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Full Length Research Paper

Polycyclic aromatic hydrocarbons (PAHs) contamination of synthetic industrial essential oils utilized in Northern Nigeria

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This paper provides supplementary information to earlier elucidations on the level of dioxin contaminations of synthetic industrial essential oils (SIEOs), commonly referred to as Turare (Hausa Language) utilized in Northern Nigeria. In this work, fifteen typical samples of this product was analysed for the EPA-16 targeted Polycyclic Aromatic Hydrocarbons (PAHs) using GC-MS methodology. The result revealed that all 15 SIEO samples indicated the presence of the EPA-16-targeted PAHs. The QC sample run for all samples gave a value within ± 19% and percentage recoveries were in the range of 76- 105%. The uncertainty of measurement is within the acceptance criteria based on a confidence level of 95%. Phenanthrene was observed to show the highest concentration at 2.87 mg/kg, while the least PAHs compounds was chrysene at 0.02 mg/kg. The results also showed that the low molecular weight (e.g. phenanthrene, anthracene and acenaphthene) PAHs constitutes the largest group of compounds with high concentrations in the SIEO samples, while the pertinent high molecular weight PAHs, benzo(b)fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(a)anthracene, benzo(a)pyrene and dibenzo(a,h)pyrene were present at relatively moderate to low concentrations. However, on the basis of form of application, the result reveals that the socio-cultural form of application had the highest composition of high molecular weight (MW) PAHs and was statistically significant ($p<0.05$). Therefore the direct forms of applications of SIEOs in Northern Nigeria portend higher likelihood of exposure enrichments of PAHs with potential hazards to human health and the environment.

Key words: Fragrance material, direct application, toxicant, persistent, human health, environment.

INTRODUCTION

The aim of this paper is to provide supplementary information to earlier elucidations in the work by Hati et al. (2008), in which the level of dioxin contaminations of synthetic industrial essential oils (SIEOs) was reported. It was necessitated by the growing risks associated with the direct application of SIEOs, commonly referred to as Turare (Hausa Language), in Northern Nigeria. SIEOs are a major source of fragrance material that is highly utilized in its neat or concomitant form by direct application. The three major forms of applications of SIEOs in Northern Nigeria as indicated by Hati et al. (2008) are presented on Table 1. A practice that is widespread in Northern Nigeria, which has grown steadily in recent years (Hati, 2005). In this work, the sixteen targeted PAHs by the United States Environmental Protection Agency (USEPA) tagged EPA-16 (EPA, 1984) was determined in some typical SIEO samples used in high volumes in this region, because toxicants to human and the environment in this product through the various forms of direct applications of SIEOs in Northern Nigeria remain unknown.

PAHs, dioxins, polychlorinated biphenyls (PCBs), toxaphene, pesticides and a number of other related compounds have been classified as persistent organic pollutants (POPs) (UNEP, 2002; Hites, 2006). They are organic compounds of anthropogenic origin that resist photolytic, biological or chemical degradation, leading to their

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Table 1. Three major categories of application of SIEOs in Northern Nigeria

Category	Description
Socio-cultural	Burning SIEOs with woods, resinous and other fragrance substances. Multiple mixtures of SIEOs applied on body.
Fashion	Applications of SIEOs as perfume/ fragrance on body, clothe and home/ office
Industrial formulations	Industrial use for production of eau de cologne, soap, pomade, perfume, etc.

Figure 1. Map of Nigeria showing major distribution points of SIEOs in Northern Nigeria

bioaccumulation in the food chain. They can be transported over long distances in the atmosphere, resulting in widespread distribution across the earth including regions where they have never been used. Owing to their toxic characteristics, they can pose a threat to humans and the environment. In recent years, the international community has called for urgent global action to reduce and eliminate the release of POPs and to identify their possible risk to human health and the environment due to their intrinsic chemical stability, high recalcitrance to deferent types of degradation and high toxicity to living organisms (DHFS, 2000; WHO, 2003; Andreoni et al., 2004).

