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A Film of Polystyrene Hydroxyl end Group Supported on SiO_2 Monoliths: Thermal Conductivity and Micro-Indentation

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Abstract - Thin films (average thickness ~1132, 2236, and 3785 nm) of polystyrene with a hydroxyl end group, PSOH (Mw= 70345 g.mol) were supported on SiO_2 monolith disks (thickness ~ 0.2, 0.4, and 0.6 cm) to measure its thermal conductivity response using the Lee's Disk method. The various analyses were carried out over a 40 minute period at intervals of 5 minutes, at a temperature range of 20 to 110°C, as a function of PSOH film and monolith disk thickness. As a result, an extremely low thermal conductivity was determined in reference to the individual materials. Additionally, the thermal conductivity was unaltered as a result of the variation of the film and monolith thickness. In contrast, the hardness and ductile behavior were increased by increasing the thickness of the PSOH film. As a result of this, monoliths with a PSOH film of 3782 nm thicknesses (and load of 100 gf) were considered materials of intermediate hardness (value of 31.5720 GPa). In addition, FTIR was the technique employed to establish the PSOH and SiO_2 monolith structures.

Keywords : Polystyrene film, SiO_2 monolith, thermal conductivity, thickness, Lee's Disk.

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Keywords : Polystyrene film, SiO_2 monolith, thermal conductivity, thickness, Lee's Disk.

I. Introduction

More and more countries around the world, with predominantly hot or cold climates, tend to experience more extreme weather during most of the year. In this case, the use of air conditioning, ventilation and heating systems can help maintain a comfortable temperature [1]. However, the energy consumption is directly affected by glass windows that are a means by which energy is gained or lost from the surrounding environment [2]. The estimated energy consumption by this means has generated high costs in environmental and economic terms [3]. This limitation can be overcome by using a thermal insulation barrier on a conventional glass [4-6].

Thin organic polymeric films are receiving more and more attention in the field of thermal insulation barriers because they present special properties, such as transparency, light-weight, easy transportability and installation, and low cost. Due to this, thin organic polymeric films have had a considerable technological importance in a wide variety of fields; most of them related to glass coating, used as solar- protective and anti-reflection coating. In both cases, these coatings have had a major impact on the temperature behavior [7, 8]. Equally important are the coating´s physical and chemical properties, related to the adhesion phenomena, humidity and friction surface [9, 10]. Polymeric thin films based on polystyrene have offered advantages in optical and thermal properties (no absorption of visible light). By using this film, acoustic insulation, as well as excellent electrical and mechanical properties can be reached [11, 12, 13]. In addition to this, polystyrene chains having a low-molecular weight can improve its orientation and inter-chain dispersion with gases, liquids, particles and polymers. This is considered to be particularly advantageous in the current study; because with the addition of a functional group as –OH, a better adhesion of polystyrene chains can be achieved, improving its coating properties. This hydroxyl group attracts other polar groups as hydroxyl and alkoxy groups. Therefore, short-chains containing a hydroxyl end group (PSOH, Scheme 1) [14-16] provide an ideal structure that can be capable of reacting with fragments that appear after the Sol-gel process.

To provide evidence between PSOH and common glass window interaction, this common glass was interchanged by a silicon dioxide (SiO_2) substrate. This is because most commercial or common glass substrates have a complex chemical composition, which contain for the most part SiO_2, alkali and alkaline earth ions. They also contain the presence of impurities, making them usually unsuitable for a research protocol. In order to obtain SiO_2 glasses with high purity and homogeneity, the Sol-gel method (Scheme 1) was used [17, 18]. This process was performed at low temperature, allowing the researchers to obtain SiO_2 monolith disks (SiO_2-D's) [19]. Thus, by controlling the hydrolysis and the rate of the gel drying, transparent and low-density SiO_2-D's were obtained [20, 21]. These monoliths contain a -Si-O-Si-O- backbone and represent

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Si-OH groups, depending on the thermal treatment used. These fragments gain importance in presence of PSOH as result of polarity of the three functional groups. Given the context discussed above, the goal of this study was to examine the possibility of using a PSOH of medium molecular weight to provide a thermal insulation barrier on conventional glass windows, thus certain aspects were analyzed such as nitrogen sorption isotherm, molecular weight, FTIR spectra, hardness (microindentation test) and thermal conductivity (using the Lee's disk method).

II. EXPERIMENTAL

a) Materials and Methods

All reagents used in the study were purchased from Sigma-Aldrich Co.: tetraethyl orthosilicate (TEOS), ethanol (ETOH), nitric acid (HNO_3), toluene and 2-mercaptoethanol (2-ME). Styrene was purified by treating it with 5 wt% aqueous NaOH to remove the inhibitor and then washed with ion-free water until a pH=7 was achieved. It was later dried by using anhydrous. 2-2' Azobisisobutyronitrile (AIBN) was purified with methanol by recrystallization.

b) Synthesis of polystyrene with hydroxyl end group (PSOH)

The PSOH was prepared using the following procedure: (1) styrene ($5x10^{-2}$ moles), 2-ME ($5x10^{-3}$ moles) and AIBN ($2.1x10^{-4}$ moles) were dissolved in toluene. (2) This mixture was degassed by several freeze-thaw cycles under high vacuum, and then polymerized for 5 hours under nitrogen gas at 70°C. Finally, (3) the solution was diluted in toluene and precipitated in methanol [22]. According to the reaction, the hydroxyl group $-S(CH_2)_2OH$ should be present at the end of the polystyrene chain (Scheme 1).

c) Silica monoliths disks (SiO_2-D´s)

SiO_2-D's were obtained by the sol-gel process, which was completed in three stages: (1) A first solution of TEOS/ETOH with a molar ratio of $4.5x10^{-3}$:$69.0x10^{-3}$ (1/4 volume relation) was heated for 15 minutes under magnetic stirring at 60ºC [23]. (2) A second solution of HNO_3/H_2O with a molar ratio of $4.7x10^{-3}$:$890.0\ x10^{-3}$ (1.0/80 volume relation) was prepared at 18ºC. In the end, (3) both solutions were mixed and stirred for 1 hour at 60ºC. The resulting mixture was left to cool at 18ºC and then transferred to 10 ml plastic vials (drilled with small holes to permit a slow solvent). The plastic vials were subsequently put under vacuum for different time periods during which the temperature was gradually raised from 20 to 250ºC.

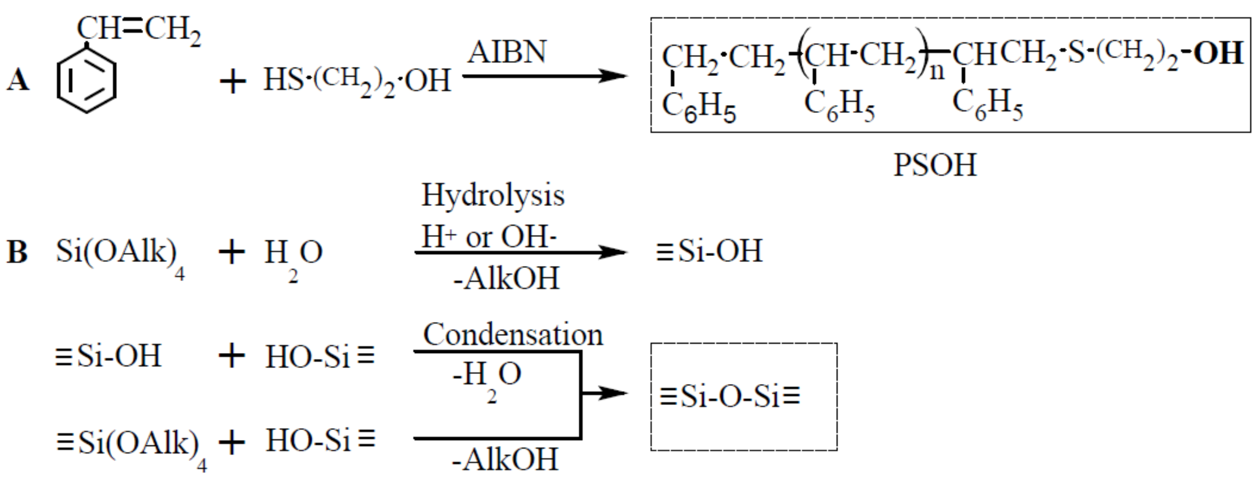
d) Coating of PSOH on SiO_2-D

By dipping SiO_2-D (on one of its sides) partly into the PSOH/toluene solution once, twice or three times, SiO_2-D´s covered with PSOH were obtained. (Figure1). The dipping processes were carried out in three replications, which were conducted at a rate of 10 cm/min for 1 second, using a digital immersion apparatus.

e) Instrumentation and characterization methods

The nitrogen sorption isotherm was obtained by the static volumetric method at 196 ºC.

Escheme 1 : A) PSOH preparation using MEOH as transfer agent and B) SiO_2-D matrix preparation bye the Sol-gel method.



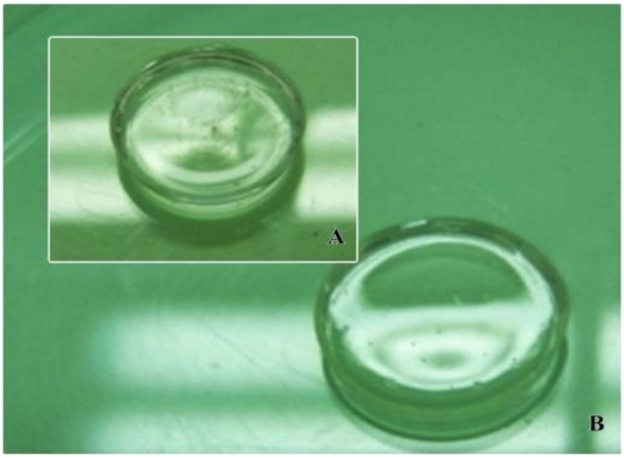


Figure 1 : Transparent silica monoliths of 1.5 cm in diameter and 2 cm along: A) uncoated and B) uncoated with PSOH.

The specific surface area (m^2/g) was determined using the BET (Braunauer, Emmet and Teller) method.

The molecular weights of the PSOH were measured using gel permeation chromatography (GPC) Waters 1525, Binary HPLC. The equipment was calibrated with polystyrene standards, and tetrahydrofuran was used as a solvent.

FTIR spectra were obtained using a Tensor 27 Bruker spectrometer in the 2000-400 cm^{-1} spectral range, at a resolution of 4 cm^{-1} in absorption mode.

The average film thickness was calculated using the polystyrene density (1.05 gcm^3) and it was assumed that the film coated totally and uniformly the SiO_2-D surface.

The microindentation tests to determine hardness (H_V) behavior were carried out using a Vickers microindentation tester (Durimet, Leitz, Wetzlar Germany), with a 10, 25 and 100 gf load (P) in the diamond shaped indentation tip (pyramid form).

Through the tester microscope, it was possible to observe (10x) the mark on the surface of SiO_2-D with and without coating.

Characterization of the experimental arrangement through Lee's disk method was carried out using *VirtualBench-Logger 2.5 Report National Instruments* software, an Analog Input, National Instrument TC-2190 data acquisition board, 5 "k" type thermocouples with chromel and alumel joints, the hot plate, two cylindrical lead pieces (1.5 cm in diameter and 2 cm along), five firebricks (silica-alumina) and diatomaceous earth. Figure 2 shows a schematic representation of the experimental arrangement of Lee's disk method, where there are two systems: one that uses pure SiO_2-D and another one that uses SiO_2-D coated with PSOH (system I and II respectively). In both systems, there was a piece of copper on both sides of the specimen having four thermocouples A, B, C and D which gave information about the interface. Each system was isolated with 5 firebricks forming a chamber filled with diatomaceous earth, where a last thermocouple (E) was inserted to monitor its temperature.

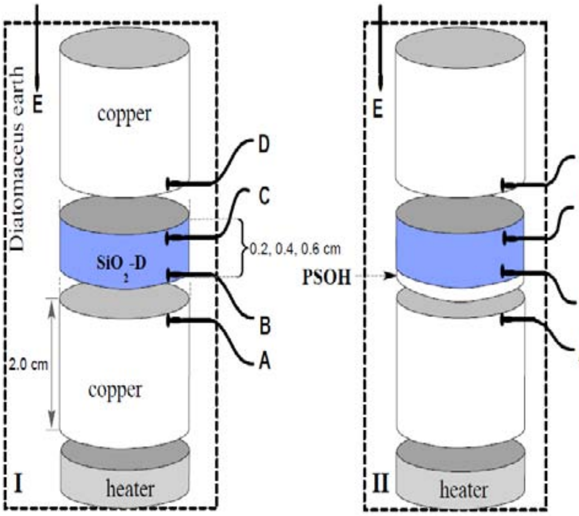


Figure 2 : Arrangement of the Lee's disk method: System I, SiO_2-D without PSOH film and System II, SiO_2-D with PSOH.

Each experiment was carried out under stable operating conditions for 40 minutes. While a plane surface heat source was set at a fixed temperature of 110°C, the diatomaceous earth temperature was kept constant at 20°C. It also revealed that there was no heat lost in the systems (I and II) toward the surroundings, and an appropriate isolate system was built.

The equation that describes heat transfer through conduction (Fourier Law) can be expressed as a linear approximation, as follows:

$$(q/A)_z \approx -k(\Delta T/\Delta z) \qquad (1)$$

where $(q/A)_z$ is the heat flux in the z-direction in W/m^2, k is the thermal conductivity in W/m K, and $\Delta T/\Delta z$ is the temperature gradient $T_n - T_{n+1}$; $T_n > T_{n+1}$) as a function of z-thickness ($z_{n+1} - z_n$; $z_{n+1} > 0$ y $z_n = 0$) in $^{o}C/m$. In regard to the equation describing specific heat, it can be expressed as heat transfer in transitory state:

$$q = mC_P(dT/dt) \qquad (2)$$

where q is the power in the transitory state, m is the mass of material in g, CP is the specific heat of material in J/g ^{o}C, and dT/dt is the differential of temperature depending on the t-time in $^{o}C/min$. In addition, the cross-sectional area of a cylinder can be expressed:

$$A = \pi D^2/4 \qquad (3)$$

where D is the diameter of material in cm.

III. RESULTS AND DISCUSSION

a) PSOH molecular weight and monolith characteristics

The weight-average molecular weight of PSOH was about MW = 70345 g mol^{-1}, having a molecular weight distribution of MW/Mn = 1.2. This value indicated that a low molecular weight PSOH was obtained.

SiO_2-D's with a single diameter of 1.5 cm and thicknesses of 0.2, 0.4, and 0.6 cm were obtained, with a relative standard deviation of 3.4 and 3.0 % for diameter and thickness respectively. These thicknesses were used to label each SiO_2-D, as SiO_2-$D_{0.2}$, SiO_2-$D_{0.4}$, and SiO_2-$D_{0.6}$, each one having an average weight of 0.8250, 1.6498 and 2.4748 g respectively, with a relative standard deviation of 2.5, 2.8 and 3.2 % respectively. Table 1 shows the relations between reagents and solvents that were used in each case.

Furthermore, according to the standard BET method, the SiO_2-D's were composed of pores having a diameter of 1.8 nm.

b) FTIR analysis

Figure 3 shows the infrared absorption spectra of the PSOH and pure SiO_2-D. The presence of the PSOH was determined by the characteristic bands of polystyrene (Figure 3A). The aromatic PSOH fraction gave a C-H stretching for the sp^2 carbon at 3067 cm^{-1}; this fraction exhibited the characteristic overtone bands in the region from 2000-1667 cm^{-1} because of the monosubstituted ring. Additionally, the phenyl ring vibrations at 1601, 1452, 753 and 695 cm^{-1} were clearly observed.

Table 1 : Initial concentration of the reactant for SiO_2-D preparation

First solution		Second solution	
TEOS	ETOH	H_2O	HNO_3
4.5x10^{-3}	6.9x10^{-2}	8.9x10^{-1}	4.7x10^{-3}
0.9330	3.1600	16.0000	0.2980
1	4	16	0.2

Peaks at 3278 and 2628 cm^{-1} were associated with the alkyl substituent group. Additionally, due to OH, the PSOH showed a broad stretched band centered at 3465 cm^{-1}, originated by the H….O-H bond.

The spectrum presented in the Figure 3B illustrates the situation of SiO_2-D. This includes intense absorption peaks at 1170, 1070, 950 and 800 cm^{-1}.

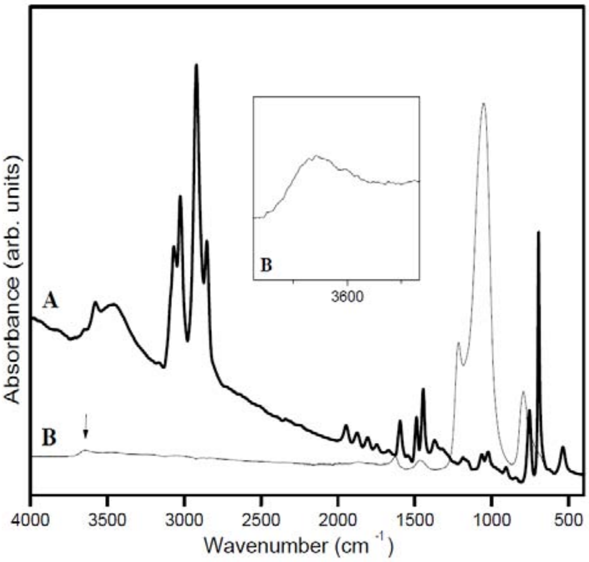


Figure 3 : FTIR spectra of A) PSOH having a OH group and B) SiO_2-D.

These peaks were assigned to the absorption of the longitudinal optic Si–O–Si asymmetric, Si–O–Si asymmetric stretching, Si–OH group, and Si–O–Si symmetric stretching, respectively. Finally, through zooming into the spectrum, a very weak broadband signal at 3645 cm^{-1}, due to a O-H stretching can be easily observed. These results conceived the existence of an intermolecular hydrogen bonding between PSOH and SiO_2-D.

c) Coating of monolith by the polymer

Table 2 shows the PSOH films thickness value (PSOHϵ) and the weight percentage (wt%) of PSOH on SiO_2-D, in relation to the number of dips. The results showed that all SiO_2-D´s coated were transparent, as well as hard and plain in consistency.

According to the experimental data (Table 2), the film thickness was independent of SiO_2-D thickness, because SiO_2-D´s of different thicknesses absorbed almost the same amount of PSOH after each dipping. This shows that the PSOH chains were absorbed on identical surfaces.

As a consequence, after each immersion, more chains were added (increasing the monolith weight) which suggests the existence of a strong chain-chain attraction. These new chain depositions were done without significant detachment (by solvation) from the previous chains.

Table 2 : PSOHϵ and gain weight percent (wt%) as function of SiO$_2$-D thickness and numbers of dips

Numbers of dips	1		2		3	
	PSOHϵ*	wt%	PSOHϵ*	wt%	PSOHΔϵ*	wt%
SiO$_2$-D$_{0.2}$	1130	0.049	2246	0.098	3782	0.215
SiO$_2$-D$_{0.4}$	1139	0.031	2206	0.049	3772	0.107
SiO$_2$-D$_{0.6}$	1128	0.015	2256	0.029	3801	0.074
Averages	*1132*		*2236*		*3785*	

** PSOH films thickness value in nm.*

d) Hardness determination

Figure 4 shows photos obtained after the microindentation hardness tests.

These tests determined the effect of PSOH film thickness on SiO$_2$-D$_{0.2}$ and SiO$_2$-D$_{0.6}$.

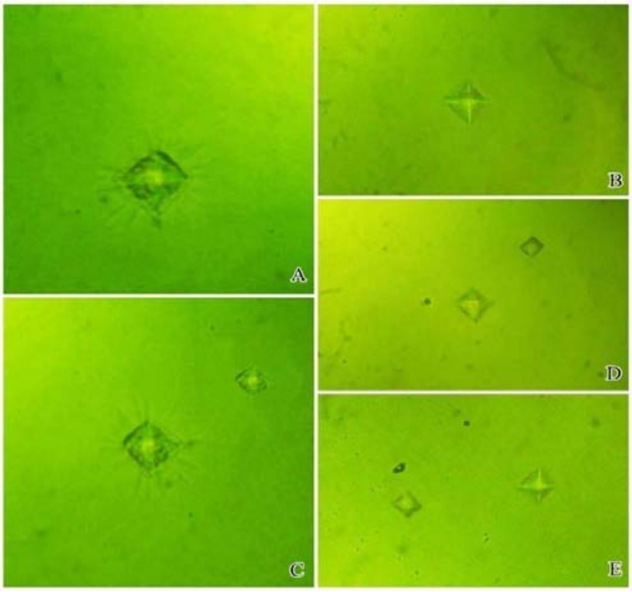


Figure 4 : Micrographs of specimens: A) pure SiO$_2$-D$_{0.2}$ (100 gf), B) SiO$_2$-D$_{0.2}$ with PSOHϵ= 3782 nm (100 gf), C) pure SiO$_2$-D$_{0.6}$ (10 gf), D) SiO$_2$-D$_{0.6}$ with PSOHϵ= 1128nm (10 gf), and E) SiO$_2$-D$_{0.6}$ with PSOHϵ= 3801nm (10 gf).

The first Vickers indentation was performed on pure SiO$_2$-D$_{0.2}$, and it was made with 100 gf *P*. In this monolith, a large number of cracks around the perimeter mark were observed (Figure 4A).

As a result of PSOH deposition, PSOHϵ=3782 nm, shorter cracks and a good geometrical definition of the mark were determined (Figure 4B).

A variant was found on the surface of the pure SiO$_2$-D$_{0.6}$ after applying a load of 10 gf *P* (Figure 4C). The cracks around the perimeter mark and the geometrical definition were lower than that of the pure SiO$_2$-D$_{0.2}$. This situation changed when the SiO$_2$-D$_{0.6}$ was coated with a PSOH film thickness of 1128 nm (Figure 4D). In this circumstance, the cracks around the perimeter mark, as well as the geometry were better defined after applying the same load. Moreover, as the PSOH film thickness was increased to 3801 nm, shorter fissures around the perimeter mark and a high geometry definition were observed (Figure 4E).

According to the above mentioned results, there was a decrease in fissure size after the PSOH film addition, which was more evident as the film thickness was increased. This was due to the lamination effect, which is produced by the strong intermolecular interaction between PSOH chains.

Table 3 indicated that *Hv* values were direct function of the geometrical mark dimension and *P* in the tip of the diamond shaped indentation. For all coated SiO$_2$-D´s, the *Hv* values were increased as the load and PSOH thickness were increased.

Additionally, the *Hv* values were direct function of the PSOH film and the SiO$_2$-D´s thickness. This behavior is mostly related to the uniform dispersion, orientation and attraction of PSOH chains on the SiO$_2$-D surface, giving it an increase of the ductile strength. This situation may be due to the medium molecular weight of PSOH, which introduced a notorious increase in the *Hv* values.

e) Temperature evaluation (Lee's Disk method)

From the System I developed for an uncoated monolith test (Figure 2), the following notes were obtained: for instance, for SiO$_2$-D$_{0.2}$: A$_1$, B$_1$, C$_1$, and D$_1$ and so forth, this monolith had a temperature reduction from An to Bn, and from Cn to Dn that were barely 0.4°C and 0.35°C respectively (Figure 5A).

