Research Journal of Environmental Sciences, 2011
ISSN 1819-3412 / DOI: 10.3923/rjes.2011.

Source Identification of Chemical Contaminants in Environmental Media of a Rural Settlement

T.O. Etchie, A.T. Etchie and G.O. Adewuyi
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

Corresponding Author: T.O. Etchie, Department of Chemistry, University of Ibadan, Ibadan, Nigeria Tel: +2348052734155

ABSTRACT

Principal Component Analysis (PCA) was used to identify the source of contaminants in Ubeji settlement. The contaminants assessed are oil and grease, TPH and related heavy metals (Cd, Cr, Cu, Ni, Pb and Zn). A total of 48 groundwater, 100 surface water, 160 soil and 100 sediment samples were collected from the study site from March to August, 2011. Measurements of oil and grease and TPH in samples were done gravimetrically, while atomic absorption spectrophotometry was used for determination of heavy metals. The results show significant contamination, as TPH levels in groundwater and surface water range from 22 to 96 mg L^{-1}, while soil and sediment levels range from 600 to 2300 mg kg^{-1}. Also, Cd, Cr and Pb levels in the groundwater and surface water range from 0.02 to 0.47, 0.51 to 1.3 and 1.7 to 4.1 mg L^{-1}, respectively while soil and sediment levels range from 0.04 to 0.48, 28 to 66, 45 to 69 mg kg^{-1}, respectively. However, Cu, Ni and Zn are within safe limits. PCA revealed that the source of the contaminants is a refinery and petrochemical company located close to the settlement.

Key words: Principal component analysis, pearson correlation coefficient, TPH, heavy metals

INTRODUCTION

Environmental studies have reported high levels of organic and inorganic chemical contaminants exceeding national and international threshold limits in different environmental media (Adeniyi and Afolabi, 2002; Osuji and Adesiyan, 2005a, b; Samecka-Cymerman *et al.*, 2005; Osuji and Onojake, 2006; Asia *et al.*, 2007; Olobaniyi and Efe, 2007; Momodu and Anyakora 2010; Adewuyi *et al.*, 2011). Some other studies (Simeonov *et al.*, 2003; Muniz *et al.*, 2004; Singh *et al.*, 2005; Kowalkowski *et al.*, 2006; Boyacioglu and Boyacioglu, 2008; Omo-Irabor *et al.*, 2008; Riccardi *et al.*, 2008; Li *et al.*, 2009; Sekabira *et al.*, 2010; Lee and Hieu, 2011; Mmolawa *et al.*, 2011; Oh *et al.*, 2011; Yisa *et al.*, 2011) have taken the extra burden to identify the sources of the contaminants as well as quantify each source contribution to the contaminant a process known as source apportionment, using statistical method of analysis; like the multivariate analysis (Kelepertsis *et al.*, 2006; Yisa *et al.*, 2011). The multivariate analysis techniques have also been employed to verify temporal and spatial variations caused by natural and anthropogenic factors linked to seasonality (Li *et al.*, 2009).

Cluster Analysis (CA), Factor Analysis (FA), Fuzzy Clustering (FC) and Principal Component Analysis (PCA) are the common multivariate techniques used for pattern recognition and source identification (Mostert *et al.*, 2010; Yisa *et al.*, 2011), while Factor Analysis (FA), Positive Matrix Factorization (PMF) and Principal Component Analysis on absolute Principal Component Scores

(PCA/APCS) are frequently used techniques for source apportionment (Mostert *et al.*, 2010). However, this study utilized the PCA technique to identify the source of petroleum hydrocarbons and heavy metals contaminants in groundwater, surface water, soil and sediment of Ubeji community; a rural settlement in the outskirt of Warri metropolis in the South-Southern Nigeria.

The study was prompted by the findings of Adewuyi *et al.* (2011) who extracted high levels of oil and grease, total petroleum hydrocarbons and heavy metals (Cd, Cr, Cu, Pb, Ni and Zn) in the settlement's river and sediment. Since the Warri Refinery and Petrochemical Company (WRPC) is located close to the settlement, Adewuyi *et al.* (2011) proposed that the company may be the principal polluter, however, there was no statistical evidence to back up the claim. Hence, the objective of this study is to re-assess the levels of these contaminants in the surface water, soil, sediment and groundwater of the settlement and further identify the source (s) of the contaminants using the Principal Component Analysis (PCA) technique. This will enable mitigation measures to be taken by appropriate authorities.

