

Assessment of contamination by trace metals and petroleum hydrocarbons in water and sediments of the Tigris and Shatt Al-Arab Rivers and NW Arabian Gulf /Iraq.

Faris J. M. Al-Imarah, Ali. H. Amteghy and Mohammad S. Moyel Dpt. Mar. Environ. Chem., Marine Science Centre, Basrah Univ. Basrah – Iraq.

ABSTRACT

For assessing water quality, during two occasions Winter and Summer of the years 2009-2011, water as well as sediment samples from 15 selected stations along Tigris River (8 stations within Mysan Governorate), Shatt Al-Arab River (5 stations within Basrah Governorate) and (2 stations within NW Arabian Gulf) were collected. Multivariate statistical techniques, Cluster analysis (CA) and Principal Component Analysis (PCA), were applied for the evaluation and interpretation of large complex water quality data sets (12 parameters) and sediments (14 parameters) at 15 different sites each were monitored. PCA resulted in four factors explaining more than 76.055% of the total variance in water guality data set. The first rotated component (PC1) explains 30.546% of the total variance in the datasets and has strong positive loading on Mn, Ni, Pb and Fe, respectively, whereas, it has moderate negative loading on DO. This factor appears to be originated from the chemical activity of the river. The second component PC2 explains 18.177% of the total variance and is positively loaded with EC and Salinity; this component can be related to mineral factor of the river water. PC3 explains 15.892% of the total variance and is negatively loaded with TPHs and positively loaded with WT and pH (r = 0.817and 0.734) respectively, this factor appears to be originated from pollution by petroleum hydrocarbons. PC4 explained 25.183% of total variance in datasets and consists of a strong positive loading of Co, Cu and V respectively. For sediments, four factors were accounted 83.790% for explaining the behavior of the studied parameters. Correlation matrix revealed that first factor PC1 accounts for 44.412 % of the total variance has positive loading on Mn, Co, Cu, Fe, Pb, V, TOC, and TPHs respectively. This factor appears to be originated from TPHs and related TOC as well as trace elements. The second factor PC2 explains 15.128% of the total variance and is positively loaded with Silt and negatively loaded with sand. The third factor PC3 explains 14.594% of the total variance and is positively loaded with pH (r = 0.737) which appears to be originated from pollution of chemical reactions, while PC4 explains 9.656% of the total variance and is positively loaded with clay, and appears to be originally for removal of pollutants by adsorption. This study illustrates the benefit of multivariate statistical techniques for analyzing and interpretation of complex data sets, and to plan for future studies. Keywords: WATER QUALITY, SEDIMENTS, IRAQ, MULTIVARIANT STATISTICS,



INTRODUCTION

Rivers play a major role in assimilation or transportation of the municipal and industrial wastewater a constant as well as occasional or seasonal polluting source. The seasonal variation in precipitation, surface interflow, ground water flow and pumped in and outflows have a strong effect on river discharge and sub the concentration of pollutants in river water (Vega *et al.*, 1998). The possible variances in water quality may be due to anthropogenic activities, natural variances during months (due to various biochemical or chemical processes) (Alberto et al., 2001).

The discharge of effluents and associated toxic compounds into aquatic systems represents an ongoing environmental problem due to their possible impact on communities in the receiving aquatic water and a potential effect on human health (Abbas *et al.*, 2008). Among the most important pollutants, petroleum hydrocarbons and metals from industrial, municipal and sewage discharge and runoff coupled with aerial deposition are of particular concern due to their environmental persistence and wide range of toxicity effects over the aquatic biota, even for some of them at low concentrations (Nix and Merry, 1990). Due to rivers constitute the main inland water resources are for domestic, industrial and irrigation purposes; it is inevitable to prevent and control the rivers pollution and to have reliable information on quality of water for effective management (Alberto et al., 2001).

The application of different multivariate approaches, such as principal component analysis (PCA) and cluster analysis (CA) for interpretation of these data matrices offers a better understanding of water quality and ecological status of studied systems, allows identification of possible factors/sources that influence water systems, and extract information about the similarities or dissimilarities among monitoring stations. These approaches provide a variable tool for reliable management of water resources as well as rapid solutions on pollution problems (Morales *et al.*, 1999 and Wunderlin, *et al.*, 2001). In the present study, the efficiency of two different multivariate statistical techniques (PCA and CA) were applied to evaluation and interpretation of a water quality data set of the Southern Iraqi Rivers, which were generated under the 3-years (2009 – 2011) monitoring program. The CA and PCA techniques were utilized to identify the source of petroleum hydrocarbons and heavy metals contaminants in surface water and sediment of Tigris and Shatt Al– Arab Rivers.

