PHYSICAL, CHEMICAL AND MICROBIOLOGY CHARACTERISTIC OF SIDOARJO MUD AND WATER

DISERTASI

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CHAPTER I

INTRODUCTION

1.1 Background of the Study

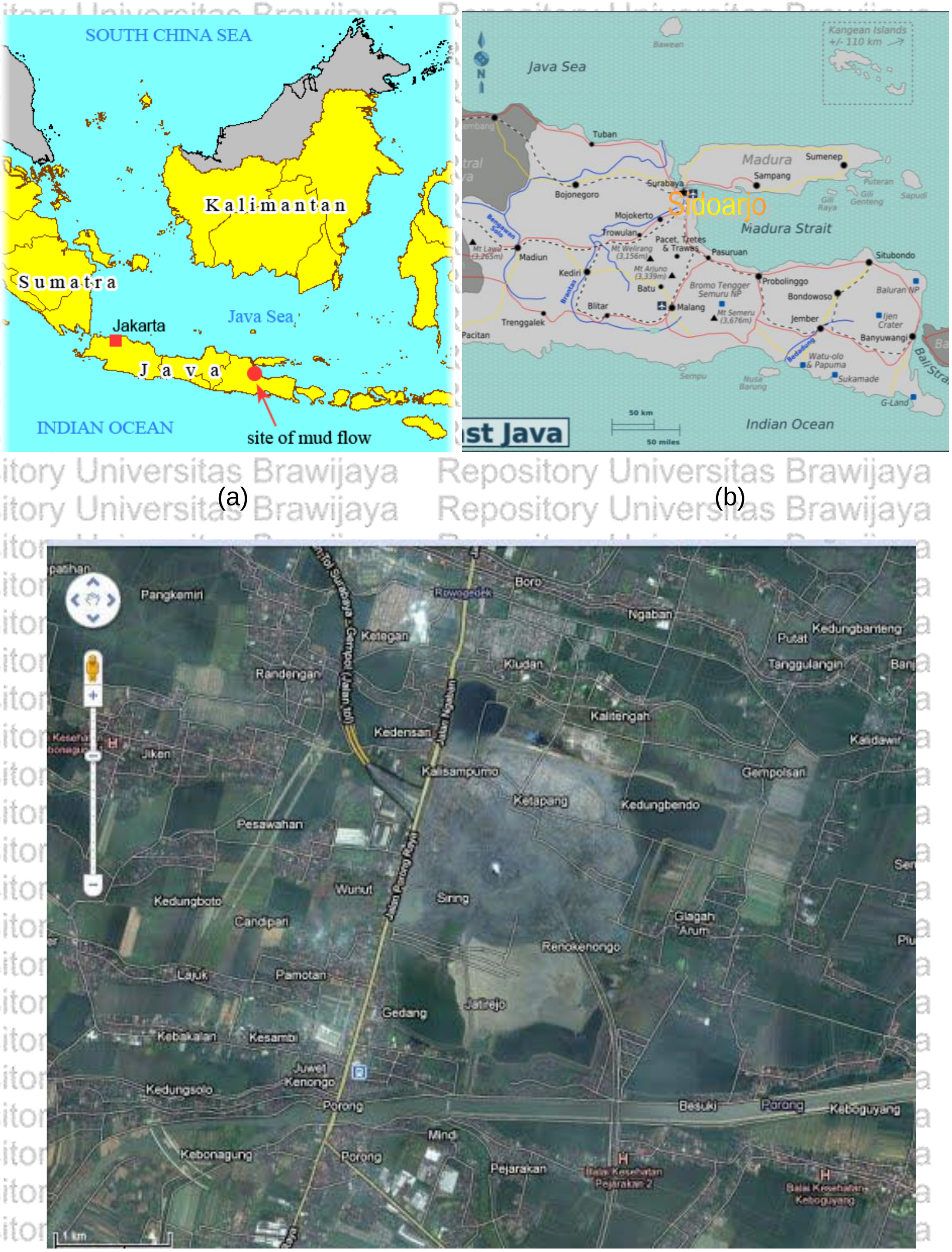
The river, lake, and ocean sediments have been contaminated by pollutants. According to Begum et al., (2009), several of these pollutants are discharged directly by industrial areas and municipal waste treatment. On the other hand, the other pollutants may come from polluted runoff in agricultural and urban areas. Contaminated sediments could endanger creature in the benthic environment. Several toxic sediments can kill benthic organisms. It can reduce the food source in the food chain in the environment. Furthermore, Begum et al., (2009) state that some contaminants can be processed by benthic organisms, it is well-knows as bioaccumulation. Consequently, when larger animals consume the contaminated organisms, the toxin will flow through food chain and it the accumulation is knows as biomagnification. As a result, waterfowl, fish, freshwater and marine mammals can accumulate the toxic chemicals in the environment (Begum et al., 2009).

Contaminated sediments are not always in the bottom the water environment. Many possiblities for this condition such as dredging that can re-suspend sediments. The re-suspension is dangerous becaiuse it exposed to toxic contaminants directly (Begum et al., 2009). One possible way is from the explosion of mud volcanoes.

According to Mazzini et al., (2007), mud volcanoes are geologically essential sources of vertically flowing fluid and the eruption in sedimentary basins in the world. Mazzini et al., (2007) explain that the mud volcanoes formation can release overpressure from clay and organic-rich sediments which may bring impressive accumulation of mud volcano in marine areas. Moreover, the existence of mud volcanoes is related to high methane fluxes in seafloor (Charlou et al., 2003), crusts of carbonate (Aloïsi et al., 2002) and hydrate gas. These volcanoes occur both on land and on the seafloor (Milkov, 2000).

Obviously, a recently born mud volcano is appearing near an active magmatic complex in the back arc sedimentary basin near Sidoarjo, Indonesia. An explosion of mud volcano happened in Sidoarjo Regency in 2006. The location which surrounded by magmatic volcanoes cause it has high temperature which triggers fast mineral transformation and geochemical reactions in the shallow depth of soil surface. The clear location of the mud explosion is shown in Figure 1.

The mud volcano explosion started on May 26th 2006. It happened when the first gas and mud volcano spewed from well in drilling activity area, Sidoarjo. Since then until two years ahead, the flowing rate of the mud was ranging from 100,000 to 180.000 m^3 per day (Plumlee et al., 2008; Jalil et al., 2010; Mazzini et al., 2007). The mud rapidly affected Sidoarjo area and has buried houses, villages, schools, factories, and forced thousands of people to evacuate and continues to pose geohazard risks in a densely populated site with many infrastructures (Istiadi et al., 2009). Although some scientists believed that the mud volcano eruption has been triggered by drilling activity, while some geologist explained that the earthquake occurred in previous day was the cause of it (Istiadi, 2007). Agency for The Assessment and Application of Technology (BPPT) stated that mud source was located in 1000-2000 meters of dept under the ground.



(a) (b)

(c)

Figure 1. (a) Site of Mud Flow Indonesia, (b) Sidoarjo, East Java, and (c) Sidoarjo mud volcano

Instead of the controversial presence of Sidoarjo mud volcano, the government and the society have to work together to overcome the mud explosion affect to the environment (Mazzini et al., 2007). In addition, legal water, land and air monitoring is urgently needed. As the eruption can be a mud volcano forming which might be impossible to stop, Indonesia government decided that the mud volcano needed to be discarded through Sidoarjo River to minimize the potential detrimental effects to the environment and local population (Mazzini et al., 2007).

In one side, the flooding mud will create sediment which can be used to study the structure of the soil. Sediments are the key determinant to study the ancient and historical environments. The sequence of sedimentary layers shows the environmental changes that happened over time (Hallberg, 1992). The recent sedimentary record will discover the cultural impacts on the environments during the industrial time. As during formation and diagenesis the sediments play an active role in the biogeochemical phases of the elements which affect the overlying water column, from the sediment, the physical characteristics of the mud can be identified.

In addition, some studies were conducted to identify the correlation between physical appearance and textural parameters of sediments (Nobes et al., 1991; Kim et al., 2001; Casas et al., 2004) explain that the sediment phisical characters depend on grain size, lithology and varied components proportion found in the sediment such as silica, biogenic carbonate, quartz and clay. Hamilton et al., (1982) stated that the wet-bulk density is linked to the grain density and porosity, while grain density itself is partially controlled by grain size. Moreover, the acoustic velocity is determined by porosity, carbonate and clay content (Hamilton et al., 1982). Physical properties are not only affected by diagenetic effects, but also by cementation and carbonate dissolution (Nobes et al., 1991). Evaluations of physical properties of the sediment samples consisted of particle size distribution analyses (mean grain size, sand silt, and sand content) and determine percent moisture (water holding capacity) and percent volatile solids or the texture of sediments.

However, according to Mazzini et al., (2007), the mud input from Sidoarjo was reported twice the amount of the suspended matter and particulate organic carbon load of the nearby river. In addition, decomposition of the additional organic matter was found to worsen the depletion of oxygen in the river that may severely impact on the aquatic organisms. Finally, the mud volcano input brings the serious impacts on human activities in the river catchment on the ecology and biogeochemistry of Madura Strait and the estuary waters due to the inorganic contents and metals in the mud (Mazzini et al., 2007).

