

**ILJS-24-054 (SPECIAL EDITION)****Health Risk Assessment of Trace Elements in Groundwater Around Marble Mine in Owa-Kajola, Southwestern Nigeria*****K. O. Ibrahim^{1,2}, S. A. Oke², M. A. Yusuf¹, M. W. Purchase³**¹Department of Geology and Mineral Sciences, University of Ilorin, Ilorin, Nigeria.²Department of Civil Engineering, Central University of Technology Free State, South Africa.³Department of Geology, University of the Free State, South Africa.**Abstract**

This study was carried out to assess health risk of trace elements in groundwater around marble mine in Owa-Kajola, Southwestern Nigeria. Groundwater samples were collected from twenty (20) hand dug wells and analyzed for trace elements (Cd, Cr, Cu, Fe, Mn, Pb and Zn). The results show that concentrations of Cd (0.016 ppm) and Pb (0.20 ppm) are above recommended limits of WHO and NSDWQ which attributed to geogenic and anthropogenic sources. The average values of exposure dose in Fe and Zn are 8.898 mg/kg/day and 3.769 mg/kg/day respectively and above standard limits. In children, average Cd is 0.622 mg/kg/day which is < 1 while other trace elements are higher in values. The hazard quotient (HQ) and hazard index (HI) values in adults and children are < 1 and these show that groundwater in study area is low non-carcinogenic risk. The average values for chronic daily intake (CDI) are < 1 and groundwater is less risk. The average carcinogenic risk values computed for Cd (6E-05 to 2E-04), Cr (8E-04 to 3E-03) and Pb (5E-02 to 2E-01) exceeded the recommended values of 10E-6 and 10E-4 in both adults and children with health implications such as kidney disease, lung cancer among others. High concentrations of some trace elements in analyzed groundwater could be from geogenic and anthropogenic sources in study area. Regular monitoring of groundwater in study area is recommended.

Keyword: Mining; marble; health risk; groundwater, health index; carcinogenic**1. Introduction**

Mining of natural resources of any kind either metallic, non-metallic minerals or fossil fuels (petroleum, coal and natural gas) play an important role in the economic development of any nation such as job opportunities in both private and public sectors, rise in foreign exchange among others (Adegbe et al., 2017). However, the mining activity has been connected with an array of environmental consequences (Tella and Danjibo, 2024). Mining not only forms a groundwater landing funnel but also pollutes aquifer, adversely affecting the groundwater environment and seriously endangering the health and safety of residents. Marble quarry is one of the wastes generating industry and about 70% of this precious mineral resource is wasted in the mining, processing, and polishing procedures. Around 40% of marble waste is generated worldwide during quarrying operations in the form of rock fragments and being dumped either in nearby empty pits, roads, riverbeds, pasture lands, agricultural fields or landfills leading to wide spreading environmental pollution.

Mining involves discharges of some effluents that contain trace elements and high amount of these trace elements in water, soil or plant may cause consequential changes in the quality of water, soil or plant (Ibrahim et al., 2024). Geochemical assessment of marble in study area for cement production has been investigated by Adedoyin et al., (2020). However, environmental impact of marble mining in study area has not been reported.

Therefore, this study was carried out to assess health risk of trace elements in groundwater around marble mine in Owa-Kajola, Southwestern Nigeria.

2. Location and geology of study area

The study area (Owa-Kajola) lies between $N8^{\circ}14'00''$ to $N8^{\circ}24'20''$ and $E5^{\circ}05'13''$ to $E5^{\circ}12'26''$ (Fig.1). The study area falls within the Basement Complex of South-western Nigeria which is northern continuation of the Ilesha Schist Belt (Adedoyin et al., 2020). It is essentially a Precambrian suite of intensely deformed metasediments which occupy a linear belt underlain by rock of migmatite gneiss, amphibolite, calc-silicate gneiss, mica schist, quartzite (member of the Omu-Aran Dyon Hills), pegmatite of Precambrian age and marble. The lenticular marble deposit occurs in the study area (Adedoyin et al., 2020) and is well exposed about two kilometers south of Owa-Kajola to the east of a major quartzite hill. The groundwater is tapped by wells located in the fractures and in extensive weathered zones which are mainly recharged by rainfall.