Table 3 : Microindentation values of pure SiO$_2$-D and with PSOH films thickness values.

		Monolith	PSOH films on SiO$_2$-D					
	P (gf)	H_v (GPa)	PSOH€	H_v (GPa)	PSOH€	H_v (GPa)	PSOH€	H_v (GPa)
SiO$_2$-D$_{0.2}$	100	23.0220	1130	25.8370	2246	29.6870	3782	31.5720
SiO$_2$-D$_{0.4}$	25	92.0408	1139	103.3380	2206	114.8042	3772	126.2701
SiO$_2$-D$_{0.6}$	10	230.1021	1128	258.3451	2256	287.0106	3801	315.6753

Consequently, two values were omitted from each pair, which only left B and C. Similarly, all B temperature values were assumed to be the same for all studies (Figure 5B).

System I and II took similar considerations, except that A' was not omitted due to its temperature difference with B'. On the other hand, because A's value is independent of the tested monolith (A'=A), it was used as an indicator in the increase of the temperature.

Table 4 shows the analysis carried out in pure SiO$_2$-D specimens, showing that the temperature decreased due to an increase of the SiO$_2$-D thickness.

This tendency was expected, however, the heat reduction was very significant, reaching up to 60% at 31.5 minutes for the monolith of higher thickness, SiO$_2$-D$_{0.6}$.

The difference of insulating temperature between B and C offered the temperature gradient ΔT, which was established for each thickness of the SiO$_2$-D. Subsequently, the temperature quotient was

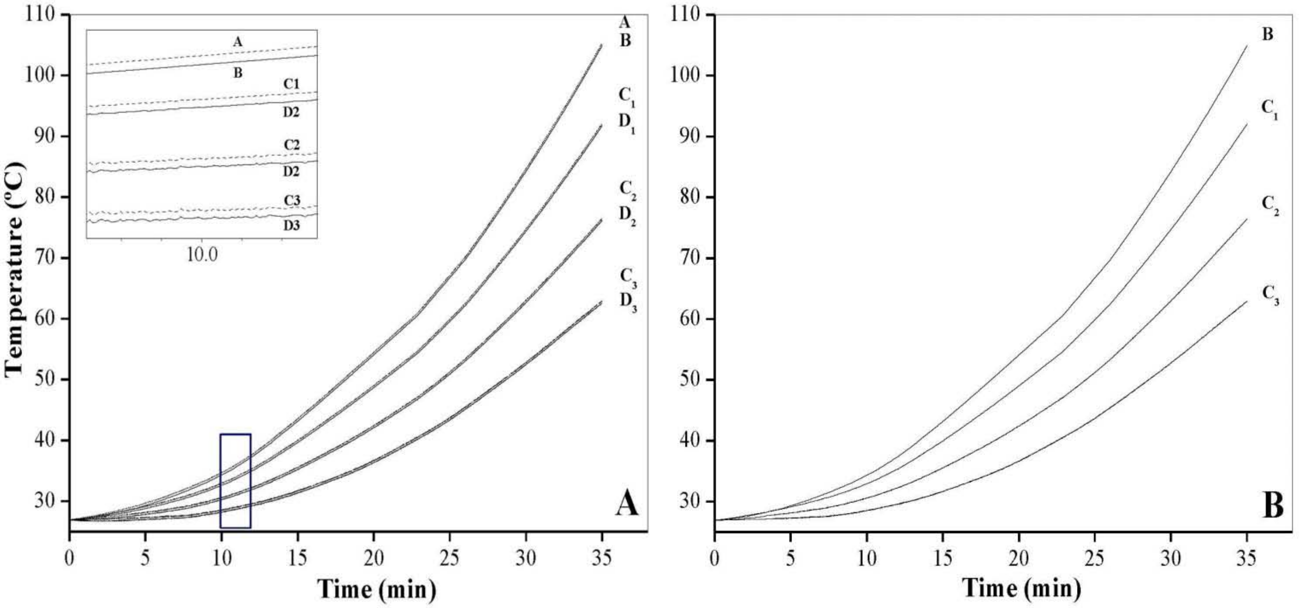


Figure 5 : System I: A) SiO$_2$-D with A and Dn and B) without A and Dn dates.

Table 4 : Temperature values (°C) and gradient, ΔT (°C) of pure SiO$_2$-D from B to C as function of time and SiO$_2$-D thickness.

Time, min.	SiO$_2$-D	SiO$_2$-D$_{0.2}$, ΔT	SiO$_2$-D$_{0.4}$,ΔT	SiO$_2$-D$_{0.6}$, ΔT
	B	C$_1$	C$_2$	C$_3$
13.4	40	37.4, 2.6	33.7, 6.3	30.4, 9.6
24.4	65	58.4, 6.6	50.1, 14.9	42.8, 22.2
31.5	90	79.6, 10.4	66.8, 23.2	55.8, 34.2

Obtained in relation to the time in the transitory state (dT/dt; slope) which was associated to the Cn value.

Figure 6 shows the thermal analysis corresponding to SiO_2-D having a PSOH film. The Figures 6A, 6B, and 6C indicate the analysis of SiO_2-$D_{0.2}$, SiO_2-$D_{0.4}$ and SiO_2-$D_{0.6}$ respectively. The subscript numbers correspond to the monolith thickness and new additional subscript numbers correspond to the PSOH thickness values, which are 1130, 2206, and 3801 nm.

Table 5 separately shows the PSOH film performance, without considering the SiO_2-D thickness, indicating the constant A´ as well as B´s values for different PSOHϵ. *ΔT* was calculated to obtain the temperature quotient for each B_1´, B_2´and B_3´ as a function of time in a transitory state (dT/dt). The insulating temperatures by PSOH thickness and by SiO_2-D were A´– B´ and B´-C´ (is equal to B-C) respectively. Thus, the difference in the insulation total (reduction temperature) is given by (A´– B´) + (B´- C´). For the systems I and II, as the experiment time runs in the interval of 0 to 35 minutes, there was an increase of *ΔT* as SiO_2-D and PSOH thickness were increased. This tendency was associated with the dielectric properties of both SiO_2 and PSOH.

Figure 7 shows the heat flux behavior as a function of temperature gradient and thickness in SiO_2-D (Figure 7A) and PSOH (Figure 7B). The heat flux increases linearly due to the thickness increase of SiO_2-D and PSOH. This was attributed to a higher temperature required to transfer heat from A´ to B' and from B' to C'. The thermal conductivity value (*k*; slope) in each SiO_2-D thickness (Figure 7A) and in each PSOHϵ (Figure 7B) was almost the same.

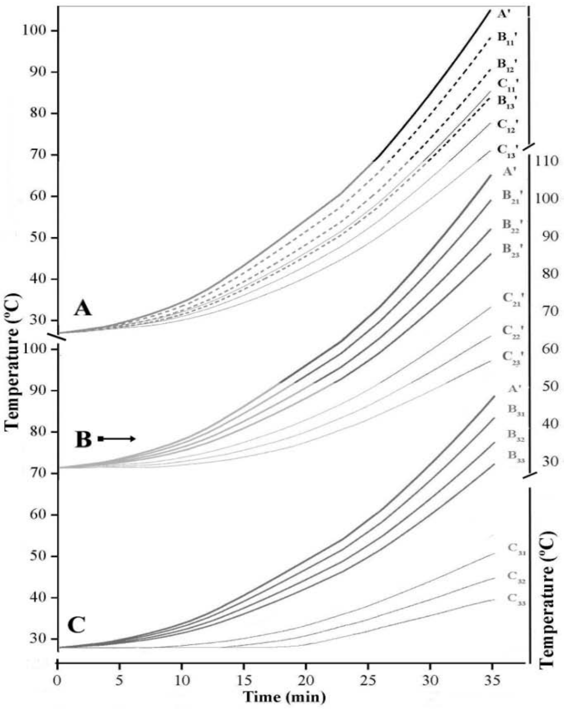


Figure 6 : System II: A) SiO_2-$D_{0.2}$ B) SiO_2-$D_{0.4}$ and C) SiO_2-$D_{0.6}$, having each monolith a PSOHϵ of 1130, 2385 and 3703nm respectively.

Table 5 : Temperature values (°C) and gradient, ΔT (°C) of PSOH films from A' to B' as function of time and PSOHϵ for no specific SiO_2-D.

Time, min.		PSOH ϵ =1130, ΔT	PSOH ϵ =2206, ΔT	PSOH ϵ =3801, ΔT
	A´	B_{11}'	B_{12}'	B_{13}'
13.4	40	38.5, 1.5	36.7, 3.3	35.2, 4.8
24.4	65	61.5, 3.5	57.4, 7.6	53.9, 11.1
31.5	90	84.6, 5.4	78.3, 11.7	72.9, 17.1

All thickness values (ϵ) in nm.

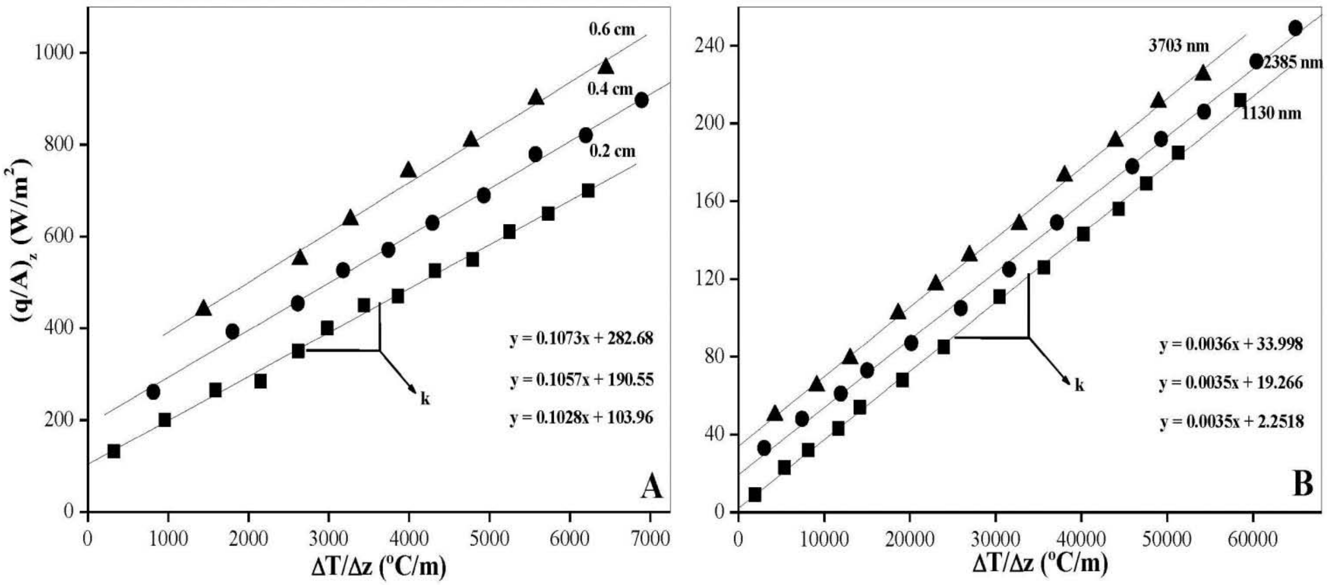


Figure 7 : Heat flux behavior as a function of temperature gradient and thickness in: A) SiO_2 -D, and B) PSOH film.

This was related to the fact that in certain materials such as SiO_2 and PSOH, *k* does not depend on its thickness, so average SiO_2-D and PSOH of *k* values were 0.1053 and 0.0035 W/m K, respectively.The SiO_2–D coated and uncoated with PSOH showed a high transparency and well defined geometry. The maximum *Hv* values and ductile behavior were found as the thickness values in PSOH increased. The individual values of SiO_2–D and PSOH film of *k* (0.1053 and 0.0035 W/m K) were lower compared to the *k* values coming from bibliographic references of pure SiO_2 and polystyrene (1.46 and 0.12 W/m K). It may be a result of a substantial air (0.02 W/m K) presence in the silica pore structure and the dispersion of polymer chains within the inorganic matrix (monolith pore size diameter 1.8 nm). Consequently, the PSOH increases its thermal insulation properties when it is supported on SiO_2–D. Preliminary, this could be attributed to the strong interfacial interaction between the polymer and the substrate, where the PSOH chains can be disassociated as a consequence of a possible affinity.

IV. ACKNOWLEDGMENTS

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Tropospheric Ozone Concentrations and Meteorological Parameters

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GJSFR-B Classification: FOR Code: 050199, 040108

TROPOSPHERIC OZONE CONCENTRATIONS AND METEOROLOGICAL PARAMETERS

Strictly as per the compliance and regulations of :

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I. INTRODUCTION

Air pollution has impacts on both the ecological equilibrium and the population health (Menut et al., 2000). Stratospheric ozone shields us from ultraviolet radiation, while tropospheric ozone can aggravate existing health conditions such as bronchitis, heart disease, emphysema and asthma (Lippman, 1989) and can result in damage to vegetation (Embersion et al., 2001). Although it is colorless and odorless, the ozone gas is very irritating to the lungs and can cause permanent lung damage. Ozone is very corrosive; it damages the human air sacs that are important for gas exchange. Repeated exposure to high levels of ozone can thus inflame lung tissues and cause respiratory infections.

Ozone damage to plants can occur without any visible signs. The gas interferes with the ability of green plants to convert sunlight into useful energy. This interferes with the normal photosynthesis processes; and causes damage to agricultural crops, commercial timber and natural forest ecosystems, ornamental plants (grass, flowers, shrubs, and trees) and other natural flora (Menut et al., 2000). The economy of the North West Province depends mostly on agriculture; therefore, interference with normal photosynthesis processes is cause for concern. Botsalano is situated in the agricultural area and high levels of ozone can have negative effects on the crops in the area, and Marikana is near the mining industry, where the ozone precursors, oxides of nitrogen and VOC's are mostly produced.

Ground-level ozone is not emitted directly into the air, but rather is formed by gases like oxides of nitrogen (NOx) and volatile organic compounds (VOC), which in the presence of heat and sunlight, react to form ozone. Emissions of NOx are produced primarily when fossil fuels are burned in motor vehicle engines, power plants, and industrial boilers.

The major anthropogenic source regions of atmospheric pollutants in southern Africa are the mining and smelting activities on the Copper belt in northern Zambia and emissions from coal combustion by industry in South Africa (Fleming and van der Merwe, 2002), where emission occurs on a continuous basis. Greenberg et al. (2003) showed that biogenic emissions of hydrocarbons from Southern African vegetation are significant sources of these important ozone precursors. Most biogenic emissions are dependent on the solar cycle and the availability of moisture. As a result, they vary with season and time of the day, being higher in summer than winter and higher during the day than at night.

Biomass of the African savannas is known to produce large amounts of photochemically active aerosols and trace gases that are necessary precursors of tropospheric ozone (Crutzen and Andreae, 1990)

Meteorology plays an important role in the formation, dispersion, transport, and dilution of air pollutants. The variations in local meteorological conditions such as wind direction, wind speed, temperature and relative humidity have a great influence on surface ozone concentrations and its precursors (Elminir, 2005). Weather conditions are also critical to ozone formation, which is greatest during summer, when long hours of sunlight and high temperatures speed up the ozone-forming photochemical reactions.

Relative humidity has an effect on the concentrations of air pollutants. A study by Li et al. (2007) reported that an increase in relative humidity leads to a decrease in average concentrations of ozone.

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High ozone concentrations are also associated with high temperatures and prolonged sunshine.

The main objectives of this study were to determine the concentrations of ozone in the lower atmosphere, and to relate the concentrations to changing meteorological conditions. The study was conducted at the Botsalano Game Reserve, which is considered a ‘clean’ environment since it is far from mines, industrial areas and human settlements; and at Marikana (Rustenburg), which is considered as relatively “polluted” environment because it is situated close to mines and industrial areas.

The Botsalano game reserve is situated 18 km east of Ramatlabama (Botswana – South Africa) border post, and 65 km north of Mafikeng. The Game Reserve is situated between longitude 25° 32’ 30.4” south and latitude 25° 45’ 17.8” east and is far from town and mining industries. Ozone concentrations and meteorological parameters were also measured at Marikana municipal offices, with a community health clinic, community hall and library buildings in the same location. Marikana is a township situated between longitude 27˚21’53.61” south and latitude 27˚28’36.58” east, located to the east of Rustenburg, a pollution hotspot in the North West Province.

II. MATERIALS AND METHODS

Environment SA 41 m UV photometric ozone analyzer was used to measure ozone concentrations. The ozone analyzer operates on a full scale of 0 – 500 ppb, at a temperature range of 10°C to 35°C, with response time setting of 11 (Automatic response time), and with or without any of the internal ozone generator, and span external control (zero/span solenoid valve) (www.epa.gov/ttn/amtic/criteria.html). The UV photometric method is not subject to interference from any of the common gaseous air pollutants.

The ozone analyzer has three major systems: the optical system, the pneumatic system, and the processing electronic system. Pneumatic system consists of sample probe, sample inlet line, particulate filter which eliminates the dust particles contained in the sample to be analyzed, solenoid valves, and scrubber, internal tubing, flow meter which maintains the necessary flow in the measurement system, and pump, all used to bring ambient air samples to the analyzer inlet (McElroy and Nees, 1997).

The air sample was taken continuously (24 hours a day) by a pump, it passed first through exchangeable Teflon filter. The filter was changed after every two weeks, and the forceps were used to hold the filter during each changing period. The detector measured the light intensity in the absence of ozone. The data logger was connected to the instruments to log the data to the computer. The data for temperature, relative humidity, rain, and wind speed and wind direction were also recorded and stored daily. The Beer-Lambert equation is used to calculate the concentration of ozone from the ratio of light intensity (US EPA, 1996).

Temperature and relative humidity were measured using Rotronic MP 101A (Vaisala HMP50), rain intensity was measured using Thies 5.4103.20.041 Adolf Thies GmbH Co.KG, and wind direction and wind speed were measured using Vector A101ML (Vector W200P).

III. RESULTS AND DISCUSSION

The hourly ozone levels are vital in determining the contribution of domestic and industrial activities in the vicinity of the study area.

a) Hourly ozone concentrations for mid week and weekend days at Botsalano Game Reserve

Figure 3.1 shows high hourly ozone concentrations during the weekend, i.e. a maximum of 49.81 and 54.18 ppb on Saturday and Sunday respectively; and low levels during mid week days with a maximum of 36.42 and 41.23 ppb on Tuesday and Wednesday respectively. The ozone starts to increase in the early hours a day from 06h00 in the morning. The afternoon maximum is due to photochemical formation of ozone and the evening minimum can be due to surface deposition, the titration of ozone by nitrogen oxides and the absence of photolysis of ozone precursors that cause ozone production at night. The maximum is also in agreement with the results obtained by Lenkopane and Matale (2000), who measured surface ozone at Gaborone and other parts of Botswana and showed that ozone reached maximum peak in the afternoon.

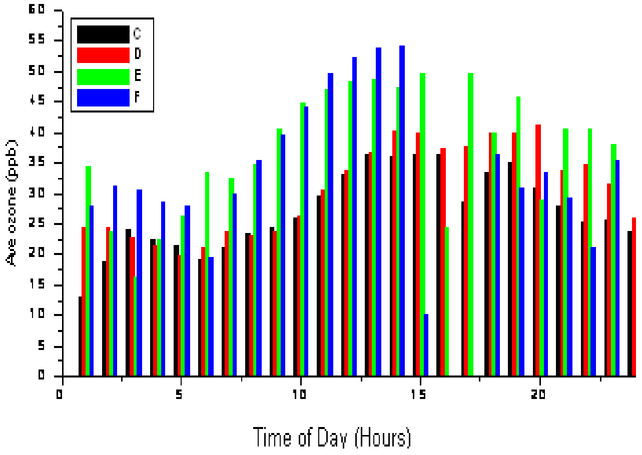

Figure 3.1 : Hourly ozone levels on 09 Jan 07 (C), 10 Jan 07 (D), 13 Jan 07 (E), 14 Jan 07 (F)

The increase of ozone concentration in the late afternoon just before sunset could be due to motor vehicle emissions because of the afternoon traffic density and domestic fuel burning activities.

The results in Figure 3.2 show higher midweek ozone levels with a maximum of 47.21 and 47.06 ppb as compared to 38.34 and 31.51 ppb maxima for the weekend.

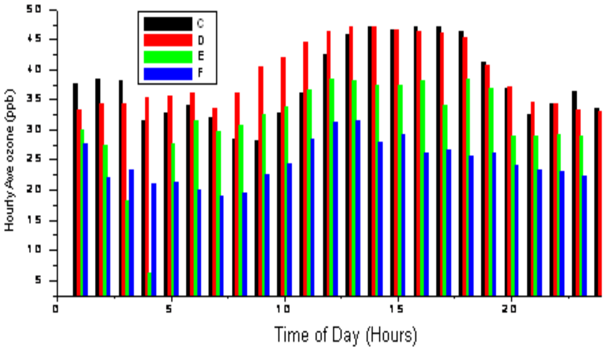

Figure 3.2 : Hourly ozone levels on 13 Mar 07 (C), 14 Mar 07 (D), 17 Mar 07 (E), 18 Mar 07 (F)

The high concentrations during the week occur because of photochemical reactions among ozone anthropogenic precursors from vehicle emissions, and the lower ozone concentration during weekend were because of lower emissions of ozone precursors on weekends. A decrease in concentrations from evening to early morning hours is in agreement with Tyson et al. (1988) who suggested that in the evening, ozone concentration decreases steadily because of the night inversion layer.

The results in Figure 3.3 show that the ozone concentrations for mid week and weekend days start to increase at 07h00 and reach a maximum of 51.37 ppb at 14h00 during the weekend, and 39.28 ppb during mid week at 16h00. It reached a minimum of 30.26 ppb during the weekend at 19h00, and 13.75 ppb during mid week at 20h00. A similar bell plot was observed for Figure 3.4, showing a concentration decrease from 01h00 to 06h00 during the weekend, and increased from 07h00 reaching a maximum of 61.76 ppb at 17h00. The mid weekdays showed an increase from 06h00, reaching a maximum of 45.91 ppb at 17h00, followed by a decrease to a minimum of 18.27 ppb at 24h00.

