VOLATILE ORGANIC COMPOUNDS AND HEAVY METALS IN ASPHALT CONCRETE USED IN ROAD SURFACING OF EAST WEST ROAD, NIGERIA

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Abstract
Volatile organic compounds and some heavy metals present in very fresh asphalt concrete to be applied on the Rumokoro-Choba axis of the East-West road of Port Harcourt were investigated with Gas chromatography (GC) and AAS. The heavy metals in the asphalts are in the following order; Vn > Ni > Zn > Cr > Cu > Pb > Cd with mean values in mg/kg of 541.44 > 477 0.4 > 149.42 > 110.89 > 100.83 > 46.86 > 24.99 respectively. The results showed ten of the thirteen detected VOCs are mono-cyclic aromatic hydrocarbons, Naphthalene being the only polycyclic aromatic hydrocarbon. Naphthalene followed closely by dichlorobenzene has the highest mean concentrations of 105.17 mg/kg and 102.63 mg/kg in the samples respectively. Chloromethane, ortho and para xylene have the least mean concentrations of 15.77 mg/kg, 17.70 mg/kg and 18.64 mg/kg respectively in the samples. These values being well above the limit for VOCs emissions, makes it expedient to drastically improve asphalt concrete quality, mode of application and reduce VOCs emissions in asphalt concretes used for asphalt paving.

Keywords: VOCs, Asphalt concrete, Heavy metals, Environment

Introduction

Modernization comes with its effects and Environmental Scientists are much worried about the possible accumulation of the various compounds and heavy metals from the Asphalt matrix used in road construction. High temperatures, rainfall and unusual humidity could lead to release of these unfriendly compounds to the environment, which may accumulate or biomagnify to unacceptable levels in the food chain and environment as well. The impact of carcinogenicity/toxicity of the released Volatile organic compounds and the toxicity of the heavy metals in the matrix on its immediate environment and humans cannot be ignored[1].

Asphalt previously known as Asphaltum also known as bitumen (Both are often used interchangeably) is a gummy, dark brown/black and extremely very viscous liquid or semi-solid form of Crude oil[2]. It occurs in nature as deposits or may be formed as the vacuum distillation product of crude oil[3]. The major use of asphalt/bitumen is in road construction, which is more than 70% of its usage. It is produced in millions of tons annually and applied as the glue or binder mixed with Construction aggregate particles to create asphalt concrete in hot mix plants[4]. Its other main applications are for bituminous waterproof materials, including production of roofing felt and for sealing flat roofs[5]. Its composition is complex and varies a lot in percentage in amount of Oxygen, Carbon, Nitrogen, Hydrogen and Sulfur elements as well as in aliphatic, aromatics, polycyclic, resins and heterocyclic compounds, which asphalt is mainly comprises in different composition[6,7,8].

Volatile organic compounds (VOCs) and other gaseous emissions are released as asphalt coating takes place and this is as a result of reduced viscosity with increasing temperature in the asphalt plant[6]. Environmental pollution due to asphalt is because of the dangerous chemicals found in it, which are emitted or released to the immediate environment.[6,7] Some of these chemicals are hydrocarbon based and include amongst others; naphthalene, acenaphthalene, Fluorene, pyrene, chrysene, benzo(a)fluoranthene, benzo(b)fluoranthene, benzo (k)fluoranthene, etc. others are, benzene, toluene, ethyl benzene, chlorobenzene, dichlorobenzene bromobenzene methylene chloride, (ortho,para,meta) xylene, oxygen, sulfur, nitrogen and heavy metals, which include Mn, Ni, V, Cr, Pb, Zn, Cd, Cu etc.[8]

According to 1999/13/EC (SED) defined VOCs as any organic compound with a vapour pressure of 0.01Kpa or more at 293.15K or having an equivalent volatility under the particular circumstance of use. In a review of 2004/42/CE (PD), VOCs was redefined as any organic compound which at standard pressure of 101.3KPa that have initial boiling point of $\leq 250^0C$[7]. The European Union set up Directives of 1999/13/CE and 2004/42/CE (PD), which fixed a limit of VOCs emissions at 150 mg/m^3 and 500 mg/m^3 respectively. Gasthauer et al in 2002, characterized asphalt fume composition by GC-MS and effects of temperature on emissions [7, 8]. Their findings suggested that oxidation mechanism was responsible for most of emissions and temperature of mixing in the industrial processes could be used to control VOCs emissions[8].