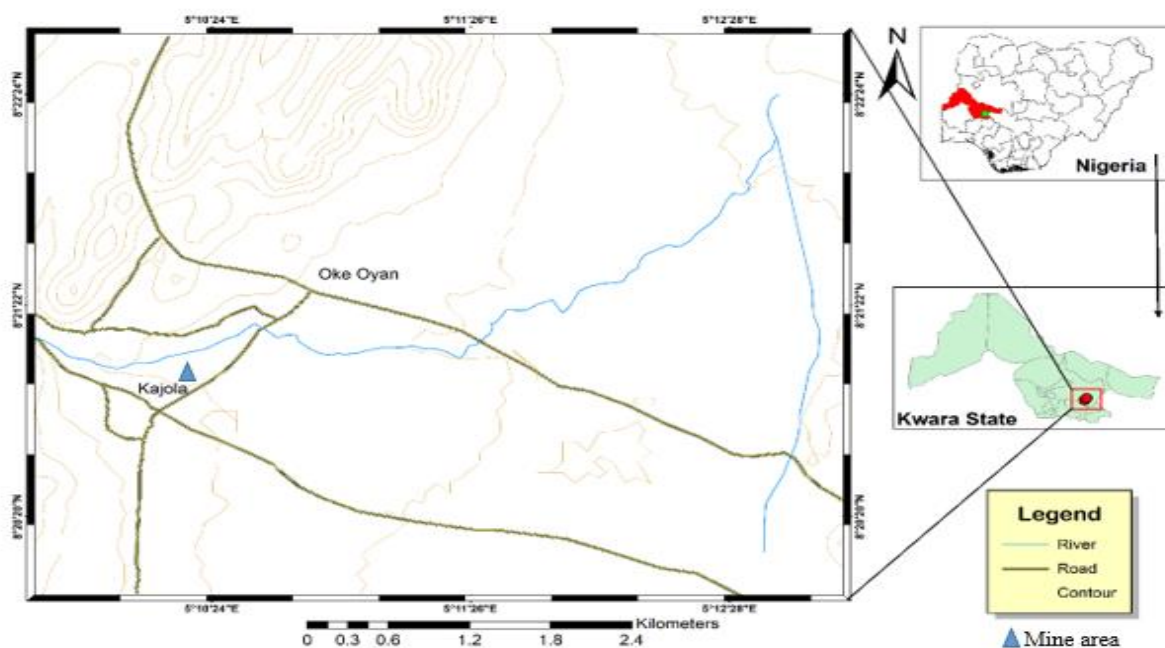


Fig.1. Location map of study area

3. Materials and Methods

Groundwater samples were collected from twenty (20) hand-dug wells and analysed for trace elements (Cd, Cr, Cu, Fe, Mn, Pb and Zn). Groundwater samples were collected using polyethylene bottles of one litre capacity during late dry season of 2023. The water from hand-dug wells were allowed to flow for about two minutes before collected, and containers were thoroughly washed and rinsed with the water to be collected. Groundwater samples collected from hand dug wells were analysed for trace element concentrations. The digestion process was monitored to ensure that it was running smoothly within normal temperature and time limits. Once the block had been digested, the tubes were taken out and left to cool at ambient temperature. A vortex stirrer was used to combine 25 cm^3 of 0.1% HNO_3 , which was then transferred to a 50 cm^3 centrifuge tube, sealed, and centrifuged for about 15 minutes at 500 rpm. A decanted sample of 10 cm^3 of the digested solution was used for Atomic Absorption Spectrophotometry (AAS). The analyses were carried out in accordance with American Public Health Association Standards and Nigerian Standard for Drinking Water Quality (NSDWQ 2007) at Central Research Laboratory, University of Ilorin, Nigeria.

