SNRU Journal of Science and Technology

Journal home page: snrujst.snru.ac.th

Non-volatile toxic heavy metals analysis in surface water collected from Moon and Shi rivers in Northeastern of Thailand by atomic absorption spectrophotometry

Amornrat Wongklom*

Program of Chemistry, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani, 34000, Thailand

* **Corresponding Author**: Amornrat_dekarnkon@hotmail.com

Received: 12 January 2016; **Revised:** 2 February 2016; **Accepted:** 12 February 2016; **Available online:** 1 August 2016

Abstract

The concentrations of heavy metals such as Cd, Cr, Cu, Mn, Ni, Pb and Zn were investigated in surface water from Moon and Shi rivers, Northeastern of Thailand. Heavy metal concentrations were analyzed by using atomic absorption spectrophotometer and compared with permissible limits set by World Health Organization. The concentrations of Cd (0.022-0.030 mg L^{-1}) were higher than their respective permissible limits (0.003 mg L^{-1}) in all samples, while Ni, Pb, Cu, Cr, Mn and Zn concentrations were observed within their respective limits. Mean concentrations of heavy metals in surface water samples were found in the order of Zn (0.178-0.286 mg/L) > Mn (0.035-0.199 mg L^{-1}) > Ni (0.033-0.072 mg L^{-1}) > Cd (0.024-0.030 mg L^{-1}) > Cu (0.013-0.027 mg L^{-1}) > Cr (BDL-0.020 mg L^{-1}) > Pb (BDL), in the six locations of Moon river and Mn (0.117-0.409 mg L^{-1}) > Zn (0.185-0.196 mg L^{-1}) > Ni (0.028-0.112 mg L^{-1}) > Cr (0.010-0.047 mg L^{-1}) > Cd (0.022-0.027 mg L^{-1}) > Cu (0.013-0.023 mg L^{-1}) > Pb (BDL), in the four locations of Shi river. The geologic and anthropogenic activities were the possible sources of water contamination with heavy metals in the study area.

Keywords: Surface water; Heavy metals; Atomic absorption spectrophotometry

1. Introduction

Surface water is considered as a substance in the environment, and its contamination with heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) is a worldwide environmental problem [1, 2]. Generally, heavy metals are released from different natural (such as weathering, erosion of bed rocks, deposits and volcanic activities) and anthropogenic (such as mining, smelting, industrial influx and agricultural activities) sources [3, 4]. They can contaminate the surface (river) and ground (spring, dug well and tube well) water that is used for domestic, agricultural and industrial purposes [5-7]. In the addition, they are contaminated in sediment and microalgae [8]. Surface and ground water contamination is a worldwide health concern, which is becoming increasingly important with the unprecedented population growth, urbanization and industrialization.

pH is one of the most important indicators of water quality and level of pollution in the aquatic ecosystem and it has no direct effects on human health. pH affects the water quality parameters such as ionic solubility and pathogens survival, which will impact the human health eventually. In addition, high range pH confers bitter taste to water [2, 9]. Heavy metal enrichment also adversely affects the drinking and irrigation quality of water. Surface water containing certain amount of heavy metals may cause health problems in human and animals. Some heavy metals like Cu, Mn and Zn are required for normal body growth and function. High concentrations of Cd, Cr, Ni and Pb are considered highly toxic in human and aquatic organisms. Their accumulation in the body can cause serious diseases. The effects of heavy metals include toxic, neurotoxic, carcinogenic, mutagenic and teratogenic effects depending upon the heavy metal species [10, 11]. Human exposures to heavy metals are of great concern due to their non-biodegradable nature. It is recognized that malnourishment and diseases such as abdominal pain, anorexia, cardiovascular diseases, immune dysfunction, hypertension, liver and kidney related disorders, as well as various kinds of cancers could be caused not only by nutrient deficiency, but also by excessive intake of heavy metals in contaminated food and drinking water [1, 7]. In the additions, A. Wongklom have determined the organochlorine pesticides [12, 13] and heavy metals contaminations (Ni, Zn, Cr, Cd, Pb, Mn, Cu) in surface water and sediment from Shi and Moon rivers revealed that the pesticides contents were observed within the respective permissible limits but the metals contaminated were higher than their respective permissible limits set by WHO [9, 14]. Therefore, it is important to assess the concentrations of heavy metals in surface water, and their possible sources of contamination. The present study is designed to investigate the concentrations of heavy metals in surface water from Moon and Shi rivers, possible sources of contamination, and their respective potential health risks, Northeastern of Thailand.

