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Geochemistry Examination of Surface Sediments from Sadong River, Sarawak, Malaysia: Validation of ICP-OES Assessment of Selected Heavy Metals

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Abstract: The dependable analytical method for the assessment of heavy metals of interest (As, Al, Mn, Ca, Cd, Cu, Fe, Cr, Ni, Co, Zn and Pb) in sediments assembled in the Sadong River, Sarawak state of Malaysia was reported. The total acid digestion extraction proceeded by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) was used for this reason. The analytical method was validated as well as the implementation of enough quality control activities in order to supply reliable information. Duplicate analysis was estimated in order to achieve the precision reproducibility conditions. To determine the accuracy of the results certified reference material was used. The limits of detection and quantification for all selected metals were below the acceptable limits in the examined sediment samples. The acquired dependable information could be used for evaluations of the correlation between anthropogenic activity in the aged and the geochemical characteristics of the sediments.

Keywords: Heavy Metals, Method Validation, ICP-OES, Sediment

INTRODUCTION

Heavy metals are distributed throughout soil and sediment components and associated with them in different ways, as well as adsorption, ion exchange, precipitation and complexation and others [1 – 2] stated that differences in environmental conditions, which includeredox potential, temperature, organic material concentrations and pH can lead trace metals to be discharged from solid phase to liquid phase which may lead to pollution of nearby water bodies in aquatic environment. In coastal sediments, heavy metals have been adjudged as a common parameter for evaluating depositional occurrences and processes including sediment provenance, due to their conservative behaviour according to [3]. Heavy metals are used to assess the relative contribution of different positions of experimental area as well as having capacity indicators of environmental pollution [2].The method validation performed was necessary to confirm the correctness of the computations. Hence to assess heavy metals in environmental materials such as sediment, there is the need to use well-known instrumental methods which possess highly responsive spectroscopic methods. These instrumental methods/techniques include AAS(Atomic Absorption Spectrophotometry) [4 – 8], ICP-OES(Inductively Coupled Plasma - Optical Emission Spectroscopic)[9 – 12]and ICP-MS(Inductively Coupled Plasma - Mass Spectrometry) [9 – 13].The objective of this research was to validate the proposed spectroscopic method (ICP-OES) in determination of heavy metals from surface sediments of Sadong River, Sarawak, Malaysia as a case study.

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STUDY AREA

A total of 15 surface sediments were collected from Sadong in March 2019, the samples were collected from five (5) stations (Fig. 1). These samples were collected using a Wedepohl stainless steel grab sampler, transferred into a polyethylene bags and kept frozen until further analysis at -40^{o} C.

Fig. 1: Map showing sampling stations of the study area

Table 1: Sampling points and their coordinates

Sampling Station	Locations	Coordinates
AQ1	Sebangan	N 01^{o}33^{1}03.2^{11}E110^{o}45^{1}56.4^{11}
AQ2	Sadong Jaya	N 01^{o}30^{1}51.0^{11}E110^{o}44^{1}24.6^{11}
AQ3	Sungai Buloh	N 01^{o}27^{1}19.4^{11} E110^{o}41^{1}08.1^{11}
AQ4	Simunjan	N 01^{o}24^{1}19.0^{11} E110^{o}40^{1}10.5^{11}
AQ5	Gedong	N 01^{o}14^{1}38.5^{11} E110^{o}40^{1}42.5^{11}

EXPERIMENTAL PROCEDURE

Materials

All the reagents used were of analytical grade. Solvent used were distilled and deionized water in the preparation of the standard. Concentrated acids and 1000.0ppm standard stock solutions were purchased from Merck in Germany. Each of the elemental standard solutions was prepared by the description obtained from the leaflet attached to the various 1000.0 ppm single-elemental standard solutions bought from Merck. Thepolyethylene containers as well as glassware were placed in 15% tetraoxosulphate (iv) acid (H_2SO_4) for 24 hours before used. Double-distilled water was used to rinse all the glassware. Certified Reference Material (CRM) Number 142Q, sewage sludge amended soil, standardized by Reference from Community Bureau was used to define the correctness of the techniques. A graduated balance was used for recording the weight of the samples. In order to evaluate the moisture content, a drying oven (MEMMERT B113.1096) at a temperature of 105 ºC was used. The loss of ignition at a temperature of 550°C was done by using muffle furnace (Ney Vulcan D-550 series).

Extraction Procedure

Heavy metals extraction was done by digestion method as reported by [14]. The dried sediment samples were digested with a mixture of concentrated HNO_3 and HCl. Absolutely 1.0 gram of the sediment samples were placed in crucible and weight of crucible with sample recorded. The samples were placed in an oven Memmert model 30 – 70 (UN 30) at 105 °C for 24 hours to degrade all organic matter and the weight recorded. Furthermore, the sample was reheated at a temperature of 550 °C for 3.5 hours in a muffle furnace Model Ney Vulcan D – 550 series, and weight recorded. 1.0 mL both of distilled water and concentrated HNO_3 was added to the cool samples and then heated to dryness on a hot plate Model Favorit HS070V2 Serial 5434. A volume of distilled water (1.0 mL) was added in addition of 2.0 mL of concentrated hydrochloric acid (HCl) and evaporated to dryness on hot plate. A volume of 15 mL distilled water and 2.0 mL concentrated HCl was added to the content in the crucible and stirred for 2 minutes for uniformity. This was followed by filtration through 0.45 μm filter paper into a 100.0 mL capacity volumetric flask and it was top up with distilled water to reach the mark.

