

Assessment of Heavy Metals and Metalloids in Water-Based Paints in Nigeria

Ajoke Fehintola Idayat Apanpa-Qasim^{a*}, Adebola Abosede Adeyi^b

^aDepartment of Chemistry, University of Ibadan, Ibadan-Nigeria

^bCSIR-National Environmental Engineering and Research Institute, Nagpur, India

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Abstract

Consumer products such as paints are potential significant sources of heavy metals and metalloids which are ubiquitous environmental contaminants. Paints may represent a significant source of heavy metals and metalloids because of the volume used and the frequency of re-application during the life of a building. Their abundance, presence and use have not been without significant health consequences as they account for significant mortality and morbidity. This study assesses the levels of heavy metals and metalloids in paints produced by 14 different manufacturers in Nigeria. There was a great variation in the concentrations of heavy metals and metalloids in the paint samples. The levels of heavy metals (dry weight) in all the samples ranged from 1.2-199 mg/kg of Ni; 742-2,910 mg/kg of Fe; 133-1,840 mg/kg of Cu; 21.4-200 mg/kg of Mn and 10.3-220 mg/kg of Zn while the level of As (a metalloid) ranged from 383-1,930 mg/kg. All the samples were above the European Union (EU) permissible limit of 25 mg/kg of As while there are no regulations presently available for Ni, Fe, Cu, Mn and Zn in paints. The concentrations of As, Fe and Cu were higher than those of Mn, Ni and Zn in all the paint samples investigated. The results showed that paints sold in Nigeria contain substantial amounts of heavy metals and arsenic, which can cause negative human health impacts with increased risk of exposure to the vulnerable groups such as children.

Keywords: *Water-based paints; Heavy metals; Metalloids; Health impact; Toxicity; Exposure.*

Introduction

Paint has been recognized to provide aesthetic and protective requirements. Its primary purpose is to protect the surface to which it is applied and to provide decorative properties. Today, paints are used for interior and exterior house paintings, boats, automobiles, planes, appliances, furniture and so on, where protection and appeal are desired.^[1,2,3] Qualities such as flexibility in different climatic conditions, less coating requirements, wide range of colours and brands make the water-based paints a better alternative.

* Corresponding author: Ajoke Fehintola Idayat Apanpa-Qasim

E-mail: ajoketola@gmail.com

The components of paint are: vehicles, pigments, extenders, binders and additives. However, not all paints have every ingredient represented. For example, gloss paints do not contain extenders,^[4] which are organic coarse particle materials. Vehicle in paints is the medium in which the pigment and other additives are carried on in the surface coating. The function of a vehicle is to provide means for easy application of the paints, provides means of adhesion to the surface, facilitates drying of the paints and acts as a moisture barrier. Pigments are insoluble particles which cover the surface to which the paint is applied. Pigments are the source of colour in paints and can be of organic or inorganic nature. In addition to solvent resistance, pigments are required to be light stable. However, for most applications, the optical properties of pigments are of prime importance. Extenders and fillers are incorporated into the paints to provide opacity, good dispersing properties and for a variety of other purposes. Binders used are the resins which bind the pigment. They are homogeneously dispersed in the dry film former.^[4,5]

Many heavy metals and metalloids are constituents of pigments and represent unique environmental and industrial pollutants, naturally distributed in all the phases of the environment.^[6,7] Heavy metals and metalloids exposure continues and is increasing in many parts of the world in consumer products such as paints, fluorescent light bulbs, drugs, auto switches, medical equipment, paints, soaps, hair dyes, candy, toys, children jewelries etc.^[8-12] Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment, raising concerns over their potential effects on human health and the environment.^[12-14] Heavy metals such as Fe, Zn and Cu are quintessential to maintain various biochemical and physiological functions in living organisms when in very low concentrations. However they become noxious when they exceed certain threshold concentrations. Metalloids such as As are known to cause cardiovascular and peripheral vascular diseases, developmental anomalies, neurologic and neurobehavioural disorders, diabetes, hearing loss, portal fibrosis, hematologic disorders (anaemia, leukopenia and eosinophilia) and carcinoma in humans.^[15-18]

Most heavy metals and metalloids present in consumer products such as paints have received very little attention. Hence, there is need to increase public awareness on exposure to these toxic metals and metalloids in water-based paints intended for sale in Nigeria.

Materials and Methods

Sample collection and metal determination

Paint samples were purchased in popular paint markets in Ibadan and Lagos, Nigeria based on colour availability and most commonly used water-based paints as presented in Table 1. A total of 174 paint samples, produced by 14 different manufacturers were collected. These samples were stored in air-tight plastic

containers and analysed at the Council of Scientific and Industrial Research - National Environmental Engineering Research Institute Laboratory, Nagpur – Maharashtra, India.

Table 1: Information on paint samples collected in Lagos and Ibadan, Nigeria

Serial No.	Manufacturer codes	Number of different paint colours collected	Number of paint samples collected	NIS-ISO registration
1	A	10	20	Yes
2	B	9	18	Yes
3	C	9	18	Yes
4	D	5	10	Yes
5	E	5	10	Yes
6	F	6	12	Yes
7	G	4	8	No
8	H	5	10	No
9	I	4	8	No
10	J	5	10	No
11	K	6	12	No
12	L	8	16	No
13	M	7	14	No
14	N	4	8	No

Note: Number of paint colours collected per manufacturer was based on availability and most commonly used. NIS-Nigerian Industrial Standard; ISO-International Organization for Standardization.

Approximately 5 mL each of the paint samples were spread on glass slides using a different brush for each sample to avoid cross contamination. The glass slides were placed in an oven at 120 °C for 2 hours. About 1.0 g each of the dried paint films was weighed into closed Teflon vessels and digested in a closed microwave digestion system using 10 mL of 70% nitric acid and 3 mL of 98% sulphuric acid. Samples were analyzed according to the standard procedure for the digestion of very difficult samples. Digestates were then filtered and analyzed using inductively coupled plasma-optical emission spectrometer (Thermo Scientific iCAP 6300 Duo). Blank determination, 100% duplicate and recovery were some of the quality control measures adopted in this study. Dilutions were performed when necessary and recovery study was between 80-110% (Table 2).

