Evaluation of Pb and Cu contents of selected component parts of waste personal computers

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ABSTRACT: Electronic waste (e-waste) is one of the fastest growing waste streams in the world. The increasing market penetration in developing countries such as Nigeria, replacement market in developed countries and high obsolescence rate, make e-waste one of the fastest growing waste streams. Thirty five (35) units of waste computer central processing unit (CPU) and 24 units of waste computer monitors of different brands, manufacturers, year of manufacture, and model were collected from different electronic repairers' shops in Ibadan, South-western Nigeria and investigated for the lead and copper contents. The devices were disassembled and the printed wiring boards (PWB) of the CPUs and monitors; and the cathode ray tube (CRT) of the monitor were milled and representative samples digested with a mixture of HNO_3-H_2O_2-HCl and analysed using Atomic Absorption Spectrophotometry (AAS). The results showed very high levels of Cu and Pb in the samples with Cu concentrations ranging from 83100-705300 mg/kg for PWB of CPUs, 39150-630300 mg/kg for PWB of monitors and 73.2-468 mg/kg for CRT. The Pb contents varied from 18060-400650 mg/kg for PWB of CPU, 8460-80850 mg/kg for PWB of monitor and 429-9900 mg/kg for CRT. The results exceeded the Toxicity Threshold Limit Concentration (TTLC) used in characterizing wastes as toxic. The adoption of inappropriate methods in the management of these wastes could result in environmental pollution and human exposure to toxins. Consequently, appropriate measures should be adopted to manage these wastes as hazardous wastes. © JASEM

Introduction

The electronics and information technology industry is the world's largest and fastest growing manufacturing industry. As a consequence of this remarkable growth combined with the phenomenon of rapid product obsolescence, discarded electronic equipment, or e-waste is now recognised as the fastest growing waste stream in the industrialised world. Electronic wastes are among the largest and fastest growing waste stream in the world (Osibanjo and Nnorom, 2007; Goodship and Stevels, 2012, Pariatamby and Victor, 2013). The absence of effective take-back systems and state-of-the-art management facilities are the main challenges to effective management of e-waste in most developing countries (Nnorom et al., 2009; Nnorom and Osibanjo, 2008)

Electronic devices and products contain an array of heavy metals such as mercury, lead, gallium, selenium, arsenic, zinc, cobalt, tin, palladium and aluminium (Puckett and Smith, 2002). At the initial stages of design and development in the electronic industry, little consideration was given to long term waste and environmental impact of the products or hazardous waste stream generated during the industrial production cycle.

Though technologies for production of electronic devices are being improved everyday in order to replace the very toxic, persistent and bioaccumulative heavy metals, the fact remains that the replaced materials still contain heavy metals that are toxic to plants and animals and even human.

The components to be examined are chosen based on the fact that they have been known to particularly consist of heavy metals such as copper, lead, cadmium which when are very hazardous to human, bioaccumulate, and have carcinogenic properties. The cathode ray tubes (CRTs) in computer monitors and TVs contain about 8% lead (Pb) by weight (Smith, *et al* 1996). They also contain small amounts of other toxic substances including barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), and zinc (Zn) (Lee and Hsi, 2002). Due to the lack of financial resources available to most people in developing countries, much of the growth in the information technology (IT) sectors in developing countries, like Nigeria has

been fuelled by the importation of hand-me-down, used equipment, from rich developed countries, and non usable electronic scraps from rich developed countries (Grossman, 2006; Ogungbuyi et al., 2012; Nnorom et al., 2011).

The management of hazardous wastes remain a central environmental issue internationally (Nnorom and Osibanjo, 2008; Ogungbuyi et al., 2012). This is clearly indicated by the existence of international conventions to regulate the movement of hazardous waste. The convention on the control of transboundary movements of hazardous waste and their disposal (22 March 1989), also known as the Basel Convention, was initiated in response to numerous international scandals regarding hazardous waste trafficking in the late 1980s (BAN, 2007). The convention on the ban of import into Africa and the control of transboundary movement and management

of hazardous waste within Africa (29 January, 1991) or Bamako Convention, in turn places a total ban on the import of hazardous waste to signatory countries.

