

INVESTIGATION OF HEAVY METAL ACCUMULATION IN WATER AND SEDIMENTS FROM PHITSANULOK PROVINCE USING X-RAY FLUORESCENCE AND ATOMIC ABSORPTION TECHNIQUES

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Abstract

This study investigated the presence of six heavy metals (zinc, copper, lead, chromium, nickel, and arsenic) in the water and sediments of four rivers in Phitsanulok province: Nan River, Yom River, Kwainoy River, and Wangthong River. Water and sediment samples were collected from eight stations and analyzed using X-Ray Fluorescence (XRF) and Atomic Absorption Spectroscopy (AAS). The study also examined the concentrations and sources of heavy metals in the sediment of these rivers. The results showed that the average levels of heavy metals in both water and sediment samples followed the order: zinc, chromium, copper, lead, nickel, and arsenic. According to water and sediment quality guidelines, chromium, copper, and nickel posed a significant threat to the water ecosystem in Phitsanulok province. The concentrations of certain heavy metals, including arsenic, lead, and nickel, exceeded normal levels at all of the studied stations, while lead, copper, and chromium concentrations exceeded normal levels at certain stations. The study also found that the concentrations of all six heavy metals in surface water samples did not exceed the drinking water guidelines set by the World Health Organization and national standards.

Keywords: Atomic Absorption Technique; Heavy Metal Accumulation; Sediments; Water; X-Ray Fluorescence

Introduction

Water is an essential element for all living things. It makes up a large part of the human body, and is necessary for the proper functioning of all cells, tissues, and organs. In addition to being a vital component of human biology, water is also crucial for the health and well-being of communities. Water is used for a wide range of purposes, including drinking, cooking, cleaning, and

irrigation. It is also used for recreational activities, such as swimming and boating, and is an important resource for the tourism and recreation industries. Water pollution is a serious problem that affects communities around the world. One of the major sources of water pollution is heavy metals, which can have serious health impacts on people and the environment. In addition to the health impacts,

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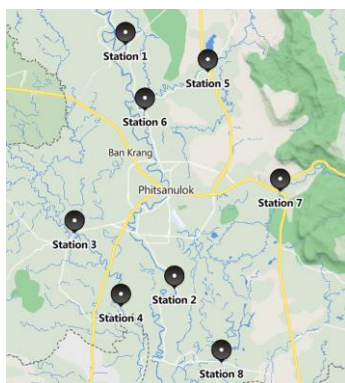


Figure 1. The location of the eight stations studied in the four rivers of Phitsanulok province

heavy metals in water can also harm the environment. They can accumulate in the food chain (Ngoc *et al.*, 2020), affecting plants, animals, and ultimately, humans. Heavy metals in fish cause cancer, damage the spine system, cause high blood pressure, inhibit enzyme activity, and cause DNA breaks (Manahan, 1992).

One major source of heavy metal contamination in water and sediments is industrial waste. Many industries release heavy metals into the environment as a byproduct of their operations, which can then enter the water supply and contaminate soil and sediment (Keepax *et al.*, 2011; Fulya *et al.*, 2020). Another source of heavy metal contamination is agricultural runoff. Fertilizers and pesticides used in agriculture can contain heavy metals, which can wash into rivers, streams, and other bodies of water. When heavy metals enter the water supply, they can accumulate in fish and other aquatic life. If people consume these contaminated fish, the heavy metals can pass into their bodies, leading to serious health problems (Rashed, 2001). Children and pregnant women are particularly vulnerable to the negative effects of heavy metals, as their bodies are still developing and are more sensitive to toxins. Phitsanulok province has four major rivers, namely the Nan River, the Yom River, the Kwae Noi River, and the Wang Thong River. All of these rivers are used for consumption and as a source of water for communities, factories, and agriculture that use chemicals. As a result, river water has the potential to be contaminated with heavy metals, leading to the accumulation of heavy metals in aquatic animals (Rashed, 2001; Terra *et al.*, 2008; Tanee *et al.*, 2013).