Instrument Operating Conditions

A MARS 6 microwave reaction system was used for sample digestion. Samples were weighed into Teflon vessels and digested at 200 °C, 25 mins ramp time and 30 min holding time, with a 1000-watt power in one cycle digestion. The temperature guard of the instrument was set not to exceed 210 °C. Cooling was automatically carried out by the instrument to 30 °C in 30 minutes. Digested samples were analyzed

using Thermo Fisher Scientific inductively coupled plasma optical emission spectrometer (model iCAP 6300 Duo) which was coupled with an auto sampler CETAC ASX-52, and a spectrometer (Echelle type) equipped with a simultaneous charge injection device and detector measuring wavelengths from 166.00 nm to 847.00 nm. The operating condition of ICP-OES was 1150W RF power, 15 L/min plasma flow, 50 rpm pump rate, 0.5 L/min auxiliary gas flow, and 0.5 L/min nebulizer gas flow. The carrier gas of the instrument was ultra-pure argon.

Table 2: Recovery study of selected elements

Metals	Spiked sample	% Recovery
As	MS	80.45
	MSD	85.28
Cu	MS	94.08
	MSD	97.65
Fe	MS	94.03
	MSD	95.13
Mn	MS	107.97
	MSD	99.28
Ni	MS	93.00
	MSD	98.00
	MSD	99.28
Zn	MS	106.34
	MSD	102.82

MS= Matrix spike; MSD= Matrix spike duplicate

Results and discussion

Six of the selected paints manufacturers were registered with NIS (Nigerian Industrial Standard) and ISO (International Organization for Standardization) while eight were unregistered manufacturers without NIS-ISO certification. The mean \pm SD of As, Mn, Fe, Ni, Cu and Zn in the paint samples collected in Lagos and Ibadan, Nigeria with respect to the various manufacturers are presented in Table 3. The variation in the concentrations of heavy metals and metalloid in the paint samples is shown in Figure 1. The concentrations of heavy metals and metalloid with respect to colours are presented in Table 4 and shown in Figure 2.

Arsenic (As)

Arsenic is one of the most important metalloids that cause disquiet from both ecological and individual health standpoints.^[19-21] Arsenic has a long-standing history of use in medicine and it is currently used to treat patients with acute promyelocytic leukemia.^[22] Arsenic is prominently toxic and carcinogenic to humans, protoplasmic and poisonous because it affects the sulphhydryl group of cells causing malfunctioning of cell respiration, cell enzymes and mitosis in plants.^[21,22] Humans may be exposed to arsenic from natural sources such as soil formations of arsenic accumulation; from industrial sources such as the production of paints or from unintended sources.^[21,23]

The concentrations of arsenic in all the paint samples with respect to manufacturers ranged from 383-1,930 mg/kg (Supplemental Material). The highest concentration of As was 1,930 mg/kg, obtained in a paint produced by manufacturer I (an unregistered manufacturer). This was followed by 1,920 mg/kg and 1,860 mg/kg in paints produced by manufacturer I and K (both unregistered manufacturers), respectively. The lowest concentration was 383 mg/kg, obtained in a paint produced by manufacturer I (an unregistered manufacturer). The highest mean concentration of As was $1,860\pm 46$ mg/kg in paints produced by manufacturer I. This was followed by $1,770\pm 15$ mg/kg in paints produced by manufacturer K and $1,720\pm 38$ mg/kg in paints produced by manufacturer J (an unregistered manufacturer) while the lowest mean concentration was 627 ± 17 mg/kg in paints produced by manufacturer B (a registered manufacturer) (Table 3). The European Union permissible limits of As in paint is 25 mg/kg.^[24] The concentrations of As obtained in all the paint samples considered in this study were higher than the EU permissible limit. Thus, users are exposed to this toxic substance in paint via occupational exposure as most of the users (i.e., painters) do not use appropriate personal protective equipment (PPEs) and vulnerable group such as children from hand-to-mouth contact with paint flakes.

Table 3: Mean concentrations (dry weight, mg/kg) of heavy metals and metalloid in paint samples with respect to manufacturers

S/N	Manufacturer codes	As	Mn	Cu	Zn	Fe	Ni
1	A	630±20	130±6.2	881±69	21.9±0.6	1150±72	3.0±0.3
2	B	627±17	25.7±0.6	690±23	25.4±0.8	1520±150	2.3±0.5
3	C	1210±18	25.0±1.5	154±6.9	16.5±0.5	2160±98	4.7±0.5
4	D	825±7.2	50.7±1.9	703±12	17.1±0.5	889±14	3.8±0.3
5	E	806±18	183±2.9	697±8	20.4±1.0	1240±19	2.3±0.3
6	F	866±19	130±6.2	506±12	93.1±2.6	1430±19	3.8±0.2
7	G	1400±27	116±3.4	699±28	154±7.5	1840±22	18.4±0.5
8	H	1690±26	145±1.5	692±13	110±3.8	1420±40	23.1±1.1
9	I	1860±46	110±2.2	1730±32	192±6.5	1160±18	85.1±2.0
10	J	1720±38	90.3±2.0	646±28	120±2.7	1660±48	86.3±3.1
11	K	1770±15	114±2.5	767±12	120±3.8	2150±46	76.5±2.3
12	L	1590±13	91.2±3.1	748±20	61.3±2.4	1530±30	89±2.0
13	M	1450±30	53.1±1.0	872±22	95.6±3.6	2180±130	78.2±2.4
14	N	1410±8	53.2±1.7	1690±66	143±12	2000±37	146±13
Range		627-1860	25.0-183	154-1730	16.5-192	889-2180	2.3-146

Table 4: Mean concentrations (dry weight, mg/kg) of heavy metals and metalloid in paint samples with respect to colours