MATERIALS AND METHODS

Site Description and Sampling: The description of the study site is available elsewhere (Ogunlaja and Ogunlaja, 2007; Adewuyi *et al.*, 2011) while the vegetation has also been documented (Omo-Irabor *et al.*, 2008). Figure 1 shows the shores of the settlement's river. Sampling was done twice, spread from March to August, 2011. In each sampling time, 12 groundwater samples were taken from 12 locally dug wells supplying water to most of the residents, 40 surface soil samples (0-15 cm soil depth) distributed over Ubeji settlement, 25 surface water and sediment samples were also randomly selected. Therefore, a total of 48 groundwater, 100 surface water, 160 soil and 100 sediment samples were collected from the study site for analysis. The sampling procedure is consistent with that described previously (Zuo *et al.*, 2007; Riccardi *et al.*, 2008).

Chemicals and reagents: Analytical grade reagents were used. Silica gel (Kieselgel 60F_{254} 0-230 mesh), nitric acid (HNO_3) hydrochloric acid (HCl), perchloric acid ($HClO_4$) and the metal standards solutions were purchased from Sigma-Aldrich, Fluka, Switzerland. Hexane (C_6H_{14}), sodium sulfate (Na_2SO_4), dichloromethane (CH_2C_{12}) and paraffine oil were purchased from Merck, Goa, India and the deionised water was purchased from the International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria.

Fig. 1: The shores of the settlement's river

Preservation of samples: Surface water and groundwater samples collected for oil and grease and Total Petroleum Hydrocarbons (TPH) were stirred and filtered using glass filter papers. The filtrates were collected while the residues (suspended particles) were discarded. After collection, the water samples were preserved on the field by adding concentrated HCl to pH = 2, while samples for heavy metals were preserved with 3 mL HNO_3 per litre of sample. The samples were stored in an ice chest. Soil and sediment samples collected from the sites were wrapped with degreased aluminum foil and polythene bags for oil and grease/TPH and heavy metals, respectively and stored in the ice chest before transporting to the laboratory for analysis (Adewuyi *et al*., 2011).

Method for analysis: The analytical test procedures used to assess environmental contamination by petroleum chemicals are total petroleum hydrocarbons and heavy metals determinations (Adeniyi and Afolabi, 2002; Osuji and Adesiyan, 2005a; Samecka-Cymerman *et al*., 2005; Osuji and Onojake, 2006; Adewuyi *et al*., 2011; UNEP, 2011).

Extraction of oil and grease: Extraction of the samples for oil and grease were carried out following standard procedures (EPA, 1999; Muniz *et al*., 2004; Mohsenzadeh *et al*., 2010). For water samples, oil and grease was extracted using EPA method 1664 (EPA 1999). Four replicates of 400 mL of homogenized water sample, acidified to pH<2, was extracted three times (sequential extraction) with 20 mL n-hexane (for each extraction) using a separating funnel. The extracts were dried over Na_2SO_4 and the solvent was evaporated with rotary evaporator. The extracts were desiccated, weighed and further evaporated. This procedure was repeated until constant weights of oil and grease were obtained.

Soil and sediment samples prior to extraction, were thawed and free of vegetation, pebbles and debris. Samples were air dried, crushed and sieved for grain size distribution using a standard set of stainless sieve. Four replicates of 100 g of soil samples were transferred into paper extraction thimbles. Oil and Grease (O/G) was extracted using Soxhlet apparatus for 8 h with a mixture of C_6H_{14} and CH_2Cl_2 (1:1, v/v). Rotary evaporator was used to concentrate the organic extracts, which were then filtered through Whatman filter paper (No. 4) with 1 g sodium sulfate. The solvent was further evaporated with a rotary evaporator to determine the weight of dry extract. Percentage of O/G was calculated and compared based on soil dry weight.

Extraction for TPH (silica gel clean-up): Silica gel chromatography was used to fractionate the oil and grease extracts. Silica gel, a polar adsorbent, absorbs polar organic substances such as vegetable oil and retains them so that non-polar hydrocarbons are eluted. The constant weights of the fractionated hydrocarbon extracts gave the TPH (Adeniyi and Afolabi, 2002; Adewuyi *et al*., 2011).

TPH analysis: The constant weights of the final extracts were determined by gravimetry (EPA, 1999; Adeniyi and Afolabi, 2002; Adewuyi *et al*., 2011).

