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Comparative Studies of Heavy Metals in Mine Water by Square Wave Stripping Voltammetry and Atomic Spectroscopy

S. Uba[1*], B. R. Horrocks[1], A. Uzairu[2], M. S. Sallau[2] and H. Abba[2]

[1]School of Chemistry, Newcastle University, NE1 7RU, United Kingdom.
[2]Department of Chemistry, Ahmadu Bello University, Samaru- Zaria, 810000, Nigeria.

Authors' contributions

Author S.Uba designed the study, managed the literature searches, performed the statistical analysis, discussed the results, and wrote the first draft of the manuscript. Author B.R. Horrocks approved the design and supervised the experiments. Authors A. Uzairu, H. Abba and M.S. Sallau read the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Inductively coupled plasma- optical emission spectroscopy (ICP-OES) and square wave voltammetry (SWV) were used to analyse and compare the concentrations of Cu, Cd, Hg, Pb and Zn in polluted mine water samples from Shilbottle in North Eastern England, United Kingdom. The results obtained revealed the concentrations of Hg, Cd and Pb, generally above the WHO (2006) toxic limits of 0.001, 0.003 and 0.001ppm across the site. The release of these metals was attributed to low pH and the metals were readily bioavailable to the environment contaminating the underground and surface waters. Analysis of variance (ANOVA) and Pearson's correlation coefficients showed strong positive correlation among the concentrations of the different metal ions across the site at P = .05 which clearly indicates their common source of pollution. However, ICP-OES technique exhibited lower detection limits compared to SWV stripping technique and only Cu, and Pb were detected in the mine water samples by the SWV stripping.

Keywords: Mine water; heavy metals; SWV; ICP-OES; UK.

**Corresponding author: Email: saniuba10@yahoo.com, s.uba@ncl.ac.uk;*

1. INTRODUCTION

1.1 Mine-water

Mine-water is known as an acidic mine drainage (AMD) or acidic rock drainage (ARD) which naturally emanates from mine tailings, pits, mine waste rocks and underground working in the mining area. From the standpoint of the chemical description, AMD/ARD is characterized by high metal concentrations, toxic heavy metals and other toxic substances (such as cyanides), metalloids and low pH waters [1]. The major source of metals in AMD is sulphide minerals, which usually have a high concentration of iron and smaller amounts of nickel, gold, lead, copper and zinc depending on the composition of local rocks. Every site possesses a special composition and as a result the potential risks related to different sites varied from site-to-site, and the remediation methods are different [1,2].

Mining industries are considered as a powerful economic source for numerous products, for instance production of precious metals (uranium and gold) and other artificial minerals which can be either fundamental or minor component of various manufactures [3,4]. The seepage AMD of such abandoned sites persists for long periods of time after their use is discontinued up to hundreds of years in some cases [2,4]. Accordingly, mining activities may cause serious threat for human health and other creatures on the earth's surface. The most dangerous and acute effect on human health is produced by cyanides resulting from gold mining operations. Other toxic elements which are released from mining processes can affect human health such as lead, cadmium and arsenic; such toxic substances reach the human body in different ways: water (groundwater and river waters affected by mines tailing), food (vegetable and fruits) and air (hydrogen cyanide). Hence, mining activities have direct effects on the environment in surrounding areas to mining sites, in turn it can be regarded as a real risk to human health when people consume polluted water and vegetables or inhale the polluted air [4-6].

Various techniques have been developed for measuring trace metals in water including anodic and cathodic stripping voltammetry, ion-exchange chromatography, ultrafiltration and dialysis [7]. Anodic stripping voltammetry (ASV) is advantageous due to its selectivity, low detection limit, high accuracy and low cost and it has a high sensitivity particularly to common toxic metals such as cadmium, copper, lead and zinc [8,9]. The effectiveness of ASV for understanding bioavailability of heavy metals in freshwater and sea waters recently has been well documented [10-14]. Hall and Vaive (1992) compared the results obtained by ASV with atomic absorption spectrosopy (AAS) technique in determining Cd, Cu, Pb and Zn and demonstrated that agreement was excellent with the exception of Zn. Previous studies on the applicability of ASV to mine water are quite lacking [15-17].

