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The Risk Assessment of Heavy Metals in Marble Building Materials used in Saudi Arabia

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Abstract: **A comprehensive analysis of heavy metals contamination was carried out in the marble building materials collected from di erent stores in Riyadh, Saudi Arabia, in which is subject to rapid construction development. In Riyadh, it has been observed environmental issues due to heavy metal pollution from new construction projects of underground metro as well as other new infrastructural developments. Therefore, it is very important to carry out an investigation of presence of heavy metals in marble materials as major unit of construction building materials. The bene t of full statistical evaluation was conducted to represent relationship models of the contents of heavy metals (Cr, Cd, Pb, Ga, and U)in marbles used in Saudi building. Four di erent methods of matrix correlations were used to obtained full spectra of relationship between studied heavy metals and other elements. Normality tests were conducted to help the statistical performance to treat the results as parametric. Moreover, Shewhart con dence limit tests were also applied to the reported data of each heavy metals to tell us the sample out of con dence limits. Lucky, all the statistical tests were within good agreement with critical values. The obtained data were compared with the value of heavy metals in upper earth crust reported by Muller. Geo-chemical indexes calculations were performed using geochemical hazard index, background enrichment index and other useful indexes. The values of hazard indexes were compared with tabulated or recommended values. The present study was found that marbles did not possess any signi cant hazard in term of heavy metals to the residents of Riyadh.**

Keywords: **Heavy Metals Contamination, Geo-chemical indexes calculations.**

1. INTRODUCTION

The term of heavy metal is used to the group of metals and semimetalss that have been linked with pollution and toxicity. It is always refers to well-known metals previously mentioned. Some researchers de ne them as metal with an atomic mass greater than Na, while others de ne as metal with greater than 3.5g/cm^3. Others term often uses to semi metals e.g As, Cu due to toxicity are similar. Some of these elements are brie y discussed.

Studies of heavy metals in the environment are an essential part to fully understand their behaviours into the environment. Most of the studies have been greatly focused on heavy metals in water, sediments and soils owing to their high potential hazards (El-Sayed et al, 2015)(Luo et al,2012). In fact, heavy metal in water environments are well organized. Thus, significant work have been expended to evaluate their presence in ecosystem (Lin et al, 2013)(Zhang, Weiguo et al, 2009)(Tchounwou, et al, 2012) whereas almost no investigation has been considered the heavy metals in building materials particularly marbles. Therefore, e orts are needed to assess presence of heavy metals in building materials.

Internal building materials can be significant contaminant emission sources. Heavy metals are often used to form coloured ions, which are utilized in making paints. For instance, in Nigeria, the reported data are logic. Nduka reported high levels of toxic metals in aked paints in four Nigerian cities (Nduka, JKC et al, 2007). In Nduka's study, Cd, Cr, Fe, Zn, and Cu levels of aked paint received from 50 building of four major cities Enugu, Onitsha, Aba, and Port Harcourt in Nigeria were investigated. He used atomic absorption spectrophotometer (AAS) as analytical tool to exam the content of heavy metals in paints. Cadmium ranged from 9.03 to 10.57 and 6.84 to 10.02 mg/kg in Enugu and Onitsha, respectively. In Aba and Port Harcourt, the levels of cadmium ranged 7.464 9.3 and 7.29 9.39 mg/kg, respectively. Chromium levels were signi cantly lower in Enugu (range 0.94 12.8 mg/kg) when compared with the values from other cities namely Onitsha (range 1.6 15.1 mg/kg), Aba (range 15.206 39.2 mg/kg) and Port Harcourt (range 33.1 55.418 mg/kg).

The use of lead connection pipes and lead pipes in building materials began in early 1800s. Although concerns with regard to health issues of pipes in Europe since 19^{th} century, the uses of lead pipes were installed in US and Europe (Troesken, Werner, 2006). It was estimated that 25% of European building are supplied with drinking water via lead pipes (Hayes, Colin R and Skubala, Nina D., 2009).

Copper pipes have been utilized for domestic water supply for over 200yrs. The reason behind using copper pipes was due to stronger, lighter, and cheaper alternative to Pb. In 1810, the first use of were made from Cu sheet. Since 1810, there have been huge of utilizations and improvements in Cu pipes (Lytle, Darren A, 2010). The major issue with Cu pipes is associated with corrosion. Lucky, this problem was sorted out with plastic pipes.

The solution of lead in building pipes was only to replace them with non-lead pipes which costed in Europe approx. 200m BP as reported by Hayes (Hayes, Colin R and Skubala, Nina D., 2009). Moreover, there were various physical parameter which a ected the presence of lead in pipes and these parameters are out of the paper's scope.

An interesting investigation of Cd and Pb in Kenyan was carried out by Constantine Kameti (2013) using AAS showed very high levels of these elements in oil based paints used for building materials. He reported high levels of lead amounts with a range of 275-37084 ppm for the paint brand with the highest lead levels. To best of authers' knowledge, it has never been reported such levels in the literature and thus we are sure there was a mistake in the analysis.

M. Vespa et al (2006) studied the presence of Co and Ni in cements. He explored the relation between Ni and Co to harden the cement pastes using XRF and XAS techniques. The study showed that Ni(II) shaped predominantly layered double hydroxide (LDH) phases. In contrast to Co, Ni was found to be present in the oxidation states II and III. Co(II) was predominately incorporated into newly formed Co(II) hydroxide-like phases ($Co(OH)_2$), Co-LDH or Co-phyllosilicates, whereas Co(III) tends to be incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate.

A study was taken by Maria F G Barreda (2016) showed presence of heavy metals in raw geological ceramic materials in Spain. Although their study was mainly concentrated on developed method by wave-length XRF, the obtained results were very valuable for literature review. The obtained results were var-ious from low up to high levels of heavy metals indicating no anthropogenic activities. Moreover, the study showed no presence of arsenic in the certified materials of ceramic materials.

Hassan studied the heavy metal contents in household, stairs, and entryway dust collected from Egyptian homes. The reported results showed that the highest levels of Cd, Co, Cu, Ni, and Cr were observed in entryway, followed by stairs and household dust. He concluded to internal sources of heavy metal in building materials . The average levels of the individual metals in dust of the small particle size (less than 38 m) were 268, 196.4 and 254.49 ppm for Pb, 49.6, 43.5 and 46.66 ppm for Ni, 2.86, 2.15 and 2.71 ppm for Cd, 4340, 3796 and 2602 ppm for Al, 2860, 2200 and 2004 ppm for Fe, 209.25, 152.3 and 103.26 ppm for Zn, 4.1, 2.88 and 1.96 ppm for Co, 85.99, 74.06 and 83.17 ppm for Cr and 168.2, 156.5 and 122.02 ppm for Cu in entryway, stairs and household, respectively (Hassan, 2012). Nevertheless, we have great doubt that lead level in Hassan study was probably wrong due to unaccepted high levels of Pb in the reported study.

Rasmussen et al quantified multi-element of indoor dusts collected from 50 houses in Ottawa, Canada. The mean levels (ppm) of these elements in house-hold dust/garden were: lead 233/42; cadmium 4.42/0.27; antimony 5.54/0.25; mercury 1.728/0.055; aluminum 24281/55677; barium 454/763; and thallium 0.14/0.29 (Rasmussen, PE et al, 2001). It was observed that dust generated from sources within the house itself can contribute significantly to exposures to certain elements, such as lead, cadmium, antimony and mercury.

Since the mud is an essential material for building materials thus, it is impor-tant to highlight it in this literature survey. Tayel El-Hasan and his colleagues carried out a study of levels of heavy metals in the Dead Sea and Jordan river sediments in the northern basin of the Dead Sea area in Jordan. The study illustrated that Dead Sea mud had low levels of heavy metals except for lead. Moreover, the study showed insignificant e ect of the mix between heavy metals content in seawater and mud (El-Hasan, Tayel et al, 2009).

Dong-Yan Liu investigated presence of trace metals in Bayer red mud and sintering used and sold in China. The nding showed high levels of As, Pb, and U (Wang, Ping and Liu, Dong-Yan, 2012).

In an Indonesian study carried out by Emad E Dagdag to analyse heavy metals in Lapindo mud in Java. The heavy metal levels in the sediments were in order B Fe Mn Co Mo Cd Cu Zn (Dagdag et al, 2015).

It is well known in KSA, most of modern buildings will last from 30-40yrs, after which they must be demolished. Aftermath, the dusts of construction wastes are spread all over the residential areas, plus carrying heavy-trucks pass-ing through the major roads which contribute as another pollution sink. In capital city, Riyadh, construction activities have intensi ed continuously and rapidly, particularly in northern part of the city owing to underground train project. Consequently, large areas of the city have been contaminated by heavy metals of construction project dusts. Honostly, at night residents breath huge amount of building dust. The question bear-in mind what type of e ect the building materials have on the environment. The answer can be carried out through assessment of heavy metals in construction building.

Therefore, this work was conducted to estimate heavy metal contamination status in building materials used in Riyadh as well as others cities of KSA. The speci c aims of out investigation can be summarized as following:

1. Study heavy metal compositions in marble building materials.
2. Perform full statistical evaluation of the obtained data.
3. Carry out all full pollution risk assessment.

2. Evaluation Of Building Material Contamination

In recent decays, different heavy metal assessment indices applied to sediments have been developed. Metal enrichment as result of pollution can be easily de-tected in a number of applied risk indexes. In heavy or toxic metal researches, many researchers have compared their results to particular environment with similar environment in different regions of the globe. Environmental quality indices are the most powerful tool for evaluation of anthropogenic activities. In recent decades, many risk indexes have been proposed, applied, and developed to facilitate the assess of heavy metal studies (Caeiro et al, 2005). The con-tamination indexes can evaluate the degree to which the effect human and are regarded as officers for the building material quality. None of these methods has been applied on building materials.

In 1980, Hkanson was the rst scientist who used contamination factor and the degree of contaminations to quantify the overall contamination roles of sediments and water.

Yovana Todorova et al (2016) studied contamination levels and ecological risks, associated with heavy metal pollution of sediments in small hydropower cascade using index approach. Yovana identi ed the content of As, Cd, Cu, Hg, Pb, Zn, total organic carbon and their correlations. Cd and Hg originated from di erent source and had specific moving. Based on the contamination and background indices the sediments were moderate contaminated and the potential ecological risk index classified the sediments with the higher risk level.

Each indices indicate the heavy metal contaminants can be broken in three categorises (Varol, Memet, 2011)(Caeiro, S, at, al ,2003) (Howard, at, al 2013):

1. Background enrichment indices which compare the results of the pollutants with baseline content of the earth crust as used in this thesis or other applied backgrounds. The enrichment factor (E.F) is de ned as the ratio of the determined level to probable e ect concentration. The following terminologies are used to describe the enrichment factor: 6 very high contamination factor, 3 C 6 considerable contamination factors, 1 C 3 moderate contamination factors, C 1 low contamination factors. Also, in some studies, researchers have used iron as a conservative tracer to di erentiate natural from anthropogenic contents. This method is more or less qualitative analysis and thus it is less accurate than above mentioned method. To express iron enrichment factor, the following mathematical relationship does de ne it as (Abrahim, GMS and Parker, RJ, 2008):

$$E{:}F = \frac{\left(\frac{m_{sample}}{Fe_{sample}}\right)}{\left(\frac{m_{shale}}{Fe_{shale}}\right)} \quad (1)$$

where;

m_{sample} is the level of the examined metal in the examined sediment or building material.

Fe_{sample} is the level of the reference metal in the examined materials.

m_{shale} is concentration of the examined metal in the average shale or the upper earth crust.

Fe_{shale} is level of the reference metal in the average shale or the upper earth crust.

Memet Varol (2011) studied enrichment factors in sediment from the Tigris River. The mean EF values for all metals studied except Cr and Mn were higher than 1.5 in the sediments of the Tigris River, suggesting anthropogenic activities on the toxic element levels in the river.

Ozkan (2012) carried out a study assessment of heavy metals using enrich-ment factor in inner Izmir Bay. The study showed that enrichment factor values of Hg and Cd were less than 5 indicating moderate enrichment whereas Pb and Cr were highly enriched.

2. Contamination indices which compare pollutant with clean areas. The contamination indices are common criterion to estimate the presence of heavy metals in uncontaminated sediment or the upper earth crust. The geo-accumulation index introduced by Muller to quantify heavy metals in sediments and the index can be computed through the following relation-ship:

$$I_{geo} = \log\left[\frac{C_n}{1{:}5B_n}\right] \qquad (2)$$

where C_n is the reported concentration of the heavy metal (n), B_n is the geochemical level value of heavy metal in the upper earth crust (n), and factor 1.5 is the correction factor due to the variations of background data. The upper earth rock given by Turkman is regarded as the background values of heavy metals in this work as illustrated in Table.1. Table.2, the scale of geo-accumulation index consists of six grades ranging from 0-6 (Caeiro, S, et al, 2005).

In addition, I_{geo} can o er an advantage of reducing the e ects of mother rocks and prominent anthropogenic effects on building heavy metal contamination.