2. Materials and Methods

Study area and sampling

Moon and Shi rivers are among the polluted rivers in Thailand because they receive large amounts of industrial wastewater and sewages, which located in a traditional agricultural production area in Northeastern Thailand. The river has long historically contaminated with heavy metals, other volatile and semivolatile organic compound. Ten sampling sites were selected to understand the distribution of difference heavy metal concentrations in surface water from Moon and Shi rivers. The sampling sites are including MW1: Amphoe Thatum, Surin province; MW2: Amphoe Rasrisalai, Srisaket province; MW3: Amphoe Yangchumnoi, Srisaket province; MW4: Amphoe Warinchamrab, Ubonratchathani province; MW5: Amphoe Thalsum, Ubonratchathani province; MW6: Amphoe Khongchaim, Ubonratchathani province; SW1: Muang Kalasin, Kalasin province; SW2 Amphoe Selaphum, Roi Et province; SW3 Amphoe Mahachanachai, Yasothorn province; SW4 Amphoe Khuangnai, Ubonratchathani province (Fig. 1). A total of 10 surface water samples from rivers were collected between March and September, 2014. All of sampling sites were near community, agriculture, fishery and domestic wastewater areas. The one meter of the surface water was sampled with far from river shore about 5-8 m by using a teflon water sampler. The water samples were collected with clean polyethylene plastic bottles from the selected sampling locations. Before water sampling, the bottles were washed with double deionized water containing 20% HNO_3. Each water sample was filtered and a few drops of 5% HNO_3 were added to prevent further microbial growth. All water samples were placed on ice and transported to Ubon Ratchathani Rajabhat University and stored at 4 ^{o}C for further laboratory analysis.

Fig. 1 The sampling sites of Moon and Shi rivers

Chemicals and Instrument

Analytical grade chemicals with 99.9% purity (Merck, Germany) were used for sample preparation and analysis. Double distilled water was used throughout the analysis. Standard solutions of all seven elements were prepared by diluting 1000 mg L^{-1} certified standard solutions of corresponding metal ions. The concentrations of selected heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) in water samples were analysed using flame atomic absorption spectrophotometer (FAAS AAS-700 Perkin Elmer, USA) under standard operating conditions. Atomic absorption spectrophotometry was carried out on a Perkin Elmer model with hollow cathode lamp (HCL). Hollow cathode lamp was used for non-volatile toxic heavy metals analysis under optimum operating conditions with an air-acetylene flame. The concentration of each parameter was read directly at their specific wavelength, Ni (232.0 nm), Cu (324.8 nm), Zn (213.9 nm), Pb (283.3 nm), Cd (228.8 nm), Mn (279.5 nm) and Cr (357.9 nm). The instrument was controlled by a personal computer using Winlab software.

Sample digestion procedures and analysis

The collected samples were filtered with filter paper (Whatman no.1). To ensure the removal of organic impurities from the samples and thus prevent interference in analysis, the samples were digested with concentrated nitric acid and hydrochloric acid (EPA method 3005A). The 2 mL of nitric acid and 5 mL of hydrochloric acid were added to 100 mL of surface water in a 250 mL beaker. The mixture was evaporated to half its volume on a hot plate at 90-95 ^{o}C after which it was allowed to cool, then filtered with a paper filter (Whatman no.1) and adjust volume at 100 mL with deionized distillation water. Concentrations of heavy metals in water samples were determined with a flame-atomic absorption spectrophotometer (FAAS) with a specific lamp for particular metal. In order to validate the method for accuracy and precision, spiked waters were analyzed for each elements. Excellent recoveries for all metals were obtained compared to the spiked samples. The recoveries were between 85 and 98% for all elements with relative standard deviation as lower than 10%. The detection limit is defined as the concentration corresponding to 3 times the standard deviation of 10 blanks. The detection limits for the methods were found to be (µg L^{-1}), Cr: 8.7, Cd: 0.85, Cu: 3.6, Mn: 2.3, Pb: 9.8, Ni: 7.5 and Zn: 2.5. The digested water samples were analysis done by using FAAS at Science Center, Faculty of Science, Ubon Ratchathani Rajabhat University. Appropriate drift blank was taken before the analysis of samples. The digested samples were analyzed in triplicates with the average concentration of metals being displayed in mg L^{-1} by the instruments after extrapolation from the standard curve.

