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Study of the Elemental Concentrations of Aerosol Particulates of Ariab Mining Area using PIXE

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Abstract: ***The goal of this work was to determine the concentration of these elements (Si, S, Ca, Cr, Mn, Fe, Cu, Zn, and Pb) in aerosol collected at six different sites of Ariab Mining area which located in the eastern part of Sudan. The samples were taken onto a nucleopore membrane filter with an air sampler that constructed to collect airborne particulate. For the quantitative determination of the investigated elements, a proton-induced X-ray emission accelerator (PIXE) was used, the accuracy of the measurements has been investigated by using certified Micro-Matter® thin film standards. The average concentration values of Si, S. Ca, and Fe in (%) are 1.52, 0.19, 0.11, and 1.86 respectively while elements Cr, Mn, Cu, Zn, and Pb showed average concentration values in (ng/m^3) 25.7, 43.3, 100.8, 82.5 and 225.8 respectively. The enrichment factor (EF) of data using Si as a reference element showed that elements, Ca, Mn, Cu and Zn are non-enriched and are considered to be due to crustal sources while Fe and Cr are enriched suggesting an origin dominated by mining sources from the ore. Also, element Pb exhibited high EF value due to its anthropogenic sources of emission from the diesel machines at the site. The results of the correlation between different elements confirmed the presence of Cu and Zn as sulfides. Comparison of the data obtained in this work with some global data showed much higher concentration values for the typical crustal elements Si and Ca, for the anthropogenic element Pb with a relatively high value for Cu and Fe, where comparable values where found for elements Zn, and Cr.***

Keywords: Elemental concentrations, Aerosol particulates, Mining area, PIXE

1. Introduction

Several natural and anthropogenic sources introduce some inorganic elements in the atmosphere in the form of aerosol particulates, which may be transported to long distances before being deposited on the ground through dry fallout or wet scavenging. Their important sources are volcanic and mining activities, fossil fuel combustion, vehicle exhaust emission, and emission from various industries. Some of the elements are toxic in trace concentration and may contaminate the biosphere. Transport of toxic pollutants from industrial regions to remote areas creates health hazards [(1)].

Mining is an essential activity that provides the raw materials four our industrialized society. However unless adequate precautions are taken, mining can be accompanied by serious negative impacts on the environment and human health. The major potential environmental impacts include soil contamination from treatment residues, spillage of chemicals, leaching of pollutants from tailings and disposal areas and contaminated soils, air emissions from minerals processing operations, and dust emissions from sites close to living areas or habitats. The understanding and prediction of aerosol effect require the knowledge of its components which includes apart from others, inorganic elements in trace concentration. A study of the elemental composition of aerosol particulates of an area is, therefore, very important to assess the quality of the atmosphere [(2)].

Air quality monitoring is important to determine whether a limit value or guideline has been exceeded. Air quality monitoring systems should mainly address population exposure toair pollution. Exposure to air pollution may result in a variety of effects on humans, animals, and vegetation, varying from mild to fatal depending on the types of pollutants. Information about the relationship between exposure and response is necessary to estimate the potential health risks [(3)].

The major objectives of monitoring air pollutant levels are to provide an early warning system for pollutant levels which may have the potential to endanger public health, to assess air quality in light of established public health and welfare standards to track air pollution trends and changes in ambient air quality due to changes in the number of pollutants emitted; toproduce information for city planning, e.g. location of new industries and housing and to access the environmental impact of industry and other activities [(4)].

The Particle Induced X-ray Emission (PIXE) technique has shown itself well suited to precisely this type of broad range analysis, covering almost the entire spectrum of elements whilst requiring only micrograms of total samples. Studies of airborne contamination using PIXE and related techniques have been undertaken by several laboratories around the world and they demonstrate its value in environmental sciences [(5)].

The main objectives of this study are determination the concentration of the crustal and anthropogenic elements in the aerosol samples throughout the mining process, compare the obtained data with the global similar studies, examine the sources attributed to the measured concentrations using the enrichment factor and draw some correlations among the investigated elements.