The VOCs and heavy metals in asphalt concrete used in some major highways in Nigeria are well published. For now there is no known published work on VOCs and heavy metals in asphalts concrete that are used in the recent road surfacing of East-West road. The focus of this research is to evaluate the levels of volatile organic compounds and heavy metals trapped in the fresh asphalt concrete matrix used in the recent road surfacing of East-West Road, from Rumokoro to Choba axis in Port Harcourt metro-polis. The possible dangers posed to humans by the Volatile organic compounds and heavy metals from asphalt concrete will be highlighted. The outcome will be used as baseline in further studies and shall enable our various regulatory bodies to enforce environmental Laws and tighten existing ones in view of the fact that VOCs reacts in complicated manners with some Environmental variables to form undesirable tropospheric Ozone.

Materials and Methods

Study Area

Port Harcourt city is the capital of Rivers State which is located South-South of Nigeria with geographical coordinates of 4^{o} 47' 21''N 6^{o} 59' 55''E. It is a metropolitan city with population of close to two million people currently. The city hosts a number of multinational oil firms, oil refineries, local and international airports. Within this metropolitan is the major East-West Road which connects it with other neighbouring states in the Niger delta. The portion of east west road under our investigation is from the popular Rumokoro to Choba axis, i.e., around the fly over, 4^{0}90'N 6^{0}98'E.

Procedure for VOC Analysis

Two fresh samples of asphalts were collected just before the fresh asphalts were laid on prepared road surface by the mechanical rollers at two different spots namely; before the flyover close to Rumokoro roundabout and after the flyover close to Choba. The fresh sample were immediately stored and sealed in a glass container to avoid contaminations. Afterwards it was taking to the Golden years limited laboratory in Port Harcourt for analysis. ASTM D 4657-92 standard procedure for VOC analysis was used. About ten grams of the asphalt concrete sample was weighed into an extraction bottle and 20ml of the extraction mixture i.e. dichloromethane (DCM). The mixture was sonicated in an ultrasonic sonicator for 2hours. The extract was concentrated to 2ml in a rotary evaporator. Later 20ml of 0.5M KOH in 100ml of methanol was added and the matrix mixture was refluxed for 1 hour in a water bath at 60^{0}C. About twenty (20) mls of Deionized water was added and extracted with hexane (20ml). The extract was dried over anhydrous sodium sulphate and was concentrated at 60^{0}C in a rotary evaporator to 2ml. This extract was eluted through a chromatographic column loaded with silica gel as the stationary phase and rinsed with hexane. The extract was eluted with 20ml of hexane for aliphatic fractions. To same column, 20ml of DCM was added for the elution of VOCs and the eluent was concentrated to 1ml and solvent exchanged with 1ml of acetonitrile. About 1µl of the eluent was injected into a pre-programmed HP 5890 GC-FID. Much later the concentration of the VOCs was calculated from the peak area of the VOC calibration standards using HP chem station software, version 4.20.

GC Operating conditions for VOC; Initial oven temp-100^{0}C, Initial Hold time-0.5min, Ramp-15^{0}C/min to 200^{0}C, then 20^{0}C/min to 300^{0}C, Final Oven Temp-300^{0}C, Detector Temp- 340^{0}C, Injector Temp- 250^{0}C, Carrier gas-Helium, Ignition gas-Hydrogen and air.

Heavy metal analysis

About one gram of the sample was weighed into a conical flask and 10mL of digestion mixture (Nitric acid: Sulphuric acid: Perchloric acid) was added in ratio 2:2:1 respectively. The mixture was placed on hot plate in a fume hood and heated gently till production of white fumes and/or clear solution was observed. The digest was allowed to cool down to room temperature and 10mL of de-ionized water was used to rinse the wall of the beaker down. The mixture was filtered using No. 42 watman filter paper into a 50mL volumetric flask and made to mark with de-ionized water and transferred into polythene bottle for heavy metal determination. Heavy metals (Mn, Cr, Pb, Zn, Cd, Cu, V and Ni) were analyzed in the digest using Atomic Absorption Spectrophotometer AAS (Biotech Engineering, Phoenix 986- UK). The digested samples were then aspirated and the actual concentrations were obtained by referring to the calibration graph and necessary calculations and the results were reported in mg/kg. Zinc, Cadmium, Zinc, Copper, Nickel, Iron and Chromium were analyzed using air acetylene mixture. Cobalt and Vanadium were analyzed using Nitrous Oxide/air/acetylene mixture[8].

Results and Discussions

The heavy metals investigated in the asphalt in mg/kg are chromium, lead, zinc, cadmium, copper, vanadium, and nickel. Surprisingly the results obtained in the samples are relatively higher when compared with the levels of heavy metals in other asphalt in other areas and Department of petroleum resource (DPR) baseline for heavy metals in asphalt.

