American Journal of Applied Sciences 9 (7): 1014-1019, 2012
ISSN 1546-9239

Determination of Heavy Metals and Other Elements in Artisanal Gold Mining Soils

[1]Girigisu, S., [2]I.G.E. Ibeanu, [2]D.J. Adeyemo and [3]S. Okoh
[1]Department of Physics, School of Science Education,
Federal College of Education (Technical) Gusau, Nigeria
[2]Health Physics and Radiation Biophysics Section,
[3]Materials Science and Development Section,
Center for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

Abstract: Problem statement: The possible exposure of heavy elements to life as a result of artisanal gold mining activities can be of great concern because of its associated effect on health. **Approach:** Soil samples from the artisanal gold mining sites of Awwal and Bagega villages in Kebbi and Zamfara states of Nigeria were collected and analyzed for heavy and other elements by X-Ray Fluorescence (XRF) technique. Ten of the element analyses are presented in this study, based on their toxicity levels. **Results:** Four of the ten elements (Pb, Si, Rb and Fe) showed relatively high concentrations. Two of these four elements presented, (Si and Pb) may pose latent and immediate hazards to health. Respiratory crystalline silica is the major element constituent of the ever-well-pronounced mining dusts of the two sites. Its form of occurrence portends irreversible health problem called silicosis and is well linked to cancer forming properties; both of which develop through latency periods. Pb at whatever concentration portends both immediate and long term hazards to women and children at the greatest risks of exposures. **Conclusion:** Based on the results presented, there exist a possibility of an immediate and long term health risks associated with the artisanal gold mining exercises in the two sites studied if the said uncoordinated and unprofessional activities of the miners are left unchecked.

Key words: Artisanal Gold mining, heavy elements, contamination, poisoning, silicosis, carcinogenesis

INTRODUCTION

Mining of minerals such as gold is found to be one of the major routes of exposure of life to heavy metals and other elements whose toxicity have been documented throughout history. It has been reported that Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology even became a science (Jerome, 1996).

The heavy metals are hazardous to life and the mining exercise is also environmentally damaging (WR, 1998). The presence of these heavy metals and other elements excavated can reside in the environment for hundreds of years. The presence of these metals in soil has been reported to affect the quality of food grown, groundwater quality, micro-organisms activity and plant growth (Popescu *et al*., 2009).

The activities that generate concentration of these heavy metals and other elements in the soil can have a serious effect on the affected communities. The effects include toxicological and environmental degradation. It is now known that exposure to some heavy metals has been linked with developmental retardation, various cancers, kidney damage and even death. Exposure to high levels of mercury, gold and lead has been reported to be associated with the development of autoimmunity in which the system's needed immune system begins to attack the cells it should protect, mistaking them for foreign bodies. And, that the autoimmunity can lead to the development of diseases of the circulatory or central nervous system (Glover-Kerkvliet, 1995).

Despite the known health effects, it is also known that mercury is still extensively used in gold mining in many parts of the world, including our research sites.

Artisanal mining is a process that is associated with generation of dust. The uncoordinated, uneducated and unprotected miners take in this dust laden with crystalline silica which is known to be a major soil forming component. The inhalation of this crystalline silica has been reported to initially cause respiratory irritation and an inflammatory reaction in the lungs (Vallyathan *et al*., 1995). Acute exposures to high

Corresponding Author: D.J. Adeyemo, Health Physics and Radiation Bio-Physics Section, Center for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

concentrations cause cough, lipoproteinosis (Chronic Toxicity, 2005). In a report on the hazards of exposure to crystalline silica, it was stated that, NIH (1997) reported that their studies from many different work environments suggest that "exposure to working environments contaminated with silica at dust levels that appear not to cause roentgenographically visible simple silicosis can cause chronic airflow limitation and/or mucus hypersecretion and/or pathological emphysema". In the result of Hnizdo and Vallyathan (2003), they concluded that "chronic levels of silica dust that do not cause disabling silicosis may cause the development of chronic bronchitis, emphysema and/or small airways disease that can lead to airflow obstruction, even in the absence of radiological silicosis" (Oxman *et al*., 1993; Park *et al*., 2002; Hnizdo and Vallyathan, 2003; Balmes *et al*., 2003)

