Liquid-liquid Extraction on Volatile Organic Compounds in Surface Water and Sediment selected Zones of Asa River, Kwara State, Nigeria

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Abstract

This research was developed in analysing volatile organic compounds in selected zones of Asa River, Kwara State. Liquid-liquid extraction procedure of two organic solvent (Hexane : Dichloromethane) (1:1 v/v) was employed to remove volatile organic compounds from river and sediment samples. The mean recovery percentage range was between 96.7 ± 1.5 - 104.0 ± 1.0 for river samples while 97.3 ± 2.2 - 104.0 ± 1.0 for sediment samples at a fortification level of 0.01 µg/l. In addition, volatile organic compounds were determined by Gas chromatography – mass spectrometry. The limit of quantification was 0.05 µg/l which was below the maximum level allowed by the European council directives for volatile organic compounds (0.5 µg/l).

Keywords: *Asa River, Volatile organic compounds, sediment, recovery, quantification*

Introduction

Liquid-liquid extraction is a method used to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. Liquid-liquid extraction (LLE), or solvent extraction, is one of the oldest and most widely used techniques in the preparation of samples for qualitative and quantitative analysis. [Frederick and Manon, 2002]. It is an extraction of a substance from one liquid phase into another and a basic technique in chemical laboratories, where it is performed using a separating funnel [Abel et al., 1994]. In liquid-liquid extraction there is a feed phase which contains a component to be removed and the addition of a second phase (solvent phase) which is immiscible with feed phase to the solvent phase. After extraction, the feed and solvent phases are called the raffinate (R) and extract (E) phases respectively [Benedikt et al., 2020].

Volatile organic compounds (VOCs) are a group of organic compounds that have a molecular structure containing carbon and their chemical properties allow them to be easily converted to steam and remain for a long period of time with diverse effects on the environment (Xin et al., 2022). Volatile organic compounds (VOCs) are organic chemicals that have a high vapour pressure at ordinary room temperature conditions. Their high vapour pressure results from a low boiling point which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air [Goldstein and Galbally, 2008]. They include both human-made and natural occurring chemical compounds. Volatile organic compounds (VOCs) among major contaminants in water matrices causes physiological adverse effects on the human body such as cancer, genetic mutations, eye irritation, nasopharyngeal mucosa, dizziness and headache, and short-term memory loss (Li et al., 2018, Song and Chun, 2021). Volatile organic compounds are primary precursors to the formation of ground level ozone and particulate matter in the atmosphere which are main ingredients of air pollutant referred to as smog. Its emissions result from natural and anthropogenic (man- made) sources [Ninemets et al., 2004]. Natural sources of volatile organic compound include vegetation, forest fires, and animals. Although natural sources of volatile organic compounds emissions are larger overall, it is anthropogenic sources in populated and industrialized areas that are the main contributors to air quality problems. The major anthropogenic sources of concern are transportation sector, the use of solvents and solvent containing products, and industrial sources [Behr and Johnen, 2009; Wang et al., 2007].

Asa River flows through Ilorin in a South-North direction dividing the plain into two, western and eastern parts [Kwara State of Nigeria Diary, 1997]. Asa River is a major river for economic, environmental and agricultural significance in Ilorin, the capital city of Kwara State, Nigeria. The river receives direct runoff of effluents from industries along its course, apart from domestic wastes and other activities which contributes to its pollution [Adekunle and Eniola, 2008]. It was observed that the river is subject to high level of eutrophication due to organic matter and industrial discharge [Eletta and Adekola, 2005]. It was also reported that Asa River catchment was found to have high precipitation and sediment yields when analysed yearly for a period of seven years [Jimoh, 2003]. Heavy metal and non-metal pollutants have been analysed on Asa River by past researchers. The aim of this research is to analyse volatile organic compounds and its hazards to health and environment using liquid-

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liquid extraction method at different concentrations of 0.01 µg/l, 0.02 µg/l and 0.05 µg/l respectively, on three zones at the course of Asa River to generate a good recovery and repeatability. Correlation analysis was done to ascertain interaction between river and sediment samples.