1.2. Chemistry of Mine Water Formation

Extensive studies have been carried out to understand the chemistry of mine water formation [18,19- 23]. The studies have simply characterized AMD as waters in both phases fluid and solid [MAS Ashtewi, Newcastle university, unpublished PhD thesis]. The major component of mine tailing disposal and waste rock dumps is metal sulfides. The most naturally abundant is pyrite (FeS_2), as well as other sulfide minerals such as marcasite (white pyrite FeS_2), sphalerite ($ZnS_{(s)}$), covellite ($CuS_{(s)}$), millerite ($NiS_{(s)}$), galena ($PbS_{(s)}$) and greenockite ($CdS_{(s)}$). All aforementioned sulfide minerals except pyrite release soluble metal ions during their exposure to the atmosphere or oxygenated water without the generation of

H^+ ion. This can be a major sources to heavy metals contamination, regardless of a real complicated reactions in acid mine drainages [MAS Ashtewi, Newcastle university, unpublished PhD thesis].

1.3 Inductively Coupled Plasma- Optical Emission (ICP-OES)

ICP-OES is an advanced tool compared to atomic emission spectrometry in which atomisation and excitation are carried out by one of the three sources (flame, arc, and spark) [MAS Ashtewi, Newcastle university, unpublished PhD thesis]. The flame emission technique is utilized only for the determination of easily excited metals such as Na, K, Ca, and Li but determination of other metals (refractory metals) using flame as atomizer is impossible as the flame temperature is about 3150^0C which is insufficient to excite such metals [MAS Ashtewi, Newcastle university, unpublished PhD thesis].

This technique is not ideal for elemental analysis as they have some drawbacks such as complex spectra, background effects, and lack of reproducibility and not well suited to measure liquid solutions and have lower temperature than ICP [24-26]. However, the technique can be used to determine the total metal contents as well as determining the metals bound to organic matrix. Plasma is an electrically conducting gaseous mixture consisting of electrons, ions and neutral particles [MAS Ashtewi, Newcastle university, unpublished PhD thesis]. The most common gas employed in the plasma is argon (Ar) from which higher gas temperature is achieved and less reactive chemical species than in flames [MAS Ashtewi, Newcastle university, unpublished PhD thesis]. The Ar^+ are capable of maintaining temperature in order to sustain ionization because Ar^+ ions are able to absorb sufficient power from an external source [25-26]. The sample is introduced into the argon flow as an aerosol or vapour via central tube [26].

1.4 Square Wave Stripping Voltammetry (SWV)

Electrochemical stripping analysis has been widely recognized as a powerful technique for simultaneous measurement of multiple trace metals in various samples. It has some intrinsic advantageous features like quick analysis speed, high precision and accuracy, relatively portable and inexpensive instrumentations and can be used 'on-site' measurement biomedical, environmental and industrial applications [27]. In the striping analysis, the proper choice of the working electrode is crucial for the success of measurement.

Traditionally, mercury-based electrodes such as hanging drop mercury electrodes (HDME) are prepared for ESA due to their reproducibility and sensitivity [27] However, the health implications and safety regulations severely restrict its application due to the toxicity of mercury [27]. The 'environmentally friendly' bismuth electrodes display many excellent properties such as low toxicity, ability to form alloys with many metals, wide cathodic potential window, insensitivity to dissolved oxygen, etc [27].

Essentially, stripping analysis is a two step technique – the first step involves the electrolytic deposition of a small portion of the metal ions in solution to pre-concentrate the metals [27]. This is followed by dissolution (stripping) of the deposit. Different versions of the stripping analysis can be employed depending on the nature of the deposition measurement steps. The two major forms of the stripping methods are the anodic and cathodic stripping methods. SWV is a rapid technique in which analysis time can only be few seconds to record a complete voltammograms, this is attributed to fast scan rate , thus, the SWV is an effective

technique to study kinetics parameters of the electrode [24]. The technique is carried out at a stationary electrode and its waveform consists of many cycles in which each tread of the stair case scan has superimposed a symmetrical double pulse one of which is in forward direction and another in the reverse direction. This shows that the background current is suppressed because the forward and reverse current are sampled at the end of each pulse, when the charging current is negligible compared to the Faradaic current [MAS Ashtewi, Newcastle university, unpublished PhD thesis].

1.5 Area of Study and Site Description and Sample Collection

The study was conducted on the Shilbottle Colliery site in Northumberland, in the north east of England. It is located about 30 miles north east of Newcastle upon Tyne and about 4 mile south east of Alnwick. The history of this site can be traced back to the early 19th century, where coal working was started on this site until 1982 when the site was closed and abandoned [23]. The major residues of these activities is a highly contaminated spoil heap, this, produces high concentrations of soluble metal ions such as Fe, Al and Mn as well as soluble SO_4^{2-} as rainwater leaches through the heap [MAS Ashtewi, Newcastle university, unpublished PhD thesis].

