

Statistical Evaluation of Environmental Geochemical Data Quality around Abandoned Barite Mine Dump Sites in parts of Oban Massif and Mamfe Embayment, South Eastern Nigeria

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ABSTRACT

All environmental geochemical data released into the public arena should undergo quality control (QC) and quality assurance (QA) so that any conclusions and decisions made based on them are accurate and truthful. Invariably, quality control checks coupled with estimation of both random and systematic errors in geochemical analysis for environmental studies have become part of good professional practice. It is in this regards that this paper evaluated statistical methods and QA/QC protocols on geochemical samples from abandoned barite mine sites in parts of Oban massif and Mamfe Embayment, South Eastern Nigeria as a case study. Analytical data quality was controlled through the analysis of reference standard materials, duplicate and blank samples and subjected to statistical analysis after a rigorous quality control protocol. The statistical methods employed included bias estimation, scatter plots, one-way analysis of variance (ANOVA) and Student's t-Test. The analysis of standard reference material revealed that the expected standards fell within the acceptable limits of $\pm 3SD$. The scatter plots showed a very high correlation of the original and repeat samples. The ANOVA and t-Tests revealed no significant procedural errors. Generally, the geochemical data were good and quite satisfactory and could be confidently used in environmental studies.

Key Words: geochemical data, geochemical variation, quality assurance, quality control, statistics, technical variation.

INTRODUCTION

Analytical sample accuracy is of great importance to all environmental geochemical studies since this form the basis on which conclusions and major decisions are made. Environmental geochemical studies often encounter challenges concerning effective delineation of the contaminated area, partly due to the inaccuracy on the part of laboratory personnel responsible for assaying or the sampling crew (Ramsey, 1992; Davies, 2016). For this reason, quality control and quality assurance (QC/QA), as well as sound statistical analysis of geochemical data, may have to be adopted in order to establish precise geochemical signatures or guide site characterization efforts (Bond, 2008).

During the measurement process, random errors will be induced from (a) sampling; handling, transportation and preparation of the samples for shipment to the laboratory; (b) taking a subsample from the field sample and preparing the subsample for analysis at the laboratory, and (c) analysis of the sample at the laboratory (including data handling errors). The magnitude of these errors can be expected to vary during the measurement process and makes it more difficult to determine the natural variability of contaminants in the environment (Geboy and Engle, 2011). According to USEPA (2006) and DES (TSQ) (2018), QA and QC measures are those activities you undertake to

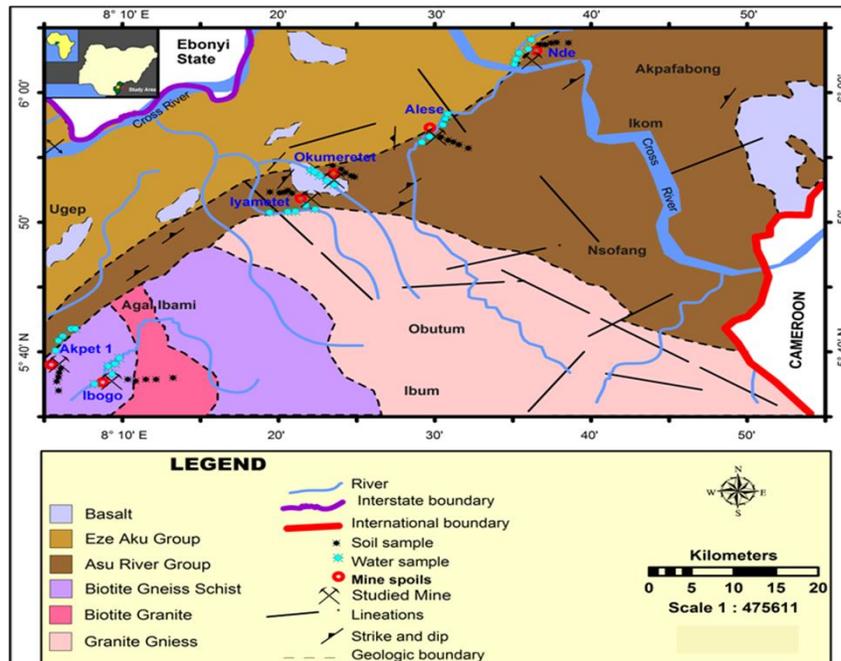


Figure 1: Geological map of the study area showing sample locations.

demonstrate the accuracy (how close to the real result you are) and precision (how reproducible your results are) of your geochemical analysis. QA generally refers to a broad plan for maintaining quality in all aspects of a project. This plan should describe how you will undertake your monitoring effort: proper documentation of all your procedures, training of volunteers, study design, data management and analysis, and specific quality control measures. QC consists of the steps you will take to determine the validity of specific sampling and analytical procedures. Quality assessment is an evaluation of the overall precision and accuracy of your data after you have run the analyses.

There are many ways to evaluate the quality of analytical data in terms of precision, accuracy, representativeness, comparability, completeness and sensitivity in relation to the intended use of the data. Precision, accuracy, representativeness, comparability, completeness and sensitivity are collectively referred to as the PARCCS parameters (Affam et al., 2012; Piercey, 2014).

In practice, inventory compilers do not have unlimited resources. Invariably, quality control requirements, improved accuracy and reduced uncertainty need to be balanced against requirements for timeliness and cost-effectiveness. A good practice system for QA/QC verification seeks to achieve that balance, and also to enable continuous improvement of inventory estimates. Judgments to select the respective parameters will need to be made on the following:

- Resources allocated to QA/QC for different categories and the compilation process;
- Time allocated to conduct the checks and reviews of emissions and removal estimates;

- The frequency of QA/QC checks and reviews on different parts of the inventory;
- The level of QA/QC appropriate for each category;
- Availability and access to information on activity data, emission factors and other estimation parameters, including uncertainties and documentation (Geboy and Engle, 2011).

Assessing data quality requires communication between the scientists responsible for designing the study and those collecting samples, analyzing samples, treating data, and interpreting results (IAEA, 2003).