Materials and Methods

Study Area and Sample Collection
Samples collected from Asa River in Ilorin, Kwara State include New Yidi/ Asa Dam Zone (RW-AS- 1), Unity Zone (RW-UN-2) and Amilegbe Zone (RW-AM-3) were assessed in this study. Sampling points were selected based on assumed diversity of input from anthropogenic impacts and pollution level. Triplicate samples were taken from each sampling points at interval of four weeks over a period of three months. Preparation of sample bottles and containers were done prior to sampling based on sample size and type of analysis to be performed. Sample containers were thoroughly washed with metal free detergents and rinsed with tap water. They were then soaked in 1% nitric acid for 24 hours and washed with distilled water and kept intact to prevent contamination. Glass bottles were used to sample Volatile Organic Compounds (VOCs). Sediment samples (SD-AS-1, SD-UN-2 and SD-EP-3) at those locations were also collected into treated aluminum foil for Volatile Organic Compounds determination using Ekman grab.
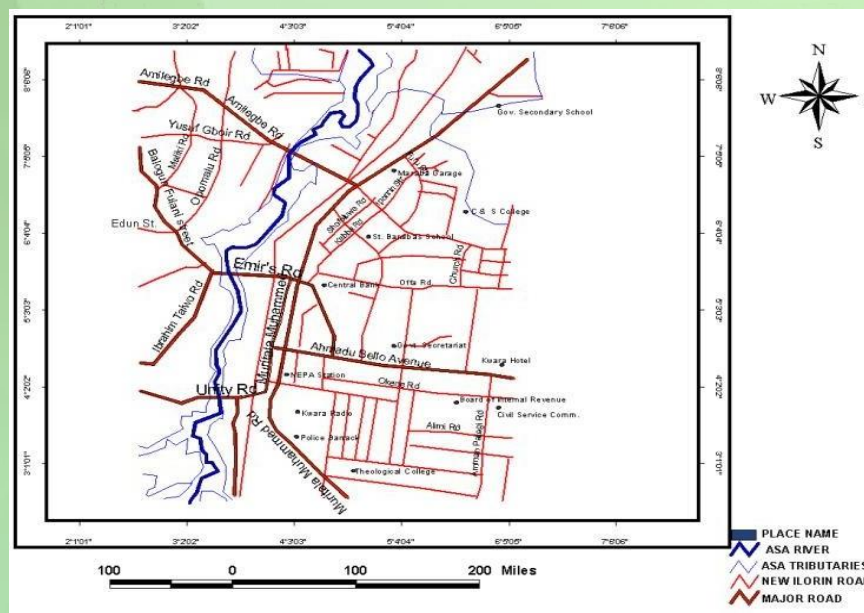

Fig. 1 Extracted Map of Asa River study Area

Reagents and solvents
All chemicals used were of analytical grade. Volatile organic compounds mixed standard include hexane, butane, propane, nonene, butene, decene, benzene, ethanoic acid, ethanedioic acid (New Haven, CT, USA).
Solvents of residue grade purity including dichloromethane, chloroform, n-hexane, 1,2- dichlorobenzene, methanol, acetonitrile were obtained from Merck Company. Standard stock solution 0.1 µg/l of mixed volatile organic compounds was prepared in methanol. All solutions were stored in the dark at 4°C. Working solutions were prepared by dilution of standard stock solution with distilled water.

Chromatographic analysis
Gas Chromatography analyses were performed with a Hewlett-Packard 7890 series gas chromatograph equipped with 5975C Mass Spectrometer detector and splitless injection mode with a pulse pressure of 5.9818psi. Chromatographic separation was carried out using a polar column (30 m length, 0.32 mm i.d., and 0.25 µm film thickness). The oven temperature was 250°C for 31 minutes followed by temperature programmed to 200°C at 17°C/min. Helium was used as carrier gas.

