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n-Alkane Profile of Underground Water near a Dump-site at Balogun-biiro in Okebaale, Oshogbo Osun State

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Abstract

Well-water samples were collected from the vicinity of Balogun-biiro dump-site located in Okebaale Oshogbo, Osun state, Nigeria. The aim of this research work is to provide background information on the concentration of *n*-alkanes in the well-water in order to assess its pollution status and probable sources. The *n*-alkane was determined qualitatively and quantitatively using GC-FID. The concentration of *n*-alkanes in the water samples was, 8.07, 9.64, 9.75, 8.43, 10.4, and 10.1 mg/L in S1, S2, S3, S4, S5, and S6 respectively. The highest concentration of *n*-alkanes was recorded in the water samples collected from a well located in a residential building very close to the dumpsite as well as the mechanic workshop (i.e. S5) while the lowest concentration was recorded in S1 (well-water relatively far from the dump-site). Various *n*-alkanes diagnostic ratios obtained indicated anthropogenic sources (i.e. both petrogenic and pyrogenic) and showed moderate level of pollution in the area under study.

Keywords: GC-FID; aliphatic hydrocarbon; pollution; anthropogenic; mechanic workshop

Introduction

Environmental pollution is any discharge of material or energy into water, land or air that may cause acute (short-term) or chronic (long-term) detriment to the earth's ecological balance or that lowers or harms the quality of life. Water Pollution involves contamination of streams, lakes, underground water, bays, or oceans by substances harmful to living things. If severe, water pollution can kill large numbers of fish, birds, and other animals, in some cases killing all members of a species in an affected area. People who ingest polluted water can become ill, and, with prolonged ingestion, may develop cancers or bear children with birth defects. Aliphatic hydrocarbon analysis can be used to fingerprint spilled oils and to provide additional information on the source of hydrocarbon contamination and the extent of

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degradation of spilled oil (Wang and Fingas, 2003). *n*-Alkanes are a class of aliphatic hydrocarbons that can be used for environmental pollution monitoring assessment (Wang *et al.*, 2002; Wang and Fingas, 2003; Commendatore and Esteves, 2004; Gao and Chen, 2008; Sakari *et al.*, 2008; Zrafi-Nouira *et al.*, 2008).

n-Alkanes are non-polar hydrocarbons and photo catalytically stable organic compounds and their bulk characteristics in suspended particle extract can be used to identify two major sources: biological source (biogenic) and incomplete combustion of fossil fuel (anthropogenic), and provide useful information for the identification of particle sources (Schauer *et al.,* 1996). Hydrocarbons of biogenic origin naturally occur at low concentrations in different substrates, such as water and sediment, and are part of the natural hydrocarbon baseline of an ecosystem (Sakari *et al.,* 2008). According to UNEP (1992), hydrocarbon concentrations in non-polluted sediments are not greater than 10 μg/g dry weight. The definition of a baseline level of hydrocarbons is essential when attempting to determine chemical changes introduced by anthropogenic effects (Commendatore and Esteves, 2004).

Some *n*-alkanes indices have been used over the years to identify biogenic and petrogenic sources. According to Commendatore and Esteves, (2004) (i) Major Hydrocarbon (MH): denotes the highest *n*-alkane concentration. This index is often around C_{18} for crude oils. C_{15}, C_{17}, C_{19} and C_{21} have been described as important components in different types of algae (both macro and micro-algae), and C_{23}, C_{25}, C_{27}, C_{29} and C_{31} for vascular land plants. (ii) The low/high molecular weight hydrocarbons (LMW/HMW): it is the ratio of the sum of *n*-alkanes ≤C20 over the sum of *n*-alkanes ≥21. Ratio values of 1.0 have been reported for petroleum, while sedimentary bacteria, seawater, marine animals, higher plants, and sediments show relatively lower values. Ratio values >1.0 indicate algae and plankton hydrocarbon inputs. (iii) n-C16 ratio: it is the sum of all *n*-alkanes/n-C_{16}. This ratio tends to be small (<15) for petroleum-contaminated samples, while it is larger (>50) for biological samples (iv) Carbon preference index (CPI): it is defined as $2(C_{27} + C_{29})/C_{26} + (2C_{28}) + C_{30}$. Petrogenic hydrocarbons show values around 1, while vascular plants and uncontaminated sediments range from 3 to 6. (viii) Sum of the resolved aliphatic/unresolved complex mixture index (U/R): this index estimates the relative degradation degree; low values suggest a degradation process, while high values suggest fresh oil presence. The UCM magnitude is related to the degree of anthropogenic contribution. UCM presence is usually associated with petroleum hydrocarbons. It has been suggested that UCM can result from bacterial degradation of organic matter. The purpose of this study is to examine the distribution of *n*-alkanes in water samples collected from wells in Balogun-biiro area Okebale Osogbo, Nigeria and used it to assess the source and variation in the level of pollution within the studied area.