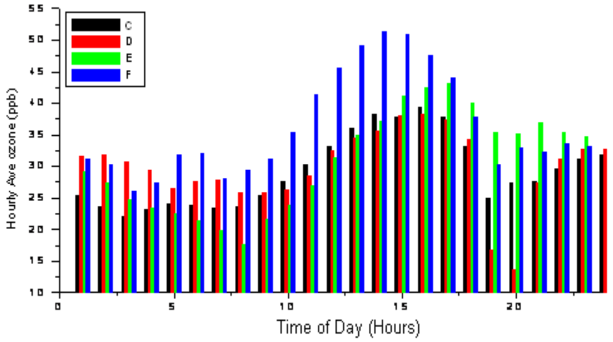

Figure 3.3 : Hourly average ozone on 10 Jul 07 (C), 11 Jul 07 (D), 14 Jul 07 (E), 15 Jul 07 (F)

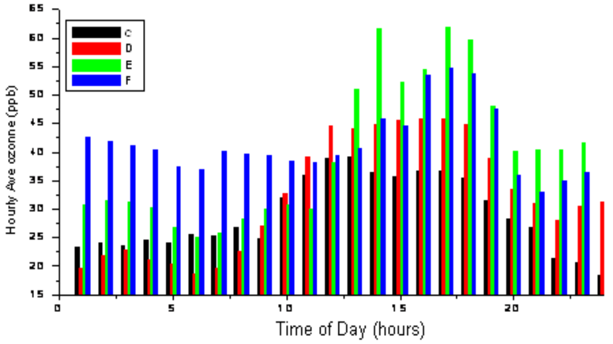

Figure 3.4 : Hourly ozone on 9 Oct 07 (C), 10 Oct 07 (D), 13 Oct 07 (E), 14 Oct 07 (F)

The ozone concentrations measured were generally higher during the weekend than in the mid week days despite the lower emissions of ozone precursors expected on weekend days. These might be because of the left over precursors from the previous day because during the weekend most companies are not operating and that decreases the emissions, most people are not working, so we expected transport emissions to be less.

The observation from the Figure 3.1, 3.3 and 3.4 may also suggest a "weekend effect". According to Qin et al. (2004) and Pudasainee et al. (2006) the phenomenon where ozone levels are higher during weekends than on weekdays is known as the "weekend effects". The mechanisms for the weekend effects on ozone formation are still not well understood. California Air Resources Board (CARB) outlined the following six potential causes of the weekend effect for ozone as described by Huess et al. (2003) and Jimenez et al. (2005): a reduction in NO_x emissions on weekends that reduces the titration of ozone; a weekend change in the timing of NO_x emissions that allows for more efficient production of ozone; increased sunlight caused by the reduction in the amount of soot in the air; carryover of vehicle emissions near the ground; carryover of vehicle emissions aloft, and increase in weekend emissions, particularly from off-road sources.

b) Hourly ozone concentrations for mid week and weekend days at Marikana

The hourly ozone levels for Marikana are presented in figures 3.5 to 3.8. Figure 3.5 show an increase in ozone from morning hours and a maximum of 56.58 ppb during the week at around 13h00, and 74.24 ppb during the weekend at around 14h00. A decrease is also observed from 20h00 to the early morning hours. Figure 3.6 shows a similar trend with a maximum of 61.80 ppb at 16h00 on the 12 March during the week, and a maximum of 30.66 ppb during the weekend. The increase from morning to late afternoon in the two figures may be associated with photochemical reactions from precursors that include industrial and vehicular emissions of nitrogen oxides and volatile organic compounds in the presence of sunlight.

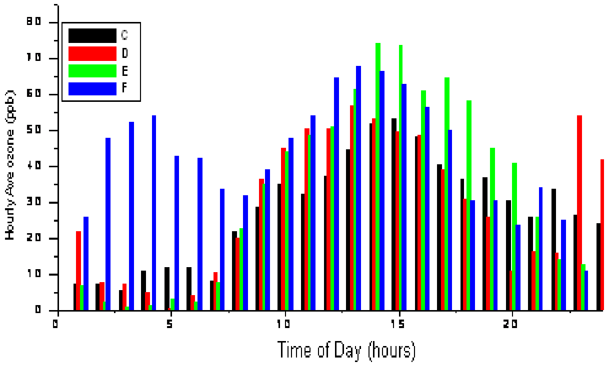

Figure 3.5 : Hourly ozone on 13 Jan 08 (C), 14 Jan 08 (D), 17 Jan 08 (E), 18 Jan 08 (F)

The increase of ozone concentrations during daylight hours is attributed to the photolysis reactions of NO_2 and photo oxidation of VOC's, carbon monoxides, hydrocarbons and other ozone precursors. It is also attributed to the downward transport of ozone by the vertical mixing, due to conventile heating, which happens during daytime hours (Lal et al, 2000).

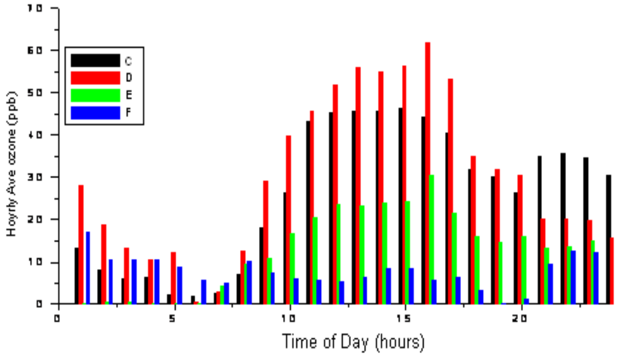

Figure 3.6 : Hourly ozone on 11 Mar 08 (C), 12 Mar 08 (D), 15 Mar 08 (E), 16 Mar 08 (F)

The high ozone concentrations during the week as observed in Figure 3.6 were the result of photochemical reactions among its anthropogenic precursors that include industrial and vehicles emissions and lower ozone concentration during the weekend were because of lower emissions of ozone precursors on weekends.

Figure 3.7 and 3.8 show higher ozone levels during weekend days than midweek days. The 'bell' features are still prominent with maxima of 80.65 ppb and 65.79 for weekend and weekday respectively in July; and 96.908 ppb and 82.982 ppb for weekend and weekday respectively in October.

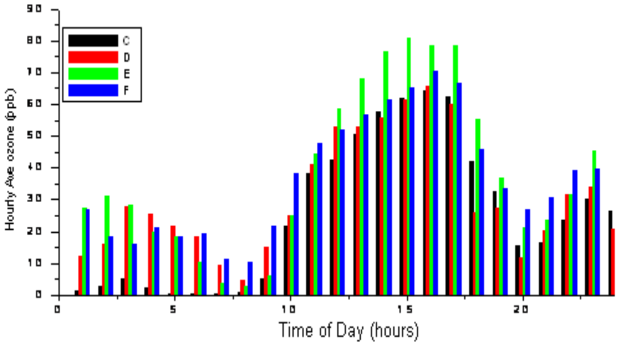

Figure 3.7 : Hourly ozone on 15 Jul 08 (C), 16 Jul 08 (D), 19 Jul 08 (E), 20 Jul 08 (F)

The rate of ozone level increase in the morning is faster than the evening one. This may imply that, in situations with significant ozone formation (including most urban and polluted rural areas weather conditions favorable formation), the removal of ozone is small compared to the rate of ozone production. The process of NO_x titration can only remove one ozone per emitted NO, whereas that of ozone formation typically produces four or more ozone per NO emitted (Sillman 1999). The slow ozone formation in the evening is attributed to the reduction of hydroxyl radical concentrations.

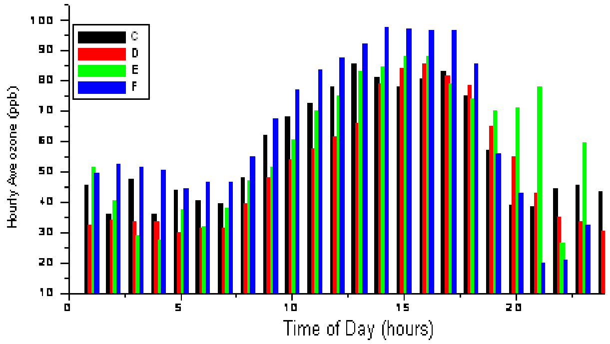

Figure 3.8 : Hourly ozone on 14 Oct 08 (C), 15 Oct 08 (D), 18 Oct 08 (E), 19 Oct 08 (F)

The hourly ozone concentrations at both sites increase from the early hours of the day and reach a maximum in the afternoon, then decreases slowly from the early hours of the evening until it reached minimum in the early hours of the morning; thus suggesting a 'bell plot' behavior, supported by several researchers including Zunckel et al. (2004), who measured surface ozone in the Southern African regions, and showed that surface ozone concentrations exhibit seasonal and diurnal variations and it increases just before sunrise and reach maximum in the afternoon then minimum in the evening. Formation of ozone is lowest in the morning and highest in the late afternoon when sunlight intensity and temperature peak. The ozone peak diminishes quickly when the sun sets; therefore an accumulation of the concentrations from one day to another is not expected. The concentrations however, are higher during the weekend than in the mid weekdays despite lower emissions of ozone precursors expected on weekends; thus suggesting a 'weekend effect'.

The hourly ozone levels at Marikana are higher than the levels observed in Botsalano Game Reserve. This is in agreement with a study by Byun et al. (2007), which concluded that ozone production in the industrial regions can be very efficient, ranging between 50 and 150 ppb h-1 due to high concentrations of reactive hydrocarbons in the presence of NO_x.

c) Daily Ozone Concentrations And Meteorology

According to Zunckel et al. (2004), mean surface ozone concentrations exhibit strong seasonal and diurnal variations. Ground level ozone concentrations increase in the spring and summer when there is more sunlight and temperatures are higher.

The daily ozone concentrations on Figure 3.9 were high during week-days with a maximum on the 4th and 15th. The maximum may be as a result of busy roads and industries, trans-border air pollution, and the biogenic emissions of hydrocarbons from vegetation. The highest daily average was found to be 44.41 ppb on the 15th of the month, which is lower than the 90 ppb daily average set by the South African Department of Environmental Affairs and Tourism; and higher than the ambient air quality standard (AAQS) for monthly average ozone of 30.00 ppb.

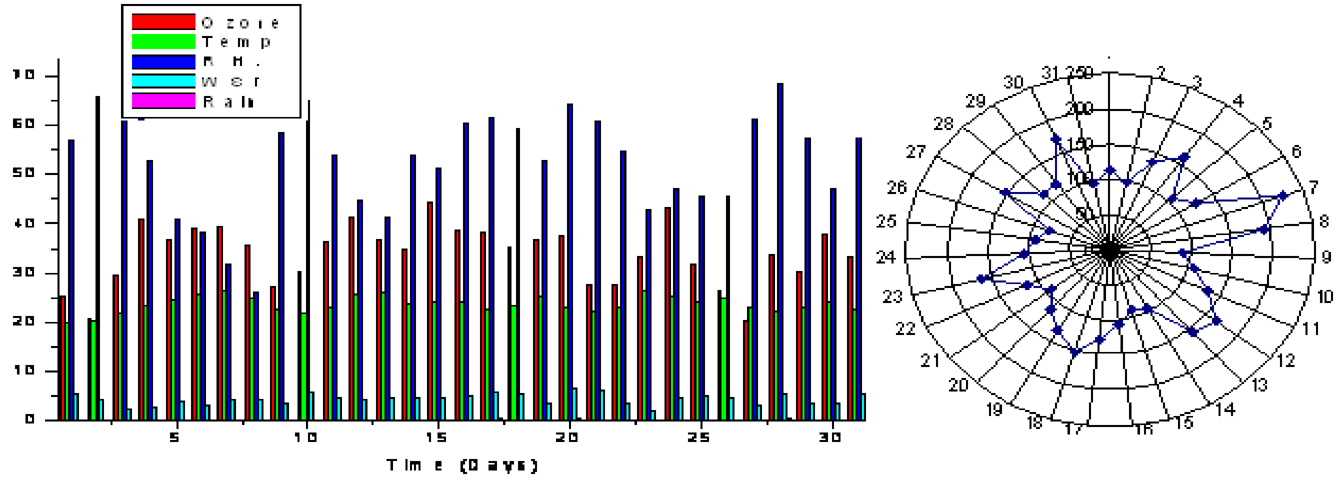

Figure 3.9 : Daily ozone levels and meteorology for January 2007

The January 2007 maximum of 44.41ppb was reached at a temperature of 24.1^{0}C and relative humidity of 51.3%; and a minimum of 20.23ppb at 22.9^{0}C, relative humidity of 61.1%, and 0.18mm rain. The measured concentrations were positively correlated with temperature (r = 0.61). A negative correlation between ozone and relative humidity, and positive correlation between ozone and the following parameters; wind speed, wind direction, and rain was also observed. The wind rose above show the direction of prevailing winds from south east (SE) and east of south east (ESE) for most of the days during this month. The wind was very light to moderate (from 2.07 to 6.77 m/s).

Figure 3.10 shows maximum mean ozone concentrations reached on the 1st and 2nd days of the month in week-days and low on the 3rd and 4th weekend days of January 2008.

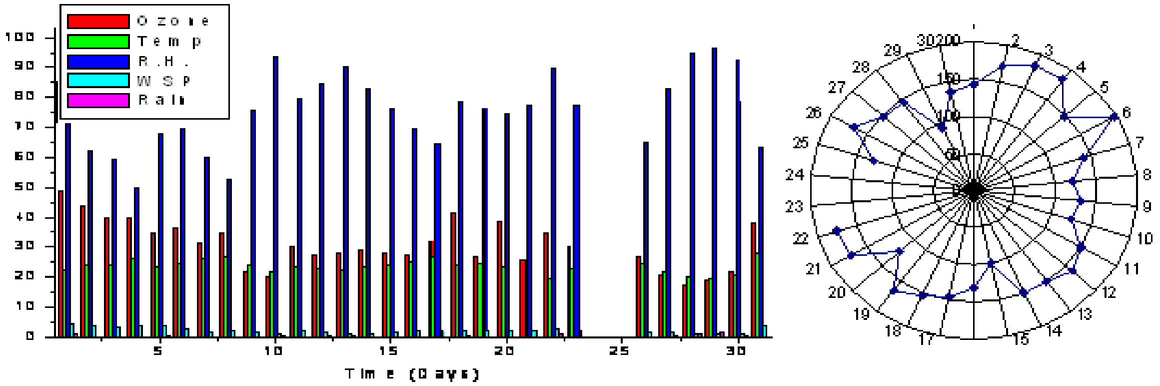

Figure 3.10 : Daily ozone and meteorology for January 2008

The January 2008 daily ozone concentrations reached a maximum of 48.80 ppb at temperature of 22.5^{0}C, relative humidity of 71.4%, and 0.96 mm of rain. The minimum average daily ozone was measured as 17.53 ppb when temperature was 20.1^{0}C, relative humidity was 94.8%, and rainfall of 1mm of rain. The ozone might be influenced by temperature and wind speed and wind direction, because they correlated positively, 0.44, 0.83 and 0.29 respectively. A negative correlation between ozone and relative humidity (r = -0.6381) was measured.

The wind rose in Figure 3.10 shows the direction of prevailing winds as SE and SSE most of the time during the month, with a very light to light wind (from 0.9 to 4.24 m/s).The wind came from locations were most of the sources (traffic, mining and industry) are situated.

The difference in ozone levels for January 2007 and 2008 can be linked to wind speed which measured 2.07 to 6.77 for January 2007 and 0.9 to 4.2 mm/s for January 2008. The low wind speed lead to the build-up of high local pollutant concentrations while high wind speeds promote the dispersion of ozone precursors and thus decrease ozone concentrations locally near sources but they also transport ozone to distant locations, often causing high ozone concentrations in areas without large sources of nitrogen oxides (NO_X) and volatile organic compounds (VOCs) (Sanchez-Ccoyllo et al., 2006).

Figure 3.11 shows the lowest daily ozone concentrations measured on weekend-days (1st and 2nd of March 2007) and this might be the results of low weekend traffic, and closure of industries in the nearby town. The ozone concentrations were high during the week-days (6th and 7th), thus showing the results of biogenic emissions, and biomass burning which are major sources of gases and aerosols in the Southern African atmosphere (Silva et al., 2003). The highest concentration was 40.96 ppb and the lowest was 4.03 ppb.

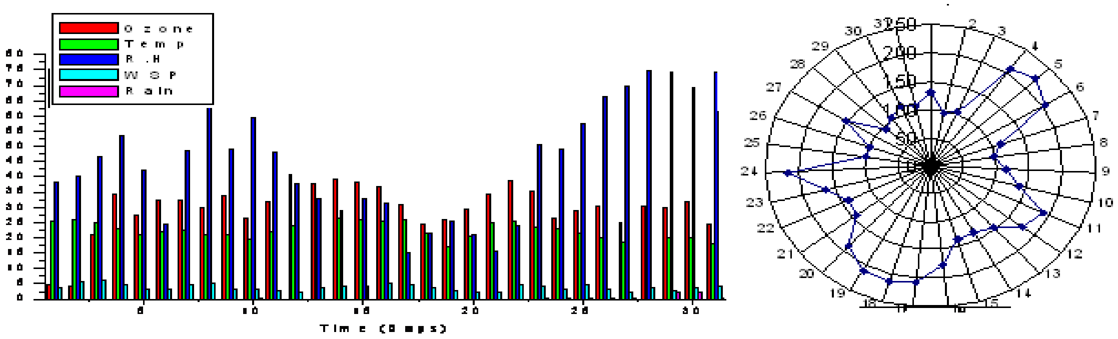

Figure 3.11 : Daily average ozone and meteorology for March 2007

The figure shows maximum concentration of 40.96ppb at temperature and relative humidity of 24^{0}C and 37.7% respectively. A positive correlation between Ozone and temperature, and wind direction, and a negative correlation between ozone and relative humidity, and wind speed was observed. The prevailing wind direction was east (E) and ESE for most part of the month and the other part was from SE and SSE, with very light to moderate wind speed; thus most of the ozone precursors might have come from south to east directions because Mafikeng the nearest town to Botsalano is situated on the south and the cement industry -

High daily ozone concentrations for the week-days 12th and 13th March 2008 that may reflect the effect of continuous emissions from transportation, industries and mining occurring in the surrounding areas are shown in Figure 3.12.

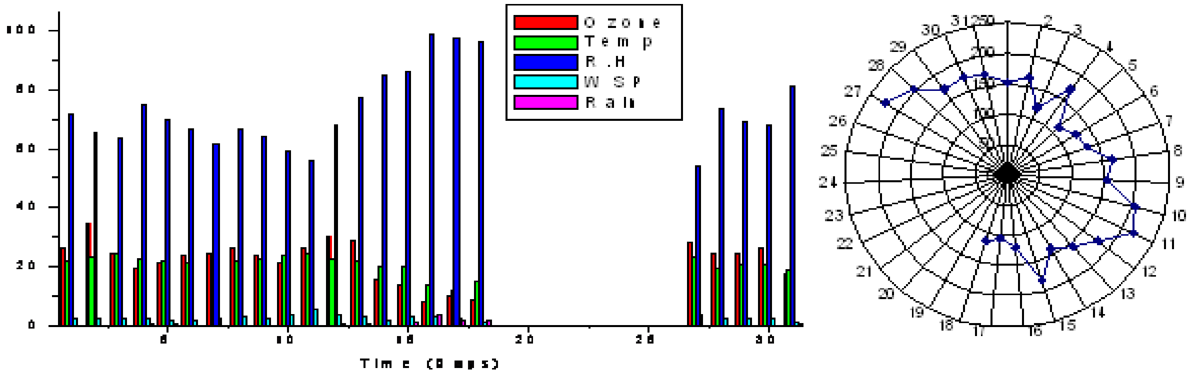

Figure 3.12 : Daily average ozone and meteorology for March 2008

The daily ozone reached a maximum of 34.43 ppb when temperature was 23.3^{0}C, and relative humidity was 65.7%, and there was no rainfall on that day. The minimum ozone was 7.78ppb when temperature was 14^{0}C, while relative humidity was 99% and rainfall was 36 mm of rainfall on that day. This minimum concentration can be as a result of washouts of air pollutants from the atmosphere by rain. Ozone and temperature are highly correlated, at 0.8047, and also ozone and wind speed and wind direction are positively

The wind rose in the figure shows the SE, SE, ESE, and SSE wind directions for most of month, with wind speed of 0.8 to 4.3 m/s. Only on three to four days the wind prevailed from SSW, where the Marikana Township, municipal dumping site and other mining industries are situated.

The March 2007 and 2008 levels are lower than the January 2007 and 2008 levels. This shows the influence of meteorological parameters like temperature, wind speed and relative humidity since the month of January is the end of summer and March is mid autumn. A decrease in temperature and an increase in relative humidity from January to March may account for the measured levels.

Figure 3.13 shows daily ozone concentrations that reached a maximum of 37.37 ppm on the 24th of July 2007, and minimum daily ozone concentration of 20.20 ppb on the 28th on the month. The maximum daily ozone concentration was reached during week-days, and this could result from emissions from buses transporting people to work and learners to different schools around the area; and the burning of wood. The minimum daily ozone concentration was reached on weekend and this might have resulted from the few transports passing by because most people are not working during weekend and even the operation in the nearby farms stops during weekend. The monthly average for the month of 28.171 ppb which is lower than the monthly average of 30.00 ppb set by AAQS.

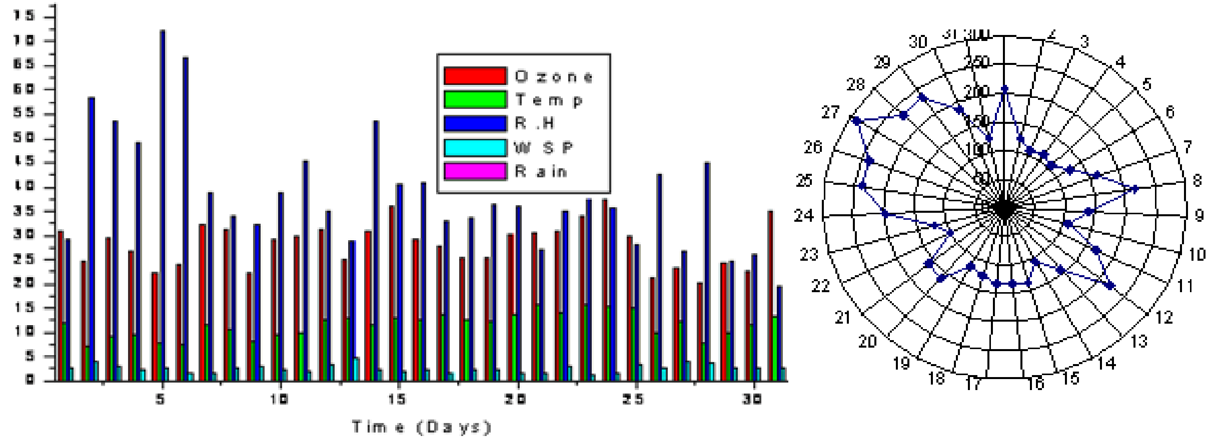

Figure 3.13 : Daily average ozone and meteorology for July 2007

A correlation coefficient of 0.6362 was obtained for ozone and temperature, and ozone and the other meteorological parameters; relative humidity, wind speed and direction showed negative correlation values, of -0.2365, -0.351 and -0.1860 respectively. The low wind speed of 1.4 to 4.8 m/s was expected to yield high ozone concentrations but this was not the case mainly because of the low winter temperatures.