Typically, errors in the taking of field samples are much greater than preparation, handling, analytical, and data analysis errors; yet, most of the resources in sampling and analytical studies have been devoted to assessing and mitigating laboratory errors. It may be that those errors have traditionally been the easiest to identify, assess and control (Bond, 2009; Plouffe, et al., 2013; Mohanty, 2015).

The Schists and gneisses of the crystalline basement, and the shales and sandstone of the Asu River Group in Mamfe Embayment (Figure 1) host the barite deposits of hydrothermal type mineralization. The mineralization is structurally controlled and restricted to gentle dipping veins, fault zones and bedding planes (Olade, 1976; Akpeke, 2008). The barite is of high quality (specific gravity, 4.26 and $\geq 92\%$ BaSO₄ (Adamu, 2011) in locations like Agoi Ibami, Yala and Agoi forest. In areas (such as the study mines) where it occurs in association with sulphides and Fe-oxides, the quality is greatly reduced. The faults and fissures are controlled by later compression related geotectonic events in the Pre-Turonian and Santonian times (Nwabufu-Ene, 1993).

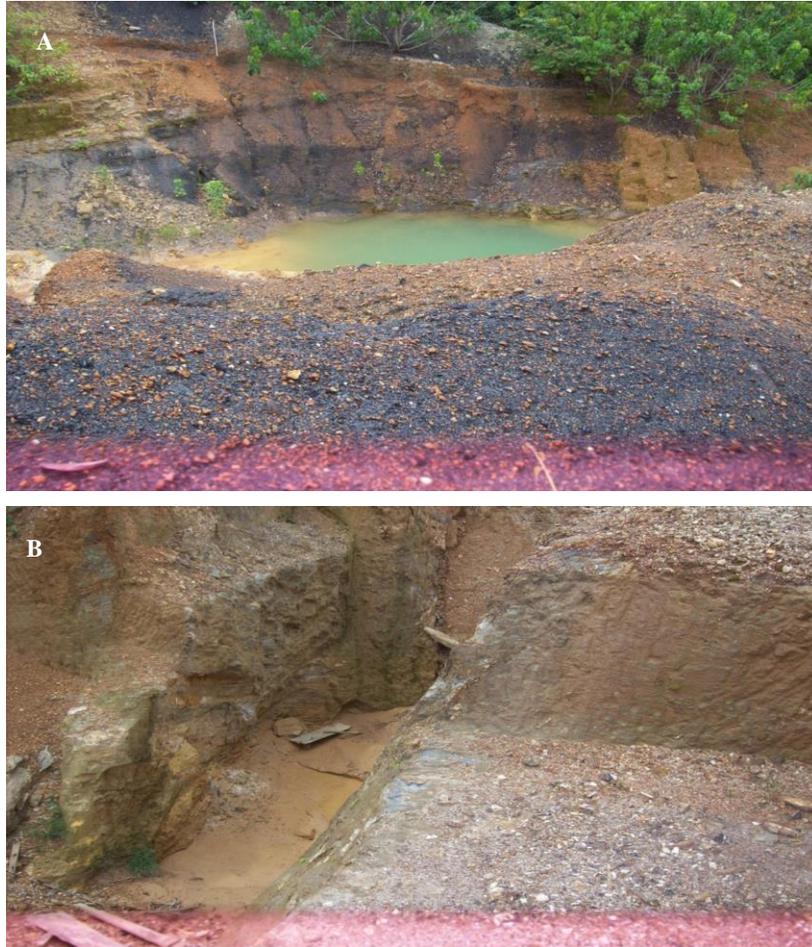


Figure 2: Abandoned barite mine dumpsites at (a) Okumuretet mine and (b) Ibogo mine.

Barite in the area was mined by opencast method for use in the oil and gas industry. The quarries have been opened in both the crystalline basement and sedimentary areas. The depth of mine pits ranges from 10-30m with widths of between 1-5m and lengths of a few metres to several kilometres (Figure 2). Tons of waste rocks are scattered on the earth surface close to mine pits. The major mining activities took place from 1996-2008. Presently, mining activities have stopped following the ban on illegal mining by the Federal Government of Nigeria.

The purpose of this paper is to evaluate the quality of geochemical data from abandoned barite mine sites in parts of Oban massif and Mamfe Embayment, South Eastern Nigeria using statistical methods and QA/QC protocols.

METHODOLOGY

Study Area

The study area lies between latitudes $05^{\circ}30'$ and $06^{\circ}10'N$ and longitudes $08^{\circ}00'$ and $08^{\circ}50'E$ (Figure 1) and

it consists of Precambrian basement complex rocks of the Oban Massif, overlain by the Cretaceous sediments of the Mamfe Embayment. The Oban Massif occupies an area of about $10,000\text{km}^2$ and includes such metamorphic rock units as phyllites, schists, gneisses and amphibolites. These rocks are intruded by pegmatites, granites, granodiorites, diorites, tonalities, monzonites and dolerites of Pan-African age, (Ekwueme, 1995; Ayodele et al., 2017). Associated with the rocks are Charnokites which occur as enclaves in gneisses and granodiorites (Oden et al., 2017).

The Cretaceous sediments cover more than 90% of the study area and occupy the Mamfe Embayment. The oldest recorded sediment in the area is the Albian-Cenomanian Mamfe Formation of the Asu River Group. It is predominantly a fluvial clastic sequence which comprises conglomeritic, immature, arkosic, cross-bedded, coarse to medium sandstones and mudstones (Petter et al., 1987; Bassey et al., 2013; Efofa et al., 2016).

The Asu River Group is overlain by the Eze-Aku group of middle Cenomanian-Turonian age. This geologic formation outcrops in the northern flanks of the study area and it consists dominantly of fossiliferous grey

Table 1: Geology and Site description of the studied mines.