Quality assurance and quality control for TPH: In the evaluation of methods for analysis of hydrocarbons, in environmental samples, the quality of a method is not judged by the percentage of fat extracted alone, but also by a number of factors like reproducibility, ease of application of method, cost and time of the analysis (Akporido, 2008). The loss of some of the hydrocarbons of interest cannot be ruled out. To this end, the extent to which the compound of interest is recovered also plays a vital role in conjunction with the factors earlier mentioned. Two replicates of the homogenized surface water, groundwater, soil and sediment samples were subjected to recovery studies by spiking samples with 2 mL of paraffine oil standard (Akporido, 2008). The spiked samples were extracted and analyzed accordingly. The recoveries of the oil in the samples ranged from 81 to 93%.

Heavy metals digestion methods: For water samples, nitric acid digestion was done following standard procedure (Hseu, 2004; Momodu and Anyakora, 2010; Adewuyi *et al.*, 2011). To ensure the removal of organic impurities from the samples and thus prevent interference in analysis, the samples were digested with concentrated nitric acid. Five mililiter of the concentrated nitric acid was added to 5 mL of the water samples and the mixture evaporated on a hot plate to a final volume of 3 mL. Another 5 mL of concentrated HNO_3 was added to the mixture and refluxed for 30 min, after which the mixture was heated on hot plate while the concentrated HNO_3 was added until the mixture was light coloured. The resulting sample was filtered and the filtrate made up to 50 mL with deionised water before analysis.

Nitric-perchloric acid digestion has been used as a standard method for digestion of heavy metals in soil and sediment samples (Hseu, 2004). Prior to digestion, the samples were thawed and free of vegetation, pebbles and debris. Samples were air dried, crushed and sieved for grain size distribution using a standard set of stainless sieve. For each sample type, 1 g of the sample was placed in a 250 mL digestion tube and 10 mL of concentrated HNO_3 was added. The mixture was boiled gently for 30-40 min to oxidize all easily oxidizable matter. After cooling, 5 mL of 70% $HClO_4$ was added and mixture was boiled gently until dense white fumes appeared. After cooling, 20 mL of deionised water was added and mixture was boiled further to release any fumes. The solution was cooled and filtered through Whatman filter paper into a 25 mL volumetric flask.

Heavy metals analysis: The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the final solutions were determined by atomic absorption spectrophotometer Buck Scientific 210VGP.s. The instrument's setting and operational conditions were done in accordance with the manufacturer's specifications. The instrument was calibrated with analytical grade metal standard stock solutions (1 mg L^{-1}).

Quality assurance and quality control: Metal recoveries was done, two replicates of the homogenized soil and filtered water samples were subjected to recovery studies by spiking samples with metal standards about the same concentrations of the analyte of interest, digested and analyzed. The average recoveries of the metals range from 78 to 94%. A blank was run for each digestion procedure to correct the measurements and to check all reagents and procedure for interferences and cross contamination.

Statistical analysis: In most applications, mathematical and statistical software are used for source grouping, by using PCA with varimax rotation and the retention of principal components having eigenvalue >1 (Ravindra *et al.*, 2008; Li *et al.*, 2009; Mohd *et al.*, 2011). The principal components that show the maximum percentage of total variance of the data set are used as factors (Li *et al.*, 2009). Loading determines the most representative parameters in each factor and generally, a value >0.5 is selected (Ravindra *et al.*, 2008).

This study chose to apply the PCA (Lee and Hieu, 2011). By using this technique, it was possible to simplify interpretation of complex systems as well as to reduce the variables to a few ones called factors (Dallarosa *et al*., 2005; Mohd *et al*., 2011). Each factor is related to an identified source (Dallarosa *et al*., 2005; Motelay-Massei *et al*., 2007; Lee and Hieu, 2011). To apply the PCA, a spearman's correlation matrix was prepared using all 8 selected parameters; oil and grease, TPH, Cd, Cr, Cu, Ni, Pb and Zn and analysed using SPSS 17.0. PCA is a data reduction technique (Dallarosa *et al*., 2005; Ravindra *et al*., 2008; Mohd *et al*., 2011). Data reduction is achieved by finding linear combinations of the original variables accounting for as much as the original total variation as possible, thus variables with similar characteristics can be grouped into factors (Dallarosa *et al*., 2005; Ravindra *et al*., 2008). The successive linear combinations are extracted in such a way that they are non-correlated with each other and account for successive smaller amounts of the total variation. The orthogonal varimax rotation on the original factors are commonly used to facilitate interpretation (Dallarosa *et al*., 2005; Motelay-Massei *et al*., 2007; Ravindra *et al*., 2008; Yang *et al*., 2010). Rotation is merely a procedure which allows new axis to be chosen so that positions of the points can be clearly described (Dallarosa *et al*., 2005; Ravindra *et al*., 2008). The technique rotates the predetermined principal components while maintaining that the individual components remain orthogonal to each other (Dallarosa *et al*., 2005). The varimax rotation technique supplies better interpretation (Dallarosa *et al*., 2005; Ravindra *et al*., 2008; Yang *et al*., 2010).