The order of heavy metals in the asphalt samples are as the follows; Vn > Ni > Zn > Cr > Cu > Pb > Cd with mean values in mg/kg of 541.44 > 477.04 > 149.42 > 110.89 > 100.83 > 46.86 > 24.99 respectively. As the asphalt concrete cures some of the heavy metals in form of oxides and leach away to the environment while some solubilized due to heavy rains thereby undermining the clean water act.

Table 1.0 shows the VOCs profile in mg/kg and heavy metals in mg/kg for asphalt 1 and asphalt 2

VOCs Profile (mg/kg)	**Asphalt concrete 1**	**Asphalt concrete 2**
Benzene	47.24	57.98
Bromobenzene	23.56	65.50
Butylbenzene	64.92	62.54
Chlorobenzene	45.87	45.97
Chloromethane	18.98	12.56
Dichlorobenzene	98.04	107.21
Ethylbenzene	81.23	101.23
Methylene chloride	99.23	81.49
Naphthalene	110.00	100.34
Toluene	26.93	46.56
M-xylene	17.00	77.67
P-xylene	16.68	20.59
O-xylene	12.90	22.50
Total	662.58	802.14
Heavy metal Profile (mg/kg)	**Asphalt concrete 1**	**Asphalt concrete 2**
Chromium	105.56	116.22
Lead	41.28	52.47
Zinc	145.05	153.78
Cadmium	21.59	28.39
Copper	95.87	105.78
Nickel	467.75	486.32
Vanadium	536.21	456.66

The heavy metals being above DPR recommended baselines in asphalt will then become major sources of heavy metal pollution to the environment. The high values of Nickel and Vanadium could be due the stable complexes they form with porphyrins. According to Osuji, petroleum products serves as major sources of metals entering into the environment as a result of, tetraethyl lead added to the gasoline, metal's compounds added to lubricants to improve its characteristics and performance and the wear metals that accumulate in used lubricants[10]. These metal salts and compounds are expected to reduce wears, resist oxidation, and inhibit corrosion etc. as the case may be. He also noted that these metals occur predominantly as the oxides are very susceptible to dissolution to surface waters and leaching.

Cadmium is known to cause kidney damage and cardiovascular diseases. It also interferes with Zinc and Copper metabolism in human[10]. It retards animal and plant growth at concentration well below that detected in the asphalt. Chromium even though needed for glucose metabolism also causes skin ulceration in human if ingested excessively. High lead ingestion in human leads to brain damage and death[10]. Lead and Zinc can also reduce heterotrophic activity in micro flora. Nickel and Vanadium can cause carcinogenesis at certain concentration. Ten mg/kg of Vanadium is fatal to rat[10]. Heavy and trace metals are usually bound to crude oil partly as porphyrins and as non-pophyrinic compounds [11, 12]. Olajire in 2006 reported that Vanadium and Nickel are the main trace metal contaminants in residues of crude oil[13]. The results obtained in this research being relatively high also show the immediate environment will be the ultimate recipient as a result of their gradual dissolution under heavy rain and eventual leaching. Bioconcentration and biomagnification of these heavy metals in the food chain could pose serious risk to plant, animals and humans.

Thirteen VOCs were detected in the asphalt and are as follows (their mean concentration in mg/kg); Benzene (52.61), Bromobenzene (44.53), Butylbenzene (63.73), Chlorobenzene (45.92), Chloromethane (15.77), Dichlorobenzene (102.63), Ethylbenzene (91.23), Methylenechloride (90.36), Naphthalene (105.17), Toluene (36.75), m-Xylene (47.34), p-Xylene (18.64) and o-Xylene (17.7).

Their respective concentrations (mg/kg) in asphalt1 are as follows; 47.24, 23.56, 64.92, 45.87, 18.98, 98.04, 81.23, 99.23, 110.00, 26.93, 17.00, 16.68 and 12.90 while the respective values in mg/kg in asphalt 2 are as follows; 57.98, 65.50, 62.54, 45.97, 12.56, 107.21 101.23, 81.49, 100.34, 46.56, 77.67, 20.59 and 22.50. The total concentration of VOCs in asphalt 1 is 662.58 mg/kg while its value in asphalt 2 is 802.14 mg/kg.

