CHEMICAL ENGINEERING TRANSACTIONS

VOL. 51, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Tichun Wang, Hongyang Zhang, Lei Tian

ISBN 978-88-95608-43-3; **ISSN** 2283-9216

DOI: 10.3303/CET1651052

Soil Heavy Metal Contamination and Microbial Ecological Risk Assessment- A Case Study

Chi Zhang[a], Jun Yao*[a,b], Cuiying Zhu[c], Mijia Zhu[a], Jingjing Sun[a]

[a]National "International Cooperation Based on Environment and Energy" and School of Civil & Environmental Engineering and, University of Science and Technology Beijing, Beijing 100083, PR China
[b]School of Water Resource and Environmental Engineering, Sino-Hungarian Joint Laboratory of Environmental Science and Health, China University of Geosciences (Beijing), Beijing 100083, PR China
[c]College of Horticulture Science and Engineering, and National Key laboratory of Crop Biology, Shandong agricultural university, Tai'an 271018, P.R. China
yaojun@ustb.edu.cn

Yinshan mine is a vital lead and zinc producer affiliated with Jiang'xi copper company, the biggest copper producer in China. In this study, nine soil samples were collected from three different functional areas of Yinshan Mine (main mining areas, farmland near acid mine drainage pipe, soils along the Jishui river). The concentrations of (consider spelling out words) Cd, Cr, Zn, Cu, Ni, Pb were determined by ICP-AES and their potential ecological risks were assessed by single factors. The results revealed that the main mining areas had serious heavy metal contamination from intensive mining activity with a single factor index reaching 8.25(Cd) and 5.06(Cu). The farmland near the acid mine drainage pipe was heavily polluted in the surface soils with a single factor index reaching 3.93(Cd) while the soils along the Jishui river was moderately polluted with single factor index values of 1.60(Zn) for the surface soils, 3.13(Pb) for middle depth and 2.55(Cd) for the deepest sample. Urease test were applied to assess heavy metal contamination in soils.

1. Introduction

Metal production and mine exploration has increased in the past few years due to a growing demand for metals, especially in developing countries such as China and India(Zhang et al., 2012, Dold, 2008). China holds varied mineral resources and large amounts of these minerals(Yang et al., 2014). There are about 171 different types of minerals in China, and China holds 12% of global mineral resources (Hu et al., 2010). In China, metal mining is at the base of development and strongly influences the economy due to its role in construction(Fu et al., 2014). The future of metal production in China is very promising and is projected to remain at current levels.

However, along with enormous economic benefits brought by mining activity, environmental problems are emerging. In China, mining activities, as well as metallic ores smelting operations and sewage irrigations are major producers of pollution (Liu et al., 2014). Heavy metal pollution is irreversible, persistent and covert(Wang, 2001). Mining activity can contaminate other resources, such as air, soil and water, which also pose threats to the environment (Zhuang and Gao, 2014). Unlike water and air pollution, soil contamination is very difficult and time consuming to clean up or remove. Meanwhile, heavy metal accumulations in soil not only harm the local plants and microorganisms, but also pose potential threats to human health as the pollutant is passed up food chains(Nabulo et al., 2010; Wang, 2001).

The Yinshan Zinc/Lead Mine is located in a very important mineral production area, and is affiliated with Jiang'xi Copper Company, the biggest cooper producer in China. Yinshan mine has more than 40 years of mining experience and mainly produces lead, zinc, copper and silver. Intensive mining and metallurgical activity produces large amounts of wastes, which contain multiple heavy metal ions. Waste is improperly discharged into the Tong river, which flows into the Le'an river. This activity has caused serious heavy metal pollution to the soil and water along Le'an river (Jiang, 2011). In 2011, there were various reports across China about heavy metals inducing cancer incidence in the downstream area of the Le'an River(Jiang, 2011).

