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DETERMINATION OF ALUMINIUM, IRON, SULFATE AND CHLORIDE IN LIKAS LAGOON, KOTA KINABALU, SABAH.

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DECLARATION

I hereby declare that all writings are based on self effort excluding quotations and summaries whereby the detail of sources has been clarified.

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ABSTRACT

Originally, Likas Lagoon was developed as a retention pond for flood water discharged from Dah Yeh Villa and Likas Jaya areas. But, it is also a well known place for fishing, bird watching and a habitat for many types of species. However, the result from the analyses of surface water for Likas Lagoon indicates that Likas Lagoon is moderately polluted. The pH is almost neutral (mean value of 7.13), sulfate concentration ranged from 30.00 to 57.00 mgL^{-1} SO_4^{2-} and chloride concentration ranged from 12.00 to 31.99 mgL^{-1} Cl^-. These three parameters were recorded as below the level that has been limited in INWQS. Meanwhile, the aluminium concentration ranged from 0.27 to 0.62 mgL^{-1} Al^{3+} and iron concentration ranged from 0.37 to 2.61 mgL^{-1} Fe, which have exceeded the level of INWQS for both parameters. Water monitoring in Likas Lagoon should be done to maintain a good quality.

PENENTUAN KEPEKATAN ALUMINIUM, FERUM, SULFAT DAN KLORIDA DI LAGUN LIKAS, KOTA KINABALU, SABAH.

ABSTRAK

Lagun Likas yang terletak berhampiran dengan Kota Kinabalu City Bird Sanctuary merupakan salah satu kawasan yang sememangnya terkenal sebagai habitat pelbagai spesies. Kajian yang telah dijalankan ke atas air permukaan Lagun Likas menunjukkan kawasan ini adalah sederhana tercemar. Nilai min pH bagi Lagun Likas ialah 7.13, julat kepekatan sulfat pada 30.00 hingga 57.00 mgL^{-1} dan julat kepekatan klorida pada 12.00 hingga 31.99 mgL^{-1}. Ketiga-tiga parameter ini berada di bawah julat yang telah ditetapkan oleh Jabatan Alam Sekitar. Kedua-dua parameter yang melebihi tahap yang telah ditetapkan dalam INWQS iaitu aluminium yang mempunyai julat kepekatan pada 0.27 hingga 0.62 mgL^{-1} dan ferum yang berjulat pada 0.37 hingga 2.61 mgL^{-1}. Pemonotoran kualiti air di Lagun Likas seharusnya dijalankan untuk mengetahui status semasa kualitinya.

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%	percent
H_2O	water
ORP	oxidation-reduction potential
DO	dissolved oxygen
BOD	biological oxygen demand
COD	chemical oxygen demand
TOC	total organic carbon
gml^{-}	gram per milliliter
$AgNO_3$	silver nitrate
NaCl	sodium chloride
DNA	deoxyribonucleic acid
Si	Silicon
F	Fluorine
Ca	Calcium
°C	degree Celsius
$mg\ kg^{-1}$	miligram per kilogram
ppm	part per million
mL	milliliter
mgL^{-1}	milligram per liter
g	gram

LIST OF ABBREVIATIONS

INWQS	Interim National Water Quality Standards
DOE	Department of environment
RSD	Relative Standard Deviation

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Since almost 71% of our Earth's surface is water, it is the most abundant substance on Earth. However, from that percentage, 97% of it is sea water and the remaining 3% is fresh water. It is widely known that the chemical formula for water is H_2O which can exists in three different conditions that are liquid, solid and gas. Physical properties, chemical properties and biological properties are the major aspects to understand the behavior of the water.

