Assessment of heavy metals concentration in the water around the area of Adipala Cilacap steam power plant using neutron activation analysis

Rozana K, Sukirno, Prabasiwi D S and Murniasih S
Center for Accelerator Science and Technology (PSTA) - National Nuclear Energy Agency (BATAN), Jl. Babarsari, Caturtunggal, Sleman, Yogyakarta, 55281, Indonesia
E-mail: kharistya.rozana@batan.go.id

Abstract. This research was conducted to assess the concentration of hazardous heavy metals (Cu, Zn, As, Cd, and Cr) in water wells and rivers, around the Adipala Cilacap steam power plant, using neutron activation analysis method. Sample of wells water and river water were taken around the Adipala Cilacap steam power plant. Samples were irradiated with pneumatic facility and Lazy Suzan in the Kartini Research Reactor, at a thermal neutron flux of approximately 0.58x10^{11} n.cm^{-2}.det^{-1}. The average concentration of hazardous heavy metals has the smallest metal value of Cr with a value of 0.0006 mg/L and the highest metal Cu with a value of 0.057 mg/L, which is examined in water wells following a decrease in the order of Cu > Zn > As > Cd > Cr. The five hazardous heavy metals under the maximum standard recommended by the WHO/USEPA and Minister of Health’s Regulation No. 492. In addition to the hazardous heavy metals, there are 13 other heavy metals that determined its concentration (Al, Ba, Mg, K, Fe, Na, Mn, Ti, La, Ce, Sm, Cs, and V), and obtained the results of the metal concentrations Al exceeds the threshold allowable by Minister of Health’s Regulation No. 492 the Year 2010.

1. Introduction
Since the beginning of human civilization, because of uncontrollable greed, excessive utilization of natural resources has occurred that led to unsurpassed destruction. Recently, with unplanned growth of industrialization, rapid urbanization and degradation of water resources, deforestation, depletion of water resources have played an important role in the worsening of the aquatic ecosystem on earth [13].

Water is the most abundant substance on the surface of the earth which is crucial for survival. Water plays an important role in the world economy, as it serves as a solvent for a wide range of chemicals, industrial conditioners, and transportation. More than 70% of freshwater consumed by agriculture [4]. Healthy drinking water is a basic need for human health. Contaminated drinking water is a significant risk to human health. Total water on earth contains 3% freshwater. Only a small portion (0.01%) from freshwater is available for human utilization [12].

Drinking water is obtained from various sources such as wells, tubes, rivers, lakes, and reservoirs. Such water can pose the greatest risk to human health because of the contamination of these sources. Water pollutants mainly consist of heavy and hazardous metals. The most common heavy metals are found in contaminated areas, such as Pb, Cr, As, Zn, Cd, Cu, Co and Hg. The metals are able to reduce crop production due to the risk of bioaccumulation and biomagnification in the food chain [4, 6, 12, 14, 18]. Heavy metals in water only occur on a sloped level but are more toxic to the human body. Noticing the harmful nature of heavy metal pollution in water, it is crucial that research is conducted to assess the nature of the problem and provide input related ways to minimize the risk of toxic metal contamination from drinking water around the Adipala Cilacap steam power plant. Since the beginning of September...
2016, steam power plant Central Java Adipala located in Buton Village, Adipala Cilacap District began to operate by generating 660 MW power, this power plant built since the year 2010.

Water pollution is water polluted by foreign objects that degrade water quality. Water pollution includes pollution in liquid forms such as marine pollution and river pollution. As the term applies, liquid pollution occurs in oceans, lakes, rivers, well water, underground and bay water, in areas containing short liquids [4, 8]. Rainwater that permeates the ground in the form of tracing and the absorption, on the way carries chemical elements. The chemical composition of groundwater provides some influence on various activities such as agriculture, industrial and domestic [10].

These toxic elements enter the human body largely through food and water and at lower levels through the inhalation of polluted air, the use of cosmetics, medicines, low-quality herbal formulations (preparations Herbo-minerals) and even materials such as toys that have a paint containing tin [20]. Water contamination has increased rapidly as a result of intentional and accidental human activity. Pollution of soil, air, water and food resources we have reached warning proportions [4]. Serayu River is one of the important rivers in central Java, stretching from northeast to southwest for 181 km, this river crosses five districts namely Wonosobo, Banjarnegara, Purwakarta and Banyumas districts, until it rises in the Indian Ocean in Cilacap Regency. In general, nowadays, the most important source of pollution, which overlooks the rivers is agricultural, wastewater towns and villages, garbage, industrial wastewater. In recent years, there has been an increase in the development of human activity every day around the Serayu River [6]. Serayu River is one of the rare habitats of various districts. All kinds of pollution will affect the variety of rivers. On the other hand, this river water is used to cultivate and fish fishing.