Liquid – liquid extraction procedure Water Analysis
The industrial and surface water samples were filtered through a membrane filter with 0.45 µm pore size before extraction procedures. Water sample of 100 ml was poured into a separating funnel and 100 ml of organic solvent (50 ml:50 ml – hexane: dichloromethane) added and the mixture separated for almost 45 minutes by thorough shaking, afterwards the extract was poured into a beaker and left for few minutes to evaporate then the remaining

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extract filtered using cotton wool as a separating medium in a pasture pipette and anhydrous sodium tetraoxosulphate (VI) (Na_2SO_4) in excess was added to absorbed the remaining water in the sample and this was totaled into a vial bottle up to 2 ml ready for Gas Chromatography analysis.

Sediment Analysis

The dry sediments were carefully collected, homogenised and passed through 60 mesh standard sieves. Sample preparation included homogeneous mixing of 10 g of sediment with 0.25 g anhydrous Sodium sulphate to remove moisture and in 10 ml of dichloromethane for 1h followed by centrifugation. Then 3 ml of supernatant was filtered through 2 g of silica gel column with 11 ml 1:1 (v/v) elution of hexane and dichloromethane. The solvent fractions were then evaporated on a rotary evaporator, and exchanged by acetonitrile with a final volume of 2 ml ready for Gas chromatography analysis.

Results and Discussion

Quality Assurance and Quality Control

The quality assurance and quality control (QA/QC) requirements included establishing Gas chromatography retention times (RT), method detection limit (MDL) and reproducibility for all compounds analyzed. In table 1, forty-six volatile organic compounds are listed along with their molecular weight (MW), boiling point (BP), melting point (MP), method detection limits (MDLs) and relative standard deviation (RSD) of each volatile organic compound. For volatile organic compound collected, method detection limits were between 0.2 and 0.7 ppbv. The relative standard deviation was between 0.6% and 5.0% which is well within the limit of ±30%. For quality assurance approximately 30% of the samples were analyzed in triplicate. The reported percentage quality is the amount present in the sample.

Recovery Studies

Recovery study was performed on investigated compounds from spiked river zone samples and sediment from three zones along Asa River route at three concentration levels. At each concentration level, three determinations were performed. The mean recoveries and relative standard deviation (RSD) of alkanes (pentane), alkenes (butene), aromatics (benzene) and carboxylic acids (acetic acid) can be observed in table 2 and 3 respectively.

Recovery study on river zones

Recovery study was done using a known amount of standard volatile organic compounds injected in the sample before extraction to check how much were recovered after completion exercise. The recoveries of volatile organic compounds from spiked river zones were done at three concentrations levels, at each concentration level, three determinations were performed. It was observed at 0.01 µg/l, 0.02 µg/l and 0.05 µg/l respectively. RW-AS-1 recorded a mean recovery percentage range and relative standard deviation of [97.1±3.2- 104±1.0] , RW-UN-2 [90.0±1.0 – 103.3±1.5] while RW-AM-3 obtained [97.7±1.5 - 104±1.0].

Recovery study on sediment zones

The recoveries of volatile organic compounds from spiked sediment was done at three concentration levels, at each concentration level, three determinations were performed. It was observed at 0.01 µg/l, 0.02 µg/l and 0.05 µg/l respectively. SD-AS-1 recorded a mean recovery range and relative standard deviation of [90.0±4.6 – 102.8±1.8], SD-UN-2 [99.1±0.5 – 104.0±1.7] while, SD-AM-3 [85.0±6.6 – 103.7±1.2].

Correlation values of volatile organic compounds based on recovery concentration

The table 4 shows the correlation analysis for volatile organic compounds targeted at river zones in relation to sediment at the same place. The degree of freedom is 5, critical table value = 0.754 at 5% significance level.