During the rainy season the soluble metals-contaminated leachate from the spoil heap seep into adjoining Tyelaw Burn, this in turn flows to the Coquet River causing spectacular ochreous pollution [MAS Ashtewi, Newcastle university, unpublished PhD thesis]. For these reasons several attempts have been adopted since the mid-1990s to reduce such severe environmental damage, including reed-beds and wetlands [MAS Ashtewi, Newcastle University, unpublished PhD thesis]. These were constructed along with a permeable reactive barrier remediation system in 2003 [23,28].

Falling rain water on the spoil heap causes an increase in the seepage of soluble contaminants. Then the leachate is discharged through the constructed permeable reactive barrier (PRB) before entering settlement lagoons. Eventually, the decontaminated water can flow to Tyelaw Burn stream via reed-bed wetland.

The samples were collected in the well labeled clean 1litre polythene bottles that were rinsed with the mine water samples prior to sample collection. Triplicates samples were collected at each sampling point. The samples were then transported to the laboratory and kept in freezer before the analysis the following day, the pH of the samples were below 4 across the sites.

1.6 Aims and Objectives of the Study

The most effective remediation technology that has been used to treat AMD in Northumberland coal sites (Shilbottle) in the last decade is the passive treatment system [8,14]. This technology included three options; (1) Permeable reactive barriers (PRB), (2) Reducing and alkalinity producing systems (PAPS) and (3) Compost wetlands [28]. For example, the PRB system was mainly constructed from carboniferous limestone mineral and less content of composted horse manure and green waste compost [28]. The significant objective of such technology is to rising up the pH which in turn encourages metal ions (e. g. iron and aluminium) to precipitate and reduce the mobility of metal contaminants [23,28].

This remediation strategy (elevated pH and contaminated precipitation) has been established and used for AMD treatment for more than five years, but the pH of the Shilbottle site is still less than 4 which might result in the release of metal ions to the environment due to increased solubility and mobility at this pH. This paper reports the concentrations of dissolved Zn, Pb, Cu, Cd and Hg in the AMD using square wave (SWV) electrochemical technique and total metal concentration by ICP-OES (spectroscopic technique).

2. MATERIAL AND METHODS

2.1 Reagents

All the chemical reagents used for the calibration plots and designed of the electrode were of analytical grades (Analar), used without any further purification and were purchased from sigma Aldrich chemicals (Gellingham, UK). The electro-analytical measurements were made in 100mM$NaNO_3$ (saturated) supporting electrolyte and a milli- (Q) plus filter Nano pure water made from RO, model D11931 (Barnstead international, Dubuque, Iowa, USA) ion exchanger and a nominal resistivity of 18.2 MΏ cm was used for the preparations of the reagent.

2.2 Instruments for the Electrochemical Measurements (SWV)

The CH instruments potentiostat (model CHI700B) was used for the square wave voltammetric measurements. It consists of a potentiostat and three electrode system comprising of bismuth working electrode, platinum a counter electrode and Ag/AgCl(s) reference electrode and 100mM saturated $NaNO_3$ was used as the supporting electrolyte. This set-up was used for the SWV measurements with a magnetic stirrer for stirring the solution to keep the solution homogeneous throughout the deposition and cleaning steps, and all the measurements were carried out in triplicate at room temperature for reproducibility.

2.2.1 Electrode polishing

Mechanical and electrochemical cleaning processes were used to polish Pt, Au and Bi electrodes while only electrochemical process was used to clean the reference electrode. Fine grade alumina with particle size 0.1 to 0.05µm was used, it was spread on smooth plastic glass plate and then slurried in de-ionized water to form a paste. The electrode was polished many times by circular motion and was eventually cleaned primarily by rinsing with de-ionized water followed by alcohol or acetone, it was finally dipped in de-ionized water for 3minutes and dried by nitrogen and the electrode was assessed by recording the voltammograms of the supporting electrolyte ($NaNO_3$) until repeatable voltammograms were exhibited after about 4cycles and very low background current [MAS Ashtewi, Newcastle university, unpublished PhD thesis].

