



Faculty of Resource Science and Technology

Determination of heavy metals in water, sediment and fishes of Bakun Hydroelectric Reservoir

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**DETERMINATION OF HEAVY METALS IN WATER, SEDIMENT, AND FISHES
OF BAKUN HYDROELECTRIC RESERVOIR**

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the requirements for the Bachelor degree of Resource Chemistry with Honours

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DECLARATION

I hereby declare that this thesis is based on my original work except for quotation and citation, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UNIMAS or other institutions of higher learning.

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List of Abbreviations

Ag	Silver
Al	Aluminium
As	Arsenic
Ba	Barium
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
EF	Enrichment factor
FAAS	Flame atomic absorption spectrometer
Fe	Iron
HCl	Hydrochloric acid
Hg	Mercury
HNO ₃	Nitric acid
IQ	Intelligence Quotient

Li	Lithium
Mg	Magnesium
Mn	Manganese
Pb	Lead
Se	Selenium
Zn	Zinc
Zr	Zirconium

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ABSTRACT

In this study, the concentration of selected metals (Cd, Cu, Fe, Hg, Mn, Se and Zn) in water, sediment and fishes of Bakun hydroelectric reservoir and the adjacent vicinity were determined. Heavy metals were analysed using a flame atomic absorption spectrophotometer and a mercury analyser. In water, only Fe, Mn and Hg were detected in the order of Fe > Mn > Hg. In sediment, Fe, Mn, Zn, Cu, and Hg were detected in the order of Fe > Mn > Zn > Cu > Hg. In fish, metals were detected in the order of Mn > Zn > Fe > Cu. The sediment was considered unpolluted according to the contamination factor, geo-accumulation index and pollution load index nonetheless the concentrations of Fe and Mn would require conventional treatment for drinking water purpose. Heavy metals in fish were generally below the permissible level of WHO/FAO except Mn where the average was found above 5.5 mg/kg.

Keywords: Heavy metals, Bakun hydroelectric reservoir, water, sediment, fish

ABSTRAK

Dalam kajian ini, kepekatan sesetengah logam berat (Cd, Cu, Fe, Hg, Mn, Se dan Zn) dalam air, sedimen dan ikan di takungan hidroelektrik Bakun dan sekitarnya telah dikesan. Logam telah dianalisa dengan menggunakan flame atomic absorption spectrophotometer dan mercury analyser. Dalam air, hanya Fe, Mn dan Hg telah dikesan dalam susunan Fe > Mn > Hg. Dalam sedimen, Fe, Mn, Zn, Cu dan Hg telah dikesan dalam susunan Fe > Mn > Zn > Cu > Hg. Dalam ikan, logam berat telah dikesan dalam susunan Mn > Zn > Fe > Cu. Sedimen tidak tercemar mengikut faktor pencemaran, indeks geo-pengumpulan dan indeks beban pencemran tetapi kepekatan Fe dan Mn memerlukan rawatan konvensional untuk dijadikan air minumam. Secara umum, logam berat dalam ikan berada di bawah had maksimum yang dibenarkan oleh WHO/FAO kecuali Mn dimana purata kepekatan didapati melebihi 5.5 mg/kg.

Kata kunci: Logam berat, Takungan Hiroelektrik Bakun, air, sedimen, ikan

Chapter 1

Introduction

Dams are constructed for various purposes including hydropower generation and seasonal flood control (Ghorefat & Yusuf, 2006). They are crucial to human economic development. About 70 % of the rivers all over the world are used as hydroelectric reservoir and 2.2% of the primary energy is generated by hydropower (Kummu & Varis, 2007). Although dams contribute some economic advantages, there are also significant negative impacts on the environment (World Commission on Dams, 2000).

Heavy metals pollution is one of the possible negative impacts of dam construction. Heavy metals are metallic elements which have a high atomic weight with density at least 5 times compared to water. Heavy metals include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), silver (Ag), zinc (Zn), and the platinum group elements (Duruibe *et al.*, 2007). They are very toxic and can cause severe negative effects even at very low concentrations (Ranjeeta, 2012).