Obviously, the presence of metals is the indication of polluted environment and the metal toxicity are biologically non-degradable. They can accumulate in water, sediment and fish (Gale et al., 2004). Metal contamination of the environment is resulted from natural sources and industrial activities. Besides, metals in soil and water can enter the food cycle through air (Gül, 2009). The Heavy metals can accumulate in the water because the product from agriculture, industrialization and mining (Olajire et al., 2003).

In addition, industrial effluents disposal also comprises about 62% of total heavy metal source such as lead, nickel, cadmium, manganese, and chromium. These heavy metals poisoned water and decreased the water biodiversity because of aquatic organism unable to survive (Garba and Abubakar, 2006). Heavy metals contained in water can be accumulated on food sources, such as fish which consumed by human. Poisoned fish will cause some health problems to human which make it unproper to be consumed (Sunday et al., 2013). The toxic metals have been reported to accumulate mainly in liver and the kidney. It can make kidney disfunction. Steoppler (1992) explain that it can enter the blood stream and it accumulate in the liver immediately.

Obviously, it was reported mud volcano in Sidoarjo have several content that consisted of 105.44 ppm Chromium (Cr), 0.99 ppm Arsenic (As), 10.45 ppm (parts per million) Cadmium (Cd), and 1.96 ppm Mercury (Hg) (Antara, 2006). Moreover, Mawardi (2006) stated that the Hg content was higher, approximately 2.5 ppm. Furthermore, the study from Pohl, the mud consisted of phenol at concentrations over the maximum residue limit. It is toxic to fish, aquatic vegetation, and health (Pohl, 2007). Based on ICBB data, mud volcano in Sidoarjo contains some dangerous bacteria that are *Staphylococcus aureu, Coliform*, and *Salmonella* (Antara, 2006). The mud volcano always emits hydrogen sulphide (H_2S) from the gushing mud centre. H_2S levels were at 700 ppm on the first day of mud flow. It is 3 ppm on the second day and it is gone on the thrid day. Furthermore, low level of H_2S still continue to spew out at certain levels. This causes the air smell foul.

Sidoarjo mud volcano has been predicted containing thermophilic bacteria with capability to adapt in high temperature environment (Akhdiya, 2003). Thermophilic bacteria possess thermostable enzyme which allow it to survive in high temperature. The exploration of this enzyme will give benefit in fish product processing which occur in high temperature condition. On the other side, some microorganisms take the role in waterborne disease outbreak. They are the most common disease-causing contaminant in private well water. Moreover, microorganisms are the source of most widely used enzyme compared to plants and animals. As a source of enzymes, microorganisms are more useful because they can grow rapidly. Besides, they can grow easily, can be modified, and also capability of producing fuctional enzymes are the other benefits (Akhdiya, 2003).

Apart from being contained metal and microorganism, sediments are solid materials that settle at the bottom of water bodies. Sediments accumulate heavy metals rapidly and usually deplete them very slowly by leaching into ground water aquifers (Enguix et al., 2000). Physical effects, such as in sediments, decrease light penetration and burg riverbed gravels used by spawning clog gills and fish. These can cause the decomposition of organic matters which uses up oxygen which is available to organisms in water. It may distort water quality, adding color and also hindering economic activities (Asonye et al., 2007). Besides, the accumulation of mud from the original vent is accompanied by subsidence in the surrounding area. It has been projected that more than 30 metres of subsidence will occur in the next few years within several kilometres of the eruption vent. The possibility exists that a massive crater will form from the hollowed-out remains of the mud volcano. Dried mud deposits could have adverse effects on river and marine environments also on the health of local residents (Plumlee et al., 2008).

Furthermore, there are many evidences that the Sidoarjo mud volcano has a harmful impact on river ecosystems and human health. The mud has been analyzed and it contain phenol in concentrations more than the maximum residue limit (Friends of the Earth International 2007). Phenol is toxic to fish, aquatic vegetation and humans. A new report from United States Geological Service has showed that several elements, namely arsenic, are present in high concentrations which overweigh the US government environmental guidelines for residential soil (Plumlee et al., 2008). Hence, it has been clear that the mud will give seious effect on the livelihoods of aquatic communities located in the Sidoarjo River and the Madura Strait.

It has been clear that there are many hazardous impacts of Sidoarjo mud sediment to the environment. Thus, a study of the current characteristics of Sidoarjo sediment and water is a beneficial measure to bring profound contribution to the government and society. Therefore, this study have three objectives. Firstly, this study aim to determine the relationships between the physical properties and the characteristics of the sediments from mud volcanoes in Sidoarjo, specifically, to identify the type of physical properties associated with mud volcanoes. Secondly, we tried to find out the characteristics of morphological and biochemical properties of the bacterial strain isolated from liquid mud and sediment in Sidoarjo for revealing the dominant bacterial species (S1 and A1). The last objective is related to the heavy metal contents. Therefore, the aim of this study is to determine the concentration of heavy metal pollution status in sediments of Sidoarjo mud volcano, in its current condition. These objectives are shown in the research problem.

1.2 Problem Statement

During industrial activities the surrounding environment is significantly polluted. The different types of pollution that can occur during industrial activities include atmospheric pollution due to smog emitted to environment, different types of solid waste generation and water resource pollution. Furthermore, the main environmental problem of industrial activities is the water pollution and sediment pollution. Ecologically, the dangerous substances and contaminants in sediments such as organic (bacteria) and inorganic (sulphate, calcite, acid, iron and zinc) affects the soil condition, water quality and aquatic ecosystem. Therefore, environmental controls are required. Thus, this research will be conducted by answering the following research questions:

1.2.1 Fundamental Research Problem

The fundamental problem of this research was the effect of mud sediment on soil characteristics of eruption location and water quality of Sidoarjo River.

1.2.2 Specific Research Problems

Specific problems that investigated on this study were:

1. How is the water quality of Sidoarjo river and mud sediment of eruption location after 9 years of eruption?
2. How is physical characteristics of Sidoarjo mud sediment?
3. How is the characteristics of soil in Sidoarjo estuary after the mud explosion?
4. What kind of heavy metals in the Sidoarjo mud sediment?
5. What kind of microorganism which able to survive in Sidoarjo mud sediment?

1.3 Research Objective

The polluted Sidoarjo River and mud sediments have caused the environment degradation in the area resulting in the reduction fishery products which impacts the farmer income and quality of local people health. Ecologically, the water pollution affects the diversity of aquatic communities. Based on that description, there are several objectives expected to achieve from this research:

1.3.1 General Objective

The general objective of this research is to to evaluate physical, chemical and microbiology characteristics of Sidoarjo mud and water.

1.3.2 Specific Objectives

The objectives of this study were to investigate or determine:

1. The current water quality of Sidoarjo River and mud sediment on the eruption location
2. The physical characteristics of Sidoarjo mud sediment
3. The characteristics of soil in Sidoarjo estuary after the mud explosion
4. Heavy metal concentration in Sidoarjo mud sediment
5. Microorganism which able to survive in mud sediment

1.4 Significance of the Study

The results of this research will provide information about current characteristics of the Sidoarjo mud after 9 years of eruption. It will be useful for the consideration in taking measure or an alternative solution to solve problems related industrial effect on the estuary quality. Therefore, the negative impacts on the environment will be minimized.

The theoretical benefits of this research will support and add more information to the previous findings about the characteristics and contaminants including heavy metal and microorganism that found in Sidoarjo mud and sediment after explosion.

The practical contribution of the research will be beneficial to the students and instructors as a material in science class, recommendation for the environment practitioners to engage re-vegetation land post mud explosion with the types of contaminants and as the guideline for land reclamation and waste treatment of industrial pollution. Besides, our study aim to give the information of the current characteristics of Sidoarjo mud sediment as the consideration in policy making by government related to industrial activities. The finding will be uploaded online to benefit other researchers who want to conduct further study on similar topic.

CHAPTER II

LITERATURE REVIEW

2.1 Mud Volcano

Mud volcanoes are geological manifestations (Mazzini, 2007). Mud volcano consisted of overpressure clay and organic-rich sediment which located in submarine and sub aerial. Moreover, the presence of mud volcanoes is associated with the presence of high methane fluxes in the seafloor as well as with the accompanying cold vents, seeps (Charlou et al., 2003), carbonate crusts (Aloïsi et al., 2002) and gas hydrates under certain conditions. These volcanoes are ceous material, and occur both on land and on the seafloor (Milkov, 2000).

There was a new mud volcano found in Sidoarjo, East Java. It is located near the magmatic volcanoes which cause it has high temperature. This condition trigger fast mineral transformation and geochemical process in soil surface surround it.

2.2 Mining Exploration in Sidoarjo

According to the geographical and geological situation, East Java Province is categorized into three areas: 1) the north as oil, gas and limestone resources; 2) the centre of the province as farming potential, water and geothermic resource area, and 3) the south as mineral resources (Dinas ESDM Propinsi Jawa Timur, 2007). Moreover, at least fourteen oil and gas fields in East Java are currently being explored. According to the report of Dinas ESDM East Java province (2007), the oil fields in East Java contain 583,475.5 million barrels of oil and 10,301.7 billion cubic feet of natural gas (Dinas ESDM Propinsi Jawa Timur, 2007).