Please cite this article as: Zhang C., Yao J., Zhu C.Y., Zhu M.J., Sun J.J., 2016, Soil heavy metal contamination and microbial ecological risk assessment - a case study, Chemical Engineering Transactions, 51, 307-312 DOI:10.3303/CET1651052

The Le'an River is an important tributary of Po'yang Lake, the biggest fresh water lake in China. This pollution will therefore affect millions of people. In recent years, the pollution in Yinshan mine attracted increasing attention (Yin et al., 2008), but no study has examined soil heavy metal pollutions in different functional areas of the Yinshan Lead/Zinc Mine.

Therefore, it is essential to evaluate the heavy metal pollution by mining activity and its potential threats on human bodies. In soils, microorganisms make up a large portion of soil biomass and are in close contact with the soil, which is very sensitive to any ecosystem pollution (Chen et al., 2014, Guo et al., 2012, Chen et al., 2013). Soil biomass is considered to be the best indicator of soil perturbations (Andreoni et al., 2004). Traditional methods for monitoring microorganism activity include carbon respiration monitoring, soil enzyme activity assays, and soil fumigation (Brohon et al., 2001, Eibes et al., 2006). Therefore, heavy metal pollution in soil caused by mining activity requires a combination of methods to allow for rapid, sensitive, and economic monitoring of microbial metabolic activity.

In this study, the combination of single factor and enzyme activity were applied to assess the degree of heavy metal contamination. Specifically, the objectives of this study were to (i) determine the concentration level and distribution patterns of different heavy metals in the soil in Yinshan Lead/Zinc Mine, (ii) assess the ecological risk of heavy metals in soil, (iii) study the effects of heavy metals on microorganism activity in soil.

2. Materials and methods

2.1. Soil collection

Nine soil samples were collected from three different functional sites in Yinshan Lead-zinc Mine: YS-1 (28°58′46.32″N, 117°36′28.57″), YS-2 (28°58′37.01″N, 117°35′55.24″), YS-3 (28°57′18.60″N, 117°33′38.58″). The three sites were: YS1 in the main mining area, YS2 in a farmland that was abandoned due to the construction of acid mine drainage pipe, and YS3 along the Jishui river about 2 kilometers away from Yinshan zinc/lead mine. A soil core was taken at each site and samples were collected from three different depths (0-20cm, 20-40cm, 40- 60cm). After collection, all soil samples were air-dried and sieved (mesh size 2 ×2mm^2) to remove large particles and root fragments. The samples were stored in polyethylene bags and kept at 4℃(Triegel, 1988).

2.2. Determination of soil physical and chemical properties

Soil pH was determined with a pH-meter (OHAUS Starter 2C). The pH-meter was dipped into a supernatant prepared from 25.0 ml distilled water and 10.0g soil. Soil total nitrogen was determined by the Kjeldahl digestion method. For organic matter analysis, the sample was titrated with a redox end point indicator. Phosphate was analyzed using the Mo-Sb colorimetric method. Total organic carbon was determined by CHNS/O (Perkin-Elmer, USA) after inorganic carbon was removed by digesting with HCl for 48 hours.

After soil samples were digested with concentrated nitric acid, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to determine heavy metals concentrations (Cd, Cr, Zn, Mn, Pb and Ni).

2.3. Determination of soil urease activity

Urease activity was measured by a modified version of x's method(Yang et al., 2007). Diploid soil samples (2.5 g) were mixed with 0.5 ml toluene for 15min in 25 mL volumetric flasks. Next, 20 mL of citrate buffer (pH 6.7) and 10 mL of 10% urea were added into each volumetric flask. Then, samples were placed in an incubator at 37 ℃ for 24h. Thereafter, 37 ℃ distilled water was added to the samples and oscillated thoroughly. The mixture was instantly filtered. Then, a 3ml filtrate was absorbed and transferred into a 50 ml volumetric flask. Next, 10 mL distilled water, 4 mL sodium phenoate (1.35 M) and 3 mL sodium hypochlorite (active chlorine 0.9%) was added to the flask. The flask was left for 20 min and then diluted to volume. A blue-colored complex formed, indicating the concentration of NH_4^+ ions produced from urea hydrolysis and was used as a measure of urease activity.