PAHs are a much more chemically diverse group of organic compounds than dioxins and PCBs. They are highly volatile compounds and the most common mechanism whereby PAHs in particular, are released into the environment is via the incomplete combustion of essential oils, fossil fuels, plastics etc. Other major sources are industrial processes, the production and use of coal tar (creosote), and similar products (Wingfors, 2004). Similar to most toxic pollutants, PAHs route of exposures are by inhalation, oral, and dermal. These have been documented to cause several health problems -death, systemic, immunological, neurological, reproductive, developmental, genotoxic, and carcinogenic effects. They are discussed in terms of three exposures periods-acute (14 days or less), intermediate (15-364 days), and chronic (365 days or more) (Carpenter, 2005; UNEP, 2002; ASTDR, 1995).

The current regulatory system allows the application of synthetic chemicals as cosmetics unless proven beyond doubt to be dangerous. However, due to the mode of application of SIEOs in Northern Nigeria and the reports (Burfield, 2003; FDA, 1995) of certain components of synthetic fragrant compounds to be bio-persistent such as the long used nitromusks and polycyclic musks, it becomes pertinent to investigate the presence and concentration levels of PAHs in some of these SIEOs utilized in Northern Nigeria.

MATERIALS AND METHODS

Study area, samples and sampling

The study area comprises the three major points of distributions of SIEO products within Northern Nigeria: Sokoto, Kano and Maiduguri (Figure 1). A total of 75 SIEO samples were collected for this study over a two year (2005 and 2006) period. This followed the detailed survey of the forms of applications of SIEOs in Northern Nigeria as described by Hati (2005) and Hati et al. (2008). Three major categories of SIEOs applications were identified. These are socio-cultural, fashion and industrial formulations. Due to the wide range of these products, samples collected for this work was obtained from narrowed statistical data of volumes of annual output distribution of the products. This was obtained from manufacturers' distributors in the study area. Thus, only SIEO products ≥ 4500 tons/yr were collected for analysis. Only 15 typical SIEO products qualified. For each of these, a composite (100 ml) of five different batches of 20 ml each was collected directly from product manufacturers distri-