According to BPK report (2007), Brantas Block Production as one of East Java's oil and gas blocks which is operated by Pertamina and Huffco Brantas Inc was authorized to explore 14.950 km^2 in 1990 (BPK report, 2007). Its share contract allowed for oil and gas exploration of over 3,041.64 km^2. By the time of first mud eruption, the location was explored by the Australian company, PT. Lapindo Brantas Inc. (BPK report, 2007; Gelder & Denie, 2007).

2.3 Sidoarjo Mud

Mud flow in Sidoarjo was the eruption of mud volcano which firstly erupted in May 2006. This mud eruption has been reported as the biggest mud volcano eruption ever happened in the world. Natural gas drilling activity by PT. Lapindo Brantas accused as the cause of the eruption which make it took the responsibility of the case. In the other side, some scientist and government agencies stated that the eruption happened as the side effect of earthquake in Yogyakarta (Mazzini et al., 2012). Since the beginning of the explosion until October 2008, it was assumed that the rate of the mud flow had been ranging between 100,000 and 180.000 m^3 per day (Plumlee et al., 2008; Jalil et al., 2010; Mazzini et al., 2012). Since then it keeps exploding small amount of mud spring. Mud volcano in Sidoarjo has erupted about 180,000 m^3 of mud per day. This eruption then has been decreased into 10,000 m^3 per day by put 15 concrete balls into the center of the volcano. The flow has been predicted to continue until 25-30 years later.

The mud affected vastly Sidoarjo area which has buried houses, villages, schools, factories, and displaced thousands of people and continues to pose geohazard risks in a densely populated area with many activities and infrastructures (Istiadi et al., 2009). Some scientists believed that Sidoarjo mud volcano is not natural disaster and it was trigger by drilling activity. However, some geologist convinced that it was natural disaster which was trigger by earthquake that was occurred the day before the eruption.

Despite the arising debate of the occurrence of Sidoarjo mud volcano, managing the impact of the mud on social and environment is more important. The efforts were not only evacuated around thousands of people (Mazzini et al., 2012), but also monitoring water, land and air quality under permit able condition is urgently necessary, due to some scientist stated that the eruption may be a mud volcano forming, and impossible to stop. The government of Indonesia which is represented by BPLS (Badan Pelaksana Lumpur Sidoarjo) decided that the only way to discharge the mud volcano is through Sidoarjo River. On the other side, Sidoarjo River is classified as level III where its main purpose is for fresh water farming, cattle farm, agriculture irrigation according to Indonesian Government Regulation No 82/2001.

2.4 Heavy Metals in the Environment

In the environment, the present of nature contaminants can range from toxic heavy metal (loid)s to present organic pollutants. It depends on the interaction of intrinsic properties contaminants with soil properties. The existence of Metal (loid)s either as cations (heavy metal such as Cd, Cu, Zn and Pb) or anions (metalloids such as Cr, As) in the soil environment is significantly affects metals absorption, mobility and solubility in soils (Violante et al., 2010). When contaminants enter the freshwater system, transformation processes will occur along with additional processes due to aqueous environment, such as mercury and arsenic. It was stated that every source of prospective contamination content on mud possesses its own hazardous effects on plants, animals and severely on human health. However, those activities which add heavy metals to the properties of soils and waters become serious concern because of their persistence in the environment and, more seriously, their carcinogenicity to humans. Those contaminants cannot be destroyed biologically but can only be transformed from one oxidation state or organic complex to another (Garbisu and Alkorta, 2001). In short, heavy metal pollution brings a potential harmful threat to the environment and human health as well. Once released to the environment, metals can remain for decades or centuries, increase the likelihood of human exposure.

Although many metals are essential, most metals are toxic at high concentrations, because they cause oxidative stress by formation of free radicals. Such metals are found naturally in the soil in trace amounts. Heavy metals like lead, mercury, cadmium, arsenic, copper, zinc and chromium that are hazardous present in disposal of some industrial wastes. Increased concentrations due to anthropogenic activities in particular areas pose serious threat to all living organisms. Another reason why metals may be toxic is that they can replace essential metals in pigments or enzymes disrupting their function (Henry, 2000). Thus, metals render the land unsuitable for plant growth and destroy the biodiversity.

The metals are classified as heavy metals if in their standard state they have a specific gravity of more than 5 g/cm^3. Approximately sixty heavy metals are known. Heavy metals are accumulated steadily in soils and plants and may bring a negative impact on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption). It causes the slower plant growth as dry matter accumulates and yields (Devkota and Schmidt, 2000). The small concentration existence of heavy metals in animal body does not count as toxic (Vries et al., 2007). However, some heavy metals such as lead, mercury, and cadmium existence in small concentration will become toxic (Galas-Gorchev, 1991). A lot of studies about soil heavy metal contents have been done with high human activities influence such as industrial cities. Regular assessment of heavy metals is needed with consideration of there are a lot of heavy metals with potential to be soil and water pollutants such as Cu, Cr, Cd, Ni and Pb.

Though several regulatory steps have been implemented to reduce or restrict the release of pollutants in the soil, they are still insufficient to control the contamination. Metal contaminated soil can be remediated by chemical, physical and biological techniques.

Heavy metals that investigated in this study have various implication for human health problems. Lead has implication with anemia, anorexia, brain damage, mental deficiency, vomiting, even death (Bulut and Baysal, 2006). Cadmium has relation with agonistic and antagonistic effects to hormones and enzymes which lead malformation of proteins (Lewis, 1991). Both of Cadmium and Lead possess high affinity to proteins in SH group such as haemoglobin, enzymes, and hormone (Manahan, 1992). These two heavy metals have been classifies as carcinogenic agents (USEPA, 1999; Pekey, 2006). The other heavy metals such as Zn and Cu have been reported caused various health problems because they are non-biodegradable and tend to be accumulated in food chain (Langston, 1990).

There has been a myriad of results reported in the literature which makes it possible to conclude that the metal has a high toxicity and been distributed in the aquatic environment worldwide. They also accumulate in sediment (Klavins et al., 1998). Data on the environmental impact of chemicals clearly represent the negative effects of the deployment accelerated and metals and metalloids in the environment by anthropogenic activities, and changes made to the global chemical cycles (Mester et al., 1998). Studies of sediment in wetlands important as wetlands act as a natural filter for the water in the system and thus act as a sink for contaminated suspended particles in the water column. Sediment also gives an indication of the potential for contamination of the temporal scale. Water analysis indicates the current status while the sediment contamination can provide information about the history of contamination systems (Shine, 2004). The wetlands also can act as a source of increased levels of contaminants in water bodies during periods of increased water flow remobilizing settled particles resulted in a re-suspension of contaminants into the water. These sediments are transported downstream and affect downstream river ecosystems and wetlands flooded (Ulbrich et al., 1997). Mobilization of sediment by water flow allowing contaminants to penetrate deep into wetlands by flood waters (Ulbrich et al., 1997). Thus, it is important to assess the quality of the sediments in the entire system.

Contaminants bind the sediment particles (Buykx et al., 2002). Contaminants may include metal compounds, or derived from chemical compounds released into the system through a number of anthropogenic activities.

Metal compounds can naturally exist in environment because they are involved in several of geochemical cycles. Categories of cycle include particular absorption, exchange, carbonate Fe-Mn oxides, organic materials, and mineral (Li et al., 1995). The quantification of metal chemical in mud sediment form is very important to estimate the mobility and bioavailability of metals in the environment (Leschber et al., 1985; Li et al, 1995).

2.5 Water Quality

Ground water systems drains water that falls on the soil. Flowing water such as river can dilute and decompose pollutants more rapidly. Furthermore, the worse condition is that many rivers all around the world are dramatically polluted (Lenntech, 2014). The main reasons are because all three major sources of pollution such as industry, agriculture and domestic are situated along the rivers. Historically, industries and cities were located along rivers because of the transportation and waste disposal needs. Moreover, agricultural activities tend to locate near rivers because the need of water to irrigate the plants and the exceptionally fertile soil containing many nutrients that are deposited in the soil when the river overflows (Lenntech, 2014).

On the other hand, the water quality of rivers depends on some interrelated factors. In its movement, water has the ability to react with the minerals contained in the soil and rocks and to dissolve a wide range of materials. Thus, it is never pure in its natural state. It always contains a variety of soluble inorganic and organic compounds. Adding to that, water can carry huge amounts of insoluble substances that are held in suspension. While the amounts and type of impurities found in natural water vary from place to place by time of year depending on a number of factors which include geology, climate, topography, biological processes and land use. Thus, the impurities determine the characteristics of a water body (Lenntech, 2014).

