

Assessing the Environmental Impacts of the Ruwais Industrial Complex (RIC), the Offshore Area, United Arab Emirates BY

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Abstract: The aim of this baseline study is to assess the impacts of the Ruwais Industrial Complex (RIC) on the marine water through measurements and analysis of the trace elements concentration levels and assessing their relationship with the Ruwais Industrial Complex (RIC) activities. Also to furnish a database references for future monitoring and protection the offshore area. The results of this baseline study will help in identifying the environmental impacts of Ruwais Industrial Complex (RIC) on the marine water and provide recommendation for further comprehensive environmental impact assessment study. The geochemical associations indicate that three groups of elements were discriminated. Group one (Sr & Mg) associated with carbonates, group two are those associated with silicates fractions (Al, Fe & Mn), and the third group discriminates those elements associated and used as indicators for petroleum hydrocarbon pollution (Ni, V). The highest values of TPH were recorded near the refinery and NGL separation plant in the western part. Copper, Lead, and Zinc concentrations showed elevated concentration levels and varied considerably from one site to another. It is obvious that the shallowest station (depth is 1 m.) contains the minimum contents of TOC, TKN as well as the coarsest sand fractions. PAHs were detected at lower concentration (below detection level) as compared to the calibration standards (EPA, 1999). PCBs generally increases towards the north western part with highest values recorded at station five.

Key words: Pollution; Organic; TOC; PAHs; PCBS; Hydrocarbons; Heavy metals, TKN; Ruwais and UAE.

INTRODUCTION

The Ruwais Industrial Complex (RIC) is situated on the southern coast of the Arabian Gulf, 235 km west of Abu Dhabi city (Fig. 1). The primary objective of the industrial development of the RIC is to most effectively utilize and enhance the added value of the hydrocarbon resources of Abu Dhabi. The projects making up the complex are dependent on the use of natural gas, gas liquids and crude oil as feedstock and fuel. The oil loading and export terminal at Jebel Dhana, a few kilometers west of Ruwais, lie alongside the RIC. Other facilities that exist in the RIC are an oil refinery, a separation plant, extraction plants, fertilizer plant (Ammonia and Urea), and a housing complex. The industries to be developed at the RIC will unfortunately introduce a large quantity of organic and inorganic pollutants into the marine environment with potential toxic effect on the ecosystem (Fig. 2).

MATERIALS AND METHODS

In order to achieve the above goals the surface and bottom sediments were collected from nine stations covering the study area. Each fully mixed sample was air dried under a hood at room temperature and sieved to pass a 35 mesh sieve. The objectives in determining the grain size distribution of sediment is to correlate the level of contaminants special organics to grain size, and determine the percentage of fine particles in the sediment. Statistical parameter of mean size was calculated according to the equation given by Folk (1966). Organic carbon content (TOC) was analyzed by treating 5 g of selected crushed sediment samples with 10 % HCl to remove carbonates. The washed residue is filtered and about 0.1 g of sample ignited in a Leco Carbon and Sulfur analyzer C-200. TKN was analyzed by taking 0.1mg of the dried sieved sample into a digestion

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tube. Add 2 tablets of catalyst mixture and 10-15 ml of concentrated sulphuric acid, heat the flask on the block digester until the liquid becomes clear and continue heating for another 30 min. digest a blank, omitting the sample. Determine the blank value by connecting the blank digestion flask to the distillation unit which is pre-programmed to disperse 80ml of distilled water and 50ml of NaOH were dispensed into the tube. The steam valve was opened on the kjektec and distilled for approximately 4 minutes. The distillate was titrated with standardized HCL acid. TPH was analyzed by taking 20 g sample of dry sediment was acidified to a low pH i.e. 2 with hydrochloric acid. Mangensum sulfate monohydrate is then added to dry the sample. Then petroleum hydrocarbons were extracted from the sample using Hexane solvent. The residue was weighed, and then dissolved in fluorocarbon-113. Infrared analysis of the extract at 2930 cm^{-1} was performed by Nicolet Fourier Transform Infrared (FTIR) Magna - IR 560 Spectrometer. PCBs were analyzed by taking 5 g of the solid sediments was mixed with equal quantity of anhydrous sodium sulphate (to absorb the water moisture in the sediments) then was placed in an extraction thimble. Then Approximately 70 ml of the extraction solvent (1:1 Hexane: Acetone) used to extract the sample using automatic soxhlet extraction (2050 Soxtec, Fosstector) for two hours (Boiling 1hrs and Rinsing 1 hrs.). An aliquot of the extract i.e. 1 mL was injected to GC/ECD from GC auto sampler 2 mL vial. PAHs was analyzed by taking 5 g of the sea bed sediment was mixed with equal quantity of anhydrous sodium sulphate (to absorb the water moisture in the sediments), placed in an extraction thimble. Then the extract was transferred into a concentrator and evaporates under nitrogen to reduce solvent to about 0.5 ml (using TurbonVap Evaporator, Zymark apparatus). Then 5.0 ml of acetonitrile was added and evaporate again till 2 ml was reached. An aliquot of the extract i.e. 20 mL was injected into HPLC, and the PAHs compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously. Heavy metals were analyzed by inductively coupled argon plasma-atomic emission spectrometer (ICP-AES), Varian, Vista - MPX-CCD, simultaneous, with background correction, auto-fit multi-calibration curve fitting, signal to background ratio signal to root background ratio. This method describes the simultaneous determination of elements such as (Al, Ba, Cr, Cu, Fe, Mn, Ni, P, Pb, V, and Zn) in geological and environmental samples and may be applicable to other matrices with appropriate sample preparation technique. Weight about 0.5 gram of the samples in to a beaker moister the sample with about 5ml of distilled water. Add 3ml of HCL and 9ml of HNO₃ and digest the mixture in hotplate for 30 minutes. Then cool the sample and filtrate the solution .after that quantitatively transfer the contents and make up to 50 ml in a volumetric flask with deionized water. Blank must be prepared at the same time an under the same conditions. Heavy metals were analyzed for the water and sediments. Total Petroleum Hydrocarbon (TPH), Poly-Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyl (PCBs), Total Organic Carbon (TOC) and Mean Grain Size (Mz) were measured only for the sediments. Heavy metals (Cu, Ni, V, Al, Fe, Sr, Ca, Mg and Ba) were analyzed for their total and leachable phases. The detection limits of our analytical compounds have been done as reference material analysis by Al katheeri (2004), Al Darwish *et al.* (2005), and Esam Abdelgawad *et al.* (2007). Analyses of samples were done at the Acme Analytical Laboratories, Canada. TPH analysis was carried out in the CLU of the UAE University according to ROPME (1999) manual. TOC, TKN, PCBs, and PAHs analysis was performed at the CLU of the UAE University.