MATERIALS and METHODS

Study area

Waters of the two main sources Tigris and Shatt al Arab Rivers within Southern part of Iraq are incorporated in different uses mainly: drinking, agricultural, industrial purposes, as well as serving population approximately five million people settled in Maysan and Basrah Governorates. These rivers usually affected by agricultural, sewage effluent, discharges of domestic wastewater, industrial effluent discharge, oil plants, wastes from hospitals, electrical power stations, and paper mill (Nix and Merry, 1990).

The Tigris River is one of the largest river in the Middle East stretching for over than 1900 km, of which 1418 km flow within Iraq, sharing with Euphrates River as the main sources for man use, especially for drinking water since they through the major cities in Iraq (AL Suhaili and Nasser, 2008).

The Shatt Al-Arab River originates from the confluence of the two major Iraqi rivers Tigris and Euphrates at Qurna city. The Shatt Al-Arab River has a length of 200 km, a width range between 400 m at Basra and up to more than 2 km at the estuary and a depth of



between 8-15 m, considering tides (Abdullah, 1990). The physico- chemical and hydrological conditions of the river's water have been affected by the quality of water coming from its tributaries, which in turn, depend on the amount of rainfall, the effects of groundwater and the water storage circumstances in the upstream areas. At its mouth, the river is also affected by the saline water tides which come from the Arabian Gulf (Hussein *et al.* 1991). **Field work**

The water samples were collected seasonally during summer and winter of three years 2009-2011 from fifteen different stations along the Tigris River within Maysan Governorate and Shatt Al-Arab River within Basrah Governorate and Northwest Arabian Gulf (Figure 1). Sediment samples were monitored, for the same sites, two seasons, summer and winter during one year, 2009. The water quality of monitoring sites comprising 12 water quality parameters were preserved and analyzed according to standard methods (APHA, 2008). Physical and chemical parameters including water temperature (WT), electrical conductivity (EC), and pH, were measured *insitu* using a HACH portable multimeter, Dissolved oxygen (DO) was measured with YSI 1000 DO meter.

Water samples were collected by clean polyethylene bottles (5 L capacity), 30 cm depths, and Sediment samples were collected by Van Veen Grap Sampler; sediments were kept in plastic bags. For Petroleum hydrocarbons analysis, water samples were collected in glass bottles (three bottles for each station) and transferred to the laboratory in an ice box. Sampling sites are shown in figure 1.



Figure 1. Map of Southern Iraq showing the sampling sites.

Petroleum Hydrocarbons analysis

Petroleum hydrocarbons were extracted from water samples according to UNEP (1993) by using carbon tetrachloride solvent (CCl_4). The samples were shaken several times; the extracts were dried by evaporation in rotary evaporator until dryness. Then to each sample, tetrachloride solvent is replaced by hexane solvent and then the Total Petroleum Hydrocarbons (TPHs) were estimated spectroflourometrically by Ultraviolet Fluorescence (UVF) analysis.

The determination of petroleum hydrocarbons in the sediment was done following Al-Saad (1995). Sediments were placed in a pre-extracted cellulose thimble and soxhlet extracted with 150 ml methanol: benzene (1:1) mixture for 24 hours. Then the extract was transferred to a storage flask and the samples were further extracted with a fresh solvent.



The combined extracts were reduced in volume to a 10 ml in a rotary evaporator. It was then saponified for 2 hours with a solution of 4N KOH in (1:1) methanol: benzene. After extracting the unsaponified matter with hexane, the extract was dried over anhydrous sodium sulfate and concentrated by a stream of N₂ for Ultraviolet Fluorescence (UVF) analysis. **Trace Element analysis:**

Trace metals analysis was performed on the <63 μ m fraction of the sediment which has been separated by sieving after drying and grinding. According to Sturgeon *et al.* (1982), concentrated HCl and HNO₃ (1:1) were added to each sample and evaporated to near dryness on a hotplate at 80 °C, then a mixture of concentrated HClO₄ and HF (1:1) were added. After heating to near dryness, 20 ml of 0.5 HCl were added and cooled for 10 min. The extraction was decanted into 25 ml plastic volumetric flask. This step was repeated twice and all supernatant were combined. Finally, samples were stored prior to trace metals analysis using a Pye-Unicam Atomic Absorption type SP9 Pye-Unicam.

