Analysis of PM10 in the Working Environment of Quarry Using ED-TXRF Technique

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Abstract

Fractionated PM10 samples consisting of coarse fraction (2-10 μm EAD) and fine fraction (<2μm EAD) were collected from airborne quarry dust using the Stacked Filter Unit aerosol sampler and analyzed for the elements Si, Al, K, Ca, Fe, Ti, Mn, V, Cu, Zn, Sr, and Pb using Energy-Dispersive Total Reflection X-ray Fluorescence (ED-TXRF) technique. The results obtained indicated that PM10 emission is dominated by coarse fractions for the major element Al, Si, K, Ca and Fe while the fine fractions are highly enriched in trace elements Cu, Zn and Pb for the various quarrying processes. The study also revealed significant crust-air fractionation of Al and Si as a result of quarrying activity as demonstrated by Si-Al ratio which is 14.7-31.4% lower than the average crustal values. The study further showed the effect of wetting agents and mechanization of the quarrying processes in reducing occupational exposure to quarry dust.

Introduction

The increasing use of crushed rock of different size aggregates in building and road construction in Nigeria has led to the establishment of several quarry businesses at locations where there are large rock deposits. The quarrying business involves several groups including small-scale operators that use simple tools like jackhammers, wedges, digger etc and fewer large companies that use the crushing machine and other instruments to reduce rock fragments into smaller size aggregates. In the process of crushing the rock, dust particles of various sizes including particles that are less than 10 microns in diameter known as PM10 are released into the atmosphere. PM10 are characterized with considerable resident time range in the atmosphere and are thus transported over long distances by the winds thereby resulting in their continual accumulation in the atmosphere, even at locations far from the source.

Mineral dusts including quarry dust are known to interact with gaseous liquid and solid constituents in the atmosphere (Ramanathan *et al.,* 2001) resulting in uptake of pollutants. This has been shown to occur at several places around the world. For example, transport of mineral dust from China to North America has been shown to be accompanied by airborne pollutants

(Jaffe *et al., 2003)* and pollutants originating from European sources had been detected in Saharan dust (Formenti *et al.,* 2001).

PM10 particles associated with mineral dusts are small enough to be inhaled into the lungs. In particular, the fine component known as $PM_{2.5}$ can be inhaled into the deepest part of the lungs, resulting in onset of respiratory problems as the body react to their presence. Thus inhalation of high concentration of PM10 associated with mineral dust often results in irritations of the upper human respiratory tract and subsequent lung function impairment, with the possibility of degenerating into pulmonary diseases (Oleru, 1984). They can thus increase the number and severity of asthma attacks, bronchitis and other lung diseases. It has been suggested that pollutants associated with mineral dust are the determining factor in asthma attacks, rather than the mineral dust itself (Glikson *et al.,* 1995). Some of the elements in the quarry dust have been linked with various health effects, most especially Si and Al which are the major elements. Inhalation of high concentration of silicon may result in silicosis, a condition that often leads to permanent damage of the cells in the lungs (Jackson *et al.,* 1989). Although Al becomes toxic only at high concentration, long time of exposure may result in pulmonary fibrosis, as it is not easily expelled from the lungs after deposition. For these reasons, indiscriminate release of quarry dust in the atmosphere should be monitored and controlled.

In the present study, PM10 was collected at various quarry industry locations in Zaria and Federal capital territory in Nigeria using the stacked filter unit (SFU) aerosol sampler (Cahill *et al.,* 1977; Maenhaut *et al.,* 1995), which consists of a PM10 pre-impaction stage that provides upper size cut-off of 10μm equivalent aerodynamic diameter (EAD). The inclusion of PM10 inlet in the sampling line results in small sample loading on the filters as a result of restriction on flow-rate and particle size and hence requirement of sensitive, specific, accurate, fast multi-elemental analytical technique that is capable of analyzing major, minor and trace constituents. The multi-element ED-TXRF technique (Wobrauschek and Aiginger, 1986), which was employed for analysis of several elements including Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, and Pb in the quarry dust is characterized with detection limit of the order of parts per billion (Okunade *et al.*, 2004) and also meet the above requirements. It was found to be a powerful tool in the analysis of PM10 resulting from the quarry activities.