3.1 Quantitative Health Risk Assessment:

The Average Daily Dose: The Average Daily Dose was computed using equation 1 to estimate the health risk of the groundwater samples in the study area.

$$ADD = \frac{C_{water} * IR * EF * ED}{BW * AT} \quad (1)$$

where, ADD is the Average Daily Dose similar to the exposure dose through ingestion of water ($\mu\text{g}/\text{kg}/\text{day}$); C_{water} is the average concentration of the estimated metals in water ($\mu\text{g}/\text{L}$); IR is the ingestion rate in this research (2.72 L/day for adults; 1.8 L/day for children); EF is the exposure frequency (365 days/year); ED is the exposure duration (70 years for adults; and 6 years for children); BW is the average body weight (70 kg for adults; 15 kg for children); AT is the averaging time (365 days/year \times 70 years for an adult; 365 days/year \times 6 years for a child), Edokpayi, *et al.* (2018). Hazard quotient (HQ) as shown in equation is used to calculate the HQ of the study area:

$$HQ = \frac{ADD}{RfD} \quad (2)$$

ADD is the average daily dose similar to the exposure dose through ingestion of water ($\mu\text{g}/\text{kg}/\text{day}$); RfD is the reference dose of a specific element. The reference dose for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 1 mg/kg/day, 0.0003 mg/kg/day, 0.2 mg/kg/day, 1.5 mg/kg/day, 0.04 mg/kg/day, 0.7 mg/kg/day, 0.046 mg/kg/day, 0.02 mg/kg/day, 0.0035 mg/kg/day and 0.3 mg/kg/day respectively (USEPA, 2001). If the value of HQ is greater than unity, that is, 1, there is possibility of non-carcinogenic negative effects on health while HQ value less than unity infers that the exposure to the surface water consumption would not likely have any practical effect on the consumers (USEPA 2001; Joel *et al.*, 2018).

Hazard index (HI) is used to assess the overall potential non-carcinogenic health effects posed by more than one metal and pathway, the addition of the computed HQ across trace elements was expressed as hazard index (HI) using equation 3 according to USEPA (1989):

$$HI = \sum_{i=1}^n HQ \quad (3)$$

$HI > 1$ is an indication of a potential adverse effect on human health (Omotoso *et al.*, 2021). Chronic Daily Intake (CDI) according to Edokpayi *et al* (2018) can be calculated using equation 4:

$$CDI = C_{water} * \frac{DI}{BW} \quad (4)$$

where C_{water} , DI and BW denote the concentration of trace elements in water (measured in mg/kg), average daily intake of water (2.72 L/day for adults; 1.8 L/day for children) and body weight (70 kg for adults; 15 kg for children), respectively. Carcinogenic Risk (CR) from Edokpayi *et al* (2018) was determined using equation 5:

$$CR_{ing} = \frac{Exp_{ing}}{SF_{ing}} \quad (5)$$

where CR_{ing} = carcinogenic risk via ingestion route and SF_{ing} = carcinogenic slope factor where Pb is 8.5E, Cd is 6.1E+03 and Cr is 5.0E+02 $\mu\text{g}/\text{kg}/\text{day}$ (Omotoso *et al.*, 2021). The CR_{ing} values for other trace elements were not computed in this study because of unobtainability of the SF_{ing} values.

4. Result and Discussion

The results of trace elements in groundwater samples are presented in Table 1 and Figure 2 which illustrates the profile of the average concentrations of the selected trace elements compared with WHO (2006) and NSDWQ (2007). The average concentrations of trace elements in analyzed groundwater samples are below standard limits except for chromium (Cr) and lead (Pb) and these could be from geogenic and anthropogenic sources such as corrosion of lead plumbing (Pb), more acidic soils (Cr), pollution through irrigation and

atmospheric deposition (Cr). High concentration of these trace elements in groundwater could result to hearing loss, anemia, kidney impairment, immune system dysfunction, lung cancer and prostate cancer.

Table 1: Statistical summary of the selected trace elements (ppm) in study area

S/N	Cd	Cr	Cu	Fe	Mn	Pb	Zn
OW-KJ 01	0.010	0.040	0.010	0.120	0.030	0.040	0.040
OW-KJ 02	0.020	0.020	0.010	0.400	0.010	0.030	0.060
OW-KJ 03	0.010	0.020	0.010	0.370	0.010	0.010	0.050
OW-KJ 04	0.010	0.030	0.030	0.210	0.010	0.010	0.050
OW-KJ 05	0.020	0.010	0.010	0.360	0.010	0.020	0.040
OW-KJ 06	0.020	0.010	0.020	0.160	0.010	0.020	0.050
OW-KJ 07	0.030	0.030	0.010	0.190	0.030	0.030	0.480
OW-KJ 08	0.010	0.020	0.020	0.140	0.010	0.010	0.050
OW-KJ 09	0.020	0.020	0.020	0.240	0.040	0.020	0.080
OW-KJ 10	0.010	0.020	0.010	0.100	0.010	0.010	0.070
Average	0.016	0.022	0.015	0.229	0.017	0.020	0.097
WHO (2006)	0.003	0.050	2.000	0.300	0.500	0.010	3.000
NSDWQ (2007)	0.003	0.030	1.000	0.3000	0.200	0.010	3.000