2.2.2 Measurements of metal concentrations for calibrations

Stock solutions (1mM) of the metal ions (Pb, Cu, Cd, Hg and Zn) were prepared in the supporting electrolyte (100mM saturated $NaNO_3$ which were then used to prepare the lower concentrations of the metal ions (0.2, 0.4, 0.6, and 1.0µM) by serial dilution. The peak currents of the solutions were measured by the SWV Stripping at 100s and then used for the

calibration plots. The metal concentrations were prepared in de-ionized water for calibration using ICP-OES.

2.2.3 Characterisation of the peak due to reduction of hydrogen ions

In order to characterize the peak due to hydrogen ion reduction, 10ml of the supporting electrolyte and 10ml of 0.015M NaOH solution used in the electrochemical cell using Bi, Pt and Ag/AgCl working, counter and reference electrodes respectively. The scan parameters used were similar to those used in section 2.2.4 and the concentrations of the metal ions were determined from the calibration plots. 0.015M NaOH was used as a control (with no H^+) to test for the H^+ reduction in the actual samples.

2.2.4 Preparation and measurements of metal concentrations by the SWV in the mine water samples

SWV voltammetric technique was used for measuring total dissolved metal ions (Cd, Cu, Pb, Hg and Zn). The mine water samples were filtered with 0.1µm milllipore and 10ml each of the filtered sample was added to 10ml of the supporting electrolyte in the electrochemical cell and the SWV were recorded according to the following scan parameters: E= -0.6V, E_{final} = +0.6V, SWV-frequency 50Hz, scan rate 0.05V/s, deposition time is 100s.

2.3 Preparation and Measurement of Metal Concentrations in the Mine Water Samples by ICP-OES Technique

The instrument used was 701V ICP-OES (Unicam Instruments Cambridge, England), quartz aqueous torch with glassy spray chamber. RF- power was 1kW, coolant flow (13ml/min), nebulizer pressure was 42psi, auxiliary flow was 0.4ml/min and the sample uptake was 1.3ml/min. The nebulizer was a standard v-groove pfa micro flow (produces a fine aerosol). the chemicals used for the calibration curves (nitrate salts of Cu, Cd, Pb, Hg, and Zn) were purchased from sigma aldrich, England, UK. The standard solution of each of the metal ion was made in glass volumetric flask using de-ionised water (18.2 mΩ cm) and the environmental samples were filtered through 0.1mm millipore and the samples were injected into the equipment with flow rate 1.3ml/min and the concentration of the elements were estimated in the Shilbottle samples [MAS Ashtewi, Newcastle University, unpublished PhD thesis].

3. RESULTS AND DISCUSSION

3.1 Quality Assurance

The SWV measurement showed good recoveries of all but zinc metal ion which was poorly recovered having percentage recovery of <23%. A blank sample which was simply de-ionized water was used as a correction factor, the true concentration of the samples were taken as the difference between the measured concentrations of the samples to those of the blanks for each metal.

3.2 Metal Concentrations in the Mine Water Samples by ICP-OES and SWV Stripping Techniques

The concentrations of heavy metal ions as recorded by the ICP-OES analytical method (Table 3.1) ranged from 0.036±0.037ppm(G) to 0.617±0.006ppm(O),0.111±0.027ppm(H) to 1.156±0.043ppm(K), 0.001±0.009ppm(H) to 2.314±0.016ppm(O), 0.003±0.008ppm(G) to 0.048±0.011ppm(K), 0.109±0.017ppm(H) to 0.545±0.016ppm(N) for Cu, Pb, Zn, Cd and Hg respectively. The concentrations ranges of Zn and Cu were below 5 and 1.5ppm of the world health organisation (WHO, 2006) limits while those of, Cd, Pb and Hg were above the limits of 0.003, 0.001 and 0.003ppm respectively across the sites which was attributed to the mobility/migration of the metals which is mostly rapid at low pH as presented in Figs. 3.1 to 3.5 below.