MATERIALS AND METHODS

Soil sample collection: An initial survey was undertaken of the two main sites to map out in each case the three mining stages where sampling was to be carried out. The two study sites are: Hawwal, located on the southern part of Kebbi state between longitudes 4°45' and 4°50' East of the prime meridian and latitudes 11°35' and 11°40' North of the equator and Bagega, which is a settlement on the North-Eastern part of Hawwal, though in Zamfara State. Baggage is on longitude 6°00' East of the prime meridian and latitudes 11°43' to 11°50' North of the equator.

About 500 g of soil from each spot was collected. All the samples were mixed thoroughly as a composite sample representative of the sampling stages. They were transferred into polythene bags, labeled and double-bagged to avoid cross-contamination in each case.

Procedure for analysis of samples: 0.5g of each sample for analysis was weighed and grounded in an agate mortar and a binder (PVC dissolved in Toluene) was added to each sample, carefully mixed and pressed in a hydraulic press into a pellet.

A compact Mini Pal 4 energy dispersive x-ray fluorescence spectrometer (PW4030) was used for the elemental analysis. The system is controlled by a computer running the dedicated Mini pal analytic software and the microprocessor controls the analytical instrument which was designed for the detection and measurement of elements in a sample from sodium to uranium. The pellets were loaded in the sample chamber of the spectrometer and voltage (30kv max.) and a current (1mA max.) were applied to produce the x-rays to excite the samples for a preset time of 10 minutes each. The spectra of the samples were then analyzed to determine the concentrations of the elements in the samples.

RESULTS

A total of ten (10) elements that were determined are presented in this study. Table 1-6 and correspondingly, Fig. 1-6 represent the analytical results for the two sites that were investigated. Table 7a and 7b on the other hand, give the comparative summary of the elemental assessments. The benchmark by regulatory bodies are presented in Table 8.