3. Results and Discussion

Selected parameters in surface water samples collected from Moon river in the six sampling locations (MW1, MW2, MW3, MW4, MW5, MW6) and Shi river in four sampling locations (SW1, SW2, SW3, SW4) are summarized in Table 1 and Table 2. The pH of the water is significant water quality parameters in the aquatic system and a high range pH confers a bitter taste to the surface water. However, according to the World Health Organization [9], the pH value in aquatic system has no direct significance in assessing health risks. In this study, the mean pH values of surface waters in the six locations of Moon river were in the decreasing order of MW1 (6.44) > MW2, MW4 (6.43) > MW3 (6.42) > MW5 (6.25) > MW6 (6.16) and the four locations of Shi river were in the decreasing order of SW2 (6.60) > SW1 (6.50) > SW3 (6.41) > SW4 (6.37).

Table 1 pH and concentrations of selected heavy metals in surface water samples from Moon river

parameter	statistics	mean concentration (mg L^{-1}), n=4						WHO
		MW1	MW2	MW3	MW4	MW5	MW6	
pH	Range	6.08-6.81	6.22-6.69	6.21-6.63	6.27-6.65	6.13-6.43	5.86-6.42	6.50 -8.50
	Mean	6.44	6.43	6.42	6.43	6.25	6.16	
	SD	±0.32	±0.24	±0.19	±0.16	±0.13	±0.24	
Cd	Range	BDL-0.043	BDL-0.043	BDL-0.040	BDL-0.040	BDL-0.040	BDL-0.043	
	Mean	0.030	0.029	0.028	0.027	0.024	0.028	0.003
	SD	±0.016	±0.012	±0.011	±0.016	±0.014	±0.014	
Cr	Range	0.015-0.025						
	Mean	0.020	BDL	BDL	BDL	BDL	BDL	0.050
	SD	±0.0041						
Cu	Range	BDL-0.020	BDL-0.027	BDL-0.017	BDL-0.013	BDL-0.017	BDL-0.020	
	Mean	0.020	0.027	0.017	0.013	0.017	0.020	2.00
	SD	±0.002	±0.002	±0.002	±0.002	±0.002	±0.002	
Mn	Range	0.057-0.16	0.023-0.207	0.04-0.097	0.060-0.517	BDL -0.083	BDL -0.067	
	Mean	0.113	0.090	0.062	0.199	0.068	0.035	0.400
	SD	±0.043	±0.082	±0.030	±0.22	±0.022	±0.029	
Ni	Range	BDL-0.063	BDL-0.080	BDL-0.060	BDL-0.043	BDL-0.050	BDL-0.043	
	Mean	0.045	0.072	0.040	0.037	0.033	0.042	0.070
	SD	±0.022	±0.012	±0.019	±0.006	±0.015	±0.002	
Pb	Range							
	Mean	BDL	BDL	BDL	BDL	BDL	BDL	0.010
	SD							
Zn	Range	0.143-0.347	0.153-0.387	0.103-0.290	0.193-0.237	0.117-0.327	0.173-0.297	
	Mean	0.256	0.286	0.178	0.208	0.217	0.248	3.000
	SD	±0.096	±0.117	±0.080	±0.020	±0.087	±0.056	

BDL = below detection limit

The lowest pH value (5.82) was recorded in the surface water of SW4, while the highest pH value (7.01) in the surface water of SW2. The results indicate that the pH values of both locations of surface water samples varied from slightly acidic to neutral. The samples of some locations were within the permissible limit as shown in Table 1 and Table 2.