2.5.1 Water Quality Degradation

The freshwater quality on the landscape reflects the combined effects of many processes along water pathways. Human activities on all spatial scales affect both water quality and quantity. Moreover, the effects of human activities on a small scale are relevant to an entire drainage basin. The water quality degradation in one part of a watershed can have negative effects on downstream users. Everyone living downstream can have the effects of some human activities on the watershed area (Peters and Michael, 2009).

2.5.2 The Impact of Water Pollution upon Freshwater Communities

a. pH effect on organisms

The effect of acidity on freshwater communities has been widely studied, not only in relation to coal mine pollution (Parsons, 1977; Armitage, 1980; Sasaki et al., 2005), but also acid rain and catchment acidification (Bell, 1971; Hall et al., 1980; Schindler et al., 1985; Maurice et al., 1987; Ormerod et al., 1987a; Courtney and Clements, 1998; Ledger and Hildrew, 1998; Ledger and Hildrew, 2001; Lepori et al., 2003; Ledger and Hildrew, 2005). pH can affect aquatic macroinvertebrates via different pathways: (a) modifying their physiology, for example disrupting cell membrane transport or changing membrane stability (Hall et al., 1980; Gerhardt, 1993; Camargo et al., 2005); (b) increasing macroinvertebrate drift, observed after acidic spells (Ormerod et al., 1987b, Courtney and Clements, 1998); (c) decreasing invertebrate emergence, observed in acidic environments (Bell, 1971); (d) affecting the availability of suitable food: algal growth (Ledger and Hildrew, 2001) and detritus conditioning by microorganisms (Nelson, 2000) may be reduced at low pH, subsequently impacting functional groups such as grazers (Hall et al., 1980; Gerhardt, 1993) and shredders; (e) trace metal bioavailability is often increased at low pH, due to three mechanisms that favor the aqueous phase at low pH: (1) changes in the hydrolysis and complexation equilibria, (2) modification of competition between metal ions and H^+ for binding sites, and (3) dependence of sorption capacity on pH (Gerhardt, 1993). However, H^+ can also out-compete heavy metal cations at binding sites in cell membrane carriers and therefore compensate for higher metal availability (Ormerod et al., 1987a; Courtney and Clements, 1998).

An increase in acidity is often associated with coal mine pollution due to H^+ produced in pyrite weathering (Equation 3.1, Chapter 3) (Langmuir, 1997; Smith, 1999; Younger et al., 2002). However in the receiving stream environment it is difficult to discern the effect of pH from that of dissolved heavy metals and ochre deposition, as they normally occur simultaneously (Chapter 3). When pH effect has been isolated in mine polluted streams, it has been associated with decreased benthic species richness but with no change in biomass (expressed as mg dry weight/m2) (Tomkiewicz and Dunson, 1977) or total abundance (Koryak et al., 1972), whereas extensive ochre deposition in combination with low pH appears to have a negative effect on both species richness and total abundance (Koryak et al., 1972; Jarvis and Younger, 1997).

Tolerance to low pH appears to vary between insect taxanomy. Plecoptera have been defined as an opportunistic order which is resistant to moderately acidic environments (Tomkiewicz and Dunson, 1977). Species of *Nemoura* (Plecoptera) are known to be common in European acidic streams (Koryak et al., 1972), probably because they are not obligate detritivores and take advantage of competitive release, occupying grazer niches when potential competitors are absent (Ledger and Hildrew, 2000; Ledger and Hildrew, 2001; Ledger and Hildrew, 2005). Chironomidae are also considered to be acid tolerant (Van Damme et al., 2008). Specialised grazers, such as many Ephemeroptera, have been shown to be very sensitive to decreases in pH (Ledger and Hildrew, 2005) and are often absent when pH is lower than 5 (Rosemond et al., 1992).

b. Trace metal effect on organisms

Organismal uptake of trace metals occurs via three main pathways; water, sediment and food. As many invertebrates ingest sediment particles containing microalgae, fungi and bacteria while feeding, distinction between biotic (food) and abiotic (sediment) input is difficult (Gerhardt, 1993).

All aquatic invertebrates take up trace metals from the environment to some extent (Rainbow, 2002). However, bioaccumulation (higher metal concentrations in organisms than in the surrounding environment) only occurs if the uptake rate is higher than the excretion and detoxification rate of the organism (Rainbow, 2002). At the food web level, this may lead to organisms in higher trophic strata accumulating metals via the food web (biomagnification) (Gerhardt, 1993).

Toxicity from trace metals is mainly associated with biochemical reactions involving: (a) competitive blockage of a functional group or macromolecule at the cell membrane, which can disrupt transport and membrane stability (Gerhardt, 1993); (b) displacement of other cations. Zinc can cause cross-linking of DNA-molecules, inhibiting transcription processes, and copper can depress the electrical response of the nervous cells (Gerhardt, 1993); (c) conformational change in proteins, for example copper can bind to certain enzymes and inhibit their action (Flemming and Trevors, 1989).

Physiological effects from heavy metal toxicity are manifested mainly as hypoxia (deficiency of oxygen reaching the body tissues), caused by a reduction in gas exchange due to coagulation and precipitation of mucus or cytological damage (Koryak *et al*., 1972; Sridhar *et al*., 2001; Niyogi et al., 2002a).

Uptake and bioaccumulation of trace metals does not always result in a toxic effect, as they can be stored as non-toxic species or bound to metallothionein (Gerhardt, 1993). Metal toxicity can depend on biotic factors: size and life stage (Kiffney and Clements, 1996), feeding characteristics such as gut volume, gut passage time and gut pH (Kelly, 1999), and alimentation habits (i.e. functional feeding groups) (Kelly, 1999). Hence, tolerance to trace metal pollution may vary between species and functional groups.

Ephemeroptera have been classified as one of the taxa most sensitive to trace metals, whereas Chironomidae appear to form one of the most tolerant groups (Arnekleiv and Storset, 1995; Hickey and Clements; 1998, Richardson and Kiffney, 2000; Hickey and Golding, 2002; Van Damme et al., 2008).

Tolerance to pollution can also be developed through adaptation (genetically based) when the population has lived under stress for several generations (Gerhardt, 1993; Morgan et al., 2007), or acclimation, when a population is pre-exposed to pollution (Gerhardt, 1993; Admiraal et al., 1999; Peeters et al., 2001). However, heavy metals can also be transferred into the sediments and potentially impact benthic organisms. This sediment-benthos association is not yet fully understood.

2.6 Sediment

The sediment texture and composition are known as a setting of river basin geology, bathymetry, and hydrologic. In the area where sediment supply is inadequate to supply drowned valleys, clay and silt are commonly deposited in the bay central part of grading shoreward and seaward into the bodies of the sand. On the other hand, in the area where sediment supply and tidal range are large, the clay and silt are commonly swept from the channels and deposited on the marginal flats. Silt and clay are usually accumulated in lagoons behind barrier bars. In short, the character and distribution of sediment are affected by many physical, chemical, and biological processes, for example, tidal currents, flocculation, bioturbation (the organism work to rework and alter the sediment), storms, estuary morphology, and human daily activities.

2.6.1 Contaminants in Sediments

There are many contaminants found in the sediments. According to Sekela et al. (1995), pollutants linked to the suspended sediments reflect one route of exposure to organisms in the water column. On the other hand, contaminants associated with bed sediments show an exposure pathway to benthic and bottom feeding organisms. The suspended sediment sampling provides an integrated sample over a known period of time with a high degree of reproducibility (Sekela et al., 1995), while bed sediment sampling is an effective method to characterize contaminant exposure over a longer period of time (weeks to years) (Sekela et al., 1995).

CONTAMINANTS	MAJOR SOURCES	EFFECTS
Dioxins and furans	- pulp and paper mills using chlorine bleaching - incinerators - commercial chemicals (PCBs, pentachlorophenol, 2,4-D) - wood and fossil fuel combustion - sewage treatment plant effluents	- teratogenic - carcinogenic - acutely toxic - endocrine disrupting - bioaccumulative
Chlorophenolics	- pulp and paper mills using chlorine bleaching - wood treatment facilities/treated wood products - incinerators - chlorinated pesticides - sewage treatment plant effluents	- immunotoxic - fetotoxic - embryotoxic - fish tainting
Polycyclic Aromatic Hydrocarbons (PAHs)	- wood and fossil fuel combustion - creosote treated products - spills of petroleum products - slash burning - plant material - natural oil deposits	- carcinogenic - bioaccumulative
Chlorinated Pesticides	- agriculture - sewage treatment plant effluents - industrial effluents - global transport and deposition	- carcinogenic - endocrine disrupting - bioaccumulative
Polychlorinated Biphenyls (PCBs)	- transformers - lamp ballasts (pre-1980) - global transport and deposition - sewage treatment plant effluents - pulp and paper mill effluents	- immunotoxic - endocrine disrupting - bioaccumulative
Nonylphenol	- pulp and paper mills - textile processing and manufacturing - plastics manufacturing - leather processing - household cleaners - sewage treatment plant effluents	- acutely toxic - estrogenic - bioaccumulative
Trace Metals*	- mining and metallurgy - paints and dyes - electrical and electronic manufacturing - cleaning and duplicating - electroplating/finishing	- acutely toxic - endocrine disrupting - bioaccumulative

Figure 2. Contaminants in Sediments

2.6.2 Sediment Problems

Mud sediment has the ability to collect, accumulate, and dispose pollutants in the environtment (US Environmental Protection Agency, 1997). Some substances such as pathogens, nutrients, metals, and organic materials are tend to transform into both of inorganic and organic materials which will deposited in the ground of water. The condition is if there is a large loading of these contaminants into the waterways, the sediments will accumulate large quantities of pollutants that disrupt the biotic and non-biotic ecosystems, either directly and indirectly. This will lead to high contamination which brings loss of important species. Several studies have reported that sediment contamination affected on ecosystem quality. Sediment contamination cases have been found in the worldwide (Burton, 1991; US Environmental Protection Agency, 1997).