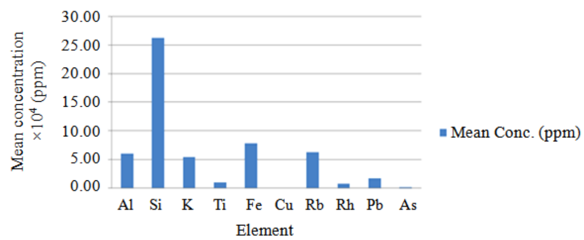

Fig. 1: Chart of result for Awwal mine zone

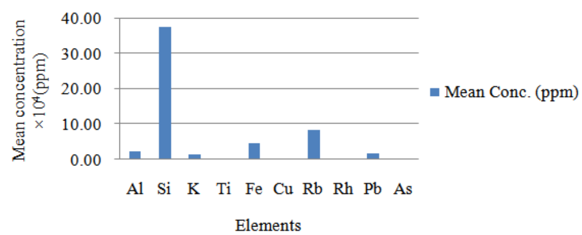

Fig. 2: Chart of result for Awwal mills zone

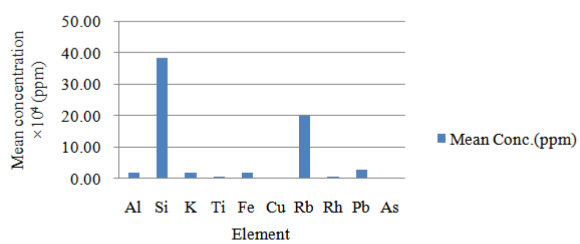

Fig. 3: Chart of result for Awwal sedimentation zone

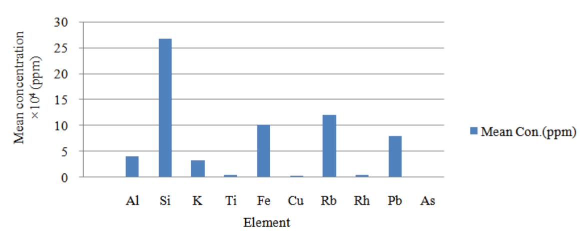

Fig. 4: Chart of result for Bagega mine zone

Table 1: Result for Awwal mines zone

	AWWAL: KEBBI state Unit 1: Mining café samples Sample code/element concentration $\times 10^4$ (ppm)									
Element	C_1S_1	C_1S_2	C_2S_1	C_2S_2	C_3S_1	C_3S_2	C_4S_1	Mean	Max.	Range
Al	7.04	6.51	4.39	6.24	6.56	6.30	5.13	6.02	7.04	4.39-7.04
Si	17.71	32.14	32.29	27.61	18.96	25.78	29.75	26.32	32.29	17.71-32.29
K	7.20	5.10	3.31	4.65	8.55	6.56	2.84	5.46	8.55	2.84-8.55
Ti	1.70	0.36	0.53	0.69	1.95	0.93	0.63	0.97	1.95	0.53-1.95
Fe	14.65	0.06	6.11	4.33	11.40	5.77	12.25	7.80	14.65	0.06-14.65
Cu	0.07	0.03	0.10	0.04	0.06	0.07	0.07	0.06	1.10	0.03-0.10
Rb	10.97	N.D	N.D	11.88	11.88	9.14	N.D	5.27	11.88	6.27-11.88
Rh	0.71	0.32	0.81	0.38	0.78	1.14	0.97	0.73	1.14	0.32-1.14
Pb	2.13	1.11	1.58	1.67	2.13	1.58	2.04	1.75	2.13	1.11-2.13
As	0.17	0.07	0.37	0.23	0.21	0.13	0.15	0.19	0.37	0.07-0.37

Table 2: Result for Awwal mills zone

	Unit 2: Mining shed samples Sample code/concentration $\times 10^4$ (ppm)								
Element	M_1S_1	M_1S_2	M_2S_1	M_2S_2	M_3S_1	M_3S_2	Mean	Max.	Range
Al	2.80	2.80	2.49	2.38	1.32	2.59	0.40	2.80	1.32-2.8
Si	39.19	39.28	37.79	35.64	34.38	39.19	37.58	39.28	34.38-39.28
K	1.83	1.68	1.49	1.48	0.97	1.47	1.49	1.83	0.97-1.83
Ti	0.17	0.17	0.14	0.17	0.20	0.15	0.17	0.20	0.14-0.2
Fe	2.77	2.79	5.23	8.21	4.91	0.53	4.57	8.21	2.77-8.21
Cu	0.09	0.08	0.09	0.10	0.11	0.04	0.09	0.11	0.04-0.11
Rb	N.D	N.D	N.D	N.D	8.59	N.D	8.59	8.59	0-8.59
Rh	0.43	0.35	0.32	0.53	0.77	0.28	0.45	0.77	0.28-0.77
Pb	0.19	1.86	2.50	2.98	2.50	0.19	1.70	2.98	0.19-2.98
As	0.37	0.30	0.36	0.55	0.23	0.07	0.31	0.55	0.07-0.55

