WASTEWATER POLLUTION AND ITS TREATMENT AT ACTIVE MINING SITES IN CHINA

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ABSTRACT: *Active mining wastewaters were analyzed for heavy metals and other physicochemical parameters to find out the hazard level to life and the environment when discharged to surface water bodies. The samples were collected from five active mines and their treatment facilities in China and analyzed for metal concentrations. The metal concentrations of all mining sites were compared with each other as well as with the safe limits set by the Ministry of Environmental Protection (MEP) of China. The concentrations of Fe, Cu, Mn, and Zn were exceeded their respective permissible limits set by MEP. In the Yongping copper mine (YCMR) wastewater, the mean concentrations of Fe (55.43 mg/L), Mn (30.77 mg/L), Cu (18.0), and Zn (6.13 mg/L) exceeded the permissible limits (0.3, 0.1, 1.0 and 2.0 mg/L, respectively) set by MEP for surface water quality. The concentration of sulfate in all mining wastewater samples was extremely high, ranging from 1200 to 5400 mg/L. In LCM, after treatment Cu, Ni, and Zn were removed 100% while Mn, Fe, and Cd were removed 77%, 70%, and 67% respectively. In NFM, after treatment Fe, Co and Cd were reduced 100% while Mn and Zn were removed 39% and 46%, respectively. In YCM, Cu, Ni, Zn, Cd and Cr were reduced 100% while Mn and Fe were removed 82% and 98% respectively. Sulfate concentration in LCM, NFM and YCM were reduced by 6.4%, 13.4% and 24% respectively. Though, the pre and post-treatment values were significantly different ($p < 0.05$) for most of the heavy metals but still the chemical treatment systems were unable to completely remove sulfates and heavy metals from the wastewater and these could portend environmental hazards to the surrounding environment and ecological life.*

Keywords: *Active mines, heavy metals, sulfates, mining wastewater, water pollution.*

1. INTRODUCTION

Heavy metals are ubiquitous in the environment because of their release from natural and anthropogenic activities world widely. Heavy metals are considered as one of the most serious pollutants in the environment and represent a serious threat to the ecosystem and all living organisms including human beings [1, 2]. In the environment, increasing amounts of heavy metals are being introduced naturally through weathering of rocks and several human activities such as mining, smelting, electroplating, and other industrial processes that release heavy metals into their waste streams [3-5]. Active and abandoned mines discharge large quantities of acidic wastewater which usually contain high levels of heavy metals and sulfate [6]. However, mining activities generate wastewater, when rock containing sulfidic minerals is come in contact with water and oxygen, producing acidity and high concentrations of metals and sulfate in the water. The contaminated mine water originates from drainage from underground workings, waste rock dumps from mining activities, mill tailings, ore stock piles, and spent ore piles from heap leach operations [7-10].

Heavy metals in wastewater released to environment are causing serious ecological problems in many parts of the world. This situation is further aggravated by lacking of remediation processes for heavy metals which continue to shift from one level to another within the aquatic environment, including biota. As a result, these metals are concentrated in the food chain and pose the greatest dangerous to organisms near the top of the food chain [11, 12].

Generally, the water body is supporting aquatic life and being suitable for other uses depending on many parameters particularly, trace elements. Heavy metals such as manganese (Mn), zinc (Zn) and copper (Cu), are needed in trace concentrations for the normal physiological functions of living tissues and regulate many biochemical processes of the body. The same metals, however, at higher concentrations in natural waters can have severe toxicological effects on humans and aquatic ecosystems. Toxic metals on the other hand are also dangerous for living organisms even present in small quantities. Highly toxic metal(loid)s such as arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg), are particularly hazardous for humans and animals [13-15].

Acid mine wastewater has high concentrations of sulfate and metals including Fe, Al, Mn, Pb, Cu, Cd, and Zn resulting from sulfide minerals oxidation exposed during coal and metal mining, highway construction, and other deep excavation [16, 17]. In the case of mining, it can be introduced to the environment surrounding a mine via surface runoff or deep-mine drainage to local waterways [18].

Today, the management of mining wastewater has become a big challenge for the world because of stricter regulations designed to protect the environment. However, environmental pollution is placing an increasing stress on various resources of the ecosystem. Metal minings are extensively carried out in China, generating huge amount of wastewater. Previously, numerous studies have been carried out regarding the adverse impacts of acid mine drainage (AMD) from abandoned mines [17, 19]. However, the present study was carried out to assess the comparative load of heavy metals and sulfate in the pre and post-treatment wastewaters from active mines in China and their associated hazardous impacts.

The present study was aimed to quantify the physicochemical parameters of active mines wastewater, and to examine the distribution of heavy metals in the wastewater from active mines and their treatment facilities (Fig. 1). The results obtained have been analyzed statistically to evaluate the relationship between the levels of metals in these media and then to identify their mutual concentrations depending on their source/origin [20]. The efficacy of wastewater treatment, used for minimizing pollution hazards to life and environment was also assessed in this study.

