT
6	0.2	Light brown clayey sandy SILT
7	0.1	Light brown clayey sandy SILT with occasional vegetation
8	0.1	Light brown clayey sandy SILT with possible bitumen, occasional medium gravel and occasional vegetation
9	0.1	Medium brown clayey sandy SILT with occasional medium gravel
10	0.1	Light brown clayey sandy SILT with occasional medium gravel
11	3.0	Dark grey wet silty Clay
12	0.15	Medium grey green sandy SILT with occasional fine gravel
13	0.1	Light brown sandy clayey SILT with occasional medium gravel
14	2.3	Dark grey wet silty CLAY
15	0.15	Medium grey green sandy SILT with occasional fine gravel
16	0.1	Light orange brown sandy SILT
17	0.1	Light greenish grey sandy SILT
18	0.2	Light to medium grey silty clayey SAND with occasional fine to medium gravel
19	0.15	Orange brown silty SAND with occasional greenish grey fragments
20	0.15	Light brown clayey sandy SILT with occasional fine to medium gravel & occasional
21	0.2	Medium brown clayey sandy SILT
22	0.15	Medium brown clayey sandy SILT

Table 2: Al-Mishraq region groundwater field monitoring results

Sample	General sample location	Depth to water m	On-site monitoring results			
			Temp.(^{o}C)	pH	EC (m/s)	TDS (g/l)
W1	5 km from the S complex boundary in the south direction. Nasser village, unusable well, the location was affected by the 2003	10	19.8	8.2	2.47	1.23
W2	2 km from the complex boundary in the east. Al-Safina village. Unusable well	1.5	19.5	7.0	3.4	1.70

W3	2 km from the complex boundary in the southwest direction. Nasser village, well usable for irrigation.	20	23.8	6.7	7.01	3.46
W4	>3.5 km from the complex boundary in the west direction. Zahra village, well unusable for eight years.	5.7	19.1	7.7	11.23	5.6
W5	>1 km from the complex boundary in the west direction. Nina'a village, a new well unusable till now due to the high sulphur content and H_2S gas.	>50	23.7	7.6	6.06	3.02

Table 3: Contaminants of Concern in Soils- Dutch Criteria

Contaminant of Concern	Tier I Screening Criteria(mg/kg)	Maximum concentration (mg/kg)	Number above applicable criteria
Chromium	380	1082	1/26
Nickel	210	310	1/26

Table ٤: Contaminants of Concern in Groundwater - Dutch Criteria

Contaminant of Concern	**Tier I Screening Criteria (µg/l)**	**Max. Concentration (µg/l)**	**Number above applicable criteria**
Arsenic	60	143	1/10
Beryllium	15	84	1/10
Cadmium	6	21.5	1/10
Chromium	30	7287	1/10
Copper	75	2704	1/10
Nickel	75	11470	1/10
Lead	75	123	1/10
Zinc	800	10320	1/10

Table 5: Contaminants of Concern in Groundwater - Australian Criteria

Contaminant of Concern	**Tier I Screening Criteria(µg/l)**	**Max. Concentration (µg/l)**	**Number above applicable criteria**
Arsenic	7	143	1/10
Cadmium	2	21.5	1/10
Copper	2000	2704	1/10
Nickel	20	11470	1/10
Lead	10	123	1/10
Zinc	3000	10320	1/10