S/No	Mine	Latitude	Longitude	Elevation	Formation	Lithology	Age
1	Okumeretet	05°59'30N	08° 20' 59"E	240m	Mamfe	Fractured shale	Albian
2	Iyametet	05°52'48N	08° 28' 06"E	216m	Mamfe	Siltstone, shale intrusive Sandstone/sa	Albian
3	Alise	05°58'31N	08° 28' 41"E	181m	Mamfe	hle	Albian
4	Nde	06°03'53N	08° 36' 20"E	140m	Mamfe	Sandstone	Albian
5	Akpet 1	05°39'20N	08° 05' 10"E	278m	Oban Massif	Gneiss, schist granodiorite	Precambrian
6	Ibogo	05°37'57N	08° 08' 30"E	280m	Oban Massif	Phyllite schist, pegmatite	Precambrian

shales and siltstones with interbedded sandstone and sparingly thin layers of limestone (Ndip et al., 2018).

The sedimentary rocks have been affected by two major tectonic episodes during the Pre-Turonian and Santonian periods. The latter involved compressional movement along an established NE-SW trend and resulted in folding and rifting with a characteristic NW-SE and N-S trending fracture system and dip values of 11 to 55° (Oden et al., 2017). The sediments are intruded by igneous rocks of basaltic/doleritic to dioritic in composition, with a few syenitic and phonolitic types (Ekwueme, 1995; Momta and Essien, 2016; Oden et al., 2017). Surficial deposits composed mainly of sands, silts, clay, gravels and local colluvials which cover most of the flood plain and river courses represent tertiary and recent sediments in the study area

Field investigation

A reconnaissance of the geology, site accessibility, land use pattern and other features of importance was carried out in order to determine factors indicative of heavy metal contamination due to barite mining. This was to enable the selection of mine sites for the study. Six barite mine sites were finally selected for this study on the basis of the risk they pose, size of mine, nature of host rock, the geology of adjacent areas and accessibility. The selected six abandoned barite mine sites are listed in Table 1 and shown in figure 1.

Sampling

Soil, sediments and water samples were collected for this study. The multistage selective sampling method was used to collect soil samples within and outside the mine areas. The latter samples served as control. The duplicate samples were taken from each mine site. A total of 60 soil samples were collected based on traverse lines and at intervals of 50m. Each sample was a composite of five subsamples within an area of 1x1m². Five samples were obtained at each mine dump site. Details of sample sites were recorded on the Forum of European Geological Surveys (FOREGS) sampling

sheet for soil following the procedure of DeVivo et al. (2008). The collected soil samples were sealed in polyethylene bags to eliminate dust contamination during transport to the laboratory. Sampling traverse lines and locations were chosen to avoid obstruction in their courses as well as areas prone to inputs not representative of the true nature of samples. Such include areas with thick vegetation cover, undecomposed leaf litter and ensuring that distance of at least 20m away from motored roads and cultivated fields to minimize effects of lead emission from vehicle exhaust and inputs from farms on the samples.

Water samples were collected from mine ponds and adjoining streams, close and away (surrounding virgin area) from mine tailings. The water samples were collected using 250ml polyethylene plastic bottles. A total of 60 water samples were collected. Five water samples were collected at each mine site during a sampling session and duplicate samples were collected at each of the six mine sites. Water samples for geochemical analysis were passed through a 0.45m filter paper, to screen out suspended particles that can possibly dissolve and affect the concentrations of dissolved metals, and acidified with concentrated HNO₃ (2ml) to keep metal ions in solution. Samples were carefully labeled and the sample locations plotted on base map (Figure 1). Prior to sample collection, the bottles were soaked in 10% HNO₃, for 24 hours and rinsed several times with deionized water as reported by Njanje et al. (2010). The water bottles were rinsed with aliquots of stream or mine pond water prior to immersing them well below the surface to collect samples free from film that is a possible source of heavy metals (Hem, 1985). All water samples were stored in a refrigerator prior to analysis, to minimize chemical reactions that can precipitate dissolved elements.

Similarly, surface (0-15cm) stream sediments samples were collected on the same sample locations as stream water samples and a duplicate sample was collected at each sampling site. Details of sampling sites were recorded on the FOREGS sampling sheets for stream water and stream sediments which were also used for recording water sample details.

Sample classification

QC/QA samples should be run with every batch of samples analyzed. Generally, 10 to 20% of the analysis run should be QC samples (DeVivo et al., 2008). Common QC samples include:

(a) **Original sample** – This is the primary sample material from the water, soil or sediment location, outcrop exposure or core cuttings. All initial analysis tests are often performed on the original samples and check analysis of randomly selected samples can also be carried out on them. They normally reflect a higher geochemical variability.

(b) **Method blank** – This is reagent water that has gone through the same procedure and has all the reagents as the other samples. Method blanks are useful in determining contamination. Ideally, the method blank should not be greater than the method detection limit.

(c) **Known sample** – This is a sample that has a known amount of analyte in it. The sample can be made in-house or it can be from an outside source. If it is made in-house, it should be made from a different source of chemicals than what the test standards are made from. The value of the known sample should fall within the result range of the other samples. Known samples help determine the accuracy of an analysis.

(d) **Spikes** – A spiked sample is a “real” sample that has a known amount of analyte added to it. The difference between the sample and the spiked sample is determined and the percent recovery is calculated. Spikes help to determine if interferences are present. Generally, 85% to 115% recovery is acceptable.

(e) **Duplicate** – Two samples are taken side by side using the same procedures and tested separately. Duplicate samples used to evaluate analytical or measurement precision.

(g) **Replicate** – A single sample that is tested twice within the batch. The results indicate precision.

(i) **Certified standards** – These are sample pulps prepared, packaged and certified by reputable laboratories to contain known values of certain elements.