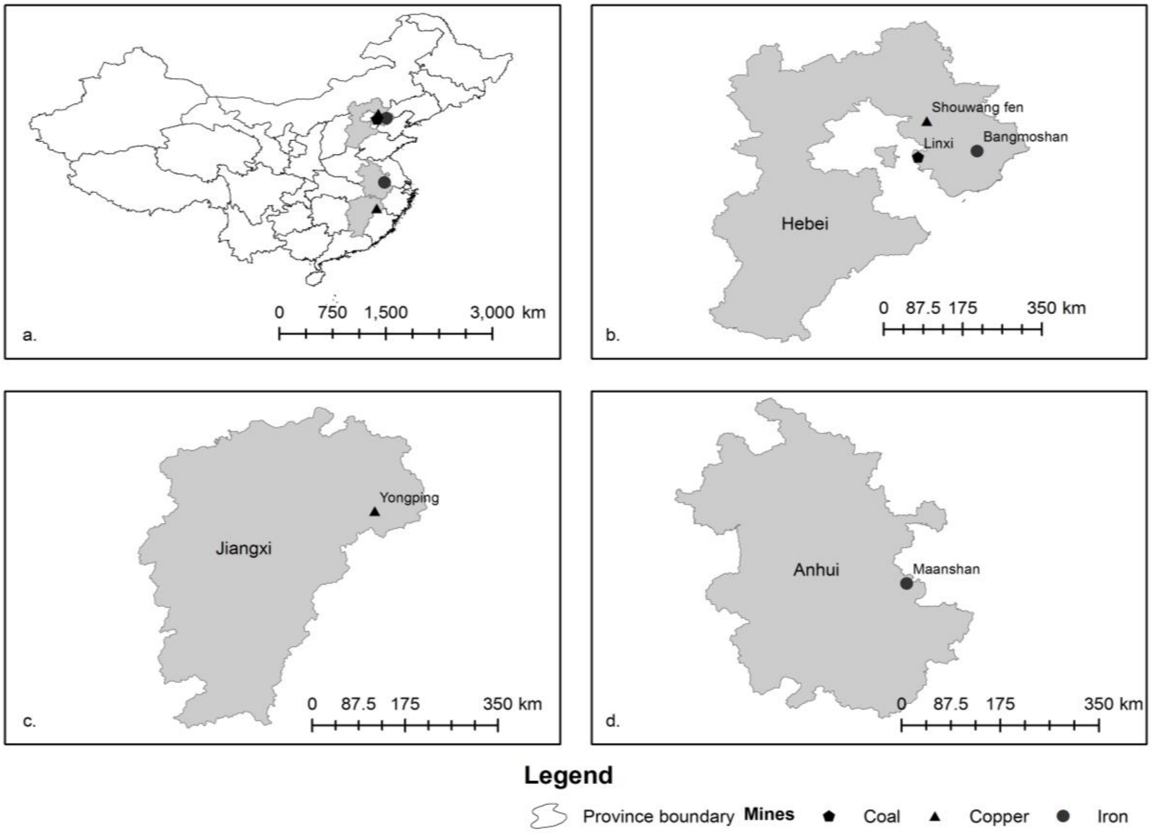
2. MATERIALS AND METHODS

2.1. Sampling Areas

Wastewater samples were collected from different mines in China as shown in Fig. 1 with the following brief information.

- Bangmoshan Ferrous Mine (BFM): an open pit mine, owned by Tangshan Iron & Steel Co. Ltd., located at Yanshan Mountains in North China. Mining and rain water were collected in a lake of 500 m diameter and 30 m depth and no treatment was provided.
- Linxi Coal Mine (LCM): a 300 m deep underground mine located in Tangshan, Hebei Province, North China. Wastewater from underground was pumped out to surface and collected in a pond for further physical treatment (sedimentation).
- Shouwangfen Copper Mine (SCM): an underground mine in Chengde City of Hebei Province, North China. The mine was 660 m deep having 11 layers. Wastewater was collected in an underground tank on the first layer 60 m deep. After physico-chemical treatment (to raise pH and sedimentation) the clean water was pumped out to the surface and collected in a tank.
- Nanshan Ferrous Mine (NFM): an open pit mine, owned by Maanshan Iron and Steel Company Limited, and located at Ma'anshan in Anhui Province, Southeast China. The mine wastewater was collected in a big dam of 8-10 km^2 area for further treatment (sedimentation).
- Yongping Copper Mine (YCM): it is also an open pit mine in Shangrao, Jiangxi Province, Southeast China. Wastewater was collected in a reservoir (1 km^2 area and 10 m depth) 2 km away from the mine site. The water was of brickish color. Wastewater from the reservoir was transported through underground pipes to a treatment plant 3 km away in the downtown. It was a physico-chemical treatment plant with capacity of 10-15 thousand cubic meters water per day by using lime to raise the pH followed by the addition of powdered Poly-aluminium chloride (PAC) as a coagulant and then sedimentation.

Fig. 1 Maps showing the locations of selected metal mining sites in China



2.2. Samples Collection and Pretreatment

Wastewater samples were collected from different points of the mining sites before and after treatment. Samples for dissolved heavy metals analyses were filtered with 0.45 μm pore size membrane filters and acidified with 50% HNO_3 to a pH <2 on the spot to minimize adsorption of trace metals to the inner surfaces of containers and collected in polyethylene bottles pre-treated with 50% HNO_3 according to the standard methods [21].

For other chemical analyses (sulfates, sulfides, COD, BOD, DOC, Alkalinity etc.) the samples were prepared and pretreated on the spot according to the standard methods. Samples were transported to the laboratory and stored at 4°C in a refrigerator for further analyses.

All laboratory glassware were pre-washed thoroughly in distilled water, soaked with 0.1 N HCl, then washed with deionized water to avoid any contamination during samplings and further analyses, as described by Sabri et al [22].

2.3. Chemical Reagents

All chemicals used were of analytical grade with high spectroscopic purity of 99.9% purchased from Beijing Chemical Co., Ltd (Beijing) and were checked for possible trace metal contamination. Ultrapure water was used throughout analysis. Standards of all nine elements were prepared from stock solution (1000 mg/L) of certified standard solutions (Fluka Kamica Busch Switzerland) of corresponding metal ions.