Table 2 pH and concentrations of selected heavy metals in surface water samples from Shi river

parameter	statistics	mean concentration (mg L^{-1}) , n=4				WHO
		SW1	SW2	SW3	SW4	
pH	Range	6.16-6.95	5.99-7.01	5.92-6.79	5.82-6.75	
	Mean	6.50	6.60	6.41	6.37	6.50-8.50
	SD	±0.33	±0.46	±0.36	±0.39	
Cd	Range	BDL-0.047	BDL-0.040	BDL-0.040	BDL-0.037	
	Mean	0.027	0.026	0.027	0.022	0.003
	SD	±0.018	±0.012	±0.012	±0.014	
Cr	Range	BDL-0.010		BDL-0.060		
	Mean	0.010	BDL	0.047	BDL	0.050
	SD	±0.001		±0.014		
Cu	Range	BDL-0.023	BDL-0.020	BDL-0.020	BDL-0.013	
	Mean	0.023	0.020	0.020	0.013	2.000
	SD	±0.001	±0.001	±0.001	±0.001	
Mn	Range	0.033-0.233	0.080-0.160	BDL-0.890	0.073-1.283	
	Mean	0.122	0.117	0.358	0.409	0.400
	SD	±0.092	±0.033	±0.460	±0.580	
Ni	Range	BDL-0.063	BDL-0.033	BDL-0.150	BDL-0.040	
	Mean	0.062	0.028	0.112	0.035	0.070
	SD	±0.002	±0.007	±0.054	±0.006	
Pb	Range					
	Mean	BDL	BDL	BDL	BDL	0.010
	SD					
Zn	Range	0.087-0.263	0.137-0.280	0.130-0.267	0.127-0.267	
	Mean	0.188	0.185	0.194	0.196	3.000
	SD	±0.074	±0.065	±0.058	±0.057	

BDL = below detection limit

Heavy metal concentrations in surface water samples were found in the order of Zn (0.178-0.286 mg L^{-1}) > Mn (0.035-0.199 mg L^{-1}) > Ni (0.033-0.072 mg L^{-1}) > Cd (0.024-0.030 mg L^{-1}) > Cu (0.013-0.027 mg L^{-1}) > Cr (BDL-0.020 mg L^{-1}) > Pb (BDL), in the six locations of Moon river and Mn (0.117-0.409 mg L^{-1}) > Zn (0.185-0.196 mg L^{-1}) > Ni (0.028-0.112 mg L^{-1}) > Cr (0.010-0.047 mg L^{-1}) > Cd (0.022-0.027 mg L^{-1}) > Cu (0.013-0.023 mg L^{-1}) > Pb (BDL), in the four locations of Shi river. The results found that Cr, Cu, Mn, Pb, Zn, and Ni concentrations in all surface water samples were found within their respective permissible limits set by WHO [9] except Cd concentrations (Table 1 and Table 2). Cadmium is relatively poorly absorbed into the body but once absorbed, it is excreted slowly. Bioaccumulation of cadmium is a serious issue as it has long biological half life in humans. High levels of cadmium in the biological system lead to impairment of brain and intellect development in children. Long term exposure also affects kidney, reproductive and nervous systems [11].

From the results obtained, the minimum concentration of Cd detected in the surface water was 0.022±0.014 mg L^{-1} (SW4) with maximum concentration being 0.030±0.016 mg L^{-1} (MW1). The Cd concentrations were higher than their respective permissible limits in all samples which the Cd concentration exceeded the permissible limit in 75% of the water samples. These results are of concern as Cadmium has been recognized for along period as a cumulative general metabolic poison. This high concentration of Cd in surface water could be attributed to the direct contact between water and mafic and ultramafic rocks, as well as agricultural and industrial contaminations [3, 4].

In the body, chromium(VI) is reduced by several mechanisms to chromium(III) already in the blood before it enters the cells. The chromium(III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism, one by which sulfate and phosphate ions also enter the cell. The acute toxicity of chromium(VI) is due to its strong oxidative properties. After it reaches the bloodstream, it damages blood cells by oxidation reactions. Hemolysis, and subsequently kidney and liver failure, are the results of this damage. From the results obtained, the minimum concentration of Cr detected in the surface water was below detection limit with maximum concentration being 0.047±0.014 mg L^{-1} (MW1). The Cr concentrations were within their respective permissible limits in all samples. This Cr concentration in surface water could be attributed to the presence of mafic and ultramafic rocks in the area, agricultural activities and weak corrosive plumbing systems [6].