In order to evaluate heavy metals contamination, the concentration of metals in fish, water and sediments can be measured. Determination of heavy metals in rivers is crucial as there is a possibility that the water is used for drinking. Besides, Mucha *et al.*, (2003) suggested that sediments are the ultimate sink of pollutants in the aquatic system. Heavy metals are non-biodegradable. Hence, once they enter the aquatic environment, they can be accumulated in fish tissue and other organisms (Ranjeeta, 2012). They also tend to accumulate in various organs of aquatic organisms, especially fish, which may in turn be transported to human *via* food chains. This will cause serious health hazards to human (Puel *et al.*, 1987) including

anaemia, brain damage, Wilson's disease, hypertension, and special types of dermatitis known as "Zinc pox" (Patil & Ahmad, 2011).

Numerous studies have been published on heavy metals in the aquatic environment (Wagner & Boman, 2003). However, there is limited knowledge on the distribution of heavy metals in Bakun hydroelectric reservoir. It is crucial to determine the heavy metals in Bakun to evaluate the heavy metal contamination status. This study aims to determine the concentration of certain heavy metals in water, sediments and fish of Bakun hydroelectric reservoir.

Chapter 2

Literature Review

2.1 Heavy metals

Heavy metal is defined as metallic elements that have a high atomic weight and at least 5 times denser compared to water. Heavy metals can be classified into several groups, according to their health importance. Heavy metals can be classified as essential, non-essential, less toxic and highly toxic. Essential heavy metals are also known as micronutrients (Reeves & Baker, 2000) and they possess toxic effect when the intake exceeds certain amount (Blaylock & Huang, 2000). Examples of essential heavy metals include Cu, Zn, Co, Cr, Mn and Fe. Heavy metals such as Ba, Al, Li and Zr are classified as non-essential heavy metals. Sn and Al are less toxic whereas Hg and Cd are highly toxic (Raikwar *et al.*, 2008).

Heavy metals are pollutants that possess significant ecological importance. They cannot be eliminated from water by natural purification process. Instead, they will be collected in suspended particulates and sediment before entering the food web through primary consumer (Ghrefat & Yusuf, 2006; Khaled *et al.*, 2006).

There are over 50 elements that can be classified as heavy metals, but only 17 that are considered to be extremely toxic and more accessible. Mercury, selenium, lead, copper, cadmium, zinc, arsenic, chromium and nickel should be given particular attention in terms of heavy metals pollution in water (Ranjeeta, 2012).

The World Health Organization (WHO) has provided the guideline values of heavy metals in drinking water. The guideline values for copper, cadmium, mercury, lead, iron, manganese, selenium and zinc were 0.003 mg/L, 2 mg/L, 0.01 mg/L, 0.006 mg/L, 2 mg/L, 0.05 mg/L, 0.04 mg/L and 3 mg/L respectively (WHO, 2011; WHO, 2003).

It is well known that mercury forms complexes with sulphur. This property can be applied to treat acute mercury poisoning. The complexes between mercury and selenium which are less known, possess higher binding affinity. Physiologically, sulphur is present more abundantly than selenium. However, due to the higher binding affinity of selenium, mercury binds to selenium selectively to form insoluble mercury selenides (Gilbert & Grant-Webster, 1995; Moller-Madsen & Danscher, 1991). This interaction prevents negative impacts of mercury toxicity to living organism (Whanger, 1992).

The median iron concentration in rivers was 0.7 mg/L. In anaerobic groundwater where iron is normally in the form of iron (II), the concentrations ranged from 0.5 to 10 mg/L. However, sometimes the concentration could increase up to 50 mg/L (NRC, 1979). Copper concentrations of an uncontaminated environment can be a few thousands mg/kg (Harrison & Bishop, 1984). The concentrations of copper is the highest in reservoirs and increase with organic matter content (Anderson *et al.*, 1994).