The daily ozone concentrations shown on Figure 3.14 reached a maximum of 39.53 ppb on the 22nd of July 2008, and minimum of 15.85 ppb on the 7th of the month. The maximum daily average ozone concentrations were reached during week-days, and this could have resulted from the industries, mining activities taking place in the area, transport from the nearby road and railway line, also from the burning of wood and coal from the nearby township because during winter some families use fire to keep their homes warm.

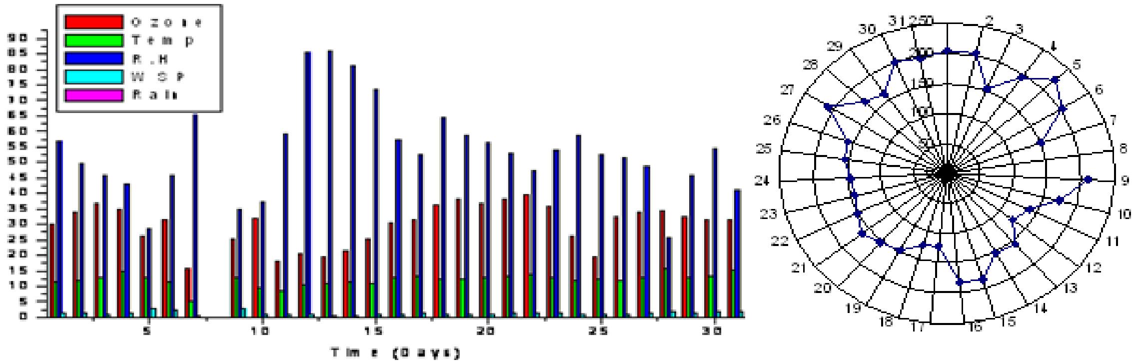

Figure 3.14 : Daily average ozone and meteorology for July 2008

The maximum of 39.53ppb was observed when temperature was 11.8°C, and relative humidity was 58.8%, and the minimum of 15.85 ppb of ozone concentration was observed when temperature was 5.02°C, and relative humidity was 66.6%. These confirm a positive correlation between ozone and temperature. Higher levels were expected for the winter month (July) since most of the biomass burning of the African savannas is observed during the winter and spring seasons (Levine et al, 1996).

Exchange processes between the stratosphere and troposphere influence ground level ozone variations, which can lead to frequent occurrences of high values in spring (Monks, 2000). The second process occurs at multiple spatial and temporal scales. High ozone concentrations might be registered within the city or at a distance downwind because of the high emissions of precursors in urban areas. These precursors may also be transported over long distances, resulting in ozone formation far from the sources under the influence of meteorological conditions (Hastile et al., 1999). The results presented in Figure 3.15 and 3.16 are representative of the Spring season, which normally lasts from August to October in Marikana and Botsalano.

The daily ozone concentrations shown in Figure 3.15 reached maximum of 52.03 ppb on the 16th of October 2007, and the minimum of 14.25 ppb on the 21st of the month. The daily average ozone concentration maximum of 53.03 ppb could have resulted from the long hours of spring day, from the plants which are found in the area and its surrounding, and from fuel burning by transports traveling in the road in that area. These maximum concentrations may cause damage to the growing maize in that area, because October is one of the months when the maize is grown. Maize is most susceptible to damage by ozone during the flowering season.

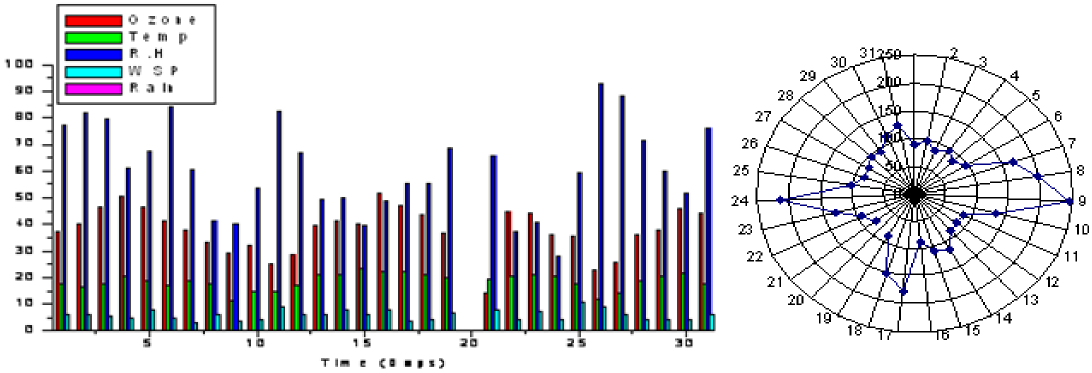

Figure 3.15 : Daily average ozone and meteorology for October 2007

The daily ozone levels shown in the figure reached a maximum of 52.03 ppb when temperature was 22.3^{0}C, relative humidity was 49.2% and there was no rainfall. on that day. The minimum ozone concentration was 22.86 ppb when temperature was 12.1 ppb, and relative humidity was 93%, with 0.2mm rainfall on that day. The high ozone might be associated with the high temperature (r = 0.6323).

The daily average ozone concentration shown in Figure 3.16 was 64.33 ppb on the 3rd of October 2008 and it was on busy working day of the week. these concentrations could be the results of long hours of spring day, fuel emission from transport sector, industries, and mining activities occurring in the surrounding area, where emission occurs continuously, and also from the waste dumping side. The minimum daily average ozone concentration was 26.25 ppb on the 26th of the month, and it was on a weekend when most of the industries are closed and the road and railway line are not busy, so the precursors are low. The average monthly ozone concentration was 50.02 ppb.

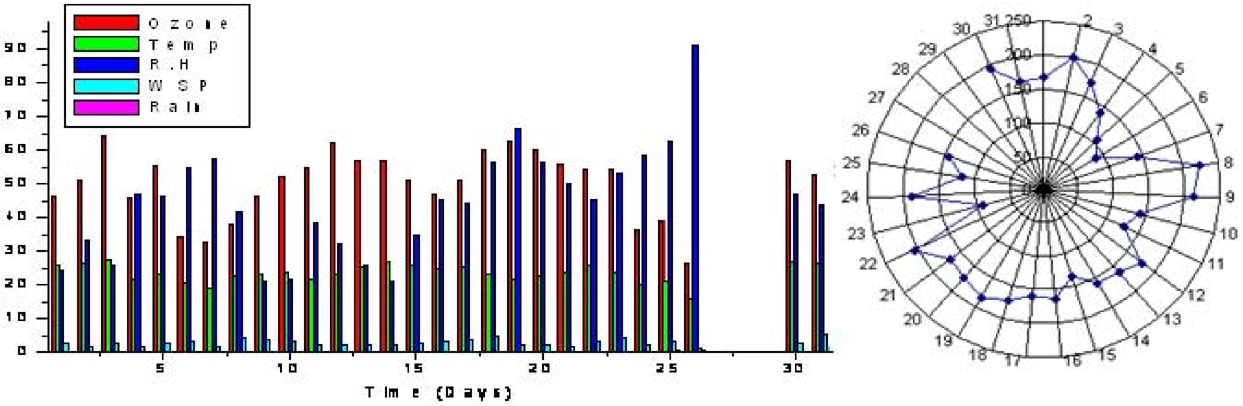

Figure 3.16 : Daily average ozone and meteorology for October 2008

The average ozone concentration reached a maximum of 64.33ppb when temperature was 27.1^{0}C, and relative humidity was 33.7%, with 0.1mm/h rainfall on that day. Ozone and temperature are highly correlated, with a correlation value of 0.6853, also ozone and wind speed and direction have positive correlation, at 0.1174 and 0.1822 respectively. This means the ozone concentration was influenced by these meteorological parameters. There is a negative correlation between ozone and relative humidity, and rain, at -0.4499 and -0.3936 respectively.

The levels observed for Botsalano (October 2007) and Marikana (October 2008) are within the range observed by Zunckel et al. (2004) in Botswana and the Mpumalanga highveld. In both regions the spring time maximum was between 40 and 60 ppb, but reached more than 90 ppb as a mean in October 2000. In these two regions the monthly minimum was between 20 and 30 ppb. The mean daytime ozone concentrations in Botswana and on the highveld reached 40 ppb as early as 10:00 and remain above that level for up to 10 hours. The seasonal maximum in this study generally occurred in the spring months from August to November and the minimum occurred in December and January. With the exception of Cape Point, a strong diurnal variation was observed at all sites. Ozone concentrations increased from a minimum near sunrise to a maximum in the afternoon then decreased again to the early morning minimum.

In general, the daily ozone levels measured during this study can be represented in order of decreasing abundance from October, January, March, July; representative of the seasons: Spring, Summer, Autumn, and Winter.

IV. CONCLUSION

The daily ozone concentration for Botsalano Game reserve ranged between 4.03 and 52.04 ppb; whereas the hourly concentrations were in the range of 6.306 to 61.762 ppb. The daily and hourly ozone concentration ranged between 21.074 and 50.019 ppb, and 0.0768 and 96.908 respectively for Marikana. The measured hourly ozone concentrations at the two study sites were below the one hour ozone standard for South Africa and also the standard set by the World Health Organization (WHO). In general, daily and hourly ozone concentrations for Marikana were found to be higher than that of Botsalano Game Reserve throughout the study period.

An increase in hourly ozone concentrations from early morning hours, reaching a peak around 15h00 and decreasing into night time was observed. The study therefore presents a ‘bell’ behavior of ozone with a peak between 12h00 and 16h00 and a low from evening to early morning; thus suggesting anthropogenic (domestic, industrial, and traffic) activities that increase emission of photochemically active aerosols and trace gases that are necessary precursors of tropospheric ozone in Botsalano and Marikana.

The fact that high ozone concentrations were observed during the weekend than in the mid weekdays, suggests a 'weekend effect' despite lower emissions of ozone precursors on weekends. This suggests the need for further studies into possible sources of ozone concentrations during weekend days, including a further investigation into the six potential causes of 'weekend effects' suggested by previous studies.

The meteorological parameters (temperature, relative humidity, wind speed and direction) were also successfully measured and related to the measured ozone concentrations. A negative correlation between ozone and relative humidity was observed at the two study sites; i.e. ozone increased with a decrease in relative humidity; whilst a positive correlation was observed for ozone and temperature, i.e. an ozone concentrations increased with increased temperature. For an increase in wind speed, a corresponding increase in ozone concentration was also observed. It was also evident during this study that wind speed cannot be separated from wind direction. Wind direction gives an indication of whether the ozone concentrations measured reach the community or not. The wind speed also gives an idea of the possible sources of the ozone levels measured.

V. Acknowledgements

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River Krishna Flood Effects on Soil Properties of Cultivated Areas in Bagalkot District, Karnataka State

By Dr. B.M.Kalshetty, Dr. T.P.Giraddi, R.C.Sheth & M.B.Kalashetti

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Abstract - During 2009 Rabi season flood of river Krishna, the cultivated area of 128 Km2 was flooded in the northern part of Karnataka catchment. The flood entirely killed the vegetations stands on the fields. After wards, the effects of the flood on the ecological properties of the soils and the conditions of agricultural production had been evaluated. A study was conducted to estimate the flood effects on heavy metals concentrations and on the nutrient status of the soils. The sediment layer left from the flood had a thickness of several mm. Boron, Molybdenum within this layer were in between proscribed values and the metal ions concentrations of Iron, Zinc , Copper, were found slightly above the prescribed limits. Thus no restriction had to be announced for food production purposes. Regarding the Major and Secondary nutrients status of the flooded soils, only the mineral Nitrogen content was substantially reduced when compared to not flooded soils. This effect could most probably be related to denitrification processes as a result of anaerobic conditions during the flood. Available Potash (K_2O) and Phosphorus (P_2O_5) found more than the prescribed limits.

Keywords : Flood effects, heavy metal concentration, soil fertility, and denitification.

GJSFR-B Classification: FOR Code: 050302

RIVER KRISHNA FLOOD EFFECTS ON SOIL PROPERTIES OF CULTIVATED AREAS IN BAGALKOT DISTRICT, KARNATAKA STATE

Strictly as per the compliance and regulations of :

River Krishna Flood Effects on Soil Properties of Cultivated Areas in Bagalkot District, Karnataka State

Dr. B.M.Kalshetty [α], Dr. T.P.Giraddi [σ], R.C.Sheth [ρ] & M.B.Kalashetti [ω]

Abstract - During 2009 Rabi season flood of river Krishna, the cultivated area of 128 Km2 was flooded in the northern part of Karnataka catchment. The flood entirely killed the vegetations stands on the fields. After wards, the effects of the flood on the ecological properties of the soils and the conditions of agricultural production had been evaluated. A study was conducted to estimate the flood effects on heavy metals concentrations and on the nutrient status of the soils.

The sediment layer left from the flood had a thickness of several mm. Boron, Molybdenum within this layer were in between proscribed values and the metal ions concentrations of Iron, Zinc , Copper, were found slightly above the prescribed limits. Thus no restriction had to be announced for food production purposes. Regarding the Major and Secondary nutrients status of the flooded soils, only the mineral Nitrogen content was substantially reduced when compared to not flooded soils. This effect could most probably be related to denitrification processes as a result of anaerobic conditions during the flood. Available Potash (K_2O) and Phosphorus (P_2O_5) found more than the prescribed limits.

The effects of the flood on agricultural management conditions were minor. However, hydrological and land use management concepts have to be developed that help to reduce the probability of such flood events in future.

Keywords : Flood effects, heavy metal concentration, soil fertility, and denitification.

I. Introduction

Soil is a specific component of the biosphere, it is not only a geochemical sink for contaminants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere. September- 2009, flood of River Krishna was the highest flood ever observed along the river. The maximum rain fall during 6 days covering the on and upper part of the catchment area.The entire catchment led to runoff responses that flooded at most of 10% of the Bagalkot District. This area was famous for cultivation purposes during the flood in these cultivated areas with a water table of 11.5 meters maximum height. Due to water logging, the vegetation stands on the cultivated fields were completely killed.

The consequences of the flood for the farmers consisted of harvest losses and the restructuration of agricultural infrastructure. Additionally, long term effects on the cultivation conditions of the soil were expected that could result from soil pollution due to sedimentation of pollutant enriched material and from changes of the nutrient status of the soil.

The main objective of our present investigation was therefore to determine the impact of the flood on the fertility and ecological properties of the flooded soils in order to provide a quick estimate of flood effects on the conditions for agricultural production in the flooded area.

After the flood we focused on two governing effects:

1. The possible enrichment of the soils with heavy metals following the sedimentation of polluted material.
2. The change of the nutrient status of the soils due to leaching effects on the hand and sorption or anaerobic conditions on the other hand.

II. Materials and Methods

Site characteristics: After Godavari, Krishna is the main River in the southern part of India, It is originated at Mahabaleshwar of Maharashtra State, it flows from west to east of Maharashtra, Karnataka, Andrapradesh, lastly it merges at Bangalkoli .

The longitude of River Krishna in Karnataka State is 480 Kms. The sub Rivers join to this Krishna River are Bhīma, Koyna, Yerla, Panchaganga, Dudaganga, Tungabhadra, HiranneKeshi, Ghataprabha and Malaprabha. The hydrological basin is that of the Koyna Dam. The River Krishna widely enters in the northern part of Karnataka state. Where as Belagavi and Bagalkot Districts of the state receive the Krishna River fist. The altitude reaches its maximum at Bagalkot District.

- Area: Jamkhandi, Mudhol, Bilagi and Bagalkot talukas of the District.
- Main stream length: 480 Kms. In Karnataka State and 128 Kms. in the Bagalkot District.
- Maximum altitude: 519.60 mtrs.
- Mean altitude: 515.8 mtrs.

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- Minimum altitude : 521.0 mrs.
- Average depth of basin : 514.63 mtrs

Floods were more frequent in September and October. There are three surface reservoirs or barrages at Hippargi & Padasalgi barrage near Jamkhandi, Galgali barrage near Bilagi and Almatti Dam at Kudalasangum of height 519.60 mtrs. The capacity of water basin is of 123.08 TMC water, catchment area of Dam 509.02 mtrs. to 514.63 mtrs.

The Almatti Reservoir situated in Bagalkot District of Karnataka State, and latitude 16°19'48'' N. the irrigation potential of 87490 hectares and hydropower generation having an installed capacity of 290 MW[1]. The water spread area is 487.87 sq .Kms. with a fetch of 124 Kms. The storage capacity at the Dam site has been 3486 m cum (123.08 TMC). The maximum flood discharge of 31,007 chums (10, 95,000 cusecs / min.) had been designed to be discharge through the 26 vents of the spill ways, having radial crest gate of size 15m X 15.25 m with crest level at RL 50.016mtrs out of 519.60 mtrs. Total catchment area of Almatti reservoir is 359.25 sq.Kms.(138.71 sq. miles).Rain fall 635 cms. In Bagalkot District and it is recorded 50 cms. In Dam site during September- 2009[1].

The Krishna River flow gradually began to rise in June, pickup in July and over flow in August and September; the flood lift reached maximum height and gradually falling through October to January and by February found to be almost dry or lean flow.

III. Sampling Design and Measurement Methods

Soil is vital eco-compartment acting as a sink for natural for anthropogenic pollutants. Partitioned between 2 micros clay fraction.A comparison in metal accumulation rates between pristine soil and anthropogenic metal contaminated soil will provide an unbiased basis for time bound accumulation of pollutants especially trace elements and others.

Impact on the fertility of lands due to the accumulation of trace elements and other pollutants from Industrial waste discharge into the River stream along with the flood.The variation of fertility of lands due to the flood in the northern part of Karnataka State, especially effect on the area of the Bagalkot District.

The samples were collected and stored in polythene bags separately. These samples were ground sieved with 200 mesh sieve. Accurately 1 gram sample weighed and digested using mixture of conc. HNO3 and HClO4 and extracted by 1 N HCl. Filtered the extract and diluted to required volume using DDW. Such prepared soil extract were analyzed for trace elements with the help of Atomic Absorption Spectrometer and also different Physico-Chemical parameters, nutrients in the soil were analyzed by standard methods[2].

The major effects of the flood on the soil properties were expected:

i. An increase in the heavy metal content as a result of the sedimentation of heavy metal enriched material, and
ii. A change in the nutrients status of the soils as a result of sorption and adsorption on the one hand, and the biological transformation, i.e.; denitrification due to anaerobic conditions on the other hand.

The nutrient status of the soils was determined by taking samples in 30 cms depth. For these samples physical parameters such as Bulk density, water holding capacity and texture were measured. The chemical parameters like pH, EC, Sodium, Potassium and Calcium carbonate were determined using standard methods [2, 9]. The major nutrients present in the selected samples of different areas were determined, the major nutrients such as Organic Carbon, available P (P_2O_5) and available Potash (K_2O). Finally the heavy metal concentrations, knows as micro nutrients such as Iron, Mn, Zn, Cu, Boron and Molybdenum were estimated using well known standard methods[10,11] .

A problem evolved due to the fact that for estimating the flood related changes of the soil properties, reference measurements before and after the flood conditions were recorded and it is required. Naturally, no samples were taken immediately prior to the flood, because of water spread over the fields. We solved the problem or estimated the sample properties before flood from the same locations not flooded but having soil properties comparable to these that were not flooded (the areas are frequently effecting by flood once in couple years). Hence, by comparing the measurement with results derived from sampling the soil at the same locations few months earlier (during summer season). The methods used for comparing the measurements are also recorded in the table 1 before and after the flood effect from the same locations of the district.

IV. Results and Discussion

According to the field survey, the sediment layer derived from the flood in the area had a maximum depth of 3/4 mm. The concentration of some heavy metals and other elemental analysis data of four flooded sediment samples and two soil samples as references, one sample from the flooded lands one year earlier to the flood and one sample from a land outside the flooded area.The element concentrations of all samples as well as the legal limits for metal concentrations, i.e., major, secondary and micro nutrients valid in WHO are also listed in the table 1.

Results of sediment analysis showed that the available Potash (K2O) was found more than legal limits in all most all 4 sample selected for investigation, the concentrations of elements (Micro nutrients) Manganese (Mn), Boron (B) were below the limit values, where as concentrations of Iron (Fe), Zinc (Zn), Copper (Cu), exceeded the legal limits, because of the sludge disposal legacy for cultivated soils.

The results of micro nutrients analysis in the fertile land which is not effected by the flood, varies with those derived from flooded area in the district. Hence, comparably slight change in heavy metal concentrations of the sediment samples lead to the conclusion that in terms of heavy metal pollution no risk must be expected for agricultural productions in the flood area. However, the limited number of samples analyzed implies a factor of uncertainty and requires more investigation.

The micro nutrients such as Zinc (Zn), Copper (Cu) and Boron (B) concentrations of a soil sample taken from not flooded area, i.e., from the spot S5 sample of the same flooded area one year earlier of flood and from a fertile land spot S6 as reference samples (table 1) found in much higher concentrations than those measured within the flooded sediment soil samples. The same trends as found high concentration of such heavy metal in the sediment of European Rivers have often measured and are a subject of environmental concern[3, 12].

Table 1 : Nutrient status of sediment soils of flooded lands and reference spots.

Sl.No.	Parameter	UNIT	Spot S1	Spot S2	Spot S3	Spot S4	SpotS5 Before flood	SpotS6 reference spot	Legal limit
I	Physical-Parameters								
	Bulk Density	g/cc	1.10	1.10	1.10	1.10	1.35	1.50	
	Water Holding Capacity	%	57.01	57.00	57.08	57.06	57.10	57.10	
	Texture		Clay loam	Clay loam	Clay loam	Clay loam	Clay loam	Clay loam	
II	Chemical Parameters								
	pH		8.15	8.20	8.18	8.14	8.60	8.62	6.5-7.5
	EC	ds/m	1.14	1.14	1.15	1.16	0.68	0.64	<1
	Sodium	%	0.32	0.38	0.35	0.37	0.18	0.17	<0.1
	Calcium Carbonate		MEDIUM	MEDIUM	MEDIUM	MEDIUM	MEDIUM	MEDIUM	
III	Major Nutrients								
	Organic Carbon	%	0.74	0.71	0.76	0.78	0.65	0.61	>0.75
	Available P	Kg/h	22.00	21.00	22.01	22.03	16.00	16.24	20-60
	Available K	Kg/h	368.00	370.00	365.02	367.67	350.00	348.00	250-300
IV	Secondary Nutrients								
	Ca	%	1.10	1.08	1.12	1.11	0.98	0.92	<1
	Mg	%	0.37	0.36	0.36	0.35	0.56	0.58	<0.5
	SO4	Ppm	21.5	22.00	21.9	21.7	16.00	16.04	10-20
V	Micro Nutrients								
	Iron	Ppm	5.10	5.06	5.08	5.09	3.92	3.68	Min.4.50
	Manganese	Ppm	1.12	1.10	1.14	1.18	0.92	0.91	Min.2.00
	Zinc (Zn)	Ppm	1.48	1.50	1.54	1.56	2.10	2.18	Min.0.75
	Copper (Cu)	Ppm	1.26	1.24	1.28	1.29	1.68	1.54	Min.0.60
	Boron	Ppm	0.23	0.22	0.24	0.26	0.40	0.48	Min.0.50
	Molybdenum	ppm	0.07	0.06	0.06	0.06	0.04	0.05	0.05-0.2

Soil analysis report in terms of the plant available potassium, Phosphorus, Magnesium content and other nutrients value including pH- values for 4 samples from the flooded fields could be compared with the measurements conducted on the same fields, one year earlier (Spot 5) and the analysis of soil sample from the reference (Spot S6), which is not effected by the flood. To isolate the effect of the soil properties of all the spots of flooded lands, spot S5 soil of land one year earlier and the Spot S6 from the fertile land which is not effected by the flood.