Table 3: Result for Awwal sedimentation zone

	Unit 3: Sedimentation zone samples Sample code/concentration $\times 10^4$ (ppm)								
Element	T_1S_1	T_1S_2	T_2S_1	T_2S_2	T_3S_1	T_3S_2	Mean	Max.	Range
Al	1.18	1.80	0.38	2.54	0.85	0.53	1.88	2.85	0.53-2.85
Si	41.43	42.04	40.12	38.86	40.68	27.28	38.40	42.04	27.28-42.04
K	2.16	1.04	2.39	3.34	1.29	N.D	2.04	3.34	1.04-3.34
Ti	0.08	0.27	0.50	2.88	0.12	0.09	0.66	2.88	0.08-2.88
Fe	0.25	1.61	2.65	2.61	1.90	2.65	2.11	2.65	1.25-2.65
Cu	0.05	0.02	0.03	0.06	0.03	0.08	0.05	0.08	0.02-0.08
Rb	N.D	N.D	N.D	N.D	N.D	20.11	20.11	20.11	0-20.11
Rh	0.97	0.41	0.48	0.81	N.D	0.66	0.67	0.97	0.41-0.97
Pb	N.D	0.58	N.D	N.D	1.02	2.69	0.86	2.86	1.02-2.86
As	N.D	N.D	N.D	N.D	0.02	0.16	0.09	0.16	0.02-0.16

Table 4: Result for Baggage Mine zone

	Baggage/Sunke: Zamfara state Unit 1: Mining zone samples Sample code/element concentration $\times 10^4$ (ppm)												
Elements	C_2S_2	C_2S_3	C_1S_1G	C_1S_1	C_1S_2	C_3S_1	C_3S_2	C_3S_3	C_3S_4G	C_4S_3	Mean	Max.	Range
Al	5.24	7.41	0.37	5.29	4.13	3.33	2.33	5.82	1.32	6.35	4.16	7.41	0.37-7.41
Si	14.95	27.84	33.16	33.68	29.61	33.07	17.28	26.48	23.82	28.82	26.87	33.68	14.95-33.68
K	5.54	5.58	N.D	4.21	2.08	1.42	2.49	3.35	0.75	3.69	3.23	5.58	1.42-5.58
Ti	0.66	0.78	N.D	0.33	0.17	0.32	0.60	0.78	0.05	0.45	0.46	0.78	0.05-0.78
Fe	15.58	8.25	7.90	6.30	8.25	5.53	17.47	11.81	8.11	12.79	10.20	17.47	6.3-17.47
Cu	0.45	0.27	0.53	0.20	0.83	0.20	0.47	0.34	0.37	0.13	0.38	0.83	0.2-0.83
Rb	8.14	N.D	11.88	N.D	N.D	N.D	16.45	N.D	N.D	N.D	12.16	16.45	8.14-11.88
Rh	0.16	0.16	0.41	N.D	N.D	N.D	1.78	0.07	N.D	N.D	0.52	1.78	0.16-1.78
Pb	11.13	3.52	1.3	1.39	9.93	9.27	4.27	7.61	30.24	1.86	8.05	30.24	1.3-30.24
As	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.00	0.00	0.00

Table 5: Result for Baggage Mills zone

	Unit 2: The milling shed samples Code/ Element concentration $\times 10^4$ (ppm)										
Elements	M_1S_2	M_1S_3	M_2S_1	M_2S_2	M_2S_3	M_3S_1	M_3S_2	M_3S_3	Mean	Max.	Range
Al	1.32	0.53	0.74	N.D	7.41	6.35	0.95	6.88	3.45	7.41	0.53-7.41
Si	25.60	12.61	21.16	26.17	24.76	27.33	23.64	29.33	23.83	29.33	12.61-29.33
K	0.73	N.D	N.D	N.D	5.82	3.67	0.20	3.57	2.80	5.82	0.20-5.82
Ti	0.10	0.06	0.02	N.D	0.75	0.53	0.04	0.28	0.22	0.75	0.02-0.75
Fe	7.54	6.95	5.25	3.78	7.13	14.04	52.17	11.53	13.55	52.17	3.78-52.17
Cu	0.49	0.46	0.32	0.81	0.14	0.16	0.53	0.13	0.38	0.81	0.13-0.81
Rb	N.D	13.71	N.D	23.77	10.97	N.D	N.D	N.D	17.82	23.77	10.97-23.77
Rh	N.D	0.97	N.D	2.59	N.D	N.D	N.D	N.D	1.78	2.59	0.97-2.59
Pb	25.05	18.55	38.50	7.24	N.D	2.23	31.26	1.67	17.79	38.50	1.67-38.50
As	0.05	0.08	N.D	N.D	N.D	N.D	N.D	N.D	0.07	0.08	0.00-0.05