RESULTS AND DISCUSSION

Heavy Metals Pollution:

Studies of the heavy metals describe the properties of heavy metals in the ecosystem and how can contribute the food chain which subsequently can impact to the human health and other organisms (Bloemen *et al.*, 1995). Heavy metals are dangerous because they tend to bioaccumulation that means the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment (Haynes and Johnson *et al.*, 2000). Nine sediment samples were collected from RIC during April 2001. The distribution of the total heavy metals indicates that the Al varied about five times in concentration compared with Fe which only varied about 4.6 times in concentration. Therefore, the the varied range of Al seems to be wider than Fe. The Fe exhibits variability, ranging between 0.14 to 0.65% Table II). On the other hand Al and Ca vary within ranges from 0.25 ppm and 1.27 ppm for Al and 14.54 % to 39.96 % for Ca (Table II). Among the minor elements, Mn fluctuates between 11.0 ppm and 174.0 ppm with an average of 70 ± 56.1 ppm. The other determined metals have limited deviation from the avearges. The distribution of heavy metals indicate that three groups of elements (Figs. 3&4) were discriminated. Group one includes those elements associated with carbonates (Sr & Mg). Group two are those associated with silicates fractions (Al, Fe & Mn). The third group discriminates those elements associated and used as indicators for petroleum hydrocarbon pollution (Ni, V). In the present study, the leached portion of the metals (Fig. 5) was determined in order to

investigate the easy-removable portion of the sediments. The average values for the L/T % calculated for the studied metals rank in descending order as follows: Cu > Mg > Zn > Mn > Ca > Ni > V > Sr > Fe > Al. The low L/T ratios for the aluminum specifies the conservative behavior of Al. On the other hand, Ca illustrates a wide range of L/T ratios. The maximum ratio is 96.3% and the minimum is 16.8%. This wide range reveals the fact that CaCO₃ can be easily dissolved with weak acid during extraction of the leached portions, besides the differentiated solubility performance of different carbonate minerals. The distribution trends of both leached and total metals shows that the leached phases almost follow the trends of their total metals. L. Sr at station number eight decreases while the total Sr increases. This may indicate that L. Sr could be associated with organic matter rather than siliciclastics/carbonate fractions. Ca attains different behavior than the other metals, where the leached portions do not follow the increasing or decreasing of the total Ca. As mentioned above, the reason for that is the solubility performance of different carbonate minerals as well as the variation of Ca concentrations contained by different minerals. The cluster analysis is also performed in order to study in more details the geochemical associations between metals. The resulting tree diagram (Fig. 6) elucidates the associations of two groups of metals. The first one assembles Ni, Cu, V and Fe together. The second group discriminates Al, Mn and Mg. These two groups cluster with Zn and Sr at higher levels. Ca on the other hand disbands from the other metals, and is clustered with them at higher level. This multivariate statistical analysis confirms the correlations between metals.