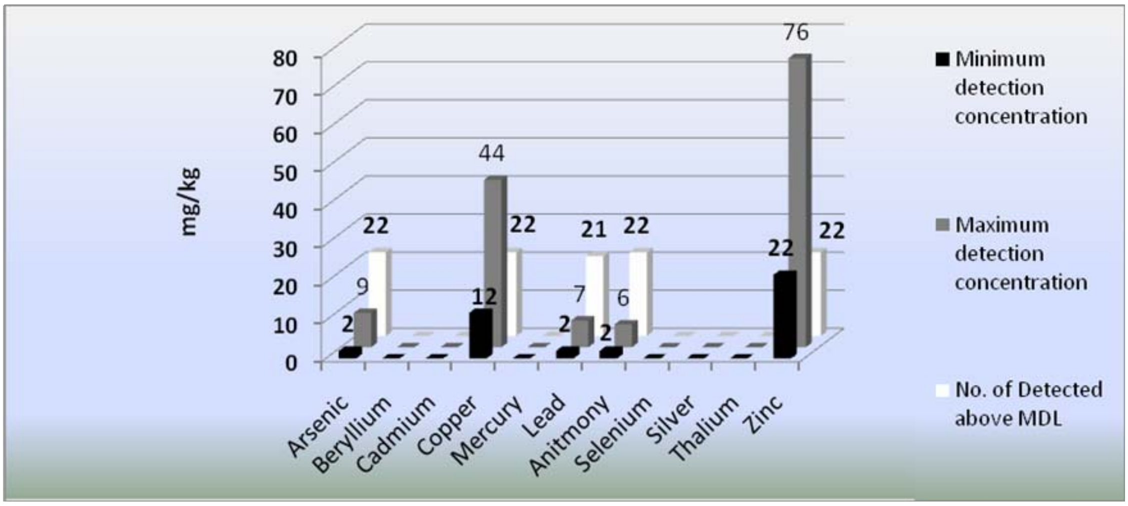

Figure 2 (a) Maximum and minimum detected heavy metal concentrations in soil, and number of samples detected above the minimum detection level of the analytical equipment used.

Figure 2 (b) Maximum and minimum detected heavy metal concentrations in soil, and number of samples detected above the minimum detection level of the analytical equipment used.

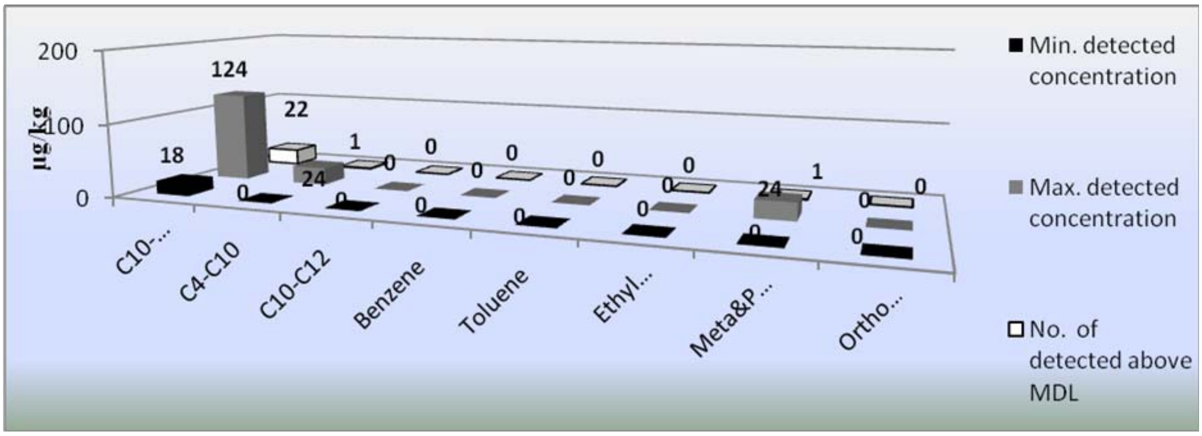

Figure 3 Maximum and minimum detected Volatile Organic Compounds (VOCs) and hydrocarbons concentrations in soil

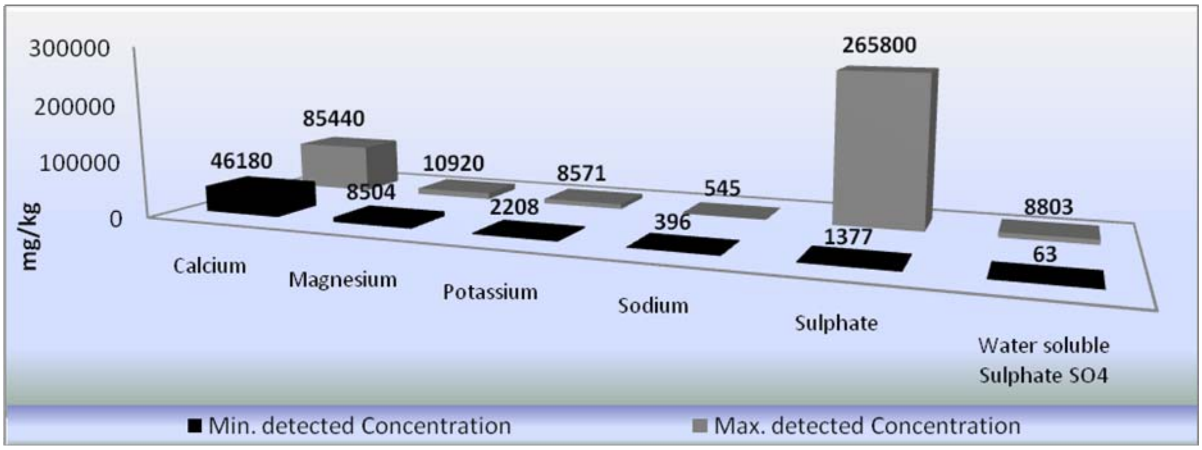

Figure 4 (a) Maximum and minimum detected Concentrations of other parameters in soil