Nevertheless, I_{geo} is only used for a single heavy metal contaminant, so this index cannot furnish a comprehensive details of the contamination status of the building materials (Guan, Yang et al, 2014).

S Odat (2013) studies the levels of heavy metal along the highway of Irbid/Zarqa in Jordan. The study used The geo-accumulation index in which Cd exhibited high level with I_{geo} of 1.4. The rest of reported heavy metals I_{geo} values were below 0.2 demonstrating background levels.

3. Metal contamination Index (MTI). In order to estimate the overall degree of sediment material contamination, the metal contamination index can be computed according to the relationship

$$MPI = (M1\ \ M2\ \ M3::Mn)^{\frac{1}{n}} \qquad (3)$$

Where Mn is the content of heavy metal n expressed in ppm (mg/kg) of dry weight basis (Qingjie, Gong, at, al, 2008).

Therefore; Metal contamination index (MTI) approach can be used for the estimate which shows the composite in uence of individual parameters on the overall quality of building materials. It is also a combined physio-chemical and microbial index which makes it possible to compare the quality of building materials and sediments.

The following description is used for MTI: 150, low risk; 150 300, mod-erate risk; 300 600, considerable risk, 600, very high risk as reported by Muller.

4. Degree of contamination (CD) was defined as the sum of all contamination factors of heavy metal M. CD classification can be found in Table.3

5. Other contamination indexes like Vector modulus and root product, and Nemerow pollution indexes are not used in this work. Newerow was ap-plied (Jie, Chen Qing, Liu Hui, Qian, 2012). Thus, Newerow is a compre-hensive pollution index and a single factor used to assess the pollution of toxic metals in building materials (Hong-gui, Deng et al, 2012).

Table 1: Concentrations of heavy metals in upper earth crust

ppm	**Element**	ppm	**Element**
610	**Sr 88**	20	**V 51**
0.4	**Mo 98**	11	**Cr 52**
0.035	**Cd 111**	1100	**Mn 55**
	Te 130	3800	**Fe 57**
10	**Ba 138**	0.1	**Co 59**
	Tl 205	20	**Ni 60**
9	**Pb 208**	4	**Cu 63**
	Bi 209	20	**Zn 66**
2.2	**U 238**	4	**Ga 69**
		1	**As 75**

Table 2: Muller's classification for the geo-accumulation index

Material Quality	**Class**	I_{geo} **Value**
Uncontaminated	0	0
Uncontaminated to moderately contaminated	1	0-1
Moderately contaminated	2	1-2
Moderately to strongly contaminated	3	2-3
Srongly contaminated	4	3-4
Strongly to extremely contaminated	5	4-5
Extremely contaminated	6	6

Table 3: Muller's classi cation for the degree of contamination (CD)

Material quality	**Values**
Very low degree of contamination	1.5
Low degree of contamination	1.5 CD 2
Moderate degree of contamination	2 CD 4
High degree of contamination	4 CD 8
Extremely degree of contamination	8 CD 16

3. ANALYTICAL WORK

The marble materials were collected from different houseware stores in Riyadh. The proposed materials weathering-effect were removed at the spot and later transported to the our lab. The materials were then crushed using crushing machine. A polyamide screen sieve (mesh size 1mm) was used and then the crushed materials were spread on the sieve by using plastic spatula and soft-shaking. Later, crushed materials were placed in an oven at 110 5 C for overnight in order to ensure no moisture is present in the crushed materials.

Approx. 5gm of each sample was milled to reduce the particle size, and to homogenize the powder sample. After drying, roughly 0.2 gm of of the homogenised sample weight was very carefully measured out into vessel, and weight was recorded with an accuracy of 0.0001gm. A solution of HCl,HF, and HNO_3 was added to the vessel.

The performance was done by microwave assisted digestion using 0.2 g dried sample. After digestion H_3BO_3 was added for complexation of fluorides. Adding boric acid to the digested solution not only complexes the free uo-ride ions in the solution, but also facilitates the dissolution of the precipitated fluorides. The solution in the bottle was the sample diluted to 50 ml in 3.5% HNO_3.

Microwave conditions were: 60 bar in PTFE (polytetra uoroethylene) ves-sels; 35 minutes at 1400 W using a Multiwave 3000 (Anton Paar; Graz, Austria) microwave digestion system. All acids were Merck Suprapur. Determination of heavy metals was carried out by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): NexION 300D (Perkin Elmer, USA) at the chemistry department, king Saud University. The selected parameters of operational system used in this analysis are listed in Table.4.

ICP standard solution was created for the analysis with eight varying levels for each element. High purity certified

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elemental standard (6 CertiPUP, Merck Plasma Standards) was used in this analysis. To ensure that acids used in this work did not a ect the ICP-MS reported data, blank was carried out and acids were used in the standard to the same levels as the sample digestion.

Table 4: Instrumentation operating System for ICP-MS

1600 W	RF power
0.92 L/min	Nebulizer gas ow
9.25 V	Lens Voltage
-1762.5 V	Analog Stage Voltage
1050 V	Pulse Stage Voltage
3	Number of Replicates
20	Reading / Replicates
Peak Hopping	Scan Mode
40 ms	Dwell Time
1200ms	Integration

It was found out that the acids did not have any affect. Every 8th sample run by ICP-MS was standard, to monitor the quality of instrument. Moreover, an internal standard was used to ensure that the instrument did not go out of calibration.

For quality assurance, five certified reference materials were used. The used reference materials were purchased from USGS and they were 69 b bauxite, 1646 a Estaurine Sediment, 1 d Limestone, GBW 07106 Rock, and GBW 07108 Rock.

The reported results of the certified reference materials by ICP-MS lab are listed in Table.5. For major elements of the certified material, the target relative standard deviation was less than 10% and thus all the results above this target were rejected and repeated. Similarly for minor and trace elements, the target relative standard deviation was less than 20%.

The target accuracy of the certified materials has to be above 85% to produce very healthy and comparable results. Fortunately, the obtained result accuracy were above 90% by ICP-MS lab. The accuracy can be computed through equation:

$$R = \frac{\text{measured value}}{\text{true value}} \quad (4)$$

Also, t-tests were conducted for the reference materials analysed in this work. The obtained results were less than the tabulated values indicating good agreement of the reported data. Nevertheless, the t-test results were not reported here.

Therefore, from the obtained results of the reference materials, the precision was less than 10% and the accuracy was better than 90% indicating the obtained data of heavy metals in the study marble material were very comparable.

Table 5: Reported results of reference materials using ICP-MS

U	Bi	Pb	Tl	Ba	Te	Cd	Mo	Sr	As	Ga	Zn	Cu	Ni	Co	Fe	Mn	Cr	V	
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	lab results
9.3	7.1	10.3	0.5	76	0.3	2.1	26.5	9.2	27.7	96	27	11.4	12.9	1.3	6.94	685.8	75.7	147.6	69 b bauxite
1.3	0.3	8.8	0.2	192	0.3	0.2	1.8	71	5.2	4.5	46.6	10.8	21.4	4.9	1.73	219.4	36.2	49	1646 a Estuarine Sediment
0.9	0.1	0.4	0	22.3	0.1	0.6	0.9	236.7	10.6	0.9	15.2	3.4	4.7	24.4	0.17	227.3	9.1	9.3	1 d Limestone
1.9	0.2	6.1	0.3	129.3	200	27	4.7	63.7	6.2	0.49	15.7	17.4	15.3	6.7	2.32	157.7	18.3	36	GBW 07106 Rock
1.4	3.3	10.4	0.2	110	57	29	6.3	876.2	7.2	0.23	47.8	22.9	18.5	8.8	1.68	414.4	24.9	35.3	GBW 07108 Rock
																			edCerti material
U	**Bi**	**Pb**	**Tl**	**Ba**	**Te**	**Cd**	**Mo**	**Sr**	**As**	**Ga**	**Zn**	**Cu**	**Ni**	**Co**	**Fe**	**Mn**	**Cr**	**V**	
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	
		11.8	.....	80	0.214						28			1.1	7.14	850	75	156	69 b bauxite
2		11.7	<0.5	210		0.148	1.8	68	6.23	5	48.9	10	23	5	2.01	234.5	40.9	45	1646 a Estuarine Sediment
1				30				260		1	18		4		0.22	233		10	1 d Limestone
2.1		7.6		143	214	29	5.3	58	5.9	0.76	20	19	16.6	6.4	2.50				GBW 07106 Rock
	3.16			120	62	32	7.1	913	6.6	0.38	52	23.4	17.8	9	1.70		32		GBW 07108 Rock

4. ANALYTICAL RESULTS AND DISCUSSION

The studied marble materials chemical data are listed in Table.33. The sta-tistical calculations are also reported in Table.33. The matrix mathematical calculations using four di erent methods are found in Table.34 and Table.35. The result calculations were subjected into statistical examination which ob-viously showed all the reported data herein passed the statistical examination indicating the reported data were con dent.

Heavy metals associated with marbles are discussed herein with more emphasized on statistical models. As carried in previous sections, only Cr, Cd, Pb, and U are given in details.

4.1 Chromium (Cr):

Cr levels in marble materials were slightly elevated with an average of 13ppm. The lowest reported level of Cr was 0.5 ppm and the highest obtained level was 66 ppm. The data pattern was as follows: 25% was 1.18 ppm, 50% was 2.24 ppm, and 75% was 22.4 ppm. The normality test using A-D test proved most of the results followed relatively the normal distribution as shown in Fig.1.

Most the obtained results for Cr in marble material passed the Shewhart confidence limit as seen in Fig.2.

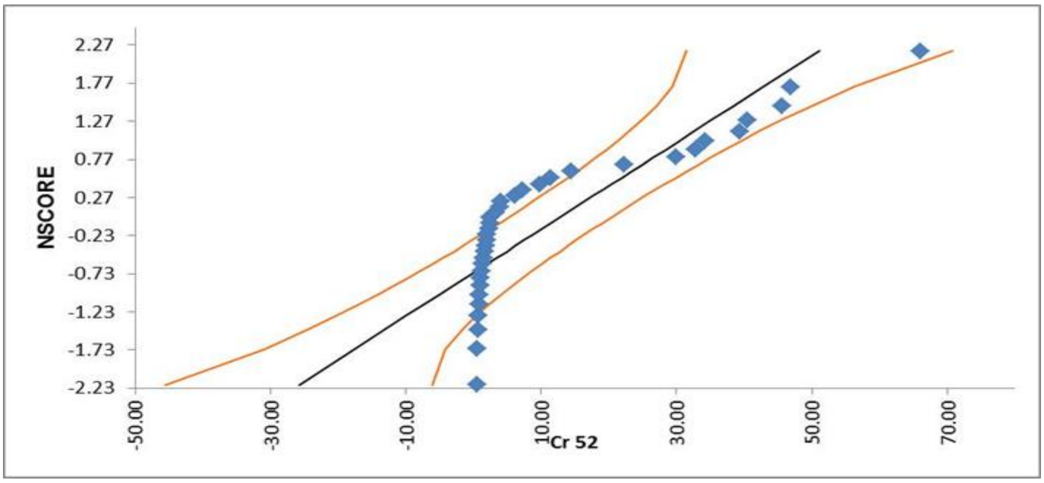

Figure 1: Normal distribution of Cr level in marble material

Matrix correlation calculations in Table.34 and Table.35 showed some positive correlation between Cr and other heavy metals.