At 0.01µg/l for RW-SD-AS-1, RW-SD-UN-2 and RW-SD-AM-3 recorded range of (-0.26 – 0.30), while at 0.02µg/l for RW-SD-AM-3 was 0.74 which indicated that $r_{cal} < r_{table}$ therefore the null hypothesis Ho cannot be rejected and this account show that volatile organic compound of river do not have association with sediment at that concentration. At 0.02µg/l, RW-SD-AS-1 and RW-SD-UN-2 obtained range (0.76 - 0.77), while at 0.05 µg/l, RW-SD-AS-1, RW-SD-UN-2 and RW-SD-AM-3 recorded range (0.91 – 0.98) and revealed that $r_{cal} > r_{table}$ therefore the null hypothesis Ho can be rejected and it would be concluded that there is a positive association between river zone and sediment at those concentration. Figure 1-3 which reveals the correlation analysis pattern at 0.05µg/l also affirm the interaction between the river and sediment zones. The R^2 determine on the graph account for the reliability of the extraction method used based on recovery studies.

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Table 1. Properties, Quality Assurance and Quality Control for targeted volatile organic compounds in river and sediment samples

Groups	VOCs Species	MW	BP (°C)	MP (°C)	MDL	RSD	% Quality	RT
Alkane	1,1-dichloro 2,2-difluoroethane	135	60	n/a	0.3	3.7	91	3.327
	BromodichloroMethane	164	87	-55	0.2	3.2	96	3.362
	Trichloromethane	119	60.5	-63	0.5	1.5	96	3.327
	Oxybis[dichloro methane]	184	39.8	n/a	0.2	3.2	96	3.785
	1,2-dimethyl – cis Cyclopentane	98	99	n/a	0.5	1.5	62	8.992
	1,2-dimethyl-trans Cyclopentane	98	92	n/a	0.5	1.5	62	8.992
	Bromomethane	94	4	-94	0.3	1.0	96	10.073
	Methylene cyclobutane	68	42	n/a	0.5	2.0	81	5.192
	2-isocyanato propane	85	74	<-75	0.3	1.0	81	3.413
	2-cyclo propyl propane	84	58	n/a	0.5	2.5	81	3.550
	Ethyl cyclobutane	84	70.7	n/a	0.5	3.6	96	4.357
	Methyl cyclopentane	98	101	-126	0.5	0.6	95	4.592
	1,3-dimethyl-cis cyclopentane	84	80.7	6.5	0.2	3.5	53	9.016
	1,3-dimethyl-trans cyclopentane	98	91	n/a	0.5	3.3	58	9.016
	2-chloro-1,1,1-trifluoro ethane	119	6.9	-106	0.5	3.5	91	7.144
	1-methyl-2-octyl cyclo propane	154	203.3	n/a	0.2	3.3	62	25.975
	1,2-diethyl cyclo butane	112	n/a	n/a	0.5	2.0	73	25.975
	1,3-dimethyl cyclo pentane	98	n/a	n/a	0.5	2.0	64	8.935
Alkenes	2-Pentene (E)	70	37	-40	0.3	2.7	93	3.613
	2-methyl-1-butene	70	31	-137	0.2	1.0	93	3.648
	2-pentene	70	37	n/a	0.3	2.0	93	3.676
	2-pentene (Z)	70	38	-180	0.3	1.0	93	3.699
	1,2-dichloro ethene (Z)	97	60.3	-81	0.4	1.5	57	6.697
	2-Hexene (E)	84	62	n/a	0.4	1.5	55	6.978
	3,4-dimethyl-1-pentene	98	n/a	n/a	0.5	1.5	77	7.464
	3,7-dimethyl-1-octane	140	156	n/a	0.5	1.0	77	7.464
	4-ethenyl cyclohexene	108	n/a	n/a	0.2	2.0	53	25.855
	1-Nonene	126	146	-81	0.5	1.6	65	26.038
	2-butene (E)	56	1	-105	0.5	1.0	91	4.883
	2-butene (Z)	56	3.7	-139	0.4	2.8	91	4.557
	2-butene	56	n/a	n/a	0.3	1.5	91	4.906
	Cycloheptene	96	112	n/a	0.2	0.6	57	27.840
	1-chloro-Z-2-heptene	133	n/a	n/a	0.4	4.6	50	5.740
	1-Hexene	84	64	-140	0.3	1.0	90	4.929
Aromatics	Fluorobenzene	96	85	-42	0.2	3.8	91	6.697
	2,3,4,5-tetrahydropyridine	83	n/a	n/a	0.4	2.5	53	6.692
	Pyridine-D5	84	115	n/a	0.6	3.2	50	6.108
	2-chlorothiophene	119	127	n/a	0.7	4.4	62	7.018
	3-chlorothiophene	119	137	n/a	0.7	3.2	62	7.018
	Indan-1,2,3-trione	178	n/a	250	0.5	5.0	53	26.581
	Ninhydrin	178	n/a	250	0.5	2.5	62	26.581
Carboxylic Acids	2,6-diamino-4-hexenoic acid	144	n/a	n/a	0.3	1.0	53	26.261
	Dichloroacetic acid	129	194	9	0.3	3.8	91	3.459
	Non-3-enyl ester acetic acid	184	234	n/a	0.3	2.0	50	28.858
	Fluoroacetic acid	78	165	33	0.5	1.0	95	7.584
	2-cyano-ethyl ester hexanoic Acid	169	n/a	n/a	0.5	1.0	54	25.820