3. Results and Discussion

3.1. Physical and chemical properties of soil samples

From table 1, Samples from YS1 (samples 1-3) show the highest conductivity due to high heavy metal concentrations in the mining area. The samples have the lowest total N concentrations, which is consistent with previous research(Wang et al., 2008). Samples from YS2 (samples 4-6) have the lowest pH measurements (3-4.63). Contamination from acid mine drainage may be responsible for low pH readings at YS2. Sample 9 from YS3 shows the highest available P, which may be due to phosphate fertilizer input. There is no significant order for other parameters.

Table 1: Physical-chemical characteristics of soil samples

Soil Samples	TOC (g/kg)	OM (g/kg)	pH	Conductivity (μs)	A- P (mg/kg)	Total N (g/kg)
1	12.200	21.033	5.93	2405.0	32.13	0.099
2	18.037	31.096	5.93	2147.5	35.31	0.068
3	14.159	24.410	7.19	2365.0	23.42	0.132
4	8.272	14.261	3.00	1197.0	87.52	0.339
5	17.812	30.708	4.63	775.0	17.33	0.688
6	8.038	13.858	3.14	754.5	16.65	0.326
7	11.783	20.314	4.44	146.0	17.23	0.514
8	10.375	12.156	5.12	180.5	21.23	0.613
9	9.379	16.169	5.01	190.7	59.65	0.774

3.2. Assessment of heavy metal concentration

Heavy metal concentrations in the different soil samples are showed in Table 2. And the single factor index was calculated and showed in Table 3. The national environmental quality standard III (GB 15618 - 1995) for soil was applied to samples from the Yinshan Lead/Zinc Mine to assess heavy metal pollution. It is obvious that samples 1-3 from mining area (YS1) have much higher heavy metal concentrations (specifically, Cd, Cu, Pb, and Zn) than the other areas. Cd, Pb, Zn are the most prevalent heavy metals in mining area, which is in consistent with the ore species found in the Yinshan Mine. The mining area has dramatically high Cd concentrations (2.11-8.26 mg/kg), which are much higher than safe levels (1.00 mg/kg) according to China national environmental quality standard III (GB 15618 - 1995). Pb and Zn concentrations are also elevated almost three times above the standard’s safe levels. The upper layers (sample 1, 3) have much higher heavy metal levels than sample 2, which may be due to the limited transformation ability of heavy metals.

At site YS2 (the abandoned farmland near the acid mine drainage tunnel), heavy metal concentrations are much lower than the mining area. For human health and environmental safety, strategies have been proposed to limit the usage of and exposure to Cd-containing phosphate fertilizers, waste water, and solid waste in agricultural farmlands (Wang, 1999). The YS2 site was used as farmland before. However the farmland was abandoned after the acid mine drainage tunnels were constructed, due to potential Cd pollution. The surface soil at YS2 shows higher concentrations of Cd (3.93 mg/kg), Cr (448.44mg/kg), Pb (1,000.83 mg/kg) and Cu (171.77 mg/kg) compared to the subsurface soil. Sample 4, taken from the surface shows a higher Cr concentration (448.44mg/kg) than all of the other samples. Previous research indicates that phosphate fertilizer usage is one of the major sources of Cr in the soil(Xing et al., 2013). Phosphate fertilizer containing Cd is used in agriculture and can lead to soil contamination (Wang, 2001). According to previous research(Chen, 1996), application of phosphate fertilizations in China is responsible for up to 37 tons of total Cd contamination. Approximately 80% of surface soil Cd originates from phosphate fertilization when soil phosphate content is well correlated with Cd content (Williams et al., 1973; Mulla et al., 1980). At YS2, subsurface samples 5 (depth 20~40cm) and 6 (depth 40~60 cm) have lower concentrations of Cd and Cr than the upper layer (depth 0~20cm). It can be inferred that the high concentrations of Cr and Cd in the surface sample at YS2 (sample 4) mainly comes from phosphate fertilizer. As this area is located near the mining ore transportation road (but at a lower elevation) mining dust may be another pollution source for high Cd concentration in the upper soil layer.

The YS3 site (samples 7, 8, 9) is located along the Jishui River, which is about 2 kilometer away from the Yinshan Mine. It is apparent that the surface soil was less polluted than the subsurface samples. This trend may imply that heavy metals may migrate from the soil surface down into the subsurface.