Colours	As	Mn	Zn	Cu	Fe	Ni
blue	1280±28	87.4±2.1	85.0±6.5	807±12	1530±48	42.4±7.6
brown	927±9.1	77.6±2.7	33.3±1.2	644±77	1710±38	24.4±2.3
chocolate	1350±17	94.0±2.7	51.9±5.7	578±30	1760±140	44.2±2.1
cream	1280±25	43.6±3.1	87.5±4.1	859.0±25	1450±51	47.3±2.5
green	1280±29	88.5±4.0	86.2±8.1	820±38	1550±63	43.2±2.0
grey	1000±21	81.5±3.5	20.8±0.1	514±102	1490±33	2.7±0.4
orange	1220±14	83.4±3.9	57.0±1.1	734±20	1680±280	56.6±1.2
pink	1200±20	108±8.2	62.8±2.5	751±25	1640±26	40.5±0.3
red	1210±21	73.1±2.0	61.3±2.1	629±30	1790±41	32.9±2.4
violet	1160±56	21.8±0.5	18.0±1.7	171±3.5	2120±7.5	4.1±0.6
white	1220±24	89.8±3.2	87.9±4.9	880±57	1740±97	47.1±5.9
yellow	860±18	66.2±4.6	36.5±1.6	600±29	1480±31	3.4±0.1
Range	860-1350	21.8-108	18.0-87.9	171-880	1450-2120	2.7-56.6

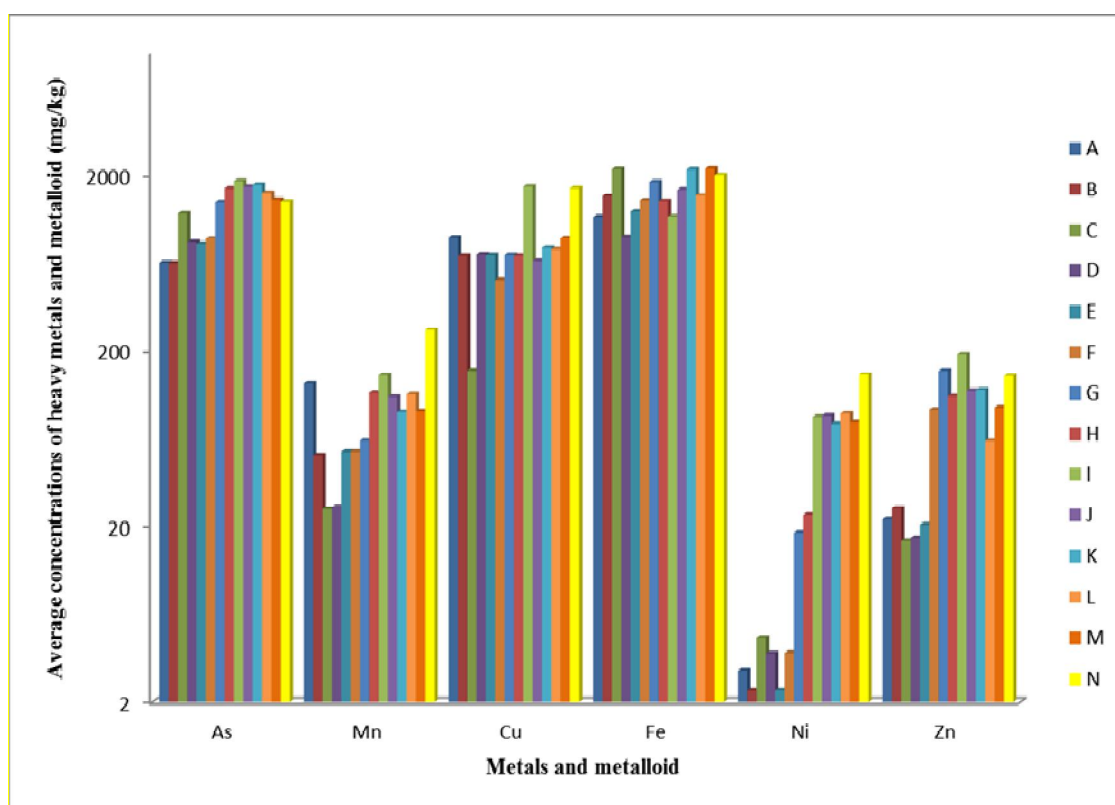


Figure 1: Variation in the concentrations (mg/kg) of heavy metals and metalloid in paint samples with respect to manufacturers.

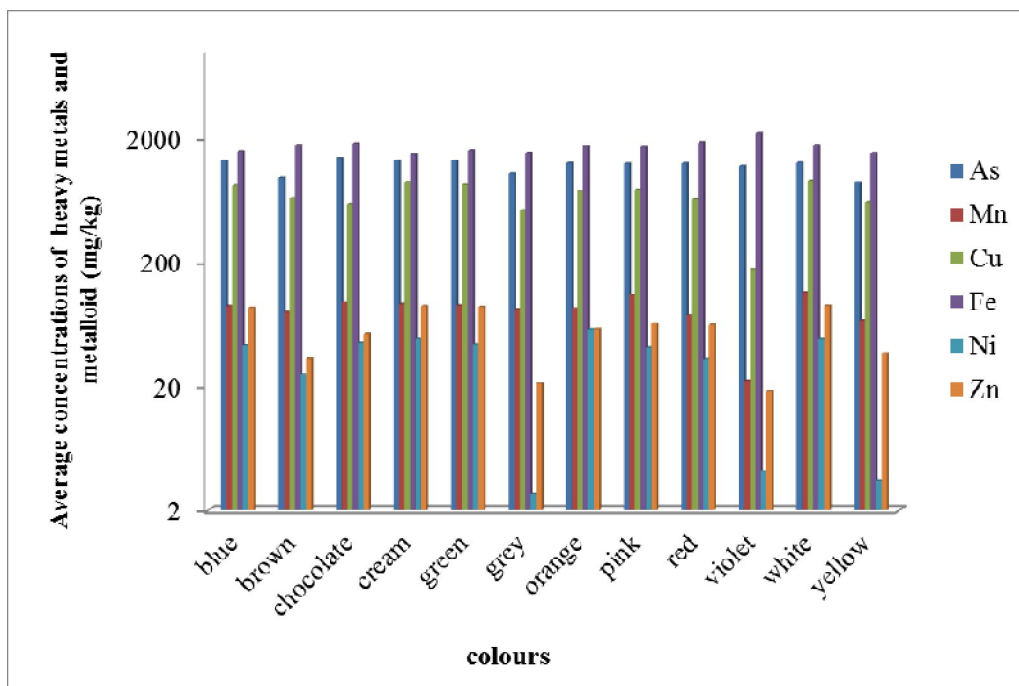


Figure 2: Variation in the concentrations (mg/kg) of heavy metals and metalloid in paint samples with respect to colours.