Sample preparation

In the laboratory the solid samples (soils and stream sediments) were air-dried and prepared for analysis as presented in Adamu (2011) and Adamu et al. (2015). The soil and stream sediment samples were crushed using agate mortar and pestle to pass through $63\mu\text{m}$ sieve. This was to obtain a fine fraction that is enriched in secondary minerals with respect to the coarser fraction (Siegel, 2002). 0.5g of powdered sample was leached in hot (95°C) aqua regia (trace-metal-grade mixture of nitric(70%) and perchloric(65%) acids, HNO₃: 1 HClO₄ ratio), dried over 24 hours (3 hours at 50°C, 3 hours at 150°C, and 18 hours at 180°C), leached in 2ml of 6M HCl and made up to 10ml with deionized water (Chukwuma, 1995). A batch of (36) samples for digestion included one procedural blank, two sample duplicates and one

standard reference material as well as an aliquot of in-house reference standard material. Repeat samples were randomly selected and prepared for assessment of precision and accuracy of laboratory procedure. Blanks were also used to account for the possible contribution of metals from reagents.

Analysis of samples

The acidified and filtered water samples were analyzed for heavy metals and major cations using inductively coupled plasma mass spectroscopy (ICP-MS; Perkin Elmer Elan 6000/9000). Leachates of soil and organic stream sediments were analyzed for heavy metals and major cations using ICP-MS in Acme Analytical Laboratories, Canada. Analytical data quality was controlled through the analysis of reference standard materials, sample duplicates and blank samples. Calibration standards for ICP-MS were prepared by serial dilution from traceable stock and verified against in-house reference materials such as OREAS and DS7, and international reference materials such as the Canadian Certificate Reference Material Project (CCMRP) SO -1 (soils) and the United States Geological Survey (USGS) G-1 (granite). The resulting metal concentrations were reported in dry weight basis.

Geochemical data Quality Assurance (QA) and Quality Control (QC) protocols

A rigorous quality control programme was employed to assess the accuracy and precision of the geochemical data. The Forum of European Geological Surveys (FOREGS) procedures were used for sampling and chemical analysis of samples in order to ensure maximum quality of geochemical data (DeVivo et al., 2008). FOREGS forms sampling sheets for soils/mine tailings, water and stream sediments allowed detailed recording of sampling information, field measurement and observations for QA. The QC programmes included reagent blanks, duplicate samples, replicate samples, certified reference materials and repeat analysis. QC/QA protocol included methods such as accuracy checks on data acquisitions and calculations, estimating uncertainties, accurate measurements and reporting of geochemical data among others. It provides routine and consistent checks to ensure data integrity and correctness. It identifies and addresses errors and omissions.

Some factors that cumulatively affect the precision of any assay result and often times the field data include the mass of material, the homogeneity of the material being assayed, the concentration of the component of interest, matrix effects due to other elements in solution, instrument calibration and drifting. Hence, according to Affam et al. (2012), Piercey (2014) and Bal (2015), QC/QC was designed to:

- (i) ensure high samples quality and result reliability
- (ii) check both field and laboratory personnel responsible

Table 2: The results of QA/QC* in chemical analysis for soil samples**

Metal	Reagent blank (mean ^a ± SD)	IDL ^b	ADL ^c
As	30 ± 0.701	0.50	1.80
Ba	643 ± 0.846	1.00	2.00
Cd	0.21 ± 0.004	0.01	0.10
Cr	130 ± 0.631	1.00	1.50
Cu	94 ± 0.423	0.10	0.50
Fe	0.8 ± 0.042	0.01	0.10
Hg	1.2 ± 0.042	0.01	0.10
Mn	866 ± 1.268	1.00	3.00
Ni	12 ± 0.423	0.10	1.00
Pb	391 ± 0.423	0.10	1.00
V	140 ± 2.114	2.00	5.00
Zn	673 ± 0.827	1.00	1.96

*QA/QC=Quality assurance / Quality Control ** Concentrations in mg/kg except Fe (%), ^a Mean ± standard deviation of 4 repeats. ^bIDL=Instrumental detection limit, ^cADL=Analytical detection limit.

for sample collection and assaying

(iii)standardize the process of sample collection

Geochemical data were then screened to evaluate the distribution characteristics of each variable in the database. Univariate and multivariate statistical methods were used to assess each variable independently, and the relationships between variables. The geochemical data was evaluated using central tendency (mean, median) and dispersion (range, standard deviation, coefficient of variation (CV %), skewness, kurtosis and graphical displays such as scatter plots. Based on these analyses, decisions were made concerning the need for and selection of, appropriate transformations to achieve a better approximation of the normal distribution (Swam and Sandilands, 1995). In this study, scatter plots, student's t-Test and analysis of variance were used to determine data precision from duplicate and replicate samples. Whereas blanks and standard reference materials were used to establish lower detection limits and to determine data accuracy respectively.

Determination of detection limits and bias

Detection limit is the concentration which is distinctly detectable above or close to a blank, determined by analysis of replicate standards and calculated as two times the standard deviation (Narayanan, 2009). Comparison of metal concentration in reagent blanks with their instrumental and analytical detection limit for soil samples is shown in Table 2. In addition, comparison between observed and recommended concentrations of metals in international certified standard materials for both soil and sediment samples are summarized in Table 3. Since the instrumental detection limits (IDLs) are less than the analytical detection limits (ADLs) for all the elements, it implies that it should not be used for compliance data reporting. However, it may be used for statistical data analysis and in comparing the attributes of different instruments (Bond, 2008; Bal, 2015).

The analysis of standard reference material revealed that the expected standards fell within the acceptable limits of

±3SD (Table 3) (Affam et al., 2012). The low values of bias for most elements in both soil and sediments indicated the accuracy of the analytical data. The procedural errors may have been reduced by calibration of standards and instruments. The observed bias may be due to temperature variations during the analysis (Fletcher, 1981).

Censored data, where concentrations of some elements were reported as less than or greater-than were replaced by unqualified values (Thompson and Howarth, 1978). These values were credited by the lower or upper detection limit of the instrument or method used. A number of techniques have been suggested for replacement of a censored value including replacement of the less-than values by 3/4 times the lower detection limit and the greater than values by 4/3 times upper detection limit (Van-Trump and Miesch, 1977). An alternative (adopted in this study) is the replacement of less than values by 0.55 times the lower detection limit and the greater-than values by 1.7 times the upper detection limit (Thompson and Howarth, 1978). For data where the proportion of the censored values is > 10%, Thompson and Howarth (1978) have suggested that the estimated mean from the normal distribution using a maximum likelihood estimate method be used to derive an estimated replacement value.