Instrumentation

1) Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The conditions of operations adopted for Inductively Coupled – Optical Emission Spectroscopic (Model) assessment include 1250W RF power, 13 $Lmin^{-1}$ plasma flows, 2.0 $Lmin^{-1}$ auxiliary flows, 0.6 $Lmin^{-1}$ nebulizer flows, 1.8 $Lmin^{-1}$ sample uptake rates. Axial view was used for trace elements assessment, while 2-point background correction and triplicate were used to compute the signal of the analysis. The discharge absorbance or intensities were received for the most sensitive lines free of spectral interference. The standards of calibration were performed by adding 1% (v/v) HNO_3 to the stock single-elemental standard solutions (1000.0 ppm).

2) Scanning Electron Microscopy (SEM) Analysis

SEM is a type of microscope that creates various images by focusing a beam of electrons onto a surface of a material and using the returned interactions to create an image. In this case the electrons are emitted via a field emission gun (FEG)/ tungsten cathode and accelerator. In the process of SEM characterization, small amount of the sediment samples was placed onto an aluminium plate with the help of double edged adhesive membrane on the plate. The sample were further mounted on a sample holder followed by coating with a conductive metal (gold) using a sputter coater. The whole sample was analysed by scanning with a focused fine beam of electrons using JOEL JSM-6390LA Analytical Scanning Electron Microscope.

Statistical Analysis of Data

Data obtained were analysed and computed statistically using the Statistical Package for Social Science (IBM SPP version 24).

RESULTS AND DISCUSSION

Figures of Advantage

Method of validation is an essential analytical requirement in the process of analysing chemical elements and it is the procedure of explaining instrumental demand, and establishing that the technique under examination has performance potentials uniform with what the approach needs.

Calibration Equation

For quantitative evaluations by ICP-OES, an establishment relation between the intensity of discharge and a given concentration of standard solution [13, 15, 16] is required. The instrumental signal was joined to the analyte concentration along calibration function [13]. The calibration curve linearity was examined by the correlation coefficient and quality control coefficient (CQC) [13]. The calibration equation of the straight line for each element was evaluated by the application of linear regression analysis [17], and these was achieved by the uniformity of the difference (variance) of the computed results divided by the mass concentration limits formerly determined and confirmed by the value of *F-statistic* [13, 18]. The results of the linear regression of all the selected elements are shown in Table 2.

Table 2: Linear regression data of As, Al, Mn, Ca, Cd, Fe, Cr, Cu, Pb, Ni, Co and Zn calibration curves

Parameters	As	Al	Mn	Ca	Cd	Fe	Cr	Cu	Pb	Ni	Co	Zn
Linear range (ppm)	0.30 – 1.00	0.30 – 1.00	0.10 – 0.30	0.10 – 0.30	0.20 – 0.60	0.20 – 0.60	0.10 – 0.50	0.10 – 0.50	0.10 – 0.50	0.10 – 0.50	0.20 – 0.60	0.03 – 0.10
R^2	0.9990	0.9984	0.9999	0.9999	0.9989	0.9990	0.9978	0.9980	0.9987	0.9989	0.9991	0.9992
Slope	1426.8	1415.6	4962.0	4907.0	2195.0	2331.5	2553.1	2446.3	2671.5	2669.8	2438.0	15413
Intercept	6.9817	12.146	5.8000	5.3000	14.900	1.8000	28.814	26.339	12.407	15.288	16.900	2.379

The testing value (TV) was defined as the quotient of the differences (variances) of 10 computations of the standards with the highest (S^2 max) and lower (S^2 min) concentrations of the working limits applied and it was achieved by the formula:

$$TV = S^2 max / S^2 min \quad \text{(Equation 1)}$$

The statistic of F_{tab} is 5.467 for f 1 = 9, f 2 = 8 and p= 0.99 probability.

The variances are homogeneous if TV < F_{tab}. Hence all the computed TV values are below the F_{tab} value (i.e. 5.467). Therefore there are no significant differences which link the variances calculated and the unmeasured least squares method that can be applied [13, 15]. Mandel's fitting test was used to verify the linearity of the calibration curves [15, 18]. While this was necessary, 1st and 2nd order calibration functions were measured from the data of calibration as well as the residual standard deviations SD_1 and SD_2. Using equation 2 and 3 [5, 13]:

$SD_1 = /)$ (Equation 2)
$SD_2 = /)$ (Equation 3)

Where

Ai = the observed absorbance or intensity result at each location i, Aic = the corresponding absorbance or intensities measured from regression analysis and N = the number of calibration locations.

$TV^i = DS^2/(SD_2)^2$ (Equation 4)
$DS^2 = (N - 2)(SD_1)^2 - (N - 3)(SD_2)^2$ (Equation 5)

From the standard deviations of the residual obtained, the TV^i results were evaluated using Equation 4 and Equation 5 as suggested by [5, 13] and tabled $F_{tab} = 98.50$ while f1 = 1, f 2 = N – 3 = 2 including p = 0.99 probability was used to compared. The best adjustment was provided in order to obtain the linear regression [13, 15] because the values of TV^i evaluated for each of the elements were lower than F_{tab}.

$CQC = / (N - 2)] * 100$ (Equation 6)

Where,

CQC is Quality Control Coefficient.