Cr had a positive relation with Fe. When using Table.6, it can be modeled as

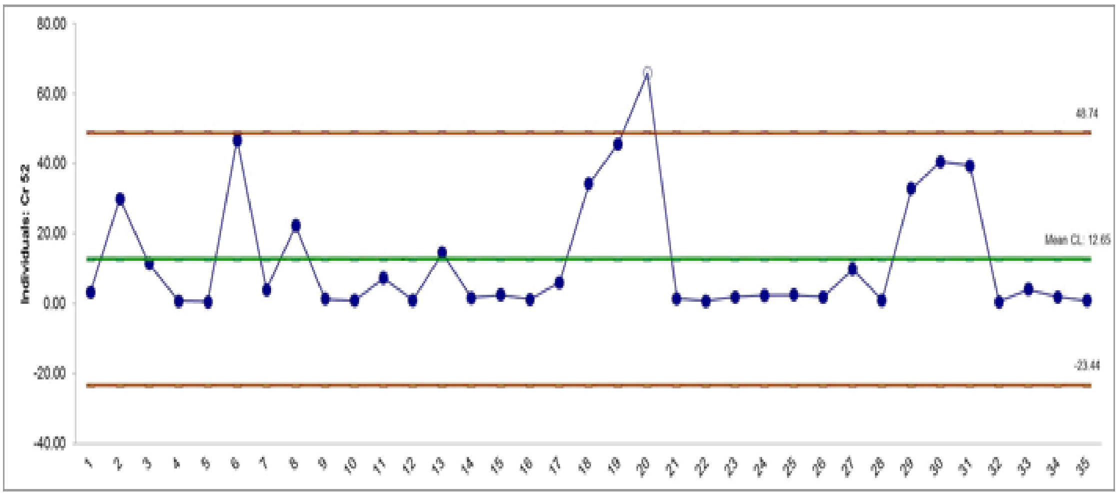

Figure 2: Shewhart con dence limit for Cr level in cement mateiral

$$\text{Cr} = (2{:}137) + (0{:}002528)\ \text{Fe} \quad (5)$$

Co and Cr were negatively correlated as shown in Table.35 and Table.34. Using Table.7 to design the mathematical calculations as:

$$(6) \qquad Cr = (26:182) + (\;\; 2:249)\ Co$$

Cr and Cu were to be positively correlated as calculated Table.35 and Table.34, thus one can compute the mathematical relationship using Table.8 as

$$(7) \qquad Cr = (3:466) + (1:956)\ Cu$$

It was found a positive correlation between Cr and Zn and this relationship can be modeled using Table.9.

$$(8) \qquad Cr = (6:707) + (0:649485)\ Zn$$

Cr and Ga were positively correlated as shown in Table.35 and Table.34. To model it using Table.10. one can get the following equation:

$$(9) \qquad Cr = (2:845) + (3:147)\ Ga$$

Cr and Ba were found to be positively correlated as shown in Table.35 and Table.34. To model it using Table.11. one can get the following equation:

$$(10) \qquad Cr = (4:677) + (0:197113)\ Ba$$

Cr and Pb were positively correlated and their model can be using Table.12 to get the following relationship:

$$(11) \qquad Cr = (0:032839) + (6:746)\ Pb$$

The matrix correlation calculation showed weak correlation between Cr and U with R=0.55. It was possible to model the relationship between Cr and U using selected parameters in Table.13 as :

$$(12) \qquad Cr = (4:039) + (23:203)\ U$$

Table 6: Summary of Cr and Fe model in marble materials using Pearsons rank correlations

					28.73%	R-Square
					26.57%	R-Square Adjusted
					15.046	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	**VIF**	**P**	**T**	**SE Coe cient**	**Coe cient**	Predictor Term
		0.5821	0.555772	3.845	2.137	Constant
1	1	**0.0009**	3.647	0.000693192	0.002528123	Fe 57
						Analysis of Variance for Model:
	P	**F**	**MS**	**SS**	**DF**	Source
	0.0009	13.301	3010.9	3010.9	1	Model
			226.37	7470.1	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.832	DW Statistic
					0.2965	P-Value Positive Autocorrelation
					0.6808	P-Value Negative Autocorrelation

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Table 7: Summary of Cr and Co model in marble materials using Pearsons rank correlations

					19.02%	**R-Square**
					16.56%	R-Square Adjusted
					16.038	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0000	4.704	5.565	26.182	Constant
1	1	0.0088	-2.784	0.807826	-2.249	Co 59
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0088	7.749	1993.1	1993.1	1	Model
			257.21	8488.0	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.437	DW Statistic
					0.0432	P-Value Positive Autocorrelation
					0.9563	P-Value Negative Autocorrelation

Table 8: Summary of Cr and Cu model in marble materials using Pearsons rank correlations

					25.19%	R-Square
					22.92%	R-Square Adjusted
					15.414	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.3674	0.913808	3.793	3.466	Constant
1	1	0.0021	3.333	0.586724	1.956	Cu 63
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0021	11.111	2640.1	2640.1	1	Model
			237.60	7840.9	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.669	DW Statistic
					0.1535	P-Value Positive Autocorrelation
					0.8352	P-Value Negative Autocorrelation

Table 9: Summary of Cr and Zn model in marble materials using Pearsons rank correlations

					34.28%	R-Square
					32.29%	R-Square Adjusted
					14.447	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0239	2.369	2.831	6.707	Constant
1	1	0.0002	4.149	0.156543	0.649485	Zn 66
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0002	17.214	3593.0	3593.0	1	Model
			208.73	6888.1	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.092582042	DW Statistic
					0.0021	P-Value Positive Autocorrelation
					0.9982	P-Value Negative Autocorrelation

Table 10: Summary of Cr and Ga model in marble materials using Pearsons rank correlations

					65.29%	R-Square
					64.24%	R-Square Adjusted
					10.500	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.1984	1.312	2.168	2.845	Constant
1	1.00000	0.0000	7.879	0.399374	3.147	Ga 69
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0000	62.075	6843.2	6843.2	1	Model
			110.24	3637.9	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.556	DW Statistic
					0.0847	P-Value Positive Autocorrelation
					0.9071	P-Value Negative Autocorrelation

Table 11: Summary of Cr and Ba model in marble materials using Pearsons rank correlations

Model Summary:

					53.36%	R-Square
					51.94%	R-Square Adjusted
					12.171	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0632	1.923	2.433	4.677	Constant
1	1	0.0000	6.144	0.032081537	0.197113	Ba 138
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0000	37.750	5592.4	5592.4	1	Model
			148.14	4888.7	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.755	DW Statistic
					0.2200	P-Value Positive Autocorrelation
					0.7596	P-Value Negative Autocorrelation

Table 12: Summary of Cr and Pb model in marble materials using Pearsons rank correlations

					70.54%	R-Square
					69.65%	R-Square Adjusted
					9.673	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.9880	0.015	2.165	0.032839409	Constant
1.00000	1	0.0000	8.889	0.758935	6.746	Pb 208
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0000	79.010	7393.2	7393.2	1	Model
			93.573	3087.9	33	Error

			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					2.019	DW Statistic
					0.4997	P-Value Positive Autocorrelation
					0.4535	P-Value Negative Autocorrelation

Table 13: Summary of Cr and U model in marble materials using Pearsons rank correlations

					28.23%	R-Square
					26.06%	R-Square Adjusted
					15.098	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.2563	1.155	3.497	4.039	Constant
1	1	0.0010	3.603	6.440	23.203	U 238
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0010	12.982	2959.1	2959.1	1	Model
			227.94	7522.0	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.926	DW Statistic
					0.4081	P-Value Positive Autocorrelation
					0.5833	P-Value Negative Autocorrelation

4.2 Cadmium (Cd):

Cd levels presented in marble materials can be described as low level with Cd levels presented in marble materials can be described as low level with an average of less than 1 ppm. From Table.33, the lowest reported level of Cd was below the detection limit whereas the highest level was 1.8 ppm. The data pattern was: 25% was 0.08 ppm, 50% was 0.1, and 75% was 0.16 ppm. The normality test of Cd in marble material showed good agreement with A-D test in Fig.3 and the Z-score was within the limit of 2 or very close to the border of Z-score.

Most of the reported results passed the Shewhart confidence limits as re-ported in Fig.3. Only first sample did not pass the Shawhart confidence limit due to high level of Cd in marble materials.

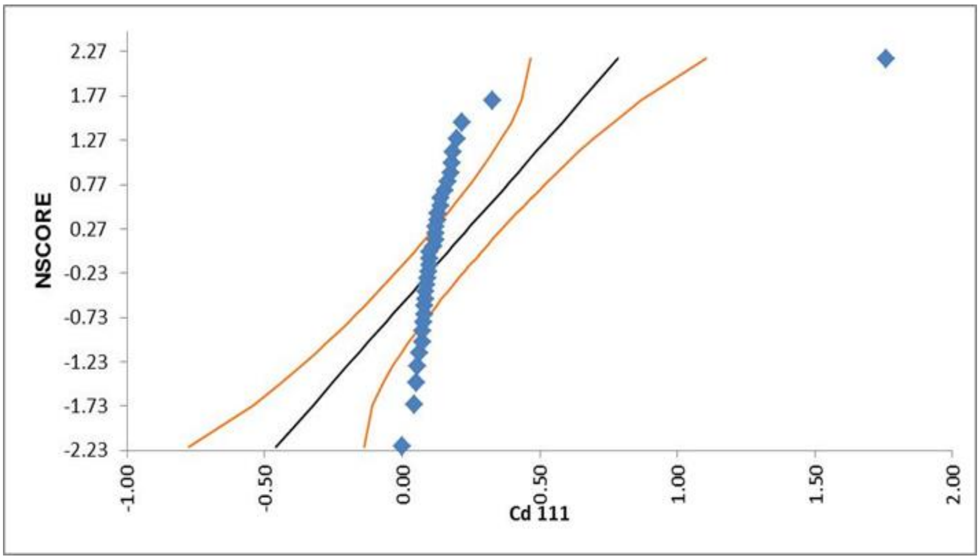

Figure 3: Normal distribution of Cd level in marble mateiral

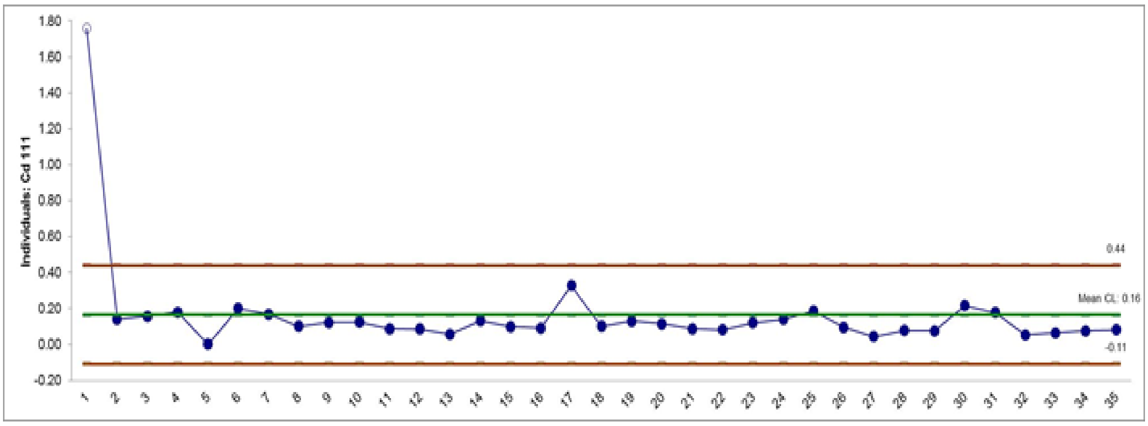

Figure 4: Shewhart con dence limit for Cd level in marble material

Pearson correlations did not show any correlation between Cd and other elements. Nevertheless, Spearman rank correlations had got different answer of Cd correlations with other elements.

As it can be seen from Table.34, Cr and Cd were positively correlated, so one can model it using Table.14 to get the following equation:

(13) Cr = (13:058) + (2:472) Cd

Cd and Mn were proven to be correlated using Spearman rank correlation calculations. Thus, when using Table.15, the following relationship can be obtained:

(14) Cd = (0:154078) + (6:81E 05) Mn

Spearman rank correlation calculations showed there was positive correlation between Cd and Fe. To make a model of this relationship, we need to use the parameters in Table.16 to get the relationship between Cd and Fe as:

(15) Cd = (0:165930) + (4:4E 07) Fe

A positive correlation was observed between Cd and As. When using Table.17, we can draw the following mathematical equation:

(16) Cd = (0:114438) + (0:036932) As rank correlations

Table 14: Summary of Cr and Cd model in marble materials using Spearman

					0.16%	R-Square
					0.00%	R-Square Adjusted
					17.807	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0007	3.742	3.490	13.058	Constant
1	1	0.8197	-0.229783	10.759	-2.472	Cd 111
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.8197	0.052800145	16.743	16.743	1	Model
			317.10	10464	33	Error
			308.27	10481	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.384	DW Statistic
					0.0248	P-Value Positive Autocorrelation
					0.9630	P-Value Negative Autocorrelation

Table 15: Summary of Mn and Cd model in marble materials using Spearman rank correlations

					0.44%	R-Square
					0.00%	R-Square Adjusted
					0.287480	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0087	2.789	0.055241753	0.154078	Constant
1.00000	1	0.7055	0.381237	0.000178578	6.80804E-05	Mn 55
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.7055	0.145342	0.012011743	0.012011743	1	Model
			0.082644744	2.727	33	Error
			0.080567303	2.739	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.030173729	DW Statistic
					0.0011	P-Value Positive Autocorrelation
					0.9991	P-Value Negative Autocorrelation

Table 16: Summary of Fe and Cd model in marble materials using Spearman rank correlations

					0.00%	R-Square
					0.00%	R-Square Adjusted
					0.288108	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0310	2.254	0.073619262	0.165930	Constant
1	1	0.9737	-0.033	1.3274E-05	-4.41138E-07	Fe 57
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	9.16759E-05	0.00110445	0.9737	9.16759E-05	1	Model
			0.083005958	2.739	33	Error
			0.080567303	2.739	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.050705627	DW Statistic
					0.0012	P-Value Positive Autocorrelation
					0.9986	P-Value Negative Autocorrelation

Table 17: Summary of As and Cd model in marble materials using Spearman rank correlations

					1.05%	R-Square
					0.00%	R-Square Adjusted
					0.286592	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.2456	1.182	0.096807047	0.114438	Constant
1	1	0.5576	0.592461	0.062337055	0.036932255	As 75
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.5576	0.351010	0.028830213	0.028830213	1	Model
			0.082135093	2.710	33	Error
			0.080567303	2.739	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.029410789	DW Statistic
					0.0010	P-Value Positive Autocorrelation
					0.9990	P-Value Negative Autocorrelation

4.3 Lead (Pb):

Pb is well-known severe toxic heavy metal. Pb concentrations in the studied adhesive materials were in average value of 2.4ppm where the lowest level was 0.8 ppm and highest level was 6 ppm. About 25% of the data were in 1.55, 50% was 1.97 ppm and 75% was 3.33. The A-d test for normality showed that the obtained results followed normal distribution as well as shown in Fig.5. The Shewhart confidence limit was carried out for Pb level in adhesive materials and was found out to be good as shown in Fig.6.