Data comparison for water samples

Due to the extremely low concentrations of elements in the analyzed water samples, most of the original-duplicate and original-replicate concentration results fell below the lower detection limits of the analyzed elements. So, only those elements pairs with significant results were compared in tabular form and scatter plot for those elements, while the other analyzed elements were compared using scatter plots only. Table 4 shows the comparison for 1st and 2nd sample results for field duplicate data. Most of the duplicate pairs with high variability between 1st and 2nd sample results were from samples with metal concentrations that fall below/within

Table 3. Comparison between observed and recommended concentration of metals (mg/kg) in standard reference materials (n=3).

Element	OBSERVED VALUES				RECOMMENDED VALUES					
	Soil		Sediment		Soil		Sediment		Bias %	
	Mean $\bar{x} \pm 2SD$	RSD%	$\bar{x} \pm 2SD$	RSD%	$\bar{x} \pm 2SD$	RSD%	$\bar{x} \pm 2SD$	RSD%	Soil	Sediment
As	54.9 \pm 3.0	2.73	54 \pm 3.16	2.88	60.0 \pm 1.10	0.92	60.0 \pm 1.10	0.92	- 8.50	- 8.50
Ba	430 \pm 18.2	2.12	427 \pm 20	2.35	436 \pm 6.0	0.69	430 \pm 5.70	0.66	- 1.36	- 0.70
Cd	5.90 \pm 0.53	4.50	6.40 \pm 0.60	4.69	5.86 \pm 0.4	3.42	6.90 \pm 0.72	5.22	+ 0.67	+ 8.44
Co	9.80 \pm 0.40	2.04	9.80 \pm 0.50	2.55	10.2 \pm 0.38	1.86	10.2 \pm 0.40	1.96	- 3.92	- 3.92
Cr	204 \pm 12.0	2.94	196 \pm 12.3	3.14	212 \pm 3.6	0.90	190 \pm 8.94	2.36	- 3.77	- 3.06
Cu	112 \pm 9.80	4.39	108 \pm 10.6	4.90	115 \pm 2.4	1.04	117 \pm 7.4	3.16	- 3.12	- 8.13
Fe (%)	2.38 \pm 0.02	6.30	2.48 \pm 0.26	5.24	2.32 \pm 0.06	1.29	2.40 \pm 0.08	1.67	+ 2.59	- 3.22
Hg	0.17 \pm 0.00	1.76	0.19 \pm 0.01	2.64	0.185 \pm 0.00	3.13	0.185 \pm 0.00	2.20	- 8.11	+ 2.70
Mn	615 \pm 27.00	2.20	662 \pm 26.20	1.98	622 \pm 10.00	0.80	670 \pm 14.22	1.06	+ 17.64	- 1.20
Ni	58.8 \pm 4.10	3.52	58.5 \pm 4.12	3.52	62.3 \pm 1.2	0.96	54.7 \pm 1.20	1.10	- 6.42	+ 6.50
Pb	68.4 \pm 3.9	2.85	78.1 \pm 3.80	2.43	73.1 \pm 2.7	1.84	75.71 \pm 2.90	1.92	- 7.07	+ 3.06
V	81.0 \pm 3.6	2.22	85.00 \pm 4.10	2.41	83 \pm 2.8	2.89	89.00 \pm 4.40	2.47	2.41	- 4.70
Zn	386 \pm 24	3.11	424 \pm 26.00	3.07	432 \pm 7.0	0.81	430 \pm 30.00	3.49	- 0.65	- 1.42

\bar{x} =Mean value \pm 2SD (95% confidence unit); RSD% = (Residual standard deviation: Standard deviation/observed mean \times 100), Bias (%) = [(observed mean – recommended mean)/recommended mean] \times 100, n = Number of samples.

their detection limits (Cd, Co, Cr, Mn, Ni, and V). High variability was also observed in the data of 1st and 2nd analysis of laboratory repeat samples for elements concentrations that fell below/within the detection limit. Table 5 shows the observed variations in the comparison of 1st and 2nd analysis of laboratory replicate samples.

Scatter Plots

Trends of 1st and 2nd sample results of field duplicate and laboratory replicate sample for heavy metals in water, soil and sediment samples are shown in figures 3, 4 and 5 respectively. The purpose of the graphical displays was to visually observe the scatter of samples pairs in the ideal 45°-line which is expected in a 1:1 relationship. Figures 3-5 also showed the scatter plots of field duplicate data and data from laboratory repeat samples. The figures

show the very high correlation of the original and repeat samples again supporting low bias.

Linear trends were observed on the scatter graphs of field duplicate and laboratory replicate sample analysis of metal concentrations indicating high precision in the analytical processes employed to determine the element concentrations in the various media. Deviations from 45°-lines were observed on Cd for water samples, and to lesser degree Pb, for soil samples, and As for duplicate pair data in stream sediments. Such variations most probably reflected randomness of the samples or may imply that these elements may not be the actual representative of the area (Mohanty, 2015).

Results of routine statistical methods

Precision analysis by scatter plots is subjective. Invariably, various statistical methods, which are

objective, have been used to assess geochemical data quality in this study. This is a more appropriate approach in analyzing data variations and providing an objective characterization of data precision. The original and duplicate soil and sediment samples were statistically compared using the simple nested one-way analysis of variance (ANOVA) and the student's t-Test.

Analysis of variance (ANOVA)

The variance of a population is defined as a measure of the deviation or scatter of values about their mean and it is given as the average of the square of those deviations of values from their mean by the formula (Swan and Sandilands 1995);

$$\sigma^2 = 1/N \sum_{i=1}^N (X_i - \mu)^2 \quad (1)$$

Table 4: Comparison of 1st and 2nd analysis results of field duplicate data for water samples.

