HEAVY METAL CONTENTS IN SURFICIAL SEDIMENT OF BANJIR KANAL BARAT AND BABON RIVERS, SEMARANG, CENTRAL JAVA, INDONESIA

HEAVY METAL CONTENTS IN SURFICIAL SEDIMENT OF BANJIR KANAL BARAT AND BABON RIVERS, SEMARANG, CENTRAL JAVA, INDONESIA

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ABSTRACT

Bottom sediment (0 - 5 cm) along the Banjir Kanal Barat (Garang River) and Babon Rivers which are situated in Semarang, Central Java, Indonesia were analyzed for their trace/heavy metals content. Eight elements namely Nickel (Ni), Copper (Cu), Lead (Pb), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Iron (Fe), and Manganese (Mn) were investigated. Their concentrations provide information related to the industrial and municipal discharge. There are serious concerns about the contamination in the study area, and previous studies found some elevated concentration of several metals (trace elements).

Total metal analyses of the fine (< 63 μm) sediment fraction by Atomic Absorption Spectrophotometer using strong acid digestion indicated high (Ni, Cu, Zn, and Mn) metal contamination. Weak acid digestion of total sediments (whole fraction) showed relatively low Cd to moderately (Cu, Cr, and Pb) levels. High Iron concentration was detected using X-RF Fluorescence.

The result of trace/heavy metal and sediment characteristic analyses were statistically processed by Spearman's Rank Correlation analyses. In the Babon River, weak acid digestion results found a strong correlation between organic carbon and Chromium. Sediment characteristics, particularly in terms of organic carbon, appeared to be the primary factor controlling metal concentration. In Babon River, strong acid digestion showed that most metals were highly correlated with Mn $(p < 0.05)$, except Zn. In Banjir Kanal Barat River, weak acid digestion results show that Copper (Cu) was highly correlated with organic carbon. From strong acid digestion results significant relationship was found between Zn and Mn $(p < 0.05)$. Analyses of surficial sediment in Banjir Kanal Barat River demonstrate very little significant correlation between metals and sediment characteristics. This condition probably reflected the diverse nature of metal input into the system, either originated from point or non-point sources. However, statistical (t-test) analyses suggested that there were contamination of Ni, Cu, and Zn in both rivers. Most of these values exceeded the Canadian Standard/Guidelines for contaminated soils and sediments. In addition, t-test result also showed different levels of contamination between Banjir Kanal Barat and Babon Rivers. Mean values indicated higher contamination in Banjir Kanal Barat River compared to Babon river.

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I. Introduction

1.2. Background

Many analyses of heavy metal contamination in Indonesian waters are often misleading because metals are reported as "not detected"/"not conclusive" whenever the trace metal levels are at the limit of detection of the technique (i.e.flame atomic absorption spectrophotometry performed in conventional laboratories). Because of those limitations, the quality of natural water system with respect to trace metals is more reliably assesed by sediment analysis.

Although the water chemistry of Banjir Kanal Barat and Babon rivers in Semarang, Central Java has been fairly well documented (Regional Development Planning Agency, 1994), few studies have focused on fluvial, estuarine , and coastal sediments. In the United States, ambient water quality standards have been established for a small number of contaminants, but no such criteria have yet been developed for sediments (Shea, 1988).

According to Salomons (1985), analyses of sediment has advantages compared to water analysis for the control and detection of metal pollution. Although there are fluctuations over time, the rate of change is well below that of water. Beside that, it can reveal an integrated record of the metal pollution with a reasonable sampling effort (Barreiro et al, 1994). Generally, in suspended sediment and the top few centimeters of bottom sediment, concentration of trace metals in most aquatic systems are significantly higher than concentrations of trace metals dissolved in the water column (Horowitz, 1989).

Bottom sediments can act as reservoirs of trace metals. Therefore, they are used in planning and design of any water quality evaluation system. The reasons are : 1) an undisturbed sediment sink may contain historical records of chemical conditions ; 2) sediment-bound trace metals can dissolve into the water column under changing environmental or physicochemical conditions such as pH, Eh, dissolved oxygen, and bacterial action ; 3) several inorganic constituents which are environmentally harmless can degrade, or react with each others, to create soluble and toxic forms ; 4) surface bottom sediments which provide a chemical environment of considerable biological importance (Barreiro et al, 1994), also considered as source of suspended sediment. In heavy storms, a localized pollution problem can become widespread and result in serious environmental impact (Horowitz, 1985).

Rivers are the most important route of transfer of matter from land to sea. The transport and distribution of metals in a river system is controlled by the interaction of water with the riverbed sediments, with suspended material, and with biogenic material (de Groot and Allersma in Krenkel , 1973 ; Borovec et al., 1993). However, this transport is dominated by sediment (Horowitz, 1985). Either naturally occurring or anthropogenically introduced, toxins are mainly associated with suspended particulate matter (Juracic et al., 1986 ; Matisoff and Eaker, 1992). River sediments also can be used as a valuable tool to show spatial and temporal trends of heavy metal contamination (Brugmann, 1995 ; Vincette-Beckett, 1991).

In addition, the < 63 μm fraction of river sediment was studied for total heavy metal contents because 1) trace metals have been found to be present mainly in clay/silt particles; 2) this fraction represents the material carried in suspension (the most important transport mode of sediments); 3) sieving does not change metal concentrations; 4) numerous metal studies have already concentrated on the < 63 μm fraction for better comparison of results (Bopp and Biggs, 1981; Salomons and Forstner, 1984 ; Lacerda *et al.*, 1990 ; Sola *et.al.*, 1991).

1.3. Previous work

The Banjir Kanal Barat and Babon rivers are the major rivers in Semarang, Central Java, Indonesia. They both drain heavily industrialized and intensively cultivated regions. The Banjir Kanal Barat River became one of the rivers prioritized in the Clean River Program in Indonesia (Environmental Impact Management Agency, 1994). Recently, due to its pollution level, Babon River also was included in this program.

According to BAPPEDA (Regional Development Planning Agency, 1988) in Astuti *et.al.*,1990, river waters in the three cities in Central Java (Tegal, Pekalongan, Semarang) were biologically and chemically polluted with heavy metals such as Cr, Cd, and Pb. The levels of pollution were categorized as middle to heavy.

Astuti et.al., 1990, reported that there was evidence of concentration of heavy metals in river mouth sediments of Semarang. The results can be depicted as follows :

Table 1.1. Concentrations (ppm) of Lead (Pb) and Cadmium (Cd) in six rivers in Semarang, Central Java

	Mangkang R	Tapak R.	Sangker R.	Banjir K.Barat R.	Banjir K.Timur R.	Semarang River
Pb	4.2	9.5	6.5	9.5	15.5	8.9
Cd	1.9	1.9	2.5	1.8	2.8	1.6

These values were based on whole fraction of sediment analysis using weak acid digestion methods.

Data from BAPPEDA (Regional Development Planning Agency, 1994), show recapitulation of industrial waste loads (kg.yr $^{-1}$) consisting of many pollutants which enter the Banjir Kanal Barat/Kaligarang River. There were heavy metals (Zn, Pb, Fe, Cr), nutrients (nitrite, sulfide, ammonia), suspended solids, BOD, COD, etc. Most of these values exceed the standard that has been established by Indonesian Ministry of the Environment, except Lead (see Appendix C-2). However, low level discharges of contaminant may meet the water quality criteria in the first time, but long term partitioning of the sediments (as pollutants sink) could result in high concentrations (Davies *et al.*, 1991).

Early in 1995, BBAP (Brackishwater Culture Agency) found that 280 hectares of shrimp farms and fish farms at Bedono and Sriwulan Subdistricts, Demak Regency, died because of industrial discharge from the Babon River (one of the study areas which is located in Semarang Regency). This evidence was very strong from the appearance (colour) of water which was reddish-brown (Suara Merdeka, 1995). Moreover, based on water and sediment/soil analysis, they reported that there were several heavy metals that exceeded the maximum levels recommended by US-EPA (Environmental Protection Agency). The high levels of heavy metal concentrations in sediments which then experience a sudden desorption can cause great danger to aquatic life and this sink could later serve as a source for many contaminants into the water column (Davies *et.al.*, 1991).

Furthermore, several researchers had done monitoring on the effect of heavy metal contaminations on organisms throughout many parts of Indonesian archipelago. Tresnalarawati (1993) examined the concentration of heavy metals (Hg, As, and Pb) in *Anadara granosa* (bivalves), water, and sediment along coastal zones of Banjir Kanal Barat River, Semarang and Bungo Beach, Demak Regency. The results showed that there was heavy metal contamination of mercury, lead and arsenic in both areas. Setiapermana and Hutagalung *et.al.*,(1994) investigated heavy metals (Hg, Pb, Cd, Cu, and Cr) in the Jakarta Bay sediments using strong acid digestion method. Mean values ($\mu g.g^{-1}$ dry weight) of heavy metal concentration were 0.54; 101.1; 1.72; 27.4; and 17.7 for Hg, Pb, Cd, Cu, and Cr, respectively. In addition, Sulistijo *et al.*,1994, examined heavy metal Pb in seaweed (*Eucheuma alvarezzi*) in Batam, Riau. The results showed that the levels of Pb found were above the standard recommended by WHO (World Health Organization).

Recently, Environmental Research Centre, Diponegoro University (1995) worked together with Regional Government to tackle the environmental conflicts that are caused by steel factory pollution (Suara Merdeka, 1995).

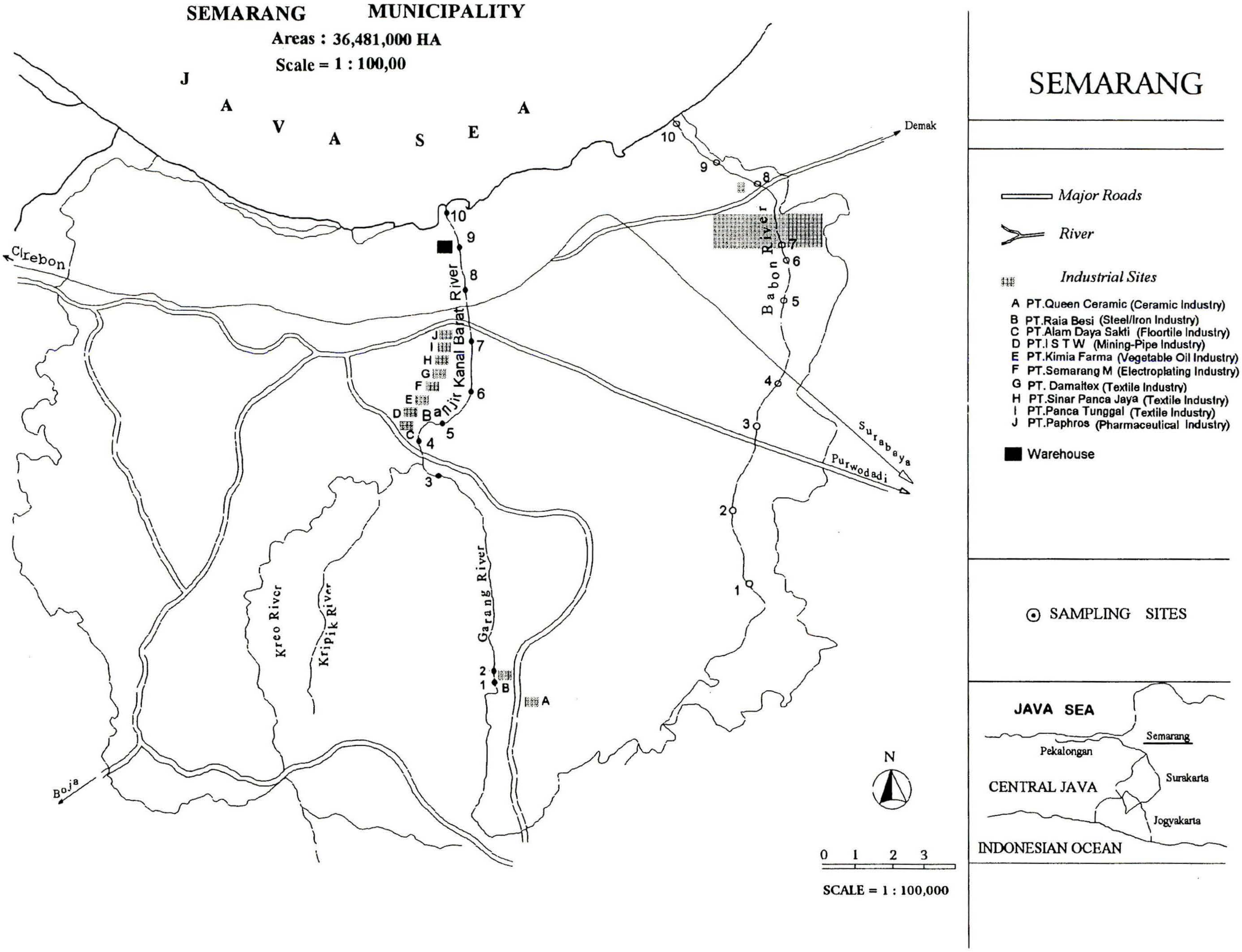
1.4. Study Objectives

The objectives of this study are to investigate and evaluate the major influences controlling the distribution and concentration of trace /heavy metal sediments such as Ni, Cu, Cd, Cr, Zn, Mn, Pb, and Fe in the Banjir Kanal Barat River and the Babon River.

In addition, this study also attempts to study the levels of trace/heavy metal contamination in both rivers and to compare their values with the Canadian Standard for Contaminated Soils and Sediments.

2. Study Area

2.1. Area of Locations


SEMARANG MUNICIPALITY
Areas : 36,481,000 HA
Scale = 1 : 100,00
J A V A S E A
Cirebon
Demak
Surabaya
Purwodadi
Boja
Banjir Kanal Barat River
Babon River
Garang River
Kreo River
Kripik River
1
2
3
4
5
6
7
8
9
10
A
B
C
D
E
F
G
H
I
J
N
0 1 2 3
SCALE = 1 : 100,000
SEMARANG
Major Roads
River
Industrial Sites
A PT.Queen Ceramic (Ceramic Industry)
B PT.Raia Besi (Steel/Iron Industry)
C PT.Alam Daya Sakti (Floortile Industry)
D PT.I S T W (Mining-Pipe Industry)
E PT.Kimia Farma (Vegetable Oil Industry)
F PT.Semarang M (Electroplating Industry)
G PT. Damaltex (Textile Industry)
H PT.Sinar Panca Jaya (Textile Industry)
I PT.Panca Tunggal (Textile Industry)
J PT.Paphros (Pharmaceutical Industry)
Warehouse
SAMPLING SITES
JAVA SEA
Semarang
Pekalongan
CENTRAL JAVA
Surakarta
Jogyakarta
INDONESIAN OCEAN

2.1. Geography and Climate

Semarang Municipality lies between Ungaran Mountain (elevation 2000 m) to the South and the Java Sea to the North, with geographic position between 6° 50' - 7 °10' South Latitude and 109° 50' - 110° 35' East Longitude. It is bordered by Kendal Regency in the West and Demak Regency in the East. The area of Semarang is 37,333,83 ha with 99 districts and 117 subdistricts. The population of Semarang city in 1991 is 1,154,536. In addition, industrial sites in Semarang are not located in one specific area, but widely distributed on the east, west, north, and southeast of the City (Environmental Impact Management Agency, 1994)

Local climate is influenced by the North West Monsoon wind that prevails between October - May (wet season) and the South East Monsoon wind that prevails between May - October (dry season). Monthly basin rainfall during the year of 1958 - 1990 ranged between 1,474 - 3,181 mm in Banjir Kanal Barat River (BKBR) and 1,414 - 3,029 mm in Babon River (BR). In average, total amount of rainfall ranges from the lowest value 70 mm on August, and the highest value 365 mm in January. Monthly average of wind flows range from 4.5 - 5.8 km/hour and temperature range from 26.5 - 28.3 ° C, the highest is 33.3 ° C, the lowest is 23.2 °C (JICA Study Team, 1994).

2.2. Hydrology and Lithology

The area of water catchment of the two rivers which were evaluated can be depicted in the table below :

Table 2.1. Characterization of River Flow Regime in Banjir Kanal Barat and Babon Rivers

River	Area (km^2)	Length (km)	Elevation (m)	FR max. ($m^3.sec^{-1}$)	FR min. ($m^3.sec^{-1}$)	AVE.
BKBR	204.0	-	-	99.2 (1987)	1.50	9.65
				123.0 (1988)	0.38	8.54
				74.4 (1990)	1.30	6.88
BR	77.0	21.0	370 - 209	39.5 (1987)	0	2.83
				162.2 (1988)	0	2.53
				354.1 (1990)	0.01	4.27

Note: (Source : JICA STUDY TEAM, 1994)

FR = Flow rates AVE = Average

At reduced flow rates and low velocities, suspended particulates settle down becoming incorporated into the bottom sediment. Usually, the chemical composition of the sediment reflects that of the overlying water column. At high flow rates, washing of the river bed may occur, leading to a lower level of contamination (Goncalves et al., 1994).

In general, soil in Semarang can be divided into 4 types: grey-yellowish alluvial, old-grey alluvial, reddish brown alluvial, and grey alluvial mediteran (brown grumusal). In the area surrounding Babon river, the soils are composed of calcareous sandstones interspersed with claystones and marls. The river itself consists of alluvial rocks and very loose sand - cobble (Regional Development Planning Agency, 1994).

2.3. Erosion and Sedimentation

Accelerated erosion of agricultural lands, urban construction, mining, forestry, and similar activities have greatly increased the sediment loads (especially large particles such as sand and silt) of many streams (Cutter et al., 1985 ; Muller and Tyler,1991) which will be usually deposited quite near the stream channel, along the banks or on the flood plain (Renwick and Ashley, 1984).

Sand and gravel are found in more energetic areas such as steep rivers, areas with strong tidal currents and along exposed coasts, while silt and clay sediments (which in general contain higher metal concentrations) accumulate in more quiet waters such as tidal flats, flood plains, etc. The different sources contributing to the sediment load of a river during high discharge are also reflected in its trace metal concentrations. Based on flows in rivers and estuaries, sand and gravel move in a thin layer along the bottom as bed load, while silt and clay are transported as suspended load (Salomons and Forstner, 1984).

Some inorganic and organic trace substances have a tendency to travel adsorbed to particles, rather than being dissolved, and substantial amounts of these pollutants may be removed from water. However, in areas that receive large amounts of urban runoff or industrial discharges, contamination levels in sediments can be quite high. Under changing environmental conditions, sediment as a reservoir may cause a remobilization of accumulated metal (Salomons and Forstner, 1984). In some environments, especially rivers, contaminated sediments may become resuspended and the contaminants reintroduced to the water (Renwick and ashley, 1984).