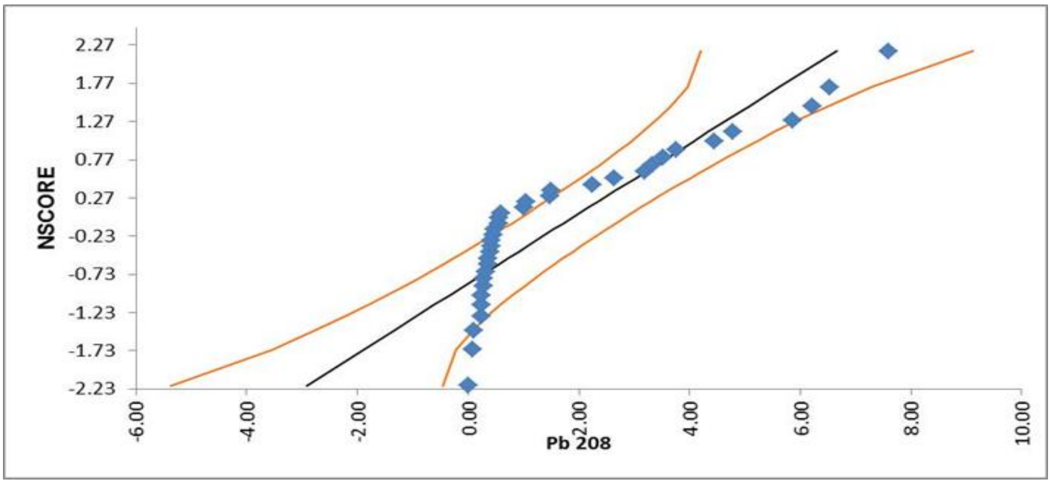

Figure 5: Non-normal distribution of Pb level in marble mateirals

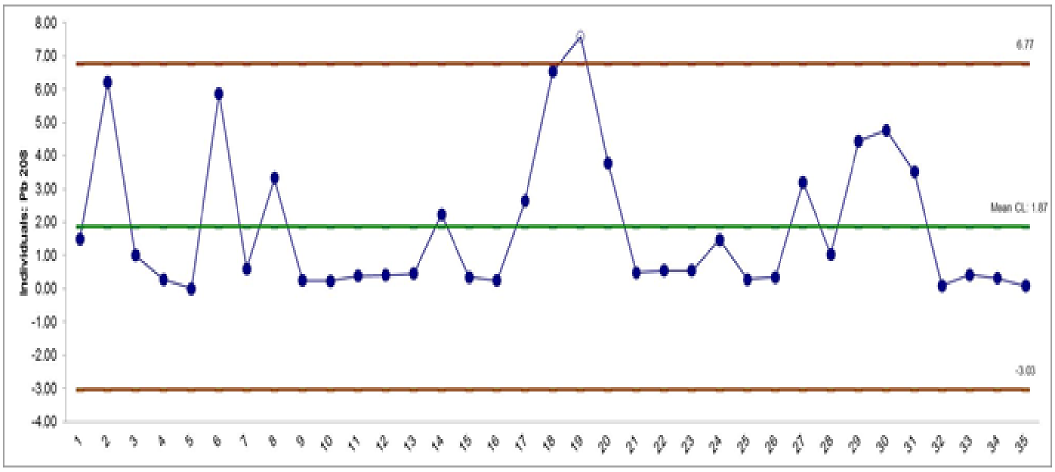

Figure 6: Shewhart con dence limit for Cd level in marble mateiral

Matrix correlation calculations using four different methods proved there was strong positive correlation between Pb and Cr with R value of 0.88. This relationship was reported in previous section of Cr and no need to repeat it.

Pb was positively associated with Fe in weak R value of 0.4. Using regression model calculation in Table.18 can be offered the following equation:

(17) Pb = (0:855428) + (0:000244) Fe

There was a weak negative relationship between Pb and Co. As done before, this relationship can be mathematically described using Table.19 as:

(18) Pb = (3:963) + (0:347846) Co

Matrix correlation calculation showed a positive correlation between Pb and Cu where it can be modelled using Table.20 as

(19) Pb = (0:895438) + (0:207616) Cu

It was found by correlation calculation that there was positive correlation between Pb and Zn which can be modelled using Table.21 to report the following equation:

(20) Pb = (1:134) + (0:080449) Zn

Pb and Ga were reported to have a positive correlation. Let's use Table.22 to obtain the following relationship:

(21) Pb = (0:627269) + (0:398925) Ga

Pb and Ba were observed to have a strong positive correlation with R-value of 0.8. Now, one can make mathematically the relationship between them using Table. as:

(22) Pb = (0:807827) + (0:026268) Ba

Table 18: Summary of Pb and Fe model in marble materials using Pearson correlations

					17.27%	R-Square
					14.77%	R-Square Adjusted
					2.018	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.1066	1.659	0.515667	0.855428	Constant
1	1	0.0130	2.625	9.29778E-05	0.000244074	Fe 57
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0130	6.891	28.064	28.064	1	Model
			4.073	134.39	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.807	DW Statistic
					0.2713	P-Value Positive Autocorrelation
					0.7069	P-Value Negative Autocorrelation

Table 19: Summary of Pb and Co model in marble materials using Pearson correlations

					29.36%	R-Square
					27.21%	R-Square Adjusted
					1.865	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0000	6.125	0.647132	3.963	Constant
1	1	0.0008	-3.703	0.093934727	-0.347846	Co 59
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0008	13.713	47.690	47.690	1	Model
			3.478	114.77	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.196	DW Statistic
					0.0060	P-Value Positive Autocorrelation
					0.9936	P-Value Negative Autocorrelation

Table 20: Summary of Pb and Cu model in marble materials using Pearson correlations

					18.31%	R-Square
					15.84%	R-Square Adjusted
					2.005	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0786	1.815	0.493391	0.895438	Constant
1	1	0.0103	2.720	0.076330113	0.207616	Cu 63

						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0103	7.398	29.751	29.751	1	Model
			4.021	132.71	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.460	DW Statistic
					0.0475	P-Value Positive Autocorrelation
					0.9483	P-Value Negative Autocorrelation

Table 21: Summary of Pb and Zn model in marble materials using Pearson correlations

					33.93%	R-Square
					31.93%	R-Square Adjusted
					1.803	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0030	3.209	0.353445	1.134	Constant
1	1	0.0002	4.117	0.019541023	0.08044949	Zn 66
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0002	16.949	55.127	55.127	1	Model
			3.252	107.33	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.012599907	DW Statistic
					0.0008	P-Value Positive Autocorrelation
					0.9993	P-Value Negative Autocorrelation

Table 22: Summary of Pb and Ga model in marble materials using Pearson correlations

					67.70%	R-Square
					66.73%	R-Square Adjusted
					1.261	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0217	2.410	0.260327	0.627269	Constant
1	1.00000	0.0000	8.318	0.047961398	0.398925	Ga 69
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0000	69.183	109.99	109.99	1	Model
			1.590	52.466	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					2.108	DW Statistic
					0.6160	P-Value Positive Autocorrelation
					0.3614	P-Value Negative Autocorrelation

Table 23: Summary of Pb and Ba model in marble materials using Pearson correlations

					61.13%	R-Square
					59.96%	R-Square Adjusted
					1.383	S (Root Mean Square Error)

						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0062	2.922	0.276460	0.807827	Constant
1	1	0.0000	7.204	0.003646034	0.026267853	Ba 138
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0000	51.905	99.315	99.315	1	Model
			1.913	63.143	33	Error
			4.778	162.46	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					2.313	DW Statistic
					0.8195	P-Value Positive Autocorrelation
					0.1637	P-Value Negative Autocorrelation

4.4 Uranium (U):

U contents in marble material are listed in Table.33 with an average of 0.4ppm which is in normal range compared with other materials studied in this work. This level of uranium is below to the upper earth crust value (2ppm).

The normality test of reported uranium result showed most of the results were normally distributed as shown in Fig.7.

The Shewhart confidence limits proved most of the reported results passed the test as shown in Fig.8. There was only one sample did not pass the test which contained high level of U in marble materials.

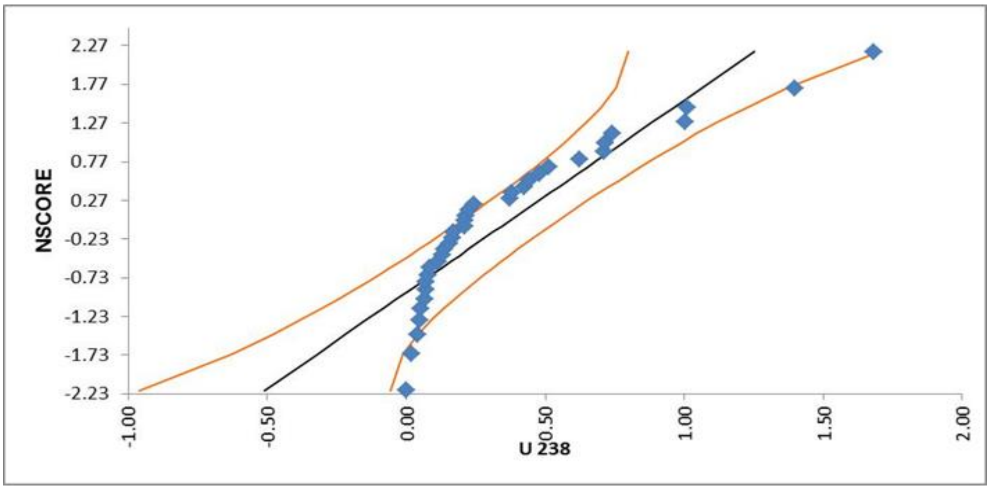

Figure 7: Normal distribution of U level in marble mateirals

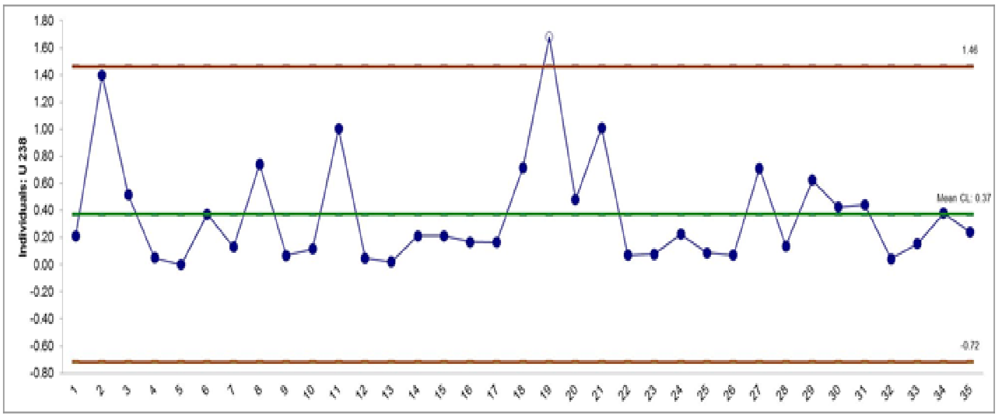

Figure 8: Shewhart confidence limit for U level in marble material

Matrix correlation calculations showed a weak positive relationship between U and Cr as previously discussed in Cr section.

Pearson matrix correlation showed weak negative correlation between U and Co with R value of -0.4. This relationship can be modeled using Table.24 as:

(23) $U = (0:678029) + (\ 0:051)\ Co$

Matrix correlation calculations showed weak positive relationship between U and Ga. The correlation between U and Ga can be modelled using table.25 as :

(24) $U = (0:215844) + (0:049845)\ Ga$

It can observed from Table.34 that U and Mo were positively correlated and this relationship can be modelled using Table.26 to get the formula:

(25) $U = (0:219735) + (0:786360)\ Mo$

U was correlated with Pb as previous reported in Pb section.