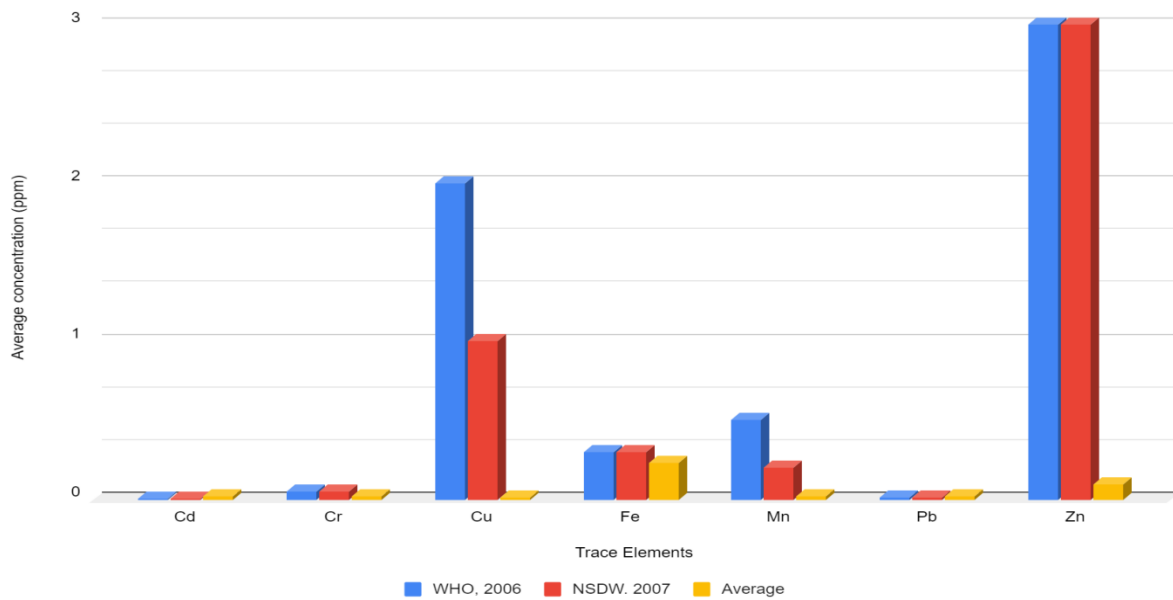


Fig.2. Average concentrations of trace elements in study area with WHO (2006) and NSDWQ (2007)

Table 2. Computed Hazard Quotient and their Statistical Descriptions in Children

Sample ID	HQ (Children)						Hazard Index
	Cr	Cu	Fe	Mn	Pb	Zn	
OW-KJ 01	0.0032	0.03	0.0206	0.0783	1.3714	0.016	1.52
OW-KJ 02	0.0016	0.03	0.0686	0.0261	1.0286	0.024	1.18
OW-KJ 03	0.0016	0.03	0.0634	0.0261	0.3429	0.02	0.48
OW-KJ 04	0.0024	0.09	0.036	0.0261	0.3429	0.02	0.52
OW-KJ 05	0.0008	0.03	0.0617	0.0261	0.6857	0.016	0.82
OW-KJ 06	0.0008	0.06	0.0274	0.0261	0.6857	0.02	0.82
OW-KJ 07	0.0024	0.03	0.0326	0.0783	1.0286	0.192	1.36
OW-KJ 08	0.0016	0.06	0.024	0.0261	0.3429	0.02	0.47
OW-KJ 09	0.0016	0.06	0.0411	0.1043	0.6857	0.032	0.92
OW-KJ 10	0.0016	0.03	0.0171	0.0261	0.3429	0.028	0.45
Average	0.0018	0.045	0.0393	0.0443	0.6857	0.0388	0.85