In developing countries, e-waste is usually disposed off in a variety of inappropriate ways including open burning, dumping into water bodies and at undesignated places and the use of crude recycling techniques to recover valuables. Leaching of harmful chemicals and toxic metals from such sites could result groundwater contamination (Nnorom et al., 2010). The physiological and health impacts of the toxic substances found in e-wastes at sufficient concentrations on humans and animals have been discussed by various researchers (Brigden *et al* 2005, Environment Victoria, 2005). Some examples of sources of e-waste, constituents and their related health effects are listed in Table 1.

Table 1: E-waste sources and their health effects

e-waste sources	Constituents	Health effects
Printed circuit boards and computer monitors	Lead	Causes damage to the nervous system, circulatory system, and kidney. Also affects brain development in children
Chip resistors and semiconductors	Cadmium	Causes neural damage
Relays and switches, and printed circuit boards	Mercury	Causes chronic damage to the brain, respiratory and skin disorders
Galvanised steels plates and decorator or hardener for steel housing	Chromium	Causes bronchitis
Cabling and computer housing	Plastics and PVC	Affect reproductive system and immune system, and lead to hormonal disorder
Electronic equipment and circuit boards	Brominated flame retardants	Disrupt endocrine system functions
Front panels of CRTs	Barium, phosphor, and heavy metals	Causes muscle weakness and damage to heart, liver, and spleen
Motherboard	Beryllium	Carcinogenic in nature causing skin diseases

Source: Boralkar (2006).

The Restriction of Hazardous Substances, (RoHS) Directive 2002/95/EC of the European Union adopted in January 27, 2003 by the European Parliament and Council and then revised in June 8, 2011 (Recast of the RoHS Directive); restrict the use of six hazardous materials found in electrical and electronic products. The Directive restricts the use of certain hazardous substances in electrical and electronic products - lead, mercury, cadmium, hexavalent chromium and flame retardants such as polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) to be substituted by safer alternatives. RoHS mandates that EEE products must not contain more than 0.1% (except cadmium with limit of 0.01%) by weight of homogenous material[1] of any of listed substances. The RoHS specifies maximum levels for the following six restricted materials:

- Lead (Pb): < 1000 ppm,
- Mercury (Hg): < 100 ppm
- Cadmium (Cd): < 100 ppm
- Hexavalent Chromium: (Cr VI) < 1000 ppm

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[1] Homogenous material means a material that cannot be mechanically disjointed into different materials.

- Polybrominated Biphenyls (PBB): < 1000 ppm
- Polybrominated Diphenyl Ethers (PBDE): < 1000 ppm

In Nigeria, e-wastes are usually disposed off at open dumps, burnt in the open while valuable materials are recovered using crude methods – all of which pollute the environment and expose humans to toxins. This study determined the levels of Pb and Cu in selected components of waste personal computer components to evaluate their potential to harm man and the environment in managed using inappropriate method as is the present practice in most developing countries.

MATERIALS AND METHODS

Sample collection and preparation: Electronic waste components were collected and used in this study. Thirty five (35) units of computer central processing unit (CPU) and 24 computer monitors of different brands, manufacturer, year of manufacture, and model were collected from different electronic repairs workshops in Ibadan, South-western Nigeria and used in this study. The devices were carefully dismantled

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separately and the components were classified into two major parts:

Millable parts: Printed wire boards (PWBs including IC packages) for the CPU, monitor, and CRT
Non-millable parts: Metal frames, rods and other metal parts.

All the millable components were separately treated by cutting into small pieces and grinding using a specially fabricated heavy duty mill to achieve the desired particle size, and then passed through a 2mm mesh sieve. Wood chips were used to clean the milling apparatus after each sample milling, and served as blanks to assess cross-contamination. Milled samples were thoroughly mixed to achieve homogeneity before removing aliquots for testing.