Pearson matrix correlation showed strong positive correlation between U and Bi with R value of 0.8. This relationship can be modelled using table.27 as:

(26) $U = (0:356690) + (0:031378)\ Bi$

Table 24: Summary of U and Co model in marble materials using Pearson correlations

					18.65%	R-Square
					16.18%	R-Square Adjusted
					0.368095	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0000	5.308	0.127732	0.678029	Constant
1	1	0.0096	-2.751	0.018540964	-0.050997501	Co 59
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0096	7.565	1.025066123	1.025066123	1	Model
			0.135494	4.471	33	Error
			0.161657	5.496	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.632	DW Statistic
					0.1349	P-Value Positive Autocorrelation
					0.8660	P-Value Negative Autocorrelation

Table 25: Summary of U and Ga model in marble materials using Pearson correlations

					31.24%	R-Square
					29.16%	R-Square Adjusted
					0.338407	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0041	3.089	0.069867748	0.215844	Constant
1	1.00000	0.0005	3.872	0.012872116	0.049845095	Ga 69
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0005	14.995	1.717	1.717	1	Model
			0.114519	3.779	33	Error
			0.161657	5.496	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					2.313	DW Statistic
					0.8203	P-Value Positive Autocorrelation
					0.1654	P-Value Negative Autocorrelation

Table 26: Summary of U and Mo model in marble materials using Pearson correlations

					12.79%	R-Square
					10.15%	R-Square Adjusted
					0.381120	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0260	2.331	0.094286503	0.219735	Constant
1	1	0.0349	2.200	0.357438	0.786360	Mo 98
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0349	4.840	0.703018	0.703018	1	Model
			0.145253	4.793	33	Error
			0.161657	5.496	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.916	DW Statistic
					0.4069	P-Value Positive Autocorrelation
					0.6045	P-Value Negative Autocorrelation

Table 27: Summary of U and Bi model in marble materials using Pearson correlations

					0.44%	R-Square
					0.00%	R-Square Adjusted
					0.407221	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0001	4.533	0.078693583	0.356690	Constant
1	1	0.7061	0.380372	0.082492756	0.031377899	Bi 209
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.7061	0.144683	0.023992579	0.023992579	1	Model
			0.165829	5.472	33	Error
			0.161657	5.496	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.863	DW Statistic
					0.3206	P-Value Positive Autocorrelation
					0.6368	P-Value Negative Autocorrelation

4.5 Gallium (Ga):

Ga was presented in marble material as trace level with an average of 3ppm as listed in Table.33.

The calculated Z-score for Ga contents showed most of the results followed normal distribution where Z-value was located within 2 as shown in Fig.9.

Only one sample out of 35 samples could not pass the Shewhart confidence limit as shown in Fig.10.

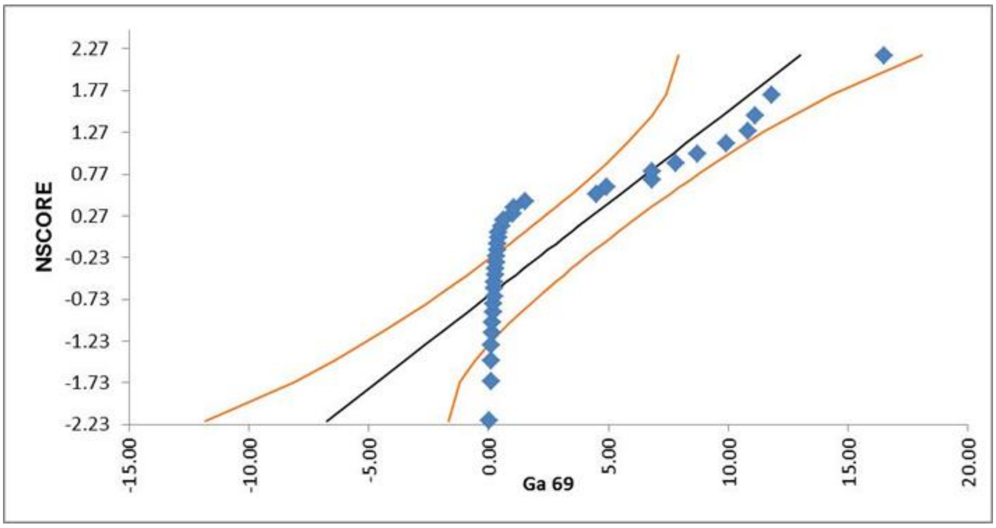

Figure 9: Normal distribution of Ga level in marble mateirals

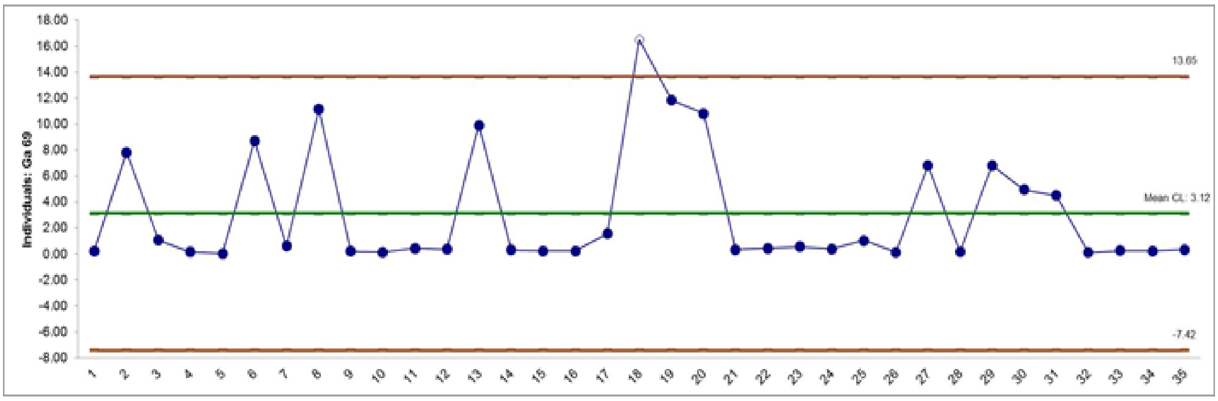

Figure 10: Shewhart confidence limit for Ga level in marble mateirals

As previously discussed, Ga and U were shown positively correlated in part (8.4.3); therefore, no need to study it again.

The use of matrix correlation calculation showed a strong positive correlation between Ga and Cr in Table.34and Table.35. This positive correlation was discussed before in Cr section.

Ga and Fe were found to be positive correlated as shown in Table.34. It was better to nd out the relationship between Ga and Fe using Table.28 as

(27) Ga = (0:780153) + (0:000562) Fe

Ga and Co were negatively correlated using Pearson correlation calculations and this can lead to the following mathematical relationship using Table.29 as:

(28) Ga = (6:712) + (0:597510) Co

The relationship between Ni and Ga were reported with positive correlations. The relationship between Ni and Ga can be modelled using Table.30 to obtain the following equation:

(29) Ga = (1:821) + (0:234919) Ni

Ga and Cu were weakly positively related as shown in Table.34. Using Table.30, one can compute the relationship as:

(30) Ga = (1:253) + (0:396711) Cu

Zn and Ga were reported with strong positive correlation. If one needs to model this relationship, parameters in Table.32 has to be used to form this equation:

(31) Ga = (1:787) + (0:145308) Zn

Table 28: Summary of Ga and Fe model in marble materials using Pearson correlations

					21.51%	R-Square
					19.13%	R-Square Adjusted
					4.055	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	Coe cient SE Coe cient		Predictor Term
		0.4568	0.753015	1.036039097	0.780153	Constant
1	1	0.0050	3.007	0.000186804	0.00056177	Fe 57
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0050	9.044	148.67	148.67	1	Model
			16.439	542.49	33	Error
			20.328	691.16	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					2.279	DW Statistic
					0.7894	P-Value Positive Autocorrelation
					0.1925	P-Value Negative Autocorrelation

Table 29: Summary of Ga and Co model in marble materials using Pearson correlations

					20.36%	R-Square
					17.95%	R-Square Adjusted
					4.084	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0000	4.736	1.417	6.712	Constant
1	1	0.0065	-2.905	0.205718	-0.597510	Co 59
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0065	8.436	140.72	140.72	1	Model
			16.680	550.44	33	Error
			20.328	691.16	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.458	DW Statistic
					0.0496	P-Value Positive Autocorrelation
					0.9499	P-Value Negative Autocorrelation

Table 30: Summary of Ga and Ni model in marble materials using Pearson correlations

					16.18%	R-Square
					13.64%	R-Square Adjusted
					4.190	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0451	2.082	0.874626	1.821	Constant
1	1.00000	0.0166	2.524	0.093069981	0.234919	Ni 60
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0166	6.371	111.85	111.85	1	Model
			17.555	579.32	33	Error
			20.328	691.16	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.840	DW Statistic
					0.3161	P-Value Positive Autocorrelation
					0.6828	P-Value Negative Autocorrelation

Table 31: Summary of Ga and Cu model in marble materials using Pearson correlations

					15.72%	R-Square
					13.16%	R-Square Adjusted
					4.201	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.2339	1.212	1.03372815	1.253	Constant
1	1	0.0184	2.481	0.159923	0.396711	Cu 63
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0184	6.154	108.63	108.63	1	Model
			17.653	582.53	33	Error
			20.328	691.16	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.930	DW Statistic
					0.4073	P-Value Positive Autocorrelation
					0.5732	P-Value Negative Autocorrelation

Table 32: Summary of Ga and Zn model in marble materials using Pearson correlations

					26.02%	R-Square
					23.78%	R-Square Adjusted
					3.936	S (Root Mean Square Error)
						Parameter Estimates:
Tolerance	VIF	P	T	SE Coe cient	Coe cient	Predictor Term
		0.0269	2.316	0.771443	1.787	Constant
1	1	0.0017	3.407	0.042651029	0.145308	Zn 66
						Analysis of Variance for Model:
	P	F	MS	SS	DF	Source
	0.0017	11.607	179.84	179.84	1	Model
			15.494	511.32	33	Error
			20.328	691.16	34	Total (Model + Error)
						Durbin-Watson Test for Autocorrelation in Residuals:
					1.589	DW Statistic
					0.1093	P-Value Positive Autocorrelation
					0.8976	P-Value Negative Autocorrelation

Table 33: Elemental Analysis and Statistical Evaluation for Marble Materials

U 238	Bi 209	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Sample code
0.21	0.02	1.50	3.47	1.76	0.12	27.46	1.11	0.23	12.97	4.10	5.35	9.60	2866	30.58	3.24	A10117
1.40	0.05	6.23	57.40	0.14	0.24	4.25	1.34	7.81	14.69	3.81	1.29	0.31	2967	65.36	29.95	A01120
0.51	0.01	1.01	15.38	0.16	0.91	198.19	2.90	1.05	3.29	1.86	6.70	9.96	10122	367.12	11.38	A01122
0.05	0.00	0.28	1.96	0.18	0.05	46.74	1.02	0.15	2.19	3.23	3.28	7.47	2996	7.10	0.67	A01123
0.00	0.00	0.00	0.07	0.00	0.00	0.11	0.00	0.03	0.09	0.29	0.15	0.08	117	2.40	0.50	A01124
0.37	1.36	5.87	90.86	0.20	0.27	11.36	1.59	8.70	88.63	6.25	4.63	1.32	1129	13.88	46.81	A01125
0.13	0.03	0.60	4.48	0.17	0.05	101.84	1.71	0.61	3.41	6.11	7.09	9.78	4227	58.16	3.96	A01126
0.74	0.03	3.33	73.28	0.10	0.23	5.70	2.21	11.13	33.61	9.96	1.35	0.28	5233	134.42	22.24	A01127
0.07	0.41	0.24	1.35	0.12	0.10	39.74	1.17	0.19	2.07	6.56	3.22	8.84	3089	10.21	1.31	A01135
0.12	0.01	0.24	0.99	0.12	0.03	34.78	1.31	0.13	2.28	19.27	3.79	9.64	3190	6.17	0.87	A01137
1.00	0.01	0.39	4.09	0.09	0.30	48.01	0.91	0.43	3.78	1.61	3.73	6.23	2032	6.16	7.28	A01041
0.05	0.00	0.41	3.64	0.09	0.12	43.28	1.46	0.36	1.96	2.08	3.20	9.06	3264	30.88	0.99	B01036
0.02	0.00	0.45	72.63	0.06	0.12	223.84	1.10	9.91	8.47	4.05	43.16	12.03	9245	136.95	14.39	B01037
0.21	0.01	2.24	2.31	0.13	0.21	147.87	1.24	0.30	23.86	5.23	4.31	8.07	6913	183.57	1.65	B01039
0.21	0.09	0.35	1.50	0.10	0.16	51.24	1.35	0.23	1.98	1.69	5.57	5.45	2449	27.45	2.42	B01045
0.17	0.01	0.25	1.74	0.09	0.16	144.58	1.32	0.22	1.41	1.00	3.70	9.67	3350	9.36	1.18	B01046 - KSU - 7
0.16	2.49	2.64	12.36	0.33	0.36	70.76	4.91	1.54	5.67	3.11	8.31	10.10	9321	1307.76	6.05	B01046 - KSU - 8
0.71	1.66	6.53	290.64	0.10	0.22	77.50	1.09	16.48	12.24	4.20	1.53	0.76	2821	79.78	34.26	B01049
1.68	1.80	7.59	136.50	0.13	0.20	34.56	1.19	11.82	16.65	14.43	16.97	5.13	13275	181.86	45.65	B01051
0.48	0.06	3.76	135.95	0.11	0.08	60.96	1.16	10.81	21.23	11.92	18.51	6.86	13800	340.95	65.99	B01052