Table 3. Carcinogenic risk values in adults and children (mg/kg)

Sample ID	Carcinogenic Risk (Adults)			Carcinogenic Risk(Children)		
	Cd	Cr	Pb	Cd	Cr	Pb
OW-KJ 01	6E-05	3E-03	2E-01	6E-04	7E-03	4E-01
OW-KJ 02	1E-04	2E-03	1E-01	2E-04	5E-03	1E-01
OW-KJ 03	6E-05	2E-03	5E-02	4E-04	5E-03	3E-01
OW-KJ 04	6E-05	2E-03	5E-02	2E-04	5E-03	1E-01
OW-KJ 05	1E-04	8E-04	9E-02	3E-04	5E-03	3E-01
OW-KJ 06	1E-04	8E-04	9E-02	2E-04	2E-03	1E-01
OW-KJ 07	2E-04	2E-03	1E-01	6E-04	1E-02	6E-01
OW-KJ 08	6E-05	2E-03	5E-02	1E-04	2E-03	1E-01
OW-KJ 09	1E-04	2E-03	9E-02	1E-06	2E-05	2E-03
OW-KJ 10	6E-05	2E-03	5E-02	3E-04	5E-03	3E-01

The computed average values of hazard quotient for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 0.0006, 0.0146, 0.0127, 0.0144, 0.2220 and 0.0126 respectively. All the average values are less than unity (USEPA 1989; Su

et al., 2017). The Hazard Index ranges from 0.14 to 0.49 with an average 0.28. It indicates a low Hazard Index (USEPA, 1989). Three carcinogenic elements were considered in this research (Cd, Cr, and Pb). The average computed values of hazard quotient for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 0.0018, 0.0450, 0.0393, 0.0443, 0.6857 and 0.0388 respectively. The Hazard Index ranges from 0.45 to 1.52 with an average of 0.85. This indicates a low to high health risk for Children. In adults Cd ranges from 6E-05 to 2E-04 with an average of 1E-04, Cr ranges from 8E-04 to 3E-03 with an average of 2E-03, Pb ranges from 5E-02 to 2E-01 with an average of 9E-02. In children Cd ranges from 1E-06 to 6E-04 with an average of 3E-04, Cr ranges from 2E-05 to 1E-02 with an average of 5E-03, Pb ranges from 2E-03 to 6E-01 with an average of 2E-01. However, the average carcinogenic risk values exceeded the prescribed limit of 10E-6 and 10E-4 respectively (Edokpayi et al., 2018). This is likely to pose a potential carcinogenic health risk hazard to both adults and children drinking the water in the investigated area. In adults, Cd ranges from 6E-05 to 2E-04 with an average of 1E-04, Cr ranges from 8E-04 to 3E-03 with an average of 2E-03, Pb ranges from 5E-02 to 2E-01 with an average of 9E-02. In children Cd ranges from 1E-06 to 6E-04 with an average of 3E-04, Cr ranges from 2E-05 to 1E-02 with an average of 5E-03, Pb ranges from 2E-03 to 6E-01 with an average of 2E-01. However, the average carcinogenic risk values exceeded the prescribed limit of 10E-6 and 10E-4 respectively (Edokpayi et al., 2018). This is likely to pose a potential carcinogenic health risk hazard to both adults and children consuming the water in the investigated area.

5. Conclusion and recommendation

Concentrations of trace elements in groundwater are less than standard limits except for chromium (Cr) and lead (Pb). The exposure dose through ingestion for adults is higher in iron and zinc. High amount of iron may cause groundwater to have poor taste and colour. High zinc intake might cause intestinal haemorrhage and muscular pains. Values for hazard quotient are less than recommended limits and hazard index for both age groups are < 1 and therefore, groundwater in study area is a low non-carcinogenic risk. Chronic daily intake values for both adults and children are generally < 1 and groundwater are of less risk. The average carcinogenic risk values computed for Cd, Cr and Pb exceeded recommended values in adults and children respectively. This could pose a serious health risk to the consumers most especially children with possible low immunity. This study recommended continuous monitoring of groundwater in study area.

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