Source: Author's fieldwork

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Table 2. Mean recoveries and standard deviation for river zones sampled

VOCs	Conc. (µg/l)	RW-AS-1	RW-UN-2	RW-AM-3
Alkanes (Pentane)	0.01	101.8±3.7	102.7±3.2	100.3±1.5
	0.02	97.1±3.2	96.7±1.5	97.7±1.5
	0.05	104.0±1.0	99.0±2.0	104±1.0
Alkenes (Butene)	0.01	101.2±2.7	103.0±1.0	102±2.0
	0.02	102.0±1.0	103.3±1.5	98.7±1.5
	0.05	103.0±1.5	95.0±1.0	103.3±1.5
Aromatics (Benzene)	0.01	99.6±3.8	99.7±2.5	101.7±3.2
	0.02	99.6±4.4	101.3±3.2	100.0±5.0
	0.05	101.3±2.52	91.0±3.61	101.3±1.5
Carboxylic Acids (Acetic Acid)	0.01	102.0±1.0	99.0±1.0	102.0±1.0
	0.02	102.3±3.8	103.0±2.0	99.0±1.0
	0.05	103.0±1.0	90.0±1.0	100.0±1.0

Table 3. Mean recoveries and standard deviation for sediment zones sampled

VOCs	Conc. (µg/l)	SD-AS-1	SD-UN-2	SD-AM-3
Alkanes (Pentane)	0.01	97.7±2.5	101.8±3.6	98.9±0.6
	0.02	97.3±3.5	99.1±3.3	103.1±2.0
	0.05	99.1±2.0	105.0±3.0	92.0±6.3
Alkenes (Butene)	0.01	100.0±2.0	99.7±1.6	104.0±1.0
	0.02	100.3±2.8	102.6±1.5	103.0±0.6
	0.05	90.0±4.6	104.0±1.0	90.0±1.0
Aromatics (Benzene)	0.01	101.7±0.6	104.0±1.7	100.8±3.2
	0.02	102.0±0.7	99.1±0.5	99.2±1.1
	0.05	85.0±2.7	102.0±2.7	85.0±6.6
Carboxylic Acids (Acetic Acid)	0.01	102.7±2.2	103.7±0.7	97.3±2.2
	0.02	102.8±1.8	101.6±1.6	103.7±1.2
	0.05	92.0±5.3	101.0±2.0	85.0±8.7

Table 4. Correlation variables of volatile organic compounds based on recovery concentration

Concentration (µg/l)	RW-SD-AS-1	RW-SD-UN-2	RW-SD-AM-3
0.01	-0.26	-0.91	0.30
0.02	0.76	0.77	0.74
0.05	0.91	0.98	0.96

$y = 0.177x + 86.64$
$R^2 = 0.821$

Fig 1. Correlation analysis of river zone and sediment at 0.05µg/l (RW-SD-AS-1)