Some of the physical properties of water that are often being discussed and analyzed are temperature, taste, odor, color, turbidity, solids, electrical conductivity and radioactivity. Water's chemical characteristics are more specific in nature such as pH, oxidation-reduction potential (ORP), alkalinity, acidity, hardness, dissolved oxygen (DO), oxygen demand (BOD, COD and TOC), nitrogen, chloride and trace organics. In the aspect of biological characteristics, living organisms play valuable roles in wastewater treatment or water treatment but some of them are also considered

as sources of potential nuisance and hazard in relation to drinking water (Tebbutt, 1992). For an example in examining water's biological properties, Daphnia can reduce the number of bacteria in water while *Escherichia coli* from human feces can cause enteric diseases to human.

Freshwater is a finite resource, essential for agriculture, industry and even human existence (Bartram and Ballance, 1996). It is true that many of our daily activities depends so much on water such as power plant, agriculture, factory, construction and mining that needs water as a cooling agent or involved in majority of the processes. Even human body needs clean water to maintain our health. Any activities that require water will then discharge waste or wastewater that cannot be used again directly and needs treatment. Treatment of water is so essential since freshwater is a finite resource and to make sure it is safe as a drinking water (Bartram and Ballance, 1996).

It is well known that Likas Lagoon has become a habitat for numbers of species and also a place for the fishermen to catch fishes using net daily. As an initiative to prevent all the living aquatic species in Likas Lagoon from threat of suffocated by solid waste such as plastic, Kota Kinabalu City Hall has to clean the lagoon everyday. However, there are still plastic, woods and aluminium tin that can be seen floating in Likas Lagoon. The monitoring of water quality for Likas Lagoon needs to be done since it has been an important habitat to a lot of birds, fishes and vegetations. Other reason is to prevent Likas Lagoon from algae blooming and to prevent from the same tragedy from happening, where a lot of fishes died suddenly.

Water treatment is important nowadays to ensure the hygienic of the water that will be consumed by all living organisms in this earth. However, human activities, high technology machines, growth of population or other activities may directly or indirectly making our clean and limited fresh water easily polluted. Determination of metal concentration in water is important to understand their role in biogeochemical processes occurring at the coastal environment. The adsorption, chemical adsorption and ion exchange processes also play a role in geochemical cycling of heavy metals in coastal water.

1.2 Objectives

The objectives of this study are:

1. To determine the concentration of Aluminium, Iron, Sulfate and Chloride in the surface water of Likas Lagoon.
2. Compare the data with Interim National Water Quality Standards for Malaysia (INWQS).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Every element occurs in water naturally in a suitable concentration. Some substances that are essential to life can be highly toxic when present in large amounts (Mason, 1996). However, human activities are the main factor that increased the concentration to an undesirable level where it could harm all the aquatic organisms. It is important to know that population growth has increased the level of pollution in this world. Environment management became an important aspect to maintain the environment in a suitable condition. Determination of metal concentration in water is important to understand their role in biogeochemical processes occurring at the coastal environment. The adsorption, chemical adsorption and ion exchange processes also play a role in geochemical cycling of heavy metals in coastal water.

Pollution can be defined as undesirable change in the physical, chemical or biological characteristic of the air, water or land that may harm health, survival or activities of humans or other living organisms. Water pollution might caused people to

die from water-borne diseases, ecosystem dysfunction, loss of diversity, contaminations of freshwater and marine ecosystem from land-based activities, contamination of groundwater resources and global contamination by persistent organic pollutants (Trudgill *et al.*, 1999).

Acid, alkali, anion, detergent, domestic sewage, farm manures, food processing wastes, gases, heat, metals, nutrients, oil, organic toxic wastes, pathogens, sediments, heat, polychlorinated biphenyls and radionuclides are some of the pollutant that have been identified as causing of water pollution. It has been identified that there are two major sources of water pollution. The first source is known as point sources where the effluent discharged is readily identified, almost in a constant volume and fixed composition. Meanwhile, the second source is known as nonpoint sources where the place of the effluent discharged is unidentified, composition and volume is unknown.