When the CQC values obtained are < 5%, then it is acceptable [13, 16]. The CQC values obtained were < 5% therefore all the values obtained are accepted. Furthermore, the square of the correlation coefficient (r^2) in each of the calibration curves of ICP-OES were higher than 0.99. After establishment of the calibration curves and equation, the limit of detection (LOD) and limit of quantification (LOQ) [13] were measured for the heavy metals of interest of ICP-OES. The results (LOD and LOQ) were measured using the equation adopted by [2], that is 3.3 * ($S.D_{blank}/m$) and 10 * ($S.D_{blank}/m$) respectively, where SD is the mean standard deviation of blanks and m is the sensitivity of calibration curve. The characteristics performance of ICP-OES calibration equation is described in Table 3.

Table 3: Properties performance in ICP-OES calibration equation

Parameters	SD_1	CQC (%)	LoDs (ppm)	LoQs(ppm)	TV	TV^1
As	3.1	1.85	0.0072	0.0220	2.86	1.04
Al	2.9	1.72	0.0068	0.0201	1.06	1.10
Mn	3.3	2.07	0.0022	0.0070	1.41	1.59
Ca	3.5	0.57	0.0024	0.0072	3.01	10.23
Cd	2.7	1.31	0.0041	0.0122	1.03	9.91
Fe	3.9	2.36	0.0055	0.0171	0.27	26.44
Cr	3.7	0.61	0.0048	0.0150	1.06	1.01
Cu	4.1	3.13	0.0055	0.0173	0.22	13.02
Pb	4.3	2.01	0.0053	0.0162	1.10	2.62
Ni	3.8	1.88	0.0047	0.0141	0.04	0.16
Co	3.5	0.26	0.0047	0.0141	0.14	0.08
Zn	4.6	1.79	0.0010	0.0031	4.41	0.01

Legend: SD_1 = standard deviation of residual measured from Equation 2, CQC = Quality control coefficient using Equation 6, LoD = Limit of detection, LoQ = Limit of quantification, TV = Variance homogeneity Test Value, and TV^1 = Linearity Testing Value

Calibration Stability

To assess the calibration stability, it is necessary to use the quality control standard (QCS) at the end of 5 samples for the measurement of the analytical instrument shift. For this purpose, a standard solution chosen from the list of the calibration solutions prepared from variety of stock solution was used [13, 16]. The following QCSs were selected and used Zn (0.1 ppm); Mn and Ca (0.2 ppm); Cd and Fe (0.3 ppm); As and Al (0.4 ppm); Ni, Cr, Cu and Pb (0.5 ppm) and Co (0.6 ppm). The results for quality control standards (QCSs) are acceptable if the bias exhibited in percentages were not greater than ± 10% of the known value. In this case, the calculated relative error values were within the acceptable range.

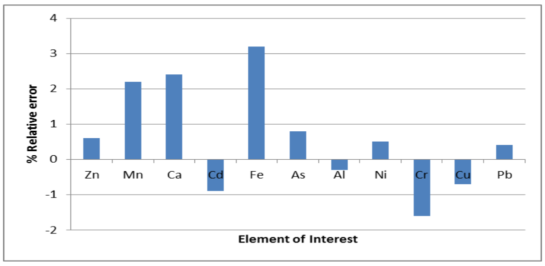


Fig. 2: Relative bias computed for QCS to check the stability of calibration for selected elements evaluated by ICP-OES

When QCS values were not within the accepted range, re-assessment should be done. After the re-assessment and if the quality control standard measurements are still not within the defined limits, ignore the old calibration and new calibration has to be set-out [5, 13]. Figure 2 shows the percentage relative errors of each of the QCS evaluations when analysing the sediments samples in ICP-OES. The values received were within the acceptable range (± 10%), showing that there is a stability of calibration possibilities which exist in all computations.

Matrix Effect

Recovery tests were used to assess the matrix effect. In order to evaluate, digested samples were spiked with analyte. Analyte of single-element standard solution for each of the metal was added to the digestion sample solution. For each of the analysis, the spiked samples were analysed three times (in triplicate) and the recovery percentages were calculated using the formula:

$$\text{Recovery (\%)} = (K - L/M) * 100\% \quad \text{(Equation 7)}$$

Where; k = the mean concentration of heavy metal after spiking; L = the mean concentration of heavy metal before spiking; M= the concentration of spiked heavy metal. The amount of heavy metals concentrations were assessed by,

$$\text{Final Conc. (mg/L)} = Cm * DF * NV\ \text{(mL)} \quad \text{(Equation 8)}$$

Where, Cm = concentration of heavy metal in sediment samples, DF = dilution factor, NV = nominal volume.

Table 4: Accuracy studied data for analysis of As, Al, Mn, Ca Cd, Fe, Cr, Cu, Pb, Ni, Co and Zn

Analyte	Spiked analyte conc. (mg/Kg)	Calculated analyte conc.(mg/Kg)	% Recovery
As	0.30	0.310	103
	0.60	0.590	98
	1.00	0.960	96
Al	0.30	0.280	93
	0.60	0.610	102
	1.00	0.990	99
Mn	0.10	0.097	97
	0.20	0.189	95
	0.30	0.291	97
Ca	0.10	0.102	102
	0.20	0.205	103
	0.30	0.291	97
Cd	0.20	0.192	96
	0.40	0.380	95
	0.60	0.602	100
Co	0.20	0.191	96
	0.40	0.402	101
	0.60	0.607	101
Fe	0.20	0.205	103
	0.40	0.373	93
	0.60	0.591	99
Zn	0.03	0.028	93
	0.06	0.061	102
	0.10	0.097	97
Cr	0.10	0.095	95
	0.30	0.290	97
	0.50	0.507	101
Cu	0.10	0.990	99
	0.30	0.282	94
	0.50	0.511	102
Pb	0.10	0.097	97
	0.30	0.296	99
	0.50	0.484	97
Ni	0.10	0.099	99
	0.30	0.310	103
	0.50	0.487	97

In the present study, it was found that the recovery range of the spiked samples analysed ranged between 90 – 104%. These values were within the acceptable range according to [5, 13] which reported that for the analyte level of roughly 1ppm, the acceptable recovery range is 90.0 –110.0%.