Table 6: Result for Baggage sedimentation zone

	Unit 3: Sedimentation zone Sample Code/Concentration $\times 10^4$ (ppm)										
Element	S_1S_1	S_1S_2	S_1S_3	S_2S_1	S_2S_2	S_2S_3	S_3S_2	S_3S_3	Mean	Max.	Range
Al	0.48	1.59	1.43	1.43	1.01	1.16	1.11	0.95	1.15	1.59	0.48-1.59
Si	10.65	31.90	17.38	21.42	15.23	25.27	29.80	26.39	22.26	31.90	10.65-31.9
K	N.D	0.56	1.41	0.26	0.56	N.D	0.39	0.58	0.47	1.41	0.26-1.41
Ti	0.01	0.12	0.23	0.18	0.13	0.11	0.07	0.05	0.11	0.23	0.01-0.23
Fe	5.19	4.97	11.53	8.23	9.78	7.34	6.03	6.42	7.44	11.53	4.97-11.53
Cu	0.33	0.25	0.61	0.41	0.58	0.38	0.30	0.42	0.41	0.61	0.3-0.61
Rb	N. D	N. D	N. D	N. D	N. D	N. D	N. D	N. D	-	-	.
Rh	N. D	N. D	N. D	N. D	N. D	N. D	N. D	N. D	-	-	-
Pb	57.60	15.77	33.49	24.72	29.69	25.97	19.48	27.18	29.24	57.6	19.48-57.6
As	N.D	0.01	N.D	N.D	N.D	0.08	0.06	N.D	0.05	0.08	0.01-0.08

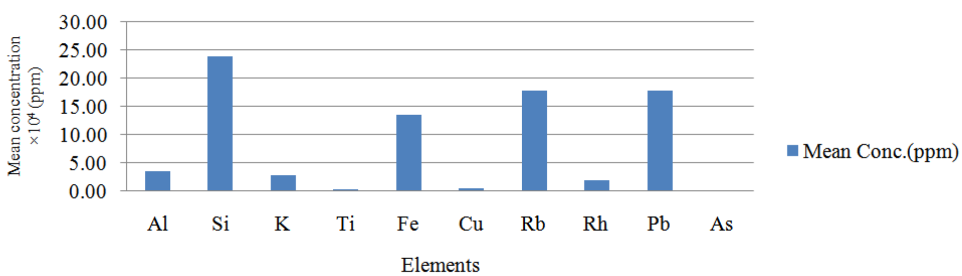

Fig. 5: Chart of result for Bagega mills zone

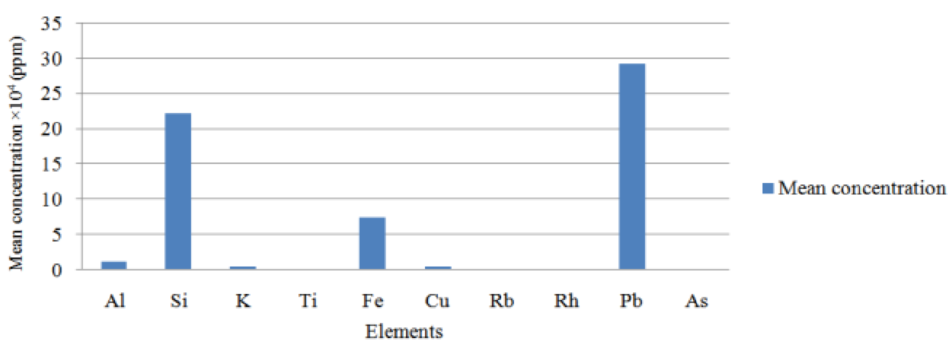

Fig. 6: Chart of result for Bagega sedimentation zone

Table 7a: Percentage composition of mean concentration values of Heavy Metals and other elements of interest from the two study sites