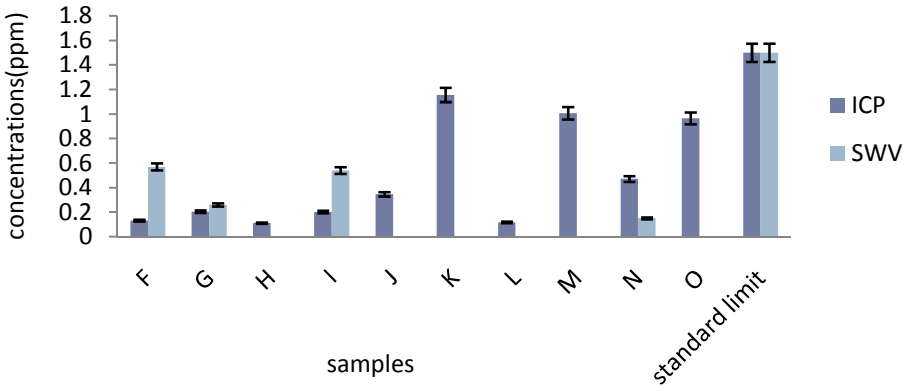


Fig. 3.2. comparative studies of lead by ICP and swv techniques in mine water samples

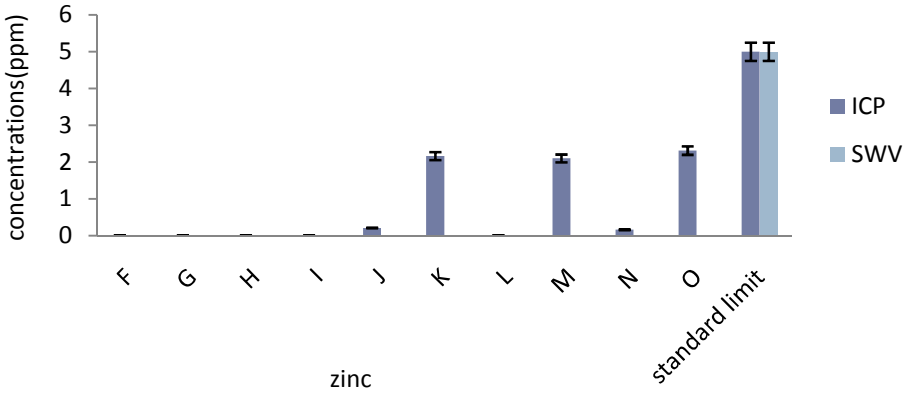


Fig. 3.3. Comparative studies of zinc by ICP and swv techniques in mine water samples

Conversely, the elevated level of cadmium was noted at F sample of the mine water by the SWV technique, it was undetected in the rest of the samples by the SWV which might be attributed to the ability of cadmium to form complex in mine waters and its presence in the dissolved form. Similarly, Hg and Zn were also undetected by SWV while Cu was detected in the G, I and J samples respectively by the SWV stripping technique, this clearly indicates the high detection limit of SWV as compared to ICP-OES. In addition, it might also indicate the sensitivity of SWV stripping to the speciation of the electrolysable species which ICP-OES is not.

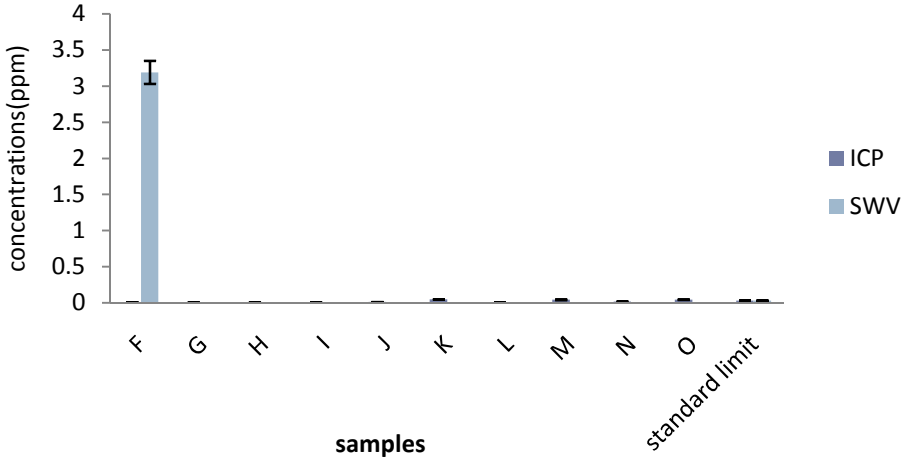


Fig. 3.4. Comparative studies of cadmium by ICP and swv techniques in mine water samples