The toxicity of Cu is associated with continuous low level exposure this can eventually lead to series health effects. As several epidemiological studies have provide evidence with respect to a possible link between Cu in surface water [7]. From the results obtained, the minimum concentration of Cu detected in the surface water was 0.013±0.002 mg L^{-1} (MW4, SW4) with maximum concentration being 0.027±0.002 mg L^{-1} (MW2). The Cu concentrations were within their respective permissible limits in all surface waters.

Manganese is an essential nutrient that is important for normal processes in the body, though adverse health effects have been noted at higher doses. Excessive Mn exposure, predominantly reported in adults exposed occupationally via inhalation, has been associated with adverse central nervous system effects includes muscle stiffness, lack of coordination, tremors, difficulties with breathing or swallowing, and other neuromuscular problems. From the results obtained, the minimum concentration of Mn detected in the surface water was 0.035±0.029 mg L^{-1} (MW6) with maximum concentration being 0.409±0.580 mg L^{-1} (SW4). The Mn concentrations were higher than their respective permissible limits which the Mn concentration exceeded the permissible limit in 7.5% of the water samples.

Ni is one of many carcinogenic metals known to be an environmental and occupational pollutant. The chronic exposure has been connected with increased risk of lung cancer, cardiovascular disease, neurological deficits, developmental deficits in childhood, and high blood pressure. Nickel exposure introduces free radicals which lead to oxidative damage and may also affect the kidneys and liver. From the results obtained, the minimum concentration of Ni detected in the surface water was 0.028±0.007 mg L^{-1} (SW2) with maximum concentration being 0.112±0.054 mg L^{-1} (SW3). The Ni concentrations were higher than their respective permissible limits which the Ni concentration exceeded the permissible limit in 7.5% of the water samples. This high Ni concentration could be attributed to the erosion of mafic and ultramafic rocks, downstream mining and industrial activities in the area [3-5].

Pb is the most recognized toxic environmental pollutant. It reacts or complexes with many biomolecules and adversely affects the human biology. Lead present in food and water account for approximately 70% of the total lead intake in humans. It can cross the placental barrier with potential toxic effects on the fetus. Infants and young children are more vulnerable than adults to the toxic effects of lead [11]. From the results obtained, the mean Pb concentrations in all surface water samples were below detection limits (BDL). The elevated Pb levels in the collected water samples could result from the weathering/leaching of mafic and ultramafic rocks, use of agricultural insecticides and weak corrosive plumbing systems [3, 4]. These results are of concern as Pb has been recognized for along period as a cumulative general metabolic poison. It is a neurotoxin and is responsible for the most common type of human metals toxicities. Also, studies have linked Lead exposures even at low levels and increase in blood pressure, as well as with reduced intelligence quotient in children and caused for attention disorders [7].

Zn is an essential trace element found almost in all food and potable water in the form of salts or organic complexes [9]. People rarely consume too much zinc. Usually, Zn excess results from consuming acidic foods or beverages packaged in a zinc-coated (galvanized) container. In certain industries, inhaling zinc oxide fumes can result in Zn excess. Consuming too much Zn for a long time can reduce the absorption of Cu, cause anemia, and impair the immune system. From the results obtained, its concentrations in surface water samples are shown in Table 1. The minimum concentration of Zn detected in the surface water was 0.178±0.080 mg L^{-1} (MW3) with maximum concentration being 0.286±0.117 mg L^{-1} (MW2). The Zn concentrations were within their respective permissible limits in all the water samples.

It could be concluded from the results discussed above that in surface water heavy metals such as Cd, Ni, and Mn showed increasing contamination from Moon and Shi rivers. This tread could be attributed to the presence of mafic and ultramafic rocks, on-going mining and agricultural and industrial contamination in the studied areas.