	Percentage composition of mean values of heavy metals and other elements							
	Pb		Si		Fe		Rb	
Mining stages	Awwal	Bagega	Awwal	Bagega	Awwal	Bagega	Awwal	Bagega
Mining zone	1.75	8.05	26.32	26.87	7.80	10.20	6.27	12.16
Milling zone	2.98	17.79	39.28	23.83	8.21	13.55	8.59	17.82
Sedimentation zone	2.86	29.24	38.40	22.26	2.11	7.44	20.11	-

Table 7b: Converted values of percentage mean concentration values to parts per million (ppm)

	Parts per million (ppm) composition of mean values of heavy metals concentrations							
	Pb		Si		Fe		Rb	
Mining stages	Awwal Baggage	Baggage	Awwal	Baggage	Awwal	Baggage	Awwal	
Mining zone	17500	80500	263200	268700	78000	102000	62700	121600
Milling zone	29800	177900	392800	238300	82100	135500	85900	178200
Sedimentation zone	28600	292400	384000	222600	21100	74400	201100	-

Table 8: Regulatory limits for comparison to obtained values of Heavy metals and other elements in Table 7b

	Regulatory limits						
	Pb		Si	Fe		Rb	
Regulatory bodies	(mean)	(range)	(mean)	(mean)	(range)	(mean)	(range)
Shacklette and Boerngen (1984)*	19 ppm	<10-700 ppm	-	26000 ppm	100 - >100,000 ppm	67 ppm	<20-210 ppm
USEPA Human Health*	400 ppm			55,000 ppm		NSL	NSL
ACGIH (2004)			3 μg m^{-3}				
NIOSH (1974)	-	-	5 μg m^{-3}	-	-	-	-

Key: NSL: No Screening Level; *: Records updated by March 21, 2008

DISCUSSION

Notable at the two main sites were volumes of dust which ranged in different concentrations from the mining to the processing units. Artisanal miners have been known, from history, as operators without the use of facilities that can provide them with respiratory protection. Thus, with such nature of operations observed in the studied sites, the levels of dust that was observed may be taken as the actual personal exposures of these miners.

The mean concentration value for Pb is 17.79 mg Kg^{-1} reaching a maximum concentration of 38.50 mg Kg^{-1}. The value is already at the action level with reference to regulatory limit as shown in Table 8. Children are known to have developed systems that are vulnerable to toxic elements even at low concentrations. The rise in concentration of Pb in the milling stage shows that Pb may be present as well in the mine but its poor mobility may not have allowed its detection on the stage. A comparative assessment of Fig. 4-6 show a trend for Pb; its presence increased with processing stages. There may be possibilities that the solubility of Pb in the sites is a function of the pH levels of the soils of each site as well as other accompanying factors. Considering these properties associated with Pb, they may have worked together in relation to the nature of the soil at the mine location to influence the elevated level of Pb as well as other elevated concentrations of metals observed in the sedimentation zone. The Pb results as indicated in Table 7 and 8 showed concentrations well above regulatory benchmark. Children could be exposed largely by their hand-to-mouth behaviors, their lower body weight and closeness of their breathing zones to the ground and thus closer to soil contaminants and low-lying layers in the air.

There were four elements all with concentrations several times above regulatory benchmarks in the two Gold mine sites that were studied. Table 7a shows the percentage composition of mean concentration values of the four elements. The compositions are all shown in parts per million (ppm) in Table 7b and Table 8 shows regulatory benchmarks. It can be seen by comparing Table 7b and 8 that almost all the elevated elements are in many folds above regulatory benchmarks. All, except Rb, have direct contamination/poisoning properties or possible direct or indirect carcinogenic characteristics. Crystalline Silica is indirectly carcinogenic, while Iron may not be directly poisonous at ordinary state. In its elevated level Fe essentially stimulates the increase in the concentration of other toxicological hazardous elements such as arsenic in soil (Chen *et al*., 2000).