2.4. Analytical Procedure

Temperature, pH and DO of the water were checked on the spot using their respective electrodes. Acidity was determined potentiometrically, while samples were prepared for measuring BOD_5 within 24 h using membrane electrode method. Sulfate concentrations were measured through turbidimetric method while sulfide was measured iodometrically [21]. COD was measured photometrically (Spectroquant TR420 and Nova60, Merck, Germany) [23]. DOC was determined with LiquiTOC-II (Elementar Analysensysteme GmbH Donaustrasse 7 D-63452 Hanau (Germany) [24].

The samples were prepared and diluted as 100%, 50%, 25%, 10% and 5% and analyzed for nine selected heavy metals, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn using flame atomic absorption spectrophotometer (AA-6300 Atomic Absorption Spectrophotometer, Shimadzu, Japan) [21].

The instrument was calibrated for determination of each element by analyzing the standard solution (concentration usually in µg/ml) of each element provided by the company (General Research Institute for Nonferrous Metals, Beijing). For quality control, the blank and standards of heavy metals were also used in triplicates. After every 6 samples, standard was run as unknown to check accuracy of the instrument. The instrumental parameters for each element are listed in Table 1.

Table 1 Atomic absorption conditions for analysis of selected heavy metals

Element	Acetylene (L/min)	Air (L/min)	Wavelength (nm)	Slit width (nm)	Lamp current (Ma)	Limit of detection (mg/L)
Cd	1.8	15.0	228.8	0.7	8	0.0005
Co	1.6	15.0	240.7	0.2	12	0.005
Cr	2.8	15.0	357.9	0.7	10	0.005
Cu	1.8	15.0	324.8	0.7	6	0.002
Fe	2.2	15.0	248.3	0.2	12	0.002
Mn	2.0	15.0	279.5	0.2	10	0.002
Ni	1.6	15.0	232.0	0.2	12	0.005
Pb	2.0	15.0	283.3	0.7	10	0.002
Zn	2.0	15.0	213.9	0.7	8	0.001

2.5. Statistical Analysis

Basic exploratory statistics were calculated for the individual group of samples i.e., pre and post treatment in order to present an overview of the measured parameters at each sampling site. Pearson correlation was calculated between the pretreatment samples only in order to assess the possible relationship between the measured parameters. A statistic correlation analysis between pertinent wastewater characteristics and metal concentrations determine the possible factors controlling the heavy metal concentrations in the wastewater from mining operations. The effectiveness of wastewater treatment was also assessed using paired t-test between pre and post treatment samples of respective sampling sites. t-test helps in understanding the pollution status and management as well as rapid solution to pollution problems [25-27]. All the analyses were performed using software IBM SPSS Statistics ver. 19 (IBM SPSS. Inc. 2010).

3. RESULTS AND DISCUSSION

The statistical summary of selected metal concentrations in all mining wastewaters is presented in Table 2. From the data related with metal distribution in mining effluents, it is clear that Fe (8.01 mg/L), Mn (4.94 mg/L), Cu (2.27 mg/L), and Zn (1.23 mg/L) were the major contributors to the overall heavy metal pollution. The selected metals were observed in order of Fe>Mn>Cu>Zn>Ni>Cr. The summary of metal concentrations in wastewater of each mine is given in Table 3. In BFM samples, the highest mean concentration (3.20 mg/L) was for Zn followed by Fe (1.60 mg/L), Ni (0.60 mg/L), Cr (0.40 mg/L), Pb (0.20 mg/L) and Cd (0.02 mg/L). The concentrations of Co, Cu and Mn were either below detection limits or within the permissible limits set by the Ministry of Environmental Protection (MEP), China. In LCM samples (both pre- and post-treatment), only Fe mean concentrations (2.34 mg/L and 0.70 mg/L, respectively), while in case of SCM, Cd concentration (0.14 mg/L) was found higher than the MEP guidelines. The mean concentrations of Fe (2.82 mg/L) and Mn (1.80 mg/L) were higher in NFMP (pre-treatment) while only Mn level (1.11 mg/L) was higher in NFMD (post-treatment) samples than the MEP guidelines. The YCMR (pre-treatment) samples were having the highest concentrations of most of the heavy metals. The concentrations of Fe (55.4 mg/L), Mn (30.7 mg/L), Cu (18.0

Table 2 Summary of selected metal concentrations in all mining wastewaters (n=24)

Metals (mg/L)	Minimum	Maximum	Mean	Std. Deviation
Cu	<DL*	21.0	2.27	6.14
Ni	<DL	2.00	0.30	0.62
Mn	<DL	36.0	4.94	10.3
Fe	<DL	57.0	8.01	18.4
Pb	<DL	0.22	0.03	0.07
Zn	<DL	9.40	1.23	2.47
Co	<DL	0.02	0.00	0.01
Cd	<DL	0.60	0.07	0.17
Cr	<DL	1.10	0.17	0.33

* <DL- Below detection limit

mg/L), Zn (6.13 mg/L), Ni (1.82 mg/L), Cr (0.93 mg/L) and Cd (0.50 mg/L) were observed greater than their respective limits set by MEP (2002).

Comparing mean metal concentrations in the mining wastewater with MEP guidelines (Fig. 2), it is clear that in YCMR samples all metals except Pb were present in greater concentrations than the MEP guidelines. The concentration of Pb was higher than MEP limit only in the wastewater collected from BFM site.