Materials and Methods

Well-water samples were collected at six different locations in the vicinity of a dump-site located in Balogun-biiro area of Osogbo, Osun state, Nigeria. The sample locations are as follows: **S1**-07^0 46^1 21N, 004^0 34^1 21E.333, **S2**-07^0 46^1 22N, 004^0 34^1 19E.335, **S3**-07^0 46^1 22N,004^0 34^1 17N.328, **S4**-07^0 46^1 20N,004^0 34^1 20E.323, **S5**-07^0 46^1 20N,004^0 34^1 19E, **S6**-07^0 46^1 20N,004^0 34^1 19E.324. 200 mL of water sample was transferred into a 1 L separatory funnel, and 60 mL of the redistilled dichloromethane was added. The separatory funnel was shaken vigorously for about 2 minutes with periodic venting to releasewater vapor pressure. The organic layer was allowed to separate for 10 minutes and was recovered into the 250 mL flask. The aqueous layer was re-extracted twice with 60 mL of the extractant. The combined extract was dried by passing through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a steam of nitrogen gas. The extracts were fractionated using silica on alumina gel column in ratio 2:1. The aliphatic fraction was obtained by elution with 20 mL of *n*-hexane. The aromatic fraction was obtained by elution with 70 mL of *n*-hexane and dichloromethane (7:3), while

the polar fraction was eluted with 25 mL of methanol. The aliphatic fraction was concentrated by rotary evaporation. The aliphatic fraction was subjected to gas chromatographic analysis for the determination of *n*-alkanes in the samples with a gas chromatography HP 5890 powered with HPCHEM software with flame ionization detector (FID). The separation was effected on 30 m x 0.25 mm i.d. HP-5 fused silica column using nitrogen as carrier gas. The oven temperature started at 68 ^0C (2 min hold) followed by 21 ^0C for 16 min at 4 ^0C/min, then 15 ^0C for 4 min and 8 ^0C/min.

Results

Representative water samples from wells in the vicinity of a dump-site and mechanic workshop located in Balogun-biiro, Okebale Osogbo were analyzed for *n*-alkanes composition using gas chromatography with flame ionization detector (FID). The parameters derived from the distribution of *n*-alkanes were used to evaluate the variation in pollution and its source within the area. The concentration of *n*-alkanes in the water samples were presented in table 1. All the samples have carbon number ranging from C_9-C_{30} except in sample 1 and 2 where carbon number ranged from C_{10}-C_{30}. The carbon maximizes at both the lower and intermediate homologues in all the samples (Table 2).

The CPI ratio in the samples ranged from 0.850 to 1.20 (Table 2). The major hydrocarbon (MH) index in the samples was C_{27}, C_{22}, C_{24}, C_{27}, C_{22} and C_{29} in S1, S2, S3, S4, S5 and S6 respectively. The values of LMH/HMW and *n*-C16 ratio in the samples ranged from 4.28 to 53.4 and 8.43 to 22.8 respectively. Presence of raised base–line humps in the chromatograms showed there are unresolved complex mixtures (UCMs). UCMs are composed mainly of branched alkanes, aromatics and cycloalkanes. They are one of indicators of petrogenic inputs (Frysinger *et al.,* 2003). The degree of petroleum contamination can be expressed as the ratio of unresolved to resolved hydrocarbon compounds i.e. U/R (Simoneit, 1984; Commendatore and Esteves, 2004). U/R values in the samples ranged from 4.28 to 53.4 (Table 2).