Samples 4,5,6 were collected from the soil core taken near the acid mine drainage area. These samples are less contaminated than the soil samples from the mining area. However, soils were also polluted heavily with Pb (single factor index: 3.18-4.50) and Cd (single factor index: 2.88-5.13). Soil sample 4 is more contaminated than samples 5 and 6. This result may be due to leaching rain from the surrounding mountains, which could increase the heavy metal concentrations in the top soil. The other reason for these elevated levels may be due to plants in the soil. Roots of plants can provide nutrients to the surrounding soils, and plants can then absorb these heavy metals. The rhizosphere effect can decrease heavy metal concentrations and so subsurface soils may be less contaminated than top soils.

The core from YS3 was collected at random from the surrounding soil in downstream area of Jishui River. Samples from this core (samples 7, 8, 9) showed elevated Cd and Pb concentrations. Also, Cu concentrations were elevated and come from mines from upstream of the sampling site.

Table 2: Total heavy metal contents in soil samples (mg/kg; GB 15618-1995: Grade III environmental quality standard for soils in China; BVSC: Background values for soils in China)

	Cd	Cr	Cu	Pb	Zn
1	6.66±0.22	69.55±2.3	489.57±17.1	1865.96±26.5	1514.05±10.2
2	2.11±0.11	80.28±1.9	2023.90±25.3	94.77±3.9	803.78±28.6
3	8.26±0.36	73.96±3.1	455.22±13.6	1913.77±20.7	1802.37±19.7
YS1 mean	5.68	74.60	989.56	1291.5	1373.40
4	3.93±0.15	448.44±12.1	171.77±8.7	1000.83±10.4	259.80±18.7
5	0.83±0.03	132.49±7.5	91.87±4.7	400.16±5.3	522.22±28.5
6	1.78±0.08	96.83±4.3	104.15±4.5	731.55±16.7	959.67±30.6
YS2 mean	2.18	225.92	122.60	710.85	580.56
7	1.15±0.11	83.71±3.6	243.89±10.6	585.30±18.2	800.84±23.4
8	2.44±0.21	99.57±2.8	58.10±3.7	1566.97±12.8	1013.32±38.6
9	2.55±0.10	63.08±3.1	223.94±8.5	179.04±7.9	228.07±13.2
YS3 mean	2.05	82.12	175.31	777.10	680.74
BVSC	0.097	61.00	22.60	26.00	74.20
GB 15618-1995	1.00	300	400	500	500

Table 3: Single factor index of heavy metals

	Cd	Cr	Cu	Pb	Zn	Ni
1	6.66	0.23	1.22	3.73	3.03	0.13
2	2.11	0.27	5.06	0.19	1.61	0.15
3	8.25	0.25	1.14	3.83	3.60	0.13
4	3.93	1.49	0.43	2.00	0.52	0.07
5	0.83	0.44	0.23	0.80	1.04	0.11
6	1.78	0.32	0.26	1.46	1.92	0.12
7	1.15	0.28	0.61	1.17	1.60	0.13
8	2.45	0.33	0.15	3.13	2.03	0.15
9	2.55	0.21	0.56	0.36	0.46	0.15

3.3. Comparison with mean values of heavy metal concentration in other areas

In order to compare the data from Yinhsan Mine to with other areas in Asia, mean heavy metal concentrations from studies in China, South Korea, and Vietnam are collected in Table 4. Cu, Pb and Zn concentrations in the Yinshan Mine (site YS1) are much higher than heavy metal concentrations in 72 other mines in China while Cd, Cr and Ni concentrations are lower. However, sites YS2 and YS3 have lower heavy metal concentrations (except Pb) than other mines in China. This comparison indicates that Cu, Pb, and Zn pollution in the Yinshan Zinc/Lead Mine is relatively serious. Compared with other countries, heavy metal concentrations at sites YS1, YS2 and YS3 are higher than those in South Korea, but much lower than those in Vietnam (except for Cu). The mines in Vietnam are the most seriously contaminated mines, with the highest heavy metal concentrations. This specific result is mainly due to the fact that the rainy season induced dike-breaking around metalliferous mines, which resulted in heavy metal pollution flowing from the upstream into the downstream, farmland areas. For the other land use types in China, the mean concentrations in the Yinshan Mine are higher, except for Ni. This trend indicates that metalliferous mining is a significant anthropogenic, source of heavy metals.