Neutron activation Analysis (AAN) is a highly sensitive nuclear engineering-based material analysis method. This method can be used to determine multi-metal simultaneously with high accuracy and sensitivity so that it is appropriate for the analysis of the trace metal in the type of sample [15]. AAN is based on thermal neutron capture reactions by the target core through a reaction \((n, \gamma)\). The nucleus of the induced nuclides will be activated and present in the metastable state [2].

The purpose of this research is to determine the concentration of heavy metals (Cd, Cu, Cr, Zn, Co and As) in the environmental wells and rivers Serayu around the Adipala Cilacap steam power plant by using the NAA method, then the concentration results compared with the raw National quality (PP Menkes No 492) and International (WHO/USEPA).

2. Methodology

2.1 Materials
Samples of wells water and river water, secondary standards for certified metals, and aquabidest.

2.2 Equipments
Kartini Research Reactor 100 kW-powered, lazy susan and pneumatic facilities, gamma spectrometer, HPGe Ortec detector, MCA spectrum, master ORTEC 92X, with maestro software, sampling tools (GPS, sample containers, etc.), electric cookers, glassware, polyethylene vial.

2.3 Location Sampling
The samples used were footage of well water and rivers. The samples in this study were taken in the surrounding area of Adipala Cilacap steam power plant, consisting of 3 different locations, including: Location 1 is ~ 2.8 km, Cibolang, Gombong Harjo, (SL: 07°41.07’3”, and EL: 109°08.15’2”). Location 2 is: ~ 2.0 km, Silang Sur, Wlahar Village. (SL: 07°40.11’,” and EL: 109°08’05.5’”). Location 3, located: ~ 2.1 km Bauton, Sawangan village (SL: 07°41’.06.0” and EL: 109°09’.22.9”), all sampling areas were in the Adipala district.
2.4 Sample Preparation and Irradiation
The sample of the water is filtered, taken 1000 mL to 20 mL by evaporation, the next 0.5 mL is inserted into the polyethylene vial, then closed tightly. Snippets are ready to be irradiated and created several sample-coded locations for the short and long half-life samples. The three-vial samples were included in the standard co-cladding and a Blanko for radionuclides of longevity irradiated 2 x 6 hours, while for the short half-life of irradiation in research reactors for 5 minutes and Irradiations performed one by one. The measurement of γ-ray is carried out with the high purity Germanium detector (HPGe). The counting is done after 5 minutes delay and minced 5 minutes for measuring Mg, Al, V, Ti, La, Cu, and Mn elements, while intermediate half-time elements i.e. K, Ba, Na, Sm, As, and Cd) after delay time for 3 days and long after 3 weeks delay time for measuring Fe, Cr, Zn, Ce, and Cs elements.

3. Result and Discussion
Safe and quality drinking water is the foundation for good human health. Water provides some kelumite metals, but when water is polluted then it can be a source of unwanted substances, harmful to human health and causes diseases such as cancer, reproductive disorders, cardiovascular disease, damage Dental and neurological diseases [9]. The water analysis of the research area showed that water samples had no color and smell. The results of the metal analysis in water well samples were shown in Figures 2, 3 and 4. Figure 2 shows the concentration of 5 hazardous heavy metals namely Cr, Cd, As, Zn, and Cu. Figure 4 shows other heavy metals that are not very danger and Figure 5 is a heavy metal histogram of leaky or heavy metals that have very small concentrations

Histogram 2 is a hazardous heavy metal content, which is the concern of metals Hg and Pb [11, 12], but both metals are not detected. Cd is metals that are not needed by both animal and human bodies and are toxic at very low concentration levels. High exposure can lead to obstructive pulmonary disease,
cadmium pneumonitis, which results from dust and inhalation [8]. This metal concentration has the smallest concentration is 0.0008 mg/L and the highest of 0.0017 mg/L with an average of 0.003 mg/L. The limit is permitted by 0.003 mg/L from WHO/USEPA [13, 14, 19] and regulation of the Minister of Health Regulation No.492/Menkes/Per/IV/2010 (PMK 492), on the drinking water quality requirement [3].