1.01	0.01	0.49	2.82	0.09	0.57	54.88	1.57	0.33	1.97	4.09	2.71	6.07	2051	19.05	1.45	B01053
0.07	0.01	0.54	3.08	0.08	0.24	41.10	1.12	0.42	2.18	1.19	2.81	8.10	2697	39.42	0.76	B01055
0.08	3.59	0.55	3.67	0.12	0.29	28.13	1.10	0.56	3.60	1.84	4.39	8.12	2721	30.55	1.87	C0530
0.22	1.56	1.47	2.83	0.14	0.14	36.31	1.18	0.37	2.79	9.55	4.00	6.97	2027	22.20	2.35	C0532 - KSU - 4
0.09	0.89	0.28	29.84	0.18	0.22	37.85	1.96	1.03	2.04	1.14	3.29	7.53	4070	996.92	2.49	C0532 - KSU - 6
0.07	0.43	0.35	1.64	0.10	0.18	132.00	1.26	0.13	1.60	2.86	2.60	6.30	1758	28.93	1.91	C0537
0.71	0.29	3.20	176.43	0.04	0.07	27.82	0.71	6.82	6.06	1.10	0.62	0.26	1988	113.98	9.88	C0539
0.14	0.01	1.04	0.95	0.08	0.01	26.03	1.09	0.14	1.33	1.11	1.52	5.72	1024	3.52	1.01	C0541
0.62	0.03	4.45	85.19	0.08	0.55	9.54	1.45	6.82	13.69	11.70	12.45	6.66	13295	344.94	32.87	C0542 - KSU - 1
0.42	0.06	4.77	101.77	0.22	0.18	20.66	0.94	4.94	8.50	3.86	2.47	1.38	3664	296.89	40.54	C0542 - KSU - 2
0.44	0.05	3.51	85.18	0.18	0.12	15.98	1.49	4.49	11.31	10.59	2.76	1.49	3542	220.73	39.43	C0544
0.04	0.01	0.09	0.84	0.05	0.03	12.90	0.66	0.11	1.05	0.89	1.58	6.08	1111	4.95	0.52	C0546
0.16	0.01	0.41	4.50	0.06	0.01	39.36	1.07	0.26	1.04	1.00	1.56	3.14	1069	3.15	4.11	C0550
0.38	1.08	0.31	1.75	0.08	0.17	30.87	0.73	0.22	1.79	1.85	2.50	6.62	1211	9.00	1.93	C0551
0.24	0.08	0.09	4.98	0.08	0.03	49.78	0.63	0.32	0.93	0.83	1.92	5.51	940.60	15.34	0.88	C0553
35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	Count
0.37	0.46	1.87	40.46	0.16	0.19	55.31	1.34	3.12	9.15	4.70	5.51	6.02	4159	147.13	12.65	Mean
0.40	0.85	2.19	65.06	0.28	0.18	53.44	0.79	4.51	15.83	4.51	7.72	3.40	3722	276.08	17.56	Stdev
1.68	3.59	7.59	290.57	1.76	0.91	223.73	4.91	16.46	88.54	18.98	43.02	11.95	13683	1305.35	65.49	Range
0.00	0.00	0.00	0.07	0.00	0.00	0.11	0.00	0.03	0.09	0.29	0.15	0.08	117	2.40	0.50	Minimum
0.08	0.01	0.31	1.75	0.08	0.07	26.03	1.07	0.22	1.96	1.19	1.92	3.14	1988	9.36	1.18	25th Percentile (Q1)
0.21	0.03	0.55	4.09	0.10	0.16	39.36	1.18	0.42	3.29	3.23	3.28	6.62	2967	30.58	2.49	50th Percentile (Median)
0.51	0.43	3.33	73.28	0.16	0.24	60.96	1.46	6.82	12.24	6.25	5.35	8.84	4227	181.86	22.24	75th Percentile (Q3)
1.68	3.59	7.59	290.64	1.76	0.91	223.84	4.91	16.48	88.63	19.27	43.16	12.03	13800	1307.76	65.99	Maximum
6.62 to 18.652.2 to 2412880 to 5438 4.8 to 7.2 2.86 to 8.163.15 to 6.23.72 to 14.591.5 to 4.661.07 to 1.6136.9 to 73.70.13 to 0.250.07 to 0.2618.1 to 62.8 1.1 to 2.60.17 to 0.750.23 to 0.51																95.0% CI Mean
14.2 to 23.0223 to 3613010 to 48772.75 to 4.466.24 to 10.123.64 to 5.912.8 to 20.7 3.6 to 5.90.63 to 1.0343.3 to 70.020.15 to 0.240.23 to 0.3752.62 to 85.21.76 to 2.80.68 to 1.110.32 to 0.53																95.0% CI Sigma
2.34	5.59	3.11	4.37	8.10	1.90	2.79	3.04	4.58	5.02	2.26	5.22	1.08	3.190	5.44	Anderson-Darling Normality Test 4.26	
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.0000	0.00	0.00	P-Value (A-D Test)
1.72	2.24	1.26	2.19	5.52	2.23	1.81	2.94	1.43	4.05	1.56	3.83	-0.48	1.574	3.20	1.52	Skewness
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.0007	0.00	0.00	P-Value (Skewness)
2.84	5.03	0.43	5.53	31.73	6.60	2.91	12.37	1.02	19.30	2.17	17.07	-0.82	1.499	10.90	1.36	Kurtosis
0.02	0.00	0.45	0.00	0.00	0.00	0.01	0.00	0.19	0.00	0.04	0.00	0.18	0.0933	0.00	0.11	P-Value (Kurtosis)

Table 34: Martix Correlation Calculations using Pearson Methods for Marble Materials

U 238	Bi 209	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Pearson Correlations
0.5313	0.0875	0.8399	0.7305	-0.0400	0.1250	-0.1586	0.0384	0.8080	0.5855	0.5019	0.3097	-0.4361	0.5360	0.1505	1	Cr 52
-0.0179	0.3171	0.1641	0.1022	0.0662	0.3270	0.0959	0.7632	0.0895	-0.0093	0.0210	0.1651	0.1826	0.4865	1		Mn 55
0.3176	0.0861	0.4156	0.3194	-0.0058	0.4156	0.3329	0.4172	0.4638	0.1343	0.4981	0.6553	0.3083	1			Fe 57
-0.4319	0.0352	-0.5418	-0.5137	0.2103	0.1539	0.5622	0.2999	-0.4512	-0.3451	0.0219	0.4236	1				Co 59
0.0335	0.0198	0.1059	0.1960	-0.0079	0.0626	0.5263	0.0901	0.4023	0.0915	0.2641	1					Ni 60
0.3054	0.0405	0.4279	0.2742	0.0181	-0.0048	-0.1528	0.0936	0.3964	0.2884	1						Cu 63
0.2239	0.1466	0.5825	0.3478	0.0968	0.1126	-0.1422	0.1178	0.5101	1							Zn 66
0.5590	0.1696	0.8228	0.9011	-0.1023	0.0766	-0.0194	0.0260	1								Ga 69
0.0261	0.3051	0.1200	-0.0623	0.1026	0.5259	0.2432	1									As 75
-0.1948	-0.1164	-0.2391	-0.0646	-0.0830	0.3006	1										Sr 88
0.3576	0.1428	0.1696	0.0340	-0.0187	1											Mo 98
-0.0662	-0.0079	0.0345	-0.0923	1												Cd 111
0.4855	0.1896	0.7819	1													Ba 138
0.6896	0.2578	1														Pb 208
0.0661	1															Bi 209
1																U 238
U 238	Bi 209	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Pearson Correlations
0.0010	0.6170	0.0000	0.0000	0.8197	0.4742	0.3628	0.8265	0.0000	0.0002	0.0021	0.0703	0.0088	0.0009	0.3881		Cr 52
0.9188	0.0635	0.3462	0.5590	0.7055	0.0552	0.5835	0.0000	0.6092	0.9579	0.9047	0.3433	0.2937	0.0030			Mn 55
0.0630	0.6228	0.0130	0.0614	0.9737	0.0130	0.0507	0.0127	0.0050	0.4419	0.0023	0.0000	0.0716				Fe 57
0.0096	0.8409	0.0008	0.0016	0.2252	0.3775	0.0004	0.0800	0.0065	0.0423	0.9005	0.0112					Co 59
0.8484	0.9103	0.5448	0.2591	0.9639	0.7209	0.0012	0.6068	0.0166	0.6012	0.1253						Ni 60
0.0744	0.8175	0.0103	0.1109	0.9178	0.9783	0.3810	0.5927	0.0184	0.0929							Cu 63
0.1961	0.4007	0.0002	0.0406	0.5801	0.5195	0.4150	0.5002	0.0017								Zn 66
0.0005	0.3301	0.0000	0.0000	0.5586	0.6619	0.9120	0.8822									Ga 69
0.8819	0.0747	0.4924	0.7220	0.5576	0.0012	0.1592										As 75
0.2621	0.5056	0.1666	0.7124	0.6356	0.0793											Sr 88
0.0349	0.4132	0.3300	0.8461	0.9152												Mo 98
0.7055	0.9640	0.8438	0.5980													Cd 111
0.0031	0.2754	0.0000														Ba 138
0.0000	0.1348															Pb 208
0.7061																Bi 209
																U 238

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Table 35: Martix Correlation Calculations using Spearman Methods for Marble Materials

U 238	Bi 209	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Pearson Correlations
0.6697	0.4255	0.8134	0.8611	0.3465	0.4269	-0.0843	0.2997	0.8555	0.7630	0.5078	0.2961	-0.2711	0.4742	0.6244	1	Cr 52
0.3535	0.3112	0.6137	0.6969	0.4308	0.5118	0.1759	0.5151	0.7280	0.6342	0.4154	0.4095	0.1639	0.7891	1		Mn 55
0.2084	0.0443	0.4204	0.4580	0.4507	0.3711	0.2821	0.5667	0.5389	0.6039	0.6031	0.6286	0.4468	1			Fe 57
-0.4496	-0.1627	-0.2944	-0.2681	0.2389	0.0759	0.5812	0.3050	-0.2003	-0.0868	0.1090	0.6560	1				Co 59
-0.0151	0.1373	0.1756	0.1711	0.4000	0.2952	0.4255	0.4224	0.2563	0.3930	0.4692	1					Ni 60
0.3510	0.2852	0.5518	0.3577	0.4972	0.2426	-0.0350	0.4552	0.4381	0.7179	1						Cu 63
0.5499	0.2961	0.8275	0.6972	0.5034	0.4711	-0.1286	0.3345	0.7669	1							Zn 66
0.6090	0.3672	0.7972	0.9415	0.2543	0.5090	-0.0171	0.3227	1								Ga 69
0.1871	0.1843	0.2955	0.1894	0.5129	0.5305	0.1714	1									As 75
-0.1258	-0.0798	-0.1966	-0.0594	0.0529	0.1202	1										Sr 88
0.5073	0.3078	0.4496	0.3784	0.3098	1											Mo 98
0.1616	0.3835	0.3835	0.2513	1												Cd 111
0.6064	0.3605	0.7585	1													Ba 138
0.6605	0.3860	1														Pb 208
0.3552	1															Bi 209
1																U 238
U 238	Bi 209	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Pearson Correlations
0.0372	0.0688	0.0001	0.0000	0.0098	0.0017	0.3121	0.0015	0.0000	0.0000	0.0131	0.0146	0.3469	0.0000			Mn 55
0.2296	0.8007	0.0119	0.0057	0.0066	0.0282	0.1007	0.0004	0.0008	0.0001	0.0001	0.0001	0.0071				Fe 57
0.0067	0.3503	0.0860	0.1195	0.1669	0.6647	0.0003	0.0748	0.2487	0.6199	0.5332	0.0000					Co 59
0.9313	0.4317	0.3129	0.3256	0.0173	0.0851	0.0108	0.0115	0.1372	0.0195	0.0045						Ni 60
0.0387	0.0968	0.0006	0.0349	0.0024	0.1603	0.8417	0.0060	0.0085	0.0000							Cu 63
0.0006	0.0842	0.0000	0.0000	0.0021	0.0043	0.4617	0.0496	0.0000								Zn 66
0.0001	0.0300	0.0000	0.0000	0.1404	0.0018	0.9224	0.0587									Ga 69
0.2818	0.2892	0.0848	0.2760	0.0016	0.0010	0.3248										As 75
0.4716	0.6485	0.2576	0.7347	0.7626	0.4917											Sr 88
0.0019	0.0720	0.0067	0.0250	0.0701												Mo 98
0.3536	0.0230	0.0230	0.1454													Cd 111
0.0001	0.0334	0.0000														Ba 138
0.0000	0.0220															Pb 208
0.0363																Bi 209
																U 238

5. RISK ASSESSMENT DISCUSSION

As the aim of our study to gure out the risk assessment of presence of heavy metals in marble materials, in this section, risk evaluation of heavy metal based in the previous analytical data are given and discussed.

Enrichment factors of the selected heavy metals were used by normalizing each value of heavy metals to their values reported by Mullers in Table.2. This can offer us an indication of presence of heavy metals in marble materials. It was chosen the upper earth crust shale heavy metal values as reference values (free heavy metal values) for normalization

Geo-accumulation Index can be very helpful to trace back the presence of heavy metals and their chemical environment. It was decided to include this index in the study due to its importance in geo-science and contamination of sediments.