RESULTS AND DISCUSSION

The mean concentrations of oil and grease in the groundwater and surface water are 380±20 and 250±10 mg L^{-1}, respectively while soil and sediment are 1300±100 and 3900±200 mg kg^{-1}, respectively. The TPH mean concentrations are 34±3 and 88±3 mg L^{-1} for groundwater and surface water, respectively and 690±40 and 1900±100 mg kg^{-1} for soil and sediment (Table 1). The difference between the concentrations of oil and grease and TPH represents the polar fraction (Pawlak *et al*., 2008). TPH have been used in various studies to assess the levels of petroleum oil pollution (Adeniyi and Afolabi, 2002; Osuji and Adesiyan, 2005a, b; Osuji and Onojake, 2006; Adewuyi *et al*., 2011; UNEP, 2011).

The levels of TPH obtained in this study is comparable with that reported by Adewuyi *et al.* (2011) for surface water and sediment of the settlement river and also with values reported in

Table 1: Parameters' concentrations and regulatory agencies' Maximum Contaminant Levels (MCLs)

			Heavy metals					
Samples	Oil and grease	TPH	Cd	Cr	Cu	Pb	Ni	Zn
Groundwater (mg L^{-1})	380±20	34±3	0.06±0.01	0.77±0.05	0.04±0.01	3.7±0.9	0.66±0.06	1.4±0.0
Surface water (mg L^{-1})	250±10	88±3	0.35±0.03	1.02±0.02	0.68±0.05	1.9±0.1	0.76±0.02	2.8±0.0
Soil (mg kg^{-1})	1300±100	690±40	0.36±0.10	34±4	42±6	56±10	33±4	260±20
Sediment (mg kg^{-1})	3900±200	1900±100	0.06±0.07	61±2	54±4	59±3	51±3	220±10
NIS (mg L^{-1})	10^{a}	0.2^{a}	0.003	0.05	2	0.01	0.02	3
SNR (mg kg^{-1})	-	1-10^{b}	0.003-0.3	5.00^{c}	5.00-20.0	2.00-20.0	2.00-750	1.00-900
ISQG (mg kg^{-1})	-	-	0.6	37	36	35	-	12

NIS: Nigerian industrial standard for drinking water quality (NIS, 2007), ^{a}WHO standard for drinking water (Adewuyi *et al*., 2011), SNR: Soil natural range (Asia *et al*., 2007), ^{b}Concentration range for unpolluted soil (Adeniyi and Afolabi, 2002), ^{c}Toxicity characteristic leachate limit (Asia *et al*., 2007) and ISQG: Interim sediment quality guidelines (Adewuyi *et al*., 2011) similar petroleum oil polluted regions in the Niger Delta area of Nigeria (Osuji and Onojake, 2006; UNEP, 2011). Osuji and Onojake (2006) reported TPH values of 20,600±4970 and 1670±361 mg kg^{-1} in subsurface and surface soils, respectively while the United Nations Environment Programme (UNEP) (2011) reported TPH levels of 49800, 63600, 14200, 32600 and 7310 mg kg^{-1} for soils of Ejama-Ebube, Bomu, Manifold, Korokoro flow station, K-Dere and Nsisioken Agbi Ogale sites, respectively in Ogoniland, while groundwater levels were 485, 3.4, 0.77, 5.65 and 86 mg L^{-1}, respectively in the same locations. Even though hydrocarbons are natural organic substances, unlike heavy metals, hydrocarbons are not generally present in the surface soil (UNEP, 2011). Hence, TPH levels can serve as an indicator of petroleum oil pollution.