Quantifications of metal pollution:

In order to compare present study with the background values, the enrichment factor (EF) is calculated (Fig. 7). The enrichment factor (EF) value is assumed to be a measure of heavy metal enrichment. It consists of 7 grades ranging from uncontaminated to extremely contaminated. In fact, the major elements (Al, Fe, Ca and Mg) in addition to Sr are not considered because these metals are lithogenic metals rather than man-made. The calculated enrichment factor (EF) indicate that stations 1, 5 and 7 can be classified as "Uncontaminated to moderately contaminated" for the elements Cu, Ni, while only stations 1 and 5 is designated as "Uncontaminated to moderately contaminated" Zn. The calculated (EF) for Mn indicate that all stations are designated as "Uncontaminated". Sr has high (EF) values, however as mentioned above it is considered as a lithogenic element associated with carbonate minerals mainly as aragonite.

Hydrocarbon and Organic Pollutants:

Hydrocarbons are important components of land derived organic inputs towards coastal areas. Studies on hydrocarbons in the aquatic environment can be based on the analysis of the water column, organisms and sediments (Medeiros *et al.*, 2005). Nine sediment samples were collected from nine stations covered the study area, aiming to estimate the concentration of the total organic carbon (TOC), total petroleum hydrocarbon (TPH), the poly-aromatic hydrocarbons (PAHs) and the polychlorinated biphenyl (PCBs). The results of grain size (Mean Size MZ in μ), total organic carbon (TOC) and total kjeldahl nitrogen (TKN) in the sediments at different stations. The total organic carbon value indicates the sum of organic carbon and represents a measure for all organic substance in sediments. These substances can be of natural organic like humic acid, mineral oils, pesticide, polycyclic aromatic hydrocarbon or chlorinated organic compounds. Industrial waste effluents may contain carbon containing compounds with various toxicity levels (Dell'Anno *et al.*, 2002). The TOC is mostly come from natural and anthropogenic contributions, such as fertilizers, pesticides, and surfactants, solvents coming from their direct use or from inefficient sewage treatment plants. Ruwais Industrial Complex (RIC) indicates that the TOC is ranging between 1.02% and 0.16% with an average of 0.37% (Table I). It generally increases towards the NW of the study area (Fig. 8). Typically some organisms fix nitrogen to either NH₄ or organic nitrogen, the term is used ammonification (nitrogen fixation); other organisms nitrify the NH₄ to NO₃, the term is used nitrification. Both, nitrification and ammonification convert gaseous nitrogen into bioavailable chemical forms (Wilson *et al.*, 1993). TKN is ranging between 0.06% and 0.02% with an average of 0.05% (Table I). It is obvious that the shallowest station (depth is 1 m.) contains the minimum contents of TOC, TKN as well as the coarsest sand fractions (Fig. 9). The correlations between different TOC and depth as well as between TPH and mean grain size (Figs. 10, 11 & 12) indicate that TOC tends to be concentrated in the fine fractions as hence it increases with depth in the offshore region. TPH is a mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons. These different compounds can expose from many sources, including petroleum extraction, transportation refining and consumption (Huang, 2005). Generally, TPH was found to be relatively high in the sediment samples of the western stations ranges from 150 mg/kg -1700 mg/kg (Table I) as compared to the TPH average concentrations of the bottom sediments in the Arabian Gulf. However, TPH generally increases towards the western parts of the study area (Fig. 13). The highest values were recorded at stations 1 & 2 which are located, near the

refinery and NGL separation plant. PAHs were detected at lower concentration (below detection level) as compared to the calibration standards (EPA, 1999). The concentration and distribution of aliphatic and polycyclic aromatic hydrocarbons (PAHs) were investigated in biota from four countries UAE, Qatar, Bahrain, and Oman (Tolosa *et al.*, 2005). The levels of TPH and PAHs in biota were relatively low compared to world wide location contaminated by oil. The concentration of chlorinated hydrocarbons (PCBs) in marine biota (fish and various bivalves) from Arabian Gulf and Gulf of Oman, collected from UAE, Qatar ,Bahrain and Oman (De Mora *et al.*, 2005). The presence of PCBs is a reflection of industrial contamination, unfortunately these properties may damage the organisms and human by accumulation in the liver, adipose tissue, brain and skin (Faroon, 2003). PCBs generally increases towards the north western part with highest values recorded at station no. five ranging between 8.03 mg/Kg to 64.49 mg/Kg with average concentration 23.84 mg/Kg (Table I & Fig. 14).

Statistical Discrimination of Scenery Similarity:

In order to study the similarities between different stations with respect to the metals concentrations, TOC, TKN, mean grain size and depth of different stations, the correspondence factor analysis (CFA) is performed Fig. (16). It discriminates three groups of samples. Group 1 mainly retains stations 1 and 5. The total and leached Zn allows a valid discrimination of these stations. Group 2, includes stations numbers 2, 3 and 6. TOC, TKN, M_z , L Al and L. Fe control this group respectively. Group 3 concerns stations numbers 7, 8 and 9. Mn, Mg (total and leached), leached Ni, Cu and Ca and total Al discriminate this group. On the other hand station 4 is not included in any of these three groups. The grouping of stations based on CFA is well-matching the spatial distribution of stations. Stations 1 and 5 are both located offshore to the east in front of the Liquid Products Jetty. Stations 7, 8 and 9 locate to the west of the Ammonia and Urea Berths and off the outfall channel. Stations 6, 2 and 3 locate near the cargo terminal, Coastal Tanker Jetty and Refinery and cooling water outfall. On the other hand station 4 locates near the water tanker.