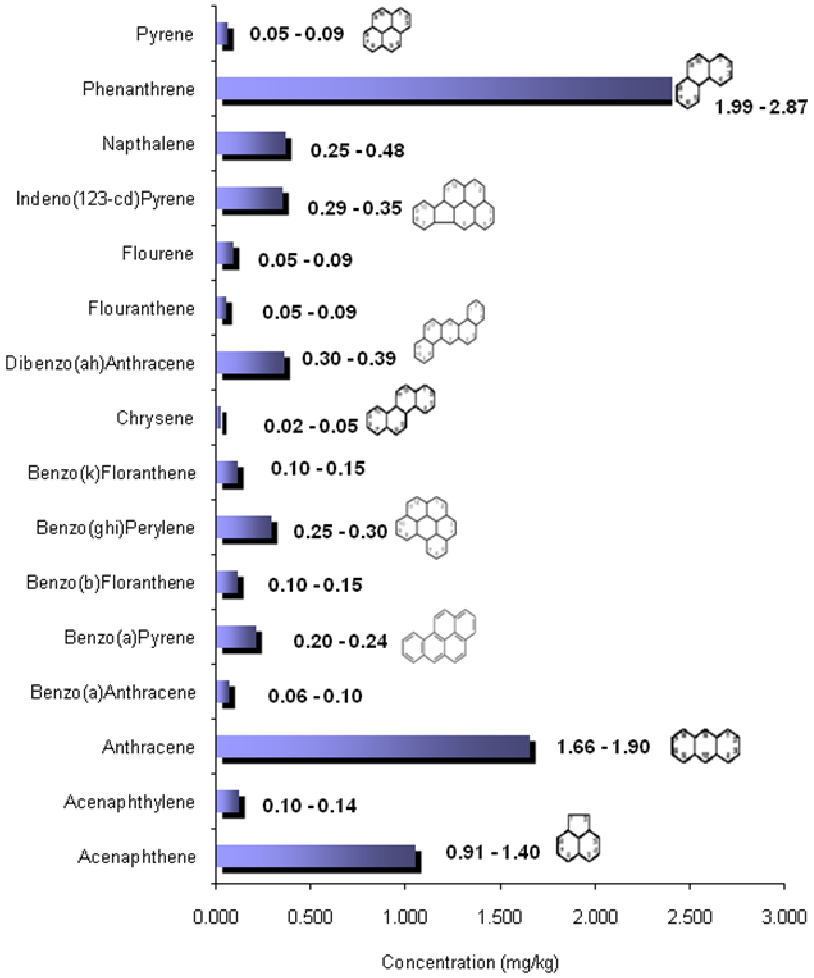

Figure 2.EPA-16PAHa concentration ranges in SIEO samples utilized in Northern Nigeria.

butors by decanting into well labeled sterile glass bottles.

Sample preparation and GC-MS (SIR) analysis

The EPA-16 PAHs determination was conducted in Scientific Analysis Laboratories Ltd (SAL), Medlock House in Manchester. SAL-in-house modification based on the EPA Method 610 and 8100 (EPA, 1984) for PAHs determination, using Gas Chromatography/Mass Spectrometry-Selective Ion Recording (GC/MS-SIR) quantitation technique was employed. In 20 ml volumetric flasks, 50 mg each of the 15 SIEO samples were dissolved in 1 ml dichloromethane (BDH, analytic grade), spiked with deuterated PAH internal standard and shaken thoroughly for proper mixing. Later transferred to the GC/MS injection vials for analysis. The standard internal addition method, using PerkinElmer TurboMass™ with HS 40XL auto sampler GC/MS was used for the determination. 2- 5 µl of each sample were injected at the GC Column conditions: Chromosorb W-AW-DCMS (100/120 mesh) coated with 3% OV-17 packed in a 1.8 x 2 mm ID glass column with nitrogen carrier gas at 40 ml/min. flow rate. Column temperature was held at 100℃ for four minutes, and then programmed at 8℃/min. to a final hold at 280℃. Safety consideration, cleanups and recoveries were observed according to procedures described by the EPA Method 610 and 8100.

Results obtained were presented as concentration (mg/kg) per analyte and statistical data analysis for variations in the 3 basic forms of application was conducted by analysis of variance (ANOVA) using coupled Microsoft Excel + Analyse-it (2006). Variations were considered significant at $p<0.05$.

RESULTS

All 15 SIEO samples indicated the presence of the EPA-16-targeted PAHs. Quality control (QC) sample run for all samples gave a value within ± 19% and percentage recoveries were in the range of 76- 105%. The uncertainty of measurement is within the acceptance criteria based on a confidence level of 95%. Figure 2 shows the concentration ranges at which each PAH compound was detected. Phenanthrene was observed to show the highest concentration at 2.87 mg/kg for one the SIEO sample, while the least PAHs compounds were chrysene at 0.02 mg/kg, followed by pyrene, flourene and flouranthene each at 0.05 mg/kg respectively. The variations were obviously very wide and high between the highest and the least 16-PAHs compounds determined. The results also