The kind of erosion and sedimentation processes and their total amount that take place in Banjir Kanal Barat River (BKBR) and Babon River (BR) can be classified as follows :

Table 2.2 : The amount of erosion and sedimentation (1000 m^3/yr) in BKBR and BR

River Flow Regime	Sheet erosion	Bank erosion	Tot.erosion	Tot.sed.transport
1. BKBR	930.30	16.50	946.80	240.20
2. BR	384.10	6.20	390.30	109.70

Note : BKBR = Banjir Kanal Barat River, BR = Babon River
(Source: JICA STUDY TEAM, 1994)

2.4. Vegetation

Vegetation along Babon River, in general, can be classified into 1) economical and agricultural plants, 2) forest and other plants. In the first category, there were 20 species. The dominant species were *Musa paradisiaca, Manihot utilissima, Arachis hypogeae, Albizia sumatrana.* The others are *Cocos nucifera, Leucauna glauca, L.macrosephala.* In the second category, there were *Ipomoea crassicaulis, Sactiarrum spontaneum, Imperata cylindrica, and Centrocema plumieri.*

Vegetation along Banjir Kanal Barat River include as much as 25 species. The dominant species were *Musa paradisiaca, Arthocarpus integra, Carica papaya, Psidium guajava, Leucaena glauca, Cocos nucifera, Mangifera indica, and Bambusa sp.* Agricultural areas consist of *Manihot utilissima, Oryza sativa, Arachis hypogaea, and Vigna sinensis* (JICA Study Team, 1994).

3. Literature Review

3.1. Sources of pollutants

There are five different sources from which metal pollution of the environment originates: (1) geologic weathering, erosion, and volcanic activity (2) industrial processing of ores and metals, (3) the use of metals and metal components, (4) leaching of metals from garbage and solid waste dumps, and (5) animal and human excretions which contain heavy metals (Forstner and Wittmann, 1983).

The geochemical contribution of heavy metal to the water system through the weathering of basement rocks is over-shadowed in many areas by anthropogenic input from a wide variety of sources. According to Salomons and Forstner (1988) in Bubb *et.al.*, (1991), those sources reflect the multipurpose usage of metals in industry and their consequent widespread occurrence in rural and urban environments. It is known that mixed inputs of industrial, agricultural, and domestic wastes into the river environment produce 2-10 fold increases in sediment metal loadings. According to Bubb *et.al.*, 1991, agriculture may also be an additional contaminant source through runoff of fertilizers/pesticides/fungicides and animal wastes.

3.1.1. Domestic effluents and urban storm runoff

In the west, domestic effluents are usually discharged from a relatively well-defined point source. They contain fairly high concentration of heavy metals (Al, Cu, Fe, Pb, and Zn) which are derived from a wide variety of household products for example cleaning materials, tooth paste, cosmetics, and human faeces (Stephensen, 1987) in Bryan and Langston (1991). In Indonesia, domestic effluents from housing become one of the largest water pollution sources. This is due to the lack of household sewage treatments (Suara Merdeka, 1995).

Urban stormwater runoff in Semarang is characterized by a diffuse drainage pattern. Together with drainage from rural areas and domestic effluents, they become the most important non-point sources of metal loads in inland waters.

Runoff from Central Semarang, which is highly populated, becomes a source of pollution because the drainage system here is a mixture of rainfall, domestic sewage, and industrial wastes. Beside this, there are sources from sand mining, farming, and fisheries activities in both rivers (Environmental Impact Management Agency, 1994).

According to Drinking Water Company in EIMA, 1994, the water usage (use) in Semarang Municipality is shown in the following table. The amount of water discharge from domestic sources can be predicted from the domestic water use.

Table 3.1. Water Use in Semarang Municipality

	Consumer	Consumption (m^3/day)	Ratio (%)
1. Domestic	52,090	39,134	83
2. Non-domestic			
a. Trade	3,604	3,599	8
b. Industry	0	0	0
c. general need	1,358	3,657	8
d. Social	401	595	1
Total	57,543	46,985	100

3.1.2. Industrial Waste

Industrial effluents are one of the most important sources of toxic contaminants in the environment. Their disposal into the surface waters is often conducted without careful consideration which can produce deleterious effect on the environment. Rivers in industrialized areas contain large amount of heavy metals. Due to random timing of discharge, it is difficult to detect metal in water analyses and it is more advantageous to use sediments as pollution indicators for metal content evaluation (Forstner and Salomons, 1989).

On Java , for example, large and middle scale industries have become the primary cause of water quality degradation. In most rivers, industrial effluents account for 50 % of the total pollution loads to the area of catchment (Suara Merdeka, 1995). Furthermore, industrial wastewater can form a very significant contribution to the effluent concentration, especially in Semarang rivers where increased emphasis is placed upon the combination of industrial and domestic wastewater and stormwater runoff (JICA Study Team, 1994).

In Banjir Kanal Barat River, which has middle - large scale industries, there are numerous sources of industrial effluents leading to heavy metal enrichment of the aquatic environment (Astuti, 1990). In the end of the year 1994, from ten factories, some of them still discharge sewage that exceeds the ambient quality (requirements). These are: Sinar Panca Jaya, Paphros, Queen Ceramic, Raja Besi, and Damaitex. Copper, iron, nickel, etc. have commonly been used in electroplating, textile, and iron factories. Semarang Makmur factory (electroplating) is considered as small scale industry. Babon River has small - middle scale of industries. Most of them use a specific heavy metal such as chromium in the tanning / leather industry. However, multipurpose usage of numerous heavy metals may lead to difficulties in tracing the source of origin of water pollution conclusively (Environmental Impact Control Agency, 1994).

Table 3.2 shows the factories that are located around Banjir Kanal Barat (No. 1 - 10) and that are located around Babon River (No. 11 - 16) describing the conditions of their industrial discharge before treatment :

No.	Name of industry	Conditions of industrial discharge
1.	PT. Queen Ceramic	- high pH and COD
2.	PT. Raja Besi	- high pH and metals
3.	PT. Alam Daya Sakti	- high pH, COD, and suspended solid (waste) for floortile
4.	PT. I S T W	- high pH, Zn, Cr, Fe, COD, and suspended solid
5.	PT. Kimia Farma	- liquid wastes from oil refining, water sanitation high COD, BOD,and suspended solid
6.	PT. Semarang Makmur	- liquid wastes from pickling, rinsing unit, and water quenching
7.	PT. Damaitex	- high pH, COD, BOD, and suspended solid from finishing, printing managed by skimming and sedimentation
8.	PT. Sinar Panca Jaya	liquid wastes from starching, spinning (cooling)
9.	PT. Panca Tunggal Knitting Mill	- liquid wastes from sinking, washing/and dyeing
10.	PT.Paphros (pharmaceutical)	- high pH, COD, and BOD (liquid wastes concentration higher than required)
11.	PT.Buana Sakti Tannery	---------
12.	PT.Puspita Sari Tannery	---------
13.	PT. Cold Storage Mina Baruna	---------
14.	PT. Jaguar Tannery	--------
15.	PT. Condro Cipto Tannery	---------
16.	PT. Fodder Company	---------

------------ information not available
(Source : Regional Development Planning Agency, 1994).

Changes in water discharge, fluctuations in the predominance of certain source areas, and irregular local emissions are responsible for variations in orders of magnitude. During high water periods, certain pollutors will empty out accumulated waste products (Forstner and Muller, 1973).

3.2. Heavy metals as Pollutants

All metals are soluble to some extent in water. Heavy metals, which in normal concentrations are essential components of biochemical function (Cu, Zn, Fe, Mn, Cr, and Co), are toxic when present in higher concentrations (Forstner and Muller, 1973). Other toxic metals that may be dissolved in water include cadmium, lead, arsenic, etc.(Bubb *et al.*, 1991). Unlike organic pollutants, inorganic pollutants such as heavy metals are very threatening because they are not decomposed by microbial activity.

However, it is difficult to detect pollution in water, because once it is released into the aquatic environment, sedimentary processes act to reduce metal concentration in the water column (Warren, 1981).

The accumulation and distribution of metals within sediments will be influenced by hydrological factors such as flow dynamics and water depth, together with physico-chemical parameters such as quantity of suspended solids, pH, redox potential, sedimentation rate, distance from the pollution source, and existing contamination within the environment (Bubb *et al.*, 1991).

Heavy metals/trace elements that are being concerned are :

3.2.1. Chromium

In Canada, chromium is commonly used as an electroplated protective coating because of its resistance to ordinary corrosive agents. At elevated temperature, chromium reacts readily with halogens, oxygen, carbon, sulfur, silicon and boron (Nriagu and Kabir, 1994). In Indonesia, chromium is used in tannery, leather, textile, electroplating and paint industries (Environmental Impact Management Agency, 1994).

According to Murray *et al.*, 1983 in Nriagu and Kabir, 1994, environmental chemistry of chromium is very complex. Chromium can exist in the environment as Cr (III) or Cr (VI). The toxicity of chromium and its aqueous concentration and its mobility in different geologic environments are dependent on its oxidation state. Cr (III) can be oxidized to Cr (VI) (Rai *et al.*, 1989), but the chemistry of Cr (VI) is radically different from that of Cr(III). Because most of its salts are soluble, Cr (VI) is very mobile in the environment, but it is not readily adsorbed to surfaces (Nriagu and Nieboer, 1988) . From a behavioural point of view, Cr (VI) can be categorized as having a relatively long residence time in the water column. Because of its high oxidizing potential, high solubility, and ease of permeation of biological membranes, Cr (VI) is more toxic than Cr (III) (EPRI, 1986).

3.2.2. Copper (Cu) and Cadmium (Cd)

In general, Copper and Cadmium were exist in the final effluent as dissolved species representing as much as much 80 % of the total, and they are the most bioavailable form. Once incorporated into sediments by adsorption processes , cadmium forms association with organics, sulphides, and manganese oxides. Copper tends to have a high affinity for the clay/ silt fraction (Bubb *et.al.*, 1991).

Cadmium is a relatively rare element and usually occur in environmental media at low concentrations. Cadmium (Cd^{2+}), cadmium carbonate ($CdCO^3$), and CdS have been considered to be the dominant inorganic forms that dissolve in river water. About 70 - 90 % of Cadmium in freshwater stream was present as the free hydrate ion (Bubb *et.al.*, 1991) or other liable complexes such as chloride complexes (Bryan and Langston, 1992).

Copper (Cu) is invariably highly complexed in polluted and unpolluted freshwater (Stiff, 1971) in Moriber, 1974. Copper may exist in the dissolved phase mainly as cupric ion.

3.2.3. Zinc (Zn)

Zinc is among the most prevalent of metal contaminants in the environment, especially in aerobic water . A significant fraction is likely to exist as simple ionic forms such as carbonate and hydroxyl complexes , hydrated ion, and stable organic or inorganic colloids particularly humics. (Bubb *et al.*, 1991).

Levels of Zn in coastal areas and estuaries are often much higher than oceanic concentrations (< 1 ug/lt) (Bruland *et al.*, 1979) in Bryan and Langston, 1992. The most available and abundant form of Zn is the free ion Zn^{2+}. Due to its comparatively high solubility, Zn tends to exist in the dissolved forms (O'Brien et al, 1990) in Bryan and Langston, 1992 ; Bubb *et al.*, 1991.

3.2.4. Lead (Pb)

Lead occurs in the environment in a wide range of physical and chemical forms which greatly influence its behaviour and its effect on the ecosystem. Most lead in the environment is the inorganic form as salts, oxides or hydroxides.

In the aqueous environment, lead is not only abundant in the earth's crust and predominantly asssociated with suspended solids but also is likely to acccumulate in sediments. However, compared with the anthropogenic inputs, the contribution of lead from natural sources tends to be insignificant, except in certain localized areas (Zabel, 1989) and its dissolved concentration in surface water is low due to its low solubility product (Prosi, 1983). Also, because of its complexity and the variability of natural environment and the log-time scale involved, the distribution, behaviour, transport, fate and bioavailability of lead in the environment is difficult to predict (Zabel, 1989).

Lead is used in mining, smelting and non-ferrous metal industries. In Indonesia, lead is used in paint and galvanizing/electroplating factories, and as leaded gasoline.

3.2.5. Iron (Fe) and Manganese (Mn)

Iron has frequently been used as an indicator of natural changes in the heavy metal carrying capacitty of the sediment and its concentration has sometimes been related to the abundance of metal-reactive compounds supposedly not significantly affected by human actions (Barreiro *et al.*, 1994).

Mn has a role in giving important information about the heavy metal content or trends in sediments (Mantei and Foster, 1991).

Iron and Manganese are not pollutants, often occur together, and present no health hazards at concentrations normally found in natural waters. They may accumulate toxic /harmful heavy metals by co-precipitation or adsorption and release them again under reducing conditions which dissolve those matrix forming elements. However, compared to organic matter, iron oxides, and clay minerals, manganese oxides have higher relative capacity to collect (accumulate) metals (Brugman, 1995).

Both iron and manganese oxides have long been known as excellent scavengers of trace metals in solution (Krauskopf, 1956) in Horowitz, 1985. While in soils, suspended sediment, and in bottom sediment, iron and manganese oxides also occur as coatings on various minerals and finely dispersed particles (Forstner and Wittmann, 1979).

3.2.6. Nickel (Ni)

Nickel enters freshwater and terrestrial environments not only from the natural weathering and leaching of rocks but also from human activities such as mining, smelting, refining, alloy processing, scrap metal reprocessing, other metal operation, fuel combustion, and waste incineration (Chau and Cordeiro, 1994).

The proportions of total nickel associated with particulates can vary from 7-99 %, reflecting variations in source rock and the impact of industrialization. Wastewater streams contribute a high proportion of dissolved nickel, usually as Ni^{2+} or stable complexes (Bubb *et al.*, 1991).

Nickel exists as a trace constituent in a wide variety of minerals that contain large amounts of iron and magnesium, such as olivine and pyroxenes (NRCC, 1981). In Canada, a nickel compound (e.g. Nickel Carbonate hydroxyde) is usually used in a variety of products and processes such as plating (as a catalyst for the hardening of fats) and in colours and glazes for ceramics. Others such as nickel carbonate are used in electric components; anhydrous nickel chloride for ammonia adsorbent in gas masks and in nickel plating; nickel oxide is primarily used in metallurgical operations as an important raw material for smelting and alloy producing processes; and nickel nitrate is used in nickel plating and nickel-cadmium batteries (IPCS, 1991). In Indonesia, some factories use Nickel for electroplating.

The heavy metal uses in major industries can be depicted in the table below :

Table 3.3 : Heavy Metals Employed in Major Industries :

****

	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sn	Zn
Organic chemicals	x	x		x	x		x		x	x
Inorganic chemicals	x	x		x	x		x		x	x
Fertilizers	x	x	x	x	x	x	x		x	x
Basic steel foundries	x	x	x	x	x		x	x	x	x
Basic non - ferrous metal	x	x	x		x		x			x
Motor vehicle plating,finishing	x	x	x		x			x		
Textile		x								
Tanning, leather		x								
Petroleum refining	x	x	x	x			x	x		x

****

Source : Forstner and Wittmann (1983)

Major industries in Semarang (especially those which are located along the study areas) that use heavy metals as a component in production processes are listed in Appendix A and Appendix B.

3.3. Trace/Heavy metals in food chain

It is a fact that some trace elements/metals are essential to organisms. For example ; Manganese has a role as an enzyme activator in biologic system; Iron as a component of hemoglobin in blood; Copper is known as essential elements in the diets of birds and mammal and it exists in combination with the blood protein of snails; Zinc has the ability to occupy low symmetry sites in enzymes, and can therefore function as an essential constituents of enzymes, etc. No organic life can develop and survive without the existence of metal ions.

However, the excessive amount of toxic metals such as mercury, cadmium, copper and many other species which are accumulated in the sediments, may be released by various processes of remobilization, and will move up the biologic chain, then reaching human beings (Forstner and Wittmann, 1983).

The following heavy metals are considered hazardous to organisms/human life:

- *Lead (Pb)*: The released of this metal to the atmosphere includes Pb smelting, refining of lead scrap, and burning of leaded gas subsequently falls out onto crops. In addition, lead solder is used on food containers. In water, Pb is widespread as a result from agricultural practices such the use of pesticides which may wash off and contaminate runoff or groundwater. Beside that, plowing and irrigation can accelerate leaching of Pb from soils. Typical Pb concentrations in urban air are about 1.3 $\mu g/m^3$ while in rural air is only 0.05 $\mu g/m^3$.

Lead enters the human body primarily via inhalation and through ingestion of contaminated food and water. Compare to mercury and cadmium, the lungs retain lead more efficiently than the gastrointestinal tract. When Pb absorbed into the blood-stream, lead is transported to all parts of the body especially by red blood cells. About 90 % of the inorganic lead in the body is deposited in the bones, where it replaces calcium. Organic lead (i.e.lead alkyls) tends to concentrate in lipid tissue (i.e. central nervous system).

In 1977, 2.4 million of waterfowl out of North American population of about 100 million die each year due to the ingestion of lead shot, and others show sublethal effects which make them more vulnerable to predation and disease. In addition, toxicity studies show that poisoning effect begin to occur on fish at Pb concentrations of about 100 ppb in soft water, and 300 - 500 ppb (12-18 weeks) values on oysters (Forstner and Wittmann, 1984). However, lead is not easily accumulated by plants (O'Neill, 1985). The lead cycle is depicted in figure below :

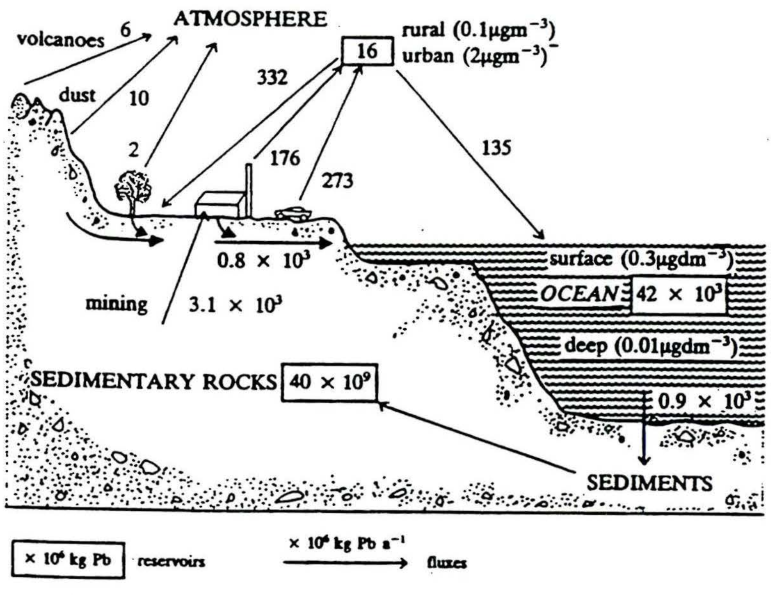


Figure 3-1. Lead Cycle

- *Cadmium :* with respect to toxicity, is not required even in small amounts for the maintenance of life. It is believed that ion Cd^{2+} exerts a toxic effects. An analysis of Cd levels in various foods stuffs, in air, and in water has indicated that people possibly ingest about 45 - 80 μg/day of Cadmium from the food, 1 - 2.5 μg/day from the water, and 0.02 - 1.0 μg/day from the air (OECD, 1975) in O'Neill (1985)..

In the body, cadmium tends to be accumulated in the liver and kidneys by thionin (Forstner and Wittmann, 1983). The body burden of cadmium increases when the age increases, too. Normal dietary intakes are in the range 0.4 - 0.5 mg per week as maximum recommended by WHO.