2. Materials and Methods

2.1 Sampling area

The Ariab district lies at the center of the western part of the Ariab-Arbaat, Belt, 210 Km South West of Port-Sudan. During the last two decades, systematic exploration along

the Ariab belt has resulted in the discovery of more than twenty goassanous outcrops of volcanogenic sulfide deposits of copper, zinc, lead, and barite, with anomalous gold.

In Ariab mining area, the mining process begins with the cutting or drilling and blasting of the ore from the parent rock. They are is then scooped or gathered and loaded into trucks or onto conveyors for transport to the crushing area where mechanical crushing of the mined material takes place by drill kits, crushers, and mining machine picks. Then the crushed soil which containing the ore transports to the heap area to be treated using dripping dissolution method by KCN solution, then the dissolved are transported through different channels to the main tank to be ready for electrolysis.

Air samples were collected from Ariab mining area choosing six different locations. The first three locations represent Hassai, Hadaymet and kamoeb mines. The other locations represent three different areas:

1) The heap's area.
2) The crushing and lab area.
3) Beer Alagam village and camp area.

Figure 1 shows the sampling locations of Ariab mining area and Table 1 shows the sampling sites, volume, and sampling duration and number of samples.

Table 1: Sampling sites, volume, and sampling duration and number of samples

Location	Location Symbol	The volume of air sampled in (l)	Sampling duration (hours)	Number of Samples
Hassai Mine	HAS.M	6260	10	5
Hadaymet Mine	HAD.M	5300	10	5
Kamoeb Mine	KAM.M	2830	6	3
Heap Area	HEP.A	5410	10	5
Crushing and Lab Area	CR. LA	3870	8	4
Camp and Village Area	CA.VG	5440	10	5

Figure 1: The sampling locations of Ariab mining area

Sampling and samples preparation

Air samples were collected at approximately 1.5 meters from the ground level. The sampling time was two hours for each. An air sampler was constructed to collect airborne particulate matter where a vacuum pump was connected to a filter holder. The filter chosen was a nucleopore membrane with a diameter of 47 µm and a pore size of 0.45 µm. The system was connected with a gas meter to measure the volume of the air sampled. The filters were stored under sterile Petri dishes and in constant humidity and temperature. Following an integrated procedure of identification of the particulate matter and determination of its concentrations using PIXE technique, each filter was cut into four quarters with ceramic scissors in a cleanroom. One quarter was used for PIXE analysis.

PIXE Measurements

In this work proton-induced X-ray Emission (PIXE) technique has been employed for the determination of trace elements in environmental air samples collected from Ariab mining area in Eastern Sudan.

The elemental composition (Si, S, Ca, Cr, Mn, Fe, Cu, Zn, and Pb) of the aerosol samples were measured by the conventional in vacuum proton-induced X-ray emission [PIXE]. It consists of a tandem Pelletron from NEC of 1.7 MV, model 5 SDH, with an Alphatross RF ion source. A proton beam of 3 MeV was routinely used in the experiments.

The high energy of the accelerated proton beam causes the excitation of the electrons followed by an electron ejection from the inner electronic shells. The rearrangement of the electrons within the electronic shell is accompanied by an X-ray emission characteristic of the element. The X-ray energy identifies the elements that compose the target; whereas the number of counts at the specific energy is proportional to the concentration of the element. The spot diameter of the beam on the target was about 2-4 mm. The X-ray induced on the target was detected using an ortec Si(Li) detector [SLP-06165] with 30 mm^2 active area, 12.7 µm thick be window, and 170 eV measured FWHM energy resolution at 5.9 keV, placed at 135° referred to the beam direction. A kapton® film of 75 µm of thickness was placed in front of the Si(Li) detector and used as X-ray background of the spectrum. Hence, the most abundant element present in the particulate matter were determined simultaneously. The Si (Li) detector calibration was performed using the X-rays of the ^{55}Fe radioactive source[6]. The deferent PIXE spectra were processed with the Gupix package [Guelph PIXE software package [7]. This program is based on the fundamental parameter approach such X-ray production cross-sections, X-ray attenuation coefficients, stopping powers, detector efficiency, collected charge, and geometry effects. Assuming a thin target approximation, thus an out-put of the elemental concentration in ng/m^2 is obtained where the ion beam loses just a negligible fraction of its energy. In order to test the method for its accuracy, Micro-Matter® thin film standards were used. The

experimental values were in agreement with the certified values. The calculated minimum detection limits (MDL) of the elements were given in ng/m^{2}Table 2. The results of the relative error as a measure for accuracy are given in Table 3.