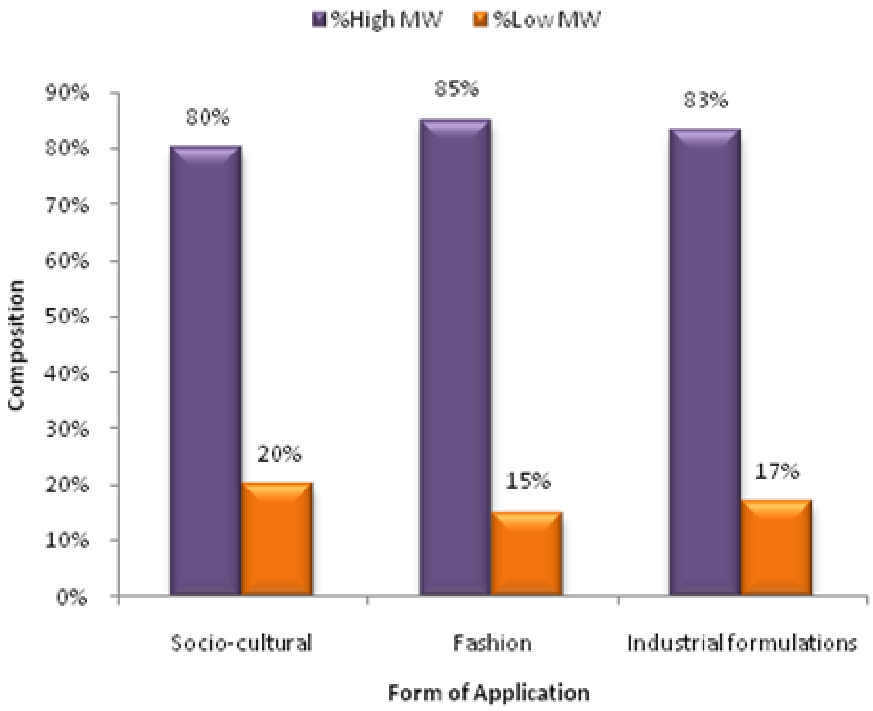

Figure 3. Percent composition of high and low molecular weight (MW) PAHs in the 3 categories of application of SIEOs in Northern Nigeria

showed that the low molecular weight (e.g. phenanthrene, anthracene and acenaphthene) PAHs constitutes the largest group of compounds with high concentrations in the SIEO samples, while the pertinent high molecular weight PAHs, benzo(b)fluoranthene, indeno(1,2,3-c,d) pyrene, benzo(a)anthracene, benzo(a)pyrene and dibenzo(a,h)pyrene were present at relatively moderate to low concentrations. On the basis of form of application (socio-cultural, fashion and industrial formulations), Figure 3 shows the percent compositions ratios of the low and high molecular weight (MW) PAHs constituents. This reveals that the socio-cultural form of application had the highest composition of high MW PAHs and was statistically significant ($p<0.05$) than in fashion form of applications.

DISCUSSION

SIEOs are solely imported from the United Kingdom, Germany, India and the Kingdom of Saudi Arabia and mainly as industrial raw materials. This is so because there is not one manufacturer of industrial essential oil in Nigeria. However, in comparism with the large tonnage of SIEOs present in Northern Nigeria markets, only a very small number of manufacturing industries require the use of this raw material. In Northern Nigerian markets, largely Maiduguri, Kano and Sokoto, there are over a hundred and fifty different types and versions of these products displayed for sale. The direct application of SIEOs in Northern Nigeria entails 'neat', straight; undiluted or unmodified use of the product in its full strength in personal and household care such as perfuming hair, body, clothes, bed, and floor and as room air freshener, bath and wood burning admixes. Through these various forms of application, toxicants can enter the human body via, especially inhalation and dermal absorption through the skin. On the other hand, volatilisation, burning or combustion and domestic wastewater effluents, these toxicants can be released into the environment (Zedeck, 2004; Smolen, 2002). SIEOs have become highly acceptable due to the relatively low cost of production, conti-nuously available alternative and the demand for large quantities of fragrant compounds for the growing industrial processes requiring the use of fragrant compounds. Both "nature identical" and newer fragrant compounds are being synthesized, rapidly reducing the dependence on natural sources in plants essential oils. Also, for carrier oils, petroleum products are now used as alternatives. Presently, more than half of the over four thousand raw materials available for fragrance production for industrial essential oils are now synthesized. They mostly serve as raw materials for the vast range of personal and household care products manufactured (Fortineau, 2004; Turin and Yoshii, 2003).