Cadmium is readily taken up by plants and enters the edible portions. Its concentration in plants are approximately the same with soil levels. In soils, the ratio of Cadmium varies from 1:300 to 1:2900 by mol; in seawater , the molar ratio is 1:35 .In Japan, due to aerial pollution from cadmium-containing fumes and particulates, plus water pollution from cadmium-containing sediments and mine wastes, rice grown in paddy fields flooded by the river contained up to 3.4 mg Cd kg^{-1} rice.

- *Zinc :* is one of the most abundant essential trace elements in the human body. Zn has a role as a cofactor of several enzymes (Forstner and Wittmann, 1983). Adult people contain 1.4 - 2.3 g Zinc, about half the amount of iron. Deficiency of this element in human can cause dwarfism, reduced rates of blood clotting and wound healing, skin abnormalities, and other problems (O'Neill, 1985).

The mobilization of Zinc (and Cadmium) by human activities outweighs natural cycling process. This is due to increasing demand for cadmium itself and the use of zinc and phosphate fertilizers which contain 5-100 mg Cd kg^{-1} (O'Neill, 1985). Normal Zinc levels in plants are 25 - 150 mg.kg^{-1}. In clams, the concentration of Zinc increases in dry season and decrease in wet season. At level of 400 ppb, Zn has lethal effect on mollusk larvae and at level of 10000 ppb is toxic to adult fish and clams (Hutagalung, 1994). The cycle of Zinc and Cadmium is depicted in figure below :

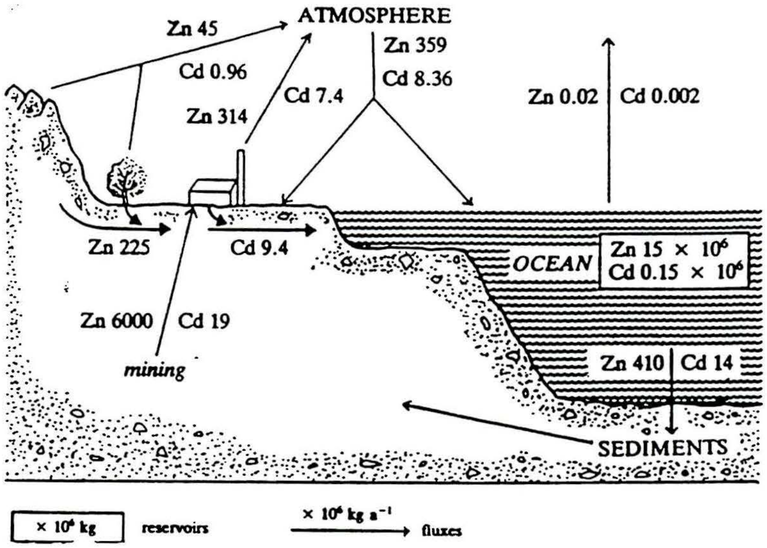


Figure 3-2. Zinc and Cadmium Cycle

- *Chromium* : In Japan, exposure by inhalation to dust containing chromium in high oxidation state (IV) and (VI) was associated with malignant growth in the respiratory tract and painless perforation of the nasal septum. In 1975, drinking water in Tokyo obtained from groundwater near the Cr (VI)-containing spoil heaps, contained more than 2000 times the official threshold limits (Forstner and Wittmann, 1984).

- *Nickel* : the toxicity of this element is lower compared to other metals such as Mercury (Hg), Cadmium (Cd), Lead (Pb), and Silver (Ag). However, in the excessive amount it will be toxic, especially for plants. Concentration of Nickel as much as 120 ppb is sufficient enough to kill oyster (Environmental Protection Agency, 1973) in Hutagalung, 1994.

3.4. Trace/heavy metal analyses

Recently, several analytical methods have been and are still being developed and applied to investigate the behaviour and fate of trace metals in the environment. Not only total concentration, but also their specific physicochemical forms are determined.

If total concentration analysis is applied, it means that all forms of a given metal are implicitly considered to have an equal effect on the environment and a similar behaviour in the biogeochemical cycle. Also, it can assess its environmental impact (only where it is present as a single well known species), but it can not predict behaviour and fate of trace elements in environment, bioavailability, toxicity, and distribution (Morrison in Batley, 1989).

3.5. Sediment Characteristics

3.5.1. Grain Size

One of the most important factors controlling sediment capacity to concentrate and retain trace metals is grain size . Most sediments tend to be comprised of material finer than 2,000 μm (very coarse sand) in lakes, rivers, and estuaries. The other factors are surface area and geochemical substrate such as Fe and Mn oxides, organic matter, clay, minerals, etc. (Horowitz, 1985).

It is believed that metals are not homogenously distributed over the various grain size fractions and that there will be large differences in total metal concentrations which are detected in sediment samples. In general, the fraction less than 63 μm is recommended for analysis for the following reasons :

- trace metals have been found to be present mainly in clay/ silt particles
- this fraction is most nearly equivalent to the material carried in suspension (by far the most important transport mode of sediments).
- numerous metal studies have already been performed on this fraction

(Forstner, 1980; Dossis & Warren,1980; Forstner & Wittmann, 1983; Salomons & Forstner, 1984; Cauwet, 1987). However, certain size fractions sometimes do not reflect the concentration in the total sediment (Windom et al., 1989).

Regarding surface area and organic content, fine grained sediments (< 2 μm) are not only rich in clay, iron, organic matter, fine grained quartz, carbonate and feldspar particles but also have great affinity for pollutants due to their large surface area and negative charge. Silt-size particles (2 - 63 μm) tend to form the major form of suspended matter under normal flow regimes and have high metal loadings associated with detrital materials (Taylor, 1986). However, metals can and do accumulate on many substrates, including sand, pebbles, cobbles, and boulders (Robinson, 1982 in Horowitz, 1985).

3.5.2. Organic matter/Organic carbon

In water, organic matter exists in dissolved and particulate forms; in the latter it occurs as individual particulate or as adsorbed matter on organic and inorganic particles (Forstner, 1977; Khalaf *et.al.,* 1981) in Ghadban *et.al.*, 1995. The role of organic matter in metal transport is important, since it is able to bind trace metals and takes part in diagenetic processes after deposition (Salomons and Forstner, 1984).

The accumulation of organic matter is a result of several factors such as high organic production (or input) and low renewal of water masses, giving rise to depletion of dissolved oxygen (Taylor, 1986). If organic matter is not removed during sewage treatment processes, it is believed that there will be metal enrichment (Salomons and Forstner, 1980). According to Swanson and others, 1966 in (Horowitz, 1985), organic matter can concentrate between 1 percent and 10 percent dry weight of Co, Cu, Fe, Pb, Mn, Ni, Zn, etc. Their concentrations in sediment produce a characteristic environment with low negative redox potential. The distribution of organic carbon values in the sediment will be low if the sedimentation rate is high, where particles are not organic rich and the sediment slightly coarser , and vice versa (Cauwet, 1987).

Owing in large part to variations in particle size distribution, organic carbon of sediments of a given water body can vary by an order of magnitude. The organic carbon values from several published reports for bed sediments range from 0.3 to 8.6 % in rivers, 1.5 to 13.8 % for harbours and bays , 0.1 to 3.0 % in the continetal shelf (Jenne in Baker, 1984).

4. METHODOLOGY

4.1. Sediment analyses

The study sites taken were based on the closeness to the industries, access to the rivers, and previous study sites. Site number 1 was choosen because this location is the first site that receives industrial discharge. The next sites were choosen because they are close to other industries along the rivers.

Surface sediment sampling were performed in the middle of the rivers. Surface sediments were collected using an Ekman grab sampler. The samples were carefully scraped only the top 2 cm, then transferred to plastic bags. At places where the water depth are low, plastic spatula was used to take the sediments. Ten samples from Banjir Kanal Barat River were collected in June 11, 1994 and ten samples from Babon River were collected in June 12, 1994. Sediments were air-dried at room temperature. Some were kept for weak acid digestion (using whole sediment fractions), and some were sieved through a 63 μm mesh sieve for strong acid digestion. The rest of the sediments were used for analyzing sediment characteristics such as organic matter (Loss on Ignition), organic carbon, and grain size analyses. In addition, temperature, pH, and related environmental parameters were measured in the field.

To know the concentration of heavy metals in the environment, several analysis methods were applied in this study. *First*, weak acid digestion using HNO_3 and $HClO_4$ gives "bioavailable" metal. *Second*, strong acid digestion using HF, HNO_3 and $HClO_4$ on fraction < 63 μm of sediments which not only gives total concentration of metals but also attacks the silicate material. *Third*, X-Ray Fluorescence. According to Hungspreugs (1988), these methods are suitable to be used in environmental studies for analyzing the environmental impact of metals in the aquatic environment .

The procedures that were used in sediment analyses are described as follows :

4.1.1. Nitric-perchloric acids attack for sediment/Weak Acid Digestion (AAS)

Atomic Absorption Spectroscopy (AAS) is based upon the absorption of resonance radiation by an atomic vapor of the analyte. The resonance radiation corresponds to the wavelength associated with excitation of gaseous analyte atoms from their ground states to excited states. The total amount of absorption depends on the number of free atoms present and the degree to which the free atoms absorb the radiation (Robinson, 1982) in Cantle (1982).

The use of nitric acid separately or with either hydrochloric or perchloric acid will provide a high degree of metal extraction by destroying organic matter, dissolving all precipitated and adsorbed metals and leaching out a certain amount of the metals from the silicate lattice, but will not dissolve silicates completely (Agemian and Chau, 1976 ; Palanquez and Diaz, 1994). In addition, significant portions of more refractive elements like Al, Cr, Fe, and Ni were left undissolved (Robinson, 1982) in Cantle (1982).

In weak acid digestion method, 10 g of sediment sample from each location were put into Erlenmeyer 125 ml and distilled water added. About 5 ml of HNO_3 and 2 ml of $HClO_4$ were poured into the solution (nitric acid was added before perchloric acid, because the latter can react explosively with untreated organic materials). Samples were put on a hot plate (100 ° C) until 3 - 5 ml volume of solution was left , diluted with distilled water until 50 ml, then placed into volumetric flasks. Trace/heavy metals such as Cu, Cd, Cr, and Pb were analyzed. Analyses were performed using Hitachi Polarized Zeeman-8000 Atomic Absorption-Flame Spectrophptometer at Centre of Physical and Chemical Analyses Laboratory, University of Gadjah Mada Yogyakarta, Indonesia. The detection limit for Cu, Cd, Cr, and Pb were 0.02 ; 0.01 ; 0.03 ; and 0.4 ppm, respectively.

4.1.2. Hydrofluoric, nitric, and perchloric acids attack for sediment/ Strong Acid Digestion (AAS)

Pre-weighed (± 0.25 g) dry sediment samples were put into teflon beaker and were digested in a gradually warmed (± 100 °C) mixture of nitric, perchloric and hydrofluoric acids in teflon 'bombs'. This method will destroy the silicates and most constituents of sediments.

Samples were evaporated overnight and after several steps of dilution (with deonized water) and filtration (using mesh 42 of ashless paper), the samples were ready for analyses by Atomic Absoption Spectrophotometry (AAS) Varian-400 (Sola, 1991). The detection limit for Ni, Cu, Mn, Fe, Zn, Pb were 0.05; 0.01; 0.05; 0.05 ; 0.01 and 0.018 respectively. The residue from filtering processes were kept for later analysis (Appendix Q). Duplicates were run in order to know the precision of the analyses.

The equation used to calculate trace metals concentration from AAS is :

Concentration (ppm) = volume/weight x AAS value x Dilution factor (DF)

In order to calculate the amount of original samples within the solution analyzed by the AAS, the insoluble residue (IR) derived during the filtering process was then subtracted from the original sample weight.

4.1.3. X-ray Fluorescence

Powdered samples (± 50 g) were ground, and then pelletized at high pressure (some materials may be sufficiently soft and homogenous as to allow direct pelletization). These samples were placed into vial and about 5 - 6 drops of supersaturated solution of moviol were added as a binding agent. The binder and sediment powder were mixed until well distributed and then put into the pelletizing dies. This mixture was pressed with a plastic piston and after 4 - 5 g of Boric acid were added to make sample more resistant and stable, pressed again under ~ 12 tonnes pressure fo about 5 - 10 minutes to make a pellet. The pellets were dried in the oven ~ 60 - 70 ° C for about 12 hours and then were ready for X-RF analysis.

4.1.4. Organic Matter Content Analyses

The organic matter (or recognized as Loss on Ignition /LOI) was expressed as volatile matter determined by calcinating the sample at 550°C (Bachtiar, 1993).

Dried sediment samples from which all carbonate was removed were weighed (10-15 g) and heated at 550°C for 1 hour. The samples were then weighed again. The organic content is given by :

$$\textbf{Organic matter content} = \frac{\mathbf{Ws - Wr}}{\mathbf{Ws}} \times 100$$

where organic matter content in percent (%) :

Ws = weight of the dried sample

Wr = weight of the inorganic residue

4.1.5. Total Organic Carbon (TOC) Analyses

Carbon (C) is a "building " element for organic matter formation, and represents 48 - 58 % of total organic matter. The principle work of total-C analyses method is changing the organic carbon compounds to CO_2 , then the total of CO_2 can be determined. Oxidation of carbon (C into CO_2) was performed by wet destruction method. The amount of organic matter can be estimated based on the total C that is being oxidized. The whole procedures can be seen in Appendix P.

4.1.6. Grain Size Analyses

One of the major considerations when evaluating contamination levels in river sediments is the relationship between heavy metals and particle size (Dept.of Environment, 1977) in Bubb et al., 1991.

In this study, sediment grain size was determined by U.S.Standard Sieve Mesh #, utilizing sieves to separate gravel and sand fractions from the dry clay and silt fractions. This analysis was performed at Centre of Chemical and Physical Analyses Laboratory, Yogyakarta, Indonesia.

In this method, sediments were weighed about 100 g and then put into sieve stacks consisting of mesh # 70; 100; 120; 140; 325; 400. After several shakes, the percentages of the sediment in every sieve were measured. The formula that was used is :

$$\textbf{\% of grain size} = \frac{\textbf{the amount of each grain size}}{\textbf{the total amount of all grain size}} \textbf{ x 100 \%}$$

4.2. Water Quality Analyses

Samples for water quality analyses were taken at each sampling site from the field work and brought to the laboratory for further analyses. Most of water quality parameter measurements were performed at Chemical Engineering Laboratory, Diponegoro University, Semarang, Indonesia.

4.2.1.. BOD (Biological Oxygen Demand)

a) BODo : - this BOD_0 is equal to the dissolved oxygen taken in the first time

- water samples were poured into dark bottles of known volume. 2 ml $MnSO_4$ and 2 ml alkali Iodide azide were added and shaken
- 2 ml concentrate H_2SO_4 was added and shaken
- this solution were poured into the beaker and amylum as an indicator was added, then were titrated with thiosulphate 0.025 N

b) BOD_5 : -samples were put on the dark bottles of known volume

- 1 ml $CaCl_2$,1 ml $FeCl_3$, 1 ml $MgSO_4$, and 1 ml phosphate-buffer were added
- after 5 days, 2 ml $MnSO_4$ and 2 ml Alkali Iodide Azide were added
- 2 ml H_2SO_4 was added, shaking was performed until the precipitate dissolved
- this solution were poured into the beaker and amylum as an indicator were added, then were titrated with thiosulphate 0.025 N

4.2.2. COD (Chemical Oxygen Demand)

(water samples were preserved with 2 ml H_2SO_4)

- 10 ml of water samples were poured into tubes and 0.2 gr $HgSO_4$ was added
- 5 ml $K_2Cr_2O_7$ 0.25 N and 15 ml $AgSO_4$ solution were added, then heated to 140 ° C for 2 hours
- the blanks were run by the same steps using distilled water
- the rest of $K_2Cr_2O_7$ was titrated with $Fe(NH_4)_2(SO_4)_2$ and Ferroin 2-3 drops

4.2.3. Suspended Solids (SS)

Total nonfiltrable residue will be retained on a standard glass fiber filter disk after filtration of well mixed water. The residue is dried at 103 - 105 ° C. The difference between the total residue and the total filtrable residue provides an estimate of the total filtrable residue (suspended solid).The procedure of suspended solids measurement can be seen in Appendix Q.

4.2.4. Temperature and pH were measured using thermometer and digital pH meter, respectively

4.2.5. Water Clarity and Surface Water Velocity are measured using Secchi disc and by counting the time that is needed by an object (stick) thrown in the water to reach a certain distance, respectively.

5. RESULTS AND DISCUSSION

General conditions in the study area

5.1. Water quality

5.1.1. Temperature

Water temperatures in the study areas vary from 26.6 - 30.2 ° C in Banjir Kanal Barat River and 26.2 - 30.4 ° C in Babon River. The highest values were recorded on the day time and at industrial complex area (location number 4, 5 and 6) (see figure 5-1, appendices E-1 and E-2).

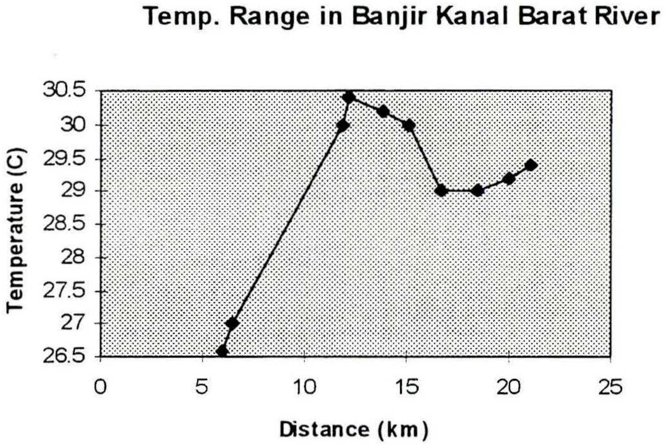


Figure 5-1 : Temperature range in Banjir Kanal Barat River

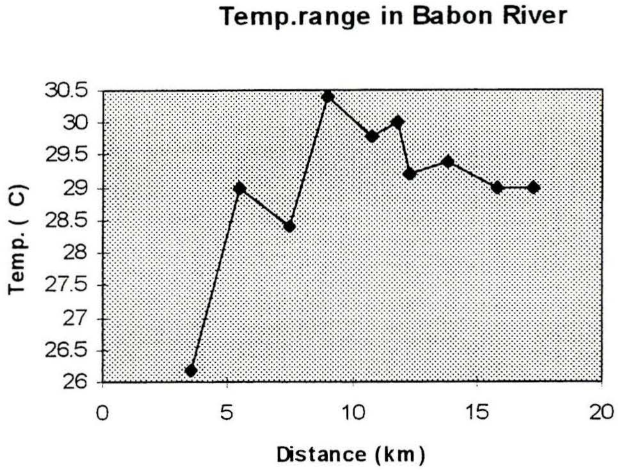


Figure 5-2 : Temperature range in Babon River

5.1.2. pH

pH ranges from 7.8 - 9.4 in Banjir Kanal Barat River and 7.3 - 8.9 in Babon River (see appendices E-1 and E-2). These alkaline pH are due to the pH of industrial discharges from textile manufactures and chemical industries which became a prominent characteristics of their liquid wastes as a result of inadequate wastewater unit works (see Appendix A).