Table 2: Detection limits obtained for the elements in ng/m^2:

Element	DL
Si	638
S	46.1
Ca	15.9
Cr	9.23
Mn	8.11
Fe	3.3
Cu	2.27
Zn	2.16
Pb	13.5

Table 3: The accuracy of PIXE measurement by using Micro-Matter® thin film standards

Micromatter® Standards		certified values (µg/cm^2)	measured values (µg/cm^2)	Relative error %
ZnTe	Zn	18.7 ± 5%	19.17 ± 0.6 %	-2.5
	Te	36.5 ± 5%	37.5 ± 0.8 %	-2.7
CaF2	Ca	24.45± 5%	23.4± 2%	4.6
SiO_2	Si	24.98 ± 5%	23 ± 2 %	7.9
Ni	Ni	52.2± 5 %	53.13± 2 %	-1.7
Cu	Cu	48± 5 %	50.13± 2 %	-5.5

3. Results and Discussion

The elemental concentrations of six different sampling sites are presented in Tables 4& 5 and the average elemental concentrations (%) and(ng/m^3) are plotted in Figures 2& 3, respectively.

From the summary of the statistical data for aerosol samples concentrations are shown in Table 6. The percentage concentration of elements Si, S, Cl, K, Ca, and Fe are in the range (0.13-5.19, 0.01-1.98, 0.03-0.32 and 0.57-4.67), respectively and the average values are 1.52, 0.19, 0.11, and 1.86, respectively. Si and Fe showed a higher average concentration value in all locations in comparison with other elements. The element concentration values of Cr, Mn, Cu, and Zn, are in the range (0.01-57.6, 17.7-124.4, 10.19-492.3, and 32.8-225.7) with the average concentrations values 25.7, 43.3, 100.8, and 82.5 (ng/m^3), respectively. The element Pb showed concentration values range between 40.89-490.6 and average concentration value 225.8 ng/m^3, which suggested this element is emitted as a result of anthropogenic activity.
Si showed the highest average concentration values in Kamoeb mine aerosol. This could be linked to its strong crustal origin from the composition of the ore which mainly contains silicon dioxide (SiO_2), while it showed the lowest concentration values in the village and camp aerosols.

The element S showed high concentration values for Hadymet mine aerosol in addition to Zn and Cu, which suggested its source from the copper and zinc sulfide ores due to mining activity. For Fe, the element showed a relatively similar average concentration value in all sites. However, the crushing area displayed the highest value due to the dust scattering from the crushing pattern in the site, and this elevating in concentration values is denoted for the different elements.

The crustal element Ca showed relatively the same concentration values in Hassai mine aerosol. The element Cu showed high concentration value in Hadaymet mine aerosol, while Mn showed high concentration value in Kamoeb mine aerosol, however, both elements showed low as well as relatively same concentration value in all other locations.

Enrichment factor analysis:
The separation of natural and anthropogenic components is a basic task of aerosol measurements. Enrichment Factor (EF) analysis is conventionally used for separating soil-derived and anthropogenic components. Therefore, to verify the contributors of crustal and non-crustal sources for trace elements, the EF was calculated for each element. In this study, Si is used as a reference element and the crustal composition given by S.R.Tylor[8]and Table 6 shows EF values obtained for the trace elements.

It has been well established that elements with EF less than 1 are due to crustal emission, while elements with EF greater than 1 are considered highly enriched and originate from non-crustal sources [9].