The concentrations of arsenic in all the paint samples with respect to available colours ranged from 383-1,930 mg/kg (Supplemental Material). The highest As concentration was 1,930 mg/kg in a cream coloured paint, followed by 1920 mg/kg and 1860 mg/kg in green coloured paints, respectively. The lowest As concentration was 383 mg/kg in a blue coloured paint. The highest mean concentration of As with respect to colours was $1,350 \pm 17$ mg/kg in chocolate coloured paints, followed by $1,280 \pm 29$ mg/kg in green coloured and $1,280 \pm 28$ in blue coloured paints. The lowest mean concentration, 860 ± 18 mg/kg, was obtained in yellow coloured paints (Table 4).

Manganese (Mn)

Manganese is a critical component of numerous metalloenzymes.^[25] It participates in blood clotting and sugar homeostasis, immune responsiveness, digestion, reproduction and bone growth.^[26,27] Despite its requirement in multiple physiological processes, elevated levels of Mn trigger toxicity, particularly within the central nervous system (CNS), causing cognitive, psychiatric and motor abnormalities.^[28] The concentrations of Mn in all the 174 paint samples with respect to manufacturers ranged from 21.4-200 mg/kg (Supplemental Material). The highest concentration of Mn was 200 mg/kg, obtained in a paint produced by manufacturer N, (an unregistered manufacturer). This was followed by 189 mg/kg and 182 mg/kg in products from the same manufacturer. The highest mean concentration of Mn was 183 ± 2.9 mg/kg, obtained in paints produced by manufacturer N. This was followed by 145 ± 1.5 mg/kg and 130 ± 6.2 mg/kg in paints produced by manufacturer I (an

unregistered manufacturer) and A (an unregistered manufacturer), respectively, while the lowest mean concentration was 25.0 ± 1.5 mg/kg, obtained in paints produced by manufacturer C (a registered manufacturer) (Table 3). There is no permissible limit of Mn in paints presently available.

The concentrations of manganese in all the 174 paint samples with respect to available colours ranged from 21.4-200 mg/kg. The highest concentration of Mn was 200 mg/kg in a white coloured paint, followed by 189 mg/kg and 182 mg/kg in a white and a green coloured paints, respectively. The highest mean concentration of Mn with respect to available colours was 108 ± 8.2 mg/kg in pink coloured paints, followed by 94.0 ± 2.7 mg/kg in chocolate coloured paints and 89.8 ± 3.2 in white coloured paints. The lowest mean concentration, 21.8 ± 0.5 mg/kg, was obtained in violet coloured paints (Table 4).

Iron (Fe)

Iron is the most crucial element for growth and survival of almost all living organisms.^[29] The toxicity of iron on cells has led to iron mediated tissue damage involving cellular oxidizing and reducing mechanisms and their toxicity towards intracellular organelles such as mitochondria and lysosomes. Iron can initiate cancer mainly by the process of oxidation of DNA molecules.^[21,30] The concentrations of iron in all the paint samples ranged from 742-2,910 mg/kg (Supplemental Material). The highest concentration of Fe was 2,910 mg/kg, obtained in a paint produced by manufacturer M (an unregistered manufacturer). This was followed by 2,730 mg/kg and 2,510 mg/kg in paints produced by manufacturer C (a registered manufacturer). The lowest concentration of Fe was 742 mg/kg, obtained in a paint produced by manufacturer D (a registered manufacturer). The highest mean concentration of Fe was $2,180 \pm 130$ mg/kg, obtained in paints produced by manufacturer M, followed by $2,160 \pm 98$ mg/kg in paints produced by manufacturer C and $2,150 \pm 46$ mg/kg in paints produced by manufacturer K (an unregistered manufacturer). The lowest mean concentration, 889 ± 14 mg/kg, was obtained in paints produced by manufacturer D (Table 3). There is no permissible limit of Fe in paints presently available.

The concentrations of Fe in all the paint colours ranged from 742-2,910 mg/kg. The highest Fe concentration was 2,910 mg/kg in a white coloured paint, followed by 2,730 mg/kg and 2,510 mg/kg in a chocolate and a brown coloured paints, respectively. The lowest Fe concentration was 742 mg/kg in a cream coloured paint. The highest mean concentration of Fe with respect to available colours was $2,120 \pm 7.5$ mg/kg in violet coloured paints, followed by $1,790 \pm 41$ mg/kg in red coloured paints and $1,760 \pm 140$ in chocolate coloured paints. The lowest mean concentration, $1,450 \pm 51$ mg/kg, was obtained in cream coloured paints (Table 4).