Digestion of sample: One gram (1g) representative sub-sample of the thoroughly mixed sample was weighed into a digestion vessel according to EPA method 3050B (EPA, 1996). 10ml of 1:1 HNO_3 (VWR Chemicals, Poole, England) was added to the sample to make a slurry, mixed and covered with a watch glass and refluxed for 15 minutes and then allowed to cool. 5ml of concentrated HNO_3 was added, covered and the solution was refluxed for another 30 minutes. This was repeated until evolution of brown fumes ceased. The sample was then heated at $95^{\circ}C$ without boiling for two hours, then allowed to cool and 2ml of de-ionised water and 3ml of 30% H_2O_2 (VWR Chemicals, Poole, England) were added to start the peroxide reaction with heating. Care was taken to ensure that losses do not occur due to excessive vigorous effervescence and less than a total of 10ml of 30% H_2O_2 was added until the general sample appearance remain unchanged. Thereafter, the sample was covered with a watch glass and heated at $95^{\circ}C$ without boiling for two hours. After two hours, 10ml concentrated HCl (VWR Chemicals, Poole. England) was added to the digest above, covered with a watch glass, and heated at $95^{\circ}C$ for 15 minutes. The digest was allowed to cool and then filtered through a filter paper and filtrate collected in a 100ml volumetric flask.

Instrumental analysis: All the sample solutions were analysed for lead and copper with flame atomic absorption spectrophotometer using appropriate lamps and resonance wavelength of the metals. The atomic absorption spectrophotometer was calibrated using the metal standards solution prepared for the purpose of calibration before the measurement took place. A flame atomic absorption spectrophotometer (Buick Scientific model 210 VGP), with air/acetylene flame and slit size 0.7nm was employed in the instrumental analysis of the metals. The determination of copper was carried out at wavelength 324.7nm while lead was carried out at 283.2nm. The detection limit for the copper and lead is 0.005 mg/L and 0.008 mg/L respectively.

Quality assurance and quality control: Appropriate quality assurance procedures and precautions were carried out to ensure the reliability of the results of the present study. Samples were carefully handled to avoid contamination while all chemicals used were of analytical grade: HNO_3 (69%, VWR Chemicals, Poole, England); H_2O_2 (30%, VWR Chemicals, Poole, England); HCl (37%, VWR Chemicals, Poole, England). Clean environment was maintained to avoid sample contamination. Before grinding the sample, the grinder was opened up and thoroughly washed with deionised water and 5 percent nitric acid, and acetone and air dried for 1 day, to eliminate any form of memory effect from any previous milling operation. After the processing of each component, the grinder was cleaned by passing dried wood chips through it and pressurised air blasted into it to ensure that it was completely free of sample particles or wood chips. This process was repeated after each sample processing. To eliminate the risk of contamination during the experiments, all plastic and glassware were carefully cleaned by washing, rinsing severally with tap water, and then soaking in 30% HNO_3 solution for a minimum of 48h. They were rinsed severally with deionized water before use. Reagent blank determinations were used to correct the instrument readings. Also, a recovery test of the total analytical procedure was carried out for some of the metals in selected samples by spiking analyzed samples with aliquots of metal standards and then re-analyzing the samples. Detection limit is defined as the concentration corresponding to three times the standard deviation of seven blanks.

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Table 2: Summary of computer components used for analysis