5.1 Chromium (Cr):

Cr levels in the study marble materials were not highly enriched as shown in Fig.11where the average value of E.F was less than one. With accordance to Muller scale, this is regarded as non-contaminated materials. This non-enriched level was expected for highly refectory element of Cr in carbonate matrix. Only one sample was high in Cr but still within the permissible limit of Cr.

As anticipated, the calculated geo-indexes of marble materials were compa-rable with safety limits reported values by Muller. Most of geo-accumulation were negative values. These negative values as shown in Table.2 indicates no contamination of the study materials. Consequently, other hazard indexes listed in Table.37 were clearly matched with geo-accumulation index. It, thus, can be declared that marble materials were safe against Cr contamination.

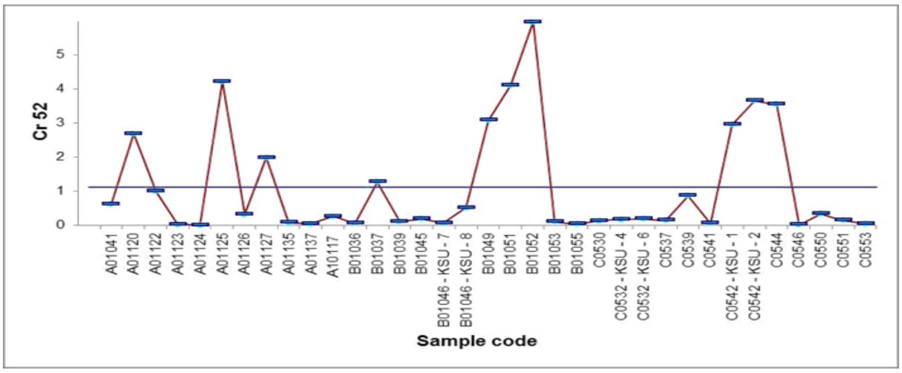

Figure 11: Enrichment distribution of Cr level in marble mateirals

5.2 Cadmium (Cd):

In Table.36, E.Fs of Cd showed normal level of enriched Cd present in marbles. The average of E.F was less than ve with accordance to Muller scale. Only one sample showed high enriched level as shown in Fig.13. Nevertheless, as stated previously, enrichment factor is not taken as indicator of hazard parameter in pollution science.

The Table.37 showed the calculated geo-accumulation indexes for Cd were less than 1.1 in average. In Fig.14, These values of geo-accumulation can offer an answer that marble materials were not contaminated with Cd.

The other pollution indexes calculated in Table.38 proved that Cd levels in marble materials were not contaminated. The calculated

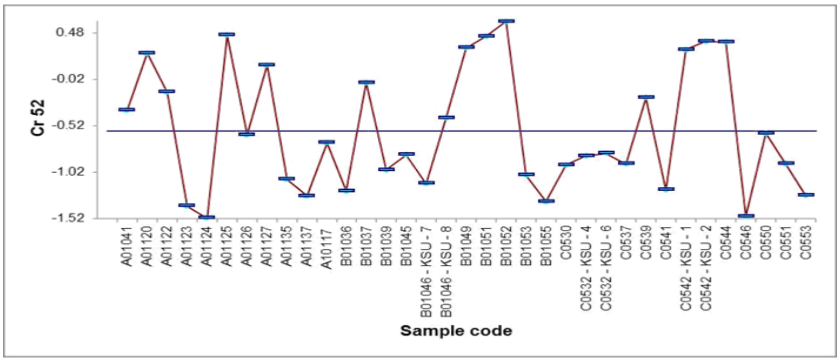

Figure 12: Geo-accumulation distribution of Cr level in marble mateirals

5.3 Lead (Pb):

The enrichment levels of Pb in marble materials were so high proved by E.F calculations in Table.36. This result was very comparable with Pb concentrations in sedimentary rocks reported by Muller.

Luckily, the calculation of geo-index of Pb in marble materials showed dif-ferent view. It proved that Pb in the studied materials of marbles was very low and regarded as unpolluted. Also, the other calculated indexes in Table.38 were in good agreement with geo-index calculations.

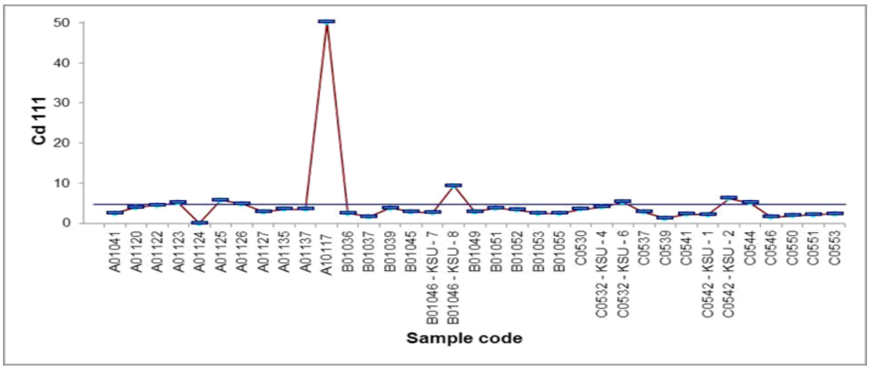

Figure 13: Enrichement distribution of Cd level in marble mateirals

5.4 Uranium (U):

U enrichment levels in marble matrix were lower than expected values reported in the upper earth crust. The reported levels of U enrichment in marble were less than 1.2 computed in Table.36.

As anticipated from the E.F of uranium in marble materials, the geo-index calculations in Table.37 with good confidence proved studied materials were free of uranium contamination. Moreover, to support this idea, other hazard indexes were computed and listed in Table.38. These hazard indexes were comparable with geo-accumulation reported values.

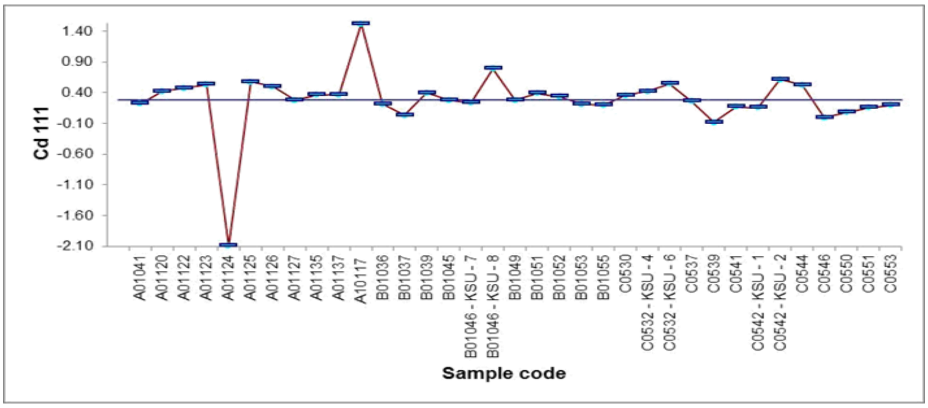

Figure 14: Geo-accumulation distribution of Cd level in marble mateirals

5.5 Gallium (Ga):

Ga enrichment factors of study materials are shown in Fig.19. The results of enrichment factors were below two in average which obviously indicated no contamination levels of Ga in the study materials.

The geo-indexes showed the marble materials were free of Ga contamination as shown in Fig19 36, 37 and, Table.38.