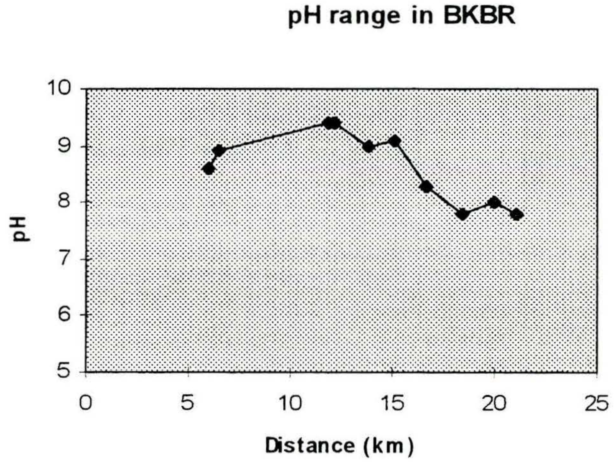


Figure 5-3 : pH range in Banjir Kanal Barat River

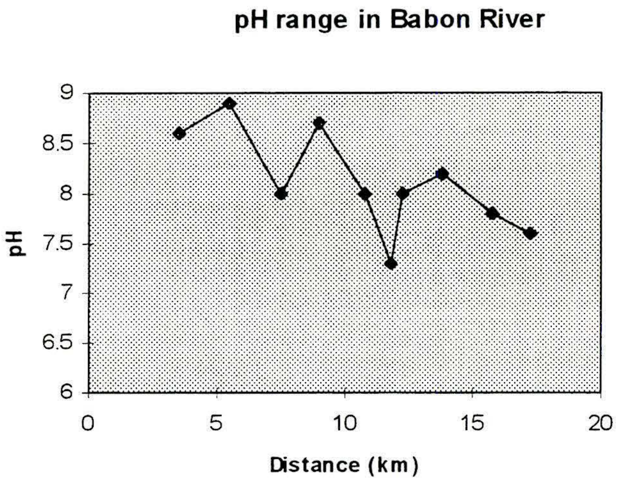


Figure 5-4 : pH range in Babon River

In addition pH has a role in determining the extent to which a metallic compound will ionize and in turn, the concentration of trace metals ions (i.e. toxic metallic ions such as Hg^{2+} Pb^{2+}) in solution (Moriber, 1974).

5.1.3. DO (Dissolved Oxygen)

Dissolved oxygen concentrations in Banjir Kanal Barat River range from 2.89 to 16.71 mg/l, and Babon River from 4.21 - 7.06 mg/l. There is a tendency to decrease near the lower end of the river. For example, in the Babon River, DO are low in value (0.0 ppm) on location 7, 8, and 9 where the tannery industrial complexes are located (Appendix B). In the mouth of these rivers, the value increases due to the seawater dilution.

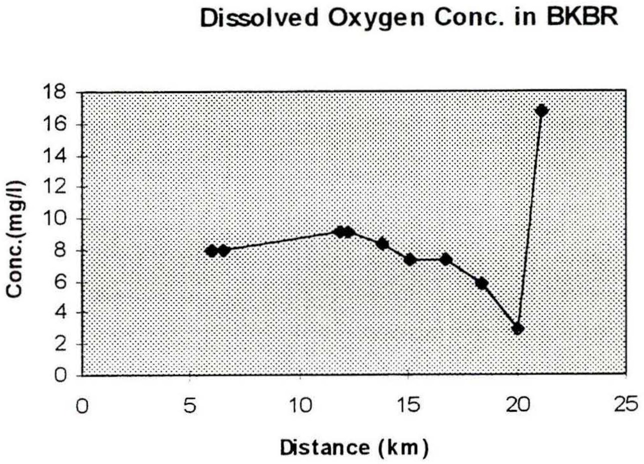


Figure 5-5 : Dissolved Oxygen Concentration in Banjir Kanal Barat River

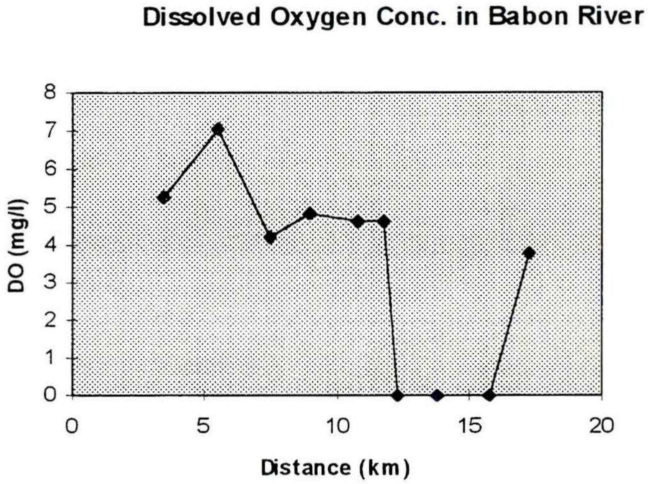


Figure 5-6 : Dissolved Oxygen Concentration in Babon River

Based on water quality criteria division (Lee, 1978) in Astuti et.al, 1990 , Banjir Kanal Barat is considered to have middle-light pollution while Babon River is categorized in heavy-middle pollution. These values are shown in table 5-1:

Table 5-1: Water Quality Criteria Division on Dissolved Oxygen (Lee, 1978)

Class	DO (mg/lt)	Water Quality
I	6.5	unpolluted/light pollution
II	4.5 - 6.4	light pollution
III	2.0 - 4.4	middle pollution
IV	< 2.0	heavy pollution

5.1.4. COD (Chemical Oxygen Demand)

The higher values of chemical oxygen demand (COD) throughout the rivers suggest that pollution sources of Banjir Kanal Barat River and Babon River are not only from industrial wastes but also domestic sewage and farming activities. Though there are no industries in upper end of Babon River (until location 5), the CODs value are relatively high. These data are matched with the data from BAPPEDA (1994).

The range of COD in Banjir Kanal Barat River is from 1.84 - 37.44 mg/l , while in Babon River the range is from 11.52 - 541.51 mg/l (see Appendix.E-1 and E-2). Most of these values exceed the standard for water receiving industrial discharges which for COD is 10 mg/l (American Public Health Association, 1976 in Talkuputra, 1978). The CODs measured can be regarded as an estimate of organic carbon content of the reference clays of the river (Jenne in Baker, 1980).

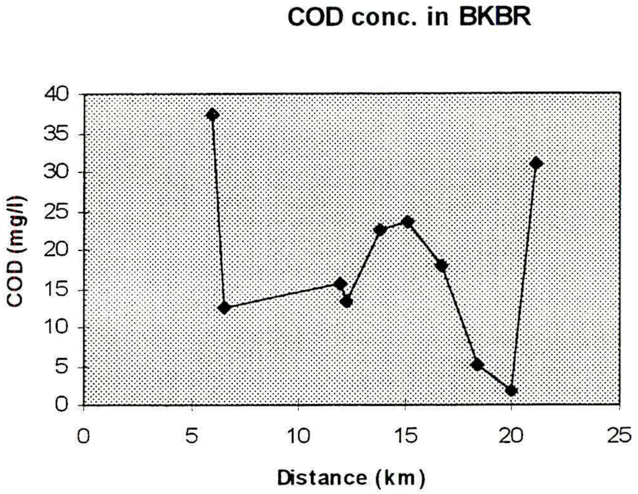


Figure 5-7 : COD values in Banjir Kanal Barat River

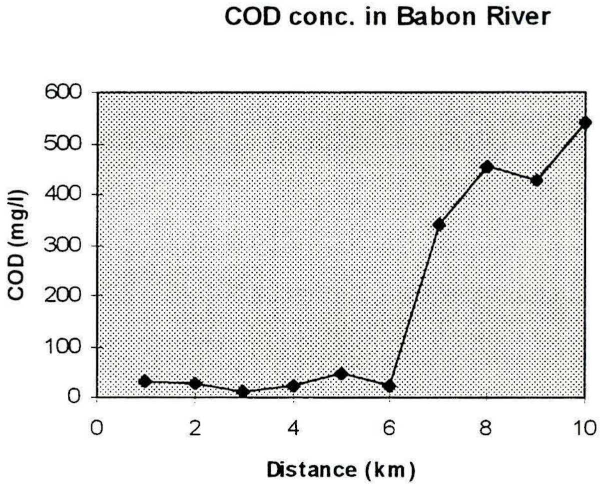


Figure 5-8 : COD values in Babon River

5.1.5. BOD (Biological Oxygen Demand)

The values of Biological Oxygen Demand (BOD) range from 1.71 to 32.26 mg/l in Banjir Kanal Barat River and 0.87 to 184.7 mg/l in Babon River. These values exceed the standard for water receiving industrial discharges which is for BOD is 6.0 mg/l (American Public Health Association, 1976 in Talkurputra, 1978).

Based on the DO, BOD, COD values, Babon River is more polluted or contaminated area than Banjir Kanal barat River. According to Sahadi (1977) in Talkuputra (1978), a river is considered to be a polluted area if the DO level reaches 0.0 mg/l, COD exceed 100 mg/l, and BOD reaches 100 mg/l. In Babon River, these conditions occured at location 7, 8, and 9 (also location 10 for COD) where the tanneries industry are located.

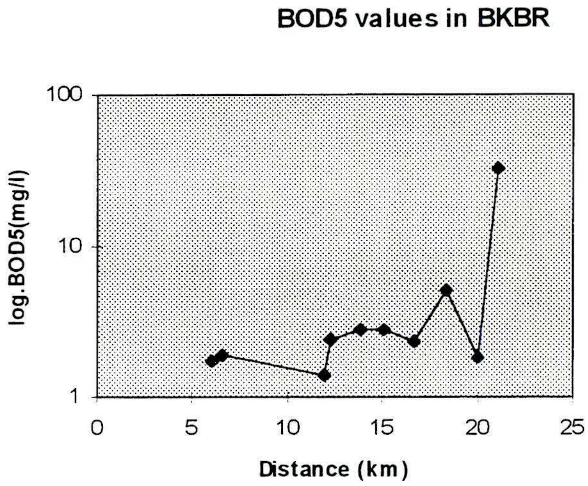


Figure 5-9 : BOD_5 values in Banjir Kanal Barat River

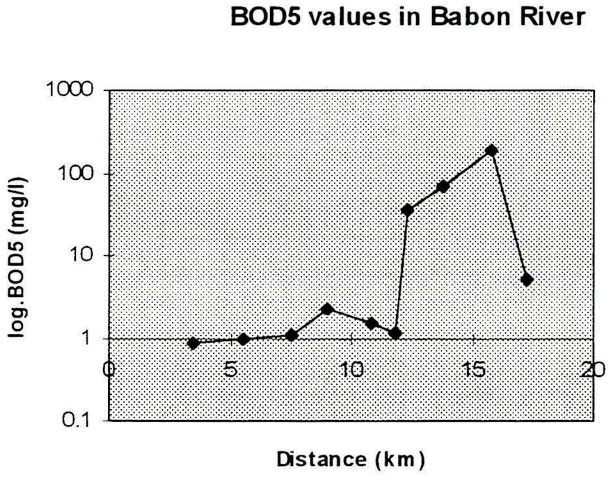


Figure 5-10 : BOD_5 values in Babon River

5.1.6. Suspended solid

Suspended solid concentration in Banjir Kanal Barat River ranges from 73.0 to 921 mg.l^{-1} while in Babon River ranges from 59.0 to 13,675,0 mg.l^{-1}. The higher values were found close to the industrial complexes (in Babon River) and close to the river mouth/lower end (in Banjir Kanal Barat River). These numbers are weak to strongly correlated with dissolved oxygen, BOD, and COD concentrations, where the increasing of suspended solid will induce both of biological and chemical oxygen demand resulting from microbial activity, which in turn, these will directly consume the provided oxygen in the waters. These conditions take place because some industries discharge their sewage directly without complete treatment prior to the discharge (Regional Development Planning Agency, 1992) (see Appendix A).

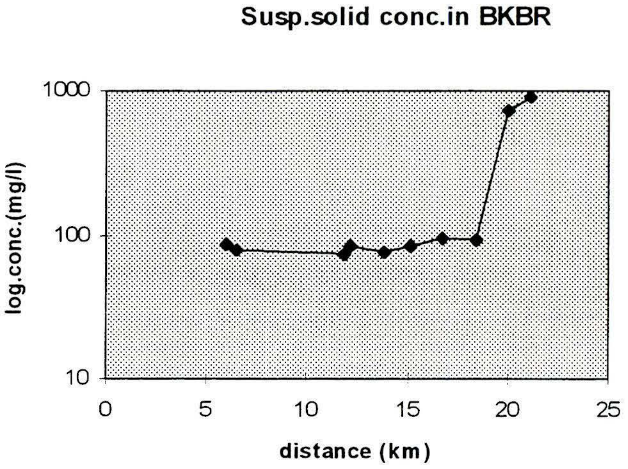


Figure 5-11 : Suspended solid concentration in Banjir Kanal Barat River

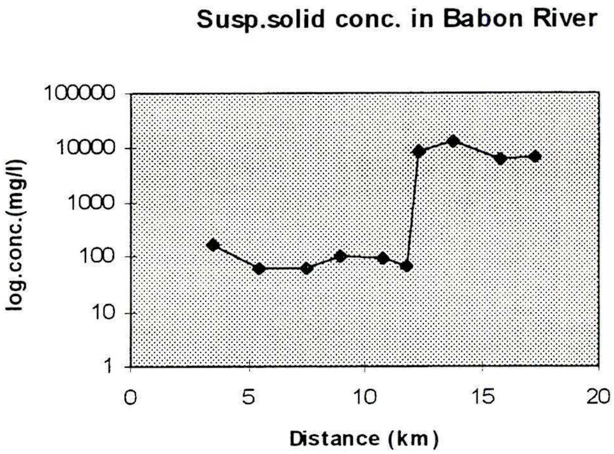


Figure 5-12 : Suspended solid concentration in Babon River

5.1.7. Water Clarity and Current Velocity

Water clarity in the study areas ranges from 20 - 50 cm in Banjir Kanal Barat River; the lower values were found in locations 4 to 7, where the industrial complexes are located (see figure 5-13). In Babon River, water clarity ranges from 15 - 50 cm and the lowest value was found at location 8, where the tannery industries are located (see figure 5-14). This agree with the suspended solid data from this area (see Appendix E-2).

Surface water velocity in Banjir Kanal Barat River ranges from 0.11 to 1.25 m.sec^{-1}. The highest value was found in the steep river[1] (see figure 5-15). The lowest values were found in the seaward sections where there was mixing between seawater and freshwater currents. In Babon River, the surface water velocity ranges from 0.08 - 0.33 m.sec^{-1} (see figure 5-16).

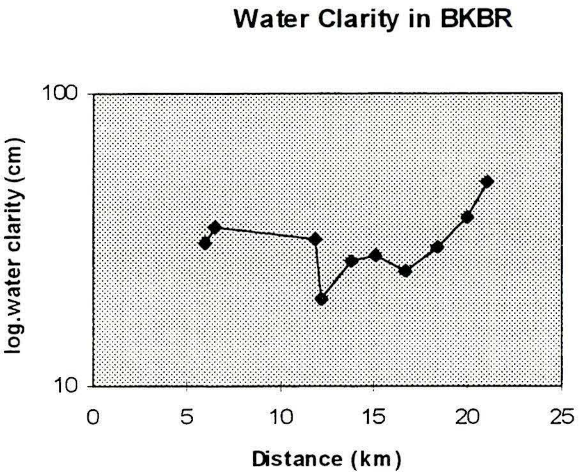


Figure 5-13: Water clarity in Banjir Kanal Barat River

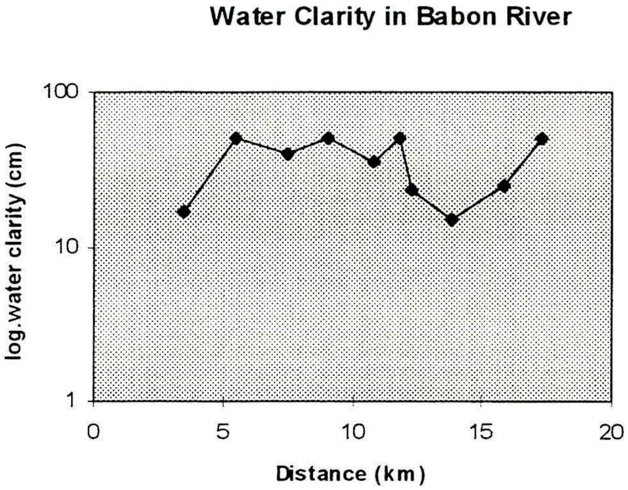


Figure 5-14: Water Clarity in Babon River

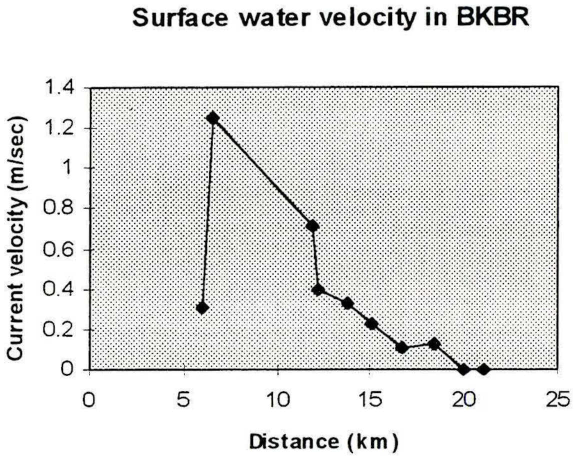


Figure 5-15: Surface Water Velocity in Banjir Kanal Barat River

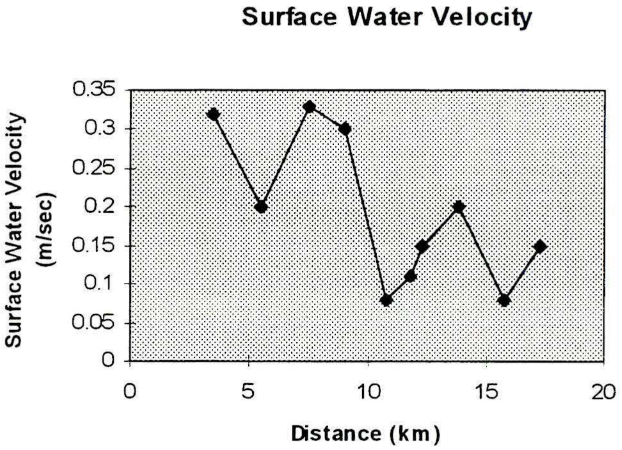


Figure 5-16 : Surface Water Velocity in Babon River

5.1.8. Rainfall (from January to December 1994)

Eventhough, in this study the temporal variation was not investigated, it is necessary to present the monthly rainfall to see the concordant value with respect to trace/heavy metals observed. Monthly Rainfall/ Annual Average Rainfall has an important role in determining the river flow and therefore the dilution available to discharges of metals. Figures below depict the monthy rainfall and total amount of days in each month in Semarang Municipality :

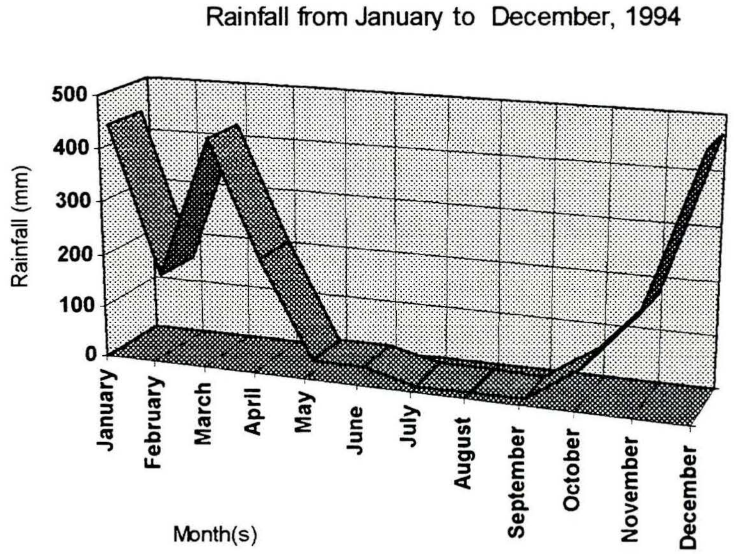


Figure 5-17 : Monthly Rainfall in Semarang Municipality from January-December 1994

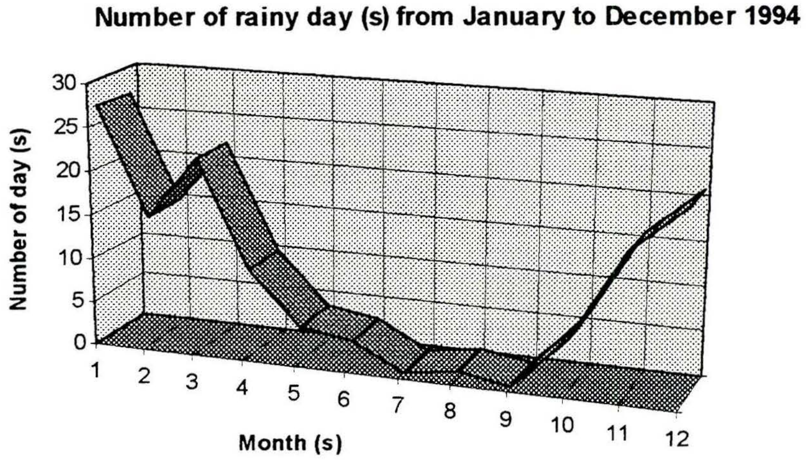


Figure 5-18 : Number of Rainy Day (s) from Januay to December 1994 in Semarang, Java, Indonesia

From June-September (dry season) 1994, the total amount of rainfall were very low . This condition will influence the metal concentrations in water, soil and sediments. Due to minimum amount of rainfall, trace elements/metals tend to concentrate and results in high concentration. It is assumed that in rainy season (October- April), due to the dilution of rain water, the metal concentration will be lower than dry season. To get a better understanding of this phenomenon, seasonal studies are desirable.