Discussion

The pattern of distribution of *n*-alkanes in the samples indicated the existence of various anthropogenic activities going on in the study area (Jacquot *et al.,* 1999; Stout *et al.,* 2002; Wang and Fingas, 2003; Commendatore and Esteves, 2004; Sakari *et al.,* 2008). This is because *n*-alkane maximized at C_{17} is characteristic of most crude oil samples (Jacquot *et al.,* 1999). Furthermore, weathered diesel-range hydrocarbons are also a possible source of *n*-alkanes especially for those in the range of C_{15}-C_{22} based on their distribution patterns for all sampling sites (Stout *et al.,* 2002; Wang and Fingas, 2003).

The CPI values indicated high anthropogenic input into the water samples (Commendatore and Esteves, 2004). Significant number of samples showed carbon maxima (i.e. MH) in the intermediate homologue, which reflected that anthropogenic sources played a very important role. Both *n*-C16 ratio and LMW/HMW in the samples showed both pyrogenic and petrogenic (anthropogenic) sources of n-alkanes in the samples. Petroleum distillates are reported to have LMW/HMW values around 1.0 while *n*-C16 ratio of value > 50 has been attributed to biogenic source i.e. uncontaminated (Stout *et al.,* 2002, Wang and Fingas, 2003, Commendatore and Esteves, 2004). The value of U/R in the samples confirmed the presence of petroleum component (Simoneit, 1984, Commendatore and Esteves, 2004).

Conclusion

This work investigated the distribution of *n*-alkanes in underground water collected from different wells in the vicinity of a dump site and mechanic workshop located at Balogun-biiro area Okebale Osogbo, Osun State Nigeria. The level of *n*-alkanes can be associated with their sources, through the use of *n*-alkanes diagnostic ratios, which provide more unique markers for the sources. Relatively high concentrations of *n*-alkanes were recorded in well water close to the dumpsite and mechanic workshop (i.e. S5 and S6) while the lowest value of *n*-alkane was recorded in S1 (i.e. relatively far distance from the dumpsite).

Table 1: Concentration of *n*-alkanes in well-water samples (mg/L) collected from the vicinity of Balogun-biiro dump-site, Oshogbo

N-ALKANE	S1	S2	S3	S4	S5	S6
C_9	-	-	0.113	0.191	0.571	0.496
C_{10}	0.103	0.303	-	-	-	-
C_{11}	0.204	0.505	0.499	0.447	0.640	0.502
C_{12}	0.288	0.610	0.812	0.608	0.488	0.209
C_{13}	0.216	0.393	0.392	0.386	0.363	0.662
C_{14}	0.422	0.678	0.495	0.711	0.554	0.602
C_{15}	0.416	0.671	0.529	0.700	0.631	0.299
C_{16}	0.379	0.575	0.427	0.545	0.500	0.877
C_{17}	0.534	0.386	0.666	0.376	0.642	0.138
C_{18}	0.599	0.394	0.761	0.348	0.682	0.440
C_{19}	0.426	0.399	0.542	0.386	0.667	0.267
C_{20}	0.519	0.523	0.675	0.512	0.858	0.864
C_{21}	-	-	-	-	-	-
C_{22}	0.563	0.811	0.687	0.486	0.894	0.453
C_{23}	0.376	0.644	0.468	0.380	0.722	0.938
C_{24}	0.990	0.753	0.951	0.737	0.675	1.06
C_{25}	0.697	0.608	0.670	0.495	0.477	0.877
C_{26}	-	-		-	-	-
C_{27}	1.07	0.569	0.745	0.823	0.821	0.848
C_{28}	-	-		-	-	-
C_{29}	0.137	0.255	0.183	0.228	0.225	1.09
C_{30}	0.010	0.563	0.167	0.104	0.042	0.086