Precision Performance Studies

The precision shows the closeness of understanding between links of computations received from two or more sampling of the same homogeneous sample in the preferred conditions and is mostly evaluated as relative standard deviation [19, 20]. The analytical accuracy was performed by evaluating the repeatability of instrument response to analyte according to the commission regulation [19]. In assessment of repeatability, measurements and the analysis were performed with three replicates. The procedures were repeated on the rest of events. The spiked concentration of each of the elements evaluated, average concentration and relative standard deviation are briefed in Table 5. According to RSD Horwitch function the highest relative standard deviation values acceptable for the concentration of less than or equal to 1000 ppm is 10% [19, 20]. Hence, the method developed showed reasonable repeatability accuracy because relative standard deviation values evaluated were within the acceptable range.

Table 5: Repeatability precision studies data for determination of selected trace elements

Analyte	**Spiked Concentration (mg/Kg)**	**Measured Concentration (n=3) (mg/Kg)**	**Mean RSD (%)**
As	0.6	0.590	7.07
Al	0.6	0.610	3.22
Mn	0.3	0.291	5.58
Ca	0.2	0.205	5.50
Cd	0.6	0.602	4.41
Fe	0.4	0.403	3.05
Cr	0.2	0.205	6.60
Cu	0.1	0.097	6.35
Pb	0.5	0.507	4.38
Ni	0.5	0.504	5.12
Co	0.6	0.601	4.37
Zn	0.1	0.105	6.81

N=number of replicates (n=3)

% RSD is Relative Standard Deviation expressed in percentage

Accuracy

The accuracy performance of computations shows how close a value or an outcome appears to the reference value. The test of accuracy can be performed in many ways, that's by comparing values received by variety of methods (by considering one of them to be a reference), by using the results of different laboratories or by applying CRM (certified reference material), and therefore any suitable method available can be used. In this present study, the test of accuracy was evaluated by considering certified reference material (CRM) the reason was that the outcome received from certified reference material analysis was the suitable evaluations of the accuracy of the method, because it was easy to compare with international standards, i.e. Community Bureau of Reference (BCR). Perhaps, the regression line was used to trace the values using SPSS Statistics. The accuracy was assessed from the Z-score value (Misa *et al.,* 2014 and Funk *et al.,* 2007) using Equation 9.

$$Z = R_{lab} - R_v/U \text{ (Equation 9)}$$

Where R_{lab} represents computed or laboratory value, R_v represents certified value accepted as the true one, and U represents the uncertainty of the Reference value. According to Ora Laboratory Procedure, evaluation of uncertainty of the certified values can be measured at the 95% confidence level by equation,

$$U = k * RSD \text{ (Equation 10)}$$

Where U represents uncertainty of the certified value and k as coverage factor (k = 1.740, for 95% and eighteen (18) points).If |z| score is less than 2 then laboratory performance is described as satisfactory and acceptable butif |z| score is greater than 2 but less than 3 then the performance is questionable. The laboratory performance becomes unsatisfactory if |z| score is greater than 3 (Misa *et al.,* 2014 and Funk *et al.,* 2007). Table 5 explains the measured values, the computed z-score results and the ratio of difference relative to the certified values expressed in percentage. The accuracy test proved that all the selected elements investigated were their |z| score<2).

Table 6: Results for CRM, sewage sludge amended soil, standardised by BCR (Community Bureau of Reference)

Element	As	Al	Mn	Ca	Cd	Fe	Cr	Cu	Pb	Ni	Co	Zn
Certified value (ppm)	41 ± 1.9	213 ± 7.0	886 ± 12	921 ± 14	75.0 ± 1.6	1061 ± 17	411 ± 10	131 ± 6.0	168 ± 5.0	37.2 ± 2.1	24.0 ± 3.0	1047 ± 18
[x]Measured value (ppm)	42.03 ± 0.25	214.70 ± 0.17	886.8 ± 0.20	923.6 ± 0.60	76.31 ± 0.13	1064.13 ± 0.04	412.24 ± 0.21	131.82*	169.41 ± 0.91	37.90*	24.77*	1048.26 ± 2.31
$R_{Lab} - R_y$	1.03	1.70	0.80	2.60	1.31	2.96	1.24	0.82	1.41	0.70	0.77	1.26
U	3.31	12.18	20.88	24.36	2.784	29.58	17.40	10.44	8.70	3.65	5.22	0.04
|Z-score|	0.31	0.14	0.04	0.12	0.47	0.10	0.07	0.08	0.16	0.19	0.15	0.04
[y]Diff (%)	2.51	0.90	0.09	0.28	1.74	0.28	0.30	0.63	0.84	1.90	3.20	0.12

[x] Mean values of triplicate analysis

[y] Diff. - Percentage of difference to true values |z scores| calculated based using Eq. 9

*Values without uncertainty due to insufficient CRM sample measurement repetitions