5.1.9. Heavy metals (Cu, Cd, Pb, Cr) dissolved in water

Although analyses of trace/heavy metals in the water column sometimes can not predict the distribution of metals, but the concentration of metals in the sediment will be reflected.

The ranges of heavy metal concentrations found in water are relatively low i.e. from "undetected" levels to 0.11 ppm for Pb ; 0.02 ppm for Cu ; 0.06 ppm for Cr in Banjir Kanal Barat River. In Babon river the ranges are from "undetected" levels to 0.36 ppm for Pb ; 0.02 ppm for Cu ; and 0.11 ppm for Cr. Most of the highest levels were found near the industrial complexes (see Appendix B). The concentration of metals (especially Pb and Cr concentrations in Babon River) found in the water column from the study areas are relatively high compared to the maximum requirement (see Appendix D). Both in Banjir Kanal Barat River and Babon River, concentrations of Cadmium are reported as "undetected". According to Engel et al., 1981 ; Zamida and Sunda, 1982 in Bryan and Langston, 1992, Cadmium usually accounts for only a minor proportion of the total dissolved metals. However, free ions of Cd are the most bioavailable inorganic forms.

According to the Regional Development Planning Agency, 1992, the water quality parameters in Babon River that exceed the requirements are Fe, Pb, and COD (at upstream areas), and ammonia, nitrite, Cadmium (Cd), and suspended solid (at downstream area). The sources of pollution in this area are human activities, agricultural activities, sand mining, and natural processes /rock weathering (upstream), and running sewage from the city, and agricultural and industrial activities. Heavy metal values in water that have been reported in this area are from "undetected level" to 0.1280 ppm for Cr; to 0.0720 ppm for Cd; to 0.0615 ppm for Pb, and to 0.0040 for Cu. Environmental Protection Agency (1973,1976) in Laws (1981) ; Regulation of Indonesian Health Minister about The Water Quality Requirement for Water Bodies (1977) suggest that the maximum concentrations of several metals that are allowed in waters are 0.05 ppm for Cr ; 0.01 ppm for Cd ; 0.05 ppm for Pb ; and 1 ppm for Cu. Beside that, the Ontario Provincial Water Quality Objectives (PWQO) had determined the threshold for trace metals (μg/L) in water which for Copper is 5 ; Nickel (Ni) : 25 ; Zinc (Zn) : 30 ; Cadmium (Cd) : 0.2 ; Lead (Pb) : 25 ; Iron (Fe) : 300 ; Manganese (Mn) : N/A (not available) (Hamilton Harbour RAP, 1992).

In conclusion, the concentration of metals (especially Pb and Cr concentrations in Babon River) found in the water column from the study areas are relatively high compared to the maximum recommended limits.

5.2. Sediment Quality

5.2.1. Heavy Metals in sediment (results from weak acid digestion)

5.2.1.1. Lead (Pb)

Lead is the most abundant of the natural heavy elements. However, Pb (II) forms compounds of low solubility ($< 10\ \mu g.l^{-1}$, above pH 8.0) with several major anions (CO_3^{-2}, OH^-, SO_4^{-2}, etc.) that occur in the natural environment. They may control the total dissolved Pb (II) in the system under certain pH, redox conditions and ions present (Bodek *et.al.,* 1988). The important sorbents of lead in soil /sediments are organic matter, clay minerals, and oxides of manganese and iron. The sorption will increase when pH increases (Rai *et.al,* 1979) in Bodek *et.al.*, 1988.

The value of lead ranges from 5.9 to 13.1 ppm in Banjir Kanal Barat River sediments. The highest values were found in location 2, where the iron factory is located. In Babon River sediments, the concentration of Lead ranges from 9.3 to 12.2 ppm (Appendices J-1 and J-2). The highest number were found in location 9 (close to rivermouth). These values are still within the range suggested by the Ministry of the Environment of Canada which for Lead is 25 ppm. This probably due to the industrial discharge containing Lead from most of the factories around Banjir Kanal Barat River were below the Maximum Target of Liquid Waste Loads from the Indonesian Ministry of Environment (see Apendix C-2). However, this study shows that Lead concentration measured in the Banjir Kanal Barat rivermouth is slightly higher compared to the data reported by Astuti, *et.al.* (1988), in the same area (see table 1-1).

In general, the primary source of Pb to aquatic sediments is atmospheric input; only a small concentration of lead reaches aquatic systems directly (Eddington and Robbins, 1976 ; Kemp and Thomas, 1976) in Baudo *et al.*, 1990.

The portion of Pb which is not soluble in the water will sink to the bottom and become part of the sediment. Pb tends to concentrate mostly in sediments containing large amounts of clay and organic matter (De Jonghe & Adams, 1982) in Baudo *et al.*, 1990.

Leaded gasoline and diesel fuel are still largely used by motor vehicles. These are diffuse sources of Pb in the atmosphere, which would eventually enter water systems (Vincette-Beckett *et al.*, 1991).

5.2.1.2. Cu (Copper)

The range of copper found is from 16.6 to 53.6 ppm in Banjir Kanal Barat River and 18.6 to 24.7 ppm in Babon River (see Appendix J-1 and J-2). Some of these values exceed the Canadian standard, which for Cu is 30 ppm. However, due to its strong affinity on the clay fraction (Bubb *et al*, 1991), copper was not found in a greater amount in the weak acid digestion compared to the values from fraction < 63 μm /strong acid digestion.

Cu is used in electroplating together with Cadmium and Nickel or with Chromium and Zinc (Indonesian Ministry of Environment, 1995).

5.2.1.3. Chromium (Cr)

For chromium, the concentrations range from 7.0 to 181.1 ppm in Banjir Kanal Barat river and 6.2 to 165.6 ppm in Babon River. The highest numbers are found in location 2 of BKBR (where the iron factory discharges its wastes) and location 8 of Babon River (immediately downstream from the tannery industries). Some of these values are above the values proposed by the Ontario Ministry of Environment which for Cr is 22 μg/g (see Appendix N). In addition, data from Regional Planning Agency (1994) showed that several industries still discharge their waste into Banjir Kanal Barat River above the maximum target that was established by Indonesia's Ministry of Environment. (see Appendix C-4).

Chromium occurs naturally in the earth's crust, in concentrations ranging from 100 to 300 μg/kg, and trace amounts are found in air and water. Moreover, this element is relatively insoluble in water. Though Cr exists in several values or oxidation state, Cr^{3+} and Cr^{6+} are environmentally the most important. Hexavalent chromium is more toxic to aquatic species because of its role as a strong oxidizing agent, and its ability to penetrate biological membranes (American Petroleum Institute, 1981).

Due to its economic importance and widespread use in industry, chromium has become an element of concern which can cause environmental effects from its discharge to surface waters. It is used in many industries such as metals finishing (including electroplating), leather and tanning, and iron and steel industry, etc.(American Petroleum Industry, 1981). In Indonesia, chromium is used mostly in the textile, leather/tannery industries and as a component in electroplating, together with Cadmium or Copper (Indonesian Ministry of Environment, 1995).

5.2.1.4. Cadmium (Cd)

Cadmium becomes a concern because of its high toxicity, and its bioavailability. Adsorption on soil and sediments will affect the mobility of Cadmium in the environment. Adsorbents such as clay minerals, carbonate minerals, oxides and, to a lesser extent, organic matter have a role in controlling the behavior of cadmium in soils and sediments (Moore and Ramamoorthy, 1984) in Baudo *et.al*, 1990.

The concentrations of cadmium found in the study areas are relatively low compare to other metals, however its concentration is higher than US.EPA standard. The range is from 0.05 to 0.08 ppm (50 - 80 ppb) in Banjir Kanal Barat River and 0.05 to 0.15 ppm (50-150 ppb) in Babon River. According to US-EPA, areas with cadmium concentration above 6 μg/kg (0.006 ppm) in sediments will be categorized as heavily polluted areas (see Appendix N). Cadmium is commonly used in electroplating, batteries, pigments, alloys, etc.(Bodek et al., 1988 ; Astuti et al., 1990).

5.2.2. Organic Matter and Total Organic Carbon (TOC) Content in Sediments

Because of the influence of organic material on metal concentration, it was considered important to determine the concentrations of organic matter in the sediments. It is assumed that the higher the organic matter concentration in one area, the higher the metals concentration will be (Horowitz,1985) and the finer the grain size, the higher the total organic carbon (Ergin *et.al.*,1993).

There is also a relationship between organic carbon/organic matter and dissolved oxygen concentration in the water column. In relatively oxygen-rich water, the decomposition of sinking organic matter proceeds much faster than in relatively oxygen-deficient or oxygen-poor waters (Ergin *et.al.*, 1993).

The percentages of organic matter (LOI) in Banjir Kanal Barat River and Babon River range from 2.6 - 15.2 % and 5.0 - 22.2 %. The relatively high concentrations found at location 6 in Banjir Kanal Barat River and Babon River are probably due to the dam construction which slightly will lower the water flow/sedimentation rate and consequently will accelerate organic material formation. The organic carbon content (TOC) of Banjir Kanal River sediment ranges from 0.5 - 5.9 %, while in Babon river it ranges from 0 - 19 %. At places where DO concentrations are very low (location 7,8, and 9 of Babon River which are 0.0 mg/l), the decomposistion of organic matter/carbon was slow, so that there were still accumulation of organic matter in the sediment.

Organic carbon also associates with clay-rich sediment and may add to the clay minerals' ability to adsorb trace metals (Presley *et.al.*, 1992).

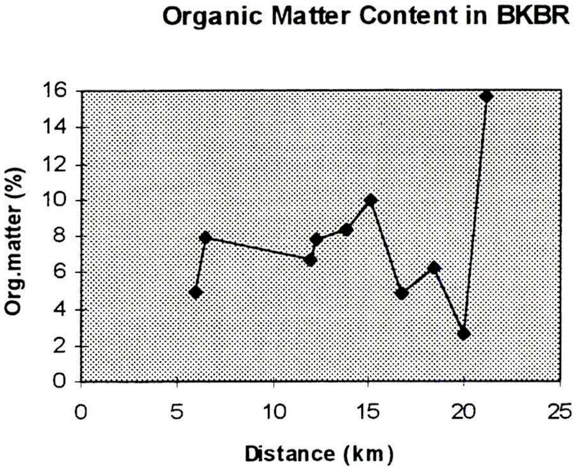


Figure 5-19 : Organic matter (Loss on Ignition) content

in Banjir Kanal Barat River

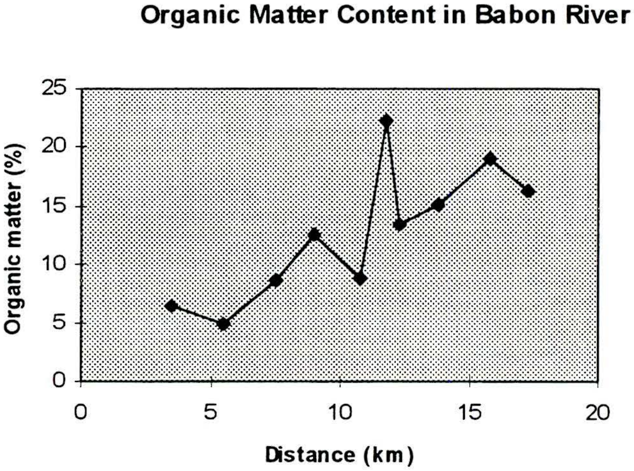


Figure 5-20 : Organic matter (Loss on Ignition) content in Babon River

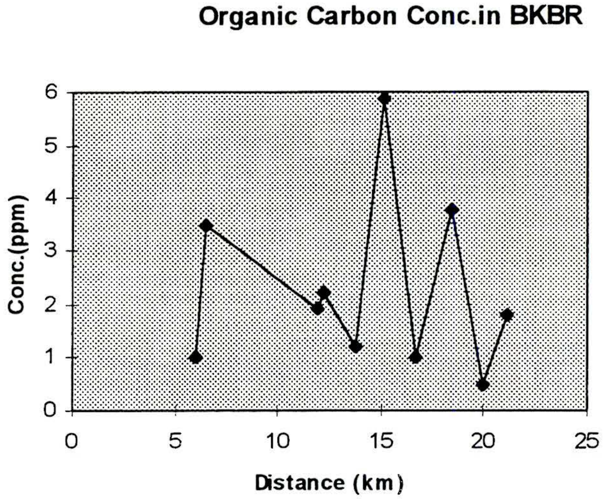


Figure 5-21: Organic Carbon content in Banjir Kanal Barat River

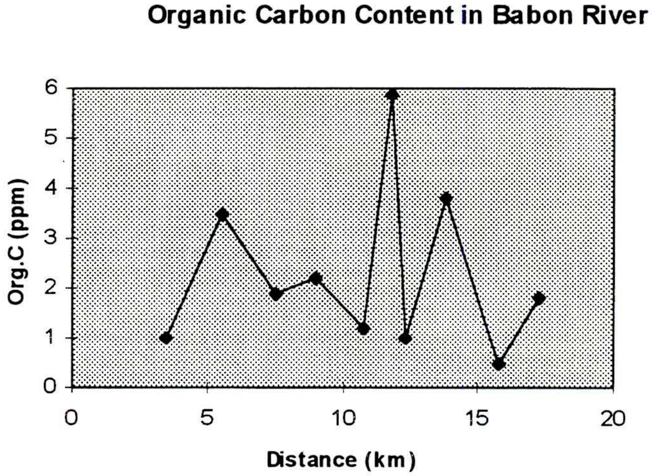


Figure 5-22 : Organic Carbon in Babon River

5.2.4. Grain size

In Banjir Kanal Barat River, grain size distributions of finest fraction increased down stream, as a result of low surface water velocity (change direction) at the end of the river channel (see Appendix F). According Palanquez and Diaz, 1994, the deposition of mud (silt and clay) will occur when the current velocity decreases below 0.05 - 0.1 m/sec or absent current. In Babon River, the grain size distribution of finest fraction of the sediment increased to the lower section. In addition, river sediments had very heterogenous particle size distributions, with a significant proportion having sandy (fine-sand) texture/fractions (see appendix L-1 and L-2).