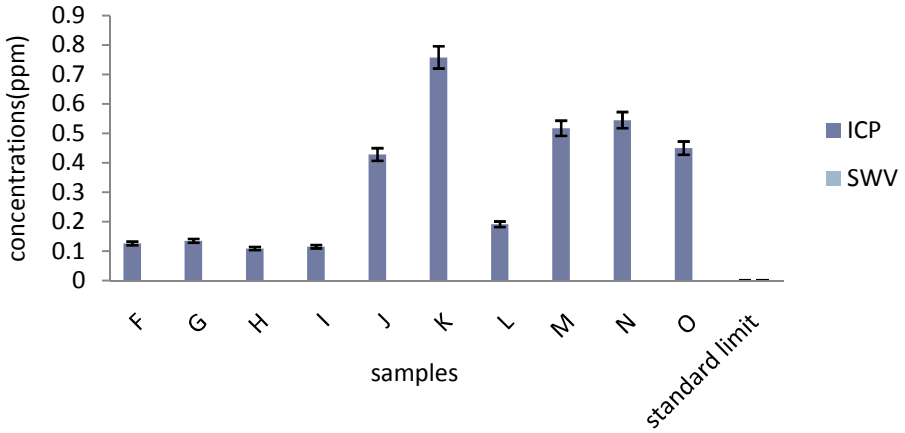


Fig. 3.5. Comparative studies of mercury by ICP and swv techniques in mine water samples

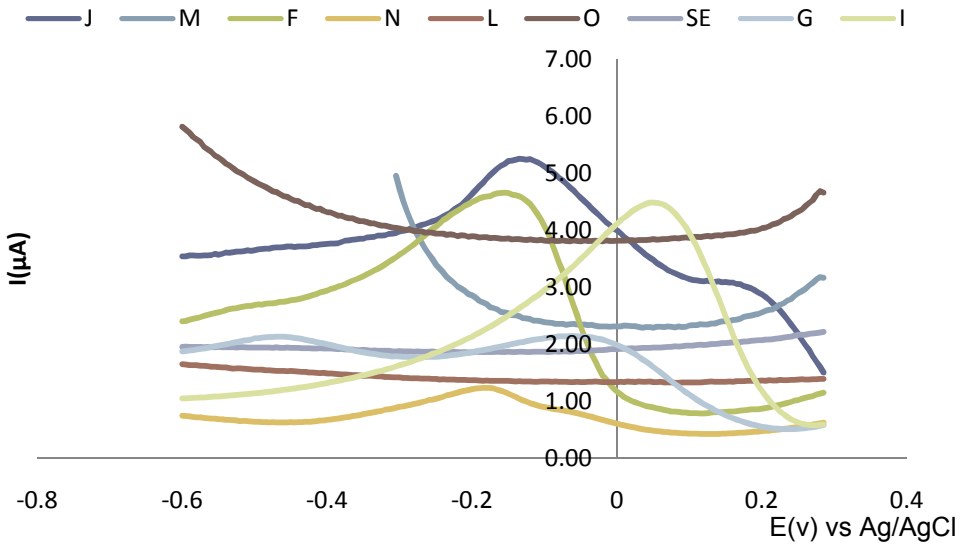


Fig. 3.6. Mine water voltamogramms for concentrations determination by the SWV on bismuth working electrode, Ag/AgCl reference and platinum counter electrode by SWV technique; the scan parameters were E_{start}= -0.6V, E_{final} = +0.6V, SWV-frequency = 50Hz,

Fig. 3.6 above shows that most of the soluble fractions of the mine water samples were lead, cadmium and copper at potentials of -0.1, -0.35, 0.25V respectively. SE was the voltammograms for the supporting electrolyte (SE) and no peak was evident. Copper metal ion was predominantly found at I and G mine water samples with concentrations of 0.27 and 0.55ppm respectively as presented in Fig. 3.1. These concentrations were below the WHO (2006) toxic limits of 1.5ppm. Furthermore, as presented in Fig. 3.2 the dissolved fractions of Pb as recorded by the SWV technique were at the J, G, I, and L mine water samples across the sites at concentrations far above the WHO (2006) toxic limits of 0.001ppm. Similarly, the concentrations recorded for zinc metal ion across the sampling points were all below the WHO tolerable limit of 5ppm as presented in Fig. 3.3 above. However, the observable concentrations for the cadmium metal ion in the mine water samples (Fig. 3.4) was noted at K, M, N and F mine water samples and undetected in the rest of the water samples. These concentrations were lower than the WHO tolerable limit of 0.003ppm in water. Generally, no metal ions were detected in the analysed samples of O and M and thus no peak was observed. Furthermore, mercury was detected by the ICP-OES spectroscopic method above the WHO (2006) tolerable limit of 0.001ppm as presented in Fig. 3.5. Comparing Figs. 3.3 to 3.5, cadmium, zinc and mercury were not detected by the SWV technique, this might be attributed to their presence in the organic phase in the analysed water samples. The limits of detection for the metal ions by the ICP-OES technique was taken as 3 x standard deviation of the blank as presented in Table 3.1. The square wave stripping voltammograms revealing the peak currents due to metal ions in the mine water samples were presented in Fig. 3.6 which clearly indicates that the metal ions were undetected in some of the analysed samples; this might be attributed to matrix effects.