Grain Size Analysis

Grain size analysis of the sediment was done according to Folk (1974), the Total Organic Carbon (TOC) of the sediment was determined using the wet oxidation method as described by El-Wakeel and Riely (1957).

Multivariate Statistical Analysis

Monitoring programs result in a huge and complex data matrix consist of a large number of physico-chemical parameters (Chapman, 1992). The application of multivariate methods such as principal component analysis (PCA) and Cluster analysis (CA) have increased tremendously during recent years for analyzing environmental data and drawing meaningful information (Vega et al., 1998; Lee et al., 2001; Wunderlin, et al., 2001; Reghunath, et al., 2002 and Saadia et al., 2005). In the present study, the efficiency of two different multivariate statistical techniques (CA and PCA) were applied to evaluation and interpretation of a water quality data set of the Southern Iraqi Rivers, which were generated under the 3-years (2009 – 2011) monitoring program. The CA and PCA techniques were utilized to identify the source of petroleum hydrocarbons and heavy metals contaminants in surface water and sediment of Tigris and Shatt Al –Arab Rivers.

RESULTS and DISCUSSION

The basic statistics calculated for Southern Iraq water quality and sediments are summarized in Table I, which presents the range, mean, and standard deviation of the results for each of the 12 parameters (WT, pH, EC, DO, Pb, Ni, Co, Cu, Fe, Mn, V, and TPHs) for water quality, and the 14 parameters (pH, EC, TPHs, TOC, Clay, Silt, Sand, Pb, Co, Mn, Fe, Cu, Ni, and V) for sediment samples .

WT showed a characteristic annual cycle, with higher values during the summer (23.5 - 35° C) and lower values in the winter season (11.4-17.5°C). The pH values of collected water Samples ranged 7 – 9.2, within the limit range of 6-9 allowed by the SEPA for water quality [21]. The EC during the annual season cycle showed significant variations, with values of 0.88 – 59.35 mS/cm and DO ranged 0.9 – 7.2 mg/l.

Trace elements can give some information about the contamination in the study area since certain elements such as Cu, Ni, V, and Zn are incorporated with crude oil (Etchie et al., 2011). In this study levels of tested trace elements has moderate mean levels, 0.144, 0.206,



0.059, 0.308, 0.352, and 0.550 $\mu g/l$ for Pb, Ni, Co, Cu, Mn, and V respectively. The lowest being reported for Co.

For sediments, Among all the heavy metals (Pb, Co, Cu, Mn, Fe, Ni, Co and V) analyzed, Pb, Mn, Fe, and Ni contents in the sediments were the Higher (106.616, 389.780, 14401.712, and 2124.659 Units) respectively and Co, Cu, and V were the lower (41.503, 26.520, and 28.234 Units) respectively. Lead is a good indicator of traffic, and is considered as an indicator of pollution by urban runoff water (Mukai et al., 1994).

TPHs used to assess the level of petroleum oil pollution (Adeniyi and Afolabi, 2002; Osuji and Adesiyan, 2005a, b; Osuji and Onojake, 2006; Adewuyi, et al., 2011 and UNEP, 2011). No comparison could be obtained for TPHs in the study area, but as a mean value of 13.910 μ g/l is represented as low level (Etchie et al., 2011).

The Pearson's correlation coefficient measures the strength of a linear relationship between two variables on the scale of -1,0,+1 (Table V), Strong positive correlations were obtained between most parameters except DO which showed negative correlations with all parameters but the EC, and TPHs showed positive correlations with trace elements which indicate that they could be arises from the same source of pollution (Yisa et al., 2011), while other parameters WT, pH, EC and DO correlate inversely with TPHs.