S/N	Product Type	Manufacturer	Model No	Serial No	Year of Manufacture	Weight
1	CPU	UNITECH	N/A	M6309U0103138359	1999	536
2	CPU	QDI	N/A	D02040303501158	1998	581
3	CPU	ZP COM	6964B	989VE1150083	1998	544
4	CPU	WINBOND	W83627F-AW	927S2C292113702	1998	476
5	CPU	V/N	VT82C686A	13C0N9800	1998	583
6	CPU	V/N	0102CG	10202400056	1999	538
7	CPU	INTEL	L942TA86	FW82810DC100	1998	579
8	CPU	INTEL	L8321L15	FW82371EB	1996	554
9	CPU	V/N	0107CD	13001901161	1998	532
10	CPU	V/N	JM 2023	2457600	2000	480
11	CPU	INTEL	SL2VH	L006VA38	1998	514
12	CPU	V/N	694X	13B007600	1999	527
13	CPU	V/N	0051 CG	M630980101067465	1998	535
14	CPU	INTEL	SL3P6	F9321J49	1998	539
15	CPU	V/N	0022CE	1EE0N2101	1998	568
16	CPU	SUMA	MS7177CT	A30EE21501784	-	588
17	CPU	UNITECH	0111CD	13B702200	-	542
18	CPU	UNISEM	W29C020	9490I2939	1998	533
19	CPU	COBRA+1	6BXA-65A	N12811XN803999	2000	560
20	CPU	ITE	0016-CYS	IT8693F-A	2000	575
21	CPU	QDI	PCI/PNP 686	249230652	1998	596
22	CPU	QDI	0360H	018196606	1998	557
23	CPU	V/N	0053 CD	0105550795	1999	593
24	CPU	INTEL	CS4610-CM	ATAKL09729	1998	679
25	CPU	WINBOND	W83977EF-AW	191483869	1998	609
26	CPU	SOYO	MC3240	272544304	1998	587
27	CPU	WINBOND	9F002U-12B	GG201080001SA	1998	546
28	CPU	WINBOND	SL2KK	FW82443LX	1995	484
29	CPU	CRYSTAL	40-04831	CS4326B-KQ	-	625
30	CPU	PRO	MS6163	93692E29084970	-	579
31	CPU	V/N	0047CE	VT82C694X	-	502
32	CPU	AMIBOS	BR66096	827SC282126702SA	1995	569
33	CPU	COMPAQ	008313	332857-W1	1998	546
34	CPU	PRO	L1084S	204708433	1998	580
35	CPU	CHIPS	M9259	00115B3D742A	-	597
36	MONITOR	ULTRASCAN	TM 4401	VP-N1B(Z)2080708	-	716
37	MONITOR	OLIVETTI	N/A	2813773	-	461
38	MONITOR	JVC	N/A	09568566	-	566
39	MONITOR	BELINEA	10 60 20	106020984125436	1998	884
40	MONITOR	NCR	B790	90-34021497	2000	609
41	MONITOR	BLUE GATE	TM-1550	2003080201804	2003	423
42	MONITOR	NEW DIAMOND	8027554	N/A	-	591
43	MONITOR	SAMSUNG	551V	AN15HMDW800567V	2003	329
44	MONITOR	CHEER	3DE	62-3VC-3DE2-E-76	2003	412
45	MONITOR	HAISI	FH-568	MF53E031100107	-	564
46	MONITOR	NEC MULTISYNC 3V	JG-1535VMB	4401216TP	1991	802
47	MONITOR	PROVIEW	MD-848FGOE	FA BE5C43169	-	492
48	MONITOR	VIEWTEC	M1454 A	4CPF13400623	-	645
49	MONITOR	KOMODO	H450	738 WK 002U02422	1997	643
50	MONITOR	PHILIPS	105S11/00	HD009947008417	1999	591
51	MONITOR	DELL	D1025HE	66052-9-4X2F-97	1997	472
52	MONITOR	ZINOX	M553	131FNAC2002729	2001	507
53	MONITOR	CTX	1569ME	0H4-81200581	1998	505
54	MONITOR	RELI SYS	TE 5559	JX92490225	1999	560
55	MONITOR	DIRECT ON PC 455	MH 455	MN43 E030612976	-	505
56	MONITOR	SAMTRON	4 BI	HMBJ501273P	1998	404
57	MONITOR	ACER	7234E	9174302003	2001	521
58	MONITOR	DIRECT ON PC 568	NH 568	MN53E030809252		579
59	MONITOR	NUTECH	N/A	0924	2002	507

RESULTS AND DISCUSSION

The results of this study showed varying Pb and Cu (Figures 1 -3) contents of the e-waste components studied. The results varied widely in some cases. The variation varied according to component type, year of manufacture, and likely exogenous contamination. A similar observation was also made in the study of heavy metal contamination of waste mobile phone plastics by Nnorom and Osibanjo, (2009a,b). A summary of the results is presented in Table 3.
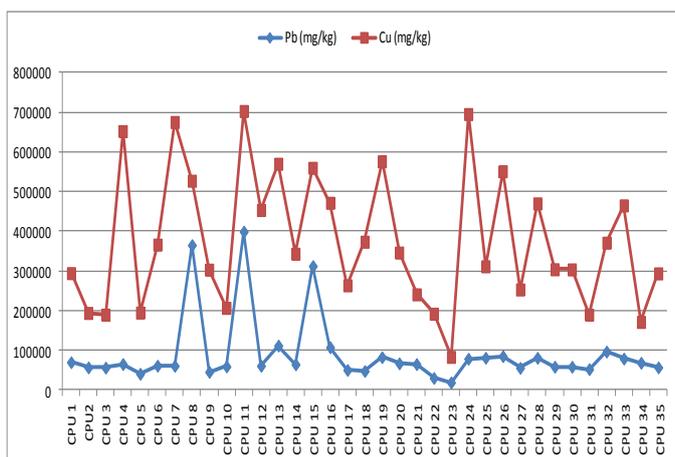
*[1]OLUBANJO, K; OSIBANJO, O[2]; NNOROM, I.C[2,3]