Element*	Detection Limit	1 st sample	2 nd sample	% difference	Remarks
As	0.05	BDL	BDL	NA	Below detection limit
Ba	0.05	9.72	9.71	0.01	Very low variation
Cd	0.05	BDL	BDL	NA	Below detection limit
Co	0.02	4.02	4.-00	NA	Below detection limit
Cr	0.50	1.80	1.90	5.55	Very low variation
Cu	0.10	0.30	0.3.00	0.00	Very low variation
Fe	0.50	0.49	0.45	8.16	Low variation
Hg	0.10	0.60	0.64	6.67	Low variation
Mn	0.05	0.38	0.18	52.63	Close to lower DL
Ni	0.20	BDL	BDL	NA	Below detection limit
Pb	0.10	0.10	0.10	0.00	Very low variation
V	0.20	0.20	0.20	0.00	Very low variation
Zn	0.50	1.2	1.2	0.00	Very low variation

BDL=Below detection limit NA=Not applicable *concentrations in mg/l.

Table 5: Comparison of 1st and 2nd analysis results of laboratory replicate data for elements concentrations (mg/l) in water samples that fell below/within lower detection limit (LDL).

Metal*	LDL	1 st analysis	2 nd analysis	% different	Remarks
As	0.50	0.40	0.40	0.00	Good precision
Ba	0.50	0.90	0.60	33.00	Close to LDL
Cd	0.05	0.70	0.68	2.89	Good precision
Co	0.02	0.06	0.05	16.67	Good precision
Cr	0.05	0.54	0.50	8.00	Good precision
Mn	0.05	1.90	0.90	50.00	Close to LDL
Ni	0.05	3.34	3.23	3.29	Good precision
Ni	0.20	3.70	3.96	7.03	Good precision
V	0.20	0.82	0.80	2.50	Good precision

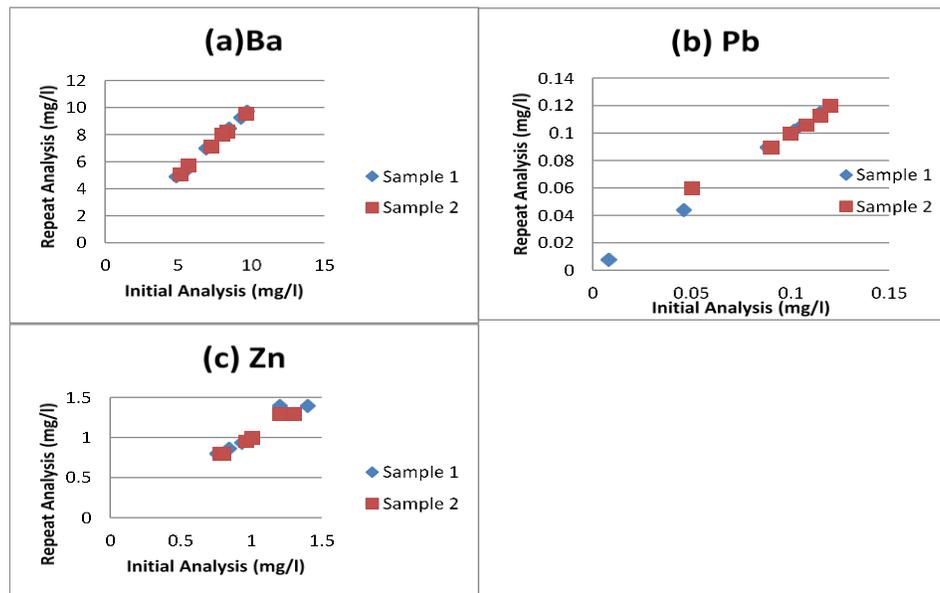


Figure 3: Scatter diagrams showing relationship between initial and repeat analysis of water samples.

where σ^2 is the population variance, μ is the population mean, X_i is the *i*th element from the population and N is the number of elements (samples) from the population. Deviations from the mean are partly due to random variations in the sample population and partly due to

procedural errors and sample inhomogeneity. Analysis of variance can be used to determine these deviation components.

The 1st and 2nd sample analysis of field duplicate data in the study area were analyzed using the simple nested

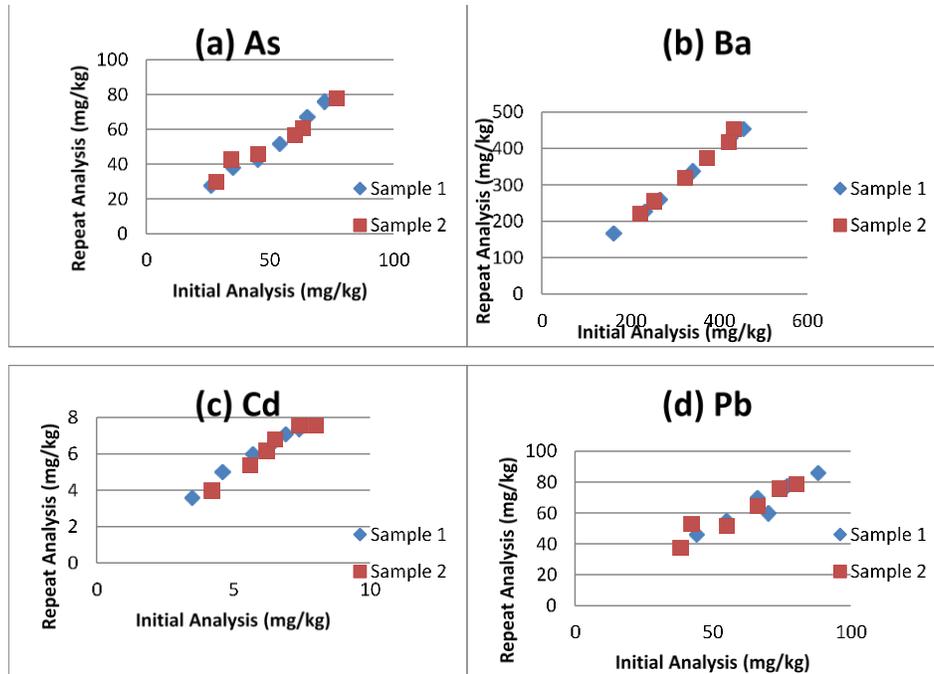


Figure 4: Scatter diagrams showing relationship between initial and repeat analysis of sediment samples.