Table 2: Total concentration and diagnostic ratios of *n*-alkanes in well-water samples (mg/L) collected from the vicinity of Balogun-biiro dump-site, Oshogbo

Parameters	S1	S2	S3	S4	S5	S6
CPI	1.08	0.850	0.972	1.08	1.14	1.20
MH(C_{max})	C_{27}	C_{22}	C_{24}	C_{27}	C_{22}	C_{29}
U/R	53.4	4.28	6.91	17.9	10.0	35.6
LMW/HMW	1.05	1.29	1.52	1.59	1.56	1.13
T*n*-alkane (mg/L)	8.07	9.64	9.75	8.43	10.4	10.1
n-C_{16} ratio	21.3	16.8	22.8	8.43	21.3	11.5

The *n*-alkanes concentration in the underground water decreased with increasing distance from moderately contaminated sites to background values as seen for *n*-alkanes values recorded from some sites under study.

The source diagnostic ratios of *n*-alkanes showed that its source could be traced to anthropogenic activities rather than biogenic. It could be recommended that regular examination and analysis should be carried out in this area so as to prevent the accumulation of anthropogenic input to a toxic level. This is to ensure the safety of residents and to prevent them from various diseases that occur as a result of consumption of polluted water.

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References

Commendatore, M. G. and Estevez, J. L. (2004). Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). *Marine Pollution Bulletin* 48, 910–918.

Frysinger, G. S., Gaines, R. B., Xu, L. and Reddy, C. M. (2003). Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science and Technology* 37, 1653–1662.

Gao, X. and Chen, S. (2008). Petroleum pollution in surface sediments of Daya Bay, South China, revealed by chemical fingerprinting of aliphatic and alicyclic hydrocarbons. *Estuarine, Coastal and Shelf Science* 80, 95–102.

Jacquot, F., Le Dreau, Y., Doumenq, P. and Munoz, D. (1999). The origins of hydrocarbons trapped in the lake of Berre sediments. *Chemosphere* 39, 1407-1419.

Sakari, M., Zakaria, M. P., Junos, M. B., Annuar, N. A., Yun, H. Y., Heng, Y. S., Zainuddin, S. and Chai, K. L. (2008). Spartial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular Malaysia. *Coastal Marine Science 32*(1), 9-18.

Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T. (1996). Source apportionment of airbone particulate matter using organic compounds as tracers. *Atmospheric Environment 30*(22), 3837-3855.

Simomeit B. R. T. (1984). Organic Matter of the Troposphere III, Characterization and Sources of Petroleum and Pyrogene Residues in Aerosols over the Western United State. *Atmospheric* 18, 51-67.

Stout, S. A. Uhler, A. D., McCArthy, K. J. and Emsbo-Mattingly, S. A. (2002). *Chemical fingerprinting of hydrocarbons In: Murphy, B.J., Morrison, R., (Eds.), Introduction of Environmental forensics*. Academy Press, Boston, pp. 137 – 260.

UNEP, (1992). *Determination of petroleum hydrocarbons in sediments*. Reference Methods For Marine Pollution Studies No 20.

Wang, Z., Lia, K., Fingasa, M., Sigouina, L., and Ménard, L. (2002). Characterization and source identification of hydrocarbons in water samples using multiple analytical techniques. *Journal of Chromatography A* 971, 173–184.

Wang, Z. and Fingas, M.F. (2003). Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin* 47, 423–452.

Zrafi-Nouira, I., Khedir-Ghenim, Z. Zrafi, F., Bahri, R., Cheraeif, I., Rouabhia, M., and Saidane- Mosbahi, D. (2008). Hydrocarbon Pollution in the Sediment from the Jarzouna-Bizerte Coastal Area of Tunisia (Mediterranean Sea). *Bulletin of Environ mental Contamination and Toxicology* 80, 566–572.