Conclusion: It is concluded that in spite of the industrial activities at RIC, the offshore sediments is still classified in general as uncontaminated sediments with except to the area in front of Liquid products Jetty which is classified as uncontaminated to moderately contaminated area. Boron, Nickel, and Strontium are at the limits of their average concentration standards. Whereas, Copper, Lead, and Zinc concentrations showed elevated concentration levels and varied considerably from one site to another. The elevated concentrations were recorded near the outlets of the refinery and ammonia outfalls exits. The Total Organic Carbon (TOC) tends to be concentrated in the fine fractions which increases with depth in the offshore sediments(range from 0.16 wt % - 1 wt %) with average 0.37wt %. The Total Petroleum Hydrocarbon (TPH) was found to be relatively high in the western part of the complex (range from 150-1700 mg/kg). Polycyclic Aromatic Hydrocarbons (PAHs) were detected at lower concentration (below detection level) as compared to the calibration standards. The concentration of polychlorinated hydrocarbons (PCBs) generally increases towards the northwestern part with highest values recorded at station no. five ranging between 8.03 mg/Kg with average concentration 23.84 mg/Kg. It is recommended that a long-term monitoring network plan for the effluents at RIC as well as guidelines for assessing on-going and proposed industries including the assimilative capacity of the study area should be established.

Table 1: Concentrations of TPH, TOC, TKN, TPCBs, and M_z in the Ruwais Industrial Complex (RIC).

Station No.	TPH mg/Kg	TOC wt%	TKN mg/Kg	TPCBs mg/Kg	M_z (pHl)
1	1.73	1.00	0.055	8.03	5.3
2	1.47	0.23	0.057	24.46	2.35
3	1.18	0.22	0.05	9.62	1.77
4	1.00	0.16	0.037	29.38	1.33
5	1.03	0.35	0.06	64.49	1.43
6	0.65	0.39	0.059	19.34	2.13
7	1.42	0.23	0.049	15.79	2.67
8	0.13	0.37	0.031	15.54	3.73
9	0.05	0.35	0.023	27.92	1.87
Average±STDEV0.	96±0.58	0.37±0.25	0.047±0.01	23.84±16.98	2.51±1.27

Table 2: Concentrations of trace elements in the Ruwais Industrial Complex (RIC).

Station No.	Cu (ppm)	Mg (%)	Zn (PPM)	Mn (ppm)	Ni (ppm)	V (ppm)	Sr (ppm)	Fe (%)	Al (ppm)
1	8	1.83	50	84	17	22	2.922	0.55	0.73
2	2	0.85	19	11	5	7	3.132	0.17	0.25
3	2	0.96	19	33	3	6	3.241	0.17	0.47
4	2.4	0.87	3	24	4	7	4.417	0.14	0.27
5	13	1.38	52	71	15	24	2.278	0.53	0.69
6	3	1.37	16	59	6	11	2.846	0.28	0.66
7	12	3.04	14	144	12	21	1.58	0.53	1.56
8	6	6.57	12	174	13	30	4.187	0.65	1.27
9	3	1.2	10	30	5	11	0.3302	0.21	0.39
Average±STDEV	5.71±4.35	2.01±1.84	21.67±17.34	70.00±56.10	8.89±5.33	15.44±8.88	2.77±1.26	0.36±0.20	0.70±0.45

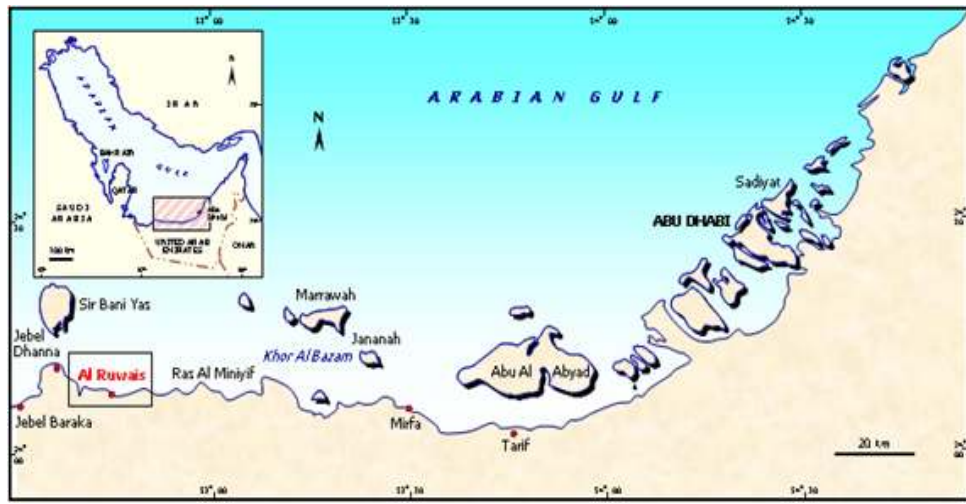


Fig 1: Location map of the Ruwais Industrial Complex (RIC).