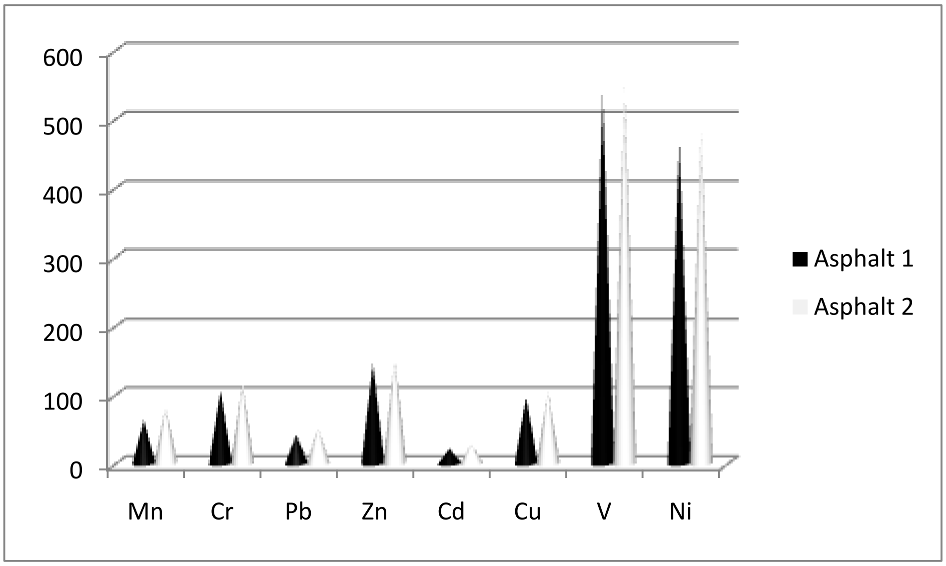

Figure 2: Graph of heavy metals in Asphalt samples 1 and 2

For asphalt concrete 1, from the decreasing order of concentrations, we have the following VOCs order; Naphthalene > Methylchloride > Dichlorobenzene > Ethylbenzene > Butylbenzene > Benzene > Chlorobenzene > Toluene > Bromobenzene > Chloromethane > m-Xylene > p-Xylene > o-Xylene. For asphalt concrete 2, from the decreasing order of concentrations, we have the following VOCs order; Dichlorobenzene > Ethylbenzene > Naphthalene > Methylenechloride > m-Xylene > Bromobenzene > Butylbenzene > Benzene > Toluene > Chlorobenzene > o-Xylene > p-Xylene > Chloromethane.

Overall the levels of detected VOCs at the operational temperature of 300^0C and FID temperature of 340^0C suggested high VOCs content of the asphalt cutbacks used for the road paving when compared with the EU directives of 2004/42/EC (PD) which fixes a reviewed limit of VOCs emission at 500mg/m^3. When this value is converted to mg/kg i.e., 0.5mg/kg one will then see the potential dangers of VOCs and Hazardous Air pollutants emissions from asphalt cutbacks. Most Diluents, which are petroleum distillates that are blended with the asphalt cement are highly energetic, and are consequently lost to environment (atmosphere) on application and after few weeks of road-surfacing. The detected VOCs are mainly monocyclic aromatic hydrocarbon, one polycyclic aromatic hydrocarbon and two polar saturates. There were no storm water prevention plans as the coatings are applied during rains by workmen who were not putting on gas masks. The application temperature being higher means higher emissions.

Connan in 1984 reported that toluene and xylene are soluble in water and hence are lost with time to the Environment[14]. The timing of this road paving is not in line the clean water act, as rain runoffs from the road surfaces carries pollutants to form sheen on surface water. Further violation of the clean water and air acts destroys the ecosystem and serious precautions must be taken in this regard

Conclusion

The level of heavy metals in asphalts 1 and 2 being above the DPR guideline makes the asphalt concrete as source of heavy metal pollution. The results showed ten of the thirteen detected VOCs are monocyclic aromatic hydrocarbons, Naphthalene being the only polycyclic aromatics hydrocarbon and we have two polar saturated compounds. Naphthalene followed closely by Dichlorobenzene has the highest mean concentration of 105.17 mg/kg and 102.63 mg/kg in the samples respectively. Chloromethane, ortho and para xylene has the least mean concentration of 15.77 mg/kg, 17.70 mg/kg and 18.64 mg/kg respectively in the samples. These values being well above the limit for VOCs emissions makes it expedient to drastically improve asphalt concrete quality, mode of application and reduce VOCs emissions in asphalt used for asphalt paving. Emulsified Asphalt (normally don't contain diluents) which are more environmentally friendly relative to asphalt cutbacks and because their low application temperatures should replace asphalt cutbacks in asphalt paving to enhance the clean air and water acts. However if asphalt cutbacks are to be used, we recommend the mixture with slow cure and its application should be during dry season to avoid possible interference with rain runoffs and associated sheen formation on surrounding surface waters.

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