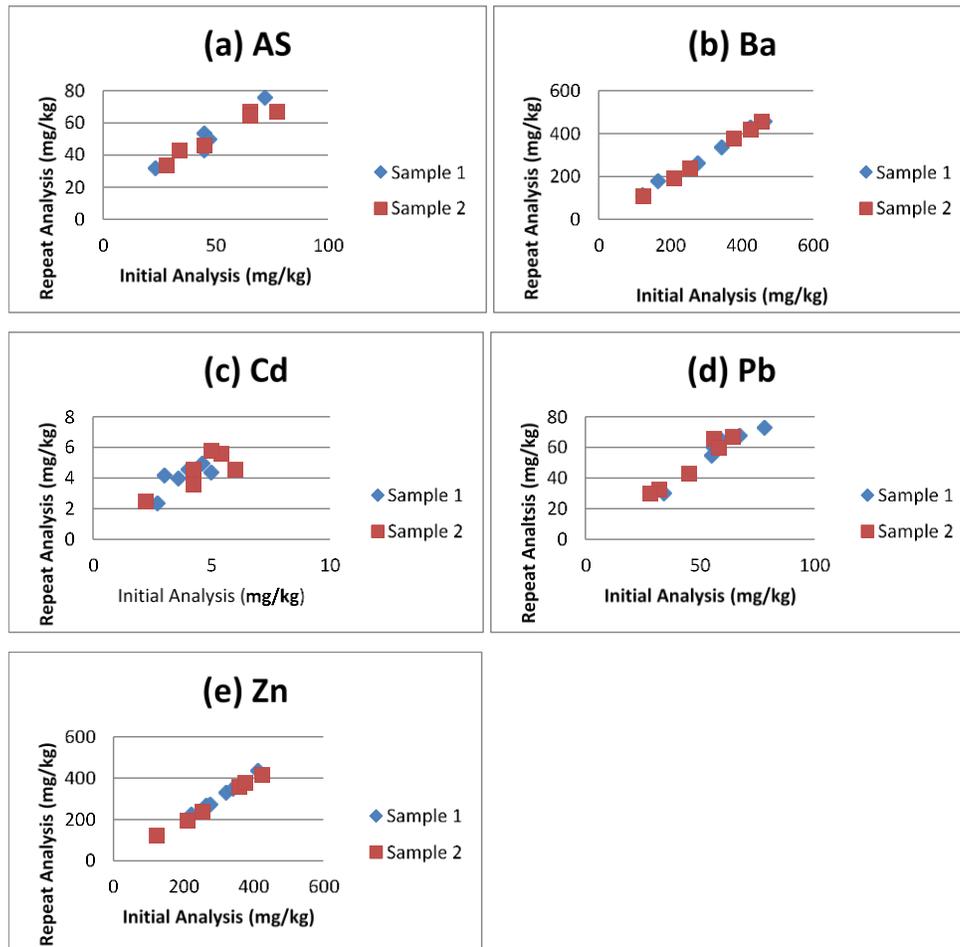


Figure 5: Scatter diagrams showing relationship between initial and repeat analysis of soil samples.

one-way ANOVA method (Ramsey, 1992). The purpose was to decompose the total variance of sample measurement into variance due to procedural errors and sample inhomogeneity, and variance due to the geochemical behaviour of the populations in the study area. Whilst the variance due to geochemical behaviour of the population can be exclusively determined, the variance introduced by procedural errors and by the inhomogeneity of the sample is not easily separated, except in water samples where the variance can be attributed to procedural errors because water is regarded as highly homogeneous. The total variance in this method can be described by the following relationship:

$$\sigma^2 = \sigma_w^2 + \sigma_b^2 \quad (2)$$

where σ^2 is the total variance measured in the data set, σ_w^2 is the sum of variances within groups and σ_b^2 is the total variance between groups.

In this study, σ_w^2 is equivalent to procedural errors and variations due to sample inhomogeneity, and σ_b^2 refers to geochemical variations in the sampled area. Because the calculation strictly involves the estimation of variances from a sample of population, the relationship can be written as:

$$MS_t = MS_w + MS_b \quad (3)$$

Where MS refers to mean squares. With the mean squares calculated, the corresponding percentages of procedural errors and geochemical variations can be determined. The "total mean squares" (MS_t) is the estimated variance of the observed measurements and comprises "mean squares between" (MS_b), which is the estimated variance between sample sites, and the "mean squares within" (MS_w), which is the estimated variance within sample sites. The mean squares between is expressed as a percentage of total mean squares estimates and represents the variance due to geochemical patterns, while the mean squares within are expressed as a percentage of total mean squares estimates and represent the variance due to procedural errors and sample inhomogeneity. According to Ramsey (1992), geochemical data is acceptable when procedural errors fall below 20%, and the analytical component of procedural variance should not exceed 4% (Ramsey, 1992).

The "mean squares terms" are calculated via the corresponding "sums of squares" (SS) as follows:

$$SS = \sum x^2 - (\sum x)^2 / n \quad (4)$$

$$SS_b = \sum_i x^2 - (\sum x)^2 / j - (\sum x)^2 / n \quad (5)$$

$$SS_w = SS_t - SS_b \quad (6)$$

$$MS_b = (SS_b) / (i - j) \quad (7)$$

$$MS_w = (SS_w) / i(j - 1) \quad (8)$$

Where, i is the number of duplicate groups (pairs), j is the number of measurements within each duplicate group, and n is the product of i and j . The F-test, which is the

ratio

$$F = MS_{\max} / MS_{\min} \quad (9)$$

can be used to determine the significances of estimated variances. With known degrees of freedom for the mean square-within and mean square-between (given by $(i - 1)$ and $(i - j)$ respectively), a critical F value can be determined from statistical tables at 5% level of variance ratio, or 95% significance level. In this study, the critical F value at 95% significance level is thus referred to as $F_{0.95}$.