Sediment samples from a reservoir in Albany County, New York with depth ranging from 0 to 1.68 m showed an average cadmium concentration of 1.69 mg/kg. This value is similar to other reservoir and stream sediments polluted by industrial pollutants (Arnason & Fletcher, 2003).

2.2 Water, sediment and fish

2.2.1 Water

Water quality is a main factor in the sustainability of aquaculture. Large scale fatality in marine organisms and poor growth in cultured species are commonly related to the contamination of water (Hashmia *et al.*, 2002).

2.2.2 Sediment

Sediment is any soil particles that are settled at the bottom of water body (Akpan & Thompson, 2013). They play an important role in identifying pollution level of aquatic systems (Casas *et al.*, 2003). Besides, they function as transporter and sinks for pollutants, thus reflects the history of pollution (Singh *et al.*, 2005), and provides a record of catchment inputs into the particular aquatic system (Mwamburi, 2003). Sediments were often found to be contaminated with various hazardous and toxic substances (Zabetoglou *et al.*, 2002), including heavy metals.

In the sediments, heavy metals accumulate *via* complicated physical and chemical adsorption mechanisms depending on the type of the sediment matrix and the properties of the adsorbed compounds. There are several physico-chemical parameters that will affect the adsorption process. These include pH, inorganic and organic carbon content, dissolved oxygen, oxidative-reductive potential, and the presence of certain anions and cations in a water phase (Ghrefat & Yusuf, 2006).

There are several indices used to evaluate the enrichment of metals in sediments. The geo-accumulation index and enrichment factor are most commonly used to measure the anthropogenic inputs in sediment (Covelli & Fontolan 1997; Ghrefat & Yusuf 2006; González-

Macías *et al.* 2006; Chen *et al.* 2007). The enrichment factor normalises the measured heavy metal concentration with respect to a reference metal such as iron or aluminium (Ravichandran *et al.*, 1995) as they are considered to act as a substitute for the clay content (Windom *et al.*, 1989; Din, 1992). Table 1 summarises the enrichment value and the degree of enrichment. The metal enrichment factor (EF) is calculated as

$$EF = \frac{\frac{M_{sample}}{Fe_{sample}}}{\frac{M_{background}}{Fe_{background}}}$$

where:

M_{sample} concentration of the examined metal in the examined sediment

Fe_{sample} concentration of the reference metal in the examined sediment

$M_{background}$ concentration of the examined metal's natural background value

$Fe_{background}$ concentration of the reference metal's natural background value

Table 1 Enrichment factor value and degree of enrichment

Enrichment factor value (EF)	Degree of enrichment
< 1	No enrichment
< 3	Minor enrichment
3-5	Moderate enrichment
5-10	Severe enrichment
25-50	Very severe enrichment
> 50	Extremely severe enrichment

The geo-accumulation index (I_{geo}) is used to identify the degree of metal pollution in sediments. The index is expressed as follows. Table 2 shows the Muller's classification of the geo-accumulation index.

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right)$$

Where:

C_n is the measured concentration of the heavy metal (n) in the sediments

B_n is the geochemical background value of element n

1.5 is the background matrix correction factor due to lithogenic effects

(Ghafar and Yusuf 2006; González-Macías *et al.* 2006; Chen *et al.* 2007).

Table 2 Muller's classification for geo-accumulation index (Muller, 1981)

I_{geo} value	Class	Quality of Sediment
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
≥ 5	6	Extremely polluted

The Pollution Load Index (PLI) is used to relate the pollution effect at different stations by different metals (Salomons & Forstner, 1984). PLI for a particular site is expressed as:

$$\text{PLI} = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)/n$$

where n is the number of metals

The contamination factor and the degree of contamination are used to examine the contamination status of sediment (Hakanson, 1980).

$$\text{Contamination factor (CF)} = \frac{\text{Concentration of metal in the sediments}}{\text{Background value of the metal}}$$

Factors Affecting Sediment-Heavy Metal Concentrations

1. Grain Size

Grain size is one of the major factors that will affect the capacity of sediment to retain heavy metals (Hirst, 1962; Jenne, 1968; Jones & Bowser, 1978; Thorne & Nickless, 1981). The concentrations of trace metal increase with decreasing grain size (Jones & Bowser, 1978).