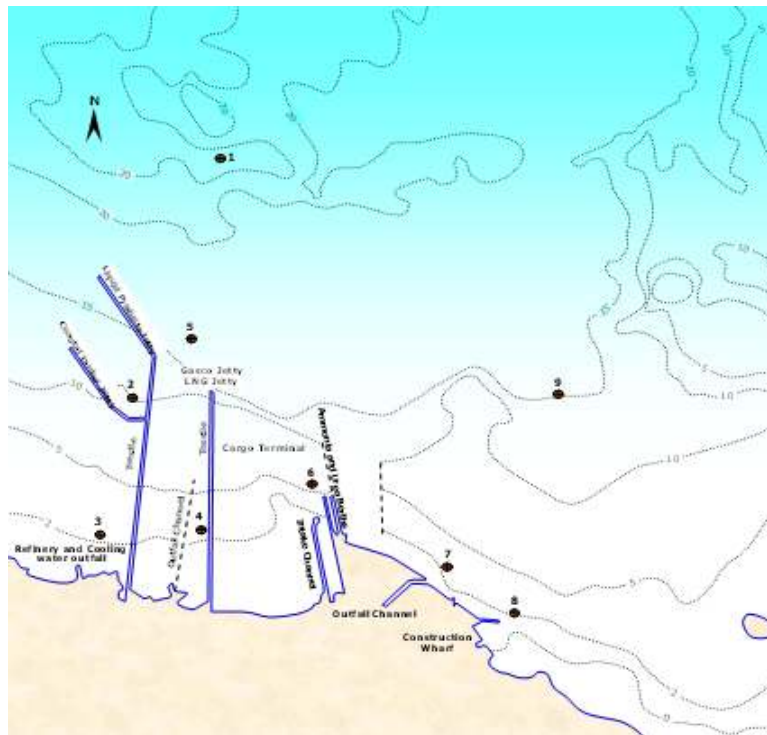


Fig. 2: Area of Study showing sampling locations.

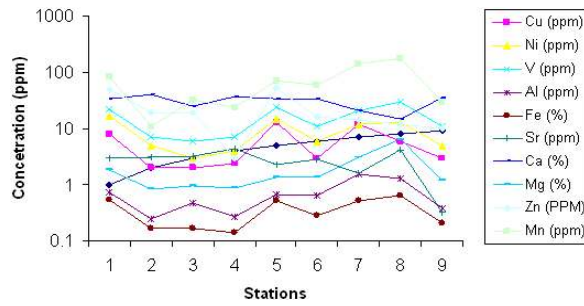


Fig. 3: Distribution of total heavy metals at different stations.

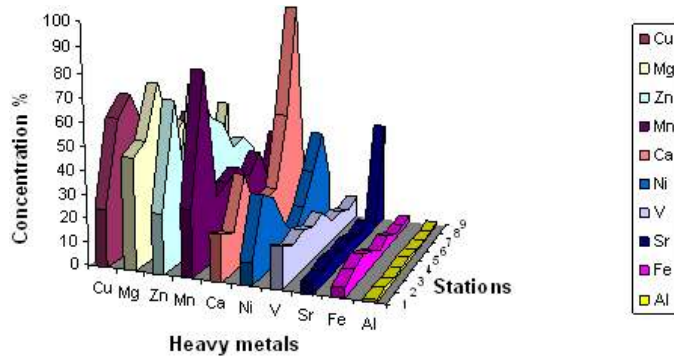


Fig. 4: Ranking of the studied leached and total heavy metal at different stations.