Statistical summary of other physico-chemical parameters (Table 4) revealed that the pH of YCMR was quite low indicating the acidic nature of the wastewater. The low pH increases the toxicity and mobility of several metal ions [28-30]. The pH values of other mining sites were within the range of MEP guidelines (6–9). Sulfates mean concentrations were extremely higher at all sites than its MEP standards. In most of mining sites, the concentrations of DO, COD and sulfides were also found higher than their respective limits set by MEP for mining wastewater.

In LCM, after treatment Cu, Ni, and Zn were removed 100% while Mn, Fe, and Cd were removed 77%, 70%, and 67% respectively. In NFM, due to treatment Fe, Co and Cd were reduced 100% while Mn and Zn were removed 39% and 46%, respectively. In YCM, Cu, Ni, Zn, Cd and Cr were reduced 100% while Mn and Fe were removed 82% and 98% respectively. Sulfate concentration in LCM, NFM and YCM were reduced by 6.4%, 13.4% and 24% respectively. The paired t-test results (Table 5) shows that treatment provided at LCM was efficient only for Zn removal ($p = 0.01$). In case of NFM, Co, Fe, Mn ($p < 0.05$), and Zn ($p = 0.05$) were removed efficiently, while the treatment provided at YCM was efficient ($p \leq 0.01$) for removal of all selected heavy metals except Zn.

The reduction/removal of these parameters to the permissible levels would not create any ecological or health problem, while if left untreated, may cause hazards to biota and even to human beings.

The statistical correlation pertaining to metal-to-metal relationship was conducted on mutual inclusive basis. The Pearson correlation (Table 6) revealed that all heavy metals (except Co and Pb) had strong positive correlation among each other ($r \geq 0.729$, significant at $p < 0.001$). Likewise, all heavy metals, except Co and Pb, had strong negative correlations with pH and DO, while strong positive correlation with sulfides. Most of the heavy metals were mildly positively affected by the temperature. SO_4^{2-} had mild positive correlation with Cd, Cu, Fe, and Mn while BOD values were positively correlated only with Co. In case of physico-chemical parameters, temperature had negative correlation with pH and DO while positively correlated with SO_4^{2-} and sulfides. pH had strong positive effect on DO, while negatively affected sulfides. The values of DO had also strong negative correlation with sulfides.

To reduce the alarming levels of heavy metals and other pollutants the mining authorities were treating those effluents using lime or sodium hydroxide neutralization, precipitation and sedimentation**.** Studies have shown that mining wastewaters usually have low pH values but most of the underground mines in China discharge effluents with pH ranged from 7-8 units. Effluents from LCM, SCM and NFM had pH in the range of 7.5-8.0 units. The wastewaters were mixed with lime underground to raise their pH level before pumping out to the surface. LCM wastewater was collected on surface in a pond of 600 m^2 area and 3 m depth for settling down suspended solids. The settling process was not able to remove dissolved heavy metals, sulfates and other chemicals completely. The effluent, discharged to the environment, still containing Fe, sulfates, COD, and sulfides at concentrations higher than their respective permissible limits. The treatment processes were not efficient (6.4%) enough to bring the sulfates level within the MEP permissible limits (250 mg/L).

Table 3 Summary of heavy metal concentrations (mg/L) in mining wastewater samples

Mine		Cu	Ni	Mn	Fe	Pb	Zn	Co	Cd	Cr
BFM (Pre)	Std. Deviation	0.02	0.20	0.01	0.36	0.02	0.20	0.00	0.003	0.10
	Minimum	0.12	0.40	0.08	1.20	0.18	3.00	0.01	0.016	0.30
	Maximum	0.16	0.80	0.10	1.90	0.22	3.40	0.01	0.021	0.50
	Median	0.14	0.60	0.09	1.70	0.20	3.20	0.01	0.019	0.40
SCM (Post)	Std. Deviation	<DL	<DL	<DL	<DL	<DL	0.00	<DL	0.002	0.003
	Minimum	<DL	<DL	<DL	<DL	<DL	0.17	<DL	0.012	0.005
	Maximum	<DL	<DL	<DL	<DL	<DL	0.17	<DL	0.026	0.01
	Median	<DL	<DL	<DL	<DL	<DL	0.17	<DL	0.014	0.01
LCMP (Pre)	Std. Deviation	0.04	0.00	0.03	0.91	<DL	0.04	<DL	0.001	<DL
	Minimum	0.02	<DL	0.02	1.44	<DL	0.19	<DL	<DL	<DL
	Maximum	0.10	0.01	0.07	3.26	<DL	0.26	<DL	0.002	<DL
	Median	0.06	<DL	0.06	2.35	<DL	0.23	<DL	0.001	<DL
LCMT (Post)	Std. Deviation	<DL	<DL	0.01	0.28	<DL	<DL	<DL	0.005	<DL
	Minimum	<DL	<DL	<DL	0.44	<DL	<DL	<DL	<DL	<DL
	Maximum	<DL	<DL	0.02	1.00	<DL	<DL	<DL	0.001	<DL
	Median	<DL	<DL	0.02	0.68	<DL	<DL	<DL	<DL	<DL
	% Reduction	100	100	77	70	-	100	-	67	-
NFMP (Pre)	Std. Deviation	<DL	<DL	0.11	0.81	<DL	0.02	0.004	0.003	<DL
	Minimum	<DL	<DL	1.70	2.02	<DL	0.07	0.01	0.001	<DL
	Maximum	<DL	<DL	1.91	3.63	<DL	0.10	0.02	0.006	<DL
	Median	<DL	<DL	1.81	2.81	<DL	0.09	0.01	0.005	<DL
NFMD (Post)	Std. Deviation	<DL	<DL	0.21	<DL	<DL	0.01	<DL	<DL	<DL
	Minimum	<DL	<DL	0.98	<DL	<DL	0.04	<DL	<DL	<DL
	Maximum	<DL	<DL	1.36	<DL	<DL	0.05	<DL	<DL	<DL
	Median	<DL	<DL	1.00	<DL	<DL	0.05	<DL	<DL	<DL
	% Reduction	-	-	39	100	-	46	100	100	-
YCMR (Pre)	Std. Deviation	3.00	0.17	5.25	1.72	<DL	4.05	<DL	0.10	0.15
	Minimum	15.0	1.66	25.5	53.6	<DL	1.60	<DL	0.40	0.80
	Maximum	21.0	2.00	36.0	57.0	<DL	9.40	<DL	0.60	1.10
	Median	18.0	1.80	30.8	55.7	<DL	7.40	<DL	0.50	0.90
YCMT (Post)	Std. Deviation	<DL	<DL	0.32	0.32	<DL	<DL	<DL	<DL	<DL
	Minimum	<DL	<DL	5.40	0.90	<DL	<DL	<DL	<DL	<DL
	Maximum	<DL	<DL	6.00	1.50	<DL	<DL	<DL	<DL	<DL
	Median	<DL	<DL	5.50	1.00	<DL	<DL	<DL	<DL	<DL
	% Reduction	100	100	82	98	-`	100	-	100	100
MEP China Guidelines*		1.00	0.02	0.10	0.30	0.05	2.00	1.00	0.005	0.05