Material and methods
PM10 sampling
PM10 sampling was limited to manual quarrying (using Jackhammers, wedges etc) and mechanized quarrying utilizing single crusher assembly (SCA), Double Crusher Assembly (DCA) and Triple Crusher Assembly (TCA). For each of these quarrying methods the sampler was situated at average position of the workers. Fractionated PM10 samples were collected with SFU consisting of PM10 pre-impaction stage and two filter cassettes for coarse and fine "Nuclepore" membrane filters arranged in series. The different filtration efficiencies of the filters result in fractionation of the PM10 into coarse fraction and fine fraction having particle size of 2-10μm EAD and <2μm EAD respectively. The SFU is thus characterized with collection efficiency that is similar to that of upper human respiratory tract (Cahill *et al.,* 1977). The SFU was mounted on a wooden pole and directed vertically downwards. In order to

prevent contamination from the pump, the exhaust of the pump was positioned far away from the sampling position and downwind from it using long POLY FLO tubing. Pre-weighing of filters including the blank filters was separately carried out in the

laboratory. After sample collection, the filter was placed in a petri dish to avoid contamination during transportation to the laboratory. Throughout the sampling campaign, the rotameter was set at a flow-rate of 16litres/min and the sampling of particulate matter conducted for specific time period depending on the dust loading.

Sample preparation and sample analysis
The Nuclepore membrane filter was cut into two and one portion of it used for analysis. The sampled particulate matter on the filters (fine and coarse fraction) was removed in 65% pure nitric acid and Ga added as internal standard following the procedure described elsewhere (Okunade *et al.,* 2004). About 5µl of dissolved material and particulate matter was then deposited on the quartz sample carrier and dried under infrared light. For the analysis of Si, plexi glass was used as sample carrier instead of quartz. This is because of the high silica content of quartz.

Multi-element analysis was carried out using the TXRF arrangement consisting of a Molybdenum target X-ray tube with a fine focus and total reflection module and ED-TXRF spectrometer. X-ray spectra from the samples were collected using a liquid nitrogen cooled Si(Li) detector characterized with 165 eV resolution at 5.9 keV and an ORTEC electronic system consisting of a high voltage power supply, spectroscopy amplifier, analog to digital converter (ADC), PC based MCA electronic card and MAESTRO acquisition software. Spectra analysis was performed using IAEA AXIL software (Nullens *et al.,* 1979; IAEA, 1995) while quantitative calculations were performed using the "Regression of count rates versus concentration" method contained in IAEA QXAS software package (IAEA, 1995). The prepared specimens were measured for 500s at a voltage of 40kV and current of 20mA.

Results and discussion
Table 1 provides the summary of the emission data for PM10 for the various quarrying methods for granitic rocks. SCA is characterized with higher PM10 concentration (than TCA and DCA) because of the dryness of the rocks and the citing of the sampler close to the average position of the workers who are exposed to the emitted dust as a result of their direct involvement in manual loading of the crusher and the evacuation of the crushed rock aggregates. On the other hand, lower concentrations of PM10 from TCA and DCA crushers are due to wetting of the rocks and the work premises. PM10 concentration from DCA crusher assembly was further reduced during the wet season due to precipitation scavenging and reduction of dust mobilization. The coarse/fine ratio of 1.8 or greater provides an indication that the emitted PM10 from quarrying activities is highly enriched in coarse fraction compared to the fine fraction. However, wetness of the rocks results in lower coarse-fine ratio due to reduction in mobilization of coarse fraction. In general, emitted PM10 concentration exceeds USE EPA PM10 standard of 70 $\mu g/m^3$ for coarse fraction and 15 $\mu g/m^3$ for fine fraction and thus may result in significant health deterioration.