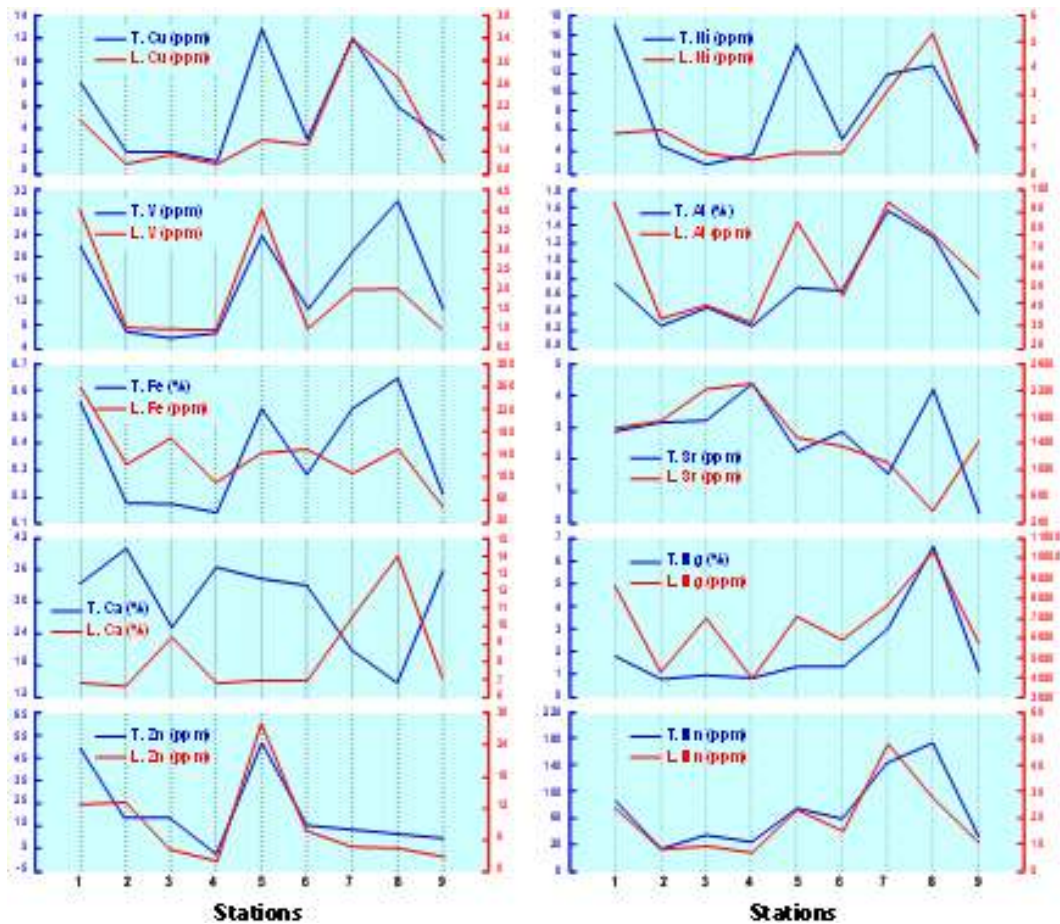


Fig. 5: Distribution of leached and total heavy metal at different stations.

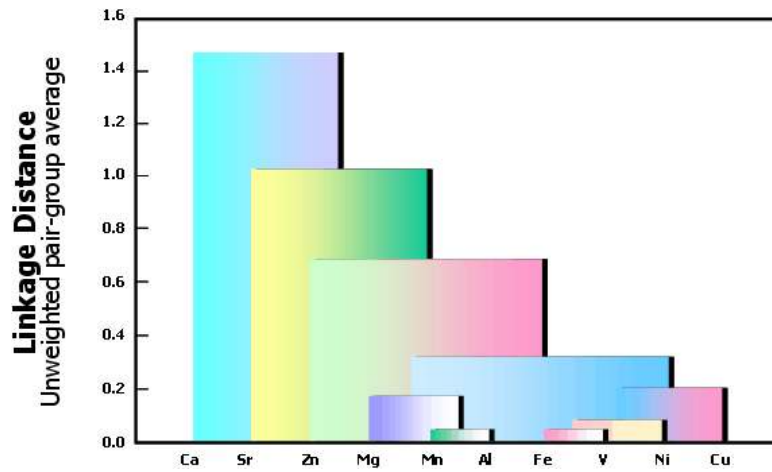


Fig. 6: Cluster analysis of the heavy metals associations at different stations.

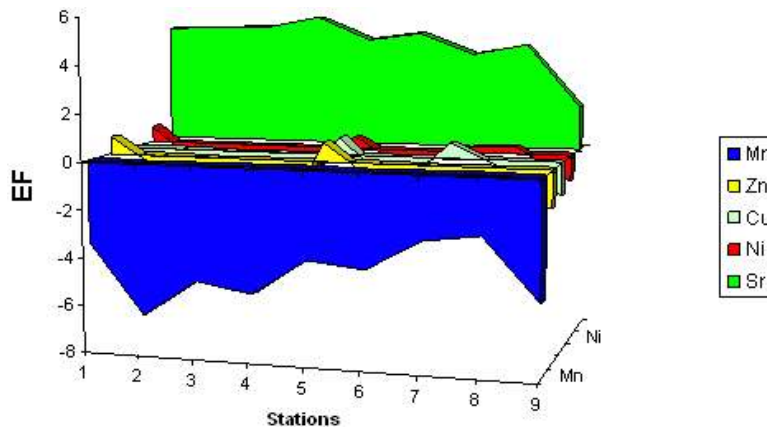


Fig. 7: Heavy metal enrichments factor (EF) at different stations.