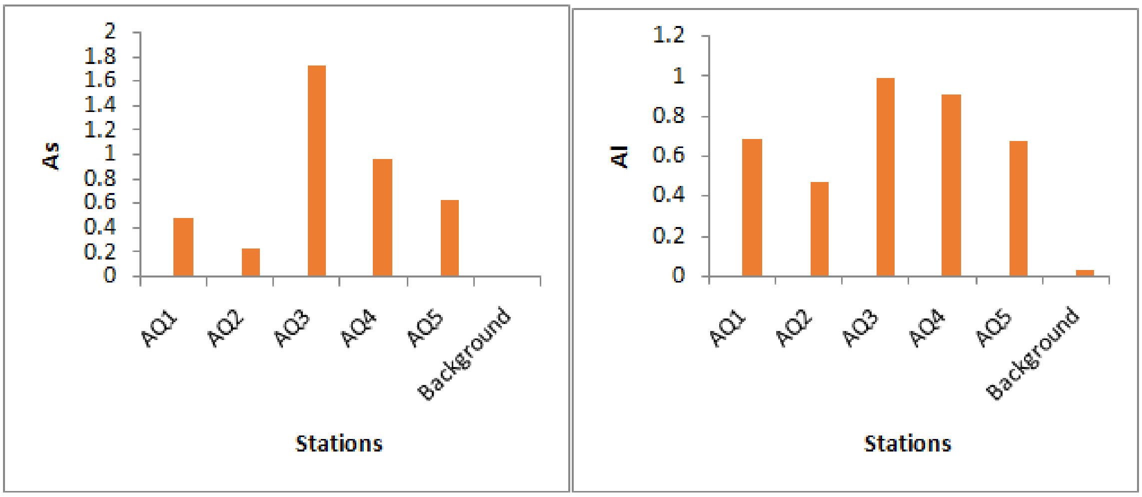
Outline of the Trace Metals Content in Sediments

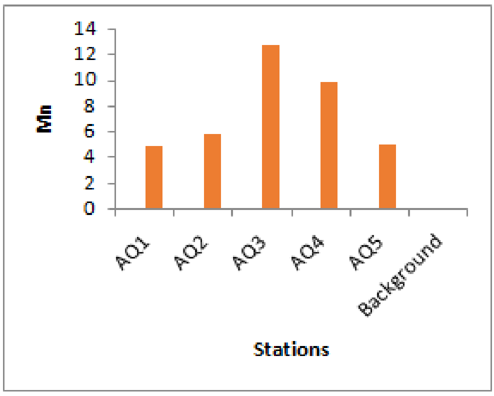
Table 7 explained the outcomes of contents of trace metals of interest in 5 sediment sample stations using ICP-OES. The results obtained from the analytical assessment are based on expression of an oven-dry weight at a temperature of 105°C. Oven-dried sediment samples were used for the analytical work because losses might happen for some trace metals through the drying process at 105°C. Hence, the values obtained were corrected in relation to the level of moisture. Table 7 and Fig. 3 shows the differences in concentrations of interested trace elements in the examined sediment samples collected from the Sadong River.

Table 7: Contents of trace metals in the sediments of Sadong River. The results are expressed in mg/Kg of dry mass at 105°C

Elements/ Station	AQ1	AQ2	AQ3	AQ4	AQ5
As	0.48±0.01	0.23±0.02	1.74±0.01	0.96±0.01	0.63±0.01
Al	0.69±0.01	0.47±0.02	0.99±0.01	0.91±0.02	0.65±0.02
Mn	4.83±0.01	5.77±0.01	12.67±0.01	9.89±0.02	4.96±0.02
Ca	6.64±0.02	7.01±0.01	8.15±0.02	7.02±0.01	5.21±0.01
Cd	0.04±0.01	0.02±0.01	1.02±0.01	0.56±0.02	0.07±0.01
Fe	28.73±0.02	28.98±0.01	36.78±0.02	30.29±0.01	16.43±0.01
Cr	0.31±0.02	0.12±0.01	1.07±0.02	0.72±0.02	0.63±0.02
Cu	0.05±0.01	0.03±0.02	0.09±0.01	0.05±0.02	0.01±0.02
Pb	0.02±0.01	0.04±0.01	0.07±0.02	0.05±0.01	0.03±0.01
Ni	0.62±0.02	0.52±0.02	1.06±0.01	0.70±0.02	0.52±0.02
Co	0.04±0.01	0.03±0.01	0.08±0.01	0.05±0.01	0.01±0.01
Zn	3.86±0.01	5.43±0.01	6.27±0.01	5.80±0.01	4.89±0.01