MEP (2002): Ministry of Environmental Protection, China

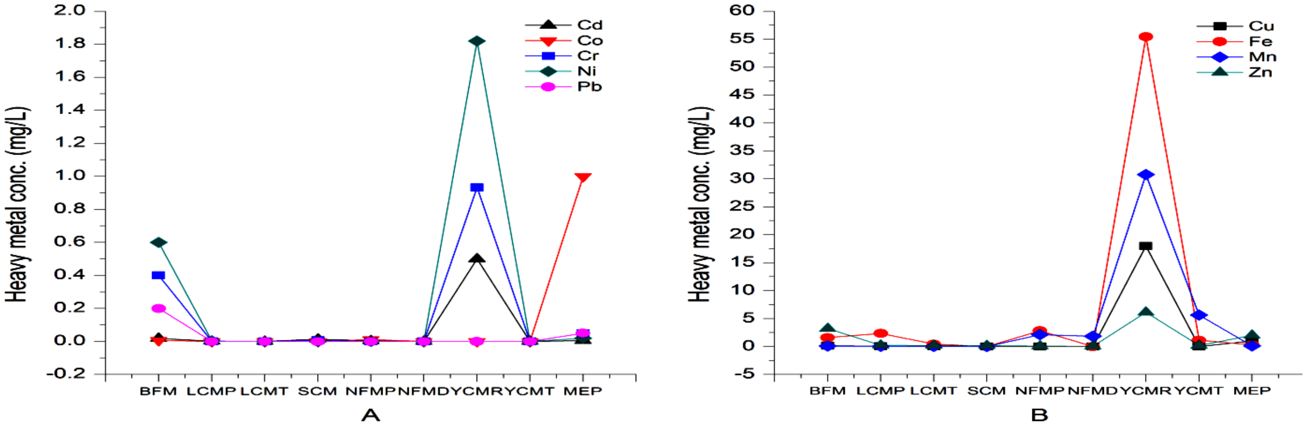


Fig. 2 Heavy metal concentrations in the eight sampling sites and MEP guidelines.

Table 4 Summary of the concentrations of physico-chemical parameters studied in water samples from selected mining and treatment sites in China