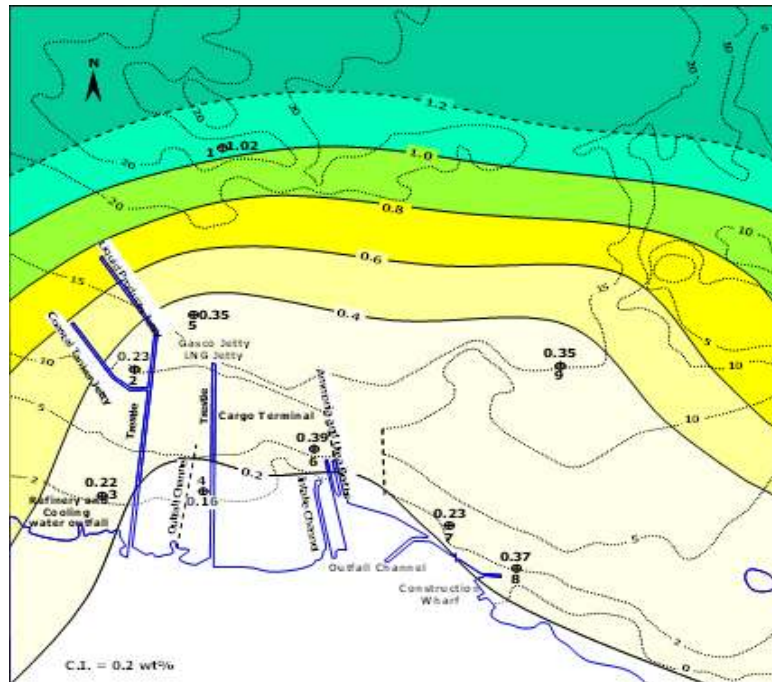


Fig. 8: Distribution of (TOC) of Al Ruwais Industrial Complex (RIC).

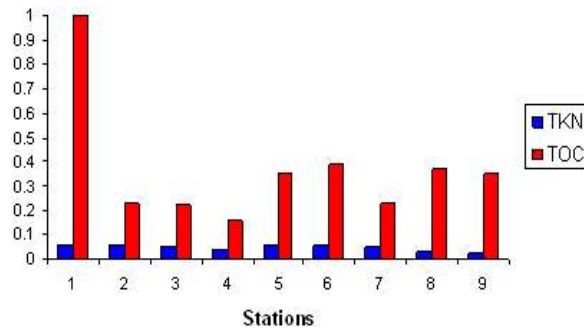


Fig. 9: Distribution of (TKN) and (TOC) at different stations.

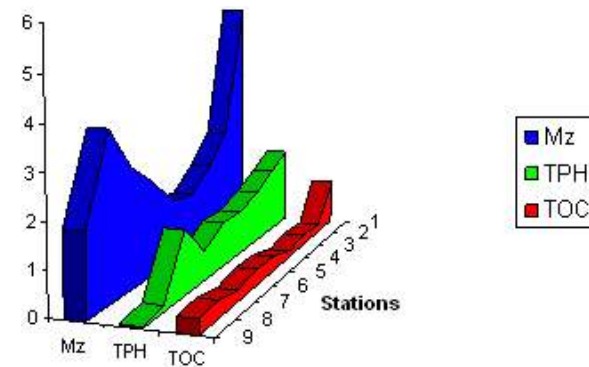


Fig. 10: Distribution of (Mz), (TPH), and (TOC) at different stations.

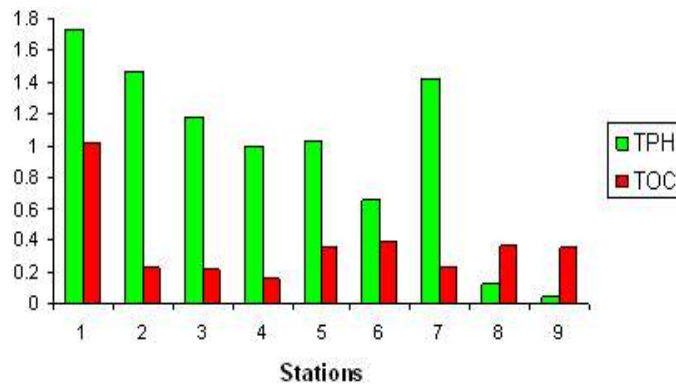


Fig. 11: Distribution of (TPH) and (TOC) at different stations.

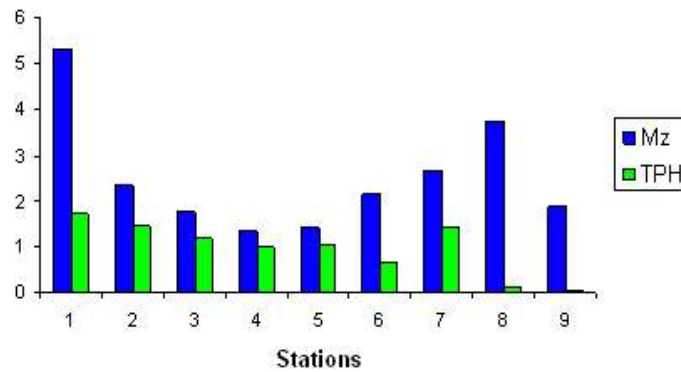


Fig. 12: Distribution of (Mz) and (TPH) at different stations.