Variables	Minimum	Maximum	Mean	Std.					
	winningini	IVIAAIITUTT	Ivicali	deviation					
Water Quality parameters									
WT º C	11.400	36.000	22.845	9.187					
рН	6.400	9.200	7.960	0.505					
EC mS/cm	0.880	59.350	10.392	16.804					
DO mg/l	0.900	7.200	4.234	1.603					
Pb μg/l	0.013	1.231	0.144	0.204					
Ni µg/l	0.035	1.244	0.206	0.195					
Co μg/l	0.005	0.198	0.059	0.046					
Cu μg/l	0.013	1.267	0.308	0.286					
Fe µg/l	0.451	9.278	2.688	1.625					
Mn μg/l	0.008	1.835	0.352	0.457					
V μg/l	0.012	2.560	0.550	0.514					
TPH μg/l	1.050	68.400	13.910	11.780					
Sedir	nent Parameters								
рН	8.100	8.711	8.324	0.171					
EC	5.000	69.980	18.231	20.802					
ТРН	36.701	163.26	71.621	34.531					
тос	0.246	1.651	0.770	0.294					
Clay	6.050	29.850	22.203	5.885					
Silt	46.417	89.124	68.079	9.798					
Sand	1.600	34.891	11.016	10.433					
Pb	57.211	160.32	106.61	29.586					
Со	24.881	67.341	41.503	10.016					
Mn	259.41	611.87	389.78	93.648					
Fe	9752.1	20168.	14401.7	3437.69					
Cu	12.411	62.334	26.520	13.441					
Ni	54.561	61443.00	2124.6	11203.4					
V	14.921	51.612	28.234	11.52					

Table I. Descriptive statistic of the parameters.



Table II. Correlation matrix (Pearson's (n)).

A)	Water Quality
----	---------------

Variables	WT	рĤ	EC	DO	Pb	Ni	СО	Cu	Fe	Mn	V	TPH
рН	0.338	1										
EC (mS/cm)	0.031	0.217	1									
DO (mg/l)	-0.493	-0.132	0.516	1								
Pb (mg/l)	0.139	-0.076	-0.148	-0.566	1							
Ni =	0.252	0.010	-0.196	-0.716	0.933	1						
Co =	0.161	0.122	0.326	-0.237	0.258	0.348	1					
Cu =	0.094	-0.116	0.188	-0.371	0.564	0.610	0.874	1				
Fe =	0.395	0.325	-0.138	-0.797	0.750	0.888	0.472	0.594	1			
Mn =	0.228	0.242	-0.298	-0.662	0.727	0.770	-0.132	0.079	0.733	1		
V =	0.325	0.104	0.156	-0.498	0.587	0.656	0.850	0.838	0.722	0.250	1	
TPH (µg/l)	-0.509	-0.433	-0.121	-0.251	0.517	0.464	0.195	0.470	0.298	0.286	0.270	1

Values in bold are different from 0 with a significance level alpha=0.05

B) Sediment Quality.

Variable	рН	EC	TPH	TOC	Clay	Silt	Sand	Pb	Со	Mn	Fe	Cu	Ni	V
рН	1													
EC	0.482	1												
TPH	-0.511	-0.083	1											
TOC	-0.222	-0.139	0.714	1										
Clay	0.025	0.123	0.058	0.021	1									
Silt	-0.102	0.309	-0.040	-0.005	-0.535	1								
Sand	0.089	-0.420	0.139	0.045	0.028	-0.760	1							
Pb	-0.148	-0.120	0.668	0.736	0.134	-0.125	0.174	1						
Со	-0.298	-0.013	0.809	0.910	0.050	0.016	0.012	0.842	1					
Mn	-0.227	-0.160	0.749	0.852	0.004	-0.046	0.114	0.892	0.915	1				
Fe	0.260	0.037	0.371	0.640	0.009	0.026	0.020	0.739	0.633	0.781	1			
Cu	-0.398	-0.320	0.841	0.887	-0.029	-0.043	0.102	0.759	0.883	0.916	0.629	1		
Ni	0.354	0.470	-0.122	-0.107	-0.108	0.217	-0.166	-0.200	-0.121	-0.112	0.118	-0.159	1	
V	-0.195	0.343	0.791	0.528	0.118	0.084	-0.018	0.690	0.725	0.629	0.503	0.587	0.094	1