Some heavy metals are essential for health but in limited concentrations, high concentrations create harmful effects for health. Zinc (Zn) and copper (Cu) are important for health but in limited concentrations [20]. In research obtained the concentration of Zn and Cu minimum respectively 0.008 and 0.02 mg/L and the maximum 0.047 and 0.057 mg/L, thus obtained the average concentration of 0.026 and 0.024 mg/L. The WHO allowable water limit for Zn is 3 mg/L and Cu is 2 mg/L [3, 14, 19]. Chromium with the maximum limit suggested in drinking water is essential in human nutrients to maintain normal glucose metabolism. However, if it is higher than the recommended level, it causes nephritis and glycosuria [4]. In research acquired the smallest concentration of Cr is 0.0006 mg/L, the highest 0.027 mg/L and the average concentration of Cr is 0.002 mg/L. Arsenic concentrations observed around the Adipala steam power plant have concentrations ranging from 0.001 to 0.0027 mg/L with an average concentration of 0.0016 mg/L, the maximum allowed by WHO and PMK 492 is 0.01 mg/L.

Results of heavy and hazardous metals concentrations in water, compared to the maximum limit of WHO/USEPA and Ministry of Health Regulation Menkes No 492, all metals are still under maximum concentration. The average concentration of heavy metals studied in water following a decrease in the order of Cu > Zn > As > Cd > Cr.

![Figure 2](image.png)

In Figure 3, a histogram of heavy metal concentration (Mg, K, Ba, Al, Mn and Fe) in samples of well water has different concentrations. The smallest concentration in Figure 3 is the metal Fe 0.006 mg/L and the highest is the Mg metal with a concentration of 1.575 mg/L. The average concentration of heavy metals studied in water following the smallest order of Fe < Mn < Al < Ba < K < Mg < Na. Specifically Na metals that have significant concentration, the lowest concentration is 6.757 mg/L and the highest 25.178 mg/L with an average concentration of 18.324 mg/L, while the highest concentration allowed by the Minister of Health Regulation number 492, is 200 mg/L [3].

The concentration of magnesium ranges from (0.56 – 1.575) mg/L with an average of 0.960 mg/L and the maximum quality raw metals from WHO for Mg metals concentration in drinking water is 500 mg/L [18]. Aluminum metals having a range of centralized (0.259 – 0.328) mg/L with an average of 0.297 mg/L, these metals have exceeded the default thresholds permitted by the minister Health number 492, the maximum quality raw for Al metals is 0.2 mg/L [3]. The aluminum concentrations found were 1.48 times greater than minimum regulation in drinking water.
Manganese is an important trace metal that is needed by our body in small quantities for the production of digestive enzymes, nutrient absorption, wound healing, bone development and immune system defense. Human exposure to a higher number of manganese may cause severe disruption of the nervous system, and long-term exposure in its worst conditions can lead to permanent neurological effects [19]. Metal Manganese has a concentration range (0.052 – 0.168) mg/L with an average concentration of 0.103 mg/L. Manganese is found lower than the permissible limit of WHO (0.5) mg/L) [19]. Iron is an important metal if it is within the allowed range, however, if the concentration of water is higher, its toxic can lead to a number of health problems in the community. Figure 3 shows the concentration of Fe in water samples with the lowest content of 0.006 mg/L and the highest 0.096 mg/L. Data shows that the Fe content is within the allowable limit range of 0.3 mg/L WHO [3, 19].

The metals of potassium and barium each have a concentration of ranged (0.151 – 1.246) mg/L and (0.405 – 0.679) mg/L, for both metals there are no recommendations for the quality standards that can be listed in this paper.

![Figure 3. Heavy metal concentrations in wells water](image)

![Figure 4. Na metal concentrations in wells water](image)

Figure 5 is a metallic histogram of a trace (four metals) that has a metal concentration detected very small V metal with concentrations of 0.00004 mg/l to the metal with the highest concentration of 0.053 mg/L namely the metal La. The two metals of Sm and Ti have an average concentration of 0.001 mg/L and 0.028 mg/L.
Any kind of pollution will affect river pollution. On the other hand, this river water is used to cultivate and fish fishing. So, to estimate the number of heavy metals that go into the river and finally up to the seawater, measuring and estimating the concentration of heavy metals in the river water is a very important thing [6]. The concentration of heavy metals contained in the water of the Serayu River around the Adipala Cilacap steam power plant is shown on the histogram Figures 5, 6 and 7, in addition to the metal concentration in the river. The image contains metal concentrations in well water, this is to compare the concentration of water studied.