Besides hydrocarbons, some heavy metals can give information about the origin of contamination, since crude oils and heavy distillates contain a wide range of trace metals (Adeniyi and Afolabi, 2002; Osuji and Adesiyan, 2005a; Adewuyi *et al.*, 2011). Cu, Ni and Zn for example are present in the oils as metallo-porphyrin complexes as well as non-porphyrin complexes and their concentration increases with increasing hydrocarbon heavy fraction contents. Pb can be useful for the age dating of a spill because Pb alkyls are the most commonly used gasoline additives (Riccardi *et al.*, 2008).

The mean concentrations (mg L^{-1}) of Cd, Cr, Cu, Pb, Ni and Zn in the groundwater is 0.06±0.01, 0.77±0.05, 0.04±0.01, 3.7±0.9, 0.66±0.06 and 1.4±0.0, respectively, while surface water is 0.35±0.03, 1.02±0.02, 0.68±0.05, 1.9±0.1, 0.76±0.02 and 2.8±0.0, respectively. The levels of Cd, Cr, Pb and Ni exceed the Nigerian Industrial Standard (NIS, 2007) for drinking water quality, though Ni levels are lower than the USEPA limit of 0.61 in drinking water (USEPA, 2010). However, Cu and Zn are within safe limits. High levels of Cd, Cr and Pb have been reported previously for the same site (Ogunlaja and Ogunlaja, 2007; Adewuyi *et al.*, 2011) and also for shallow wells and boreholes used as drinking water sources in neighboring communities (Nduka and Orisakwe, 2009).

Also, the levels of the metals (mg kg^{-1}) in soil and sediment are 0.36±0.10 and 0.06±0.07 for Cd, 34±4 and 61±2 for Cr, 42±6 and 54±4 for Cu, 56±10 and 59±3 for Pb, 33±4 and 51±3 for Ni and 260±20 and 220±10 for Zn. The levels of Cd, Cr, Cu and Pb in the soil exceed the soil natural range (Asia *et al.*, 2007), while Cr, Cu and Pb in the sediment exceed the Canadian interim sediment quality guidelines (Adewuyi *et al.*, 2011). However, Ni and Zn levels in the soil and sediments are within these limits.

Unlike the other metals, Cu, Ni and Zn are essential metals for plants metabolic activities, so the metals may have been used up by aquatic and terrestrial plants in the river and soil, thereby reducing the levels that ultimately get to the groundwater and sediment. Previous studies conducted in Warri have also reported safe levels of these metals in environmental media (Aremu *et al.*, 2002; Emoyan *et al.*, 2006; Ogunlaja and Ogunlaja, 2007; Oribhabor and Ogbeibu, 2009; Kaizer and Osakwe, 2010; Nwankwo and Ogagarue, 2011) including high spill areas (Adewuyi *et al.*, 2011).

Source identification of the pollutants: The Pearson's correlation coefficient measures the strength of a linear relationship between two variables on the scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect direct relation) (Yisa *et al.*, 2011). Strong positive correlations were observed for the contaminants in all the environmental media, except for Cd, which shows

Table 2: Correlation matrix

		Oil and grease	TPH	Cd	Cr	Cu	Pb	Ni	Zn
Correlation	Oil and grease	1.000	0.996	-0.461	0.955	0.873	0.800	0.925	0.704
	TPH	0.996	1.000	-0.379	0.975	0.907	0.841	0.951	0.755
	Cd	-0.461	-0.379	1.000	-0.251	-0.101	-0.027	-0.191	0.097
	Cr	0.955	0.975	-0.251	1.000	0.978	0.940	0.996	0.882
	Cu	0.873	0.907	-0.101	0.978	1.000	0.990	0.993	0.961
	Pb	0.800	0.841	-0.027	0.940	0.990	1.000	0.967	0.989
	Ni	0.925	0.951	-0.191	0.996	0.993	0.967	1.000	0.921
	Zn	0.704	0.755	0.097	0.882	0.961	0.989	0.921	1.000

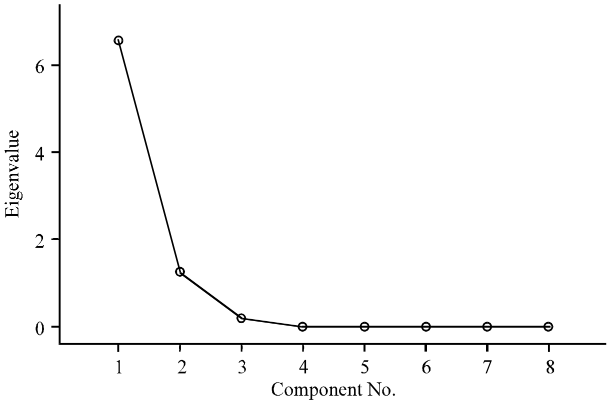

Fig. 2: Scree plot of eigenvalues and components

negative correlations with the other contaminants (Table 2). Significant correlations between contaminants are indications that they are from the same source (Yisa *et al.*, 2011). Hence, the PCA will confirm the relationships between the contaminants with respect to their sources.