Values in bold are different from 0 with a significance level alpha=0.05

Principal component analysis

PCA is a pattern recognition technique that attempt to intercept the variance within a large set of intercorrelated variables by converting them into smaller variables (Simeonov et. al., 2003). It provides information on the most significant parameters used to describe the entire data set, data reduction, and to summarize the statistical correlation among constituents in the water with a minimum loss of original information (Alberto et al., 2001; Helena et al., 2000). PCA has been used on a correlation matrix of rearranged data to explain the structure of the underlying dataset and to identify the unobservable, latent pollution sources. PCA was carried out on the data set to compare the compositional patterns between analyzed water and sediment samples and to identify the various factors (principal components (PCS)) that influence each of them. Eigen values >1 were taken as criterion for the extraction of the PCS required for explaining the source of variances in the data set. Results of PCA analysis, eigen values for different factors, percentage variance accounted and cumulative percentage variance are given in Table VI. PCA of the entire data set allowed forming PCS with four eigen values greater than 1 explaining that 89.798% of the total variance in the water quality data set as indicated in table III (A). The PCA was actually performed on the correlation matrix between different parameters followed by Varimax rotation and the same has been used to examine their inter relationship. Correlations between parameters are shown in Fig.3.



The water parameters loading for the four identified PC_S from the PCA analysis of the data which are given in Table III (A). The first rotated component (PC_1) which explains 30.546% of the total variance in the datasets and has strong positive loading on Mn, Ni, Pb and Fe, respectively, whereas, it has moderate negative loading on DO (Table III (A) and Fig. 3). This factor appears to be originated from the chemical activity of the river. PC_2 , on the other hand, explains 18.177% of the total variance and is positively loaded with EC and Salinity; this component can be related to mineral factor of the river water. PC_3 explains 15.892% of the total variance and is positively loaded with WT and pH and negatively loaded with TPHs (Table III (A) and Fig. 3). This factor appears to be originated 25.183% of total variance in datasets and consists of a strong positive loading of Co, Cu and V respectively.

For sediments, the entire data set allowed forming PC_s with four eigen values greater than 1 explaining that 83.790% of the total variance in the sediment data set as indicated in table VI (B). Factor loading between sediment parameters are shown in Table III and Fig. 4. PC_1 accounts for 44.412 % of the total variance with strong positive loading on Mn, Co, Cu, Pb, TOC, TPHs and Fe respectively. This factor appears to be originated from TPHs and related TOC and trace elements. PC_2 explains 15.128% of the total variance and is positively loaded with Silt and negatively loaded with sand, their loading are high and as shown in fig.4 (B). PC_3 explains 14.594% of the total variance and is high positively loaded with pH, whereas, it has moderate positive loading on EC and Ni. This factor appears to be originated from pollution of chemical reactions. PC_4 explains 9.656% of the total variance and is positively loaded with clay, and appears to be originally for removal of pollutants by adsorption

Cluster analysis:

CA is defined as the classification of similar objects into groups (clusters) where the number of groups as well as their forms are unknown (Kaufman & Rousseeuw, 1990), with the primary purpose being the assembly of objects based on the characteristics they possess. Hierarchical agglomerative clustering is the most common approach, which provides instinctive similarity relationships between any one sample and the entire data set, is typically illustrated by a dendrogram (tree diagram). The dendrogram presents a picture of the groups and their proximity to one another, with a dramatic reduction in the dimensionality of the original data (Alberto et al., 2001). The clustering procedure as a dendrogram of sampling sites obtained in this study generated four groups of stations (Fig. 5). Cluster 1 corresponded to sites 9, 10, 11 and 12, which were located in an area of slightly saline water. Cluster 2 corresponded to sites 13, 14, and 15, which were located in the deep south of Iraq and affected by saline water from Northern Arabian Gulf. Cluster 3 corresponded to sites 1, 2, 3, 4, 5, 7, and 8, which were located down streams Tigris River within Maysan Governorate and the water quality measured in these sites of lower salinity and moderately effected by pollutants discharge to the river. Clustre 4 corresponded to site 6 as a discharging point of sewage from the city to the river. The cluster analysis revealed different properties at each set of sites with respect to physical and chemical variables. The four groups vary according to natural backgrounds features. Additionally, the water quality measured at these sites appeared to be affected by different pollutant sources (Zhao et al., 2012).