Mine		Temp	pH	DO	SO_4^{2-}	DOC	COD	BOD	Sulfides
BFM (Pre)	Mean	12.0	8.03	7.13	1997	8.27	53.3	2.80	0.24
	Std. Deviation	0.55	0.15	0.60	138	0.80	4.51	0.80	0.14
	Median	12.0	8.00	7.20	2050	8.20	53.0	2.80	0.25
	Minimum	11.4	7.90	6.50	1840	7.50	49.0	2.00	0.10
	Maximum	12.5	8.20	7.70	2100	9.10	58.0	3.60	0.38
SCM (Post)	Mean	12.0	7.80	7.60	1197	54.4	42.7	2.60	0.14
	Std. Deviation	0.87	0.10	0.61	193	0.55	2.52	0.05	0.02
	Median	11.6	7.80	7.90	1260	54.4	43.0	2.61	0.14
	Minimum	11.4	7.70	6.90	980	53.8	40.0	2.55	0.12
	Maximum	13.0	7.90	8.00	1350	54.9	45.0	2.64	0.16
LCMP (Pre)	Mean	20.1	7.63	7.97	3633	17.3	142.3	3.10	2.63
	Std. Deviation	0.12	0.06	0.06	152.8	0.32	10.3	0.95	0.57
	Median	20.0	7.60	8.00	3600	17.4	145	3.00	2.80
	Minimum	20.0	7.60	7.90	3500	16.9	131	2.20	2.00
	Maximum	20.2	7.70	8.00	3800	17.5	151	4.10	3.10
LCMT (Post)	Mean	19.7	7.53	7.83	3400	8.73	125.7	2.42	3.19
	Std. Deviation	0.31	0.25	0.29	200	2.97	7.64	0.39	0.40
	Median	19.8	7.50	8.00	3400	8.00	124	2.60	3.23
	Minimum	19.4	7.30	7.50	3200	6.20	119	1.98	2.77
	Maximum	20.0	7.80	8.00	3600	12.0	134	2.69	3.56
	% Reduction	2	1.3	1.8	6.4	50	11.7	22	-21
NFMP (Pre)	Mean	12.0	7.97	6.90	3797	7.47	39.7	6.62	0.33
	Std. Deviation	0.08	0.06	0.10	145	0.25	1.53	2.07	0.13
	Median	12.0	8.00	6.90	3800	7.46	40.0	6.53	0.32
	Minimum	12.0	7.90	6.80	3650	7.23	38.0	4.60	0.20
	Maximum	12.1	8.00	7.00	3940	7.72	41.0	8.74	0.46
NFMD (Post)	Mean	7.33	7.80	7.87	3287	9.30	39.0	3.60	1.48
	Std. Deviation	0.83	0.20	0.61	110.6	1.21	2.65	0.20	0.37
	Median	7.60	7.80	8.00	3300	9.50	40.0	3.60	1.49
	Minimum	6.40	7.60	7.20	3170	8.00	36.0	3.41	1.10
	Maximum	8.00	8.00	8.40	3390	10.4	41.0	3.80	1.84
	% Reduction	39	2.1	-14	13.4	-25	1.8	46	-349
YCMR (Pre)	Mean	23.7	2.37	2.87	4600	3.83	13.4	16.4	29.1
	Std. Deviation	0.58	0.15	0.81	721	0.15	0.35	0.72	1.01
	Median	24.0	2.40	2.50	4400	3.80	13.4	16.8	29.2
	Minimum	23.0	2.20	2.30	4000	3.70	13.0	15.6	28.0
	Maximum	24.0	2.50	3.80	5400	4.00	13.7	16.9	30.0
YCMT (Post)	Mean	19.3	5.7	4.73	3500	9.17	12.5	<DL	22.3
	Std. Deviation	1.53	2.38	0.93	458	4.32	0.50	<DL	2.52
	Median	19.0	5.50	5.00	3400	7.80	12.6	<DL	22.0
	Minimum	18.0	2.50	3.70	3100	5.70	12.0	<DL	20.0
	Maximum	21.0	7.20	5.50	4000	14.0	13.0	<DL	25.0
	% Reduction	19	-140	-65	24	-139	7	100	23
Guidelines*			6-9	2	250	-	30	6	0.5

**MEP (2002): Ministry of Environmental Protection, China*

Table 5 Evaluation of treatment processes for the removal of HMs by applying paired t-test to the pre- and post-treatment samples

Mine		Cu	Ni	Mn	Fe	Pb	Zn	Co	Cd	Cr
LCM	*p*-value	0.14	0.12	0.10	0.08	NA	0.01	NA	0.67	NA
	t-value	2.38	2.60	2.54	2.98	NA	11.16	NA	-0.48	NA
NFM	*p*-value	NA	NA	0.02	0.03	NA	0.05	0.04	0.12	NA
	t-value	NA	NA	5.05	6.06	NA	3.62	4.76	2.62	NA
YCM	*p*-value	0.01	<0.001	0.01	<0.001	NA	0.12	NA	0.01	0.01
	t-value	10.39	18.45	8.28	53.88	NA	2.62	NA	8.66	10.58

Table 6 Pearson correlation among heavy metals and other physicochemical parameters in pre-treatment samples

	Cu	**Ni**	**Mn**	**Fe**	**Pb**	**Zn**	**Co**	**Cd**	**Cr**	**Temp**	**pH**	**DO**	**SO4**	**DOC**	**COD**	**BOD**	**Sulfides**
Cu	1	.940**	.998**	.991**	-.322	.797**	-.513	.999**	.904**	.758**	-.981**	-.970**	.577*	-.617*	-.572	.940**	.987**
Ni		1	.927**	.931**	.006	.859**	-.420	.945**	.992**	.612*	-.914**	-.916**	.338	-.689*	-.639*	.842**	.919**
Mn			1	.990**	-.351	.784**	-.478	.997**	.889**	.739**	-.977**	-.976**	.599*	-.639*	-.598*	.954**	.983**
Fe				1	-.347	.729**	-.509	.986**	.885**	.764**	-.996**	-.962**	.637*	-.624*	-.579*	.953**	.996**
Pb					1	.154	.325	-.297	.108	-.557	.371	.273	-.871**	-.106	-.101	-.452	-.369
Zn						1	-.320	.820**	.896**	.447	-.687*	-.800**	-.002	-.572	-.536	.645*	.716**
Co							1	-.498	-.382	-.861**	.561	.359	-.379	-.247	-.310	-.315	-.572
Cd								1	.914**	.742**	-.973**	-.972**	.547	-.626*	-.582*	.934**	.980**
Cr									1	.547	-.862**	-.886**	.226	-.691*	-.643*	.787**	.870**
Temp										1	-.798**	-.610*	.665*	.022	.077	.646*	.810**
pH											1	.943**	-.665*	.578*	.529	-.937**	-.997**
DO												1	-.527	.753**	.719**	-.946**	-.944**
SO_4													1	-.200	-.181	.716**	.650*
DOC														1	.990**	-.690*	-.562
COD															1	-.660*	-.512
BOD																1	.937**
Sulfides																	1

In case of SCM, both chemical and physical treatment of the wastewater was provided underground. The final discharge had Cd in excess than the MEP limits for agricultural purposes, while Zn was more than the allowed limits for surface water. Here again sulfate level was of concern. In NFM, after chemical treatment the effluent was discharged into a big dam for sedimentation and pollutants removal. The post-treatment dam effluent analysis showed that all heavy metals and other pollutants were completely removed or were within the permissible limits except for Mn (1.11 mg/L) (though pre and post-treatment values were significantly different; t=5.05, p=0.02) and sulfates (3287 mg/L). The YCMT treated water still contained high levels of sulfates, Fe and Mn. Other heavy metals (Cu, Ni, Pb, Zn, Co, Cd, and Cr) and chemicals (DOC, COD, BOD and Sulfides) were completely removed. Wastewater from BFM was collected together with rain water in a big lake near the mine without any treatment facilities.