The concentrations of the 8 contaminants (parameters) were subject to principal component analysis using ones as prior communality estimates. The principal component method was used to extract the component and this was followed by a varimax (orthogonal) rotation.

Only the first two components displayed eigenvalues greater than 1 (Dallarosa *et al.*, 2005; Ravindra *et al.*, 2008) and the result of a scree test (Fig. 2) also suggested that only the first two components where meaningful. Therefore, only the first two components were retained. Combined components 1 and 2 accounted for about 98% of the total variance.

In interpreting the rotated factor pattern, an item was said to load on a given component if the factor loading was 0.5 or greater, for that component and was less than 0.5 for the other (Ravindra *et al.*, 2008). Using these criteria, 7 parameters (oil and grease, TPH, Cr, Cu, Pb, Ni and Zn) were found to load on the first component, while only Cd loaded on the second component, signifying a different source of pollution. The loading of oil and grease, TPH, Cr, Cu, Pb, Ni and Zn on component 1 show a common source and is traceable to the Warri Refinery and Petrochemical Company (WRPC) as the source of the pollution (Table 3) and thus confirmed the proposal of Adewuyi *et al.* (2011). High levels of TPH, Cr, Cu, Pb, Ni and Zn have been reported previously for petroleum oil polluted regions of the Niger Delta region of Nigeria (Adeniyi and Afolabi, 2002) and elsewhere (Muniz *et al.*, 2004; Rauckyte *et al.*, 2006; Riccardi *et al.*, 2008).

Table 3: Rotated factor pattern and final communality estimates from principal component analysis

Parameters	Component 1	Component 2	h^2
Oil and Grease	0.851*	0.493	0.968
TPH	0.892*	0.410	0.963
Cd	-0.025	-0.975*	0.950
Cr	0.968*	0.246	0.997
Cu	0.997*	0.067	0.998
Pb	0.989*	0.032	0.979
Ni	0.985*	0.172	1.000
Zn	0.966*	0.169	0.962

h^2: Final communality estimates, *Factor loadings on components above 0.5

CONCLUSION

Samples of groundwater, surface water, soil and sediment collected from the Ubeji settlement and river showed significant contamination by oil and grease, TPH and the non-essential hydrocarbons (Cd, Cr and Pb). Pearson's correlation coefficient used to study the linear relationship of the contaminants with each other gave a strong correlation for all the contaminants except Cd that was negatively correlated with the rest of the contaminants. PCA revealed that all the contaminants but Cd are from the WRPC.

REFERENCES

Adeniyi, A.A. and J.A. Afolabi, 2002. 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., O.T. Etchie and A.T. Ademoyegun, 2011. Determination of total petroleum hydrocarbons and heavy metals in the surface water and sediment of Ubeji river, Warri, Nigeria. Biorem. Biodiver. Bioavail., 5: 46-51.

Akporido, S.O., 2008. Assessment of water, sediment and soil pollution arising from crude oil spillages in the vicinity of Esi River Western Niger Delta. P.hD. Thesis, Chemistry Department, University of Ibadan, Nigeria.

Aremu, D.A., J.F. Olawuyi, S. Meshitsuka, M.K. Sridhar and P.A. Oluwande, 2002. Heavy metal analysis of groundwater from Warri, Nigeria. Intern. J. Environ. Health Res., 12 : 261-267.

Asia, I.O., S.I. Jegede, D.A. Jegede, O.K. Ize-Iyamu and E.B. Akpasubi, 2007. The effects of petroleum exploration and production operations on the heavy metals contents of soil and groundwater in the Niger Delta. Int. J. Phys. Sci., 2: 271-275.

Boyacioglu, H. and H. Boyacioglu, 2008. Water pollution sources assessment by multivariate statistical methods in the Tahtali Basin, Turkey. Environ. Geol., 54: 275-282.