Figure 6 Histogram of hazardous heavy metal there is 6 very noted heavy metals namely Cr, Cd, As, Zn, Co and Cu. The six metals are the heavy metals most commonly associated with human poisoning coupled with the metals Hg, Ni and Pb [1, 6]. While the heavy metals needed by humans in the amount of kelumite are copper, zinc, cobalt and chromium are needed by the body in small quantities [9, 14, 19]. The metal concentration in the water of a different Serayu river is illustrated in Figure 5. The concentration of toxic heavy metals in water is found in the following order: Zn > Cu > Cd > Cr > As > Co. Comparison of existing metals in water well around and river water for Zn = 19, Cu = 1.5, Cd = 8, Cr = 3 and As = 2 times whereas for metal Co in its concentration wells are not detected.

According to the United States Environmental Protection Agency (USEPA), the World Health Organization (World Health Organization WHO), the number of heavy metals that can be received such as cadmium in a liter of river water or lake water is 0.01 mg/L, for arsenic is 0.03 mg/L, Chromium 0.1 mg/L for zinc is 3 mg/L, and copper 0.05 mg/L [1, 7, 17], as well as cobalt metal 0.05 mg/L [4]. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring the concentration of such metals [13].

The concentration range observed during the study is below the allowable limit for the standard river or lake water. Furthermore, the concentration level of hazardous metals Zn (0.41 ± 0.02) mg/L, Cu (0.0347 ± 0.001) mg/L, Cd (0.007 ± 0.0008) mg/L, Cr (0.005 ± 0.001) mg/L, As (0.003 ± 0.001) mg/L, and Co (0.001 ± 0.0001) mg/L. The average concentration of hazardous heavy metals has the smallest metal value of Cr with a value of 0.0006 mg/L and the highest metal Cu with a value of 0.057 mg/L, which is examined in water wells following a decrease in the order of Cu > Zn > As > Cd > Cr. River water flow has taken at a distance of about 2 km from the sea and about 2.8 km from Adipala steam power plant has a metal concentration under the international recommended concentration (WHO and USEPA). From the six hazardous heavy metals, the cobalt metal has the smallest concentration. Cobalt is beneficial to humans because it is a part of vitamin B12, which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. However, too high cobalt concentrations can damage human health [12].
Figure 6. The concentration of Heavy Metals in Rivers and Wells Water

Figure 7 is a heavy metals histogram of relatively dense metal or metalloid known for its limited toxic potential, particularly in the context of the environment. The group consists of Al, Ba, Mg, K, Fe and Na. The concentration is shown in Figure 8, where the lowest concentration is Al metal with a concentration value Al (0.705 ± 0.012) mg/L and the highest concentration value for the metal Fe (4.224 ± 0.30) mg/L. Sodium metal has a significant concentration of (365.46 ± 0.30) mg/L, this water is drunk does not meet the requirements specified Menkes No 492 is 200 mg/L [3].

The concentration of aluminum metal and iron in river water has exceeded the maximum limit on the USEPA/WHO recommendation, i.e. Fe concentration with a value of 1.0 mg/L and aluminum with a value of 0.05-0.2 mg/L [17]. The metallic concentrations in river water are found in the following order: Fe > K > Mg > Ba > Al The comparison of existing metals in water well around and river water for, Fe = 86, K = 6, Mg = 2, Ba = 2.5 and Al = 2.5 times, metal Fe has a comparison that is too significant the other metals.

Figure 7. Concentration Heavy Metals in River and Wells Water
Figure 8. The concentration of Na Metals in Rivers and Wells Water

Figure 9 is a trace heavy metal histogram (Mn, Ti, La, Ce, Sm, Cs and V) which have low concentrations with the concentration range \((0.0001 \pm 0.00001)\) mg/L, metal V and Mn metals \((0.220 \pm 0.03)\) mg/L. According to the seven trace metals, only Mn has the maximum allowable limit for seawater or river water according to WHO is 0.5 mg/L [17, 18]. Mn is a low toxicity element that has considerable biological significance. Mn is one of the more biogeochemical and active transition metals in the aquatic environment [17]. The concentration of metals in river water is found in the largest order as follows: Mn > Ti > La > Ce > Sm > Cs > V. Comparison of existing metals in water well around and river water for, Mn = 2, T = 3, La = 2, Sm = 7 and V = 5 times, metal Ce and Cs are not in the water of the well as shown in Figure 9.

Figure 9. The concentration of Heavy Metals in River and Wells Water

4. Conclusion
Healthy water is a basic necessity for life. At this time, NAA is able to detect contaminated and healthy water. The excess amount of heavy metals present as pollutants in well water and river water. Heavy metals in water potentially pose a threat to the environment and can damage human health through the food chain. Results of heavy and hazardous metal concentrations in water Cu, Zn, As, Cd and Cr, compared with the maximum limit of WHO/USEPA still below the maximum allowable, except the Al
metal according to the Minister of Health No. 492/Menkes/Per/IV/2010, concerning drinking water quality requirements, as both metals have exceeded the maximum threshold. It is recommended that drinking water is monitored by regular heavy metals to prevent excessive accumulation of heavy metals in the body.