Generally, the results of PAHs in this study shows significant variations between the SIEO samples investigated. These variations are very likely to reflect immensely from one sample to another when the large number of various products and versions used in Northern Nigeria are

considered since only less than 50% of the total products range of SIEOs that can be found in Northern Nigeria market were investigated in this study. Significant factors such as differences in batch production (Byrne and O'Grady, 1990), essential oil formulations (RUK, 2004), which include the economic considerations in the proliferations of lower SIEO versions; physical and chemical changes through production, transportation, storage and exposure may be responsible for the observed variations.

The present levels of PAHs found in this study indicates a higher likelihood that the products consist of synthetics and or additives of petroleum products, which are usually accompanied by high levels of PAHs in related finished products. The result of this study also shows correspondence in the levels of PAHs reported by Goodpaster, et al. (2001) in their comparison on the levels of PAHs in motor oil, petroleum jelly and petroleum. Burfield, (2003) have also reported instances of adulteration of natural essential oils with petroleum products used as carrier oils, in other to increase the volume of final product. The health implications of PAHs in petroleum products used in the production of personal care products have also been well documented (Goldie, 2006; Burfiled, 2003). Some of the products labels indicate only fragrant compounds as contents, e.g. terpenes and Galaxolide®, while other product indicate presence of compounds such benzoic acid, 2- (phenylmethylene-1-trans 3)-ester, as substances of various allergic potentials. These are likely precursor compounds and sources of the PAHs in the samples. On the other hand, the safety and precautionary background information are not observed.

On the toxicity levels of PAHs, UNEP (2002) have reported that the acute toxicity of low PAHs is moderate with an LD_{50} of naphthalene and anthracene in rat of 490 and 18000 mg/kg body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10 mg/kg body weight. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic actions of these substances produce intermediates that bind covalently with cellular DNA. The carcinogenicity of benzo(a)pyrene have also been well documented by Duffus and Worth (1996). IARC (2006) has classified benz(a)anthracene, benzo(a)pyrene, and dibenzo[a,h]anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno(1,2,3-c,d)pyrene were classified as possible carcinogens to humans.

As anticipated, the levels of PAHs recorded in this study would pose greater health and environmental risks as the modes of utilization of SIEOs continue to grow in Northern Nigeria and as these compounds continue to receive enrichments through burning (UNEP, 2002). In Northern Nigeria, one of the most significant modes of application is in the burning of SIEOs in concoction with other fragrance exuding agents such as wood, resins, and certain fish scales, etc. In this, the SIEOs are often employed as fuel. Consequently enrichment of these POPs will be introduced from low temperature and incomplete combustion processes (UNEP, 2002; DHFS, 2000; WHO, 2003).Again, inhalation which is likely to cause more harm than other routes of exposures (Duffus and Worth, 1996) is given greater precedence through this forms of applications. It has been reported that an indoor pollution (e.g. PAHs) are 45 times higher in homes where residents smoke exist, and as much as 118 times higher than in areas with no indoor source of burning incense, candles, air fresheners or other synthetic fragrances have been recorded (Downey, 2005). Another mode of possible enrichment of toxic substance exposure is in the practice of local blending and concoctions of different types of SIEOs. This results in the formation of compounded aggregates such as the Uhmra that are directly applied on the body. Synergistic and antagonistic effects are possible with blends of essential oils. Also the permeation of toxicant through the skin is high since it is dependent upon the lipid solubility of toxicants, concentration at skin surface and nature of toxicants matrix, which this mode of application satisfy (Duffus and Worth, 1996; Halcon, 2002).

Conclusion

The levels of PAHs found in SIEO samples analyzed in this study are higher than levels permissible in cosmetics, pertinent amongst which are those classified by IARC as carcinogenic. The direct forms of utilization of these products in Northern Nigeria portend high risks for human health and environment upon continuous usage.

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