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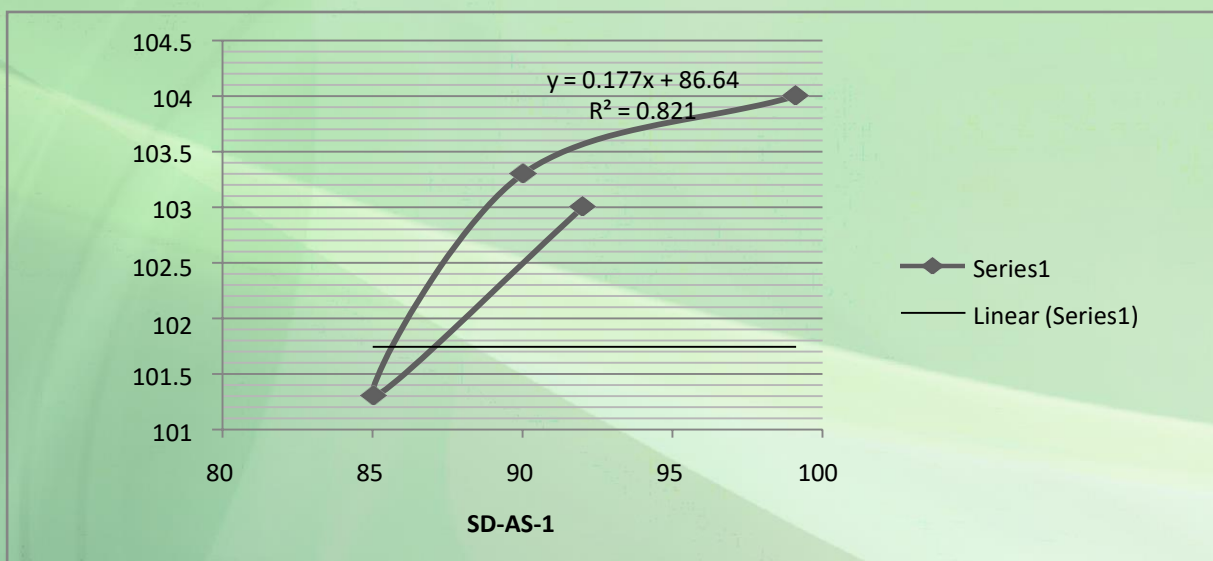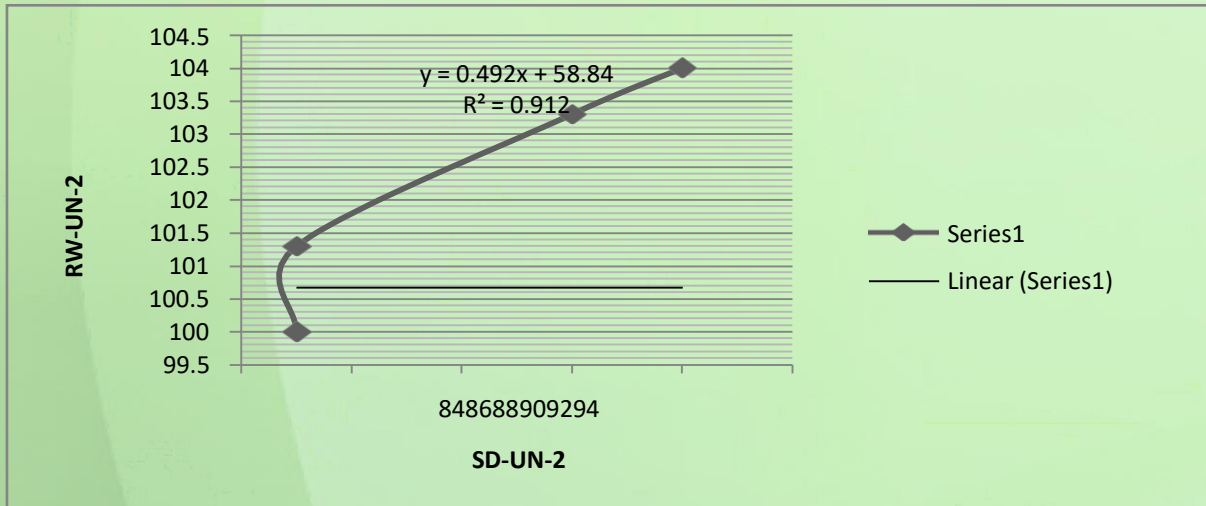Turkish Science and Technology Publishing (TURSTEP)