In this research, the researchers were interested in studying the accumulation of heavy metals, including zinc, copper, lead, chromium, nickel, and arsenic in water and sediments using X-Ray

Fluorescence (XRF) and Atomic Absorption Techniques (AA). Both techniques are convenient, fast, and highly accurate, which is beneficial for the people in terms of health, sanitation, and the economy, as well as for finding guidelines for planning, prevention, solving problems, or managing water sources in the future. Many studies have used XRF (Ene *et al.*, 2010), and AA (Mohammed *et al.*, 2023), to investigate heavy metal accumulation in water and sediment samples, which has helped to understand the sources and fate of heavy metals in the environment and has provided valuable information for the development of strategies to address heavy metal contamination.

Materials and Methods

This research was conducted in four rivers located in the Phitsanulok province in northern Thailand, which is about 380 kilometers north of the capital city of Bangkok. The study area encompasses a total of 10,816 square kilometers and has a population of 865,247 as of 2019. In the same year, the per capita income in this region was 81,919 Thai Baht (equivalent to approximately \$2,428). The study are shown in Figure 1. include eight stations.

1. Nan river, Phrom Phiram Subdistrict, Phrom Phiram District 17° 2' 0.96"N 100° 11' 52.08"E
2. Nan river, Wang Nam Khu Subdistrict, Mueang Phitsanulok District 16° 40' 56.41"N 100° 16' 18.14"E
3. Yom river, Bang Rakam Subdistrict, Bang Rakam District 16° 45' 43.55"N 100° 7' 15.54"E
4. Yom river, Wang Itok Subdistrict, Bang Rakam District 16° 39' 21.80"N 100° 11' 27.30"E
5. Kwainoy river, Wat Bot Subdistrict, Wat Bot District 16° 59' 19.74"N 100° 19' 15.54"E
6. Kwainoy river, Tambon Makhm Sung, Amphoe Mueang Phitsanulok 16° 45' 43.55"N 100° 7' 15.54"E
7. Wangthong river, Wang Thong Subdistrict, Wang Thong District 16° 45' 43.55"N 100° 7' 15.54"E
8. Wangthong river, Phai Lom Subdistrict, Bang Krathum District 16° 45' 43.55"N 100° 7' 15.54"E

In November 2022, water and sediment samples were collected from four rivers in Phitsanulok province, including the Nan River, Yom River, Kwainoy River, and Wangthong River. The samples were taken from areas within a radius

of 500 meters, 500 to 1000 meters, and 1000 to 1500 meters from the sampling area. The collected samples were immediately placed in an airtight insulating box. A total of surface water samples and drinking water samples were collected. To collect surface water samples for analysis, researchers took three samples from each of four different habitats, located at a specific distance from each site. The drinking water samples were collected from households that reported using well water and were selected through a survey administered to 200 residents. The samples at each location were mixed in a plastic bucket and a 1-liter sample was stored in a polyethylene bottle. Water and sediment samples were collected from all four rivers before and after entering urban communities. It is expected that there will be significant differences in the values obtained from these two locations.

The water samples were acidified with nitric acid to pH less than 2 and transferred on ice to the laboratory for analysis. A 10-milliliter sample of each water sample was filtered through a 0.45-micrometer pore-size disposable capsule filter before elemental analysis. The surface water and drinking water samples were collected following the regulations for water sampling and quality control from the Pollution Control Department Ministry of Natural Resources and Environment.

All sediment samples were dried. Then soaked in hydrochloric acid for 24 h to remove organic matter in the sediment samples. After filtering, the samples were dried at 110°C for 8 h, and the samples were ground in a rock labs grinder and sieved at 250 µm particle sizes.

Heavy metal contamination of water and sediment is a major environmental concern because heavy metals can be toxic to humans and wildlife. X-ray fluorescence (XRF) and atomic absorption (AA) are two techniques that are frequently used to determine the concentration of heavy metals in water and sediment samples.

To analyze the data collected in this study, the researchers calculated several descriptive statistics, including the mean and standard deviation (SD). The statistical significance of the results was determined by setting a threshold of $P < 0.05$. All statistical analyses were carried out using the SPSS statistics software.