Table 4: Comparison of heavy metal concentrations in this study with those of mean values in other areas

	Cd	Cr	C	Pb	Zn	Ni
China	11.0	84.28	211.9	641.3	1163	106.6
South Korea	1.99		79.09	111.1	183.2	22.00
Vietnam	135	1501	271.4	30,635	41,094	2254
China (21 urban soils)	0.88	76.80	99.20	61.30	133.0	99.60
China(9 urban road dusts)	2.03	109.2	149.6	238.7	655.9	56.75
China(12 agricultural soils)	0.43	58.87	31.71	37.55	117.7	27.53

3.4. Effects of heavy metal pollution on urease activity

Urease activity in soil originated from soil microbes containing urease. Almost 17 to 77% of soil bacteria and 78 to 98% of soil fungi have the ability to hydrolyze urea. Urease activity may be considered as the ability of the microbes to release ammonium to the soil. Fig. 1 shows the variation in urease activity in contaminated soil. Soil enzyme activity can be inhibited when contamination has a toxic effect on soil microflora, and thus can be a reliable indicator of the current microbial state of the soil. Many soil bacteria possess the enzyme urease, which catalyzes the conversion of the urea molecule and amine to produce ammonia.

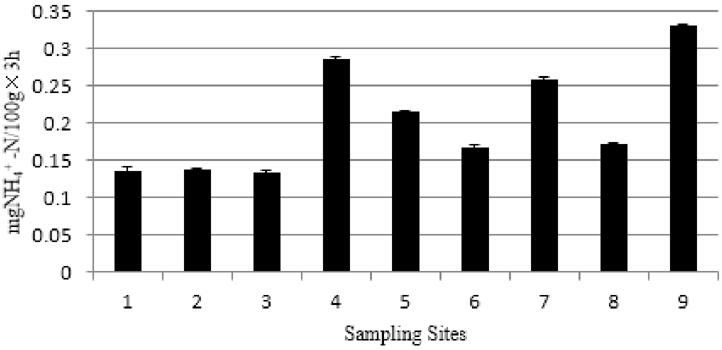

Figure 1. Urease activities in the polluted soils

4. Conclusion

Based on the results of the pollution and health risk assessments, it is apparent that the soils surrounding the Yinshan Mine are seriously polluted by heavy metals. Moreover, microbial activities in the surrounding soils are influenced by heavy metal pollution. This paper provides quantitative evidence demonstrating the critical need for strengthened mining regulations in order to protect residents from heavy metal discharges.

Acknowledgements

This work is supported in part by grants from the Key project from National Science Foundation of China(41430106), National Natural Science Foundation of China (41273092, 41430106, U1402234), Public welfare project of Chinese Ministry of Environmental Protection (201509049) .

References

Andreoni V., Cavalca L., Rao M. A., Nocerino G., Bernasconi S., Dell'amico E.,Colombo M., Gianfreda, L., 2004, Bacterial communities and enzyme activities of PAHs polluted soils. Chemosphere, 57, 401-12.

Bremner J. M., 1965, Total nitrogen, Madison, American Society of Agronomy.

Brohon B., Delolme C., Gourdon R., 2001, Complementarity of bioassays and microbial activity measurements for the evaluation of hydrocarbon-contaminated soils quality. Soil Biology and Biochemistry, 33, 883-891.

Chen H., 1996, Heavy Metal Contamination in Soil—Plant Systems, Beijing, Scientific Press of China.

Chen H., Zhuang R., Yao J., Wang F., Qian Y., 2013, A Comparative Study on the Impact of Phthalate Esters on Soil Microbial Activity. Bulletin of Environmental Contamination and Toxicology, 91, 217-223.