Heavy metal refers to a number of metals that have a relatively high atomic number (Botkin and Keller, 2003). The natural processes of weathering, erosion and volcanic activity are known to be the sources of trace metals in the environment (Salomans and Förstner, 1984). However, human activities such as extraction of ore from earth's crust also become a source of trace metals. Sources of trace metals in lakes are the atmosphere (from wet or dry deposition), riverine inputs (fluvial input of dissolved or particulate form) and various waste discharges (Salomans and Förstner, 1984). Even though the atmosphere is one of the sources of trace metals in lakes, but it is a minor source for aluminium, iron and cobalt.

Metals can be found in aquatic systems in many forms. According to Salomans and Förstner (1984), the major metal forms that have been identified are:

i. Oxidized form : iron oxides, manganese oxides or sulfur precipitated by oxidation of reducing solution. Usually caused by water emergence at the surface or a flow reducing water out of a swamp,

ii. Reduced form : uranium, vanadium, copper, selenium and silver precipitated as metals or lower-valency oxides by reduction of oxidizing water. Usually caused by an encounter with organic matter or mixing with reducing waters or gases,

iii. reduced sulfide form : iron, copper, silver, zinc, lead, mercury, nickel, cobalt, arsenic and molybdenum are precipitated as sulfides by reduction of oxidizing sulfate waters. It is usually caused by the action of sulfate-reducing bacteria. Uranium, vanadium and selenium can also be precipitated through the same reducing type but dissolved sulfates are required,

iv. sulfate-carbonate form : barium, strontium and calcium precipitated by increased sulfate or carbonate as a result of mixing of waters, the oxidation of sulfide or passage into carbonate rock,

v. alkaline form : calcium, mercury, strontium, manganese, iron, copper, zinc, lead, cadmium and other elements precipitated by increased pH. The interaction of acid waters with carbonates or silicate rocks and the mixing with alkaline water are the main cause of this type,

vi. absorptive form : adsorption or coprecipitation of ions on accumulations of iron-manganese-oxides, clays and organic materials. It is known that the cations from transition metals and those with high valence tend to be more strongly adsorbed than anions and low valency cations.

Both forms, dissolved and particulate can be found in water. Usually, the dissolved metals will be removed from water by absorption or by uptake by biota. Meanwhile, the particulate form will settle to the bottom with sediment. The changes in trace metal concentrations are determined directly or indirectly by the carbon cycle in the lake. Higher concentration of trace metal in lakes especially for manganese and aluminium are due to the acidic pH.

An atom or a group of atoms with a net positive or negative charge are known as ion. An ion with a net positive charge is called cation that results from the loss of one or more electrons from a neutral atom. Meanwhile, anion is an ion whose net charge is negative due to an increase in the number of electrons (Chang, 2005). Enrichment of anions might cause acidity, water hardness by binding with metallic ions or influence the water's alkalinity.

Generally, lagoon is a lake of salt water that is separated from the sea by a reef or an area of rock or sand. The formation of lagoon can be naturally by the impacts of waves or indirectly due to the reclamation activities. However, lagoon might loss its salinity if the input of seawater into the lagoon is being controlled. Lagoon is one of the most important habitats for many kinds of living organisms such as birds, fishes, algae and others. Likas Lagoon was originally developed as a retention pond for flood water discharged from Dah Yeh Villa and Likas Jaya areas. Due to the sediments that carried by inland water, the depth of the Likas Lagoon are reducing and allowing vegetation to grow there such as grass, sedges, water hyacinth and mangroves trees.

2.2 Aluminium (Al)

Aluminium is an important parameter for evaluation of acidic deposition effects in drainage systems because of its influence on acid neutralizing capacity and also because of its toxicity to aquatic biota (Sullivan, 2000).