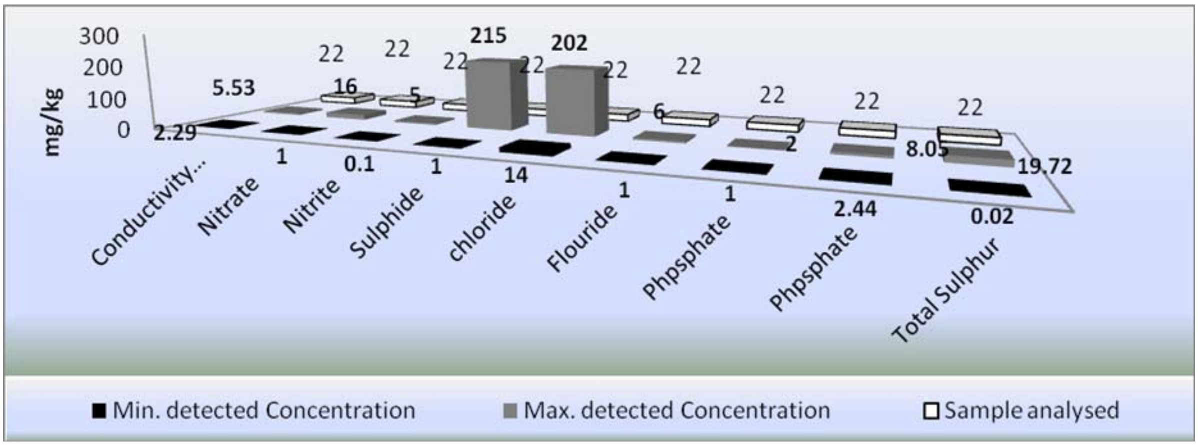

Figure 4 (b) Maximum and minimum detected Concentrations of other parameters in soil

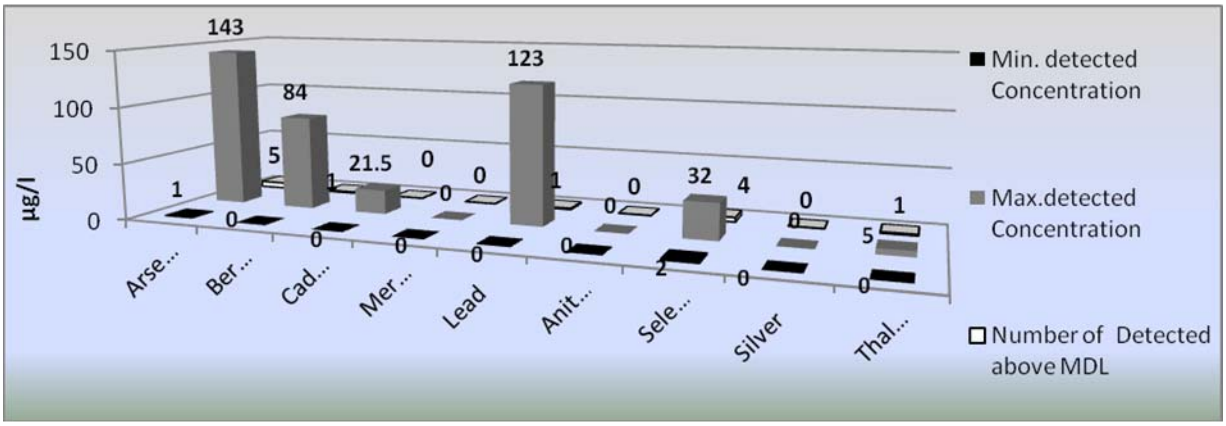

Figure 5 (a) Maximum and minimum detected heavy metal concentrations in water and number of samples detected above the minimum detection level of the analytical equipment used.