Results revealed that in case of physical parameters such as bulk density, water holding capacity and texture found to be the same in all most all spots. The pH value of the samples from flooded field were found to be less when compared to the conditions of the soil before flood spot S5 and soil from fertile land. This is because; of normal washing by the flooded water. The variation in pH value was not pronounced, may be coursed by the fertilizer application and plant uptake. The Electrical conductivity found to be more than the prescribed limit in case of all the four spots of flooded lands, this may be due to the deposition of more total dissolved solids (TDS). The values of sodium and Calcium carbonate had increased and found more than the legal limits in all four samples (S1 to S4) of flooded sediment soils.

The amount of major nutrients available Potassium (Potash K2O) was increased after the flood in most of the spots S1 to S4. The increase in the Potassium content might be possible due to the saturations of the soil might have resulted in the widening of smectitic clay minerals and thus release of previously fixed Potassium and also due to large fertilizer storage have been resulting in the dissolution of the stored fertilizers within the flood water. The later might also be the reason for the increase in the available Phosphorus and the secondary nutrient Magnesium content on the sediment soils of flooded lands. However, the measured changes in the Potassium content were also within the range variation yearly due to the fertilization.

The Calcium and sulphur content of the sediment soils of flooded fields were found to be more when compared to the conditions from spots S5 and S6. The table 2 contains the micronutrients levels (Cation exchange capacity CEC). The CEC measured for 4 flooded sediment soils and one of the fertile field S6 and another one from the field of one year earlier of flood S5. The CEC of the flooded soil simples was higher in average than that of the not flooded samples as shown in figure I. However, due to the pronounced variation of the clay content in the different soil samples, the CEC values were within a wide range varying in between 08 to 26 mval/100g. The relative contribution of the different cations to the CEC might therefore be a better basis for comparing the situation of the flooded and not flooded soils (Spots S1 to S6).

Table 2 : Cation Exchange Capacity and Relative Contribution to the elements to the CEC (%).

Sl.No.	Spots	CEC mval/100gr.	K^+	Na^+	Ca^{++}	Mg^{++}	EC	pH
1.	S1	10	368	0.32	1.10	0.37	1.14	8.15
2.	S2	08	370	0.38	1.68	0.36	1.14	8.20
3.	S3	11	365	0.35	1.12	0.36	1.15	8.18
4.	S4	12	367	0.37	1.11	0.35	1.16	8.14
5.	S5	23	350	0.18	0.98	0.56	0.68	8.60
6.	S6	26	348	0.17	0.92	0.58	0.64	8.62

The monovalent and divalent cations contributed to a higher degree and the contribution of protons was lower in the flooded soils when compared to the not flooded soils respectively. The displacement of protons in to the solution was in agreement with the results from pH measurements which is also showed the lower pH –values on the flooded soils. One reason for the decreased pH – values in the flooded soils might have been anaerobic fermentation process that took part during water storage conditions. The increase of the relative contribution of cations to the CEC might be the displacement of protons by cations that were released from clay minerals due to widening during saturated conditions and increased cation availability as a consequence of the flooding of the fertilizer storage.

V. Mineral Nitrogen Content, Available Nutrients (n.p.k) and Organic Carbon in the Soil Samples

The mineral nitrogen content measured for 4 samples from flooded sediments and 2 reference samples one sample spot S5 from field of one year earlier from the effect of flood and another sample S6 from the fertile land. The Nitrogen, phosphorus and Available Potash contents derived for the three different soil depths as listed in table 3.

Table 3 : N P K measurements of soil samples of flooded and reference soils at Different Depths.

Fields	N (Kg/ha)	N (Kg/ha)	N (Kg/ha)	P (Kg/ha)	P (Kg/ha)	P (Kg/ha)	K (Kg/ha)	K (Kg/ha)	K (Kg/ha)
	0-20cm	20-40cm	40-60cm	0-20cm	20-40cm	40-60cm	0-20cm	20-40cm	40-60cm
S1	134	135	128	11.8	11.4	11.6	377	380	371
S2	151	142	150	12.3	12.2	12.8	377	370	369
S3	160	154	141	13.2	12.8	13.0	358	364	363
S4	138	146	135	12.0	9.8	10.8	362	392	388
S5	222	210	206	21.8	22.0	21.6	348	350	354
S6	251	246	231	36.3	35.2	34.8	346	352	349

The nitrate content expressed in Kg/ha was calculated from the measured values assuming a soil density of 1.5 g/cm.The ammonium content as below the value of 0.05 mg/100g dry soil for all samples.

In most of the samples derived from the flooded fields, the nitrogen content was appreciably lower than that in the reference spot S5 and S6. This might be loss in nitrate concentration due to the flood event, the dissolution of nitrate in the flood water and removal with the flood stream and denitrification of nitrate due to anaerobic conditions during the flood. The major amount of nitrogen removed by water runoff[4], and the high vegetation stands on the fields being killed due to water logging provided a source of easily decomposable carbon. This together with the anaerobic conditions during the flood might have triggered the denitrification process[5]. Similar effects have frequently been observed for other areas as a result of flood events or water saturation due to high intensity irrigation [6, 7, 8].

All the values were compared the standard limits shown in table 4, guidelines for soil evaluation and soil gradation in order of production potential based on specific value/range.

Table 4 : Guidelines for soil evaluation

Gradation in order of production potential based on specific values.

Soil quality parameter	Soil with high production potential Grade A (Fertile Soil)	Soil with average production potential Grade B (Normal Soil)	Soil with poor production potential Grade C (Unfertile Soil)
pH(Saturation extract)	6.5-8.3	5.5-6.5 or 8.4-9.0	<5.5 or >9.0
Electrical conductivity m mhos/cm(Saturation extract)	0.2-0.5	0.5-4.0	4.0 & <0.2
Cation exchange capacity meg/100 grams	>30	10.0-30.0	<10
Exchangeable Sodium percent	<5	5-15	>15
Available P kg/ha 17cm plough layers	40-60	20-40	<20
Available N kg/ha in 17 cm plough layer,	>200	100-200	<110
Organic matter % on dry wet. Basis (organic Carbon)	>4	2-4	<2
Available K kg/ha in 17 cm plough layer	>280	110-280	<110
Organic Carbon %	>0.75	0.5-0.75	<0.5

VI. SUMMARY AND CONCLUSION

The objective of our present investigation was to determine the impact of the flood on chemical properties and nutrients status of flooded soils of cultivated areas in order to provide a quick estimate of flood effects on the conditions for agricultural production in flooded area. The possible effects were observed to be heavy metal ions (micronutrients) enrichment in the sediment, and the change of the nutrient status of the soils. The concentration of heavy metals in the sediment layer left from the flood was more or less below legal limits except Iron, Zinc and Copper.

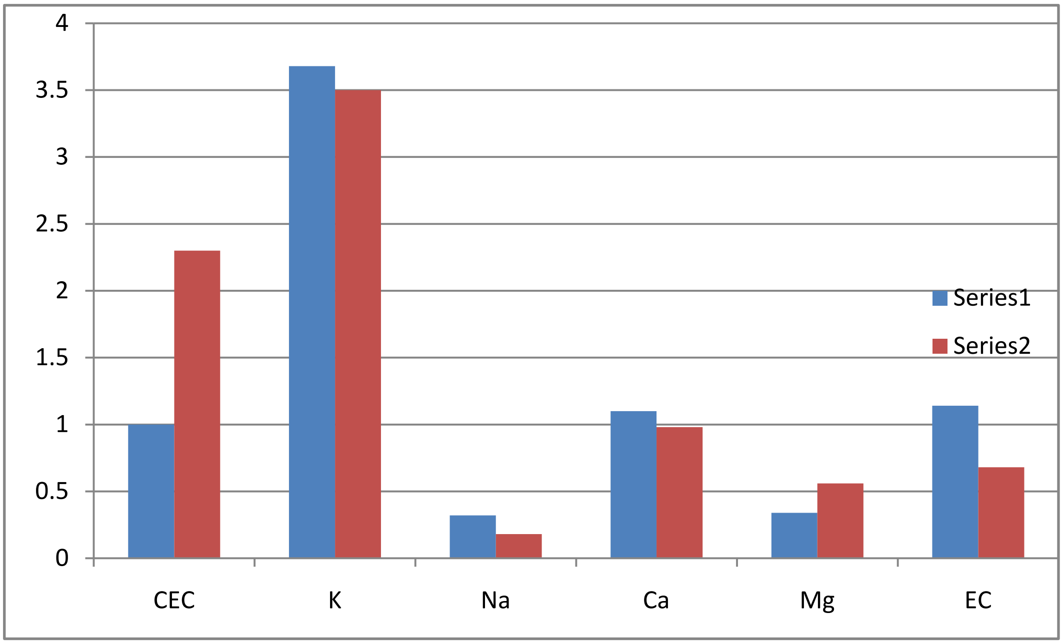
The nutrient status of the soils, the reduced in available Phosphorus and the percentage of Magnesium (Mg) and increase in Potassium contents were measured in the soils of flooded area. The pH-values recorded in almost all spots of flooded area were more than the legal limits. The relative contribution of protons to the CEC was also reduced. The mineral nitrogen content was appreciably decreased in the area of flooded sediment soils. This effect could most probably be related to denitrification processes as result of anaerobic conditions during the flood.

The conclusion is drawn that the effects of the September-2009 flood on the conditions for agricultural production in the 128 Km^{2}area. The total soil evaluation be recorded as the fertile land sample spot S6 showed, the soil with high production potential (Grade A). The spot S5 sample soil from land one year earlier of flood showed the soil with normal/ average production potential (Grade B), this may be due to the fertilizer use. The spots S1 to S4 soil sample analysis showed the soil with poor production potential (unfertile) Grade C. Major Effects on the flood were the direct crops losses and the destruction of agricultural infrastructure. However, given the major damage to leaving beings and social casts the flood caused in the entire catchment, precautions are urgently needed that help to reduce the probability of such flood events in future. Aiming not only reducing the effect of the flood, but reduce the probability of flood events requires a better understanding of the physical nature of rainfall – runoff

Relationships as well as the effects of land use systems on the hydrological response of the catchment as a whole and in its parts.

The political support to farmers for land use, co-operation and financial supports. The multinational co-operation and mutual research activities are of high importance for success in this research field.

Figure 1 : Cation Exchange Capacity and Relative Contribution to the elements to the CEC (%).



Series 1: Flood Area

Series 2: Reference Spot

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The Kinetics and Effect of pH on Removal of Manganese, Cadmium and Lead from Aqueous Solution by Maize Cobs

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Keywords : Kinetics study, Cadmium, Manganese, Lead, maize cob, sorption.

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I. INTRODUCTION

Heavy metals released by a human of anthropogenic emission in the environment are some of the major pollutants of soil and water resources (Loubna et al., 2007). Some metals such as Copper, Zinc and iron are considered bio-essential while others such as Cadmium, Lead, Mercury and chromium are highly toxic. However, even bi-essential metals may cause physiological and ecological problems if present at significant concentration. From an environmental protection point of view, heavy metals ions should be removed at the source in order to avoid pollution of natural water and subsequent metal accumulation in the food chain. Various physical and chemical techniques for removing metals ions from the wastewater include chemical precipitation, adsorption, ion exchange, extraction and membranes processes chemical precipitation is most common utilized conventional technique. However, the application of these methods is often limited due to their inefficiency, high capital investment or operational costs. Consequently, there is a growing requirement for novel, efficient and cost effective techniques for the remediation of metal bearing waste water before their discharge into the environment. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from waste water and water supply (Peterlene et al., 1999, Dakiky et al., 2002). Biosorption technology, utilizing natural metals or industrial and agricultural wastes to remove metal form aqueous media, often an efficient and cost-affordable alternative compound to traditional chemical and physical remediation and decontamination technique since the cost of this process are rather expensive, the use of agricultural residue or industrial by product have been studied. These includes the use of sago waste (Quek et al., 1998), maize-starch, hazelnut shell (Bulut and Zeki., 2007), waste tea leaves, etc. Despite the relative simplicity and potential cost effectiveness of bio sorption, metal removal using low-cost bio-sorbents is relatively improve and need further development before it may be applied routinely in practice and thus considered an alternative to use of ion-exchange resins or activated carbons. Maize cob is an abundant agricultural waste product with millions of tons being generated annual polluting the environment in Nigeria. The maize cobs have been recognized to have significant potential as a bio sorbent for metal removal after simple pre-treatment. In this work, we investigated the potential of maize-cobs to act as a bio sorbent for Mn^{2+}, Cd^{2+}, and Pb^{2+} removal from aqueous media.

II. MATERIALS AND METHODS

a) Sorbent preparation

The maize cobs collected from a local maize mill were cut into small pieces; air dried, powdered in a grinder and sieved through 450 μm and 300 μm mesh screens. The portion of the maize cob meal retained on the 300 μm mesh was steeped in dilute nitric acid solution for 8 hours rinsed with deionized water and air dried.

b) Sorbate preparation

1000 mg kg^{-1} of each of each metal stock was prepared by dissolving calculated amount equivalent of 1.00g of each metal in a specific compound ($MnSO_4.H_2O$, $CdCl_2$ and $Pb(NO_3)_2$) in 1litre distilled water (1000mg/L). Standard Mn^{2+}, Cd^{2+}, and Pb^{2+} solutions of

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10, 20, 40 and 50 mg kg^{-1} were prepared serially by diluting the stock solutions respectively.

c) Contact time study

Equilibration time for the adsorption and adsorptions model of Mn^{2+}, Cd^{2+}, and Pb^{2+} on maize cob was carried out on the metals ions. 30 ml of each selected concentration of salt solutions of heavy metals in distilled water were added each into 1g of maize cob meal weighed into shaking bottles at room temperature (25°C) under neutral pH each to determine the time required for each of the metal ion to reach adsorption equilibrium. Two drops of toluene was added to each solution in the bottles to inhibit microbial growth. The cob suspensions were shaken on a mechanical shaker at a speed of 200 rpm for 30, 60, 90, 120, 150 and 180mins. After the specified shaking time, the solution phase was filtered by using filter paper (whatman 110mm and 11mm pore size) for removing the suspended cob particles. A 10 ml of aliquot of supernant were analyzed for residual Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively by Flame Atomic Absorption Spectrophotometer. The adsorbed heavy metal concentration in maize cob was taken as the difference between metal added in initial solution and the remaining metal in supernatant solution after equilibration. The time for metal adsorption to reach equilibrium was determined graphically from the plot of adsorption values against time of equilibrium. The adsorbed metal ions individually on miaze cob per unit adsorbent mass was calculated as follows:

$$Qe = (Co - Ce)\, V / m \qquad (1)$$

Co is the initial heavy metal concentrations (mg/L); Ce is the concentration of heavy metal at equilibrium (mg/L), m is the maize cob mass (m), V is the solution volume (L). Calculations were made by using these data and adsorption curves were obtained.

d) pH study

One gram of maize cob was weighed into different shaking bottles and 30 ml each of 10 mg kg^{-1} of salt solution of Mn^{2+}, Cd^{2+}, and Pb^{2+} was added. The pH of each solution was adjusted to the required pH value (2.0, 3.0, 4.0, .5.0 and 6.0) using 0.1N HCl and 0.1NNaOH solution from the stock solution. Then, the mixture was stirred in a shaker with speed of 200 r p m at 25°C for each of the equilibration time for Mn^{2+}, Cd^{2+}, and Pb^{2+}. After, the solution phase were fiitered by using filter paper (whatman 110mm and 11mm pore size) for removing the suspended particles. A 10 ml of aliquot of supernant were analysed for residual Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively by Flame Atomic Absorption Spectrophotometer. The adsorbed heavy metal (Mn^{2+}, Cd^{2+}, and Pb^{2+}) on maize cob was taken as the difference between metal added in initial solution and the remaining metal in supernatant solution after equilibration. The optimum pH for metal adsorption was determined graphically from the plot of adsorption values against the design pH values.

III. RESULTS AND DISCUSSION

a) Effect of contact time

The time taken to attain equilibrium for Mn^{2+}, Cd^{2+}, and Pb^{2+} at neutral pH, temperature of 25°C and centrifugation speed of 200 r p m using 1g of maize cob is shown in fig 1, 2, 3. It was observed that the amount of Mn^{2+}, Cd^{2+}, and Pb^{2+} adsorbed per unit mass of maize cob increased significantly with increase in initial concentration. The adsorbed rate was very rapid in the first few minutes after which the rate decreased sharply and eventually reached a constant peak after at 120 minutes of the adsorption irrespective of concentrations (10 mg kg^{-1} to 50 mg kg^{-1}). Two hours was therefore indicated as the time for Mn^{2+}, Cd^{2+}, and Pb^{2+} adsorption to reach equilibrium. The necessary contact time to reach the equilibrium depends on the initial metal ion concentration. The uptake rate is controlled by the rate at which the metals (Mn^{2+}, Cd^{2+}, and Pb^{2+}) were transported from the exterior to the interior sites of the adsorbent. The adsorption capacity was observed to increase with the initial metal concentration for the series (10, 20, 40 and 50 mg kg^{-1}) for the selected heavy metals .This is due to larger surface area of the cob at the beginning of adsorption reaction. The amount of the metal ion each in their different series shows the same magnitude in their removal but varies in the adsorption capacity. However, the differential sorption of Mn^{2+}, Cd^{2+}, and Pb^{2+} ions may be ascribed to the difference in their ionic sizes. The ionic sizes of Mn^{2+}, Cd^{2+}, and Pb^{2+} are 0.67, 0.97, and 1.20 respectively. The smaller the ionic size the greater its affinity to reactive sites. The adsorption capacity increased in the substrate with stronger bond for smaller size metal ion indicative that the competition of manganese with ionic radius of 0.67A has higher binding site than cadmium with ionic radius of 0.97A on maize cob. The lowest adsorption capacity of lead with weak bond on maize cob could be attributed to its highest ionic radius 1.20A. Mn^{2+}, $Cd^{2+}$and Pb^{2+} adsorbed by complexation reaction. This general trend of the sorption is due to the fact that metal ion with smaller ionic radius diffuse faster in aqueous systems and compete better for exchange site than for those with larger sizes. This trend in smaller ionic size was also observed for Cu^{2+},Cd^{2+} and Zn^{2+} using other biological adsorbents (Gardea-Torresdey *et al.*1996; Ho and Mckay, *2000* ; Horsfall *et al.* 2006). According to Cho *et al.* (2005) metal with smaller hydrolysis constant (Pk_H) has the increasing tendency to hydrolyse because of their larger charge-size function (z^2/r). The Pk_H for manganese to cadmium shows that cadmium will be hydrolyze to a greater extent than manganese indicating a higher binding for manganese > cadmium and lead has the least adsorption. So the adsorption capacities increases from $Mn^{2+} > Cd^{2+} > Pb^{2+}$. The long contact time of 2 hours observed to reach equilibrium for all the metal ions indicated that the predominant mechanism was physisorptions which encourage easy removal of the adsorbed heavy metals or regeneration of the spent adsorbent.

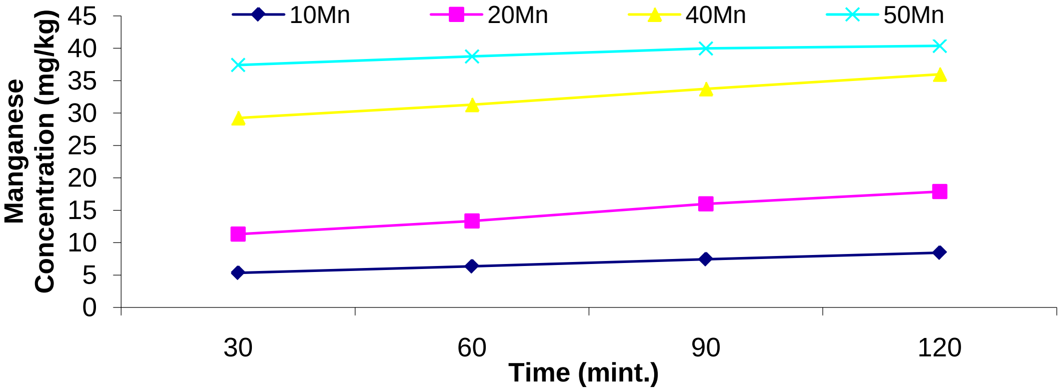

Figure 1 : Time of attainment of manganese adsorption equilibrium at pH of 7.0, 10mg kg^{-1} and temperature of 25°C and centrifugation speed of 200 rpm.

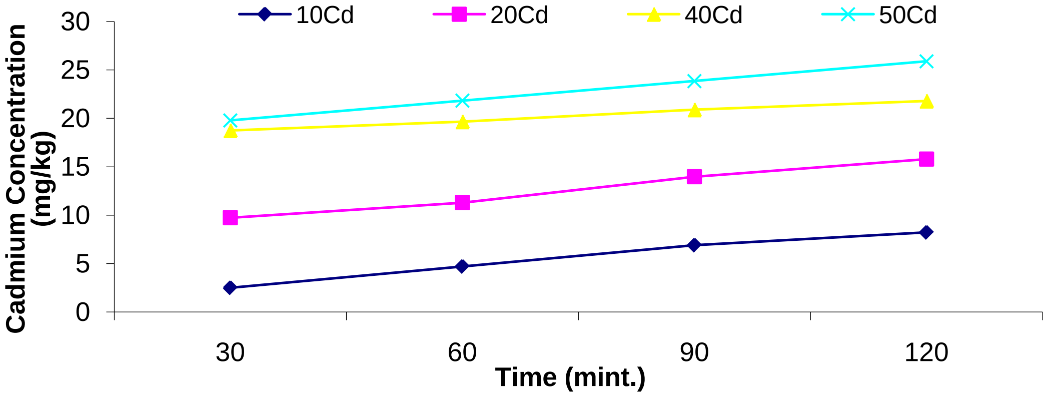

Figure 2 : Time of attainment of cadmium adsorption equilibrium at pH of 7.0, $10mgkg^{-1}$ and, temperature of 25°C and centrifugation speed of 200 rpm.