Values are means ± SD of three replicates

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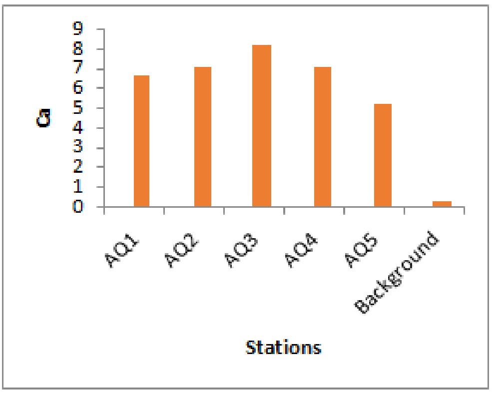
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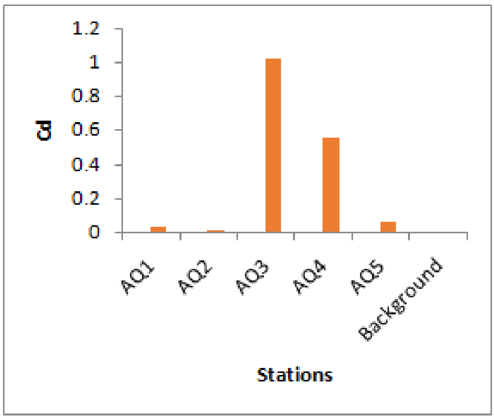
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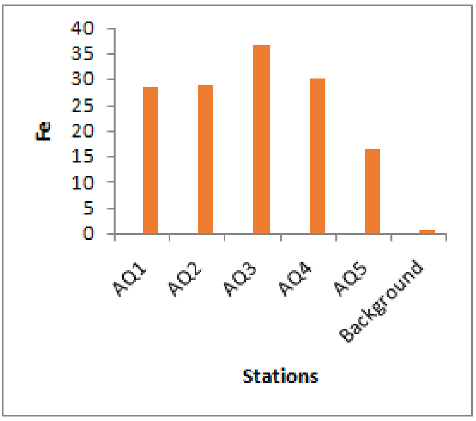
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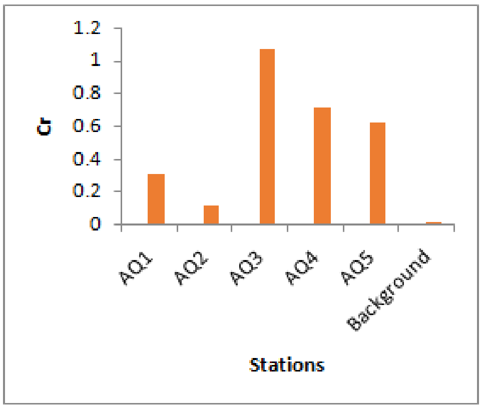
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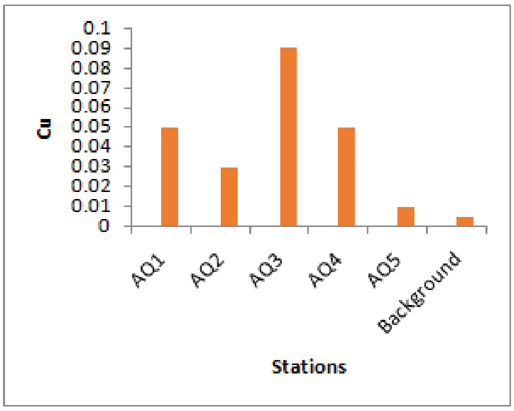
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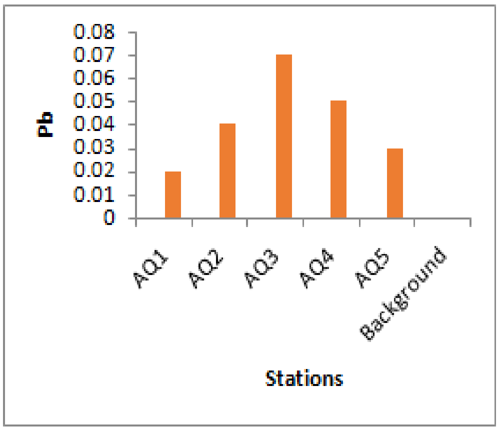
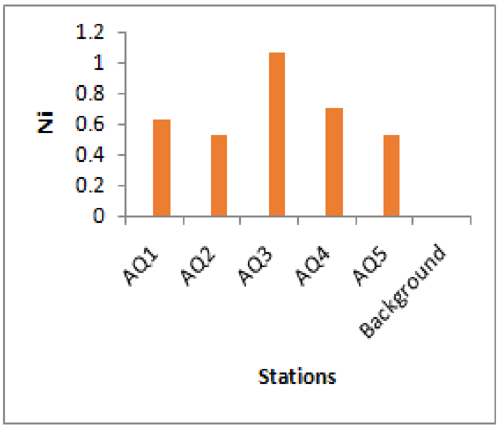
AQ1
AQ2
AQ3
AQ4
AQ5
Background
Stations


Pb
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
AQ1
AQ2
AQ3
AQ4
AQ5
Background
Stations