2. Iron and Manganese Oxides

Iron and manganese oxides are excellent scavengers of heavy metals from solution regardless of their form (Forstner & Wittmann, 1979).

3. Organic Matter

It is well recognized that organic matter are able to concentrate heavy metals in and on soils as well as sediment (Kononova, 1966; Nriagu & Coker, 1980; Ghosh & Schnitzer, 1981; Forstner, 1982a,b). The organic matter is generally known as humic substances and is categorized into four categories, namely humic acids, humins, yellow organic acids and fulvic acids (Jonasson, 1977). The ability of organic matters to concentrate metals depends on their constituents and type (Swanson *et al.*, 1966; Rashid, 1974; Jonasson, 1977).

4. Clay Minerals

Clay minerals is another collecting and concentrating agent of heavy metals in aquatic systems (Hirst, 1962; Jones & Bowser, 1978; Forstner & Wittmann, 1979; Forstner, 1982a,b). The major function of clay as metal concentrating agent is to act as a site for the precipitation and flocculation of organic matter and other minerals.

2.2.3 Fish

Fish are basically one of the most important protein sources for humans (Eletta *et al.*, 2003).

They act as a bioindicator in determining the heavy metal pollution since they are the top consumers in aquatic ecosystems (Dallinger *et al.*, 1987; Wildianarko *et al.*, 2000).

Food chain and water are the possible channels for accumulation of heavy metals. Heavy metals may enter fish bodies through their digestive tract, gills or body surface (Pourang, 1995).

Factors including the life cycle, life history and food items will affect the uptake of metals in fish. Other factors such as ecological needs, size and age of individuals, season of capture as well as physico-chemical parameters of water may also affect the heavy metals uptake by fish (Canpolat & Çalta, 2003).

In fish, concentrations of almost all the metals (except for mercury) are generally inversely associated to the age and size. A study revealed that the concentrations of Cu, Fe, Ni, Mn, Zn, and Pb have an inverse relation with body mass of fish from a mine-polluted impoundment. The field data in addition shows that the concentration of mercury in fish is linearly proportional to the age and size, probably associated with the affinity of mercury to the muscle tissue of fish (Munn & Short, 1997; Green & Knutzen, 2003).

2.3 Impacts of heavy metals

2.3.1 Impacts of heavy metals on fish

The concentrations of heavy metals bioaccumulated in fish depends on the variability in size and age of fish (Salanki & Salama, 1987). According to Ebrahimi and Taherianfard (2011), exposure of fishes to heavy metals will induce some pathological changes.

Metals such as lead, mercury, arsenic and cadmium are examples of non-essential heavy metals that are very toxic to living organisms (Amiard *et al.*, 1987; Barka *et al.*, 2001; Hanna *et al.*, 1997). For instance, lead in water can cause generative damage in some aquatic life and cause blood and nervous alteration in fish and other living organisms (Kalay *et al.*, 1999; Weis & Weis, 1989).

Other heavy metals such as zinc can cause changes in behaviours of fish including deficiency of balance, restless swimming, air guzzling, periods of dormancy and death (Kori & Ubogu, 2008). Besides, it also leads to development of certain degree of anaemia in fish (Caring, 1993).

2.3.2 Impacts of heavy metals on human

Heavy metals possess hazardous effects on human because they interfere with the biochemistry of the metabolic processes. When consumed, they are converted to stable oxidation states, combining with the biomolecules in body forming strong and stable chemical bonds (Ogwuegbu & Ijioma, 2003).