4. Conclusion

Heavy metal concentrations in surface water samples were found in the order of Zn > Mn > Ni > Cd > Cu > Cr > Pb, in the six locations of Moon river and Mn > Zn > Ni > Cd > Cu > Cr > Pb, in the four locations of Shi river. The Cr, Cu, Mn, Pb, Zn, and Ni concentrations in all surface water samples were found within their respective permissible limits set by WHO except the concentrations of Cd (0.022-0.030 mg L^{-1}) were higher than their respective permissible limits (0.003 mg L^{-1}) in all samples. The Cd concentration exceeded the permissible limit in 75% of all water samples from Moon and Shi rivers. Therefore, it is strongly recommended that water from contaminated locations should not be used for drinking purposes without proper treatment and lead to health risk to bio-organisms.

5. Acknowledgement

I would like to acknowledge Ubon Ratchathani Rajabhat University for financial support.

6. References

[1] S. Khan, Q. Cao, Y. M. Zheng, Y. Z. Huang, Y. G. Zhu, Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China, Environ. Pollut. 152 (3) (2008) 686–692.

[2] S. Muhammad, M. T. Shah, S. Khan, Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan, Microchem. J. 98 (2) (2011) 334–343.

[3] H. U. Shah, T. J. Simpson, S. Alam, K. F. Khattak, S. Perveen, Mould incidence and mycotoxin contamination in maize kernels from Swat Valley, North West Frontier Province of Pakistan, Food and Chem. Toxicol. 48 (4) (2010) 1111–1116.

[4] M. T. Shah, S. Begum, S. Khan, Pedo and biogeochemical studies of mafic and ultramfic rocks in the Mingora and Kabal areas, Swat, Pakistan, Environ. Earth Sci. 60 (5) (2010) 1091–1102.

[5] M. Arif, D. J. Henry, C. J. Moon, Host rock characteristics and source of chromium and beryllium for emerald mineralization in the ophiolitic rocks of the Indus Suture Zone in Swat, NW Pakistan, Geol. Rev. 39 (1-2) (2011) 1–20.

[6] K. Khan, Y. Lu, H. Khan, S. Zakir, Ihsanullah, S. Khan,A. A. Khan, L. Wei, T. Wang, Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan, J. Environ. Sci. 25 (10) (2013) 2003-2013.

[7] K. Siraj, S. A. Kitte, Analysis of Copper, Zinc and Lead using Atomic Absorption Spectrophotometer in ground water of Jimma town of Southwestern Ethiopia, Int. J. chem. Anal. Sci. 4 (2013) 201-204.

[8] D. O. Ogoyi, C.J. Mwita, E.K. Nguu , P.M. Shiundu, Determination of heavy metal content in water, sediment and microalgae from Lake Victoria, East Africa, The Open Environ. Eng. J. 4 (2011) 156-161.

[9] WHO, Guidelines for Drinking-Water Quality 3rd ed., Recommendations. World Health Organization, Geneva, 2008.

[10] A. K. Patra, S. S. Wagh, A. K. Jain, A. G. Hegde, Assessment of daily intake of trace elements by Kakrapar adult population through ingestion pathway, Environ Monit and Assess. 169 (1-4) (2010) 267–272.

[11] S. Gupta, P. Pandotra, A.P. Gupta, J.K. Dhar, G. Sharma, G. Ram, M.K. Husain, Y.S. Bedi, Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of Zingiber officinale collected from different locations of North Western Himalayas by Atomic Absorption Spectroscopy, Food and Chem. Toxicol. 48 (2010) 2966-2971.

[12] A. Wongklom, J. Intaraprasert, Analysis of 5-organochlorine pesticides in sediment samples by gas chromatography–electron capture detection, KKU. Sci. J, 40 (2012) 278-282.

[13] A. Wongklom, J. Intaraprasert, Monitoring of organochlorine pesticides in water and sediment samples of Moon river, Thailand, Pure and Applied Chemistry International Conference (PACCON 2012), Chiang Mai, Thailand, 11-13 January 2012. 621-623.

[14] A. Wongklom, T. Thanachatchairathana, Assessment of the water quality and the heavy metal contamination of surface water from Shi and Moon river, 9th MAEJO University Fishery Conference, Chiang Mai, 26-28 February 2014. 107-108.