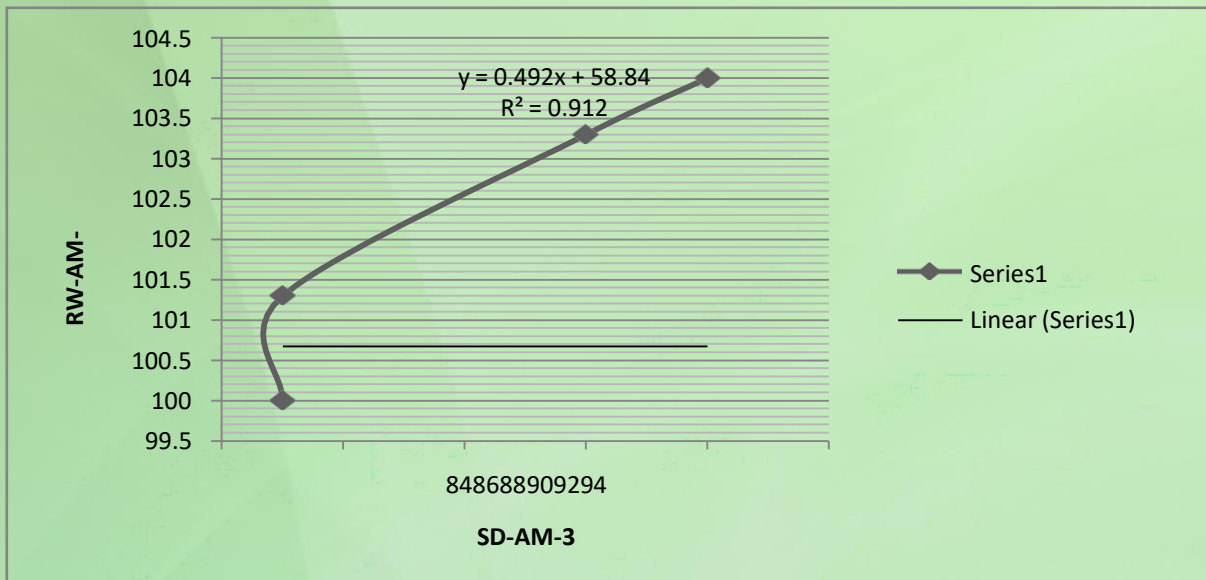Fig.2 Correlation analysis of river zone and sediment at 0.05µg/l (RW-SD-UN-2)

Fig.3 Correlation analysis of river zone and sediment at 0.05µg/l (RW-SD-AM-3)

Conclusion

Liquid-liquid extraction method was performed on the river and sediment zones to confirm their applicability on Ilorin environs, Kwara State which had in general a relatively transparent aspect. Previous experiment had shown that the type and volume of solvent could increase the emulsion formation. The recovery experiments were carried out for optimization of liquid-liquid extraction for volatile organic compounds and the following summaries were made: For river samples at 0.05 µg/l recorded 90.0±1.0% – 104.0±1.0% while sediment samples obtained (85.0±8.7% - 105.0±3.0%). Both the river and sediment zones revealed a derivative of benzene (Fluorobenzene) which is a human carcinogen and a chemical compound found in environmental tobacco smoke, stored fuels and exhaust from cars. It has also been found to contaminate food and water and when digested can lead to vomiting, dizziness, sleepiness, rapid heartbeat and at high levels, even death may occur. Other volatile organic compounds like chlorofluorocarbons and chlorocarbons also determined in this experiment are harmful to health and should be thoroughly monitored because this is the river that serves has drinking water source for Kwara state. In summary, though the volatile organic compound gave a good recovery due to their concentration being below limit of quantification, it is evident that the studied area presents a critical situation and offering risks to environmental compartments.

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