Thus, the dominant heavy metals recorded in the present study were Fe, Mn, Zn and Cd in the wastewater samples of all selected sites. Although the physico-chemical treatment methods applied to the mining wastewater were quick and removed most of the heavy metals but still were unable to bring down heavy metal concentrations to the limits suggested by MEP (2002). The contaminated water was discharged into the surface water bodies or infiltrate to underground and somehow entering into the food chain. Heavy metals are non-biodegradable and can accumulate in tissues of living organisms, causing various disorders and diseases; therefore, their removal or reduction to acceptable limits is necessary before their discharge into surface water bodies [31]. The chemical methods applied were also not able to bring down the high concentrations of sulfates to acceptable limit. These high concentrations of sulfate in wastewater confine the use of anaerobic treatment technologies because of toxic, corrosive and odorous hydrogen sulfide (H_2S) production [32, 33]. The H_2S production causes many problems, such as toxicity [34], and corrosion [35].

In all mining sites, chemicals were mixed to raise the pH of wastewater but the techniques used for removal of heavy metals and their efficiency were different from each other. In case of LCM, after chemical treatment the water had little time for sedimentation because of smaller sedimentation pond size as compared to NFM where water collected in a bigger dam allowing longer time for complete sedimentation.

In case of YCM, the wastewater treatment plant surface area was smaller but showed greater efficiency because of using poly-aluminium chloride (PAC) for coagulation and sedimentation purposes.

Although lime treatment along with coagulation is simple and robust, it does, however, it presents several environmental problems. The volume of sludge produced after lime treatment is usually greater, enriched with toxic metals rich and usually contains a significant amount of water. It often requires special waste disposal facilities which further increase the costs of disposal. The water content increases the volume and weight of the waste which means that money is being spent to dispose of water (both in transport and landfill fees) which might otherwise be avoided. The general methods to reduce the water content are often laborious or require more energy which also increases the costs and are often unable to keep up with the flow of material from the treatment system. In view of the likely environmental hazards, effective monitoring and comprehensive treatment methods are needed to be applied for the treatments of mining wastewater.

4. CONCLUSION

It is concluded from the findings of this study that active mines are the major sources of heavy metals and other inorganic pollutants in surface water which in turn can contaminate soil and groundwater if not treated properly. Several toxic metals were exceeded the maximum permissible limits set by MEP. The Pearson correlation showed good relationships between different metal pairs and other physico-chemical parameters present in wastewater. It can also be concluded from the paired t-test results applied to the pre and post-treatment HMs data that the treatment processes were not good enough to completely remove all heavy metals except in case of YCM site where the differences between pre and post-treatment values were significantly higher ($p \leq 0.01$). The concentrations of heavy metals and sulfates in all mining sites reported in the present study were higher than the MEP prescribed limits and the treatments provided were not capable of removing heavy metals and sulfates completely from wastewater.

REFERENCES

1. Wang, L., Wang, Y., Xu, C., An, Z. and Wang, S. Analysis and evaluation of the source of heavy metals in water of the River Changjiang. *Environ. Monit. Assess.*, **173**(1-4), 301-313 (2011).
2. Khan, S., Reid, B.J., Li, G. and Zhu, Y.-G. Application of biochar to soil reduces cancer risk via rice consumption: A case study in Miaoqian village, Longyan, China. *Environ. Int.*, **68**(154-161 (2014).
3. Shine, J.P., Ika, R.V. and Ford, T.E. Multivariate Statistical Examination of Spatial and Temporal Patterns of Heavy Metal Contamination in New Bedford Harbor Marine Sediments. *Environ. Sci. Technol.*, **29**(7), 1781-1788 (1995).
4. Goh, B.P.L. and Chou, L.M. Heavy metal levels in marine sediments of Singapore. *Environ. Monit. Assess.*, **44**(1-3), 67-80 (1997).
5. Nawab, J., Khan, S., Shah, M.T., Khan, K., Huang, Q. and Ali, R. Quantification of Heavy Metals in Mining Affected Soil and Their Bioaccumulation in Native Plant Species. *Int. J. Phytoremediat.*, **17**(9), 801-813 (2015).
6. Moosa, S., Nemati, M. and Harrison, S.T.L. A kinetic study on anaerobic reduction of sulphate, Part I: Effect of sulphate concentration. *Chem. Eng. Sci.*, **57**(14), 2773-2780 (2002).

7. Brown, M., Barley, B. and Wood, H. Minewater Treatment - Technology, Application and Policy *The Mine water Problem*, 1-31 (2002).

8. Changul, C., Sutthirat, C., Padmanahban, G. and Tongcumpou, C. Chemical characteristics and acid drainage assessment of mine tailings from Akara Gold mine in Thailand. *Environmental Earth Sciences,* **60**(8), 1583-1595 (2010).

9. Dave, S.R. and Tipre, D.R. Coal Mine Drainage Pollution and its Remediation. T. Satyanarayana, B. N. Johri and A. Prakash. *Microorganisms in Environmental Management*, 719-743 (2012).