Nickel (Ni)

Nickel is believed to play a role in physiological processes as a co-factor in the absorption of iron in the intestine. Based on studies on nickel workers and laboratory animals, all nickel compounds, except metallic nickel, have been classified as human carcinogens by the International Agency for Research on Cancer^[31] and the U.S. Department of Health and Human Services.^[32] Nickel is the most observed cause of immediate and delayed hypersensitivity noticed in occupationally exposed humans as well as the general population.^[33] The concentrations of Ni in all the paint samples ranged from 1.2-199 mg/kg (Supplemental Material). The highest concentration of Ni was 199 mg/kg, obtained in a paint sample produced by manufacturer N (an unregistered manufacturer). This was followed by 167 mg/kg and 166 mg/kg in paints produced by the same manufacturer. The lowest concentration of Ni, 1.2 mg/kg, was obtained in a paint produced by manufacturer D (a registered manufacturer). The highest mean concentration of Ni was 146 ± 13 mg/kg, obtained in paints produced by manufacturer N followed by 89 ± 2.0 mg/kg and 86.3 ± 3.1 mg/kg in paints produced by manufacturer L and manufacturer J (both unregistered manufacturers), respectively. The lowest mean concentration was 2.3 ± 0.3 mg/kg, obtained in paints produced by manufacturer E (a registered manufacturer) (Table 3). There is no permissible limit of Ni in paints presently available.

The concentrations of nickel in all the available paint colours ranged from 1.2-199 mg/kg. The highest Ni concentration was 199 mg/kg, followed by 167 mg/kg in white coloured paints. This was followed by 166 mg/kg in a blue coloured paint. The lowest Ni concentration was 1.2 mg/kg, obtained in a green coloured paint. The highest mean concentration of Ni was 56.6 ± 1.2 mg/kg in orange coloured paints, followed by 47.3 ± 2.5 mg/kg in cream coloured paints and 47.1 ± 5.9 in white coloured paints. The lowest mean concentration, 2.7 ± 0.4 mg/kg, was obtained in grey coloured paints (Table 4).

Copper (Cu)

Copper plays a critical role in human metabolism as a co-factor of key metabolic enzymes involved in respiration, neurotransmitter biosynthesis, radical detoxification, iron metabolism and many other physiological processes.^[34] In recent years, nutritionists have been more concerned about copper toxicity than copper deficiency. Excessive copper intake can cause nausea, vomiting, abdominal pain and cramps, headache, dizziness, weakness and diarrhea^[17] The concentrations of copper in all the paint samples ranged from 133-1,840 mg/kg (Supplemental Material). The highest concentration of Cu was 1,840 mg/kg, obtained in a paint produced by manufacturer I (an unregistered manufacturer).

This was followed by 1,810 mg/kg and 1,790 mg/kg in paints produced by manufacturer I and N (both unregistered manufacturers), respectively. The lowest concentration of Cu was 133 mg/kg, obtained in a paint produced by manufacturer C (a registered manufacturer). The highest mean concentration of Cu was 1,730±32 mg/kg, obtained in paints produced by manufacturer I, followed by 1,690±66 mg/kg and 881±69 mg/kg in paints produced by manufacturer N and manufacturer A (a registered manufacturer), respectively. The lowest mean concentration was 154±6.9 mg/kg in paints produced by manufacturer C (Table 3).

The concentrations of copper in all the available paint colours ranged from 133-1,840 mg/kg in a blue and a white coloured paints, respectively. The highest Cu concentration was 1,840 mg/kg in a white coloured paint, followed by 1,810 mg/kg and 1,790 mg/kg in a blue and a green coloured paints, respectively. The lowest Ni concentration was 133 mg/kg in a blue coloured paint. The highest mean concentration of Cu with respect to colours was 880±5.0 mg/kg in white coloured paints, followed by 859±25 mg/kg and 820±38 mg/kg in cream and green coloured paints, respectively. The lowest mean concentration, 171±3.5 mg/kg, was obtained in violet coloured paints (Table 4).

Zinc (Zn)

Zinc is an essential metal responsible for the catalytic activity of more than 200 enzymes and plays a role in immune function, wound healing, protein synthesis, DNA synthesis and cell division. It supports normal growth and development during pregnancy, childhood and adolescence.^[35] Excessive absorption of Zn suppresses Cu and Fe absorption.^[36] Acute adverse effects of high Zn intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea and headaches.^[37-39] The concentrations of Zn in all the paint samples ranged from 10.3-220 mg/kg (Supplemental Material). The highest concentration of Zn was 220 mg/kg in a paint produced by manufacturer I (an unregistered manufacturer). This was followed by 196 mg/kg and 195 mg/kg in paints produced by the same manufacturer. The highest mean concentration of Zn was 192±6.5 mg/kg, obtained in paints produced by manufacturer I. This was followed by 154±7.5 mg/kg and 143±12 mg/kg in paints produced by manufacturer G and N (both unregistered manufacturers), respectively. The lowest mean concentration was 16.5±0.5 mg/kg, obtained in paints produced by manufacturer C (an unregistered manufacturer). There is no regulatory standard of Zn in paints presently available.

The concentrations of Zn in all the available paint colours ranged from 10.3-220 mg/kg. The highest Zn concentration was 220 mg/kg in a white coloured paint, followed by 196 mg/kg and 195 mg/kg in a green and a blue coloured paints, respectively. The lowest Zn concentration was 10.3 mg/kg, obtained in a brown coloured paint. The highest mean concentration of Zn with respect to colours was

87.9±4.9 mg/kg in white coloured paints, followed by 87.5±4.1 mg/kg and 86.2±8.1 mg/kg in cream and green coloured paints, respectively. The lowest mean concentration, 18.0±1.7 mg/kg, was obtained in violet coloured paints.

The order of metal concentrations in the paint samples with respect to colour was:

As: chocolate > cream > green > blue > white > orange > red > pink > violet > grey > brown > yellow;

Mn: white > pink > chocolate > cream > green > blue > orange > grey > brown > red > yellow > violet;

Cu: white > cream > green > blue > pink > orange > brown > red > yellow > chocolate > grey > violet;

Fe: violet > red > chocolate > brown > white > orange > pink > green > blue > grey > yellow > cream;

Ni: orange > cream > white > chocolate > green > blue > pink > red > brown > violet > yellow > grey;

Zn: white > cream > green > blue > pink > red > orange > chocolate > yellow > brown > grey > violet.

Results of statistical analysis

The correlation coefficients of heavy metals and metalloid investigated are presented in Table 5. There was a strong significant correlation between As versus Ni and Zn; Ni versus Cu, Mn and Zn; Cu versus Mn and Zn; and Fe versus Zn.