Table 1: Summary of the emission data for PM10 for various quarrying methods

Quarrying Method	Mean Conc. Fine Fraction (μg/m^3)	Mean Conc. Coarse Fraction (μg/m^3)	Mean Conc. PM10 (μg/m^3)	Coarse- Fine Ratio
MQ	81.48	238.27	319.75	2.92
SCA	555.56	2888.89	3444.45	5.20
DCA-D	64.81	157.41	222.22	2.43
DCA-W	18.53	19.65	38.18	1.06
TCA	116.67	270.37	387.04	2.32

Multi-element analysis of the PM10 samples displayed in Table 2 and 3 shows the mean elemental concentrations for coarse and fine fractions for elements Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, and Pb in the PM10 samples relative to their background values. The concentration of all the elements monitored exhibit high variation in accordance with variation in their PM10 concentrations. The presence of Pb in significant concentration can be attributed to emission from exhaust of vehicles used for loading and offloading within the quarry premises and windblown soil dust. Table 2 also shows that Si-Al ratio for the various quarrying methods ranges from 2.34-2.91. This is much lower than Si-Al ratio of 3.41 (Mason, 1966), 3.42 (Taylor, 1964), 3.90 (Wedepohl, 1971) and 4.02 (Turekian, 1971) in average crustal rock indicating that there is significant reduction of Si-Al ratio of 14.7-31.4% compared to Mason's crustal value of 3.41. This provides an indication of crustal-air fractionation of silicon and aluminium since Al is strongly correlated with Si (with correlation coefficient of 0.97).

Table 2: Mean elemental concentration of coarse fraction (μg/m^3) in PM10
samples resulting from various quarrying methods.

Element	MQ	SCA	TCA	DCA-D	DCA-W
Al	10.757±0.621	127.176±4.783	10.803±0.675	8.411±0.500	-
Si	26.172±1.410	311.218±3.711	25.256±0.347	24.480±0.294	-
K	7.632±0.044	144.141±0.358	8.017±0.065	7.946±0.043	0.920±0.011
Ca	7.172±0.037	66.419±0.255	7.101±0.047	1.608±0.027	0.314±0.006
Ti	0.865±0.015	10.774±0.089	1.534±0.017	0.167±0.011	0.026±0.002
V	0.097±0.007	0.910±0.056	-	-	-
Mn	0.176±0.007	1.763±0.045	0.406±0.010	0.031±0.005	0.010±0.001
Fe	6.652±0.017	66.827±0.125	13.455±0.038	0.627±0.012	0.260±0.002
Cu	0.330±0.009	3.635±0.066	0.083±0.011	0.102±0.007	0.054±0.003
Zn	0.310±0.010	4.874±0.047	0.123±0.011	0.085±0.008	0.048±0.003
Sr	0.321±0.020	3.201±0.235	0.230±0.009	-	-
Pb	0.382±0.026	3.351±0.178	0.132±0.023	0.134±0.029	0.061±0.013
Si /Al ratio	2.43	2.45	2.34	2.91	-

Table 3: Mean elemental concentration of fine fraction ($\mu g/m^3$) in PM10 samples from various quarrying methods.

Element	MQ	SCA	TCA	DCA-D	DCA-W
K	1.349±0.040	31.815±0.588	2.209±0.078	.277±0.026	0.603±0.023
Ca	1.620±0.022	13.619±0.362	1.424±0.048	0.561±0.016	0.293±0.012
Ti	0.011±0.006	-	0.153±0.019	-	-
Fe	0.714±0.007	8.784±0.092	1.786±0.018	0.306±0.005	0.151±0.004
Cu	0.373±0.012	7.307±0.164	0.328±0.041	0.220±0.007	0.169±0.007
Zn	0.363±0.013	5.661±0.234	0.338±0.027	0.244±0.007	0.159±0.007
Pb	0.453±0.030	7.363±0.291	-	0.260±0.019	0.186±0.031