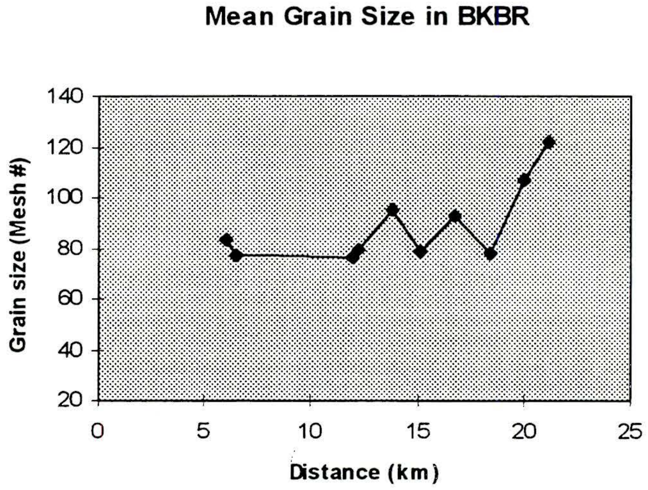


Figure 5-23 : Mean grain size of Banjir Kanal Barat River sediments

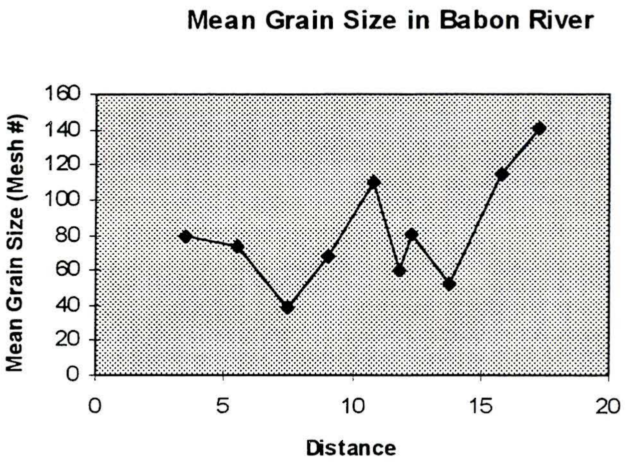


Figure 5-24 : Mean Grain Size of Babon River sediments

The interelationship between water quality parameter and trace/heavy metals in the sediment and its characteristics (organic carbon, loss on ignition/organic matter) will be depicted in table 5-2 :

Table 5-2: Correlation amongst water quality, heavy metals, and sediment characteristics
in Banjir Kanal Barat River , Semarang, Central Java, Indonesia

	° C	pH	SS	DO	BOD	COD	WCla	SV	Pb	Cr	Cu	Cd	LOI
pH	0.577												
SS	-0.498	-0.850**											
DO	0.476	0.402	-0.365										
BOD	0.287	-0.396	0.195	0.139									
COD	0.012	-0.092	-0.018	0.515	0.139								
WCla	-0.384	-0.463	0.285	0.006	-0.139	-0.067							
SV	-0.153	0.028	-0.085	-0.365	0.146	0.189	-0.730*						
Pb	-0.031	-0.335	0.249	-0.103	0.576	-0.224	0.387	-0.337					
Cr	0.396	-0.207	0.268	-0.224	0.042	-0.285	-0.176	0.386	0.094				
Cu	-0.274	0.390	0.136	0.030	0.236	-0.030	0.456	-0.416	0.738*	-0.135			
Cd	-0.369	-0.307	0.251	-0.413	-0.117	-0.110	0.024	0.604	-0.287	-0.048	-0.094		
LOI	0.457	0.232	-0.280	0.634	0.588	0.442	0.067	-0.219	0.564	0.309	0.358	-0.398	
Org.C	0.211	0.288	-0.329	0.097	0.377	-0.103	-0.164	0.207	0.505	0.255	0.833**	-0.079	0.571

* significantly correlated, (α = 5 %), critical values for Spearman Correlations is 0.683
**significantly correlated, (α= 1 %), critical values for S[peraman correlation is 0.833

In the Banjir Kanal Barat River, not many strong correlations were observed. The increasing concentration of suspended solid were followed by the decreasing of dissolved oxygen, pH (result from microbial activity) and the increasing of chemical and biological oxygen demand. On the relationship amongst dissolved oxygen, biological oxygen demand, suspended solids, and organic matter/carbon in the sediment, the relatively high values of BOD and COD were simultaneously found together with high DO and organic materials . These anomalies can be explained by the low level of water in the study area and the physical processes such as sand mining, and row boat activities which can cause high turbidity (suspended solids). A relatively high BOD/COD indicates that there is a lot of organic waste material in the water and that a lot of oxygen is being used to decompose the material. However, due to the low level of the river basin and the water movement (relatively high surface water velocity), it is easy for water to be reoxygenated (oxygen is always available). In addition, increasing surface water velocity was followed by decreasing water clarity which can be seen from the strong correlation between them (rs = - 0.730). High surface water velocity tend to carry river materials to downstream in which it will increase the turbidity.

In Banjir Kanal Barat, because of industrial discharges coming from many industries (multipurpose of metal use), there is no significant correlation found. In addition, source of origin of water pollution can not be traced .

Table 5-3 : Correlation amongst water quality, heavy metals, and sediments characteristics in Babon River, Semarang, Central Java, Indonesia

	° C	pH	SS	DO	BOD	COD	WCla	SV	Pb	Cr	Cu	Cd	LOI
pH	-0.081												
SS	0.055	-0.178											
DO	-0.044	0.565	**-0.718***										
BOD	0.337	-0.362	**0.746***	**-0.853****									
COD	-0.086	-0.252	**0.809***	-0.585	0.581								
WCla	-0278	-0.133	-0.604	0.437	-0.454	-0.414							
SV	-0.396	0.601	-0.184	0.359	**0.710***	-0.466	0.070						
Pb	0.153	-0.301	-0.261	-0.252	0.340	-0.274	0.113	0.303					
Cu	-0.546	-0.460	-0.321	-0.178	0.368	-0.134	0.169	0.304	0.340				
Cr	-0.080	-0.546	0.600	**-0.841****	0.535	**0.693***	**-0.256**	0.146	0.304	0.052			
Cd	-0.088	0.467	-0.368	0.536	-0.385	-0.525	0.206	-0.468	0.102	-0.449	-0.441		
LOI	0.423	**-0.792***	0.467	-0.681	**0.697***	0.423	0.056	-0.612	0.382	0.649	0.442	-0.667	
Org.C	0.055	-0.558	0.455	**-0.770***	0.730	0.608	-0.094	-0.526	0.382	**0.927****	0.212	**-0.866****	**0.746***

* significantly correlated, (α = 5 %), critical values for Speraman Correlation is = 0.683
**significantly correlated,(α = 1 %), critical values for Spearman Correlation is = 0.833

SS = Suspended Solid
Wcla = Water clarity
SV = Surface Water Velocity
LOI = Loss on Ignition

Due to Chromium discharge, there was water quality degradation in Babon River. As can be seen, increasing organic pollutants such as BOD, COD, suspended solids, and organic matter/carbon values were followed by the decreasing value of DO. Weak to strong correlations were observed between those parameters with oxygen *($p < 0.05$)*. A high BOD/COD indicates that there is a lot of organic waste material in the water and that a lot of oxygen is being used to decompose the material. In addition, BOD and COD are well correlated with suspended solids.

Weak correlations are shown between most water quality parameters with heavy metals (except Cr) concentration in sediments. This permanent accumulation of contaminants (especially heavy metals) poses problems, because the sediment acts as a source of pollutants long after the pollution of waterways has been abated and/or the levels of heavy metals already decreased (very low). Weak *($p> 0.05$)* and strong *($p < 0.05$)* correlations were observed between Chromium and water quality parameters or sediment parameters (organic matter/carbon). This condition occured because most of industries that are located around Babon River are tannery industries and use chromium in the production process.

What is surprising in the metals data from weak acid digestion is that there were positive correlations amongst trace/heavy metals (Pb, Cu, Cr, and Cd), organic matter/carbon content and coarse and medium fraction/ mesh # 70 (see table 5-4). Some plausible reasons responsible for this are the use of whole fraction of sediments for trace/heavy metals analyses and the formation of agglomerates in sediments. According to Krumgalz, 1989, the formation of agglomerates occurs during the generally accepted drying procedures. Possibly the standard method for sieving was not vigorous enough to destroy the formed agglomerates. In this case, the total amounts of either trace metals or organic matter retained by each agglomerates particle will be much larger compared to the amounts which could be adsorbed only on the outer surface of such agglomerates. According to Morse *et al.*, 1993, the metals which are not well associated with finer grain sediments may be incorporated into the sediment by processes other than simple sedimentation or may be associated with fractions such as large carbonate particles.

Moreover, it is likely that the surface sediments in relatively shallow (20 - 120 cm) water in the study areas are mobile and shift with changing currents, as has been suggested by Dinnel (1988) in Presley *et.al.*, 1992. Both phenomena result in variability in the trace element concentrations of the sediment and changes in grain size & organic carbon/matter in this study. Rank 's Spearman Correlation amongst these parameters are shown in table below :

Table 5-4: Correlation amongst sediment characteristics (parameters) and between heavy metal (whole fraction) and organic matter, organic carbon, and percentage (%) of grain size with mesh # 70, 100, 120, 140, 325, and 400 in BKBR

****

	Pb	Cu	Cr	Cd	% LOI	Org.C	# 70	# 100	# 120	# 140	# 325
Cu	0.176										
Cr	0.527	-0.067									
Cd	-0.226	-0.123	0.439								
% LOI	0.564	0.358	0.309	-0.400							
Org.C	0.505	0.833**	0.255	-0.079	0.571						
#70	-0.358	0.733*	-0.079	0.206	-0.091	0.523					
#100	0.127	-0.733	-0.127	0.027	-0.139	-0.596	-0.903				
#120	0.309	-0.697	-0.030	-0.281	0.127	-0.499	-0.976	0.903**			
#140	0.612	-0.455	0.393	-0.192	0.188	-0.614	-0.794	0.539	0.673		
#325	-0.200	-0.636	-0.212	-0.082	-0.127	-0.790	-0.685	0.685*	0.685*	0.479	
#400	-0.171	-0.732	0.031	0.166	-0.189	-0.719	-0.482	0.524	0.457	0.287	0.701*

****

* significantly correlated (α = 5 %), critical value for Spearman's correlation is 0.683

** significantly correlated (α= 1%), critical value for Spearman's correlation is 0.833

All metals, except Cd, have positive correlation with either organic matter or organic carbon. The strongest relationships were observed for Cu , with 'r_s' value of 0.833. This higher value obtained for Cu in comparison with other metals could indicate that Cu tends to associate with organic matter/carbon. Many negative correlations derived between metals and finer sediments (mesh # 325 and 400) implied that finer grain size was not a controlling factor. Other factors may have been responsible for dictating the localized metals distribution (content). Metals may be correlated with medium or coarse sand fraction in which, they become component of industrial discharge or input of coarse particles. According to Singh and Subramanian, 1984 in Bubb *et.al.*, 1991, finer fraction deposits probably contained sufficient binding capacity to immobilize the majority of metals with which they were in contact, so other physico-chemical parameters such as Fe/Mn oxides and hydroxides and sulphides may become the controlling factors. Moreover, the interrelationships are complex, but there seems to be a lack of any significant correlation amongsts metals such as cadmium, copper, and other elements.

In Babon River, most metals, except Cd, were more associated with organic carbon and organic matter rather than with finer fraction (mesh # 325 and 400). The strongest correlation was observed for Cr ('r_s'= 0.927). This is because the single source of this pollutant comes from tannery industries, which release most of the Cr, not combined with any other of the investigated metals, into the river.

Various heavy metal concentrations and organic matter content can be used to identify the sources of anthropogenic heavy metals in a particular area, provided only one point contamination source exists for that area (Krumgalz & Fainshtein, 1991). The relationships between metal concentration with sediment parameters are depicted in table 5-5:

Table 5-5 :Correlation amongst sediment characteristics (parameters) and between heavy metals, organic matter, organic carbon, and grain size with mesh # 70, 100, 120,140, 325, and 400 in Babon River :

	Pb	Cu	Cr	Cd	% LOI	orgC	# 70	#100	#120	#140	#325
Cu	0.479										
Cr	0.188	0.333									
Cd	-0.237	-0.399	-0.773*								
% LOI	0.382	0.212	0.649	-0.667							
orgC	0.382	0.442	0.927**	-0.866*	0.746*						
# 70	-0.418	-0.358	-0.624	0.324	-0.406	-0.527					
# 100	0.442	0.176	0.346	-0.156	0.139	0.297	-0.770*				
# 120	0.527	0.515	0.346	-0.262	0.382	0.382	-0.879*	0.606			
#140	0.673	0.491	0.418	0.337	0.406	0.455	-0.903*	0.733*	0.952**		
# 325	0.115	0.530	0.164	0.006	0.309	0.176	-0.515	0.285	0.697*	0.479	
# 400	-0.176	0.394	0.467	-0.137	0.382	0.285	-0.552	0.188	0.455	0.333	0.721*

* significantly correlated (α = 5 %), critical value for Sperman's correlation is 0.683
** significantly correlated (α= 1%), critical value for Spearman's correlation is 0.883

In these areas, due to the industrial discharges, the suspended solids were observably very high. It is assumed that the high values of organic carbon as well as organic matter (obtained from solid material decomposition by microorganisms) concentration on sediment can easily adsorb the available metals. In this case, organic carbon/matter will predominantly control the metals distribution. However, the absence of further significant associations between metals and other measured variables could indicate that the distribution of metals was influenced by other physico-chemical parameters such as pH or redox condition. From all of these, most of heavy metal values found in sediments that have been analyzed using weak acid are still within the range from

Canadian Standard for contaminated Soils and Sediments. However, in some places there are several high levels found.

From Atomic Absorption Spectrophotometer, duplicate analyses show that most of the RSD (Relative Standard Deviation) of the samples measured did not deviate much from the original reading. The results are depicted in the following table:

Table 5-6: Duplicate Analyses on Banjir Kanal Barat River Sediment

Station	Lead (Pb) (ppm)	Copper (Cu) (ppm)	Chromium(Cr) (ppm)	Cadmium(Cd) (ppm)
BKBR1	5.9± 0.4	19.4± 0.9	7.0± 1.3	0.08 ±0.06
BKBR2	13.1± 0.5	22.8± 0.6	181.1± 14.8	0.075 ±0.11.
BKBR3	6.35± 4.9	24.3± 3.3	8.6± 0.9	0.1 ±0.06
BKBR4	8.6± 0.4	28.9± 2.6	2.9± 1.3	0.05± 0.01
BKBR5	8.9± 1.4	22.4± 3.2	7.4 ± 1.7	0.05± 1.7
BKBR6	10.9± 0.5	24.2± 0.6	7.6±1.2	0.05 ± 1.04
BKBR7	7.2± 0.8	16.6± 0.6	7.9 ± 1.3	0.08 ± 0.02
BKBR8	9.2± 3.3	53.6±22.1	7.4 ±0.5	0.05 ± 0.05
BKBR9	9.2 ± 0.7	19.0± 1.8	7.4 ±1.7	0.07 ± 0.07
BKBR10	11.1± 1.1	21± 0.4	76.9 ±0.5	0.07 ± 0.05

Table.5-7: Duplicate Analyses on Babon River Sediment

	Lead (Pb) (ppm)	Copper (Cu) (ppm)	Chromium (Cr) (ppm)	Cadmium (Cd) (ppm)
BR1	10.5 ± 0.7	21.9 ± 0.6	6.2 ± 0.6	0.1 ± 0.08
BR2	10.7 ± 0.3	23.4 ± 1.4	7.3 ± 0.5	0.08 ± 0.1
BR3	12.1 ± 1.1	24.1 ± 1.7	8.1 ± 0.3	0.11 ± 0.1
BR4	11.3 ± 0.4	18.6 ± 1.3	5.4 ± 0.7	0.15 ± 0.05
BR5	11.3 ± 0.5	19.9 ± 0.9	6.3 ±1.3	0.1± 0.14
BR6	12.1 ± 0.5	23.8 ± 0.7	8.9 ± 0.4	0 .06 ± 0.08
BR7	9.3 ± 1.8	21.3 ± 0.7	16.6 ±	0.08 ± 0.12
BR8	12.0 ± 1.71	21.2 ± 2.0	165.6 ± 10.6	0.06 ± 0.02
BR9	12.2 ± 0.4	24.7 ± 1.5	70.9 ± 3.1	0.06 ± 0.07
BR10	10.7 ± 0.3	22.4 ± 1.3	57.4 ± 40.5	0.05 ± 0.07

Note : All values are in : (Mean ± Total Error) ppm

Total Error $= \sqrt{\text{Sample}_{error} + \text{Instrument}_{error}}$

There was rarely any significant difference between replicate AA (Atomic Absorption) analyses from weak acid digestion. However, in some cases, considerable variation in analytical results were found between field samples from the same area. This reflects the variation in metal concentrations which could occur between sites.

5.2.3. Heavy Metals in sediments (results from Strong Acid Digestion)

5.2.3.1.Nickel (Ni)

Ni can have a valence of +1, +3, or +4, but the only oxidation state of importance under environmental condition is Ni (2+). Based on heavy metals study, nickel, together with chromium and mercury, is among the most generally mobile metals in the environment (Fuller, 1977) in Bodek *et.al.*, 1988. Though the mechanism for sorption in soils and sediments is not being investigated, it is believed that iron and manganese oxides, clay minerals and (to some extent) organic matter have the importance role as sorbents of nickel. In addition, the presence of other cations such as other heavy metals are possibly effective in reducing sorption of nickel (Rai *et al.*, 1984) in Bodek *et al.*, 1988. In organic rich, polluted systems, the mobility of nickel increases due to the presence of humic and fulvic acids (Jackson *et al.,* 1978) in Bodek *et.al.*, 1988.

In the Banjir Kanal Barat River, Semarang, the values of nickel range between 27.6 - 58.2 ppm and 14.0 - 31.1 ppm in the Babon River . Most of these values exceed the Canadian Council of Ministers of The Environment (1991) requirement, which for Nickel is 20 ppm. In Banjir Kanal Barat River, the highest level was found in location 9 (3.3 km from Pharmaceutical Factory) (see fig.5-25a). Indonesia is becoming the fifth largest leading producer and consumer of Nickel in the world (Moore, 1991). Ni is used in many industries for its corrosion resistance, high strength and durability. The major source of discharge are nickel-bearing geologic formations, municipal waste water and sludge, smelting and refining non-ferrous metal foundries (Moore, 1991).

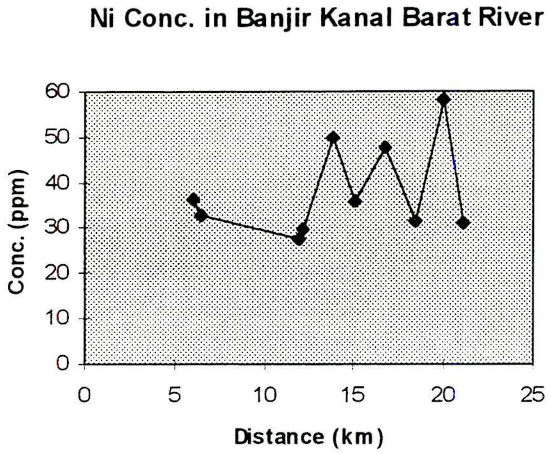


Fig.5-25a : Nickel concentration in Banjir Kanal Barat River, Semarang Indonesia

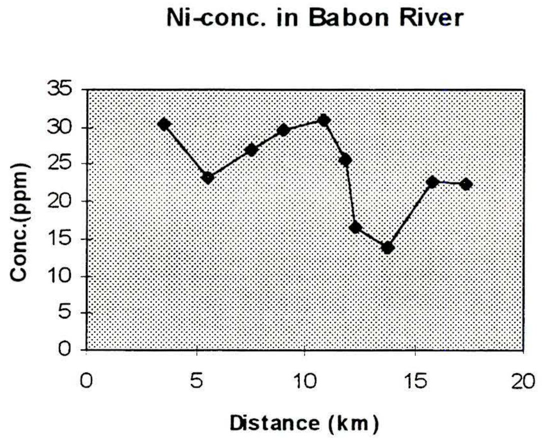


Fig.5-25b : Nickel concentration in Babon River, Semarang Indonesia

5.2.3.2. Zinc (Zn)

Under environmental conditions, the only oxidation state of importance for zinc is +2. Because Zn has high solubility, it tends to exist principally in the dissolved form (Forstner and Wittmann, 1979). In polluted areas, however, organic materials can affect the chemical form in which zinc is present (Callahan et.al., 1979) in Bodek *et al.*, 1988. Like other metals, the sorption of zinc on soil and sediments strongly impacts its mobility in the environment. For this reason, severe zinc contamination tends to be confined to region of the source. Several factors that control the behavior of zinc in soils and sediments are hydrous iron and manganese oxides, clay minerals, carbonate minerals (Moore, 1984) in Bodek *et al.*, 1988. To a lesser extent (less than 5 %) is bound to organic matter (Salomons and Forstner, 1984). In addition, there is an inverse correlation between sediment grain size and the concentration of zinc sorbed; the finer the grain size, the more zinc sorbed.