Different heavy metals could cause different health hazards to human. Cadmium exposure during human pregnancy causes reduced birth weights and premature labor (Henson & Chedrese, 2004). Intensive exposure to water contaminated with copper may result in anaemia,

kidney and liver damage (Madsen, *et al.*, 1990). Copper toxicity is also the main cause of the Wilson's disease (Patil & Ahmad, 2011).

Excess amount of iron can cause rapid increase in pulse rate and coagulation of blood in blood vessels, high blood pressure and drowsiness. Zinc compounds on the other hand are corrosive to skin, eye and mucous membrane. They cause distinct types of dermatitis known as "zinc pox" and irritate the digestive tract resulting in nausea and vomiting (Patil & Ahmad, 2011).

Fish and human are primarily exposed to lead by consuming contaminated food and breathing. Lead typically accumulates in muscles, bones, blood and fat (Elder & Collins, 1991). Possible adverse effects caused by lead includes critical damage to liver, kidneys, brain and nerves, reproductive disorders, increase in heart disease, high blood pressure, anaemia, behavioural disorders as well as learning deficits (Afshan *et al.*, 2014; Patil & Ahmad, 2011). In young children, it also cause hormonal imbalance of metabolite of vitamin D and diminished IQ (Tandon *et al.*, 2001; Siddiqui *et al.*, 2002; Lindbohm *et al.*, 1991).

Selenium is an essential heavy metal. It is crucial to humans, animals and even some plants. However, the safety tolerance is very narrow (Nève *et al.*, 1987; Dubois & Belleville, 1988; Oldfield, 1997). One of the important functions of selenium is to protect the cells and tissues against oxidative damage, leading to normal functioning of immune system as well as protect human from various tumours (McKenzie *et al.* 1998; Rayman, 2000; El-Bayoumy, 2001). Selenium deficiency causes development of some viral infections due to weakened immune system (Baum *et al.* 1997).

Besides, selenium has anti-oxidative and anti-inflammatory effects that will inhibit the production of free radicals and reactive forms of oxygen (McKenzie *et al.* 1998). This anti-oxidative and anti-inflammatory effects exist not only during cardiovascular disease, but also during some other inflammatory disease such as rheumatoid arthritis or pancreatitis (Rovensky *et al.*, 2002).

Although selenium is an essential heavy metal, it can be toxic if it exceeds certain concentration. Selenium is found to be inversely associated to bladder cancer risk (Eliane *et al.*, 2006).

Mercury is a heavy metal of increasing concern that can be considered as a global pollutant. Primarily, human are exposed to methyl mercury *via* fish consumption. Due to the toxic effect of methyl mercury which will cause health problem, it is listed as one of the most unsafe chemicals in the environment by the International Program of Chemical Safety (Gilbert & Grant-Webster, 1995).

Adults may experience neurological effects when exposed to methyl mercury in high concentration. Unborn and growing children are even more susceptible to the exposure. It is well known that placental barrier can block many toxic elements. Unfortunately, methyl mercury is the only toxic element that can cross the placenta and even tends to be accumulated at higher concentration on the fetal side than on the maternal side (Iyengar & Rapp, 2001). Moreover, mercury also crosses the blood-brain barrier and shows long-term retention once it gets across (Kerper *et al.*, 1992).

The accumulation of chromium in human body depends on the uptake and elimination from the body (Karadede *et al.*, 2004). Some hazardous effects of chromium to human include faded immune system, various skin diseases, disruption to respiratory systems, mutation and thus cancer (Afshan, 2014).

Arsenic has been known to be related to high blood pressure and severe impacts on the cardiovascular system (Lee *et al.*, 2003; Yoshida *et al.*, 2004) whereas exposure to cadmium increases calcium excretion thus causes skeletal demineralization. This may further lead to increase in bone fragility and risk of fractures (Wu *et al.*, 2001).

Nickel results in embryo toxic and allergic reactions, nephrotoxic effects, and contact dermatitis. Nickel sensitization may also cause conjunctivitis, eosinophilic pneumonitis and asthma. It is a probable human carcinogen that results in lungs and nasopharyngeal cancers (Sharma *et al.*, 2011).