Based on the computed EF values, we can deduce that S, Ca, Mn, Cu, and Zn are non-enriched (EF less than1) and are considered to be due to crustal sources. Fe and Cr showed high EF (greater than 1), indicating its anthropogenic sources and suggesting an origin dominated by mining sources from the ore. Also, element Pb exhibited high EF value due to its anthropogenic sources of emissions from the drilling and crushing machines, and diesel trucks used for transporting ores.

Correlation between Various Aerosol Components:
The correlation matrix for the various elements combined from six sites is shown in Table 7 Significant positive correlations ($r > 0.8$) were observed between Cu-S, Zn -S, and Cu- Zn. While, slightly positive correlations ($r \geq 0.8$) were observed between Fe- Si, and Fe- Pb.

An appositive correlation between Fe-Si could be indicative of the presence of Fe- Silicates, while the positive correlation between Cu-S, Zn- S Cu- Zn Suggest zinc and copper sulfides, where Zn and Cu are always present as sulfide deposits at the mining site.

Comparison between the present study data with the global data:
Table 8 predicted the comparison of average elemental concentration (ng/m^3) between the present study and the global data. It showed that the average elemental concentration of S, Zn, and Cr is relatively same as the most of the global studies, Some typical crustal elements, such as Si exhibited much higher average concentrations. The obtained result also showed a relatively high average concentration for Cu and Fe when compared with the available data, suggesting strong local anthropogenic sources for these elements in Ariab mining area. The element Pb showed average concentration higher than all

different global studies[10]. This could be referred to as the emission from the digging machines and the transport pattern of ore by diesel trucks from the mining sites to the crushing area.

Table 4: Mean elemental concentrations (%±SD) in different locations in Arib area

Elements	Si%	S%	Ca%	Fe%
HAS. M	1.1±0.8	0.05±0.1	0.14±0.22	1.32±1.3
HAD. M	1.3±0.8	0.7±0.8	0.1±0.02	1.7±1.4
KAM. M	2.6±1.1	0.03±0.01	0.1±0.03	1.7±1.3
HEP. A	1.4±1.2	0.1±0.04	0.2±0.2	1.5±1.9
CR. LR	2.4±2.2	0.2±0.1	0.3±0.3	3.7±4.5
CA. VG	1±1.3	0.02±0.19	0.12±0.12	0.6±0.6

Table 5: Mean elemental concentrations (ng/m^3±SD) in different locations in Arib area

Elements	Cr	Mn	Cu	Zn	Pb
HAS. M	27±17	35±25	107.5±109.4	28 ±22	142.5±203
HAD. M	14±20	41±28	1227±2020	511±875	442±452
KAM. M	36±19	755±908	50±57	21±5.3	37.4
HEP. A	40±39	75±101	104±116	85±122	225±218
CR. LR	26±10	80±90	124±30	132±144	542±728
CA. VG	20±9	74.5±92	51.6±7.8	29±15	44.7±5.3