On the other hand, the contamination cases were ignored in the past with because they commonly identified as industrial discharge. The total cases then continued to rose by years which accumulated as pollution sources. These accumulation of pollution then contaminated aquatic systems. It dramatically affected to benthic communities. The effects were varied which associated with sediment (Canfield et al., 1994; Swartz et al., 1994). The contamination will affected on the food chain balance (Bishop et al., 1999; McCarty and Secord, 1999; Ludwig et al., 1993; and Foley et al., 1988).

Excessive transformation of substances into organic and inorganic materials in water is the main cause of contamination (Burton, 1991). Somehow, contaminants will attach to anything on the water surface which caused it become less degradable. Absorbed contaminant in sediment will stay on it for long period of time into small and fine-grained particles. This condition is related to sediment ability to absorbed contaminants in high concentration. Sediment is one of the essential parts of aquatic system because of this ability (Burton, 1991). Moreover, sediment provides source of substances from contaminant accumulation for food web and some biological pathways (Mackay, 1991). Contaminants will keep moving in water which sometimes there are transfers occur of one compartment to another compartment (Barrie et al., 1992). The transfer can cause some contaminant become persistent in sediment.

Pollution formed naturally in the area with high population number or high activities such as industrial and agricultural area. There are about 1.2 billion from 12 billion cubic of sediment surface found in US which considered has the potential to harm fish, humans, and wildlife (US Environmental Protection Agency, 1997). However, there is only 11% of river with toxicity information available in nations worldwide. Other 77% of river was reported to be contaminated.

Sediments with contaminant were found in every type of aquatic ecosystems, such as rivers, lakes, estuaries, bays, and oceans (US Environmental Protection Agency, 1997). North Carolina estuaries have been reported with pollution sediment which previously not contaminated. Apparently, there were huge quantities of sediment found in United States and other industrial countries which contaminated with metal and organic matters. These contaminants level have high risk to harm aquatic ecosystem (Pelly, 1999).

There were efforts, resources, and huge amount of money allocated to remove the contaminant sediment from aquatic ecosystem in order to restore water quality (US Environmental Protection Agency, 1997). The contaminant sediment remediation is becoming an important issue nowadays. On the other hand, the failure to identify whether or not the sediment is contaminated causes both an ecological and human health risks. Thus, the process of identifying sediments as contaminated is importantly crucial (US Environmental Protection Agency, 1997).

2.6.3 The Impact of Polluted Sediments upon Freshwater Communities

Sediments form a sink for heavy metals due to the adsorption capacity of clay, organic matter and other solids such as ochre flocs (Smith, 1999; Peeters et al., 2001). Trace metal loaded sediments may pose a threat for benthic organisms, but they can also be a source of pollutants when physico-chemical properties of the stream (e.g. low pH, high discharge) favour desorption of heavy metals or erosion of contaminated sediment (Bervoets et al., 1997; Kelly, 1999; DeNicola and Stapleton, 2002).

Benthic organisms are able to take up metals while burrowing in sediments or when feeding from particulate matter (Bervoets et al., 1997; 1998). Nevertheless, a direct link between sediment trace metal concentration and an adverse effect on invertebrates has not always been found (Bervoets et al., 1998, Van Damme et al., 2008). Some authors suggest that invertebrates collect trace metals from sediment pore water or from the boundary layer between the surface of the sediment and the overlying water column (Bervoets et al., 1998; Courtney and Clements, 2002). It is probably a combination of substratum, water and organism physiology that play an important role in the biogeochemical cycling of metals from the sediment (Kelly, 1999).

Thus, it becomes apparent that further study is needed to fully understand the role of all these factors on the toxicity of mine pollution, and trace metals associated with it, on freshwater ecosystems. Sediments may also integrate long term metal exposure of lotic ecosystems, whereas metal concentrations in water are generally more variable (Van Damme et al., 2008).

Gray (1998) have observed a seasonal effect on mine discharge (l/s) and metal discharge rates (kg/s), both reaching their maximum in wetter months (February) and minimum in drier periods (October). Pollution input from spoil heap runoff has also been seen to vary seasonally (Younger et al., 2002; Gandy and Younger, 2008; Canovas et al., 2008). Spoil heaps that do not develop a water table appear to produce maximum contamination during wet periods, when surface runoff dissolves metals from spoil material and transports them to the receiving water body. On the contrary, some spoil heaps are big enough to develop a localized water table, and in this case, high rainfall dilutes the drainage from the spoil heaps, resulting in lower trace metal concentrations and acidity during wet periods (Gandy and Younger, 2008). Additionally, these processes may be counteracted by greater dilution in reaching the receiving stream during high flow events, which often coincide with wetter periods (Canovas et al., 2008). Therefore, trace metal concentrations in water may be highly variable depending on the hydrology of the streams, and sediment toxicity may be a better predictor of benthic species variation.

However, sediment analysis is often disregarded in routine monitoring work. The detrimental impact of polluted sediment in mine drainage is not always associated with trace metal toxicity. In streams impacted by coal mine drainage, extensive deposition of ochre often covers the stream bed (Chapter 3). This may cause a series of physical effects on the benthic community by (a) limiting food resources by lowering primary productivity (Koryak et al., 1972; Hall et al., 1980) or coating detritus preventing grazer access (Nelson, 2000) (Chapter 5), (b) clogging of invertebrate gills (Koryak et al., 1972; Hall et al., 1980) (Plate 4.1), and (c) reducing habitat availability due to fine sediment deposition (Rabeni et al., 2005). However, ochre flocs have high adsorption capacity for heavy metals dissolved in the water

(Parkman et al., 1996; Jain and Ram, 1997; Smith, 1999), thus their toxic effect may also be relevant.

2.6.4 The Development of Sediment Quality Criteria

Contaminant sediments have been categorized based on restricted degraded material disposal, industrial and residential cleanups, effluent, extension area, risk to ecology and human being, fish tissue contamination, contaminated sites, and beneficial (US Environmental Protection Agency, 1987). Traditional determination of sediment contamination level was based on the assessment of chemical bulk concentrations with make the comparison with the reference values (Great Lakes Water Quality, 1982; Gambrell et al., 1983; US Environmental Protection Agency, 1987; Thomas, 1987). Water pores has been made as the indicator of sediment quality by USEPA Region VI (USEPA, 1999). Furthermore, similar program has been arranged to be focused on the contaminant equilibrium partitioning (EqP) of water (US Environmental Protection Agency, 1989).

Statistical analysis of the relationship between contamination and toxic response has been used to evaluate the hazardous level of sediment according to its chemical components (Long and Morgan 1991; Persaud et al., 1993; Smith et al., 1996; Ingersoll et al., 1996; Cubbage et al., 1997; WDOE 2000). On the other side, the theoretical approach also has been used to compare the differences of bioavailability based on EqP (DiToro et al., 1991; NYSDEC 1994; US Environmental Protection Agency, 1997).

Original sediment quality guidelines (SQGs) has been used to compare a reference with background with consideration of the ecological impact possibility from sediment contaminants. This method is commonly used in metal contaminants determination. New empirical SQGs with combination of biology laboratory assessment has been proven as effective way to predict the biological effect of contamination in water (Long et al., 1998, 2000; Ingersoll et al., 1996; MacDonald et al., 2000a,b).

However, the bioavailability issue is not well addressed by the empirical SQGs since SQGs are based the analysis on total sediment concentrations. Therefore, the EqP approach attempts to address this issue more specifically. As a result, it suggests that pore water concentrations resemble the primary exposure pathway for aquatic organisms. As it is assumed that sediment contaminant exposure was driven by the pore water concentration, the toxicity of contaminants could be directly related to the USEPA water quality database. By normalizing sediments based on their organic carbon concentration, differences in bioavailability (toxicity) were largely accounted for. The method has been useful for some situations. Using this method, the toxicity of DDT and its metabolites in sediments were reasonably explained for a field site near Huntsville, Alabama (Hoke et al., 1994). However, carbon normalization has not completely removed the variability in expected toxicity in several nonpolar compounds (Meyer et al., 1993).