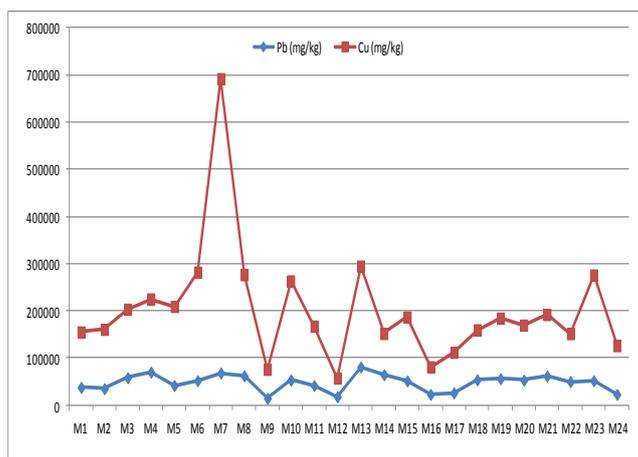**Fig 1:** Variation in lead and copper contents of the PWB of CPU

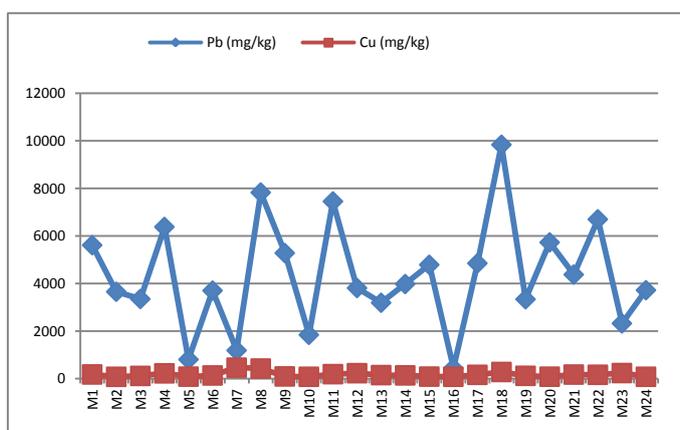**Fig 2:** Variation in l ead and copper contents of the PWB of Computer monitor

Fig 3: Variation in lead and copper contents of the CRT of Computer monitor

The results show (Table 3) that the lead and copper contents in the printed wiring board (PWB) of the Central Processing Unit (CPU) of all the samples exceed the threshold limits for these metals by 400 times and 282 times respectively, while in the printed wiring board of the monitors, the threshold limit was exceed by 81 times and 252 times respectively. It was observed that the copper content in the CRT is far below the threshold limit for all the samples, while lead content is very high in this part of the component, exceeding the regulatory limit by 10 times. Printed wiring boards contain 10 – 40% copper by weight (Ernst *et* al, 2003), and this is line with the results obtained in the experiments, indicating high level of copper in the printed wiring board of the CPU and the monitor, and a low level (far below the threshold limit) in the cathode ray tube.

Previous e-waste study (DTSC, 2004) reported that the copper and lead content exceed the TTLC of both elements, although at a lower concentration than the average reported in this present study. This discrepancy is likely due to the fact that in the DTSC study, the printed wiring board was milled without any capacitor on it, but in this present study, the capacitors were milled together with the printed wiring board which may have accounted for the higher level of concentration reported in this study.

A comparison of our computer data used for this study and other e-waste analyses (Lincoln *et al*, 2007) indicate also that the two elements are above the regulatory limit, though at a lower concentration of 81 times for Cu as compared to 282 times for Cu in the PWB of the CPU and 252 times in the PWB of monitor for the present study, but lead was found to be 10 times more than the regulatory limit, which is the same value obtained for lead in CRT in the present study.

A comparison of the concentration of the two metals in the three parts analysed showed that Cu has a higher concentration than Pb in the printed wiring board of the CPU and monitor while Pb has a higher concentration than Cu in the cathode ray tube.