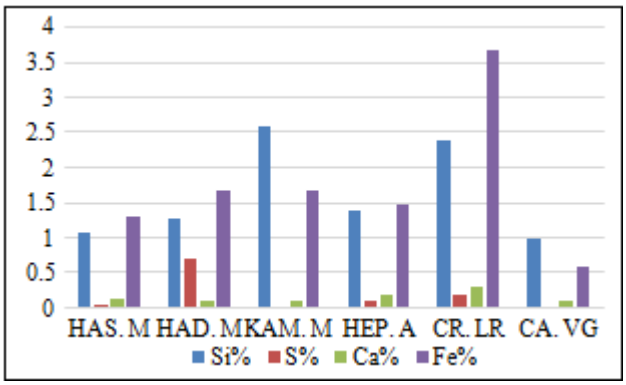

Figure 2: Average elemental concentrations (%) in different locations

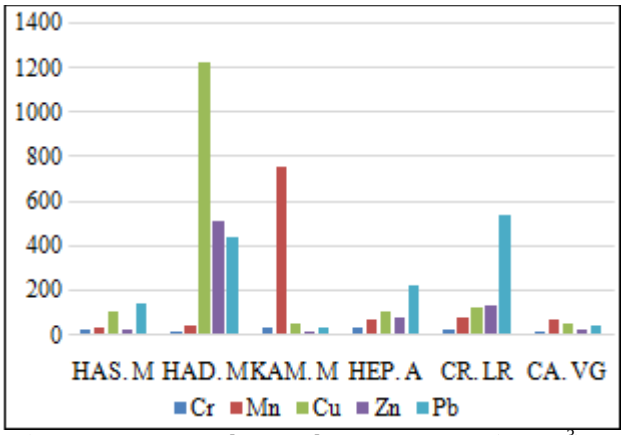

Figure 3: Average elemental concentrations (ng/cm^3) in different locations

Table 6: Summary of statistical data obtained for aerosol samples concentrations (ng/m^3)

Element	Mean	SD	Med	Min	Max
Si%	1.52	1.28	0.9	0.13	5.19
S%	0.19	0.39	0.05	0.01	1.98
Ca%	0.11	0.06	0.01	0.03	0.32
Fe%	1.86	1.30	1.46	0.57	4.67
Cr	25.7	14.2	26.7	0.01	57.6
Mn	43.3	26.2	40.6	17.7	124.4
Cu	100.8	82.7	60.4	10.19	294.3
Zn	82.5	61	63.4	32.8	225.7
Pb	225.8	185.6	123.8	40.89	490.6

Table 7: Crustal enrichment factors of trace elements

Elements	Enrichment Factors
S	0.14
Ca	0.49
Cr	4.76
Mn	0.84
Fe	6.12
Cu	0.03
Zn	0.22
Pb	3.38

Table 8: Correlations among trace elements combined from six sites

	Si	S	Ca	Cr	Mn	Fe	Cu	Zn	Pb
Si	1								
S	0.167	1							
Ca	-.573	-.029	1						
Cr	0.363	0.261	0.223	1					
Mn	0.449	0.092	0.145	0.380	1				
Fe	**0.747**	0.228	0.427	0.509	0.176	1			
Cu	0.149	**0.964**	-.040	-.196	-.039	0.172	1		
Zn	0.132	**0.961**	-.052	-.295	-.096	0.142	**0.982**	1	
Pb	0.556	0.641	0.196	0.062	-.118	**0.786**	0.527	0.517	1

Table 9: Comparison of average elemental concentration (ng/m^3) between this study and literature data

	Si%	S%	Ca%	Fe%	Cr	Mn	Cu	Zn	Pb
Sudan[10]	-	-	1.46	0.64	-	230	130	95	41
India[11]	0.68	0.27	0.38	0.37	46	104	50	38	158
Lebanon[12]	0.35	0.08	0.59	0.18	-	24.7	47.3	77.3	104.6
Italy[13]	-	-	0.09	0.01	38	3	4	6	12
Norway [14]	-	-	0.43	0.51	-	83.3	12.3	41.2	18
Korea[15]	-	-	-	0.14	17.3	48.2	-	146	-
This Study	1.5	0.2	0.1	1.9	25.7	43.3	100.8	82.5	225.8

4. Conclusion and Recommendation

- Elemental analysis of Ariab aerosols using PIXE analysis showed the presence of Si, S, Ca, Cr, Mn, Fe, Cu, Zn, and Pb, with higher concentration for Si and Fe in all locations.
- Based on E.F calculation, the crustal elements were defined as S, Ca, Mn, Cu, and Zn, while the rest were classified as non-crustal.
- It has been confirmed from the positive correlation between the elements Cu, Zn, and S, the presence of Cu and Zn as sulfide deposits at the mining site.
- Elements Si, Fe, Cu, and Pb showed average concentration values higher than all different global studies.

5. Recommendation

- The camp where most of the labor and engineer where settling must be constructed far away from the mining sites due to the strong emissions of some toxic elements like Pb.

- To do more future studies in the crushing and heap area due to that they both generate different pollutants from the dust, the emissions of diesel machines, and the chemical treatments of crushed ore in the heap.

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