Dallarosa J.B., E.C. Teixeira, M. Pires and J. Fachel, 2005. Study of the profile of polycyclic aromatic hydrocarbons in atmospheric particles (PM_{10}) using multivariate methods. Atmos. Environ., 39: 6587-6596.

EPA, 1999. Method 1664, revision A: N-hexane extractable material (HEM; Oil and grease) and silica gel treated N-hexane extractable material (SGTHEM; Non-polar material) by extraction and gravimetry. Office of Water, Washington, DC., USA.

Emoyan, O.O., F.E. Ogban and E. Akarah, 2006. Evaluation of heavy metals loading of river Ijana in Ekpan-Warri, Nigeria. J. Applied Sci. Environ. Manage., 10: 121-127.

Hseu, Z.Y., 2004. Evaluating heavy metal contents in nine composts using four digestion methods. Bioresour. Technol., 95: 53-59.

Kaizer, A.N. and S.A. Osakwe, 2010. Physicochemical characteristics and heavy metals levels in water samples from five river systems in Delta State, Nigeria. J. Applied Sci. Environ. Manage., 14: 83-87.

Kelepertsis, A., A. Argyraki and Alexakis, 2006. Multivariate statistics and spatial interpretation of 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.

Kowalkowski, T., R. Zbytniewski, J. Szpejna and B. Buszewski, 2006. Application of chemometrics in river water classification. Water Res., 40: 744-752.

Lee, B.K. and N.Y. Hieu, 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.

Li, Y., L. Xu and S. Li, 2009. Water quality analysis of the Songhua River Basin using multivariate techniques. J. Water Res. Protect., 2: 110-121.

Mmolawa, K.B., A.S. Likuku and G.K. Gaboutloeloe, 2011. Assessment of heavy metal pollution in soils along major roadside areas in Botswana. Afr. J. Environ. Sci. Technol., 5: 186-196.

Mohd, I., M.A. Mansor, M.R.A. Awaluddin, M.F.M. Nasir, M.S. Samsudin, H. Juahir and N. Ramli, 2011. Pattern recognition of Kedah River water quality data implementation of principal component analysis. World Applied Sci. J., 14: 66-72.

Mohsenzadeh, F., S. Nasseri, A. Mesdaghinia, R. Nabizadeh, D. Zafari, G. Khodakaramian and A. Chehregani, 2010. Phyto remediation of petroleum-polluted soils: Application of Polygonu aviculare and its root-associated (penetrated) fungal strains for bioremediation of petroleum-polluted soils. Ecotoxicol. Environ. Saf., 73: 613-619.

Momodu, M.A. and C.A. Anyakora, 2010. Heavy metal contamination of groundwater: The surulere case study. Res. J. Environ. Earth Sci., 2: 39-43.

Mostert, M.M.R. and G.A. Ayoko and S. Kokot, 2010. Application of chemometrics to analysis of soil pollutants. Trends Analyt. Chem., 29: 439-445.

Motelay-Massei A., D. Ollivon, B. Garban, K. Tiphagne-Larcher, I. Zimmerlin and M. Chevreuil, 2007. PAHs in the bulk atmospheric deposition of the Seine River Basin: Source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy. Chemos., 67: 312-321.

Muniz, P., E. Danulat, B. Yannicelli, J. Garcia-Alonson, G. Medina and M.C. Bicergo, 2004. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediment of Montevideo Harbour (Uruguay). Environ. Int., 29: 1019-1028.

NIS, 2007. Nigerian standard for drinking water quality. ICS 13.060.20,Approved by Standard Organization of Nigeria (SON)Governing Council, Lagos and Abuja, Nigeria. http://www.unicef.org/nigeria/ng_publications_Nigerian_Standard_for_Drinking_Water_Quality.pdf

Nduka, J.K. and O.E. Orisakwe, 2009. Effect of effluents from warri refinery petrochemical company WRPC on water and soil qualities of contiguous host and impacted on communities of delta state, Nigeria. Open Environ. Pollut. Toxicol. J., 1: 11-17.

Nwankwo, C.N. and D.O. Ogagarue, 2011. Effects of gas flaring on surface and ground waters in Delta State Nigeria. J. Geo. Mining Res., 3: 131-136.

Ogunlaja, A. and O.O. Ogunlaja, 2007. Physicochemical analysis of water sources in Ubeji community and their histological impact on organs of albino mice. J. Appl. Sci. Environ. Manage., 11: 91-94.