Acknowledgments
The authors would like to thank Government through the DIPA 2018 PSTA BATAN for the aid of funds i.e. this research can be done. Also, the author thanks to Reactor Division Officer: Wantana, Sigit. P, Rochim, Umar S H, and M Subchan.

References
[1] Saeed S A and Shaker I M 2008 Assesment of Heavy Metals Pollution in Water and Sediments and Their Effect on Oreocromis Niloticus in the Northern Delta Lakes 8th International Symposium on Tilapia in Aquaculture 475-490
[2] Shahabuddin M et al 2010 Soil Contamination in Nuclear Reactor Surrounding Areas in Savar, Bangladesh using Instrumental Neutron Activation Analysis Method. Int. J. Environ. Sci. Vol 1 3 (2010), 282-295
[3] Ministry of Health Regulation Number 492/Menkes/Per/IV/2010 regarding drinking water quality requirements
[4] Khan S A, Din Z U, Ihsanullah, Zubair A 2011 Levels of Selected Heavy Metals in Drinking Water of Prshawar City Int. J. Sci. Nat. 2 648-652
[5] World Health Organization 2011 Guidelines for Drinking Water Quality ISBN 978 92 4 154815
[6] Fatemeh N et al 2012 Heavy Metal Distributions in Water of the Aras River J. Water. Resour. Protect 4 73-78
[7] Ogundowokan A O 2013 Speciation Study of Heavy Metals in Water and Sediments from Asunle River of the Obafemi Awolowo University, Ile-Ife, Nigeria. Int. J. Environ. Protect 3 6-16
[8] Verma R and Dwivedi P 2013 Heavy metal water pollution - A case study : Recent Research in Science and Technology 5 98-99
[9] Afrasiab K T et al 2014 Detection of heavy metals (Pb, Sb, Al, As) through atomic absorption spectroscopy from drinking water of District Pishin, Balochistan, Pakistan. Int. J. Curr. Microbiol. App. Sci 3 299-308
[10] Barbara Szpakowska et al 2014 Contents of Cu, Zn, Cd, Pb and Fe in rainwater effluents discharged to surface waters in the city of Poznań. J. Elem 3 779–794
[11] Radulescu C et al 2014 Determination of Heavy metal Level in Water and Therapeutic Mud by Atomic Absorption Spectrometry. Rom. Journ. Phys. 59 1057–1066
[12] Rajeswari. T.R, and Sailaja. N 2014 Impact of Heavy Metals on Environmental Pollution Journal of Chemical and Pharmaceutical Sciences Special. 3 175-181
[13] Braich O S and Jangu S 2015 Evaluation of Water Quality Pollution Indices for Heavy Metal Contamination Monitoring in the Water of Harike Wetland International Journal of Scientific and Research Publications 5 1-6
[14] Ramchander J, et al 2015 Quantitative Determination of Heavy Metals in the Water Samples of Four Areas of Hyderabad in Telangana State IOSR J. Applied Chemistry (IOSR-JAC) e-ISSN: 2278-5736 8 18-19
[15] Iga K, Motrenko H P and Danko B 2016 Determination of chromium in biological materials by radiochemical neutron activation analysis (RNAA) using manganese dioxide. J. Radioanal. Nucl. Chem. 310 559–564.
[16] Verma C, Madan S and Hussain A 2016 Heavy metal contamination of groundwater due to fly ash disposal of coal-fired thermal power plant, Parichha, Jhansi, India. Cogent Engineering . 3 1 - 8
[17] Golam M M and Fahad A A 2017 Environmental Contamination and Assessment of Heavy Metals in Water, Sediments and Shrimp of Red Sea Coast of Jizan, Saudi Arabia. J. Aquat. Pollut. Tox. 1 1-8

[18] Ojo A A 2017 Review on Heavy Metals Contamination in the Environment. Eur. J. Earth. Environ. 4 1-6

[19] Jamshaid M, Khan A A, Kashif A A and Saleem M 2018 Heavy metal in drinking water and its effect on human health and its treatment techniques - a review Int. J. Biosci. 12 223-240

[20] Sabber W, Rahman M Z, Hasan M M, Khan M N 2018 Assessment of Heavy Metals in River, Sediment and Fish Mussel in Rupsha River Under Khulna District Bangladesh. Int. J. Expt. Agric 8 1-5