Ni
1.2
1
0.8
0.6
0.4
0.2
0
AQ1
AQ2
AQ3
AQ4
AQ5
Background
Stations

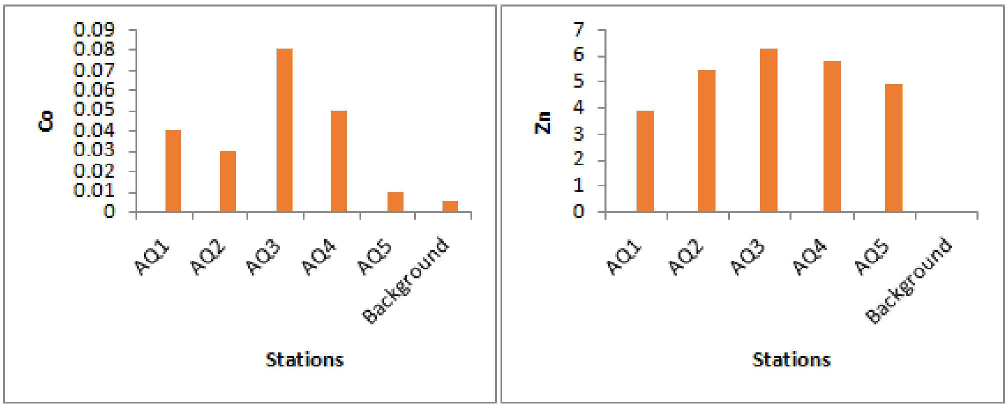
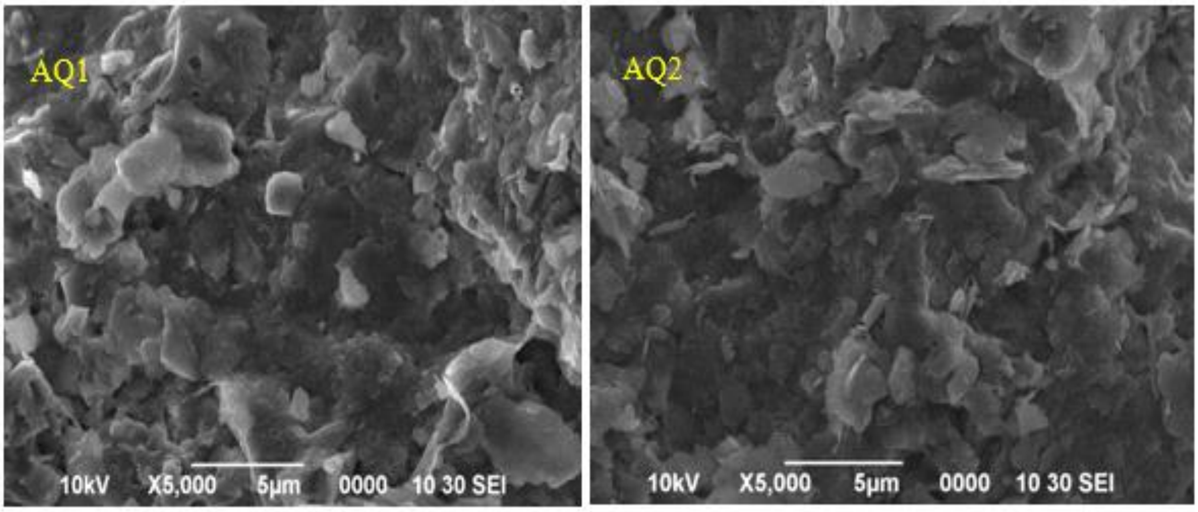


Fig. 3: Variations of analysed heavy metals contents in the sediments from the Sadong River

Brief observations are as follows: the highest concentrations of trace elements were observed in sample areas accumulated immediately downstream of the Sungai Buloh region where about 30% of the industrial activities are located and also the lower part of the Simunjan region of the river. Furthermore, lower contents of heavy metals was obtained from the samples collected in the middle station because of the reduction in content with the displacement from the origin of contamination and, also as a result of reduction in concentrations (dilution) due to uncontaminated sediments collected from the riverbanks because of erosion (lateral and splash type) of the waterway. This occurred at the median segment of the Sadong River, in which there are countless undercut banks possessed of Pleistocene non-polluted sediments. In addition, an extensive decrease in the concentration levels of heavy metals was noticed owing to their deepness and distance from the bottom of the river. The present – day sediments deposits gather together on the bottom of the river including the riverbanks are distinguished by reduction in heavy metals contents, except natively the river wear away and gather its aged polluted sediment. Also, mineralogical investigation is necessary when assessing the levels of concentration of trace elements and examining the origin of contamination by trace elements in sediment samples. The geological formof the eastern Kuching, where river Sadong runs, is influenced by sediments of quaternary which consist of sands, silts and clays of sediment source, glacial tills, fluvio-glacial sands and gravels and different types of organic and organo-mineral sediments including humic acid, fluvic acid, peat and peaty muds (accumulated organic sediment obtained from the fungal and bacterial degradation of dead plants biopolymers). Due to the nature and form of the geology and native used of land (predominantly farming activities due to excellent texture and high fertility of the soil); there is an occurrence of typological distinction of sediments materials in the river of Sadong. Looking at the mineralogical perspective in Sadong sediments the dominated are the igneous materials (granite and quartz grains) of various fragments, forming at least 55-85% of aggregate mass. Around 15% constitutes other mineral particles including orthoclase feldspar and clay minerals (Kaolinite, illite and montmorillonite). The portion of dead remains of plants and animals (organic matter) consisted of scattered charcoals, humus as well as peat in the samples analysed was mainly 4-13%, an area where the humid is more the portion can extend to 15 to 47%.