Oh, M.S., T.J. Lee and D.S. Kim, 2011. Quantitative source apportionment of size-segregated particulate matter at urbanized local site in Korea. Aerosol Air Qual. Res., 11: 247-264.

Olobaniyi, S.B. and S.I. Efe, 2007. Comparative assessment of rainwater and groundwater quality in an oil producing area of Nigeria: Environmental and health implications. J. Environ. Health Res., 6: 111-118.

Omo-Irabor, O.O., S.B. Olobaniyi, K. Oduyemi and J. Akunna, 2008. Surface and groundwater water quality assessment using multivariate analytical methods: A case study of the Western Niger Delta, Nigeria. Phys. Chem. Earth, 33: 666-673.

Oribhabor, B.J. and A.E. Ogeibu, 2009. Concentration of heavy metals in a Niger Delta mangrove creek, Nigeria. Global J. Environ. Sci., 8: 1-10.

Osuji, L.C. and C.M. Onojake, 2006. Field reconnaissance and estimation of petroleum hydrocarbon and heavy metal contents of soils affected by the Ebocha-8 oil spillage in Niger Delta, Nigeria. J. Environ. Manage., 79: 133-139.

Osuji, L.C. and S.O. Adesiyan, 2005a. Extractable hydrocarbons, nickel and vanadium contents of ogbodo-isiokpo oil spill polluted soils in Niger Delta, Nigeria. Environ. Monitor. Assess, 110: 129-139.

Osuji, L.C. and S.O. Adesiyan, 2005b. The Isiokpo oil-pipeline leakage: Total organic carbon/organic matter contents of affected soils. Chem. Biodivers., 2: 1079-1085.

Pawlak, Z., T. Rauckyte and A. Oloyede, 2008. Oil, grease and used petroleum oil management and environmental economic issue. J. Achieve Mater. Manuf. Eng., 26: 11-17.

Rauckyte, T., D.J. Hargreaves and Z. Pawlak, 2006. Determination of heavy metals and volatile aromatic compounds in used engine oils and sludges. Fuel, 85: 481-485.

Ravindra, K., R. Sokhi and R. van Grieken, 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos. Environ., 42: 2895-2921.

Riccardi, C., P. di Filippo, D. Pomata, F. Incoronato, M. di Basilio, M.P. Papini and S. Spicaglia, 2008. Characterization and distribution of petroleum hydrocarbons and heavy metals in groundwater from three Italian tank farms. Sci. Total Environ., 393: 50-63.

Samecka-Cymerman, A., K. Kolon and A.J. Kempers, 2005. Differences in concentrations of heavy metals between native and transplanted *Plagiothecium denticulatium*: A case study of soil contaminated by oil well exudates in South-East Poland. Arch. Environ. Contam. Toxicol., 49: 317-321.

Sekabira, K., H.O. Origa, T.A. Basamba, G. Mutumba and E. Kakudidi, 2010. Assessment of heavy metal of pollution stream sediments and its tributaries. Int. J. Environ. Sci. Technol., 7: 435-446.

Simeonov, V., J.A. Stratis, C. Samara, G. Zachariadis and D. Voutsa *et al.*, 2003. Assessment of the surface water quality in Northern Greece. Water Res., 37: 4119-4124.

Singh, K.P., A. Malik and S. Sinha, 2005. Water quality assessment and apportionment of pollution sources of Gomti River (India) using multivariate statistical techniques: A case study. Anal. Chim. Acta, 538: 355-374.

UNEP, 2011. Environmental assessment of ogoniland. http://postconflict. unep.ch/ publications/ OEA/UNEP_OEA.pdf

USEPA, 2010. Drinking water contaminants, national primary drinking water regulations. http://water.epa.gov/drink/contaminants/index.cfm#Primary

Yang, F., Y.B. Zhai, L. Chen, C.T. Li and G.M. Zeng *et al*., 2010. The seasonal changes and spatial trends of particle-associated polycyclic aromatic hydrocarbons in the summer and autumn in Changsha city. Atmos. Res., 96: 122-130.

Yisa, J., J.O. Jacob and C.C. Onoyima, 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.

Zuo, Q., Y.H. Duan, Y. Yang, X.J. Wang and S. Tao, 2007. Source apportionment of polycyclic aromatic hydrocarbonsin surface soil in Tianjin, China. Environ. Pollut., 147: 303-310.