Chen, H., Zhuang R., Yao J., Wang F., Qian Y., Masakorala K., Cai M., Liu H., 2014, Short-term effect of aniline on soil microbial activity: a combined study by isothermal microcalorimetry, glucose analysis, and enzyme assay techniques. Environmental Science and Pollution Research, 21, 674-683.

Dold B., 2008, Sustainability in metal mining: from exploration, over processing to mine waste management. Reviews in Environmental Science and Bio/Technology, 7, 275-285.

Eibes G., Cajthaml T., Moreira M. T., Feijoo G., Lema J. M., 2006, Enzymatic degradation of anthracene, dibenzothiophene and pyrene by manganese peroxidase in media containing acetone. Chemosphere, 64, 408-414.

Fu J., Zhao C., Luo Y., Liu C., Kyzas G. Z., Luo Y., Zhao D., An S., Zhu H., 2014, Heavy metals in surface sediments of the Jialu River, China: their relations to environmental factors. J Hazard Mater, 270,102-9.

Guo H., Yao J., Cai M., Qian Y., Guo Y., Richnow H. H., Blake R. E., Doni S., Ceccanti, B., 2012, Effects of petroleum contamination on soil microbial numbers, metabolic activity and urease activity. Chemosphere, 87, 1273-80.

Hu R., Liu J., Zhai M., 2010, Mineral Resources Science in China: A Roadmap to 2050.

Klutte A., 1986. Methods of Soil Analysis, Madison, American Society of Agronomy.

Liu G., Yu Y., Hou J., Xue W., Liu X., Liu Y., Wang W., Alsaedi A., Hayat T., Liu Z., 2014, An ecological risk assessment of heavy metal pollution of the agricultural ecosystem near a lead-acid battery factory. Ecological Indicators, 47, 210-218.

Nabulo G., Young S. D., Black C. R., 2010, Assessing risk to human health from tropical leafy vegetables grown on contaminated urban soils. Sci Total Environ, 408, 5338-51.

Triegel E. K., 1988, Sampling variability in soils and solid wasters, Washington, American Chemical Society.

Wang Q., Ding M. Y., Zhang Z. J., Jiang X., Jin X. Q., Xu Z. X., 2008, Seasonal varieties and influential factors of heavy metals in sediments of Taihu Lake. Ecology and Environment, 17, 1362-1368.

Wang Q. A. L., J, 1999, Fertilizer proper use and sustainable development of soil environment in China. Advances of Env. Sci., 7(2), 116–124.

Wang Q. Y., Dong Y., Cui X., Liu, 2001, Instances of Soil and Crop Heavy Metal Contamination in China. Soil and Sediment Contamination, 10, 497-510.

Xing Y., Si Y. X., Hong C., Li, Y., 2013, Impact of Long-Term Heavy Metal Pollution on Microbial Community in Iron Mine Soil. Research of Environmental Sciences, 26, 1201-1211.

Yang C.L., Sun T.H., He W.X., Zhou Q.X., Chen S., 2007, Single and joint effects of pesticides and mercury on soil urease. Journal of Environmental Sciences, 19, 210-216.

Yang J., Chen L., Liu L. Z., Shi W. L., Meng X. Z., 2014, Comprehensive risk assessment of heavy metals in lake sediment from public parks in Shanghai. Ecotoxicol Environ Saf, 102, 129-35.

Yin H., Cao L., Xie M., Chen Q., Qiu G., Zhou J., Wu L., Wang D., Liu X., 2008, Bacterial diversity based on 16S rRNA and gyrB genes at Yinshan mine, China. Systematic and Applied Microbiology, 31, 302-311.

Zhang X., Yang L., Li Y., Li H., Wang W. & Ye B., 2012, Impacts of lead/zinc mining and smelting on the environment and human health in China. Environ Monit Assess, 184, 2261-73.

Zhuang W., Gao X., 2014, Assessment of heavy metal impact on sediment quality of the Xiaoqinghe estuary in the coastal Laizhou Bay, Bohai Sea: inconsistency between two commonly used criteria. Mar Pollut Bull, 83, 352-7.