International Journal of Environment & Water ISSN 2052-3408

A) Water samples B) Sec	diment paramete	ers		
A	PC ₁	PC ₂	PC ₃	PC ₄
WT	0.151	-0.137	0.817	0.248
рН	0.215	0.298	0.734	-0.093
EC	-0.144	0.954	0.085	0.176
Sal.	-0.152	0.951	0.086	0.181
DO	-0.622	0.565	-0.267	-0.341
Pb	0.858	-0.070	-0.179	0.313
Ni	0.873	-0.151	-0.042	0.399
Со	0.027	0.199	0.054	0.946
Cu	0.283	0.097	-0.192	0.909
Fe	0.806	-0.118	0.244	0.466
Mn	0.945	-0.158	0.129	-0.154
V	0.385	0.064	0.107	0.867
ТРН	0.447	-0.039	-0.784	0.232
Eigenvalue	3.970	2.360	2.060	3.270
Variability (%)	30.546	18.177	15.892	25.183
Cumulative %	30.546	48.723	64.615	89.798
В	PC ₁	PC ₂	PC ₃	PC ₄
рН	-0.204	-0.224	0.897	-0.035
EC	-0.040	0.548	0.644	0.405
ТРН	0.823	0.093	-0.339	0.196
TOC	0.894	-0.036	-0.095	-0.076
Clay	0.020	-0.217	-0.004	0.872
Silt	0.008	0.859	0.052	-0.446
Sand	0.071	-0.867	-0.045	0.014
Pb	0.899	-0.168	-0.010	0.073
Со	0.954	0.066	-0.113	0.063
Mn	0.963	-0.100	-0.049	-0.082
Fe	0.783	-0.128	0.431	-0.166
Cu	0.918	-0.071	-0.264	-0.111
Ni	-0.045	0.291	0.648	-0.027
V	0.769	0.270	0.070	0.356
Eigenvalue	6.210	2.110	2.040	1.350
Variability (%)	44.412	15.128	14.594	9.656
Cumulative %	44.412	59.541	74.134	83.790

Table III. Factor loading after Varimax rotation.

Values in **bold** correspond for each variable to the factor for which the squared cosine is the largest.



Figure 3. Factor loading of water quality parameters for southern Iraqi. A) With factors 1 and 2, B) With factors 2 and 3, and C) with factors 3 and 2.





Figure 4. Factor loading of sediment parameters for southern Iraqi. A) With factors 1 and 2, B) with factors 2 and 3, and C) with factors 3 and 2.



Figure 5. Dendrogram obtained by agglomerative hierarchal clustering analysis (Ward's method) for sampling stations.



CONCLUSION

Among the whole components appeared in Table VI, for water quality, the first four components are sufficient to explain the monitoring area. As can be seen in this table, these components explain more than 76.055% of the total variance of the original data set.

Principal components analysis of water quality data from the Southern Iraq monitoring station showed that WT, pH, and PHCs are the main causes of variations in water quality in that region. The results of the correlation matrix revealed that there are negative significant correlation between TPHs with WT and pH (r = -0.509 and -0.433 respectively).

For sediments, four factors were accounted 83.790% for explaining the behavior of the studied parameters. Correlation matrix revealed that factor 1 which accounts for 44.172 % of the total variance has positive loading on TPHs, TOC, Pb, Co, Cu, Fe, Mn, and V. This factor indicates strong association (r=0.710-0.957) for all correlated parameters which appears to be originated from TPHs and related TOC and trace elements. Factor 2, on the other hand, explains 15.128% of the total variance and is positively loaded with EC, Silt and Ni (r=0.776, 0.748 and 0.610 respectively) and negatively loaded with sand (r = -0.706), their loading are high and as shown in fig.4 (B). Factor 3 explains 14.594% of the total variance and is positively loaded with pH (r = 0.737) which appears to be originated from pollution of chemical reactions. Factor 4 explains 9.656% of the total variance and is positively loaded with clay (r = 0.700) and appears to be originally for removal of pollutants by adsorption. This study illustrates the benefit of multivariate statistical techniques for analyzing and interpretation of complex data sets, and to plan for future studies.

REFERENCES

- Adamo, P., Arienzo, M., Imperato, M., Naimo, D., Nardi, G., and Stanzione, D. (2005). Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. Chemosphere, 61(6):800-809.
- Adeniyi, A. A. and Afolabi, J. A. (2003). Determination of total petroleum hydrocarbons and heavy metals in the soil within the vicinity of facilities handling refined products in Lagos metropolis. Environ. Int. 28:79-82.
- Adewuyi, G.O., Etchie, O. T. and Ademoyegun, A. T. (2011). Determination of total petroleum hydrocarbons and heavy metals in the surface water and sediments of Ubegi river, Warri, Nigeria. Biorem. Biodiver. Bioavail. 5:16-51.
- Alberto W. D., Del Pilar D. M., Valeria A. M., Fabiana PS, Cecilia H. A., and De Los Angeles B. M. (2001). Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia River basin (Cordoba—Argentina). Water Res, 35: 2881–94.
- Al-Tamir, M. A. (2008). Interpretation of ground water quality data variation in Erbil city, Northern Iraq. Al-Rafidain Engineering, 16(2):24-30.
- Alvin, C. R., (2002). Methods of Multivariate Analysis. John Wiley & Sons.INC. USA.
- APHA (American Public Health Association) (2008). Standard Methods for the Examination of Water and Wastewater. 30th Edition. Washington, DC.
- Asia, I. O., Jegede, S. I., Jegede, D. A., Ize-Iyamu, O. K. and Akpasubi, E. B. (2007). The effects of petroleum exploration and production operations on the heavy metals contents of soil and ground water in the Niger Delta. Int. J. Phys. Sci. 2:271-275.