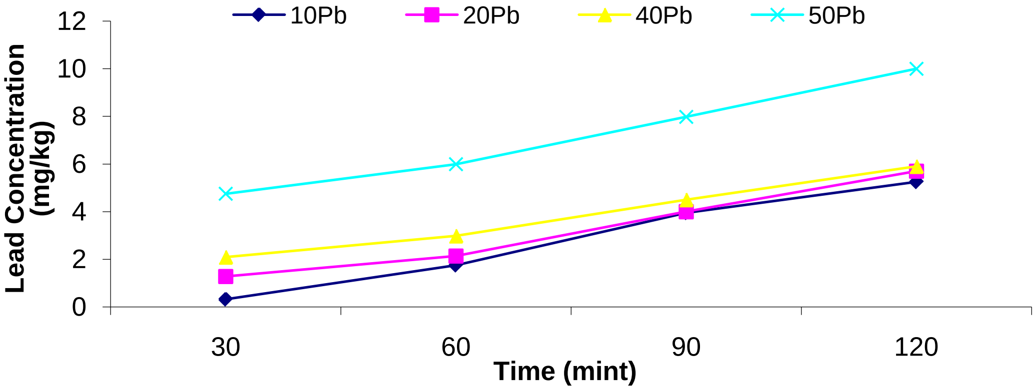

Figure 3 : Time of attainment of lead adsorption equilibrium at pH of 7.0, $10mgkg^{-1}$, temperature of 25°C and centrifugation speed of 200 rpm.

b) Effect of initial rate concentration

The initial concentration provides a driving force to overcome all mass transfer resistances of the metals ion in the aqueous and solid phase. This led to higher probability of collision between the metal and active sites of the maize cob. The surface adsorption sites become exhausted at some point in time, it reached a constant value in which no more metal is removed from solution. At this point, the adsorbed amount of heavy metals on maize cob was in a state of dynamic equilibrium (Demibas, 2004). The equilibrium uptake increased with the increasing of initial metal ions at the range of experimental concentration. Initial rate of the sorption capacity was greater for higher initial heavy metals concentrations, because the resistance to each of the metal uptake decreased as the mass transfer driving force increased so the initial rate of adsorption in metals was greater for higher initial adsorbate concentrations (50 mg kg^{-1}) than for the lowest concentration (10 mg kg^{-1}) of metals ions (manganese, cadmium, and lead) on maize cob.This agree with the work of Okiemen et al (1987) work on the adsorption on cellulosic material.

c) Kinetic treatment of experimental data

The mechanism of adsorption for the heavy metals was subjected to both pseudo-first order Lagergren, (1898) and pseudo second order Ho and Mckay (1999) equations at the initial metal concentrations of 10 mg kg^{-1}

Pseudo first order or Lagergren equation

$$\text{Log}\,[Qe - Q] = \log Qe - k_1/2.303t \qquad (2)$$

A linear plot of log [Qe-Q] against't' indicates the conformity with the model

Qe = mass of metal adsorbed at equilibrium (mg kg^{-1})

Q= mass of metal adsorbed at time "t" (mg kg^{-1})

"t"= time for adsorption (hrs)

k_1 = equilibrium rate constants for 1st order

Pseudo second order or Ho (2004) equation

$$t/Qe = 1/k_2Qe^2 + t/Qe \qquad (3)$$

A linear plot of t/Qe against't' indicates conformity with the model

Qe = mass of metal adsorbed at equilibrium (mg kg^{-1})

"t"= time for adsorption (hrs)

k_2 = equilibrium rate constants for 2nd order.

First order kinetics for Mn^{2+}, $Cd^{2+}$and Pb^{2+} onto maize cob are shown in Fig.4, 5, 6.

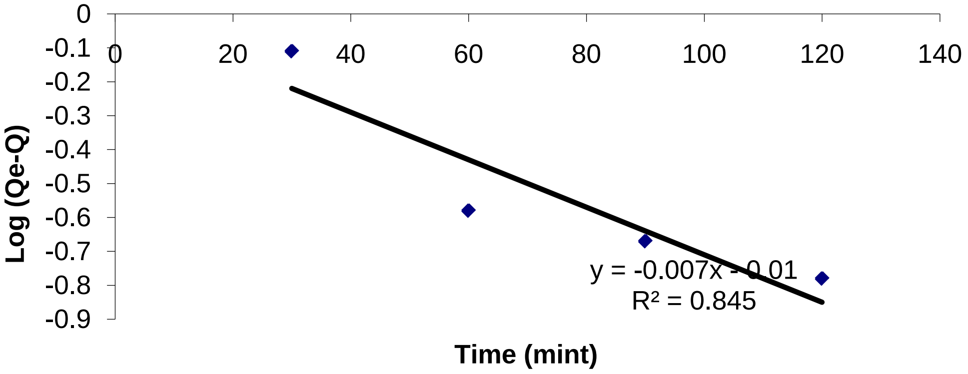

Figure 4 : Lagergren pseudo first order kinectic plot for manganese at pH of 7.0, initial metal concentration of 10mg kg^{-1} and temperature of 25°C

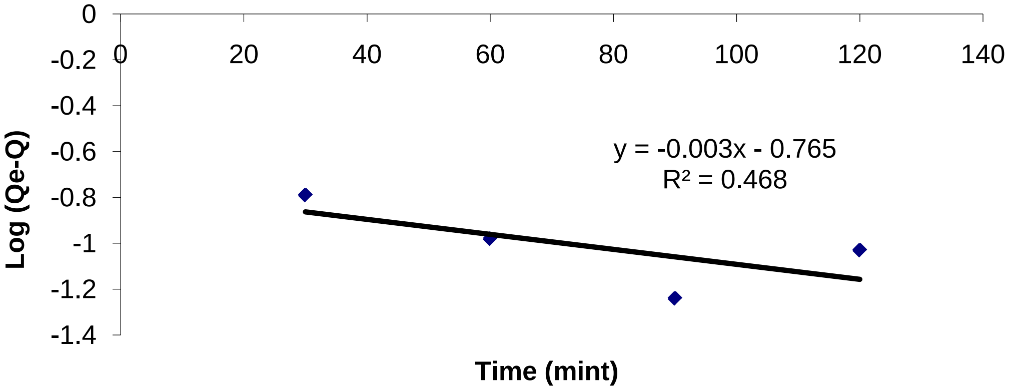

Figure 5 : Lagergren pseudo first order kinetic plot for cadmium at pH of 7.0, initial metal concentration of 10 mg kg^{-1} and temperature of 25°C.

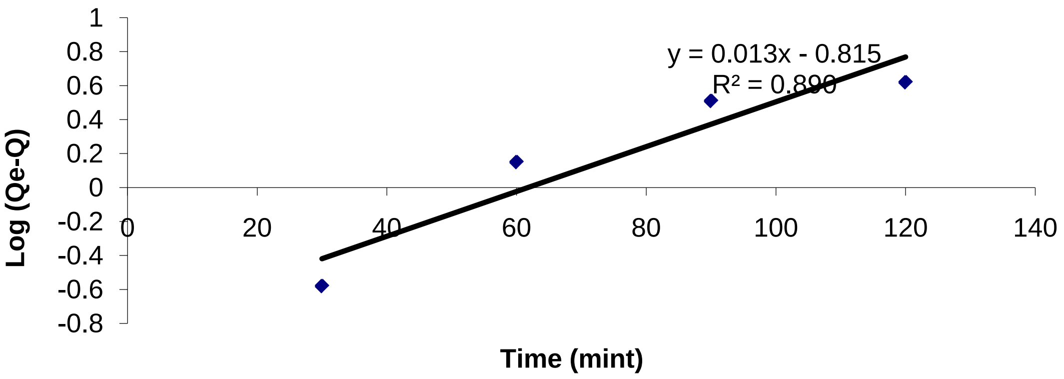

Figure 6 : Lagergren pseudo first order kinectic plot for lead at pH of 7.0, initial metal Concentration of 10 mg kg^{-1} and of 25°C.

Figures7, 8, and 9 illustrates the pseudo second order (Ho) equations of Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively at the initial metal concentrations of 10 mg kg^{-1}.

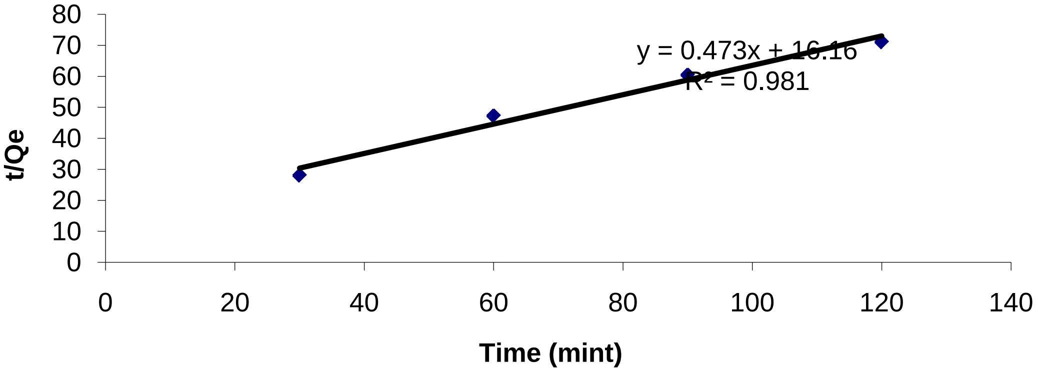

Figure 7 : Ho pseudo second order kinetics plot for manganese at pH of 7.0, initial metal concentration of 10 mg kg^{-1} and 25°C.

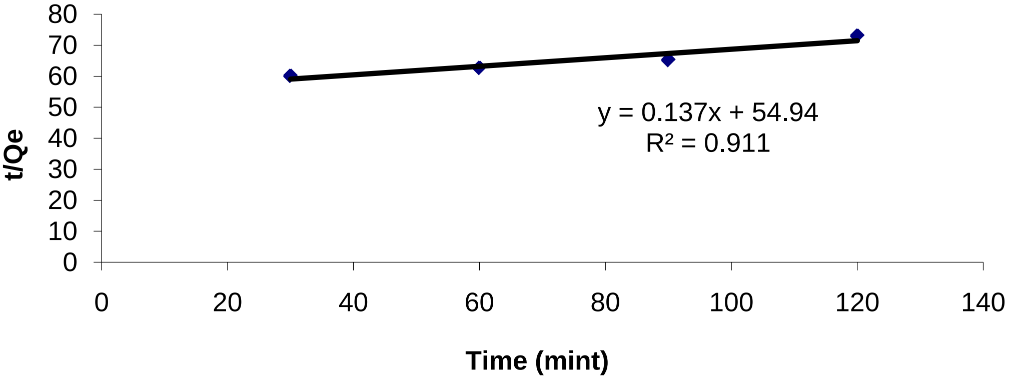

Figure 8 : Ho pseudo second order kinetics plot for cadmium at neutral pH, initial metal concentration of 10 mg kg^{-1} and 25°C.

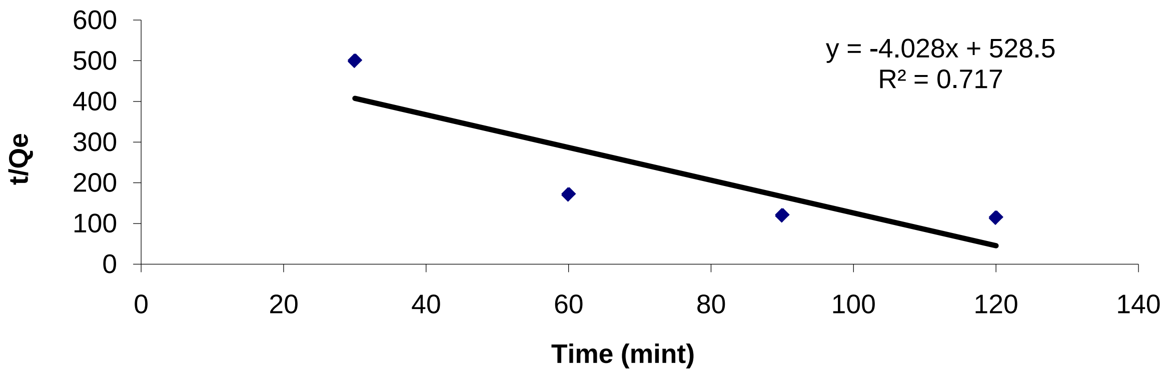

Figure 9 : Ho pseudo second order kinetic plot for lead at neutral pH, initial metal concentration of 10 mg kg^{-1} and 25°C.

The rate of the metals sorption has the highest conformation with pseudo second order (Ho) rate model each, with coefficient of determination (R^2) of 0.98, 0.91and 0.72 for Mn^{2+}, Cd^{2+}, and Pb^{2+} respectively.

d) Effect of pH

The acidity of solution (pH) is one of the most parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Heavy metals adsorption on maize cob with varying range of pH of 2.0, 3.0, 4.0, 5.0 and 6.0, 1g adsorbent, 2 hours contact time and 10mgkg^{-1} of adsorbate concentration were kept constant. This pH range was chosen in order to avoid metal solid hydroxide precipitation (8-14). Results showed in Fig 10 that, the initial pH on the adsorption dynamics for manganese, cadmium and lead ions on maize cob were significantly affects the extent of sorption of the metals by maize cob and the adsorption capacities increases for the metals when the pH increases from 2.0 to 6.0.

The variation in the removal of the metal ions by maize cob with respect to pH can be elucidated by considering the surface charge of the sorbent materials and speciation of each of the metals ion (the -COO- ligands attract the positively charged Mn^{2+}, $Cd^{2+}$and Pb^{2+} and binding occurs, indicating that the binding process is an ion exchange mechanism that involves an electrostatic interaction between the negatively charged groups in the cell walls and the metallic cations). The minimal adsorption capacity obtained for all the metals ions at low pH is partly due H^+ ion that competes with Mn^{2+}, $Cd^{2+}$and Pb^{2+} for the surface of the adsorbent. This could be due to the excess of H^+ ion surrounding the binding sites making sorption unfavourable. The solution pH affects the sorbent surface charge and makes the active site reactive for Mn^{2+}, $Cd^{2+}$and Pb^{2+}removal. The pH_{max} was found to be 6.0, 5.0 and 4.0 for Mn^{2+}, $Cd^{2+}$and Pb^{2+} respectively.

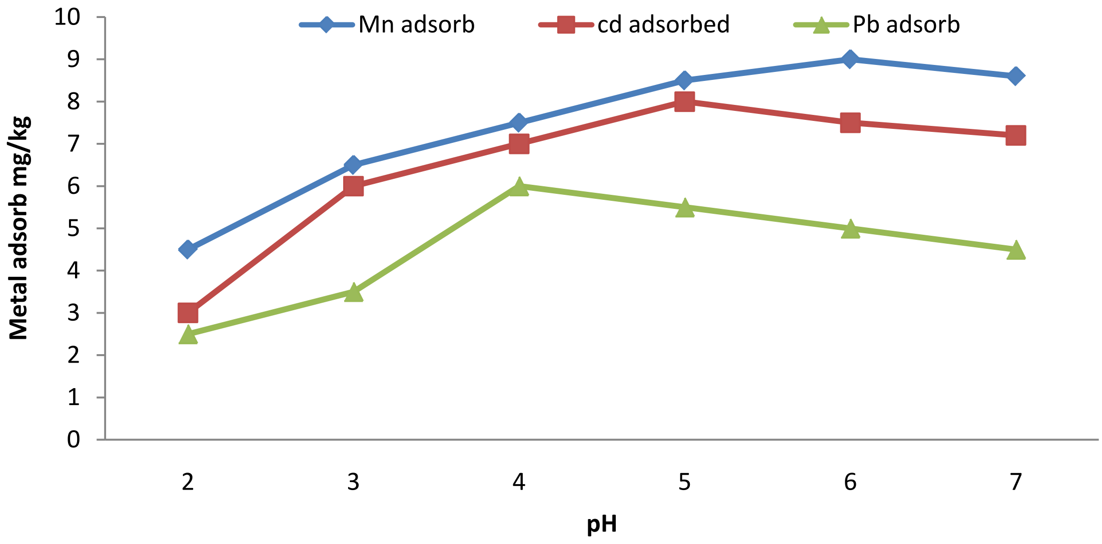

Figure 10 : Fitted Curve showing the effect of maize cob pH on manganese, cadmium, and lead adsorption by maize cob.

e) Adsorption isotherms

The adsorption characteristics of manganese, cadmium and lead was determined by fitting the adsorption data into both Freundlich, (1926) and Langmuir (1918) equations respectively.

Freundlich isotherm: This is use for modeling the adsorption on heterogenous surfaces. This can be explained by the equation

$$Qe = K_f Ce^{1/n} \qquad (4)$$

The linear form of equation (4) can be written as:

$$Log\ Qe = 1/n \log Ce + \log k_f \qquad (5)$$

Qe = the quantity of ions absorbed per unit weight of absorbent .

Ce = the equilibrium concentration of the adsorbate after adsorption has taken place.

"K_f" = Freunlich constant; and "1/n" = adsorption intensity.

Mn^{2+}, $Cd^{2+}$and Pb^{2+} adsorption isotherm using Freundlich approach in the study is presented as a function of the equilibrium concentration of metal ions in the aqueous medium at neutral pH, 25°C and contact time of 120 minutes is shown in Figure 10, 11 and 12. These adsorptions gave a linear fit form of the model with the coefficient of determination ($R^{2)}$ of 0.96, 0.96 and 0.81 for Mn^{2+}, $Cd^{2+}$and Pb^{2+} which are strong correlation. The order of the distribution of coefficient (R^2) decreased from $Mn^{2+} > Cd^{2+} > Pb^{2+}$, it showed that the adsorbent surface had maximum capacity for $Mn^{2+} > Cd^{2+} > Pb^{2+}$.

The Freundlich adsorption co-efficients (k_f and 1/n) were numerical values that characterized the maize cob surface for its affinity for the metals. All the metals exhibited a slope (1/n) defined as adsorption intensity which is less than unity thereby exhibiting a favourable condition for the maize cob surface which agrees with Horsfall and Abia (2003). The 1/n that was less than unity implies that the surface site heterogeneity was predominant for the adsorption of the metals on maize cob that is, there was broad distribution of adsorption of the ions on the maize cob surface. The adsorption capacity (k_f) for Mn^{2+}, $Cd^{2+}$and Pb^{2+} by maize cob were positive value which predicted that the quantity adsorbed on maize cob corresponds to complete heterogenous layer coverage.

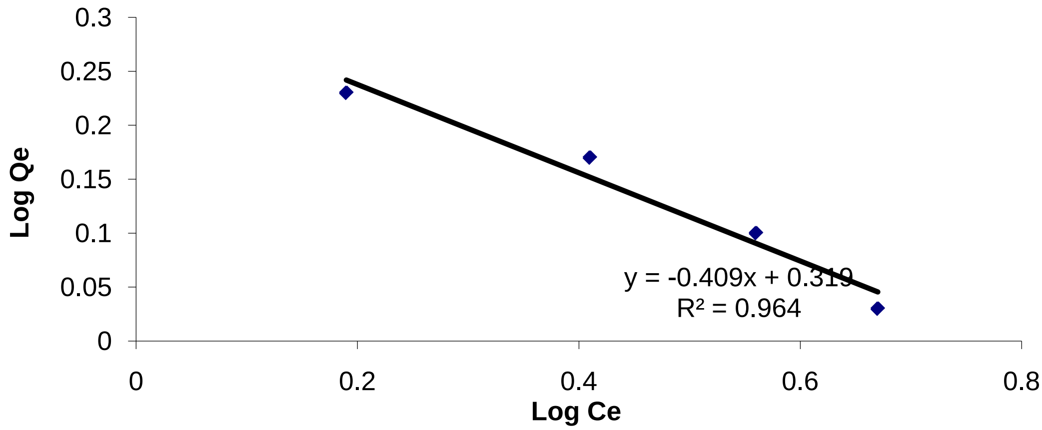

Figure 11 : Freundlich adsorption isotherm for manganese at neutral pH, 10 mg kg^{-1} initial concentration and 25°C.

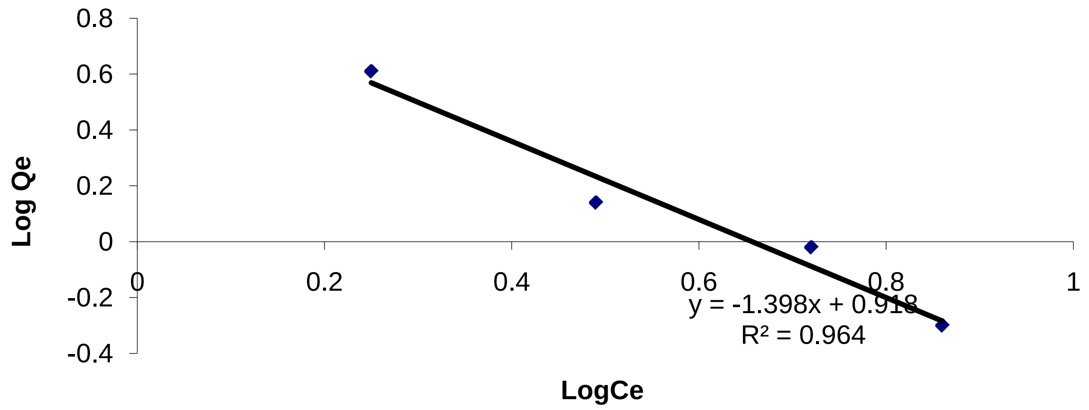

Figure 12 : Freundlich adsorption isotherm for cadmium at neutral pH, initial concentration of 10 mg kg^{-1} and 25°C.

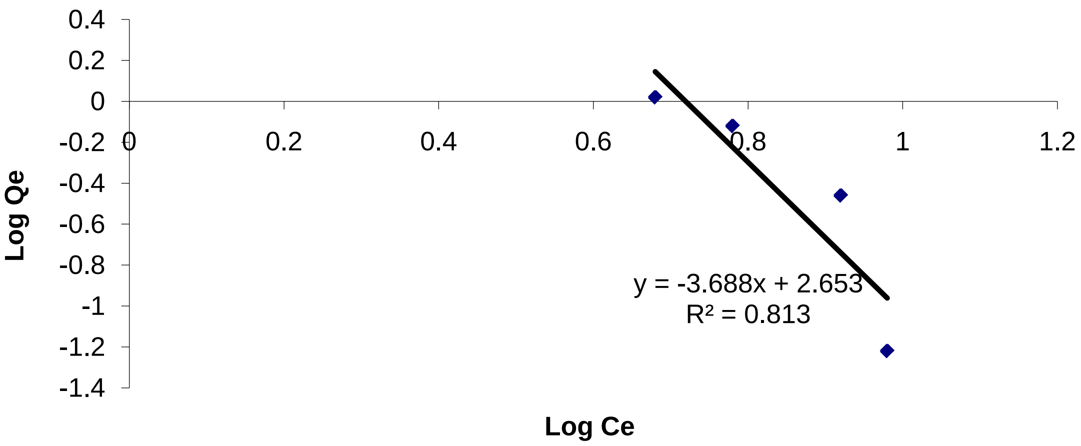

Figure 13 : Freundlich adsorption isotherm for lead at neutral pH and initial concentration of 10 mg kg^{-1} and 25°C

Langmuir adsorption isotherm:

This model suggests that the uptake occurs on homogenous surface by monolayer sorption without interaction between sorbed molecules. The model assume uniform energies of adsorption onto the surface. Langmuir isotherm can be defined according to the following

$$Qe == V_m kCe /1 + kCe \qquad (6)$$

Qe = the quantity of ions absorbed per unit weight of absorbent .