This method has also been applied to metals by accounting for the interactions with acid volatile sulfide (Ankley et al., 1993). Five metals including Cd, Ni, Pb, Zn, and Cu, form insoluble sulfides. Thus, their toxicity is limited by the amount of sulfide in the sediment. Toxicity is seen when the amount of metal stoichiometrically exceed the amount of sulfide that can bind it. A clear demonstration of the implementation of this approach was described for Cd toxicity to amphipods, (*Ampelisca abdita* and *Rhepoxynius hudsoni*) in marine sediments (DiToro et al., 1990). However, as in the case of organic contaminants, this approach has sometimes over-predict toxicity, usually because of the other substances (Ankley et al., 1993).

2.6.5 Sediment Quality Guideline Values

USEPA has developed national equilibrium partitioning sediment guidelines (ESGs) for a broad range of sediment types. They have finalized the methodologies for deriving ESGs for nonionic organic chemicals (USEPA, 2000) and mixtures of certain metals (cadmium, copper, lead, nickel, zinc, and silver (USEPA, 2000). Moreover, in determining the level of contaminants in the sediment, sediment quality guideline values can be used. The values of sediment quality guideline are used to identify the condition of the sediment. It represents contaminant level. The recommended values of sediment quality standard are presented in Figure 3.

Metal	mg/kg dry wt.[++]							Source of SQG Effect-Based Concentrations
	Level 1 Concern ≤ TEC	TEC	Level 2 Concern > TEC ≤ MEC	MEC	Level 3 Concern > MEC ≤ PEC	PEC	Level 4 Concern > PEC	
Antimony	←	2	↔	13.5	↔	25	→	NOAA (1991) [1.]
Arsenic	←	9.8	↔	21.4	↔	33	→	CBSQG (2000a)[2]
Cadmium	⇐	0.99	⇔	3.0	⇔	5.0	⇒	CBSQG (2000a)
Chromium	⇐	43	⇔	76.5	⇔	110	⇒	CBSQG (2000a)
Copper	⇐	32	⇔	91	⇔	150	⇒	CBSQG (2000a)
Iron	⇐	20,000	⇔	30,000	⇔	40,000	⇒	Ontario (1993) [3]
Lead	←	36	↔	83	↔	130	→	CBSQG (2000a)
Manganese	⇐	460	⇔	780	⇔	1,100	⇒	Ontario (1993)
Mercury	←	0.18	↔	0.64	↔	1.1	→	CBSQG (2000a)
Nickel	⇐	23	⇔	36	⇔	49	⇒	CBSQG (2000a)
Silver	⇐	1.6	⇔	1.9	⇔	2.2	⇒	BC (1999) [4.]
Zinc	⇐	120	⇔	290	⇔	460	⇒	CBSQG (2000a)

Figure 3. Recommended Sediment Quality Guideline Values of Heavy Metals in Sediment

The CBSQGs for organic compounds are expressed on a dry weight concentration at 1% TOC in sediments. However, unlike the organic compounds, the CBSQG and study site metals concentrations can be compared on a bulk chemistry basis and do not need to be adjusted to a 1% TOC basis to do the comparison. TOC does not play the same role in determining metals availability as it does in determining organic compound availability.

2.7 Passive Treatment

Passive treatment is known as process that does not need regular human intervention (operation and maintenance). It is made by natural material such as clay, soil and broken rock, plants, manure and wood (INAP, 2013). Passive treatment is a process of sequentially removing metals or/and acidity in a natural-looking, man-made bio-system that capitalizes on ecological and geochemical reactions (INAP, 2013).

The great advantage of this process is that it can last for many years with limited human intervention and once constructed it does not need chemical or electrical power to work (INAP, 2013). There are different types of passive treatment but the most known are: aerobic wetlands, anaerobic wetlands, anoxic limestone drains, open limestone drains, and also reducing and producing alkalinity system (INAP, 2013). When it comes to design of passive treatment system for AMD the critical parameters are flow rate, water quality characteristics of AMD and land availability (Zipper et al., 2011).

The simplest type of passive treatment is the aerobic wetland, but it cannot treat efficiently certain type of water (Zipper et al., 2011). It is used to treat net alkaline water which has high content of iron and the capacity to neutralize acidity is limited (Zipper et al., 2011). Mine water is aerated while it is flowing slowly through vegetation and dissolved iron is oxidized and the oxidation product will precipitate (Zipper et al., 2011). As result of precipitation of iron, the pH will drop due to generation of H^+ ions and effluent water can have pH lower than influent water even if the iron concentration is higher (Zipper et al., 2011). Aerobic wetlands can also remove Mn but oxidation of Mn will start when oxidation of Fe is completed (Zipper et al., 2011). To remove Mn using aerobic wetlands it is necessary to have big area to allow completely Fe oxidation and begin Mn oxidation or it can be done by adding another wetland cell (Zipper et al., 2011). Composted organic matter or natural soil can be used as substrate and water level between 10 to 30 cm are used to maintain aerobic condition and to allow cattails to growth in order to help in wetland performance (Zipper et al., 2011).

Passive treatments have the advantage that they are often more cost effective, however they require more land than active techniques and can be less controlled. The most commonly used are engineered wetlands. There are three main types of wetlands, designed to remediate different types of pollutants: Aerobic wetlands are more applicable to ferruginous, net-alkaline waters. They remove iron and manganese, although the latter to a limited extent, via oxidation, hydrolysis and sedimentation (Younger et al., 2002). However, this hydrolytic process generates protons, thus lowering pH. For this reason, this technique is only applied to net-alkaline waters or to acidic waters previously neutralized. Aerobic wetlands consist of shallow water bodies typically supporting vegetation communities of Phragmites australis, Typha latifolia and Juncus effusus (Younger, 2002). Macrophytes appear to assist in water remediation by reducing the flow, providing adsorption surfaces and releasing oxygen into the water (Batty et al., 2008). Additionally, they have proved to be crucial as a polishing step, removing iron when concentrations are too low to be removed by abiotic processes (Batty and Younger, 2002).

In contrast, compost wetlands are suitable for net-acidic waters. They are very similar to aerobic wetlands, but a compost layer is added to provide an organic substrate that supports sulphate reducing microbial communities. In this anoxic substrate, sulphate reduction and calcite dissolution take place, decreasing acidity and removing iron and zinc as sulphides (Younger, 2000). A rise in pH leads to aluminium and manganese precipitation as (hydr)oxide and carbonate respectively (Younger, 2000). Reducing and alkalinity producing systems (RAPS). RAPS are similar to compost wetlands, but have an additional limestone gravel bed, which maximises alkalinity generation (Batty and Younger, 2004). The compost layer holds sulphur reducing bacteria, produces alkalinity and allows insoluble Fe^{3+} to be converted to soluble Fe^{2+} before reaching the limestone bed, avoiding coating of the bed with ochre which would reduce its reactivity. Thus, RAPS are normally followed by aerobic wetlands to remove dissolved Fe^{2+} from the water. These systems are more efficient in removing trace metals from solution than compost wetlands on their own. However they require the water to flow downwards through the system and not superficially, thus it is only applicable if there is enough head in the system (Batty and Younger, 2004). Passive treatments are effective at removing iron from acidic and alkaline waters, but their efficacy with respect to other contaminants is still the subject of on-going research (Younger et al., 2002; Johnston and Rolley, 2008).

CHAPTER III

RESEARCH METHOD

3.1 Research Design and Study Area

This research was designed following descriptive qualitative and quantitative approaches using real laboratory experiment. It is descriptive since the objective is to describe the characteristics of sediment and water in Sidoarjo mud, Sidoarjo, East Java (Johnson & Christensen, 2004). Descriptive quantitative approach was applied to identify heavy metals which were potentially dangerous for soil and microorganisms in contaminated aquatic ecosystem in the area near Sidoarjo mud, Sidoarjo, East Java. Moreover, quantitative research was based on the measurement of quantity or amount. It is applicable to phenomena that can be expressed in terms of quantity (Kothari, 2004). Qualitative approach was used to obtain information and plan solutions for the future development of in situ wetland re-vegetation in the area. Therefore, this research study was primarily based on the principles of qualitative-quantitative research. Strauss and Corbin (1991) refer to qualitative research as any kind of research that produces findings which are meaningful, testable and scientifically free from contradictions. This type of research focuses on understanding rather than predicting or controlling phenomena. It attempts to evaluate condition such as what can be predicted to happen in the same condition. This study is done in qualitative naturalistic inquiry strategy (Johnson and Christensen, 2004) to obtain information concerning the current condition of Sidoarjo mud sediment and water including the microorganism as they exist at the time of the study. Thus, this study was done through real laboratory experiment with qualitative-quantitative descriptive approach.

The research was done in two different areas, observations and measurement of water and sediment in the area of research (Sidoarjo mud) and sample analysis in the experiment laboratory (Brawijaya University). The research location was part of Sidoarjo district, East Java. Identification of sediment characteristics including sediment physical properties, heavy metal contents and microorganisms were conducted at Ecology Laboratory, Faculty of Mathematics and Natural Sciences, University of Brawijaya.