- Champan, D., (1992). Water quality assessment. In; Chapman, D. (Ed.), on behalf of UNESCO, WHO and UNEP, Chapman & Hall, London.
- Eisler, R.(2000). in Handbook of Chemical Risk Assessment. Health Hazards to Humans, Plants and Animals. Vol. 1-2, Lewis Publishers, 2000; pp. 1500).
- Etchie, T. O., Etchie, A. T., and Adewuyi, G. O. (2011). Source identification of chemical contamination in environmental media of a rural settlement. Res. J. Environ. Sci., 5(9):730-740.
- Fedo C.M., Eriksson K., Krogstad E.J. (1996). Geochemistry ofshales from the Archean Abitibi greenstone belt, Canada: Implications for provenance and source-area weathering. Geochimica et Cosmochimica Acta, 60:1751-1763.
- Förstner U. & Salomons W. (1980). Trace metal analysis inpolluted sediments. Part I: Assessment of sources and intensities. Environ. Sci. Technol., 1:494-505.
- Förstner V. & Wittmann G.T.W. (1981). Metal Pollution in theAquatic Environment. N. York, Springer Verlag, 486p.
- .Helena B., Pardo R., Vega M., Barrado E., Fernandez J. M., and Fernandez L. (2000). Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga river, Spain) by principal component analysis. Water Res, 34: 807–16.
- Hussain, N. A., Al-Najar, H. H., Al-Saad, H. T., Yousif, U. H. and Al- Saboonchi, A. A. (1991). Shatt Al-Arab basic scientific studies. Marine Science Centre Publ. Basra Univ. 391pp.
- Kaufman L., and Rousseeuw P. J. (1990). Finding groups in data: an introduction to cluster analysis. New York: Wiley.
- Kelepertsis, A., Argyraki, A., and Alexakis,. (2006). Multivariate stastistics and spatial interpretion geochemical data for assessing soil contamination by potentially toxic elements in the mining area of Stratoni, North Greece. Geochem. Explor. Environ. Analysis, 6:349-355.
- Kelly A.G., Wells D.E., Fryer R.J. (1994). Sampling strategy to detect a change in concentration of trace organic contaminants in marine sediment. Sci Total Environ, 144:217-230
- Liaghati T., Preda M., Cox M. (2003). Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. Environment International., 29:935-948.
- Lee,B.K. and Hieu, N. Y. (2011). Seasonal variation and sources of Heavy metals in atmospheric aerosols in a residential area of Ulsan, Korea. Aeros. Air Qual. Res. 11:679-688.
- Lee, J.Y., Cheon, J.Y., Lee, K.K.,Lee,S.Y., Lee, M.H., (2001). Statistical evaluation of geochemical parameter distribution in a ground water system contaminated with petroleum hydrocarbons. J. Environ. Quality, 30: 1548-1563.
- Li, Y. Xu, L. and Li, S. (2009). Water quality analysis of the Songhua river basin using multivariate technique. J. water Res. Protect. 2:110-121.
- Mmolawa, K. B. Likuku, A.S. and Gaboutloeloe, G. K. (2011). Assessment of heavy metal pollution in soils along major roadside area in Botswana. Afr. J. Environ. Sci. Technol., 5:186-196.
- Nath B.N., Kunzendorf H., Pluger W.L. (2000). Influence of provenance weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bed load sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India. J. of Sedimentary Petrology, 70:1081-1094.
- Nesbitt H.W., Young G.M., Mclennan S.M., Keays R.R. (1996). Effects of chemical weathering and sorting on the petrogenesis of siliclastic sediments, with implications for provenance studies. J. of Geology , 104:525-542.
- Nix, P.G. and C.H. Merry, (1990). Use of sediment bags as a monitor of fecal pollution in streams. Bull. Environ. Contam. Toxicol., 45: 864-869.
- Oh. M. S., Lee, T. J., and Kim, D. S., (2011). Quantitative source apportionment of size-segregated particulate matter at urbanized local site in Korea. Aerosol. Air Qual. Res., 11:247-264
- .Olobamyi, S. B. and Efe, S. I., (2007). Comparative assessment of rain water and ground water quality in an oil production area of Nigeria. Environmental And Health implications. J. Environ. Health Res. 6:111-118.
- Otto, M., (1998). Multivariate methods. In: Kellner, R., Mermet, J. M., Otto, M., Widmer, H.M.(Eds), Analytical Chemistry. Wiley-VCH, Weinheim, Germany.