Ce = the equilibrium concentration of the adsorbate after adsorption has taken place.

Vm is the monolayer capacity and “k” is the equilibrium constant.

The linear form of equation (6) can be written as follow:

$$Ce/Qe = 1/kV_m + Ce/V_m \qquad (7)$$

The sorption of the metals ions (Mn^{2+}, Cd^{2+} and Pb^{2+}) on maize cob showed a non linearity with Langmuir linear equation. This indicates that the adsorption in Mn^{2+}, Cd^{2+} and Pb^{2+}did not occur at the homogeneous surface molecules to each other in the plane of the active site maize cob.

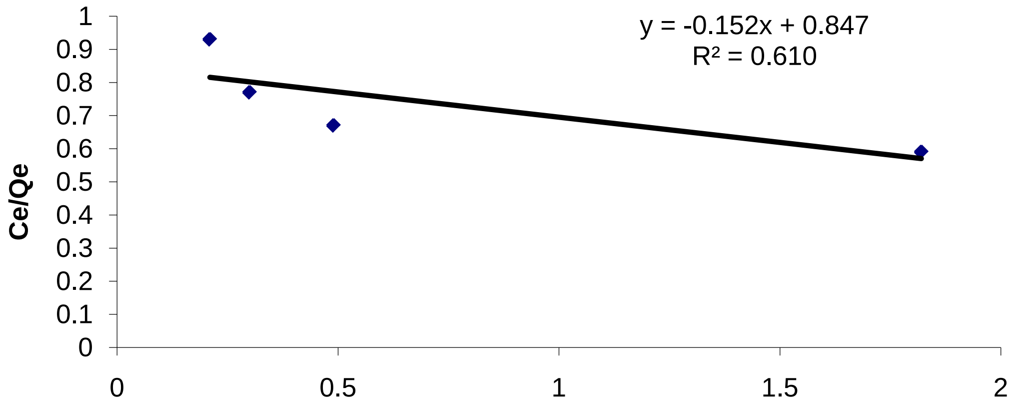

Figure 14 : Langmuir adsorption isotherm for manganese at neutral pH and initial concentration of 10 mg kg^{-1} and 25°C.

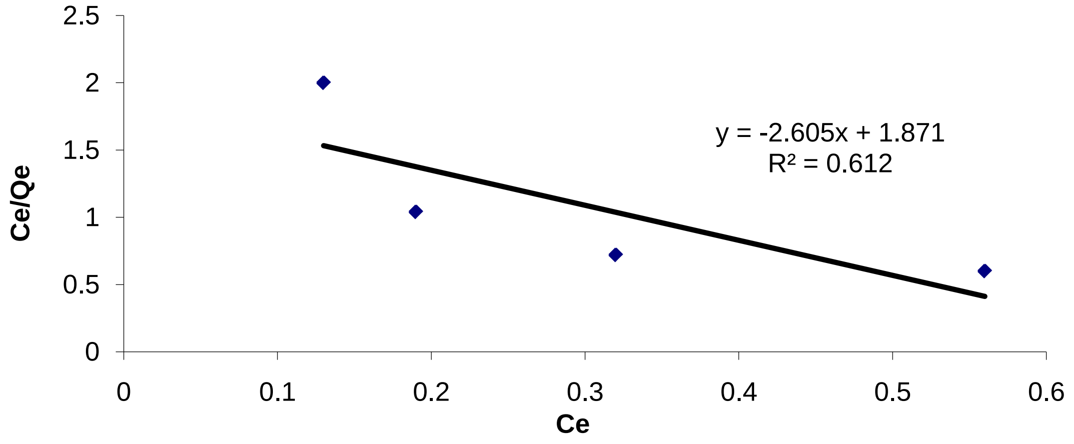

Figure 15 : Langmuir adsorption isotherm for cadmium at neutral pH and initial Concentration of 10 mg kg^{-1} and 25°C.

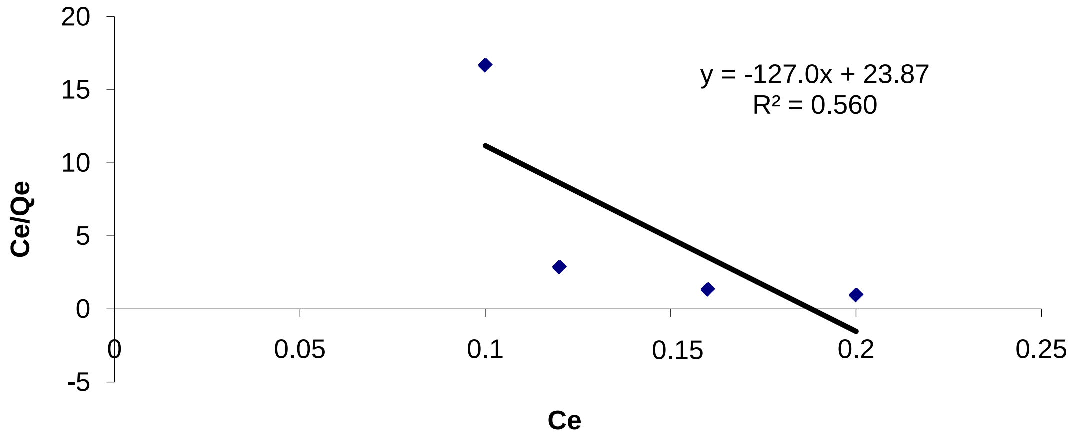

Figure 16 : Langmuir adsorption isotherm for lead at neutral pH and initial concentration of 10 mg kg^{-1} and 25°C.

IV. CONCLUSION

This study clearly suggest that the use of maize-cobs as sorbent is much economical, effectual and more viable. It can be efficiently used to remove ions from aqueous solution. The different operational parameters observed during the process of investigations reveal that the adsorption of manganese, cadmium and lead ions was dependent on initial rate concentrations, solution pH, ionic strength and contact-time with same magnitude in their removal but different adsorption capacities. The long contact time of 2hrs at which equilibrium for manganese, cadmium and lead ions was reached indicated that the predominant mechanism is physisorption and the kinetic of their reactions is best described by pseudo- second order rate model. The maximum adsorption capacity was attained at pH$_{max}$ of 6.0, 5.0 and 4.0 for Mn^{2+}, $Cd^{2+}$and Pb^{2+} respectively. It is common to describe the goodness of it in terms of R^2, which is the square of the correlation coefficient. Langmuir isotherm shows an inadequate fit of experiment data in the whole range of concentrations generally giving the R^2 values lower than 0.90. the poor ability of this model to represent the experiment data could have been due to the fact that the Langmuir isotherm does not take into account adsorbent - adsorbate interactions. The correlation of Freundlich adsorption isotherm showed that this isotherm yielded the best fitted to experiment data that is, the adsorption of the metals ions conform with Freundlich isotherm of heterogeneous adsorption but non linear with Langmuir equation and the coefficient of distribution (R^2) decreases from Mn^{2+}, $Cd^{2+}$and Pb^{2+} respectively. As a result of this study, it may be concluded that maize cob may be used as alternative and effective material for elimination of heavy metal pollution from waste waters since it is low cost, abundant and locally available adsorbent.

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Analytical Assessment of Cadmium, Lead and Iron in Hand Dug Wells of Ilaro, South-Western Nigeria

By Eruola, A.O. & Adedokun, N.A
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Abstract - The levels of selected heavy metals; Cadmium, Lead and Iron in the hand dug wells of Ilaro town was critically assessed at strategic points of the area to determine the level of pollution caused by anthropogenic activity within the town using different physical and chemical processes. The Mean ± S.D of the results obtained are; Cadmium 0.017±0.016 mg/l; Lead 0.229±0.061 mg/l; Iron 1.076±2.393 mg/l. All the parameters were higher than the standards that were specified for drinking water by WHO. Consequently, the well water in the study location is not suit for drinking.

Keywords : Ilaro, Heavy metals, Pollution, Metal, Water quality, Contaminants.

GJSFR-B Classification: FOR Code: 030199

ANALYTICAL ASSESSMENT OF CADMIUM, LEAD AND IRON IN HAND DUG WELLS OF ILARO, SOUTH-WESTERN NIGERIA

Strictly as per the compliance and regulations of :

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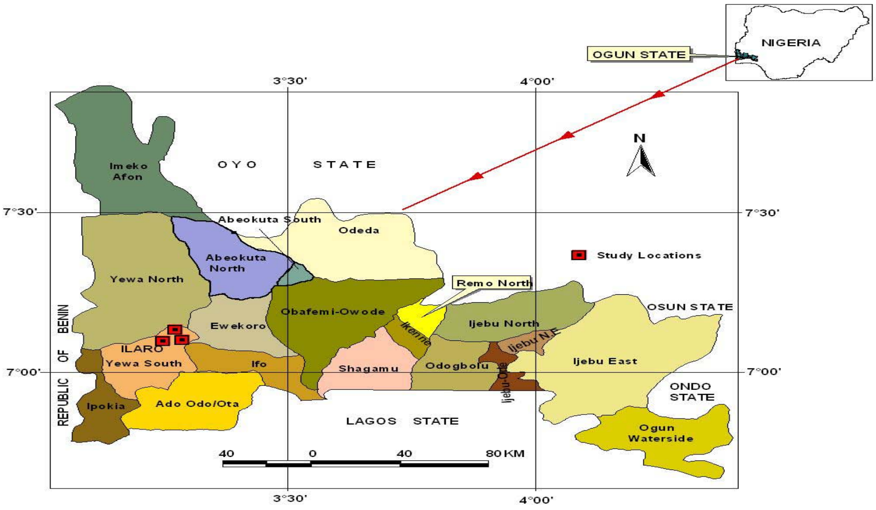
I. INTRODUCTION

A primary concern of people living in developing countries is that of obtaining clean drinking water. The quality of groundwater is a function of natural processes as well as anthropogenic activities [9]. Quality drinking water is essential for life. Unfortunately, in many developing countries of the world, including Nigeria, good, portable and hygienic water has become a scarce commodity [6].Several human activities have constituted great havoc to the quality of water which we are not taking cognizance of and the health implication of any water that is polluted either lightly or heavily with heavy metal is highly significant. Due to the frequent and sometimes lengthy periods of interruption in the supply of treated piped water, many households rely on other sources of water such as wells, boreholes, springs and surface waters. The use of groundwater as the only source of portable water supply is increasing worldwide. In the United States, 90 - 95% [5] of rural and suburban water comes from this source and in Ghana, it is 62 - 71% [3]. Water has unique chemical properties due to its polarity and hydrogen bonds which means it is able to dissolve, absorb, adsorb or suspend many different compounds [10], thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities [7].

II. STUDY AREA

Ilaro is found in South-western part of Nigeria as shown in figure 1.The land is flat and sloppy where mainly we have streams. Some areas are swampy and low lying. Generally, the soil is firmed and rich for agricultural farming. Ilaro town is about 50 km from Abeokuta, the Ogun State capital, and about 100 km from Ikeja, the capital city of Lagos State. The landform is that of eroded pediment plain with well-incised valleys forming a trellis pattern. The soils are developed over a deeply weathered layer of sedimentary rocks consisting of false bedded sandstones which underlies the area. The sediments are of lower cretaceous rocks or Abeokuta form.



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III. Material and Method

Water samples were collected from hand dug wells which are used for drinking and domestic purposes in Ilaro. The well water samples were collected using 500ml screw-capped plastic containers that have been washed with detergents, dried and rinsed with 10%HNO_3 to avoid contamination by any physical or chemical means. The choice of the sampling locations was carefully selected with some factors in view. Before collection of the water samples, small volume of the water was allowed to run without collection for 3-4 minutes so that sample collected would actually be a true representative of the water, to get fresh water and also to have homogenous mixture. Water sample were obtained to rinse the container before collection. On collection, the samples collected were preserved immediately with HNO_3 to keep the metals in solution. The samples were tested for four physico-chemical parameters; Total Dissolved Solid, pH, Electrical Conductivity and Temperature. Samples without preservative was tested for the previously listed physical parameters by taking about 50mls volume into a beaker that have been previously rinsed with distilled water and later with the water sample to be tested

The collected water sample in 500ml container were return to the laboratory for further analysis and kept in the refrigerator at low temperature to minimize physical and chemical reactions. Digested water samples were sent to be analyzed using Atomic Absorption Spectrophotometer (AAS) to test for the interested heavy metals (Cd, Pb and Fe)

IV. Result and Discussion

The summary of the physical and chemical results of the water samples analyses from the 10 points are given below in Tables 1 and 2. pH in Ilaro ranges from 3.90-7.03.The water is generally acidic except for F.P.I, Ilaro which is neutral. The effects of acidic water on human health and the environment have been widely reported. For example, acidic water has been known to be aggressive and enhance the dissolution of iron and manganese, causes unpleasant taste in water [4]. The water samples has actually shows the relationship between the physical parameters .The higher the temperature, the more the dissolved solids in the water and the higher the electrical conductivity Temperature of the points is from 27-28.8^{0}C. TDS ranges from 12mg/l-286mg/l. TDS values generally are not up to the MCL of 500ppm, but it implication is that it impair the water quality and affect the clarity of water.High concentration of TDS could result to salty and unpalatable taste in water. High concentration of TDS could result to gastrointestinal irritation. Electrical Conductivity of the sampled points is from 25-560μs/cm. It was observed from result that most of these wells were not suitable for domestic purposes for which they are presently used for. 70% of tested samples contain detectable amount of cadmium with concentration above the maximum contaminant level (0.003mg/l) suggested by WHO (fig.2). This is of concern because cadmium has carcinogenic properties as well as long biological half-life [8] leading to chronic effect as a result of accumulation in the liver and renal cortex [4]. It can also cause kidney damage as well as produce acute health effects resulting from over exposure to high concentrations [8].

Table 1 : Physical Parameters.

Parameters	S01	S02	S03	S04	S05	S06	S07	S08	S09	S10
P^H	6.52	5.71	5.89	5.16	5.25	4.77	3.90	5.12	6.22	7.03
TDS (mg/l)	86	12	50	58	32	108	202	286	216	20
Temperature (^{0}C)	27	27.4	27.6	28.8	27.6	28.1	27.4	27.5	28.4	28.2
E.C (μS/cm)	169	25	99	113	63	213	398	560	426	40

Table 2 : Heavy Metals Concentrations in Water Samples.

Parameters Sample	Locations	Coordinate	Cadmium (mg/l)	Iron (mg/l)	Lead (mg/l)
S01	Oke- ola, Ilaro	N06.89821, E003.00829	0.011	ND	0.249
S02	Express,Ilaro	N06.89228, E003.99855	0.014	0.024	0.221
S03	Orita, Ilaro	N06.88520, E003.00235	0.012	0.134	0.303
S04	Musa Str, Ilaro	N06.89123, E003.01600	0.003	ND	0.262
S05	Otegbeye,Ilaro	N06.89525, E003.01499	ND	ND	0.317
S06	Lesli,Ilaro	N06.88650, E003.01347	0.003	0.049	0.236
S07	Aderogu,Ilaro	N06.88329, E003.01118	0.018	0.041	0.196
S08	Akiniku,Ilaro	N06.88723, E003.02233	0.004	0.039	0.284
S09	Gbogodi, Ilaro	N06.87657, E003.00357	0.066	8.406	0.261
S10	F.P.I. Ilaro	N06.88972, E003.98886	0.008	ND	0.291

Table 3 : Statistical summary of the investigated Physico-Chemical Variables.

Variables	Mean ± S.D (Range)	MCL	No above MCL	% above MCL
pH	5.33 ± 0.73 (3.9-7.03)	6.5-8.5	8	80%
Temperature (^{0}C)	27.52 ± 0.76 (26.1-28.9)	-	-	
E.C (µS/cm)	197.2 ± 150(25-560)	1000	-	
TDS (mg/l)	100.25 ± 76.6 (12-286)	500	-	
Cadmium (mg/l)	0.017 ± 0.016 (0.003-0.066)	0.003 mg/l	7	70%
Lead (mg/l)	0.229 ± 0.061(0.102-0.317)	0.01mg/l	10	100%
Iron (mg/l)	1.076 ± 2.393 (0.009-8.406)	0.3 mg/l	1	16.67%

NOTE: MCL is Maximum Contaminant Level set by [7] for drinking water

70% of tested samples contain detectable amount of cadmium with concentration above the maximum contaminant level (0.003mg/l) suggested by WHO (fig.1). This is of concern because cadmium has carcinogenic properties as well as long biological half-life [8] leading to chronic effect as a result of accumulation in the liver and renal cortex [4]. It can also cause kidney damage as well as produce acute health effects resulting from over exposure to high concentrations [8].

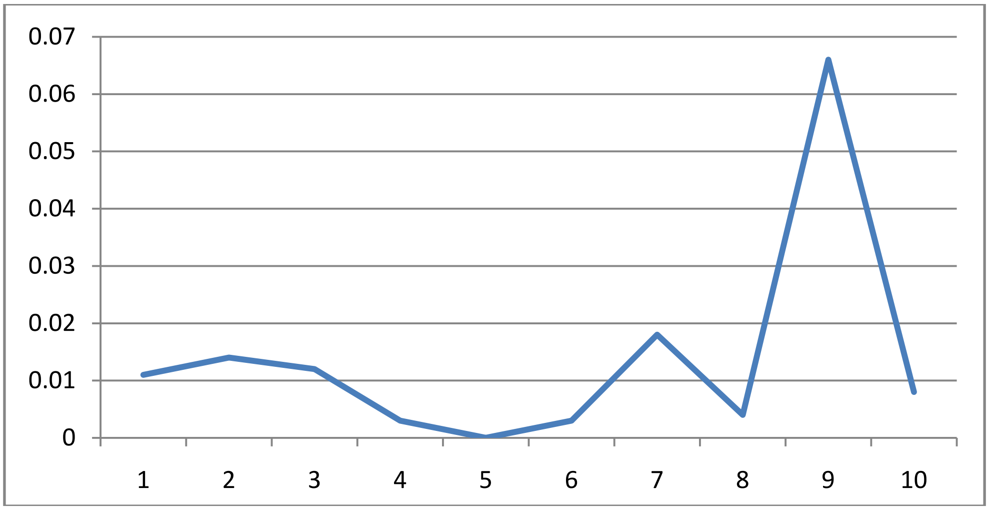

Figure 2 : Cadmiumlevels in water samples.

Table 3 showed the comparison of the heavy metal contamination in the sampled wells in the two study locations. Although the metals concentrations in water samples were generally above the maximum Contaminants Level; Cadmium concentration is higher in Ilaro wells (0.019 mg/l) than in Aiyetoro wells (0.015mg/l). Also, the Lead concentration in Aiyetoro wells (0.262 mg/l) is higher than that of Ilaro wells (0.195 mg/l). Finally, the Iron Level in Aiyetoro wells (1.280 mg/l) is higher than in Ilaro wells (0.704 mg/l)

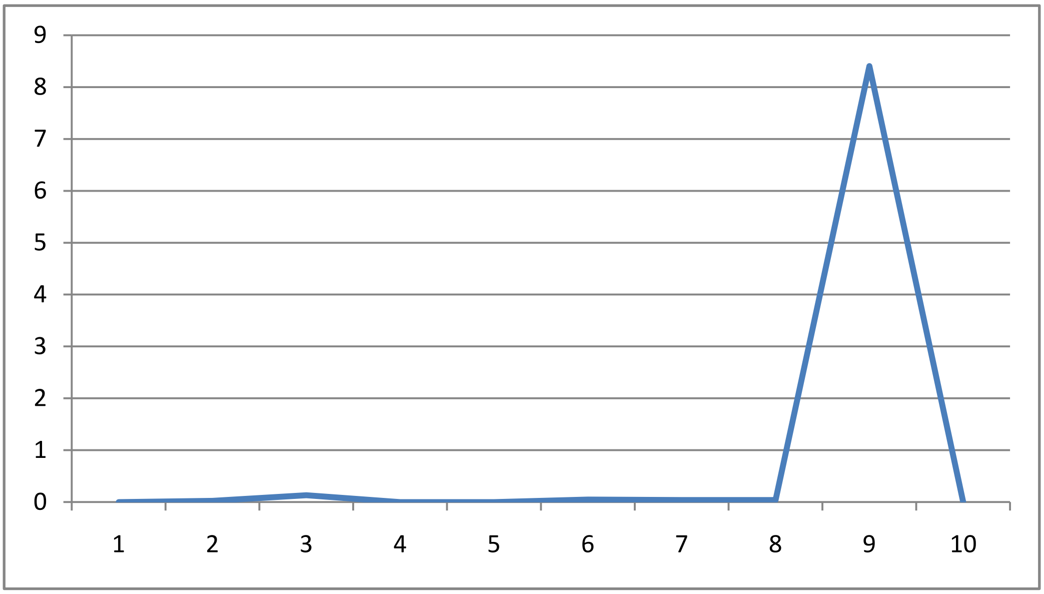

Figure 3 : Iron level in water samples.

Furthermore, the result showed that all water sample contained lead concentration that does not conform with the maximum contaminant level 0.01mg/l. The lead concentration in well samples in the study area fell in the range of 0.102mg/l - 0.317mg/l concentration (fig. 2). This result is of great concern as lead has been recognized for centuries as a cumulative general metabolic poison [1]. It is a neurotoxin and it is responsible for the most common type of human metal toxicosis. Also studies have linked lead exposures even at low concentration and increases in blood pressure (Zietz et. al., 2007) as well as with reduced intelligence quotient in children (Needleman, 1993) and with attention disorders (Yule and Rutter, 1985). Thus the danger of lead poisoning becomes very critical and real for the users.

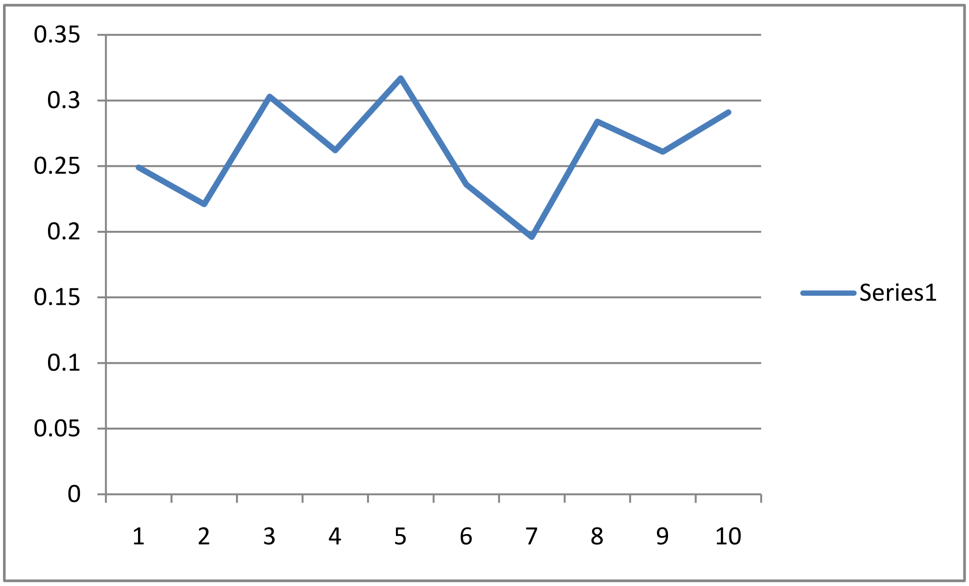

Figure 4 : Lead Level in water samples.