3.3 Correlation Matrices of the Metals Across the Sites for the Mine Water Samples

The analysis of variance showed that there was significant difference in the concentrations of the analysed metals at P = 0.05 as presented in Table 3.2. Similarly, the correlation coefficients of 0.843, 0.944, 0.947, 0.521, 0.838 and 0.653 were recorded among Pb and Cu, Zn and Cu, Zn and Pb, Cu and Hg, Pb and Hg, and Hg and Zn metal ions at 99% (P = 0.01) and indicated by ** in Table 3.3 respectively. The strong positive correlation might not be unconnected to the stability constants and bioavailability of these metals in the mobile phase of the samples for bioavailability and bioaccumulation. In addition, this shows that the metals have a common source of pollution which is majorly the abandoned mine site.

Table 3.1. The limit of detection of the analysed metal ions by the ICP-OES technique

Metals	Blank standard deviation	Detection limit (ppm)
Cu	0.002	0.005
Pb	0.010	0.029
Zn	0.011	0.033
Cd	0.009	0.027
Hg	0.016	0.570

Table 3.2. Analysis of variance (ANOVA) of the metals across the sites

		Sum of Squares	df	Mean Square	F	Sig.
Cu	Between Groups	1.133	10	.113	7620.367	.000
	Within Groups	.000	22	.000		
	Total	1.133	32			
Pb	Between Groups	4.518	10	.452	342.096	.000
	Within Groups	.029	22	.001		
	Total	4.547	32			
Zn	Between Groups	29.656	10	2.966	7275.624	.000
	Within Groups	.009	22	.000		
	Total	29.665	32			
Cd	Between Groups	.043	10	.004	326.395	.000
	Within Groups	.000	22	.000		
	Total	.043	32			
Hg	Between Groups	1.563	10	.156	308.860	.000
	Within Groups	.011	22	.001		
	Total	1.574	32			

Table 3.3. Correlations matrix of metals across the sites

Metals	Cu	Pb	Zn	Cd	Hg
Cu	1				
Pb	**0.843	1			
Zn	**0.944	**0.947	1		
Cd	0.224	0.147	0.240	1	
Hg	**0.521	**0.838	**0.653	0.003	1

***. Correlation is significant at the 0.01 level, *Correlation is significant at 0.05 (2-tailed).*

4. CONCLUSION

Spectroscopic method mainly inductively coupled plasma - optical emission (ICP-OES) and square wave (SWV) analytical methods were used to analyse and compare the concentrations of Cu, Cd, Hg, Pb and Zn metals in the abandoned mine water samples from the North Eastern England, United Kingdom. The concentrations of Hg, Cd and Pb were generally above the WHO (2006) toxic limits of 1.5, 0.003 and 0.001ppm across the sites. The release of these metals was attributed to low pH (acidic) noted in all the water samples. Thus, the metals were readily bioavailable to the environment due to increased solubility at this pH contaminating the underground and surface waters at the vicinity of these sites. There was strong relationship of the metals across the sites at $P = .05$ and were positively correlated which clearly indicates their common source of pollution. However, ICP-OES technique exhibited lower detection limits where virtually all the metals were detected unlike the SWV technique in which only Cu and Pb were detected, a clear indication of the bioavailability of these metals for bioaccumulation.

ETHICAL APPROVAL

All experiments have been examined and approved by the major supervisor, Dr B.R. Horrocks, School of Chemistry, Newcastle University, Newcastle Upon Tyne, United Kingdom.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Akcil A, Koldas S. Acid Mine Drainage (AMD): Causes, treatment and case studies. Journal of Cleaner Production. 2006;14(12-13):1139-1145.
2. Egiebor NO, Oni B. Acid rock drainage formation and treatment: a review. Asia-Pacific Journal of Chemical Engineering. 2007;2(1):47-62.
3. Azapagic A. Developing a framework for sustainable development indicators for the mining and minerals industry. Journal of Cleaner Production. 2004;12(6):639-662.
4. Abdalla OAE, Sulaiman FO, Al-Ajmi H, Al-Hosni T, Rollinson H. Cyanide from gold mining and its effect on groundwater in arid areas,Yanqul mine of Oman. Environmental Earth Sciences. 2010;60(4):885-892.
5. Zhuang P, McBride, MB Xia HP, Li NY,Lia ZA. Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Science of the Total Environment. 2009l407(5):1551-1561.
6. Kjeldsen P. Behaviour of cyanides in soil and groundwater: A review. Water Air and Soil Pollution. 1999;115(1-4):279-307.