Of the four high-concentration-elements at various stages, two of them present latent and immediate hazards to health; Respiratory crystalline silica (Si) is the major element constituent of the ever-well-pronounced mining dusts of the two sites. Its form of occurrence portends irreversible health problem called silicosis and is well linked with cancer forming properties; both of which develop through latency periods. Lead (Pb), at any concentration portends both immediate and long term hazards to women and children at the greatest risks of exposures. Consistently high concentrations of respiratory Silica and up surging Pb in the two sites (especially in Bagega), are signs of possible risk of exposure to contamination/poisoning by these elements.

CONCLUSION

Based on the work carried out and the results presented, the artisanal gold mining exercises in the two zones are likely to have immediate and long term health risks to the exposed populations if left unchecked. The hazard is not limited to the miners only, but because of the unprofessional practice of the miners, the whole village and its visitors may be equally at risk.

REFERENCES

ACGIH, 2004. Guide to Occupational Exposure Values. 1st Edn., ACGIH, Cincinnati, ISBN-10: 1882417550, pp: 172.

Balmes, J., M. Becklake, P. Blanc, P. Henneberger and K. Kreiss *et al*., 2003. Environmental and occupational health assembly. Am. Thoracic Soc.

Chen, M., L.Q. Ma and Y.C. Li, 2000. Concentrations of P, K, Al, Fe, Mn, Cu and As in Marl Soils from South Cited. In: Heavy Metals and Toxic Trace Elements Contents in Soils of Selected Areas of the Kavala Prefecture, Papastergios, G., (Ed.). Northern Greeceulletin of the Geological Society of Greece, Greece, pp: 263-272.

Chronic Toxicity, 2005. Silica (crystalline, respirable). CAS Registry Number, 7631-86-9.

Glover-Kerkvliet, J., 1995. Environmental assault on immunity. Environ. Health Perspect., 103: 236-239. PMID: 7768222

Hnizdo, E. and V. Vallyathan, 2003. Chronic obstructive pulmonary disease due to occupational exposure to silica dust: A review of epidemiological and pathological evidence. Occup. Environ. Med., 60: 237-243. PMID: 12660371

NIH, 1997. Adverse effects of crystalline silica exposure. American thoracic society committee of the scientific assembly on environmental and occupational health. Am. J. Respir Crit Care Med., 155: 761-768. PMID: 9032226

NIOSH, 1974. National Institute for Occupational Safety and Health. NIOSH.

Oxman, A.D., D.C. Muir, H.S. Shannon, S.R. Stock and E. Hnizdo *et al*., 1993. Occupational dust exposure and chronic obstructive pulmonary disease. A systematic overview of the evidence. Am. Rev. Respir. Dis., 148: 38-48. PMID: 8317812

Park, R., F. Rice, L. Stayner, R. Smith and S. Gilbert *et al*., 2002. Exposure to crystalline silica, silicosis and lung disease other than cancer in diatomaceous earth industry workers: A quantitative risk assessment. Occup. Environ. Med., 59: 36-43. PMID: 11836467

Popescu, I.V., C. Stihi, G.V. Cimpoca, G. Dima and G. Vlaicu *et al*., 2009 Environmental sample analysis by Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma-optical Emission Spectroscopy (ICP-AES). Rom. J. Phys., 54: 741-746.

Shacklette, H.T. and J.G. Boerngen, 1984. Element concentrations in soils and other surficial materials of the conterminous United States. USGS.

Vallyathan, V., V. Castraova, D. Pack, S. Leonard and J. Shumaker *et al*., 1995. Freshly fractured quartz inhalation leads to enhanced lung injury and inflammation. Potential role of free radicals. Am. J. Respir. Crit. Care Med., 152: 1003-1009. PMID: 7663775

WR, 1998: Heavy metals and health. World Resources Institute, Washington, D.C.