Table 5: Correlation coefficients of heavy metals and metalloid in the paint samples.

	As	Ni	Fe	Cu	Mn	Zn	Colours	Manufacturers
As	1	0.723(**)	0.392(**)	0.233(*)	0.284(**)	0.722(**)	-0.101	0.792(**)
Ni		1	0.346(**)	0.593(**)	0.660(**)	0.649(**)	-0.076	0.897(**)
Fe			1	-0.18	0.008	0.217(*)	0.117	0.395(**)
Cu				1	0.686(**)	0.565(**)	-0.041	0.411(**)
Mn					1	0.453(**)	0.034	0.429(**)
Zn						1	-0.071	0.690(**)
Colours							1	-0.088
Manufacturers								1

Note: ** significant at 0.01, * significant at 0.05

Conclusion

The present study demonstrated wide variations in the concentrations of heavy metals and metalloid in water-based paints in Nigeria. It was found that all the paint samples contained As, a regulated metal, in concentrations far above the permissible limit of 25 mg/kg. Generally, high levels of the investigated heavy metals and metalloid were obtained in paint samples produced by both the registered and unregistered manufacturers. Water-based paints classified as decorative paints must depict beautification and decorative properties but not at the expense of jeopardising human health. With regard to the growing evidence of the effects of heavy metals on cognitive development from both excessive Fe and Cu intake, more research on the bioavailability and exposure of children to heavy metals and metalloids in paints due to hand-to-mouth contact with paint flakes is urgently needed. It should be noted that children have both higher absorption and less effective excretion of several elements in comparison to adults. ^[40,41] Other components of paints such as additives and raw materials may also introduce toxic elements into the paints. Effective legislation, guidelines and strict enforcement is necessary in Nigeria to safeguard public health from exposure to toxic substances in paints and other consumer products.

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References

1. Mohanty, A.; Budhwani, N.; Ghosh, B.; Tarafdar, M.; Chakravarty, S., *Environment, Development and Sustainability*, 2013, 15(6), 1653-61.
2. Beetseh, C. I.; Oragbe, D., *Chemistry and Materials Research*, 2013, 3.
3. Odior, A. O., *Industrial Engineering Letters*, 2012, 2, 18-26.
4. Adamu, A. K.; Yakubu, M. K.; Sunmonu, O. K., *International Conference on Biological, Chemical and Environmental Sciences*, 2014 (BCES-2014).
<http://iicbe.org/upload/8184C614005.pdf>.
5. Karakaş, F.; Pyrgiotakis, G.; Çelik, M.S.; Moudgil, B.M., *KONA Powder and Particle Journal*, 2011, 29, 96-106.
6. Li, J., *International Journal of Environmental Research and Public Health*, 2014, 11, 12441-12453.
7. Sherene, T., *Biological Forum*, 2010, 2, 112-121.
8. Apanpa-Qasim, A. F. I.; Adeyi, A. A.; Mudliar, M.N.; Raghunathan, K.; Thawale, P., *Journal of Health and Pollution*, 2016, 6, 43-49.
9. Galadima, A.; Garba, Z.N., *Elixir Pollution*, 2012, 45, 7917-7922.
10. Sindiku, O. K.; Osibanjo, O., *Journal of Toxicology and Environmental Health Sciences*, 2011, 3, 109-115.
11. Omolaoye, A. U.; Gimba, C. E., *Journal of Environmental Chemistry and Ecotoxicology*, 2010, 2, 126-130.
12. Tchounwou, P. B.; Yedjou, C. G.; Patlolla, A. K.; Sutton, D. J., Heavy metal toxicity and the environment. In *Molecular, Clinical and Environmental Toxicology* 2012, 133-164.
13. Basu, A.; Panda, S.S.; Dhal, N.K.; *Bulletin of Environment, Pharmacology and Life Sciences*, 2015, 4, 158-169.
14. Mamtani, R.; Stern, P.; Dawood, I.; Cheema, S., *Journal of toxicology*, 2011, Article ID 319136.
15. Frisbie, S.H.; Mitchell, E.J.; Dustin, H.; Maynard, D.M.; Sarkar, B., *Environmental Health Perspectives*, 2012, 120, 775.
16. Das, K.K.; Das, S.N.; Dhundasi, S.A., *Indian Journal of Medical Research*, 2008, 128, 412.
17. Araya, M.; Pizarro, F.; Olivares, M.; Arredondo, M.; Gonzalez, M.; Méndez, M., *Biological Research*, 2006, 39, 183-187.
18. Aras, M. A.; Aizenman, E., *Antioxidants and Redox Signaling*, 2011, 15, 2249-2263.
19. Vahter, M., *Annual Review of Nutrition*, 2009, 29, 381-399.
20. Fowler, B. A. (Ed.), *Biological and Environmental Effects of Arsenic*, 2013, Elsevier, Chicago
21. Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N., *Interdisciplinary Toxicology*, 2014, 7, 60-72.
22. Xu, J.; Shi, H.; Ruth, M.; Yu, H.; Lazar, L.; Zou, B.; Zhao, J., *PLoS one*, 2013, 8, e70618.
23. Keil, D.E.; Berger-Ritchie, J.; Gwendolyn A. M., *LabMedicine*, 2011, 42, 735-742.
24. European Union EN71-3. 2009. 8 Major Metal Migration Test.
https://twap.sgs.com/sgsrsts/en/mini-site/Testing%20Service/2-Testing%20Service%20DM/EN71-3_8_Major_Heavy_Metal_Migration_Test.pdf