7. Pickering WF. General strategies for speciation In Ure CM, eds. Chemical speciation in the environment. London: Chapman & Hall. 1995;9-32.
8. Florence TM. The Speciation of Trace Elements in Waters. 1982;Talanta 29:345-364.
9. Florence TM. Electrochemical approaches to trace element speciation in waters,; a review. 1986;Analyst 111:489-505.
10. Nurnberg HW. Investigations on Heavy metals speciation in natural waters by voltammetric procedures. Fresenius J. Anal. Chem. 1986;316:557-565.
11. Kozelka PB, Sanudo-Wilhelmy S, Flegel AR, Bruland KW. Physicochemical speciation of lead in south san Francisco bay. Estuar Coast Shelf. Sci. 1997;44:649-658.
12. Kozelka PB, Bruland KW. Chemical speciation of dissolved Cu, Zn, Cd, Pb in Nawangansett bay, Rhode Island. Mar Chem. 1998;60:267-282.
13. Rozan TF, Benoit G. Geochemical factors controlling free Cu ion concentrations in river water, Geochim Cosmochim Acta. 1999;63:3311-3319.
14. Huang S, Wang Z. Application of anodic stripping voltammetry to predict the bioavailable /toxic concentrations of Cu in natural water. Appl Geochem. 2003;18:1215-1223.
15. Yun ST, Jung HB, So CS. Transport, fate and speciation of heavy metals (Pb, Zn, Cu Cd) in mine drainage geochemical modeling and anodic stripping voltammetric analysis. Environ Technol. 2001;22:749-770.
16. Archterg EP, Herzl VMC, Branngardt CB, Milward GE. Metal behavior in an estuary by acid mine drainage; the role of particulate matter. Environ pollut. 2003;21:283-292.
17. Alonso E, Santos A. Callejon M, Jimeng JC. Speciation as a screening tool for the determination of heavy metal surface water pollution in the Guardiamar river basin. 2004;56:561-570.
18. Singer, PC and Stumm, W. Acidic mine drainage, rate - determining step. Science. 1970;167(3921):1121-&.
19. Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB. Mine-water chemistry: the good, the bad and the ugly. Environmental Geology. 1997;32(3):157-174.
20. Colmer AR, Hinkle ME. The Role of Microorganisms in Acid Mine Drainage: A Preliminary Report. Science. 1947;106(2751):253-256.
21. Colmer AR, Temple KL, Hinkle ME. An iron-oxidizing bacterium from the acid drainage of some bituminous coal mines. Journal of bacteriology. 1950;59(3):317-28.
22. Leathen WW, Braley SA, McIntyre LD. The role of bacteria in the formation of acid from certain sulfuritic constituents associated with bituminous coal. II. Ferrous iron oxidizing bacteria. Applied microbiology. 1953,1(2):65-8.
23. Kleinmann RLP, Crerar DA, Pacelli RR. Biogeochemistry of acid mine drainage and a method to control acid formation. Journal Name: Min. Eng. (N.Y.); (United States) Journal. 1981;33(3):300-305.
24. Settle FA. Handbook of Instrumental Techniques of Analytical Chemistry. New Jersey: By Prentice Hall PTR; 1997.
25. Skoog DA, Holler FJ, Niemann TA. The principles of Instrumental analysis. Fith edition, 1998. Brookscode Thomson learning. 849.
26. Vandecasteele C, Block CB. Modern methods for trace elements determination John wiley; 1993.

27. Wang J. Analytical Chemistry. Vol. third edition, New Jersey: by John Wiley; 2006.
28. Jarvis AP, Moustafa A, Orme PHA, Younger PL. Effective remediation of grossly polluted acidic, and metal-rich, spoil heap drainage using a novel, low-cost, permeable reactive barrier in Northumberland, UK. Environmental Pollution. 2006;143(2):261-268.

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