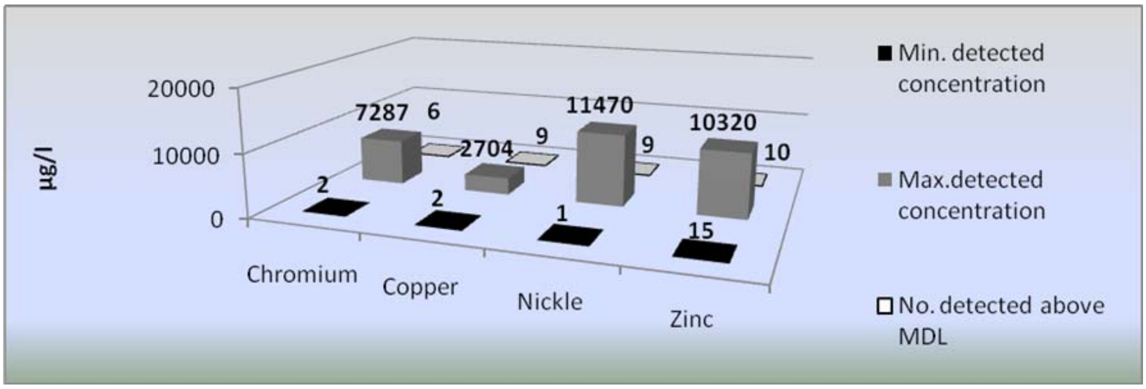

Figure 5 (b) Maximum and minimum detected heavy metal concentrations in water and number of samples detected above the minimum detection level of the analytical equipment used

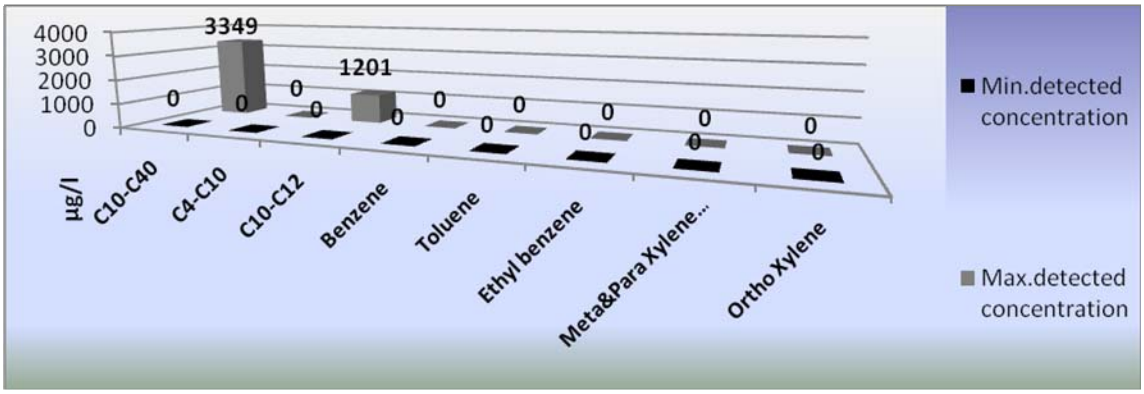

Figure 6 Maximum and minimum detected Volatile Organic Compounds (VOCs) and hydrocarbons concentrations in water

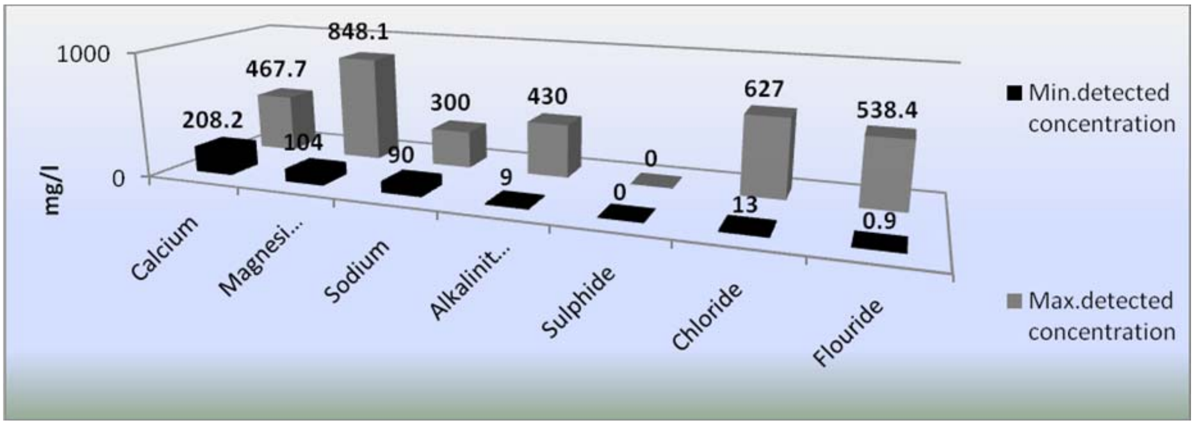

Figure 7 Maximum and minimum detected concentrations of other parameters in water

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