These data demonstrate that electronics manufacturers who seek to design product that will be exempted from current hazardous waste classifications will need to address not just Pb (as the

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current wave of responses to European and Japanese regulations has shown, but also the copper content. However, extensive testing of replacement materials should precede the selection of alternative materials for electronics.

A comparison of the Pb and Cu contents of the samples and the TTLC limit are presented in Figures 5 and 6 respectively.

Table 3: Summary of the Range and Mean (in Parenthesis) of Copper and Lead Concentration in the Components Analysed in mg/kg

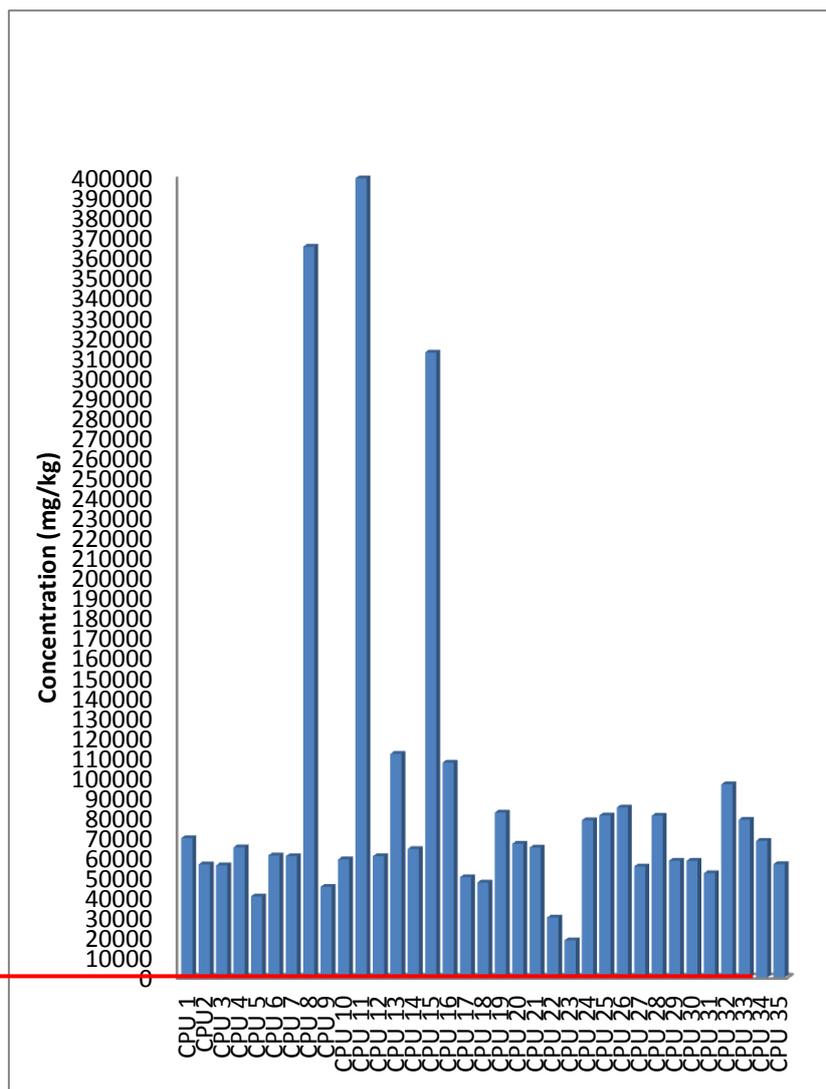| TTLC Limit	/kg)	1000 (mg/kg)
Component	**mg/kg)**	**Lead (mg/kg)**
PWB of CPU	83100 – 705300 (376196)	18060 – 400650 (89882)
PWB of monitor	39150 – 630300 (149819)	8460 – 80850 (47044)
Cathode ray tube	73.2 – 468 (166)	429 – 9900 (4341)

Fig 4*: Lead Concentration of Printed Wiring Board (PWB) of CPUs (TTLC Limit = 1000 mg/kg)*