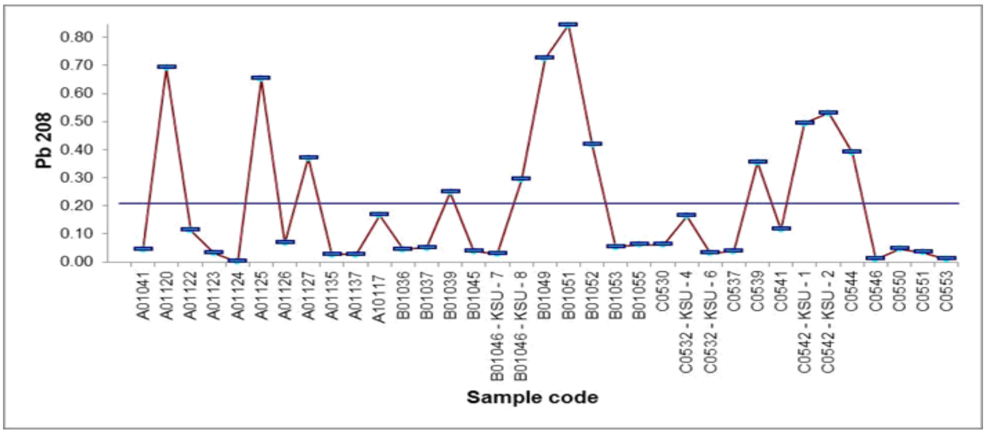

Figure 15: Enrichment distribution of Pb level in marble mateirals

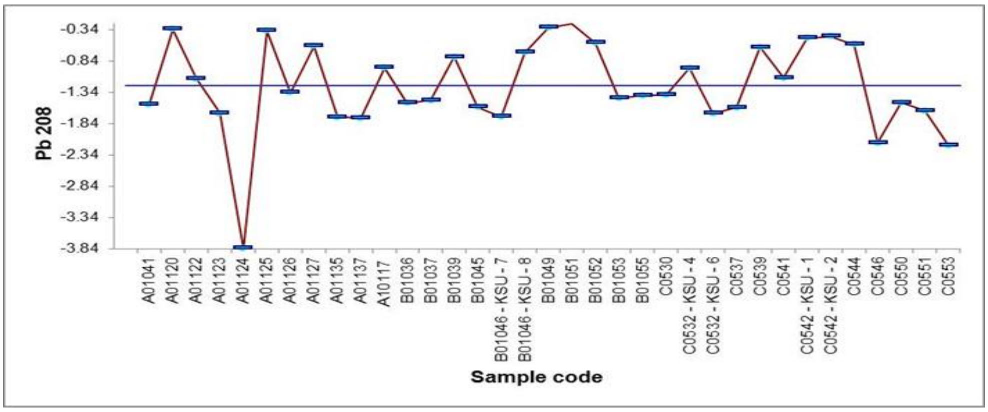

Figure 16: Geo-accumulation distribution of Pb level in marble mateirals

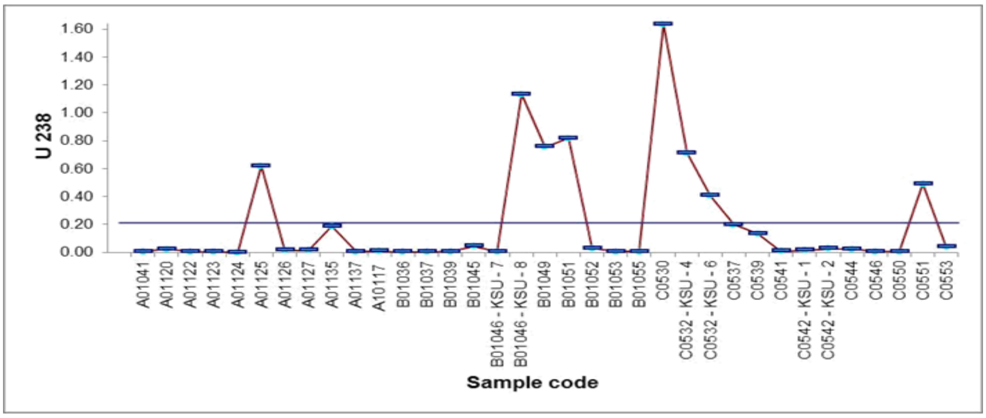

Figure 17: Enrichment distribution of U level in marble mateirals

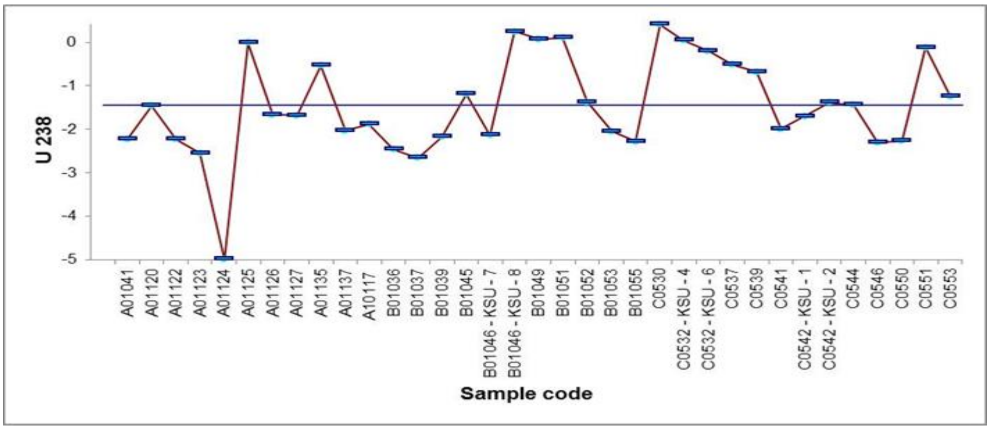

Figure 18: Geo-accumulation distribution of U level in marble mateirals

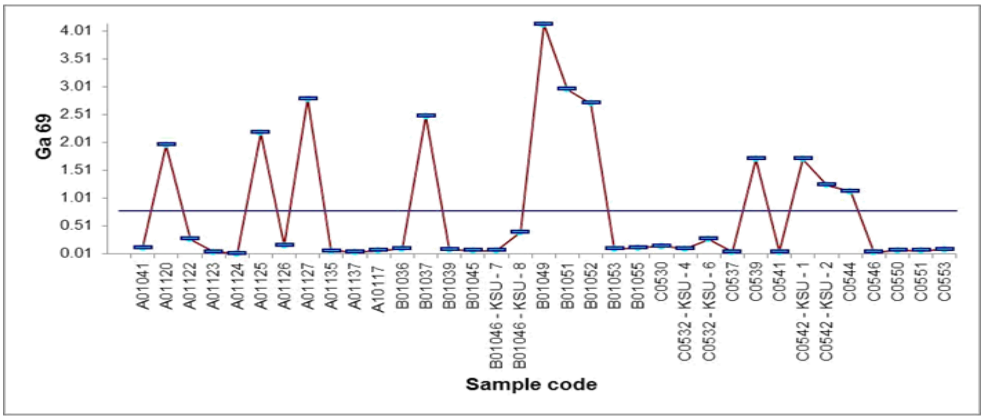

Figure 19: Enrichment distribution of Ga level in marble mateirals

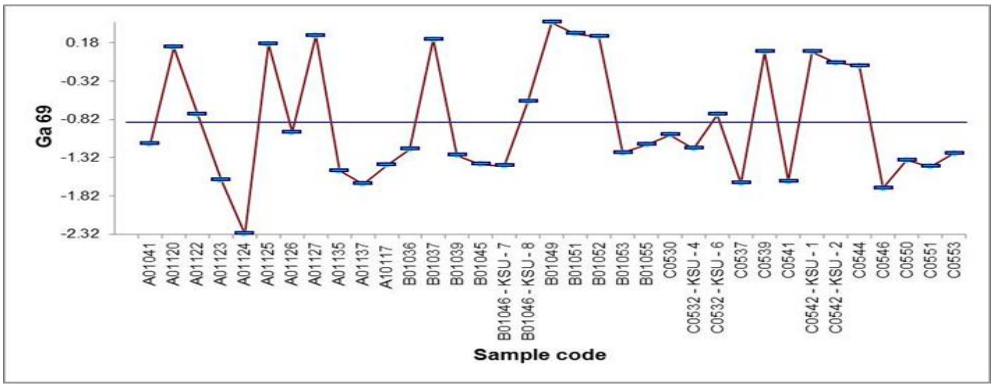

Figure 20: Geo-accumulation distribution of Ga level in marble materials

Table 36: Enrichment Factor for marble materials

U 238	Pb 208	Ba 138	Cd 111	Mo 98	Sr 88	As 75	Ga 69	Zn 66	Cu 63	Ni 60	Co 59	Fe 57	Mn 55	Cr 52	Sample code
0.01	0.17	0.35	50.26	0.29	0.05	1.11	0.06	0.65	1.02	0.27	96.00	0.75	0.03	0.29	**A10117**
0.02	0.69	5.74	3.96	0.61	0.01	1.34	1.95	0.73	0.95	0.06	3.12	0.78	0.06	2.72	**A01120**
0.00	0.11	1.54	4.45	2.29	0.32	2.90	0.26	0.16	0.47	0.33	99.56	2.66	0.33	1.03	**A01122**
0.00	0.03	0.20	5.12	0.13	0.08	1.02	0.04	0.11	0.81	0.16	74.70	0.79	0.01	0.06	**A01123**
0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.07	0.01	0.81	0.03	0.00	0.05	**A01124**
0.62	0.65	9.09	5.72	0.67	0.02	1.59	2.17	4.43	1.56	0.23	13.20	0.30	0.01	4.26	**A01125**
0.01	0.07	0.45	4.78	0.13	0.17	1.71	0.15	0.17	1.53	0.35	97.77	1.11	0.05	0.36	**A01126**
0.01	0.37	7.33	2.87	0.58	0.01	2.21	2.78	1.68	2.49	0.07	2.77	1.38	0.12	2.02	**A01127**
0.19	0.03	0.13	3.50	0.26	0.07	1.17	0.05	0.10	1.64	0.16	88.45	0.81	0.01	0.12	**A01135**
0.01	0.03	0.10	3.52	0.08	0.06	1.31	0.03	0.11	4.82	0.19	96.37	0.84	0.01	0.08	**A01137**
0.00	0.04	0.41	2.52	0.76	0.08	0.91	0.11	0.19	0.40	0.19	62.30	0.53	0.01	0.66	**A01041**
0.00	0.05	0.36	2.47	0.30	0.07	1.46	0.09	0.10	0.52	0.16	90.56	0.86	0.03	0.09	**B01036**
0.00	0.05	7.26	1.63	0.30	0.37	1.10	2.48	0.42	1.01	2.16	120.29	2.43	0.12	1.31	**B01037**
0.00	0.25	0.23	3.74	0.52	0.24	1.24	0.08	1.19	1.31	0.22	80.67	1.82	0.17	0.15	**B01039**
0.04	0.04	0.15	2.85	0.40	0.08	1.35	0.06	0.10	0.42	0.28	54.46	0.64	0.02	0.22	**B01045**
0.00	0.03	0.17	2.59	0.39	0.24	1.32	0.06	0.07	0.25	0.18	96.72	0.88	0.01	0.11	**B01046 - KSU - 7**
1.13	0.29	1.24	9.34	0.91	0.12	4.91	0.39	0.28	0.78	0.42	101.00	2.45	1.19	0.55	**B01046 - KSU - 8**
0.76	0.73	29.06	2.87	0.56	0.13	1.09	4.12	0.61	1.05	0.08	7.64	0.74	0.07	3.11	**B01049**
0.82	0.84	13.65	3.71	0.49	0.06	1.19	2.95	0.83	3.61	0.85	51.26	3.49	0.17	4.15	**B01051**
0.03	0.42	13.59	3.26	0.19	0.10	1.16	2.70	1.06	2.98	0.93	68.61	3.63	0.31	6.00	**B01052**
0.01	0.05	0.28	2.48	1.41	0.09	1.57	0.08	0.10	1.02	0.14	60.69	0.54	0.02	0.13	**B01053**
0.00	0.06	0.31	2.36	0.59	0.07	1.12	0.10	0.11	0.30	0.14	81.01	0.71	0.04	0.07	**B01055**
1.63	0.06	0.37	3.44	0.72	0.05	1.10	0.14	0.18	0.46	0.22	81.21	0.72	0.03	0.17	**C0530**
0.71	0.16	0.28	3.98	0.35	0.06	1.18	0.09	0.14	2.39	0.20	69.68	0.53	0.02	0.21	**C0532 - KSU - 4**
0.40	0.03	2.98	5.27	0.55	0.06	1.96	0.26	0.10	0.28	0.16	75.30	1.07	0.91	0.23	**C0532 - KSU - 6**
0.20	0.04	0.16	2.72	0.45	0.22	1.26	0.03	0.08	0.71	0.13	62.98	0.46	0.03	0.17	**C0537**
0.13	0.36	17.64	1.25	0.17	0.05	0.71	1.71	0.30	0.28	0.03	2.62	0.52	0.10	0.90	**C0539**
0.01	0.12	0.10	2.21	0.03	0.04	1.09	0.03	0.07	0.28	0.08	57.22	0.27	0.00	0.09	**C0541**
0.01	0.49	8.52	2.16	1.37	0.02	1.45	1.70	0.68	2.93	0.62	66.58	3.50	0.31	2.99	**C0542 - KSU - 1**
0.03	0.53	10.18	6.18	0.45	0.03	0.94	1.24	0.42	0.97	0.12	13.79	0.96	0.27	3.69	**C0542 - KSU - 2**
0.02	0.39	8.52	5.05	0.30	0.03	1.49	1.12	0.57	2.65	0.14	14.93	0.93	0.20	3.58	**C0544**
0.00	0.01	0.08	1.49	0.06	0.02	0.66	0.03	0.05	0.22	0.08	60.85	0.29	0.00	0.05	**C0546**
0.00	0.05	0.45	1.82	0.03	0.06	1.07	0.07	0.05	0.25	0.08	31.39	0.28	0.00	0.37	**C0550**
0.49	0.03	0.18	2.15	0.43	0.05	0.73	0.05	0.09	0.46	0.12	66.20	0.32	0.01	0.18	**C0551**
0.04	0.01	0.50	2.35	0.07	0.08	0.63	0.08	0.05	0.21	0.10	55.09	0.25	0.01	0.08	**C0553**
35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	**Count**
0.21	0.21	4.05	4.69	0.48	0.09	1.34	0.78	0.46	1.17	0.28	60.17	1.09	0.13	1.15	**Mean**
0.38	0.24	6.51	8.11	0.46	0.09	0.79	1.13	0.79	1.13	0.39	34.05	0.98	0.25	1.60	**Stdev**
1.63	0.84	29.06	50.25	2.28	0.37	4.91	4.11	4.43	4.75	2.15	119.48	3.60	1.19	5.95	**Range**
0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.07	0.01	0.81	0.03	0.00	0.05	**Minimum**
0.00	0.03	0.18	2.35	0.17	0.04	1.07	0.06	0.10	0.30	0.10	31.39	0.52	0.01	0.11	**25th Percentile (Q1)**
0.01	0.06	0.41	2.87	0.40	0.06	1.18	0.10	0.16	0.81	0.16	66.20	0.78	0.03	0.23	**50th Percentile (Median)**
0.20	0.37	7.33	4.45	0.59	0.10	1.46	1.70	0.61	1.56	0.27	88.45	1.11	0.17	2.02	**75th Percentile (Q3)**
1.63	0.84	29.06	50.26	2.29	0.37	4.91	4.12	4.43	4.82	2.16	120.29	3.63	1.19	6.00	**Maximum**
1.81 to 6.28 0.12 to 0.29 0.078 to 0.34			1.9 to 7.47	0.05 to 0.22 0.75 to 1.43 48.5 to 71.9 0.14 to 0.41 0.79 to 1.56 0.18 to 0.73 0.39 to 1.17 1.07 to 1.61 0.06 to 0.12 0.32 to 0.64										0.6 to 1.7	**95.0% CI Mean**
0.31 to 0.5	1.29 to 2.09 0.2 to 0.33 0.79 to 1.28 27.5 to 44.61 0.31 to 0.5 0.91 to 1.47 0.64 to 1.04 0.91 to 1.47 0.64 to 1.03 0.07 to 0.11 0.37 to 0.59 6.56 to 10.62 5.26 to 8.52 0.19 to 0.32														**95.0% CI Sigma**
5.59	3.11	4.37	8.10	1.90	2.79	3.04	4.58	5.02	2.26	5.22	1.08	3.19	5.44	4.26	**Anderson-Darling Normality Test**
0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**P-Value (A-D Test)**
2.24	1.26	2.19	5.52	2.23	1.81	2.94	1.43	4.05	1.56	3.83	-0.48	1.57	3.20	1.52	**Skewness**
0.00	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	0.21	**0.00**	**0.00**	**0.00**	**P-Value (Skewness)**
5.03	0.43	5.53	31.73	6.60	2.91	12.37	1.02	19.30	2.17	17.07	-0.82	1.50	10.90	1.36	**Kurtosis**
0.00	0.45	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	0.19	**0.00**	**0.04**	**0.00**	0.18	0.09	**0.00**	0.11	**P-Value (Kurtosis)**

Table 38: Degree of contamination and Pollution load Index for marble materials

	Pollution load Index		Degree of contamination
0.47	Cr 52	40.26	Cr 52
0.04	Mn 55	4.68	Mn 55
0.86	Fe 57	38.31	Fe 57
39.45	Co 59	2105.81	Co 59
0.20	Ni 60	9.65	Ni 60
0.89	Cu 63	41.10	Cu 63

0.24	Zn 66	16.02	Zn 66
0.24	Ga 69	27.27	Ga 69
1.19	As 75	47.06	As 75
0.07	Sr 88	3.17	Sr 88
0.33	Mo 98	16.85	Mo 98
3.11	Cd 111	164.10	Cd 111
0.90	Ba 138	141.61	Ba 138
0.11	Pb 208	7.27	Pb 208
0.03	U 238	7.36	U 238

6. CONCLUSION

A comprehensive assessment of presence of heavy metals in marble building materials used in Saudi building market was conducted. Over 40 samples were assembled from major marble stores in Riyadh. Quality control measurements were precisely performed to offer us very good reported data with regard to the carried out statics. The reported precision of used reference materials which are matrix-matched was over 90% and relative standard deviation was better than 5-8%.

In this assessment, the risk indexes indicated the levels of Cr, Cd, Pb, U, Ga concentrations were likely to be insignificant with regard to the critical values reported in literature of sediments in the upper earth crust. The cal-culation of enrichment factor was located within less Muller scale. Also, the geo-accumulation calculations were in negative values indicating the study mar-ble materials free of heavy metals contamination.

Therefore, using marble materials can be considered safe for workers as well as residents.

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