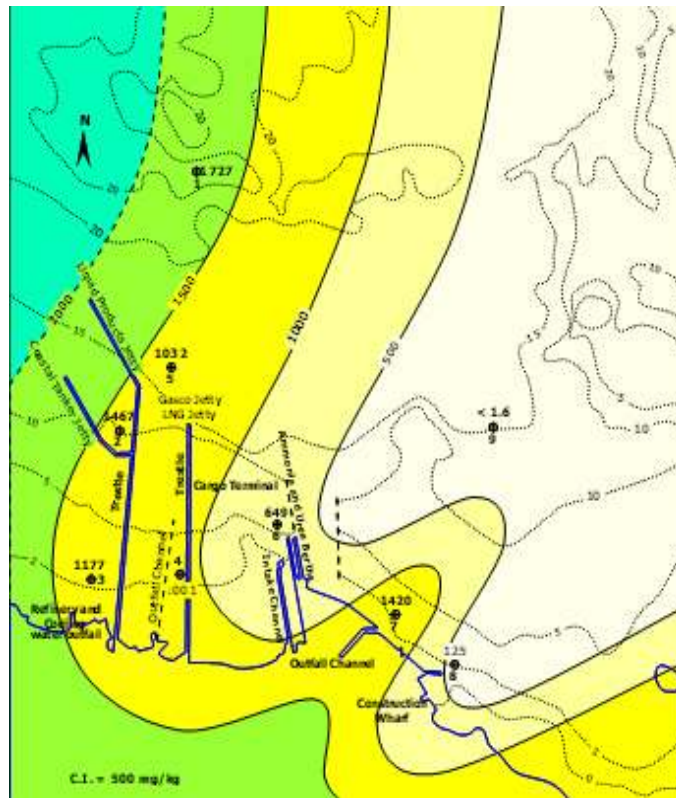


Fig. 13: Distribution of (TPH) of Al Ruwais Industrial Complex (RIC).

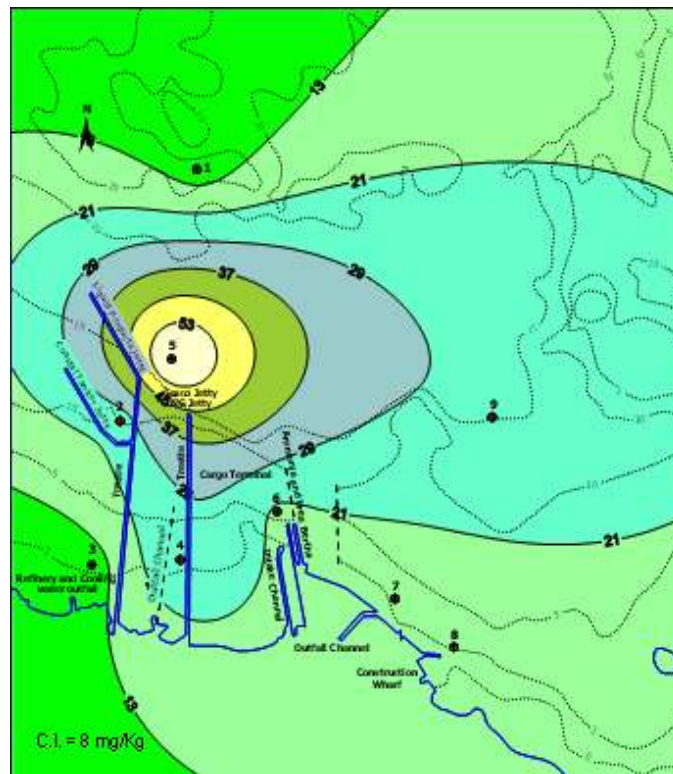


Fig. 14: Distribution of (PCBs) of Al Ruwais Industrial Complex (RIC).

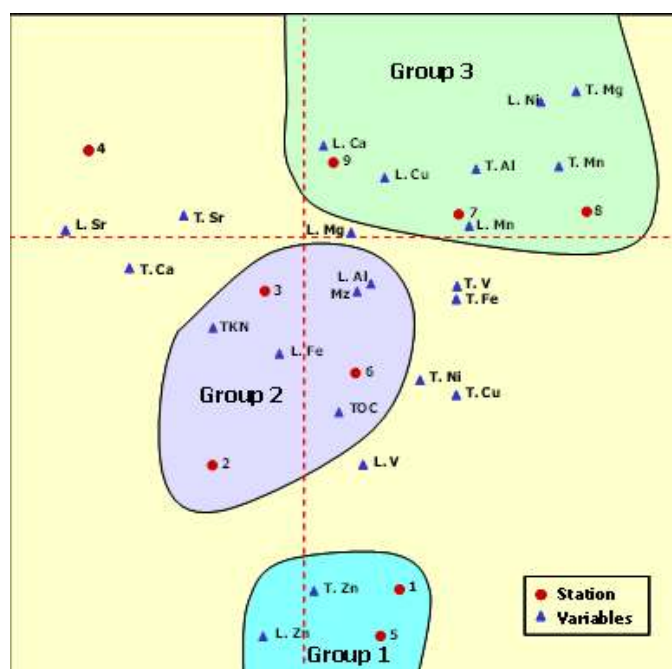


Fig. 15: Factor analysis of the heavy metals, TOC, TKN and Mz at different stations.

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