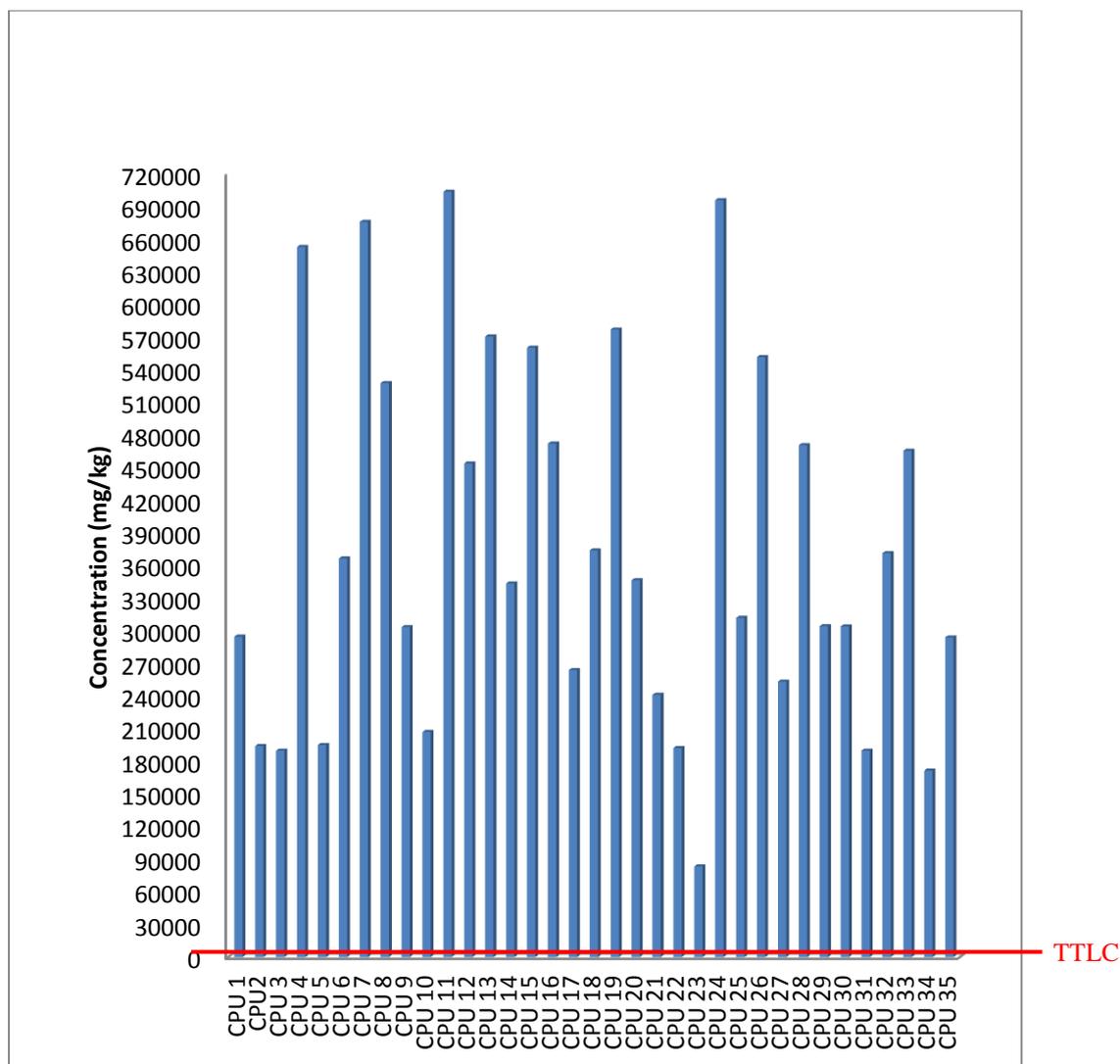*[1]OLUBANJO, K; OSIBANJO, O[2]; NNOROM, I.C[2,3]*

Fig 5: *Copper concentration of Printed Wiring Board (PWB) of CPUs (TTLC limit = 2500 mg/kg)*

Conclusion: This study have shown that PWB of contain elevated levels of lead and copper. Considering that inappropriate methods are adopted in the management of waste computers and e-wastes in general, the observed high levels of Pb and Cu would pose harm to man and the environment. Challenges facing effective e-waste management in Nigeria poor consumer awareness, inadequate legislations dealing specifically on e-waste, lack of waste management facilities. The success of any environmental policy depends on the fact that all sections of the population understand the functioning of the environment and the potential environmental challenges. Environmental education will be required to create awareness of this problem to ensure that the society fully assume responsibility in safeguarding the environment.

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