Results and Discussion

Sediment samples

The XRF analysis of the collected sediment samples revealed the presence of major elements such as calcium, iron, potassium, manganese, and titanium, as well as minor elements including

Table 1. The heavy metal content found in sediment samples collected from eight different stations (mg/kg)

	As	Cr	Cu	Ni	Pb	Zn
1	11.09	93.80	33.76	59.35	27.65	102.21
2	9.52	110.74	33.01	60.41	24.78	97.83
3	7.19	81.36	26.08	48.57	18.67	78.05
4	5.87	84.06	31.02	51.48	17.94	80.22
5	10.98	101.15	36.11	62.34	25.59	92.29
6	12.53	98.35	34.23	60.77	51.21	106.14
7	8.54	59.50	13.56	40.12	11.66	34.10
8	9.05	62.67	17.29	41.83	11.02	32.69

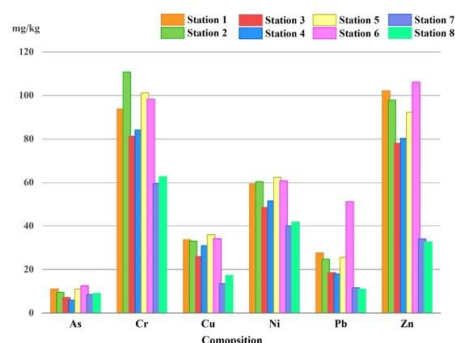


Figure 2. The heavy metal content in sediment samples collected from eight different stations

arsenic, chromium, copper, magnesium, nickel, lead, rubidium, phosphorus, strontium, and zinc. The average concentrations of heavy metals such as arsenic, chromium, copper, nickel, lead, and zinc were measured in five separate samples of each sediment sample and are presented in Table 1. and Figure 2. Results for the elements silver, cadmium, mercury, antimony, selenium, and tin were not reported because their concentrations were below the detection limits of 30 mg/kg, 40 mg/kg, 2 mg/kg, 120 mg/kg, 3 mg/kg, and 105 mg/kg, respectively. The concentrations of chromium and zinc in the sediment samples showed significant variations. The concentrations of arsenic and nickel exceeded normal levels (5 mg/kg for arsenic and 20 mg/kg for nickel) in all of the studied stations, while lead concentrations exceeded normal levels (20 mg/kg) at six stations, including Phrom Phiram District, Mueang Phitsanulok District, Bang Rakam District, and Wat Bot District, and exceeded the alert level in the sensitive area (50 mg/kg) at one location (Mueang Phitsanulok District). Zinc concentrations exceeded normal levels (100 mg/kg) at two stations in the Phrom Phiram District and one station in the Mueang Phitsanulok District. Copper concentrations exceeded normal levels (20 mg/kg) at all studied stations, while chromium concentrations exceeded normal levels (30 mg/kg)

at all studied stations and exceeded the alert level in the sensitive area (100 mg/kg) at two locations (Mueang Phitsanulok District and Wat Bot District). The results of the XRF analysis indicate that the sediment samples collected from the various locations contained a range of both major and minor elements. The concentrations of certain heavy metals, including arsenic, lead, and nickel, exceeded normal levels at all of the studied stations, while lead, copper, and chromium concentrations exceeded normal levels at certain stations. The presence of these heavy metals at elevated levels suggests that the sediment may have been contaminated by various sources, such as industrial discharge or the use of pesticides and fertilizers containing these metals. It is important to note that the accumulation of heavy metals in sediment can have negative impacts on the health of aquatic organisms and the overall ecosystem. Further research may be necessary to identify the specific sources of heavy metal contamination in these sediment samples and to develop strategies to mitigate any negative impacts.

Concentration of heavy metal in water samples

Using atomic absorption (AA), the average concentrations of As, Cr, Cu, Ni, Pb, and Zn in surface water from waterfront communities in Phitsanulok province were studied. Research has revealed that contains varying levels of As, Cr, Cu, Ni, Pb, and Zn that are represent in Table 2. The highest concentrations were found to be of Zn, followed by Cr, Ni, Cu, Pb, and then As. It's important to note that these levels of As, Cr, Cu, Ni, Pb, and Zn in the water may have potential health risks to the local population, as exposure to these heavy metals can cause a variety of health problems, including neurological and developmental disorders, cancer, and organ damage. It's important to investigate the source of these contaminants and take appropriate measures to reduce exposure to them. Additionally, it's worth noting that the levels of these metals in well water may indicate contamination of the local groundwater, which can have a more widespread impact. Further study may be needed to determine the potential health risks and identify the sources of these contaminants.