Using the individual fine and coarse concentration data, fine-coarse ratios were calculated for each of the elements K, Ca, Ti, Fe, Cu, Zn, Pb in every PM10 sample and these ratios were subsequently averaged over all the samples. As shown in Fig. 1, the mean fine/coarse ratios for the elements K, Ca, Fe, Ti, ranges between 0.2 to 0.4, while the trace elements Cu, Zn and Pb have fine/coarse ratios above 2.0, thus showing that PM10 from the various quarrying methods are dominated by coarse fractions for the major elements K, Ca, Fe and Ti, while the fine fractions are enriched in trace elements Cu, Zn and Pb. It is instructive to note that proper application of water alone is capable of suppressing emission of Al and Si during quarrying since they were only detected in the coarse fractions but neither in any of the fine fractions nor in samples collected during wet season. Lower concentrations were also observed for other elements during the wet season as shown in Table 4 for DCA samples collected during the dry season (DCA-D) and DCA samples collected during the wet season (DCA-W). This again can be attributed to precipitation scavenging. In addition, fine-coarse ratio for DCA samples collected during the wet season is generally greater than the value obtained during the dry seasons for all the elements monitored, again indicating that application of water has greater effect in reducing the concentration of elements when they are in coarse fraction than in fine fraction.

Conclusion
Size fractionated sampling has been applied for the assessment of PM10 resulting from occupational exposure to quarry dust using the stacked filter unit aerosol sampler whose collection efficiency is similar to that of upper human respiratory system. The multi-elemental data obtained from the TXRF analysis of fractionated PM10 from the various quarrying methods indicated that PM10 emission is dominated by coarse fractions for the major element Al, Si, K, Ca and Fe while the fine fractions are highly enriched in trace elements Cu, Zn and Pb. The study also revealed the effect of quarrying on crust-air fractionation of aluminum and silicon as demonstrated by Si-Al ratio which is 14.6-31.3% lower than the Mason's average crustal values. The study further showed that significant reduction in PM10 emission and hence lower occupational exposure from quarrying activities could be achieved with regular usage of wetting agents and mechanization of the quarrying processes.
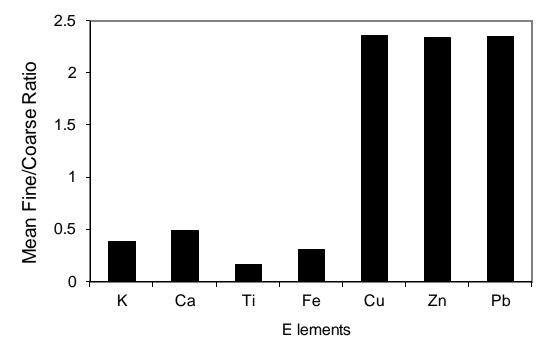
Fig. 1: Mean fine/coarse concentration ratios for selected elements in PM10
samples collected from quarry industries.

Table 4: Comparison of mean concentration of PM10 for dry and Wet Seasons

Element	Coarse fraction ($\mu g/m^3$)			Fine fraction ($\mu g/m^3$)		
	DCA-D	DCA-W	DCA-W/DCA-D	DCA-D	DCA-W	DCA-W/DCA-D
`K	7.946	0.920	0.116	0.277	0.060	0.217
Ca	1.608	0.314	0.195	0.561	0.293	0.522
Ti	0.167	0.026	0.156	-	-	-
Mn	0.031	0.010	0.322	-	-	-
Fe	0.627	0.260	0.414	0.306	0.151	0.493
Cu	0.102	0.054	0.529	0.220	0.169	0.768
Zn	0.085	0.048	0.565	0.244	0.159	0.652
Pb	0.134	0.061	0.455	0.260	0.186	0.715

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