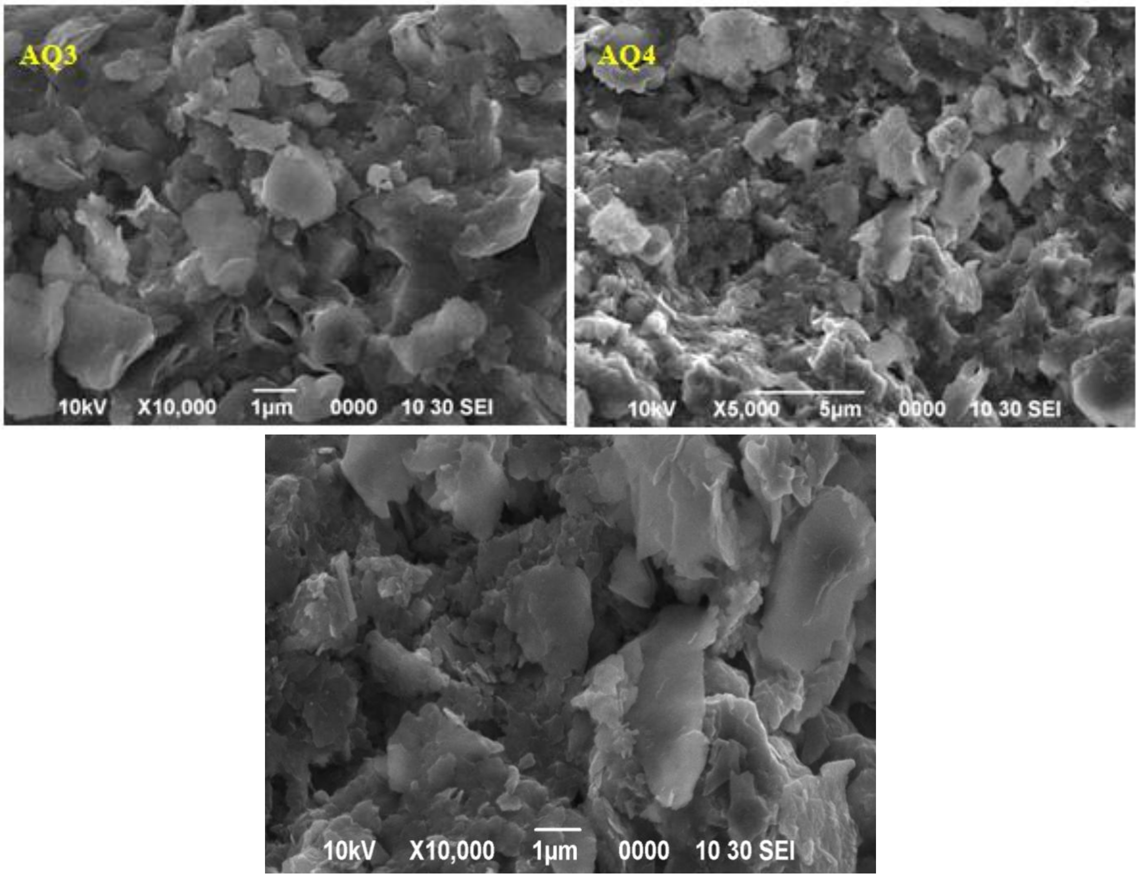


Fig.4: Scanning electron microscope micrographs of five stations sampled from Sadong River

The mineral constituents of geochemically investigated samples were performed by a SEM (scanning electron microscope). The scanning electron microscope micrographs apply to the Sadong river sediment samples. Fig.4, exhibits the scanning electron microscope (SEM) illustrations of samples from geological reference in which the levels of trace metals were evaluated. A huge portion of sharp teeth granite and quartz particles of distinctive tetrahedral structure plus size was available in the samples analysed, as exhibited in Fig. 4.The results from the SEM micrographs demonstrated that sediment samples were flakes or petal types. Although a greater proportion of the particles were agglomerated indicating a greater portion of granite and quartz in the sediment samples, a few were dispersed proving that there is a presence of sand minerals. Clay minerals were found on the sandy particles of quartz isolated and in groups or in aggregation form. The examined sediments were distinguished not just by different levels of shapes (tetrahedron), but also a portion of organic materials and its classifications, as well as carbonates and pH presence. There is an absence of carbonates and the pH range of samples was from 6.5 - 8.3 in the samples collected. In all the samples analysed, igneous materials (granite and quartz grains) of various size were establish as a controlling constituents as it can be observe in Fig 4.

In Fig. 4, it can also be observe from the SEM micrographs that the quantity of granite and quartz particles is indistinguishable in all the analysed samples. As indicated, the maximum concentration levels of metalloids are in relation with the groups of minreals made up of clay minerals and organic materials which are accountable for sorbing and bonding. Hence, there is a reasonable highest concentration of trace elements in the samples analyzed. Sorbing and bonding of trace elements in Sadong river sediments is also correlated with anthropogenic activity in the aged. The considerable response in heavy metals contents of the sediments accumulated in the river was as a result of heavily pollutants related to stronger agricultural and industrial activities in the zone.

CONCLUSIONS

In conclusion, the inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements of metals of interest, as available in the samples from the Sadong River, were validated by applying the quality control steps and actions. As described in Table 5, analytical values obtained are expressed on a dry-mass basis at a temperature of 105°C.Based on the results obtained from the experiment proved that the method validated was easy and convenient for assessment of the 12 metals examined: As, Al, Mn, Ca, Cd, Cu, Fe, Cr, Ni, Co, Zn and Pb in the analysed samples (sediment).

The calibration equations are acceptable because of well-established un-weighted least squares method. The relative error of the quality control computations was used to investigate the calibration stability in the process of sediments analysis and the results obtained were within the acceptable limits, showing the stability of calibration throughout the computations. The recoveries were within the defined range of 90.0 – 110.0% and therefore the matrix effect is regarded as insignificant. The accuracy test proved that all the selected elements investigated, their z-score values were satisfactory (i.e. |z| score values were less than 2).The values obtained after the experiment also indicate that the selected elements in the vertical profiles from the Sadong River could produce data about anthropogenic activity. Sediments from stations closer to industrial activities recorded highest concentrations of trace metals under examination. In addition, the wide reduction in the level of heavy metals in relation to the depth and distance from the bottom of the river is observable as a result of new sediment deposits assembled at the bottom of the river and the riverbanks.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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