- Preda M. & Cox M.E. 2000. Sediment-water interaction, acidity and other water quality parameters in a subtropical setting, Pimpama River, Southeast Queens land. Environ Geol., 39(3-4):319-329.
- Razmkhah, H., Abrishamchi b, A. and Torkian, A. (2010). Evaluation of spatial and temporal variation in water quality by pattern recognition techniques: A case study on Jajrood River (Tehran, Iran). J. Environ. Manag., 91: 852–860.
- Reghunath, R., Murthy, T.R.S., Raghavan, B.R.,2002. The utility of Multivariate statistical techniques in hydrogeo-chemical studies: an example from Karanataka, India. Water research, 36: 2437-2442.
- Richard A. Johnson and Dean W. Wichern, (2002). Applied Multivariate statistical analysis. Prentice-Hall, London.
- Saadia R. Tariq, Munir H. Shah, N. Shaheen, A. Khalique, S. Manzoor, M.anzoor, M. Jaffar, (2005). Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water: A case study from Peshawar, Pakistan. Journal of environmental management.
- Sameaka-Cymerman, Kolon, A. K., and Kemoers, A. J. (2005). Differences in concentrations of heavy metals between native and transplanted Plagiothecium denticulatisum: A case study of soil contaminated by oil well exudate in South-East Poland. Arch. Environ. Contam. Toxicol., 49:317-321.
- Schiff K.C. & Weisberg S.B. 1999. Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. Marine Environ. Res., 48:161-176.
- Shrestha, S., Kazama, F., (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of Fuji river basin. Japan. Environ. Model. & software, 22:464-475.
- Simeonova, V., Stratisb, J. A., Samarac, K., Zachariadisb, G., Voutsac, D., Anthemidis, A., Sofonioub, M. and Kouimtzisc, Th. (2003). Assessment of the surface water quality in Northern Greece. Water Research 37 (2003) 4119–4124
- Singh. K.P., Malik,A., Mohan, D., Sinha, S., (2004). Multivariate statistical technique for the evaluation of spatial temporal variation in water quality of Gomti River (India): A case study. Water research 38,3980-3992.
- Tiri, A. and Boudoukha, A. (2010). Hydrochemical Analysis and Assessment of Surface Water Quality in Koudiat Medouar Reservoir, Algeria. European J. Sci. Res., 41 (2):273-285
- UNEP, (1993). Developing Large Environmental Databases for Sustainable Development:UNEP / IUFRO International Workshop,July 14-16, 1993, Nairobi, Kenya, Proceedings.
- UNEP (2011). Environmental assessment of Ogoniland. http://postconflict. Unep. Ch/publication/ OEA/UNEP_OEA.pdf
- Vega, M., Pardo, R., Barrado, E., Deban, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. Water research, 32, 3581-3592.
- Wunderlin, D. A., Diaz, M.P., Ame, M.V., pesce, S.F., Hued A.C., Bistoni, M.A., (2001). Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia river basin (cordoba-Argentina). Water Res. 35,2881-2894.
- Yisa, J., Jacob, J. O. and Onoyima, C.C. (2011). Identification of sources of heavy metals pollution in road deposited sediments using multivariate statistical analysis .J. Emerg. Trends. Eng. Appl. Sci., 2:658-663.
- Zhou, F., Liu,Y. and Guo, H. (2007). Application of Multivariate Statistical Methods to Water Quality Assessment of the Water courses in Northwestern New Territories, Hong Kong. Environ Monit Assess, 132:1–13.