25. Smith, S. J.; Hadler, K. S.; Schenk, G.; Hanson, G. R.; Mitić, N., *Manganese Metalloproteins In Metals in Biology*, 2010, 273-341, Springer, New York.
26. Aschner, J. L.; Aschner, M., *Molecular Aspects of Medicine* 2005, 26, 353-362.
27. Erikson, K.M.; Thompson, K.; Aschner, J.; Aschner, M., *Pharmacology & Therapeutics*, 2007, 113, 369-377.
28. Dobson, A.W.; Erikson, K.M.; Aschner, M., *Annals of the New York Academy of Sciences*, 2004, 1012, 115-128.
29. Valko, M.; Rhodes, C. J.; Moncol, J.; Izakovic, M. M.; Mazur, M., *Chemico-Biological Interactions*, 2006,160 (1), 1-40.
30. Bhasin, G.; Kauser, H.; Athar M., *Cancer Letters*, 2002, 183(2), 113–122.
31. International Agency for Research on Cancer (IARC), *Monographs on the Evaluation of Carcinogenic Risks to Humans*, 1990. <http://monographs.iarc.fr/ENG/Monographs/vol49/>,1990.
32. United States Department of Health and Human Services, *Toxicological Profile for Nickel*, 2005. <http://www.atsdr.cdc.gov/toxprofiles/tp15.pdf>, 2005.
33. Das, K.K.; Das, S.N.; Dhundasi, S.A., *Indian Journal of Medical Research*, 2008, 128, 412.
34. Osredkar, J.; Sustar, N., *Journal of Clinical Toxicology*, 2011, S3, 2161-0494.
35. Johnstone, J.; Roth, D. E.; Guyatt, G.; Loeb, M., *Canadian Medical Association Journal*, 2012, cmaj-111990.
36. Whitney, E.N.; Rolfes, S.R., *Understanding Nutrition* (10th edition), 2010, 447-450.
37. Frazzini, V.; Rockabrand, E.; Mocchegiani, E.; Sensi, S. L., *Biogerontology*, 2006, 7 (5-6), 307-314.
38. Aras, M. A.; Aizenman, E., *Antioxidants and Redox Signalling*, 2011, 15 (8), 2249-2263.
39. Blake, S., *Vitamins and Mineral Demystified*, 2007, McGraw-Hill Professional, p. 242.
40. Oskarsson, A.; Hallén, I.P.; Sundberg, J.; Grawé, K.P., *Analyst*, 1998, 123 (1), 19-23.
41. Ljung, K.; Vahter, M.; *Environmental Health Perspectives*, 2007, 115 (11), 1533–1538.

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Supplemental material: Concentrations (mg/kg, in dry weight) of metals and metalloid in paint samples with respect to manufacturers

Manufacturer codes	Primary colours in samples collected	As		Mn		Cu		Fe		Ni		Zn	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
A	blue	383	414	109	120	813	868	1000	1280	4.88	3.57	20.5	24.6
	brown	432	454	135	134	733	986	1010	1140	1.74	3.09	20.7	22.8
	chocolate	675	673	126	128	724	743	1050	1040	4.19	4.38	20.0	22.5
	cream	653	708	123	134	711	771	1120	1110	3.48	4.63	18.1	22.3
	green	435	472	116	135	1040	988	1130	1120	2.34	3.15	26.0	29.1
	grey	809	873	143	135	774	991	1170	1040	1.83	2.89	19.8	22.9
	pink	459	529	121	153	800	717	1060	1120	1.76	2.33	21.7	19.7
	red	735	826	119	130	890	757	1270	1160	2.40	2.09	20.3	23.0
	white	743	768	124	136	1020	1330	1320	1580	3.22	2.30	24.5	21.1
	yellow	786	773	136	153	1030	931	1190	1180	2.90	3.59	18.3	20.4
B	blue	526	547	46.2	49.8	654	624	2020	2180	1.46	1.43	22.4	20.0
	green	603	558	48.2	55.1	757	756	1110	1100	1.57	2.12	25.7	25.2
	orange	532	605	46.9	52.2	640	617	1840	1120	1.63	3.94	20.6	22.3
	pink	774	766	57.5	57.9	658	763	1130	1220	4.00	2.23	16.2	19.4
	red	920	921	50.6	58.2	741	761	2150	2220	2.02	3.09	23.1	22.9
	white	520	570	48.7	49.4	674	714	1210	1490	2.44	1.86	26.6	26.8
	yellow	612	662	51.7	54.2	600	600	1080	1190	2.14	3.12	23.6	25.7
	brown	475	449	48.3	46.8	674	625	1710	1950	2.67	2.59	34.7	37.1
cream	594	644	43.0	47.9	775	791	1260	1370	1.23	2.04	31.9	32.2	

Supplemental material: Concentrations (mg/kg, in dry weight) of metals and metalloid in paint samples with respect to manufacturers

Manufacturer codes	Primary colours in samples collected	As		Mn		Cu		Fe		Ni		Zn	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
C	blue	1260	1250	24.8	26.7	159	133	2040	2010	6.91	5.29	10.7	12.9
	brown	1220	1270	28.6	21.9	136	165	2510	2380	4.51	5.99	10.3	12.7
	chocolate	1210	1260	24.2	24.6	151	149	2730	2300	3.82	3.89	19.9	17.3
	green	1200	1220	23.7	22.9	149	165	1950	2200	7.00	7.25	15.8	16.7
	grey	1190	1170	23.7	25.0	151	139	1910	1850	3.21	2.92	21.7	18.7
	red	1280	1220	24.2	28.9	162	134	2000	2070	5.78	3.64	16.0	17.5
	violet	1120	1190	21.4	22.1	168	173	2130	2120	3.62	4.52	16.8	19.2
	white	1070	1070	27.6	25.1	154	142	2210	2110	3.21	3.62	14.4	13.2
	yellow	1290	1280	28.7	26.5	168	182	2210	2230	3.97	5.15	20.3	22.7
D	blue	876	840	35.2	33.0	784	742	940	988	5.28	4.98	11.4	10.9
	cream	845	824	22.6	23.4	674	700	742	742	7.71	8.22	15.4	15.9
	green	740	760	24.0	23.8	542	542	989	999	1.18	1.01	18.2	20.2
	red	910	890	22.8	24.6	773	782	880	880	2.04	2.94	20.2	19.2
	white	789	781	23.8	24.1	742	752	859	870	2.45	2.12	20.2	19.7
E	blue	797	765	59.1	60.1	731	725	1110	1000	2.95	3.11	23.2	19.8
	cream	790	854	50.1	49.2	620	640	1350	1300	3.85	2.76	18.7	19.7
	green	819	822	54.4	50.0	734	701	1290	1240	1.48	1.27	18.7	21.8
	white	844	855	52.0	54.3	739	734	1170	1100	1.81	2.90	19.7	22.5
	yellow	778	733	50.2	51.7	677	668	1400	1440	1.33	2.00	19.7	20.0