In this study, the values of zinc range between 85 - 572.5 ppm in the Banjir Kanal Barat River and 45.5 - 350.5 ppm in the Babon River sediments. The highest values for both rivers are found in location 9 and 2 respectively (see fig.5-26). The higher value in further downstream compared to Zn-roof plating factory (6.2 km from location 9) was probably due to an additional contamination of Zn coming from sources such as populated areas and domestic sewages. Most of these values are above the standards for Zn (60 ppm). According to Moore (1991), sediments are primary sink for zinc. By comparison, sediments from uncontaminated waters typically contain residues of 5 - 50 ppm. The recent uses of Zn are in coatings to protect iron and steel, in alloys for die casting, galvanizing, and in brass. Major sources include the discharge of domestic waste water, manufacturing process involving metals and atmospheric fallout. According to Forstner and Wittmann (1983), Zn is characteristic of domestic and industrial waste effluents.

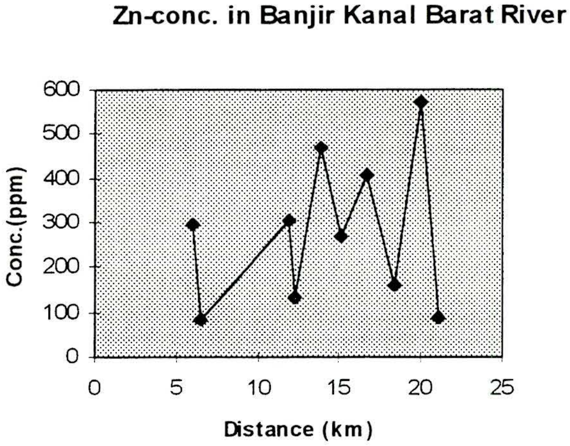


Figure 5-26a: Zinc (Zn) concentration Banjir Kanal Barat River Semarang, Indonesia

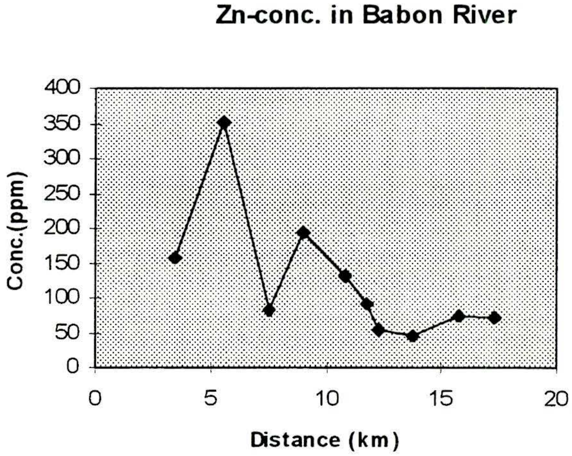


Figure 5-26b: Zinc (Zn) concentration Babon River, Semarang, Indonesia

5.2.3.3. Copper (Cu)

Copper exists as Cu (II) under aerobic conditions and Cu (I) under anaerobic conditions (Sillen, et.al., 1977) in Bodek et.al., 1988. Compared to other metals such as zinc, lead, and cadmium, copper has stronger affinity for clays (finer grain size), iron and manganese oxides, organic matter, and carbonate material. Sometimes, residues are often elevated in sediments, both freshwater and marine (Salomons and Forstner, 1984).

The values range between 40 - 176.9 ppm in the Banjir Kanal Barat River and 18.1 - 71.7 ppm in the Babon River. The highest values are in location 1 at BKBR and location 2 at BR, where farming activities and housing are located along the rivers (see fig.5-27). The high concentration at relatively unpolluted area in Babon River is probably because of local mineralization and the use of pesticides and fungicides from farming activities. According Fillipek & Owen (1978, 1979) in Rosental *et.al.,* 1986, elevated concentration of Cu in sediments suggested C-organic complexes as the major form of Cu. Almost all of these values exceed the Canadian Standard which for Copper is 30 ppm. Modern uses of Cu include electrical wiring, construction, and electroplating. The primary sources are from domestic wastes, manufacturing process involving metals and the dumping of sewage sludge (Moore, 1991).

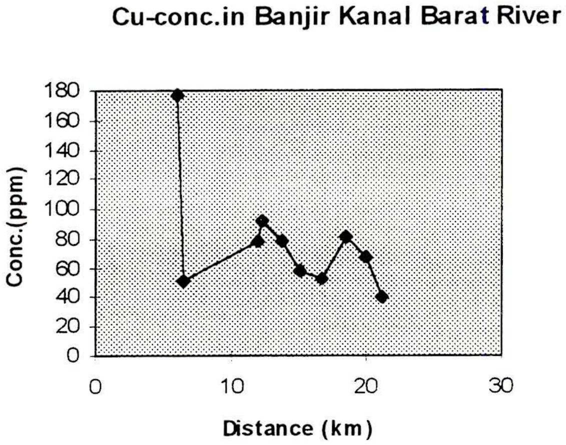


Figure 5-27a : Copper (Cu) concentration in Banjir Kanal Barat River

Semarang, Indonesia

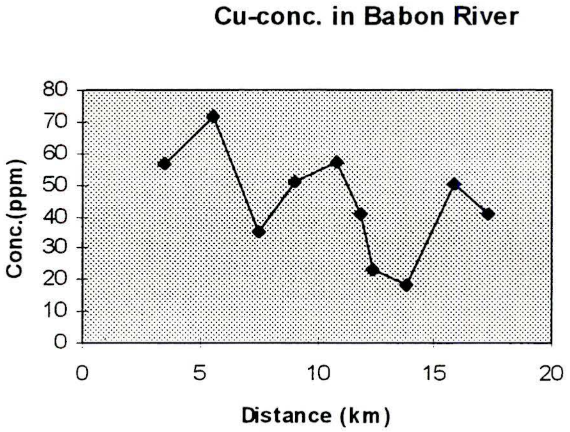


Figure 5-27b : Copper (Cu) concentration in Babon River, Semarang, Indonesia

5.2.3.4. Manganese (Mn) and Iron (Fe)

Iron and Manganese are not pollutants and often occur together and present no health hazards at concentrations normally found in natural waters. They may accumulate toxic /harmful heavy metals by co-precipitation or adsorption and release them again under reducing conditions which dissolve those matrix forming elements (Brugman, 1995).

Manganese is an essential nutritional and multi valent element. It can exist in the +2, +3, +4, +6, and +7 oxidation states. Manganous ion (Mn^{2+}) is considered labile metal ion. When Mn^{+2} adsorbed by clay minerals in soils/sediments, iron oxides or manganese oxides are released. However, copper, zinc, and nickel strongly adsorbed by clay minerals and hydrous iron oxides than they do manganese (Rai *et.al.*, 1984) in Bodek *et.al.*,1988.

The values of Mn range between 719.4 - 2199.0 ppm in the Banjir Kanal Barat and 418.1 - 1708.6 ppm in the Babon River sediments (see fig.5-28). The higher values are in location 5, 7, and 9 at BKBR. Between location 5 and 7 there are some factories such as electroplating, textiles, and pharmaceutical that applied several heavy metals such as Ni, Zn, Cr, etc. Most of these metals are well correlated with Mn as a metal scavenger. In the Babon River, the highest concentration at location 1 (relatively unpolluted area) may due to local mineralization.

Mn has a role in giving important information about the heavy metal content or trends in sediments (Mantei and Foster, 1991). Iron has frequently been used as an indicator of natural changes in the heavy metal carrying capacitty of the sediment and its concentration has sometimes been related to the abundance of metal-reactive compounds supposedly not significantly affected by human actions (Barreiro *et al.*, 1994).

There was no standard for both trace elements. Though Mn and Fe are of little direct toxicological significance, they may control the concentration of other elements, including toxic heavy metals , in surface water.

The main use of manganese is in iron alloys, nonferrous alloys and dry cells, while Fe is used for the production of steel. Total environment flux of Mn is greater than that of all other metals except Fe. Of that total, municipal wastewater is the prominent source, followed by dumping of sewage sludge, smelting and refining, and metal manufactured processes (Moore, 1991).

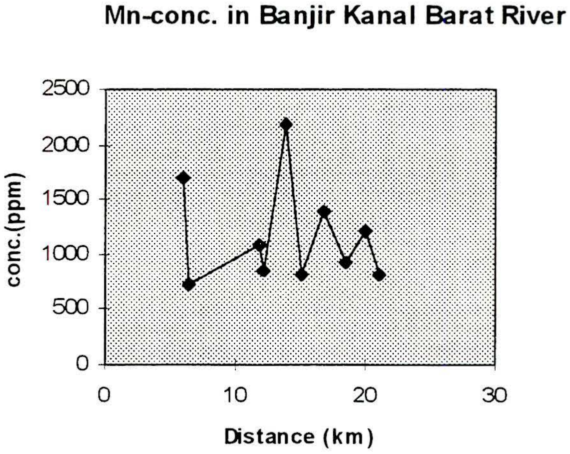


Figure 5-28a: Manganese (Mn) concentration in Banjir Kanal Barat River Semarang , Indonesia

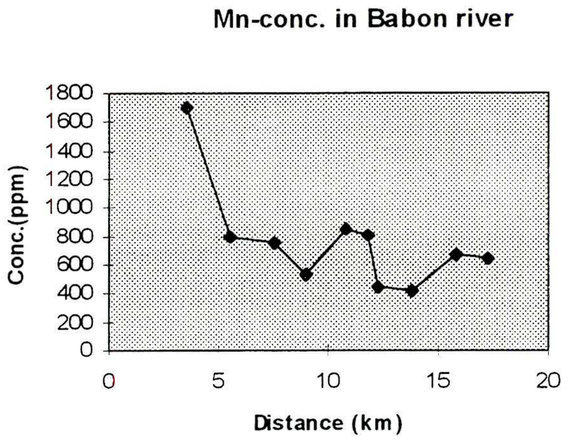


Figure 5-28b: Manganese (Mn) concentration in Babon River, Semarang , Indonesia

In addition, Lead, data were not included because of the instrumentation problem on this element.

In general, the Banjir Kanal Barat River where many kind of industries (see Appendix A) and activities are located, has higher concentration of Ni, Cu, Zn, and Mn compared to the Babon River which is only dominated by tannery/leather industries that mainly use Chromium (Cr) in their industrial processes (see Appendix B). The following table is the t-test result of comparison of metal concentration in both rivers :

Table 5-8: Two Sample t (t-test) between BKBR and BR

	Nickel	**Copper**	**Zinc**	**t-table (5 %),df=9**
t - value	3.74*	2.52*	2.56*	1.883

*** significantly different**

The comparison of the mean concentration of each trace/heavy metals calculated for the two rivers reveals that such concentration are different from each other for most of the metals in Banjir Kanal Barat River (ANOVA, $p < 00.05$). This difference could be due to causes such as different metal sources, sedimentation rates, and bioturbation of sediments in each location. The results are shown in the following table :

Table 5-9: Mean (M) and Confidence Interval (CI) of metal data in BKBR and BR

River	**Nickel**			**Copper**			**Zinc**		
	M	**CI (95%) Low**	**CI 95% Upp.**	**M**	**CI 95% Low**	**CI 95 % Upp**	**M**	**CI 95 % Low**	**CI 95% Upp**
BKBR	38.13	.199	8.381	77.82	20.32	75.32	278.9	100.0	337.8
BR	24.29	10.84	25.42	44.57	2.96	26.18	125.3	.574	131.1

M = Mean , CI = Confidence Interval

The higher values of metal concentrations found probably result from a combination of factors, including industrial discharges to the rivers, inputs from weathering and erosion of the highly mineralized Ungaran Hill, etc. In addition, internal factors such as grain size, organic matter/carbon content, and probably physico-chemical factors play important role in determining sediment metal concentrations. In the areas where industries are absent, the high concentration is presumably due to a product of local mineralization (natural process such as progressive erosion exposing underlying sediments richer in trace/heavy metals). In areas where sewage discharge are rapidly dispersed away from dumping sites (i.e. by high current velocity), the levels input of metals are unlikely to be reflected in the fine fraction of the sediment and vice versa (i.e. location no.2 of BKBR)

Moreover, it can be seen from the figures 5-24 to 5-28 that toward the seashore the concentration of most trace elements decrease because of the sea water dilution. It is assumed that this decrease is also correlated with the high suspended solid concentration in seaward directions (possibility of metals bound to suspended solids rather than the dissolved one).

Duplicates of samples have been taken randomly and compared with original samples in order to determine the precision of the analysis. The results show that some of the RSD (Relative Standard Deviation) of the duplicates deviate from the RSD of the original samples probably due to homogenization.The results are depicted in table below:

Table 5-10: Duplicate Analyses in BKBR and BR sediments

		Ni	Cu	Zn	Mn
BKBR5	Mean	40.5	69.95	391.1	1396.65
	Total Err.	13.398	12.39	110.89	1134.698
	%Tot.Err	32.84	17.8	28.35	81.24
BKBR6	Mean	26.85	42.15	208.55	721.9
	Total Err.	12.77	22.27	84.36	132.25
	%Tot.Err	47.56	52.85	40.45	18.32
BKBR8	Mean	28.15	88.1	160.1	927.95
	Total Err.	4.9	9.07	2.33	15.89
	%Tot.Err	17.39	10.29	1.46	1.71
BR3	Mean	24.08	31.15	79.2	861.05
	Total Err.	4.13	5.88	5.49	151.57
	%Tot.Err	17.22	18.86	6.93	17.6
BR4	Mean	27.15	47.5	173.1	964.9
	Total Err.	3.62	5.25	29.43	621.13
	%Tot.Err	13.33	11.06	17	64.37
BR9	Mean	24.15	49.35	91.65	714.75
	Total Err.	2.07	1.17	25.12	58.35
	%Tot.Err	8.55	2.37	27.41	8.16

Note: All concentrations are expressed in : Mean ± Total Error

$$\text{Total Error} = \sqrt{\text{SD}^2 + \text{Instrument Error}^2}$$

The big difference/variations of standard deviation in the results (see appendices H-1 and H-2) could be due to the differences of location (the nearer to the industrial and populated area, the higher the concentration) and depend on what kind of metals that are being used and discharged mostly.

Statistical analyses (t-test) shows that concentration of Ni, Cu, and Zn in both rivers are significantly higher than the concentrations set by the Canadian Standard for Contaminated Soils and Sediments. The following table shows t-test result of metal/element concentrations compared to the Canadian Standard for Contaminated Soils and Sediments.

Table 5-11: t-test for each element in Banjir Kanal Barat and Babon Rivers

****

	Nickel	**Copper**	**Zinc**	t-table (5 %, df=9)
BKBR	5.62*	3.93*	4.16*	1.833
BR	2.37*	2.84*	2.24*	1.833

****

*** significantly different from Canadian Standard**

All of t-test result in table 5-11 are higher than t-table, so that the heavy metal contaminations in both rivers exceed the Canadian Standard for Contaminated Soils and Sediments.

Spearman's Rank Correlation analyses show that there are correlations between Manganese with Ni, Cu, and Zn in Babon River. This agrees with Brugmann (1995) who suggested that though iron and manganese are not pollutants, but they may accumulate harmful heavy metals. These correlation are depicted/ shown in Table 5-12:

Table 5-12: Correlation amongst metals in Banjir Kanal
Barat River, Semarang, Indonesia

****

	Ni	**Cu**	**Mn**
Cu	-0.127		
Mn	0.539	0.455	
Zn	0.661	0.212	0.806*

****

*** significantly correlated ($\alpha = 5$ %), critical value for Rank's Spearman Correlation is 0.683**

In Banjir Kanal Barat River, correlations amongst metals show positive associations to some extent, especially between Zn and Mn ($p<0.05$). Other metals were also correlated with Mn but correlation decreased in the following order: Zn>Ni>Cu.

From all of these, Banjir Kanal Barat River (where many industries are located) shows a very complex relationship between certain metal pairs such as Nickel-Copper. This could have happened within the contamination regime, in which it receives various individual sources of heavy metals (diverse nature of metal) and organic inputs into the system which both originated from a variety of point and non point sources. It probably reflected the heterogeneity of sediment nature/texture. Therefore, it is very difficult to determine the relationship amongst metals (the behavior and the fate of metals) and their effects on the environment because these metals which are coming from one particular industrial source may well be quickly obscured by the superimposition, interaction, and mixing of metals from other quite different industrial sources (Jonasson and Timperley in Baker, 1980). One metal may by its presence facilitate the toxic effect of another metal, in addition to exerting its own effect. This results in a combined toxicity that is greater than the toxicity of the individual metals. As an example, copper and zinc has been shown to exert synergistic effects (Moriber, 1974).

The following table shows correlations amongst metals in Babon River.

Table. 5-13: Correlation amongst metals, between metals in Babon River, Semarang, Indonesia

	Ni	**Cu**	**Mn**
Cu	0.697*		
Mn	0.770*	0.709*	
Zn	0.758*	0.891**	0.636

*** significantly correlated (α= 5%), critical value for Spearman's Correlation is 0.683**
****significantly correlated (α=1%), critical value for Spearman's Correlation is 0.833**

All metals are correlated with maganese but correlation decreased in the following order:

Ni > Cu > Zn.

5.2.3. Heavy Metals in Sediments (results from X-Ray Fluorescence Analyses)

The results obtained from this method were almost comparable to those that are analyzed by weak-acid digestion (HNO_3 and $HClO_4$) (see Appendix K). Most of the metals were reported as below detection limit levels (< 50 ppm). According to Gorton (distinguished lecturer University of Toronto, personal communication),1996, XRF is an insensitive method compared to other analytical instruments such as AAS, ICP.MS, etc. Even though Iron is not a pollutant, its concentrations were reported very high (above detection limit that Atomic Absorption Spectrophotometer can detect). From X-RF measurement, iron concentrations range from 11,400 to 26,900 ppm in Banjir Kanal Barat River sediments and 6,900 to 9,700 ppm in Babon River sediments. According to US.EPA (Anonym, 1977), an area considered as heavily polluted area if the concentration of iron exceeds 25,000 μg/kg. As a “metal scavenger”, Iron (and Manganese) will determine /control the other metals concentration in the environment. Vincette-Beckett, 1991, had observed a fair agreement on the total metal analyses of lake sediments using X-Ray Fluorescence spectroscopic and graphite furnace AAS data, on the same samples.

5. CONCLUSIONS

From Strong Digestion Analyses, it can be concluded that :

- In general, the Banjir Kanal Barat River where many kind of industries and activities are located, has higher concentration of Ni, Cu, Zn, and Mn compared to the Babon River which is only dominated by tannery/leather industries that mainly use Chromium (Cr) in their industrial processes.
- Towards the seashore the concentration of most trace elements decreases because of sea water dilution. It is assumed that this also correlated with the high suspended solid concentration (which are 93,0 - 921 $mg.l^{-1}$ in Banjir Kanal Barat and 6,738 - 13,675 $mg.l^{-1}$ in Babon River) to the seaward directions/river mouth (possibility of metals bound to suspended solid is higher compared to the dissolved one).
- In Babon River, almost all of trace/heavy metal concentrations tend to decrease in tannery/leather industry areas which are using Cr only in their production process. It seems that the concentration of trace elements in Babon river does not fluctuate greatly.
- The concentration ranges of five elements in Banjir Kanal Barat River are : 27.6 - 58.2 ppm for Nickel ; 40.0 - 176.9 ppm for Cu ; 85.0 - 572.5 ppm for Zn ; and 719.4 - 2199.0 ppm for Mn. In addition, the concentration ranges of five elements in Babon River are : 14.0 - 31.1 ppm for Ni ; 18.1 - 71.1 ppm for Cu ; and 45.5 - 350.5 ppm for Zn. For these concentration, Zinc (Zn), Nickel (Ni) and Copper (Cu) are higher than the values from "Canadian Standard for Contaminated Soils and Sediments.