Decision rule:

$$H_0: \mu_0 = \mu_d$$

$$H_1: \mu_0 \neq \mu_d$$

Reject if : $F > F_c$

Accept if : $F \leq F_c$

Where F_c is the theoretical value.

When F falls below the critical F-value, it implies that the populations, from which the two variances are drawn, are statistically indistinguishable. On the other hand, an F value that exceeds the critical value indicates that true geochemical patterns can be adequately reflected in the measurements (Ramsey, 1992), and therefore a decision can be made to reject or accept the hypothesis (Davis, 2003).

Computed ANOVA results for soil and sediment samples are shown in Tables 6 and 7 respectively. All the computed F – values are less than the critical F value at 95% significance level, which implies that true geochemical patterns can be adequately reflected in the data. In other words, there is no significant analytical error.

Student's t-Test

The student t-Test is another useful method for assessing the significance or the difference between the means of two samples. It can account for the uncertainty introduced into estimate based on samples by using probability distribution which has a wider spread than the normal distribution. It establishes a likelihood that a given sample may be a member of a population with specific characteristics for testing hypothesis about the equivalency of two sample populations with two types of errors: (a) Random errors and (b) Systematic errors. Random errors cannot be avoided but it is important to determine if the systematic error is present (Davis, 2003). The t-Test determines if there is a difference between two sample populations and whether the error is significant. The t-Test is computed from:

$$t = \frac{|x_0 - x_d| \sqrt{n-1}}{Sdiff} \quad 10$$

Where x_0 and x_d are the means of original and duplicate samples respectively. $Sdiff$ is the standard deviation and n is the number of observations.

Table 6: Results of Single factor analysis of variance for the soil geochemical data.

ANOVA		As				
Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	56.33333	1	56.33333	0.247474	0.629615	4.964603
Within Groups	2276.333	10	227.6333			
Total	2332.667	11				
ANOVA		Ba				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3	1	3	0.000161	0.990134	4.964603
Within Groups	186630.7	10	18663.07			
Total	186633.7	11				
ANOVA		Cd				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.240833	1	0.240833	0.298492	0.596807	4.964603
Within Groups	8.068333	10	0.806833			
Total	8.309167	11				
ANOVA		Pb				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.333333	1	0.333333	0.001488	0.96999	4.964603
Within Groups	2240.333	10	224.0333			
Total	2240.667	11				
ANOVA		Zn				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	184.0833	1	184.0833	0.036715	0.851882	4.964603
Within Groups	50138.83	10	5013.883			
Total	50322.92	11				

Table 7: Results of single factor analysis of variance for the sediments geochemical data.

ANOVA		As				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	4.083333	1	4.083333	0.012789	0.912198	4.964603
Within Groups	3192.833	10	319.2833			
Total	3196.917	11				
ANOVA		Ba				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.333333	1	1.333333	0.000102	0.992135	4.964603
Within Groups	130539.3	10	13053.93			
Total	130540.7	11				
ANOVA		Cd				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.12	1	0.12	0.056057	0.817619	4.964603
Within Groups	21.40667	10	2.140667			
Total	21.52667	11				
ANOVA		Pb				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.083333	1	2.083333	0.008902	0.926693	4.964603
Within Groups	2340.167	10	234.0167			
Total	2342.25	11				
ANOVA		Zn				
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.333333	1	0.333333	7.67E-05	0.993186	4.964603
Within Groups	43474.67	10	4347.467			
Total	43475	11				

Decision rule:

$$H_0: \mu_0 = \mu_d$$

$$H_1: \mu_0 \neq \mu_d$$

$$\text{Reject if: } t > t_{\alpha/2}$$

$$\text{Accept if: } t \leq t_{\alpha/2}$$

Where $t_{\alpha/2}$ is the theoretical value.

Table 8: Computed t-Test results for soil and sediment samples.

(a) Soil samples			
Element	Calculated Results	Critical Values of t at 95%	
As	0.05	2.57	
Ba	0.82	2.57	
Cd	0.17	2.02	
Pb	0.43	2.02	
Zn	0.04	2.02	
(b) Sediment samples			
As	0.16	2.02	
Ba	0.37	2.02	
Cd	0.01	2.57	
Pb	0.69	2.57	
Zn	0.42	2.02	

Calculated results from the available sample data using the t-Test empirical formula are presented in Table 8. The results showed that the calculated values are less than the critical range at 5% significant level. The null hypothesis is thus accepted. This implies that there is no significant difference between the sample means at 5% level of significance. In other words, there is a minimal systematic error associated with the sample populations. This confirms and supports the results from ANOVA that true geochemical patterns can be adequately reflected in the data

Conclusions

There are many ways to evaluate the quality of analytical data in terms of precision, accuracy, representativeness, comparability, completeness and sensitivity in relation to the intended use of the data. This study evaluates the data quality of geochemical samples from abandoned barite mine sites in parts of Oban massif and Mamfe Embayment, South Eastern Nigeria using statistical methods and QA/QC protocols. Analytical data quality was controlled through the analysis of reference standard materials, sample duplicates and blank samples and subjected to statistical analysis after a rigorous quality control protocol. The statistical methods employed include estimation of bias, scatter plots, one-way analysis of variance (ANOVA) and student's t-Test. The analysis of standard reference material revealed that the expected standards fell within the acceptable limits of $\pm 3SD$. The scatter plots showed a very high correlation of the original and repeat samples indicating the accuracy of the analysis. The ANOVA and t-Tests revealed no significant procedural or analytical errors. Generally, the results of laboratory procedures are good and quite satisfactory and can be confidently used in environmental studies.

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