Moreover, this research also investigated Sidoarjo River condition which part of Brantas River. Since mud eruption in 2006, there was alteration in the coastal area environment of Sidoarjo River estuary. The location of mud eruption was surrounded by industries. Because of located in the tropics area, case study temperatures are very steady throughout the year and range from 25°C up to 35°C in the lower areas. This region have Rainfall rate 1500 and 4500 mm per year (MacKinnon et al., 1996// Jennerjahn et al., 2013). This brings the dried sediment wet and flown to the nearby River. Consequently, the contaminants in the mud sediment will be transported to the river. Therefore, this study was conducted in the rainy season to benefit in collecting the reliable sample as the some samples is sediment in the river. This is done to analyze the mud contaminants transported to river. The setting of sample locations is presented in Figure. 4.

Figure 4. Location of Study Sites

Sidoarjo mud is situated in the backarc area 10 km northeast from the Penanggungan volcano. It is located in Sidoarjo area. Sidoarjo is near by Surabaya city. It has an area of 634.89 km^2. The explosion of mud volcano happened in Sidoarjo the location of the mud volcano is close to magmatic volcanoes. The areas of the sample include Location A which is situated at West Siring village, Location B which is in Jatirejo village, Location C in Mindi village, Location D which is located in Pejarakan village, Location E in Reno Kenongo, and Location F which is near the center of the mud explosion.

3.2 Research Materials

Sample materials which used in this research were taken from mud eruption location. The complete list of the materials and each function are mentioned in Table 1.

Table 1. Materials Used in the Experiment

No.	Material	Function
1	Water sample in Sidoarjo River	Experiment material for acidity analysis and microorganism component
2	Sediment sample in Sidoarjo mud	Experiment material for physical texture and heavy metal content

The tools were used in this study include tools for water and sediment sample taking process, physical and chemical water parameter measurement, and acidity level experiment. The tools are listed in the Table 2.

Table 2. Tools Used in the Research Experiment

No.	Tool	Function
1	Water Thermometer	To measure water temperature
2	Clinometer	To measure salinity
3	Turbid meter	To measure clearness of the water
4	Electric pH meter	To measure pH level
5	Winkler bottle	To take water sample
6	Measuring glass	To adjust water volume
7	Spade	To take sediment and plant sample
8	Plastic bowls	To take sediment sample
9	Plastic containers	As the water and sediment place
10	Small aquariums	As the media of experiment
11	Scale	To adjust the sample
12	Camera digital	To take pictures and record the experiment and the sample condition
13	Spectrophotometer UV/VIS	To analyze the level of metal and acid in the sample
14	Beaker glass	To analyze the level of metal and acid in the sample
15	Erlenmeyer	To analyze the level of metal and acid in the sample
16	Reaction tube	To analyze the level of metal and acid in the sample

3.3 Instruments

The researcher was active as a data collector or a key instrument that is supported by other instruments, such as field notes, interview guides, questionnaires and tools to take water sample. Johnson & Christensen (2004) stated that a qualitative researcher is said to be the data-collection instrument who must decide what is important and what data are to be recorded. The tools and material samples for the laboratory experiment were the other primary instrument to obtain the primary data about the condition of research location and soil and sediment quality in Sidoarjo mud, Sidoarjo, East Java, Indonesia.

3.4 Research Procedures

This research will be conducted in three stages which include: 1) observation of research location, 2) laboratory analysis of the water and sediment sample, and 3) describing the finding of sample analysis.

3.4.1 Observation of Research Location

The first stage was observation of the research area. Observations were conducted to collect data from the specific area where research was being conducted (Sidoarjo mud and Sidoarjo river in Sidoarjo, East Java). According to Strauss and Myburgh (2003), observation is at the basis of all research. In this case the researcher will focus on two of the five scientific observation steps indicated by Strauss and Myburgh (2003). 1. A natural phenomenon is observed and 2. Conclusions are drawn from what happens. Moreover, Strauss and Myburgh (2003) indicated that the researcher reports what she or he observes. The researcher used a qualitative observation technique. According to Strauss and Myburgh (2003) the observation process therefore entails that the researcher or observer has a list of certain specifics that she/he will observe, often called an observation schedule. When observing qualitatively, observation is much more open when compared to observation as a quantitative technique. The observation was done in March 2014 to identify and observe the location. During the observations, the researcher wrote notes of important information in the field notes. Therefore, in this study, the researcher was responsible for collecting the data and use camera digital to take pictures of the sources of data in term of condition of mud sediment in the research location.

3.4.2 Laboratory Analysis of the Water and Sediment Sample Quality

The second stage was analyzed the condition of sediment sample of Sidoarjo mud. The living microorganism was analyzed to find the potential of living organism which can live in the polluted areas. The purposes of this stage are to find out the physical characteristics of Sidoarjo mud sediment resulted from mud volcano eruption to know the basic materials of the mud volcano, to discover the level of acidity and metal contained in this muddy ecosystem, and discover the microorganism which can survive in this extreme environment. The experiment was conducted from December 2014 to May 2015 in the polluted aquatic ecosystem area. At the sample was analyzed at the Ecology Laboratory, Faculty of Mathematics and Natural Science, University of Brawijaya. Identification of physical characteristic of the sediment, analysis of metal and acid level in the sediment samples, and analysis of living microorganism was also conducted at Ecology Laboratory, Faculty of Mathematics and Natural Science, University of Brawijaya.

In the third stage procedure, the samples of sediment and soil were collected, measured and analyzed to find the parameters including salinity, temperature, pH, turbidity, and metal contaminants. The acidity level and metal level in the aquatic ecosystem were analyzed by taking water and sediment samples from the research location and analyze them at Ecology Laboratory, to find out the distribution and level of acidity and metal in the water and sediment samples. The data will then be recapitulated and saved for further analysis.

3.5 Data Analysis

Along with the data collection, the data were then analyzed in the laboratory experiment to find the acidity, pH level, contents, physical properties, and existing microorganism in the Sidoarjo mud sediment. The results of the experiment are served as the main data to be described. Johnson & Christensen (2004) stated that qualitative data analysis involves the analysis of the information from field notes which the procedures are reading the data, segmenting and coding the data, and coded categories, searching for relationship and patterns in the data, and generating tables and/or figures to help in interpreting the data.

According to Hasan (2002), data analysis is the process of organizing and sorting data into patterns, categories, and a description of the basic unit in order to discover themes, therefore, working hypotheses can be formulated as suggested by the data. In analyzing data, the method used is descriptive quantitative-qualitative, where data obtained describe the characteristics of the study site condition of polluted environment. Quantitative approach is used by applying table analysis obtained from the laboratory experiment to understand the current condition of Sidoarjo mud sediment and the nearby river.

The investigation result of this research will be presented on tables and figures and documented in a paper. The process of paper writing and the examination will be on September to October 2015. Paper will be published on scientific journal also will be presented in scientific conferences.

3.6 Operational Framework

Mud volcanoes can be important manifestations because of vertical fluid flow and mud eruption in sedimentary basins worldwide. They can release organic-rich sediment to their environment (Mazzini et al., 2007). Moreover, the existence of mud volcano correlated with the existence of high methane flux in the seafloor as well as the existence of cold vents, hydrate gas, and carbonate crusts under the exact conditions (Aloïsi et al., 2002; Charlou et al., 2003). These volcanoes are ceous material, and occur both on land and on the seafloor (Milkov, 2000).

A new mud volcano was found in Sidoarjo Indonesia and it close to an active magmatic complex in a back arc sedimentary basin. The mud volcano location is near by magmatic volcanoes so it has high temperature that initiate transformations of mineralogical and geochemical reactions at low level depth (Plumlee et al., 2008; Jalil et al., 2010).

The operational framework of the research started with the need to analyze the three aspects of the sediments. They include the physical or texture of the sediment, heavy metal in the sediment, and the microorganism that can live under extreme condition of mud sediment.

In one side, the flooding mud will create sediment which can be used to study the structure of the soil. Sediments can be ancient key and historical environments. A sedimentary layers sequence can give information about environmental changes (Hallberg, 1992). Cultural impact in industrial era can be revealed by recent sedimentary record. In the process of diagenesis and formation, the sediments also take an active part in the biogeochemical cycles of the elements which affect the overlying water column. Physical characteristics of volcano mud can be identified from its sediment.

3.6.1 Physical Properties of Sidoarjo Mud Sediment

Factors that determined the physical properties of sediment were grain size, sediment components, and some lithology scope (clay, quartz, silica, and biogenic carbonate) (Nobes et al., 1991). Grain density and porosity were related to wet-bulk density which affected by grain size. While, determination of acoustic velocity were influenced by carbonate, clay content, also porosity (Hamilton et al., 1982). The physical properties of Sidoarjo mud sediment were influenced by diagenetic effects, cementation, the increasing of compaction, decreasing porosity, and carbonate dissolution (Nobes et al, 1992). The evaluated sediment physical properties were particle size distribution analysis (mean grain size, sand silt, and sand content) and determinations for percent moisture (water holding capacity) and percent volatile solids or texture of sediments.

3.6.2 Chemical characteristics and heavy metals in Sidoarjo mud sediment

Indication of pollution in environment can be know by metal presences. They are toxic because metal is biologically non-degradable and tend to accumulate in water, fish and sediment (Gale et al., 2004). Industrial activities and natural sources are common cause for evironment contamination. Metals in water and soil can enter the food cycle (Gül, 2009). Heavy metals can contaminate the aquatic environments because of agriculture, industrialization and mining. The contamination can accumalate in the sediment (Olajire et al., 2003).