10. Gaikwad , R.W. and Gupta, D.V. Review on removal of heavy metals from acid mine drainage. *Appl. Ecol. Environ. Res.,* **6**(3), 81-98 (2008).

11. Kotze, P., Preez, H.H.d. and Vuren, J.H.J.v. Bioaccumulation of copper and zinc in Oreochromis mossambicus and Clarias gariepinus, from the Olifants River, Mpumalanga, South Africa. *Water SA*, **25**(1), 99-110 (1999).

12. Oostdam, J.V., Gilman, A., Dewailly, E., Usher, P., Wheatley, B., Kuhnlein, H., Neve, S., Walker, J., Tracy, B., Feeley, M., Jerome, V. and Kwavnick, B. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci. Total Environ.,* **230**(1-3), 1-82 (1999).

13. Peavy, H.S., Rowe, D.R. and Tchobanoglous, G. Water quality: definitions, characteristics, and perspective *Environmental engineering*, (1985).

14. Zadorozhnaja, T.D., Little, R.E., Miller, R.K., Mendel, N.A., Taylor, R.J., Presley, B.J. and Gladen, B.C. Concentrations of arsenic, cadmium, copper, lead, mercury, and zinc in human placentas from two cities In Ukraine. *J. Toxicol. Environ. Health, Part A*, **61**(4), 255 - 263 (2000).

15. Aremu, D.A., Olawuyi, J.F., Meshitsuka, S., Sridhar, M.K. and Oluwande, P.A. Heavy metal analysis of groundwater from Warri, Nigeria. *Int. J. Environ. Health Res.,* **12**(3), 261–267 (2002).

16. Sato, M. Oxidation of sulfide ore bodies, II. Oxidation mechanisms of sulfide minerals at 25°C. *Econ. Geol.,* **55**(6), 1202-1231 (1960).

17. Bohan, C.M. Chemical and Physical Properties of Acid Mine Drainage Floc (2002).

18. Ferrell, G.M. Ground-water quality: West Virginia, (1986).

19. Benassi, J.C., Laus, R., Geremias, R., Lima, P.L., Menezes, C.T.B., Laranjeira, M.C.M., Wilhelm-Filho, D., Favere, V.T. and Pedrosa, R.C. Evaluation of remediation of coal mining wastewater by Chitosan microspheres using biomarkers. *Arch. Environ. Contam. Toxicol.,* **51**(4), 633–640 (2006).

20. Jan, F.A., Ishaq, M., Ihsanullah, I. and Asim, S.M. Multivariate statistical analysis of heavy metals pollution in industrial area and its comparison with relatively less polluted area: A case study from the City of Peshawar and district Dir Lower. *J. Hazard. Mater.,* **176**(1-3), 609-616 (2010).

21. APHA, AWWA and WEF. *Standard Methods for the Examination of Water and Wastewater*, 20th, p.1325 (1998).

22. Sabri, A.W., A. R. Khalid and Thaer., I.K. Heavy metals in the water, suspended solids and sediment of the river tigris impoundment at Samarra. *Water Res.,* **27**(6), 1099-1103 (1993).

23. Ehlers, G.A. and Rose, P.D. Preliminary Evaluation of a White-Rot Fungal Reactor in the Treatment of a Waste Oil–Recycling Wastewater. *Bioremediat. J.,* **9**(1), 21-32 (2005).

24. Liu, C.P. and Sheu, B.H. Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. *For. Ecol. Manag.,* **172**(2-3), 315-325 (2003).

25. Vega, M., Pardo, R., Barrado, E. and Deban, L. Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Res.,* **32**(12), 3581-3592 (1998).

26. Adams, S., Titus, R., Pietersen, K., Tredoux, G. and Harris, C. Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. *Journal of Hydrology*, **241**(1-2), 91-103 (2001).

27. Ghrefat, H. and Yusuf, N. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere,* **65**(11), 2114-2121 (2006).

28. Richards, B.K., Steenhuis, T.S., Peverly, J.H. and McBride, M.B. Effect of sludge-processing mode, soil texture and soil pH on metal mobility in undisturbed soil columns under accelerated loading. *Environ. Pollut.,* **109**(2), 327-346 (2000).

29. Park, E.J., Jo, H.J. and Jung, J. Combined effects of pH, hardness and dissolved organic carbon on acute metal toxicity to Daphnia magna. *Journal of Industrial and Engineering Chemistry,* **15**(1), 82-85 (2009).

30. Franklin, N.M., Stauber, J.L., Markich, S.J. and Lim, R.P. pH-dependent toxicity of copper and uranium to a tropical freshwater alga (Chlorella sp.). *Aquat. Toxicol.,* **48**(2–3), 275-289 (2000).

31. Wan Ngah, W.S. and Hanafiah, M.A.K.M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.,* **99**(10), 3935-3948 (2008).

32. Shayegan, J., Ghavipanjeh, F. and Mirjafari, P. The effect of influent COD and upward flow velocity on the behaviour of sulphate-reducing bacteria. *Process Biochem.,* **40**(7), 2305-2310 (2005).

33. Muyzer, G. and Stams, A.J.M. The ecology and biotechnology of sulphate-reducing bacteria. *Nat. Rev. Microbiol.,* **6**(6), 441-454 (2008).

34. O'Flaherty, V., Mahony, T., O'Kennedy, R. and Colleran, E. Effect of pH on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria. *Process Biochem.,* **33**(5), 555-569 (1998).

35. Vincke, E., Boon, N. and Verstraete, W. Analysis of the microbial communities on corroded concrete sewer pipes – a case study. *Appl. Microbiol. Biotechnol.,* **57**(5-6), 776-785 (2001).