2.2.1 Properties of Aluminium

The atomic number for aluminium is 13 and it has an atomic mass of 26.98. Aluminium is not a heavy metal because of its density is 2.70 g ml^{-1} (Yokel, 2004). It is known to be the third most abundant element (7.5%) and the most plentiful metal that can be found in the earth's crust and oceans. Aluminium is amphoteric (behaving both as Brønsted acid and base), its solubility increases at pH values below about 5.5 (Sullivan, 2000) and it is not one of a transition element because its d or f shells do not have unpaired electrons. Although aluminium is considered an active metal, it does not react with water as do sodium and calcium because the metallic properties of an element decreased from left to right of a periodic table (Chang, 2005). Usually, aluminium reacts with hydrochloric acid or strong bases. At a normal temperature, aluminium exists in two valence states, +3 and 0 that cannot be found in the environment because aluminium is one of the most reactive of the common metals. The melting point of aluminium is at 660.4°C and the boiling point is 2467°C.

Aluminium oxide readily forms on the surface of aluminium making it less reactive than elemental aluminium and it protects the metal from further chemical attack (Meyer, 1990) due to the exposure of aluminium to water, oxygen and other

oxidants. This nanometer thick film, aluminium oxide, is very high resistance to corrosion and it is insoluble from pH 4.5 to 8.5. Basically, aluminium is a small, hard metal ion (Lewis acid) with a high charge density that prefers to coordinate with hard Lewis base such as OH^-, SO_4^{2-}, PO_4^{3-}, COO^-, ROH and RO^- or might also bind with amines as part of a multidentate ligands system.

2.2.2 Sources of Aluminium

The sources of aluminium in environment are from natural sources and acidification that increases its concentration. Almost all aluminium is obtained from bauxite that contains up to 60% alumina. Aluminium never occurs as the free metal in nature but generally will combine with oxygen, silicon and fluorine due to its reactivity. Majority of the aluminium that is found in the earth's crust occurs in primary minerals which combine with silica (in feldspars and micas) and in aluminosilicate clay minerals (kaolinite and smectites). When weathering occurs, the silica will be dissolved away and aluminium will remain in oxide or hydroxide form. However, in subsoil water, lakes, rivers and seawater, the concentration of aluminium at neutral pH is low due to the formation of secondary hydroxo phases (Frech and Cedergren, 1992).

In natural waters, aluminium is mainly derived from chemical weathering of rocks and minerals. According to Bache (2000), acid deposition onto land surface has decreased the pH and increased the aluminium solubility. With pH below 5 in aqueous solution, $AlOH(H_2O)_6^{3+}$, $AlOH(H_2O)_5^{2+}$ and $Al_8(OH)_{40}^{4+}$ are the principal ionic species that will occurs but at higher pH, formation of colloidal particles [$Al(OH)_3$] will occurs.

Others anions will successfully compete with the hydroxide in complexing aluminium and majority of the aluminium found in natural water complexed to humic substances (Almer, 1978). The concentration of aluminium in lake sediments is small if the acidity of the soil water is low due to the contents of hydromorphic aluminium. The soluble aluminium will increase if the soil is acidified. In surface waters with pH above 5.5, the aluminium will be predicated out while at the pH below 5, large amounts of aluminium will be present in the incoming solution and can dissolve aluminium from the lake sediment. So, acid waters are highly enriched in aluminium.

Activities such as refining of the primary metal, manufacturing or welding aluminium and people living near the industrial emission sources or hazardous waste sites are the population that is at risk from elevated aluminium exposure. Aluminium compounds are often used in many activities such as water purification, sugar refining, brewing, paper production, glass, ceramics, rubber, wood preservatives, waterproofing textiles, abrasives, furnaces lining and as leavening agents (Yokel, 2000). Aluminium is mostly used in structural materials in building, construction, transportation, packaging, containers because of its physical properties; it is light, strong and easily machined. In many applications, aluminium and aluminium alloys are used because of their ability to resist corrosion at pH 4.5-8.5 due to the build up of aluminium oxide on its surface. Aluminium is a component that can be found in many consumer products such as antacids, buffered aspirin products and antiperspirants. Some of the products that might contains aluminium are acne cleaning preparations, dental rinses, toothpastes, first aid antibiotics, antiseptics, sunscreen, insect sting and bite and diaper rash. There is also evidence that aluminium increases with water treatment where the

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