The highest concentrations of heavy metals were detected in both surface and well water for zinc, and the lowest concentrations were observed for arsenic. The study also found that the concentrations of all six heavy metals in surface water samples did not exceed the drinking water guidelines set by the World Health Organization and national standards. The study concludes that the levels of heavy metals in both surface and well water samples did not exceed the standards, as shown in Table 2.

Table 2. Heavy metal concentrations (mg/L) in water samples

Station	Heavy Metal	Surface Water	Well Water
1	As	0.02±0.68	0.03±1.62
	Cr	1.16±1.15	1.12±2.01
	Cu	0.19±2.69	0.09±2.04
	Ni	1.56±1.67	1.25±0.51
	Pb	0.13±2.45	0.07±0.55
	Zn	2.57±2.06	0.75±0.86
2	As	0.02±1.87	0.03±2.41
	Cr	1.37±0.51	1.32±1.30
	Cu	0.19±2.43	0.09±1.32
	Ni	1.59±1.34	1.27±1.97
	Pb	0.12±0.61	0.06±1.64
	Zn	2.54±2.01	0.72±0.87
3	As	0.01±0.91	0.02±2.07
	Cr	1.01±1.39	0.97±2.13
	Cu	0.15±2.41	0.07±0.89
	Ni	1.28±2.55	1.02±1.91
	Pb	0.09±2.14	0.05±0.77
	Zn	1.96±2.19	0.57±2.00
4	As	0.01±1.53	0.02±1.18
	Cr	1.01±1.95	0.97±0.91
	Cu	0.15±1.15	0.07±0.71
	Ni	1.28±0.64	1.02±2.64
	Pb	0.09±1.99	0.05±1.29
	Zn	1.96±1.73	0.57±1.59
5	As	0.02±0.47	0.03±1.49
	Cr	1.25±0.76	1.21±0.77
	Cu	0.20±2.03	0.10±0.78
	Ni	1.64±1.21	1.31±0.96
	Pb	0.12±2.07	0.06±0.73
	Zn	2.32±0.85	0.68±0.62
6	As	0.02±0.82	0.02±1.52
	Cr	1.22±1.15	1.17±1.13
	Cu	0.19±2.69	0.09±1.84
	Ni	1.60±1.67	1.28±1.18
	Pb	0.24±2.45	0.13±2.55
	Zn	2.67±2.06	0.78±0.49
7	As	0.02±1.97	0.02±1.78
	Cr	0.74±1.01	0.71±1.62
	Cu	0.08±1.86	0.04±2.62
	Ni	1.05±2.37	0.84±1.74
	Pb	0.05±0.70	0.03±1.40
	Zn	0.86±1.43	0.25±2.40
8	As	0.02±0.68 ^a	0.02±0.95
	Cr	0.78±0.76	0.75±1.65
	Cu	0.10±2.23	0.05±0.63
	Ni	1.10±0.55	0.88±1.41
	Pb	0.05±1.44	0.03±1.44
	Zn	0.82±1.16	0.24±1.08

Conclusions

In conclusion, the XRF analysis of sediment samples collected from various locations revealed elevated levels of heavy metals, including arsenic, lead, and nickel. These findings suggest the sediment may have been contaminated by industrial discharge or the use of pesticides and fertilizers containing these metals. The presence of these heavy metals in sediment can have negative impacts on the health of aquatic organisms and the overall

ecosystem. Additionally, the atomic absorption analysis of surface and well water from waterfront communities in Phitsanulok province found varying levels of heavy metals, with zinc having the highest concentrations and arsenic having the lowest. The study found that the concentrations of all six heavy metals in surface water samples did not exceed the drinking water guidelines set by the World Health Organization and national standards. Further research is needed to identify the specific sources of heavy metal contamination and develop strategies to mitigate any negative impacts on the local population and the environment.

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