V. CONCLUSION

The result of this study showed that the groundwater of the study areas contain all the analyzed heavy metals; 70% of water samples contain Cadmium above the maximum Contaminants Level, all the water samples contain Lead higher than the Maximum Contaminants Level while 10% of the water samples contain Iron higher than the Maximum Contaminants Level. The results for Conductivity and Total Dissolve Solids were generally low to the Maximum Contaminants Level while 90% of the water samples were generally acidic. These suggest a significant risk of this population to heavy metal toxicity and acidic water thereby making the water unsuitable for drinking.

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Ocimum Gratissimum : the Brine Shrimps Lethality of a New Chemotype Grown in South Western Nigeria

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Abstract - Hydro-distilled volatile oils of leaves and seeds of *Ocimum gratissimum* L. (*Lamiaceae*) were investigated for chemical constituents and brine shrimp lethality activity. The essential oil of the leaves of *O. gratissimum* consisted of γ- *terpinene* (52.86%), Z-tert-butyl-4-hydroxy anisole (13.93%), caryophyllene (10.37%) and p-cymenene (7.16%) as the major compounds while the essential oils of the seeds yielded α- pinene (48.19%), caryophyllene (10.71%), and 3-tert-butyl-4- hydroxyanisole (11.14%) as the major compounds. The volatile oils showed significant toxicity against brine shrimps, *Artemia salina*, as 100% mortality was recorded at 1000 ppm for the different essential oils.

Keywords : Essential oil, Hydro-distillation, Ocimum gratissimum, Artemia salina, toxicity.

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Abstract - Hydro-distilled volatile oils of leaves and seeds of *Ocimum gratissimum* L. (*Lamiaceae*) were investigated for chemical constituents and brine shrimp lethality activity. The essential oil of the leaves of *O. gratissimum* consisted of **γ**-*terpinene* (52.86%), Z-tert-butyl-4-hydroxy anisole (13.93%), caryophyllene (10.37%) and p-cymenene (7.16%) as the major compounds while the essential oils of the seeds yielded **α**-pinene (48.19%), caryophyllene (10.71%), and 3-tert-butyl-4-hydroxyanisole (11.14%) as the major compounds. The volatile oils showed significant toxicity against brine shrimps, *Artemia salina*, as 100% mortality was recorded at 1000 ppm for the different essential oils.

Keywords : Essential oil, Hydro-distillation, Ocimum gratissimum, Artemia salina, toxicity.

I. Introduction

Ocimum gratissimum L. (*Lamiaceae*) is known by different people of the world by different local names. It is commonly called Scent leave, 'Nchu anwa' or 'Ahuji' by the Igbo speaking populations of South Eastern Nigeria. 'Effirin-nla' by the Yoruba speaking people of South Western Nigeria and known as 'Daidoya' by the Hausa Speaking populations of Northern Nigeria (Odugbemi, 2006, Saliu et al, 2011). In India it is known by its several vernacular names, 'Vriddhutulsi' (Sanskrit), 'Ram tulsi' (Hindi), 'Nimma tulasi' (Kannada) (Prabhu et al, 2009). In northern Brazil the plant is commonly known as 'Alfavaca-cravo' where it is used in medicine and other culinary purposes (Rabelo et al, 2003).

The nutritional importance of *Ocimum gratissimum* centres on its usefulness as a seasoning because of its aromatic flavour (Okwu, et al, 2006). *O. gratissimum* is an essential ingredient in the local Cuisine popularly known as 'pepper soup' and relished by many in South Western Nigeria. It is an important herbal medicinal plant not only in Nigeria but also in the sub-Saharan Africa. In the southern part of the country, crude aqueous extract of *O. gratissimum* is commonly used in the treatment of epilepsy, high fever and diarrhoea (Effraim et al, 2003). In the Savannah areas, decoctions of the leaves are used to treat mental illness (Akinmoladun, 2007). It is used by the Igbo community of south eastern Nigeria in the management of the baby's cord, to keep the wound surfaces sterile. It is also used in the treatment of fungal infections, fever, cold and catarrh (Ijeh et al, 2005).

Brazilian tropical forest inhabitants use a decoction of *O. gratissimum* in the treatment of digestive disorders (Madeira et al, 2003). In Kenya, it is an important herbal medicine; the leaves are rubbed between the palms and sniffed as a treatment for blocked nostrils (Kokwaro, 1993). They are also used for abdominal pains, sore eyes, and ear infections, for coughs, barrenness, and fever, convulsions, and tooth gargle, regulation of menstruation and as a cure for prolapsed of the rectum (Lexa et al, 2007; Kokwaro, 1993). In India, the whole plant has been used for the treatment of sunstroke, headache, and influenza, as a diaphoretic, antipyretic and for its anti-inflammatory activity (Tania et al, 2006).

Numerous publications have presented data on the composition of the Essential oils of *O. gratissimum*. In early investigations of the Nigerian variety of *O. gratissimum*, the essential oil was found to possess appreciable antibacterial activity against a wide range of organisms (El-Said et al, 1969). Thymol was identified as the major principle which was responsible for the antibacterial activity of *O. gratissimum* but the essential oils of *O. gratissimum* from Europe contain eugenol as the dominant component as well as traces of ocimene and myrcene (Ekundayo, 1986). Analysis of the leaves and flowers volatile oils from different locations in Nigeria confirmed the occurrence of thymol as the main constituent and eugenol was not detected (Sofowora, 1970). However, a recent study of the central Nigerian grown *O. gratissimum* essential oil yielded eugenol (61.9%) as the most abundant compound (Saliu et al, 2011).

The aerial parts of *O. gratissimum* harvested in Togo were composed of thymol (31.79 %), p-cymene (15.57 %) and γ-terpinene (12.34 %) as the major compounds of the essential oil (Koffi et al, 2009).

A Brazillian variety produced eugenol (52.14 %); 1,8-cineole (29.17%), β-seline (5.56%), trans-

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caryophyllene(3.35 %) (Rabelo et al, 2003). Hydro-distilled volatile oils from the leaves of *O. gratissimum* from Meru district in Eastern Kenya were found to be dominated by monoterpenes, eugenol (68.8%), methyl eugenol (13.21%), cis-ocimene (7.47%), trans-ocimene (0.94%), pinene (1.10%) and camphor (0.95%) (Lexa et al, 2007).

Variation of chemical compositions of the essential oil of *O. gratissimum,* eugenol type, was studied for 11 h during the daytime using microwave oven technique, a considerable variation was observed in the eugenol yield, 98% at 12.00 a.m. to 11% at 05.00 p.m. These results show the influence of the solar light on eugenol production and can be useful to indicate the optimal time for collection of the plant (Vasconcelos et al, 1990).

The composition of essential oils from a particular species of plant can differ between harvesting seasons, geographical sources and parts of plant (Burt, S; 2004). Genetic differences in plants of the same species that are otherwise indistinguishable (chemotypes) can also result in widely different essential oil content (Rahimi-Nasrabadi et al, 2009). These may serve to explain the differential medicinal uses of *O. gratissimum* by people of different climes around the world.

Brine Shrimps (*Artemia salina*) is a small aquatic organism which is ideal for toxicity test because it can be cultivated in massive numbers in a limited amount of water and possess a short life span, enabling many experiments to be conducted in a short time. Also, its abundance facilitates replication for statistical analyses (Puente et al, 1992).

It appears that brine shrimp lethality bioassay is predictive of cytotoxicity and pesticidal activity (Pisutthanan et al, 2004). On the basis of these, we investigate the chemical compositions and Brine shrimp lethality of the leaves and seeds essential oils of *Ocimum gratissimum* grown in south western Nigeria.

II. EXPERIMENTAL

a) *Collection of Plant material*

The *Ocimum gratissimum* leaves and seeds were harvested at Apatapiti estate, near the Federal University of Technology, Akure, Ondo state, Nigeria. The identification was done at the Forest Research Institute of Nigeria (FRIN), Ibadan were voucher specimens were deposited.

b) *Isolation of essential oils*

The plant parts of *O. gratissimum* were carefully separated, washed and then subjected to hydro-distillation separately for 2-3hrs using a Clevenger-type glass apparatus, according to European *Pharmacopoeia* (2008) specification. The weight of fresh plant material was 1kg for each plant part. The oil yield was calculated in percentage of volume per weight (v/w) of plant samples.The oil samples were stored in air-tight containers at 0^0C before going for GC-MS analysis without any further treatment

c) *Gas chromatography/mass spectrometry analysis*

The essential oils were analyzed using GC-MS Agilent 6890N GC Coupled with MS-5973-634071 Series. The capillary column type was DB-1MS [30.0m (length) X320.00μm (diameter) X1.00μm (film thickness)]. The carrier gas was Helium at constant flow rate of 1.0ml/min and average velocity of 37cm/s; the pressure was 0.78psi. The initial column temperature was set at 100^0C to the final temperature of 250^0C at the rate of 50C/min, volume injected was 1.0μl and split ratio was 50:1.The total chromatogram was auto-integrated by ShemStation and the constituents were identified by comparison of the GC-MS data with published mass spectral database (NIST02.L) and data from literature.

III. TOXICITY TEST

The cytotoxicity test was conducted on the brine shrimps, *Artemia salina*, using the method of Krishnaraju et al (2005) with some modification.

a) *Hatching of Artemia salina (brine shrimps)*

An improvised aquarium of plastic container with two compartments was used. Holes were created into the divider to allow water circulation and to enable hatched shrimps swim to the side exposed to light. The container (Aquarium) was filled with fresh sea water prior to the introduction of a spatula of brine shrimps to one side which was covered with a booklet as to produce a dark environment which was favoured for hatching, while the other side was left exposed to light. The aquarium was then left for two days until the hatched brine shrimps swam across the divide to the side exposed to light.

b) *Preparation of samples' test solutions*

Stock solution was prepared by emulsifying 20 mg of the essential oils separately in 0.3ml of dimethylsulphoxide (DMSO) and the volume was made up with 1.7ml of fresh sea water to equal 1000 ppm concentration. After this, serial dilution was done to obtain two additional Concentrations of 100ppm and 10 ppm.

c) *Stationing the Brine Shrimps*

Fresh sea water (3.0ml) was transferred into the specimens' vials prepared in triplicates. Then, 0.5ml of each prepared concentrations was introduced into the specimen vials followed by introduction of ten brine shrimps into every specimen vial including the control vial. Finally, every specimen vial was topped up with sea water until it reached 5.0ml. All the vials containing the shrimps were left opened for 24 hours. Finney's probit analysis was used to determine the LC_{50} of each essential oil. Percentage mortality was calculated as number of dead *nauplii* divided by initial number of *nauplii* (10) multiply by 100.Toxicity of the extracts against the brine shrimps were determined by a statistically significant decrease in the survival of brine shrimps exposed to essential oils relative to the survival of shrimps in the control.

IV. RESULTS AND DISCUSSIONS

Hydro-distillation of the leaves and seeds of *O. gratissimum* gave light yellow and orange volatile oils respectively. The essential oil yields of the leaves and seeds were 0.97% and 0.83% respectively. Nine constituents representing 97.09% of total oil from the leaves were identified and Twenty-two compounds representing 98.41% of the total oil were identified from the seeds essential oil (Table 1). The main constituents of the leaves essential oils were found to be γ-terpinene (52.86%), z-tert-butyl-4-hydroxy anisole (13.93%), caryophyllene (10.37%), and P-cymene (7.16%). Other notable representative compounds were identified as thymol (3.65%), γ-selinene (3.45%) and caryophyllene oxide (2.68%). On the other hand, the major constituents of the seeds essential oil were α-pinene (48.19%), 3-tert-Butyl-4- hydroxyl anisole (11.14%) and caryophyllene (10.71%). Other constituents were α- selinene (4.00%), caryophyllene oxide (3.45%), p-cymenene (3.86%) and thymol (3.29%). Six compounds were found to be common constituents of the leaves and the seeds essential oils of *O. gratissimum*. They were caryophyllene, caryophyllene oxide, p-cymenene, γ-selinene, tert-butyl-4-hydroxy anisole and thymol.

Artemia salina nauplii were found to be highly susceptible to the essential oils of *O.gratissimum* (Table 2). At concentration of 1000 ppm for all the extracts, the ten brine shrimps used in the triplicate determination died after 24hrs which equal100% mortality of the *nauplii.* Mortality of 93-97% was recorded for 100ppm concentrations. The susceptibility of the *nauplii* at 10ppm ranges between 55-86% mortality.

Table1 : Chemical compositions of the essential oil of leaves and seeds of *Ocimum gratissimum*.

	Chemical compounds	Retention times (Min.)	Percentage composition (%) Leaves	Seeds
1	γ-Terpinene	2.20	52.86	-
2	α-Pinene	2.22	-	48.19
3.	p-cymenene	22.29	7.16	-
4	(Z)-β-Terpineol	2.34	-	0.92
5	1,3,8-p-Menthatriene	2.42	-	0.51
6	(4)-Terpineol	2.92	-	1.39
7	Thymol methyl ester	3.45	3.65	3.29
8	Unbellulone	3.91	1.57	1.23
9	Methoxy mesitylene	4.72	-	1.11
10	m-Eugenol	5.34	-	0.96
11	α-Cubebene	5.87	-	0.67
12	β-Elemene	6.15	-	2.11
13	Caryophellene	6.66	10.37	10.71
14	1-Ethyl-3-(propen-1-yl)adamantane	6.94	-	1.03
15	α-caryophyllene	7.17	1.42	1.70
16	2-tery-Butyl-4-hydroxyanisole	7.80	13.93	-
17	3-tert-Butyl-4- hydroxyanisole	7.81	-	11.14
18	γ-Selinene	8.01	3.4	-

19	α –Selinene	8.04	-	4.0
20	α –Panasinsen	8.34	-	0.64
21	Caryophyllene oxide	9.45	2.68	3.45
22	2-Methylene-6, 8, 8-trimethyl Tricyclo [5.2.2.0](1,6)undecan-3-ol	11.87	-	0.60
23	Monoamide, N-(3-acetylphenyl) benzene-1, 2-dicarboxylic acid	17.51	-	0.99
24	3, 4-Xylenol	18.43	-	0.65
25	Trimethyl-8-(-1-methylethyl) -2,4(1H,3H)-phenanthrenedione	22.93	-	0.93
26	2-(4-Hydroxy-3-methoxyphenyl) -3,7-dimethoxy-4H-chromen-4-one	22.95	2.96	-
	Total		97.04 %	96.22%

Table 2 : Toxicity of the essential oils using brine shrimps (*Artemia salina*) lethality assay.

Essential oil	No. of dead Shrimps; conc.1000ppm	%Mortality	No. of dead Shrimps; Conc. 100ppm	%Mortality	No. of dead Shrimps; Conc. 10ppm	%Mortality	LC_{50} µg/ml
OGL	10,10,10	100	9,10,9	93.3	7,7,6	66.7	3.6031
OGS	10, 10, 10	100	10,10,8	93.3	6,6,4	55.5	8.1588

Key: OGL= *O. gratissimum* leaves' essential oil, OGS= *O. gratissimum* seeds' essential oil.

VI. SUMMARY AND CONCLUSIONS

The major constituents of the leaves' essential oils of *O. gratissimum* were γ-terpenene, caryophyllene, p-cymene, Z-tert-butyl-4-hydroxyanisole while the seeds essential oils of *O. gratissimum* yielded α-pinene, caryophyllene, 3-tert-Butyl-4-hydroxyanisole and α-selinene as the major products in this study. The genus *Ocimum* has been reported to yield essential oils of varying chemical compositions around the globe. Guenthor, (1948) grouped *O. gratissimum* into thymol and eugenol chemotypes based on literature reports on the essential oils of *O. gratissimum* around the world which suggested thymol, and or eugenol as the major constituents. Previous reports from Nigeria (Sofowora, 1970; Iwalokun et al, 2001; Saliu et al, 2011) were in agreement with this classification. However, many other chemotypes have been reported in literature around the world subsequently. Chemotypes characterized by high contents of geraniol (Charles et al, 1992), methyl cinnamate (Fun et al., 1990), ethylcinnamate (Ali et al, 1968), eugenol/methyl eugenol (Lexa et al, 2007) and citral (Hegnauer, 1967) have been reported. Accordingly, the extracted essential oil in this study could be classified as the γ-terpenene/ α-pinene chemotype. This chemotype is similar in chemical compositions to a Togo variety (Koffi et al, 2009) which had γ-terpenene (12.34%) as one of the major constituent of the leaves' essential oils of *O. gratissimum.* Keita et al. (2000) have also reported thymol (46%), p-cymeme (12%) and γ-terpene + trans-sabinene hydrate (17%) for *O. gratissimum* in the Republic of Guinea. The occurrence of tert-butyl-4-hydroxy anisole in the leaves and seeds essential oils of this chemotype is of particular health benefits; tert-butyl-4-hydroxy anisole is known to prevent or delay the propagation of harmful radicals in the living cells.The essential oils of *O. gratissimum* (leaves and seeds) were lethal to *Artemia salina* which is predictive of cytotoxicity and pesticidal activity.

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5. Ask your Guides: If you are having any difficulty in your research, then do not hesitate to share your difficulty to your guide (if you have any). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work then ask the supervisor to help you with the alternative. He might also provide you the list of essential readings.

6. Use of computer is recommended: As you are doing research in the field of Computer Science, then this point is quite obvious.

7. Use right software: Always use good quality software packages. If you are not capable to judge good software then you can lose quality of your paper unknowingly. There are various software programs available to help you, which you can get through Internet.

8. Use the Internet for help: An excellent start for your paper can be by using the Google. It is an excellent search engine, where you can have your doubts resolved. You may also read some answers for the frequent question how to write my research paper or find model research paper. From the internet library you can download books. If you have all required books make important reading selecting and analyzing the specified information. Then put together research paper sketch out.

9. Use and get big pictures: Always use encyclopedias, Wikipedia to get pictures so that you can go into the depth.

10. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right! It is a good habit, which helps to not to lose your continuity. You should always use bookmarks while searching on Internet also, which will make your search easier.

11. Revise what you wrote: When you write anything, always read it, summarize it and then finalize it.

12. Make all efforts: Make all efforts to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in introduction, that what is the need of a particular research paper. Polish your work by good skill of writing and always give an evaluator, what he wants.

13. Have backups: When you are going to do any important thing like making research paper, you should always have backup copies of it either in your computer or in paper. This will help you to not to lose any of your important.

14. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several and unnecessary diagrams will degrade the quality of your paper by creating "hotchpotch." So always, try to make and include those diagrams, which are made by your own to improve readability and understandability of your paper.

15. Use of direct quotes: When you do research relevant to literature, history or current affairs then use of quotes become essential but if study is relevant to science then use of quotes is not preferable.

16. Use proper verb tense: Use proper verb tenses in your paper. Use past tense, to present those events that happened. Use present tense to indicate events that are going on. Use future tense to indicate future happening events. Use of improper and wrong tenses will confuse the evaluator. Avoid the sentences that are incomplete.

17. Never use online paper: If you are getting any paper on Internet, then never use it as your research paper because it might be possible that evaluator has already seen it or maybe it is outdated version.

18. **Pick a good study spot:** To do your research studies always try to pick a spot, which is quiet. Every spot is not for studies. Spot that suits you choose it and proceed further.

19. Know what you know: Always try to know, what you know by making objectives. Else, you will be confused and cannot achieve your target.

20. Use good quality grammar: Always use a good quality grammar and use words that will throw positive impact on evaluator. Use of good quality grammar does not mean to use tough words, that for each word the evaluator has to go through dictionary. Do not start sentence with a conjunction. Do not fragment sentences. Eliminate one-word sentences. Ignore passive voice. Do not ever use a big word when a diminutive one would suffice. Verbs have to be in agreement with their subjects. Prepositions are not expressions to finish sentences with. It is incorrect to ever divide an infinitive. Avoid clichés like the disease. Also, always shun irritating alliteration. Use language that is simple and straight forward. put together a neat summary.

21. Arrangement of information: Each section of the main body should start with an opening sentence and there should be a changeover at the end of the section. Give only valid and powerful arguments to your topic. You may also maintain your arguments with records.

22. Never start in last minute: Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

23. Multitasking in research is not good: Doing several things at the same time proves bad habit in case of research activity. Research is an area, where everything has a particular time slot. Divide your research work in parts and do particular part in particular time slot.

24. Never copy others' work: Never copy others' work and give it your name because if evaluator has seen it anywhere you will be in trouble.

25. Take proper rest and food: No matter how many hours you spend for your research activity, if you are not taking care of your health then all your efforts will be in vain. For a quality research, study is must, and this can be done by taking proper rest and food.

26. Go for seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

27. Refresh your mind after intervals: Try to give rest to your mind by listening to soft music or by sleeping in intervals. This will also improve your memory.

28. Make colleagues: Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

29. **Think technically:** Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

30. Think and then print: When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

31. Adding unnecessary information: Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

32. Never oversimplify everything: To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

33. Report concluded results: Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

34. After conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

INFORMAL GUIDELINES OF RESEARCH PAPER WRITING

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

Final Points:

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.

Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

· Adhere to recommended page limits

Mistakes to evade

- Insertion a title at the foot of a page with the subsequent text on the next page

- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

· Use standard writing style including articles ("a", "the," etc.)

· Keep on paying attention on the research topic of the paper

· Use paragraphs to split each significant point (excluding for the abstract)

· Align the primary line of each section

· Present your points in sound order

· Use present tense to report well accepted

· Use past tense to describe specific results

· Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives

· Shun use of extra pictures - include only those figures essential to presenting results

Title Page:

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.

Abstract:

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript--must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for briefness. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

Approach:

- Single section, and succinct
- As a outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

Introduction:

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.
- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

Procedures (Methods and Materials):

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently.You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.

- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

ADMINISTRATION RULES LISTED BEFORE SUBMITTING YOUR RESEARCH PAPER TO GLOBAL JOURNALS INC. (US)

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- Methods to avoid Plagiarism is applied by us on every paper, if found guilty, you will be blacklisted by all of our collaborated research groups, your institution will be informed for this and strict legal actions will be taken immediately.)
- To guard yourself and others from possible illegal use please do not permit anyone right to use to your paper and files.

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Topics	Grades		
	A-B	**C-D**	**E-F**
Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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