Supplemental material: Concentrations (mg/kg, in dry weight) of metals and metalloid in paint samples with respect to manufacturers

Manufacturer codes	Primary colours in samples collected	As		Mn		Cu		Fe		Ni		Zn	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
F	blue	870	879	52.5	53.5	419	420	1340	1310	3.89	3.99	96.8	96.9
	cream	888	845	56.3	51.2	459	422	1430	1420	3.60	3.82	97.9	88.4
	green	898	889	56.3	54.5	442	420	1400	1390	3.69	3.50	78.9	76.7
	red	888	878	56.7	50.1	547	552	1520	1510	2.60	3.59	95.9	94.8
	white	826	879	45.7	52.5	657	620	1470	1530	3.27	3.89	98.8	96.8
	yellow	795	863	52.2	57.3	536	572	1420	1480	4.52	5.34	94.2	101
G	blue	1720	1560	59.9	57.6	645	679	1800	1900	17.2	18.9	167	143
	cream	1120	1220	57.4	59.8	726	849	1830	1760	18.6	18.5	137	147
	green	1590	1460	68.7	55.4	658	700	1810	1770	18.2	17.7	181	180
	white	1290	1220	64.8	68.6	697	636	1860	1960	18.4	19.5	139	140
H	blue	1680	1700	105	102	624	613	1100	1010	11.8	11.0	100	118
	cream	1670	1570	124	110	711	657	1170	1380	17.8	18.6	110	121
	green	1720	1720	112	124	669	653	1210	1100	28.2	30.6	118	114
	pink	1760	1780	117	127	694	712	1880	1830	29.4	28.1	106	116
	white	1680	1630	112	125	788	796	1680	1820	30.0	25.7	99.0	104
I	blue	1820	1810	155	158	1810	1790	1290	1210	85.0	91.0	195	182
	cream	1830	1930	132	130	1640	1550	1020	1060	81.3	80.9	189	172
	green	1920	1910	141	148	1740	1760	1150	1130	90.1	90.0	196	190
	white	1760	1900	150	144	1840	1740	1240	1190	81.2	81.0	193	220

Supplemental material: Concentrations (mg/kg, in dry weight) of metals and metalloid in paint samples with respect to manufacturers

Manufacturer codes	Primary colours in samples collected	As		Mn		Cu		Fe		Ni		Zn	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
J	blue	1710	1770	119	125	634	586	1610	1500	73.5	71.7	127	117
	cream	1700	1800	92.0	102	611	646	1100	1160	92.3	99.2	109	108
	green	1720	1700	106	101	793	742	1630	1460	83.7	93.1	126	123
	red	1700	1680	121	117	607	579	2140	2000	86.9	97.1	118	117
	white	1760	1710	113	102	694	568	1910	2150	82.4	83.0	118	121
K	blue	1740	1680	88.0	87.9	767	791	2080	2070	80.1	79.9	113	123
	chocolate	1790	1830	91.9	99.8	784	730	2060	2050	79.1	72.8	112	93.0
	cream	1720	1740	92.1	90.4	880	839	2180	2170	70.9	79.8	144	151
	green	1860	1860	90.1	91.2	723	743	2130	2230	74.7	71.2	102	121
	red	1710	1730	91.8	87.7	638	687	2170	2330	75.1	80.0	109	100
white	1770	1780	88.9	83.9	797	783	2190	2180	77.8	76.5	130	140	
L	blue	1530	1560	109	100	779	743	1070	1080	73.6	81.5	69.8	60.1
	brown	1580	1540	99.0	107	934	901	1420	1560	83.9	91.1	61.0	66.8
	chocolate	1680	1670	132	124	622	720	1410	1470	94.6	90.8	62.1	68.5
	cream	1650	1670	109	107	660	651	1850	1770	84.0	85.3	55.2	55.5
	green	1620	1580	123	119	653	710	1611	1700	94.6	88.0	50.1	58.9
	orange	1600	1540	117	105	752	679	1570	1510	87.4	91.5	58.3	54.0
	pink	1600	1610	121	128	748	712	1640	1650	91.8	93.1	66.8	67.5
white	1540	1520	102	113	838	867	1570	1630	92.2	93.4	64.8	61.5	

Supplemental material: Concentrations (mg/kg, in dry weight) of metals and metalloid in paint samples with respect to manufacturers

Manufacturer codes	Primary colours in samples collected	As		Mn		Cu		Fe		Ni		Zn	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
M	blue	1560	1570	78.6	81.2	893	944	1920	1980	77.7	75.9	103	93.4
	cream	1530	1540	94.5	92.3	968	897	1610	1830	78.3	87.8	95.1	88.1
	green	1520	1400	86.6	88.5	886	867	2120	2390	76.8	75.6	87.7	105
	orange	1470	1570	90.6	89.4	823	895	2040	2010	77.8	77.2	95.7	91.0
	pink	1410	1350	103.4	89.9	830	877	2440	2450	76.3	75.5	97.8	96.8
	red	1520	1560	96.8	90.2	721	730	2180	2200	76.2	81.0	89.2	94.1
	white	1110	1130	94.8	100	891	991	2910	2410	79.2	79.0	105	96.4
N	blue	1480	1430	174	177	1640	1600	2040	1960	166	125	166	135
	cream	1470	1410	178	182	1740	1740	1890	1990	135	140	110	123
	green	1400	1340	180	182	1790	1580	2080	1970	118	122	165	123
	white	1350	1390	200	189	1750	1680	2150	1950	167	199	164	159