However, the Sidoarjo mud input was reported that doubled the suspended matter or more and particulate organic carbon load of the river. In addition, decomposition of the additional organic matter can worsen oxygen depletion in aquatic environment that can affect to aquatic organisms. The mud volcano input have some adverse effects of human activities in the river of estuary and Madura Strait coastal waters. It is because of inorganic contents and metals in the mud (Mazzini et al., 2012).

Obviously, it was reported that Chromium (Cr), Arsenic (As), Cadmium (Cd), and Mercury (Hg) was found in high concentrartion 105.44 ppm, 0.99 ppm, 10.45 ppm and 1.96 ppm (respectively) in Sidoarjo mud in early December 2006 (Antara, 2006). The East Java province Public Works Department reported that the Hg content was higher (2.5 ppm) (Mawardi, 2006).

3.6.3 Microorganism in Sidoarjo Mud

There are three dangerous bacteria that are *Salmonella, Coliform* and *Staphylococcus aureus*. This study was conducted by the ICBB in Sidoarjo mud (Antara, 2006). Furthermore, the mud volcano always emits hydrogen sulphide (H_2S) from the gushing mud centre. H_2S levels were at 700 ppm on the first day of mud flow. It is 3 ppm on the second day and it is gone on the thrid day. Furthermore, low level of H_2S still continue to spew out at certain levels. This causes the air smell foul.

Moreover, mud flow in Sidoarjo was considered as suitable condition for thermophilic bacteria that can survive in extreme environmental conditions. The thermophlic bacteria have thermostable enzyme and it is useful for fishery product processing industry, especially in high temperature process. Microorganisms are common cause of waterborne disease. They are usually contaminated in private well water. Moreover, microorganisms are the source of most widely used enzyme compared to plants and animals. As a source of enzymes, microorganisms are more useful because they can grow rapidly. Besides, they can grow easily, can be modified, and also capability of producing fuctional enzymes are the other benefits (Akhdiya, 2003).

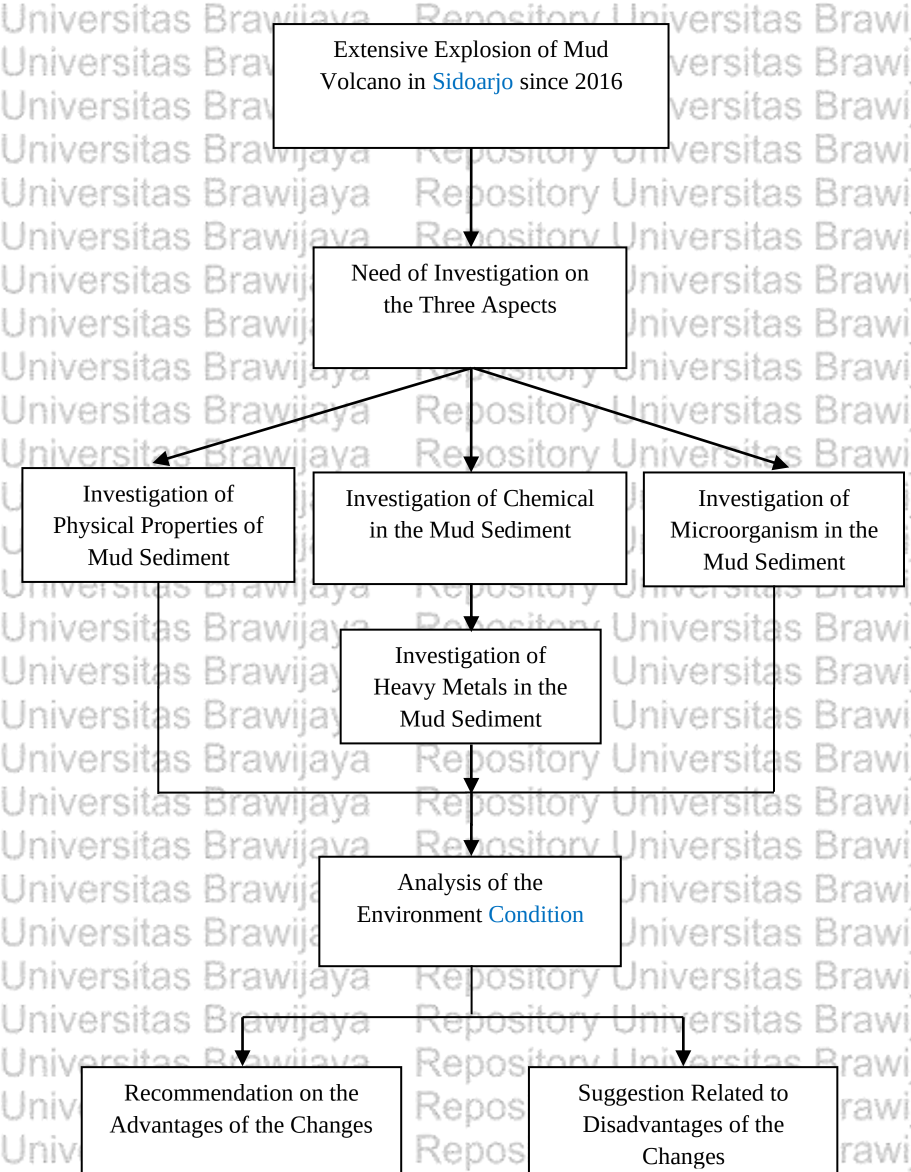


Figure 5. Flow chart of operational frameworks

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CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The result can be concluded that water quality in all research location (West Siring, Jatirejo, Miindi, Penjarakan, Reno Kenongo, Near Explosion Center) has pH average of 6 > and < 8 measured in H_2O and KCl 1N. The highest physical property in the sediment from Sidoarjo mud is silt. The high content of silt is beneficial for the environment as it helps to fertilize the soil. It is nutritious for plants. The highest silt content can be found in Reno Kenongo and near the center of the explosion. The second biggest component of the sediment is clay. Finally, sand contributes the least in the physical properties of Sidoarjo mud sediment.

Organic matter in surface sediments is an important source of food for benthic fauna. The result showed that Reno Kenongo area has the highest carbon content. Therefore, there is possibility that more organisms will survive in this area. However, higher levels of Total Organic Carbon often correlate with increasing concentrations of other potential chemical contaminants which lead to a sharp decline in most benthic variables. On the other hand, the nitrogen content in the six locations is lower than the carbon content.

The main chemical compositions of Sidoarjo mud are calcium, natrium, magnesium, and kalium. The sediments of Sidoarjo mud are high in calcium which is found West Siring. Calcium can reduce the uptake and therefore the effects of lead in fish. The second biggest chemical content is natrium. The next is magnesium content. In contrast, kalium is the lowest chemical found in the sediment in all locations.

Physico-chemical analysis was carried out to investigate the concentration of heavy metal status in sediments of Sidoarjo mud. The metals detected in the sediments include copper (Cu), iron (Fe), manganese (Mn), cobalt (Co), zinc (Zn), cadmium (Cd), molybdenum (Mo) and boron (Bo). Pb and Hg were not detected in Sidoarjo mud sample. The highest heavy metal found in the mud sediment is iron. The second biggest component of the sediment is Manganese. Cobalt content is also seen to be high in all sediment samples. Molybdenum is the fourth biggest heavy metal found. On the other hand, molybdenum has the same potential effect on the plantation. Cadmium is found to be the fifth biggest component in the sediment from Sidoarjo mud with the highest level found in Mindi Village. Cadmium was found at the high average of 1.8%. This concentration may bring the negative effect for the environment. In human, long-term exposure of cadmium is associated with renal disfunction.

Isolate identification showed that bacterial isolates A1 was suspected as *Enterobacter gergooviae* and based on 16s rRNA analysis showed that it is *Marinobacter lutaoensis*. In addition, biochemical test result show that it is *Klebsiella rhinoseleromatis* was obtained from bacterial isolates S1 and based on 16s rRNA analysis showed that it is *Marinobacter hydrocarbonoclasticus*. Bacterial isolates in Siodarjo mud are dominated by thermophilic bacteria that can survive in high temperature ($T > 45^oC$).

5.2 Recommendation

The level of heavy metals on Sidorajo mud sediment was below environmental soil quality guidelines. The levels of physical and chemical on Sidoajo mud sediment were considered acceptable for the environment and in this level it is not dangerous. However, regular monitoring of Sidoarjo River is necessary to protect human health and further environmental disaster.

This research, however, does not compare the condition of the sediment content in dry season. Therefore, it is suggested to conduct another further research on using samples taken during the rainy and dry seasons to compare the result. Moreover, the possible benefits of the sediment on plantation and other industries need to be researched.

Due to the existence of some heavy metals, new treatment needs to be done to normalize the level of heavy metals. In addition, the thermopile bacteria may be effective in fishery products. Thus, further research should digest deeper on the topic.