- Statistical analyses (t-test) shows that there were differences of contamination levels of Ni, Cu, and Zn between Banjir Kanal Barat and Babon Rivers. In addition, the levels of contamination in Banjir Kanal Barat River was higher than Babon River. Moreover, the big difference/variations of standard deviation in the results could be due to the differences of location (the nearer to the industrial and populated area, the higher the concentration) and depend on the kinds of metal that are being used and discharged mostly.
- Spearman's Rank Correlation shows that there were strong correlation amongst heavy metals such as Ni, Cu, and Zn $(p < 0.05)$ in Babon Rivers, and weak $(p>0.05)$ correlation in Banjir Kanal Barat River.

From Weak Acid Digestion analyses, it can be concluded that :

- Most of the metals found in sediments using weak acid digestion analyses are lower compared to strong acid digestion with finer grain size(< 63 μm).
- In weak acid digestion which used whole fraction of sediment, the positive correlation were found between metals concentration and organic matter or organic carbon.
- In Banjir Kanal Barat River, Copper (Cu) is strongly correlated organic carbon. In Babon River, Chromium (Cr) is strongly correlated with organic carbon.
- Most of trace/heavy metal values found using this method are still within the range from Canadian Standard for Contaminated Soils and Sediments.
- Most of the results obtained in this method are almost comparable with results from X-Ray fluorescence.

From Atomic Absorption analytical procedures point of view (strong and weak acids digestion analyses), it seems that weak acid digestion shows higher precision (less total error) than strong acid digestion. One plausible reason is in the weak acid digestion, one sample was taken from each location and measured three times (three readings). In the strong acid digestion, two samples were taken from each location (one of them is the duplicate) and measured two times. The samples in the weak acid digestion were more homogenous than the samples from the strong acid digestion.

Suggestions

- More studies on metal studies are needed, especially on speciation, in order to really understand the distribution, behavior and fate of trace/heavy metals in the environment and the effect of heavy metals on organisms.
- The use of Standard Reference Material is very critical because it can give an idea of the degree of metal extraction provided by the methods.
- The most contaminated metals in Banjir Kanal Barat River such as Ni, Cu, and Zn are associated with the industries (steel, electroplating, textile, etc) that use most heavy metals in their productions. Therefore, discharge from those industries should be regulated.
- The most contaminated metal in Babon River is Cr. Therefore, the waste from industries (tanneries) that use Cr, should be regulated, too.

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APPENDICES

Apppendix A.Wastewater Characteristics, Treatment, and Disposal Situation in Industries Around Banjir Kanal Barat River, Semarang :

1. *PT. Queen Ceramic (Ceramic Industry)*

Prominent parameters of waste water are pH, suspended solids, and COD. Waste treatment is physico-chemical treatment by adding coagulant and floculant, continued with sedimentation. Sediment results from Waste Water Treatment is recycled.

2. *PT. Raja Besi (King of Iron) (Steel/ Iron Plating Industry)*

Waste water discharge contains pH and metals. Waste water is neutralized with soda caustic the treated with physical sedimentation. Waste Water Treatment Unit need to be improved/completed.

3. *PT.Alam Daya Sakti (Floortile Industry)*

Parameters of untreated waste water are pH, suspended solids, and COD. Waste water treatment is discharged to the sedimentation pond, then recycled for the process. The sediments result from sedimentation are used for floortile and the rest of them are discharge to other areas (outside factory).

4. *PT. I S T W (Mining-Pipe Industry)*

Water discharge parameters which are prominently apparent before treatment are pH, suspended solids, Zn, Cr, Fe and COD. Waste water comes from pickling, degreasing, water quenching unit. Waste water treatment is by neutralization, aeration, coagulation, filtration. This treated wastes are recycled.

5. *PT. Kimia Farma (Vegetable Oil Refinery)*

Liquid waste are coming from iol refinery, water sanitation. Prominent characteristics waste water before treatment are COD, BOD, and suspended solids, and oil. Waste water treatment is oil separation based on their specific gravity.

6. *PT. Semarang Makmur (Zn-Electroplating)*

Waste water treatment that has been implemented is :

Waste water process from pickling and rinsing unit with excessive HCL and from galvanizing unit which still contains Zn, Pb

7. *PT. Damaitex (Textile Industry)*

Waste water is from finishing, printing (which is managed by skimming and sedimentation process). Characteristics of waste water before treatment are pH, COD, BOD and suspended solids, color, and oil. Waste Water Treatment Unit need to be improved because the one that already existed do not fulfill the standard/requirements criteria.

8. *PT. Sinar Panca Jaya (Textile Industry)*

Liquid wastes from starching are discharged together with wastes from spinning (cooling). No Waste Water Treatment Unit available (the old one is already malfunction).

9. *PT. Panca Tunggal Knitting Mill*

Due to the absence of location for Waste Treatment Unit, the liquid wastes from sinking, washing and dyeing are transported into other river.

10. *PT. Paphros (Pharmaceutical industry)*

The prominent parameters are high pH, COD, BOD. Here, liquid wastes concentration are higher than required. Waste water is treated with an aerated pond. However , it is still not fulfill the criteria for sewage discharge.

(Source : Institution of Environmental Impact Control, 1994)

Appendix B. Factories around Babon River:

1. *PT. Buana Sakti Tannery*
2. *PT.Puspita Sari*
3. *PT.Cold Storage Mina Baruna*
4. *PT.Jaguar Tannery*
5. *PT.Condro Cipto Tannery*
6. *PT.Fodder Company (PT.Proteina Prima)*

(Source : Environmental Impact Management Agency, 1994)

Appendix C-1 :Recapitulation of Waste Pollutant Load of Zinc (kg/yr) from 1989/90 to 1992/93 which enter Banjir Kanal Barat River

No.	Industry	Year 1	year II	Year III	Year IV	Max.target
1	PT.Queen Ceramic	1,058.4	957.5	652	163.38	120.00
2	PT. Iron King	17,605.52	57181		35354.55	84.00
3	PT. Alam Daya Sakti	965.37	101.8	60.9	--	22.92
4	PT.I S T W	2311.875	2129.2	1605	--	0.48
5	PT.Kimia Farma	6249.98	186	245	2614.511	264.00
6	PT.Semarang Makmur	609.93	210.6	61.4	--	5400.00
7	PT.Damaitex	864	49.5	741	1489.02	48.00
8	PT.Paphros	160.987	278.8	457	672.388	198.00
9	PT.Sinar Panca Jaya	1353.35	774.6	586	1223.272	204.00
10	PT.Panca Tunggal	2238.75	1229	--	--	--
	Total	33,418.64	63097.8	4408.3	41517.1	6341.4

Appendix C-2: Recapitulation of Waste Pollutant Load of Lead (kg/yr) from 1989/90 to 1992/93 which enter Banjir Kanal Barat River

No.	Name of the industry	Year I	Year II	Year III	Year IV	Max target
1	PT.Queen Ceramic	2.85	0.57	0.63	1.11	1.8
2	PT. Iron King	5.82	7.29	1.2	6.84	2.73
3	PT. Alam Daya Sakti	0.29	0.09	0.6	--	0.33
4	PT.I S T W	0.2	0.39	0.27	--	--
5	PT.Kimia Farma	3.56	0.55	0.29	0.47	3.96
6	PT.Semarang Makmur	0.99	0.15	0.1	--	0.81
7	PT.Damaitex	0.72	--	4.86	2.97	7.2
8	PT.Paphros	5.6	5.41	0.55	0.85	3.96
9	PT.Sinar Panca Jaya	1.29	0.71	1.17	4.98	4.08
10	PT.Panca Tunggal	0.33	1.23	0.15	--	--
	Total	21.65	16.39	9.82	17.22	24.87

Appendix C-3: Recapitulation of Waste Pollutant Load of Iron (kg/yr) which enter Banjir Kanal Barat River

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No.	Name of the industry	Year I	Year II	Year III	Year IV	Max target
1	PT.Queen Ceramic	10.8	17.16	20.82	6.81	60
2	PT. Iron King	2120.25	3923.01	2208.3	1440.93	90.9
3	PT. Alam Daya Sakti	5.685	3.255	29.04	--	11.46
4	PT.I S T W	6.93	0.66	6.0	--	9.0
5	PT.Kimia Farma	22.308	79.464	10.322	2.059	132
6	PT.Semarang Makmur	1.65	4.77	5.96	--	27
7	PT.Damaitex	30.12	3.0	160.08	18.09	240
8	PT.Paphros	18.704	25.954	20.988	3.485	198
9	PT.Sinar Panca Jaya	3.278	3.976	27.254	10.934	204
10	PT.Panca Tunggal	5.265	2.555	3.27	--	-
	Total	2219.725	4067.249	2488.764	1482.308	972.36

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Appendix C-4: Recapitulation of Waste Pollutant Load of Chromium (kg/yr) from 1989/90 - 1992/93 which enter Banjir Kanal Barat River

****

No.	Name of the industry	Year I	Year II	Year III	Year IV	Max target
1	PT.Queen Ceramic	589.5	1958.81	22.8	24.75	6
2	PT. Iron King	1667.56	888.51	1382.16	691.06	212.4
3	PT. Alam Daya Sakti	92.43	38.63	70.23	--	1.14
4	PT.I S T W	118.8	55.89	89.76	--	1.2
5	PT.Kimia Farma	463.48	785.10	214.95	2.79	13.2
6	PT.Semarang Makmur	349.11	368.55	5.54	--	13,500
7	PT.Damaitex	3816	0.0	271.16	261.95	180
8	PT.Paphros	751.65	209.41	104.54	51.81	19.8
9	PT.Sinar Panca Jaya	1886.65	268.48	551.05	391.65	1769.09
10	PT.Panca Tunggal	640.0	1124.85	--	--	--
	Total	9735.18	4898.23	2712.19	6553.2	15702.83

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Note :

-- = Either data not available or wastes were discharged to another place

Appendix D.

The Regulation of Indonesian Health Minister No.173/Men.Kes./VII/'77 Year of 1977 about Water Quality Requirement of Water Bodies

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No.	Parameter Chemistry	Unit	Minimum Allowed	Maximum suggested	Maximum allowed	
	A. Inorganic chemistry					
1	Arsen	mg/l		nil	0.05	as As
2	Barium	mg/l		nil	0.05	as Ba
3	Total Fe	mg/l		nil	1	as Fe
4	Bor	mg/l		nil	1	as B
5	Chrom	mg/l		nil	0.05	as Cr^{6+}
6	Chrom	mg/l		nil	0.5	as Cr^{3+}
7	Cadmium	mg/l		nil	0.01	as Cd
8	Cobalt	mg/l		nil	1	as Co
9	Mangan	mg/l		nil	0.5	as Mn
10	Nickel	mg/l		nil	0.1	as Ni
11	Silver	mg/l		nil	0.05	as Ag
12	Quicksilver	mg/l		nil	0.005	as Hg
13	Selenium	mg/l		nil	0.01	as Se
14	Zinc	mg/l		nil	1	as Zn
15	Copper	mg/l		nil	1	as Cu
16	Lead	mg/l		nil	0.05	as Pb
17	Ammonia	mg/l		0.01	0.05	as N
18	Chloride	mg/l		25	600	as ion Cl
19	Cholor (free)	mg/l		-	nil	as Cl_2
20	Fluoride	mg/l		-	1.5	as ion F
21	Hardness	* D	5	10		
22	Nitrat and Nitrit	mg/l		nil	10	as N
23	Sulphate	mg/l		50	400	as ion SO_4
24	Sulphide	mg/l			nil	as ion S
25	Uranyl	mg/l		nil	5	as ion uranyl
	B. Organic Chemistry					
1.	Extract C Chloroform	mg/l		0.01	0.5	
2.	Herbicide	mg/l		nil	0.1	
3.	Oil and Fat	mg/l		nil	nil	
4.	Phenol	mg/l		nil	0.002	

5 Pesticide:	Unit	Min.allwd	Max.sgstd	Max.allwd	
a.Aldrin	mg/l		nil	0.017	
b.Chlordane	mg/l		nil	0.003	
c.D.D.T.	mg/l		nil	0.042	
d.Dieldrine	mg/l		nil	0.017	
e.Endrine	mg/l		nil	0.001	
f.Heptachlor epoxide	mg/l		nil	0.018	
h.Lindane	mg/l		nil	0.056	
i.Metoxy chlor	mg/l		nil	0.035	
j. Organophosphat and carbamate	mg/l		nil	0.1	
k. Toxaphene	mg/l		nil	0.005	
6 Cyanide	mg/l		nil	0.1	as ion CN
7 Subtances which react with methyl blue	mg/l		nil	0.5	
Radioactivity					
1 Gross beta	pCl/l		100	1	
2 Radium 226	pCl/l		1	3	
3 Strontium 90	pCl/l		2	10	

List. 2 Water Quality Requirements from Water Bodies

Parameter	Unit	Class A		Class B		Class C	
		Min.allwd	Max.allwd.	Min.allwd.	Max.allwd	Min.allwd.	Max.allwd
Physics							
1 Temperature	C		air temp.		air temp.		air temp.
Chemistry							
1 BOD	mg/l		3		3		5
2 DO	mg/l	6		4		6	
3 pH		6.5	8.5	6.5	8.5	6	9
4 Dissolved matter	mg/l		1,000		2,000		2,000
Microbiology							
1 Nearest estimation of total Coliform	per 100 ml		10,000		1,000		20,000
2 Nearest estimation of tot. feces coliform	per 100 ml		2,000		400		4,000

Appendix D-1: Ministry of Environment Regulation on Liquid Waste Standard Quality for Industrial Activities (October, 1995)

No.	Parameter	Unit	Liquid Waste Standard Quality Category I	Liquid Waste Standard Quality Category II
	Physical			
1.	Temperature	°C	38	40
2.	Dissolved solids	mg/l	2000	4000
3.	Suspended solids	mg/l	200	400
	Chemical			
1.	pH		6.0 - 9.0	
2.	Dissolved Fe	mg/l	5.0	10
3.	Dissolved Mn	mg/l	2.0	5.0
4.	Barium (Ba)	mg/l	2.0	3.0
5.	Copper (Cu)	mg/l	2.0	3.0
6.	Zinc (Zn)	mg/l	5.0	10
7.	Hexavalent Chrom	mg/l	0.1	0.5
9.	Total Chrom	mg/l	0.5	1.0
10.	Cadmium	mg/l	0.05	0.1
11.	Mercury (Hg)	mg/l	0.002	0.005
11.	Lead (Pb)	mg/l	0.1	1.0
12.	Stanum (Sn)	mg/l	2.0	3.0
13.	Arsenic (As)	mg/l	0.1	0.5
14.	Selenum (Se)	mg/l	0.05	0.5
15.	Nickel (Ni)	mg/l	0.2	0.5
16.	Cobalt (Co)	mg/l	0.4	0.6
17.	Cyanide (C)	mg/l	0.05	0.5
18.	Sulphide (H_2S)	mg/l	0.05	0.1

19.	Fluoride (F)	mg/l	0.05	0.1
20.	Chlorine (Cl_2)	mg/l	1.0	2.0
21.	Ammonia (NH_3-N)	mg/l	1.0	5.0
22.	Nitrate (NO_3-N)	mg/l	20	30
23.	Nitrite (NO_2-N)	mg/l	1.0	3.0
24.	BOD_5	mg/l	50	150
25.	COD	mg/l	100	300
26.	Methylene blue	mg/l	5.0	10.0
27.	Phenol	mg/l	0.5	1.0
28.	Vegetable oil	mg/l	5.0	10.0
29.	Mineral oil	mg/l	10.0	50.0
30.	Radioactivity *		---	--

* Radioactivity value follow the valid regulation

Appendix D-2: Standard Quality of Liquid Waste for Cu and Ni Electroplating Industry by Indonesian Ministry of the Environment

Parameter	Electroplating using Cu		Electroplating using Ni	
	Max. Conc. (mg/l)	Max poll. load (gr/m^2)	Max.Conc. (mg/l)	Max.poll.load (gr/m^2)
1. TSS	60	6.0	60	6.0
2. Cadmium (Cd)	0.05	0.05	0.05	0.005
3. Cyanide (CN)	0.5	0.05	0.05	0.05
4. Total metal	8.0	0.8	8.0	0.8
5. Copper (Cu)	3.0	0.3	-	-
6. Nickel (Ni)	-	-	5.0	0.5
7. pH	6.0 - 9.0		6.0 - 9.0	

Appendix D-3: Standard Quality of Liquid Waste for Cr and Zn Electroplating/Galvanizing Industry by Indonesian Ministry of the Environment

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Parameter	Electroplating using Copper (Cr)		Electroplating using Zn (Zn)	
	Max. Conc. (mg/l)	Max poll. load (gr/m^2)	Max Conc. (mg/l)	Max poll.load (gr/m^2)
1. TSS	60	6.0	60	6.0
2. Cadmium (Cd)	0.05	0.05	0.05	0.005
3. Cyanide (CN)	0.5	0.05	0.05	0.05
4. Total metal	8.0	0.8	8.0	0.8
5. Crhrom total (Cr)	2.0	0.2	-	-
6. Hexavalent Cr $^{6+}$	0.3	-	5.0	0.5
7. Zinc (Zn)	-	-	2.0	0.2
8. pH	6.0 - 9.0		6.0 - 9.0	

****

Appendix D-4 : Standard Quality of Liquid Waste for Tannery/Leather Industry by Indonesian Ministry of the Environment

****

Parameter	Max. Concentration (mg/l)	Max.Pollution Load (kg/tonnes)
1. BOD $_5$	150	10.5
2. COD	300	21.0
3. TSS	150	10.5
4. Sulphide (as H_2S)	1.0	0.07
5. Total Chrom	2.0	0.14
6. Oil and Fat	5.0	0.35
7. Total ammonia	10.0	0.70
8. pH	6.0 - 9.0	
Max. flow rate	70 m^3 per tonnes basic material	

****

Appendix D-5: Standard Quality of Liquid Waste for Textile Industry by Indonesian Ministry of the Environment

****

Parameter	Max. Concentration (mg/l)	Max.Pollution Load (kg/tonnes)
1. BOD $_5$	85	12.75
2. COD	250	37.5
3. TSS	60	9.0
4. Total Phenol	1.0	0.15
5. Total Chrom	2.0	0.30
6. Oil and Fat	5.0	0.75
7. pH	6.0 - 9.0	
Max. flow rate	150 m^3 per tonnes basic material	

****

Appendix D-6: Standard Quality of Liquid Waste for Monosodium Glutamate (MSG) Industry Indonesian Ministry of the Environment

****

Parameter	Max. Concentration (mg/l)	Max.Pollution Load (kg/tonnes)
1. BOD $_5$	85	12.75
2. COD	250	37.5
3. TSS	60	9.0
4. pH	6.0 - 9.0	
Max. flow rate	120 m^3 per tonnes MSG products	

****

Appendix D-7: Standard Quality of Liquid Waste for Pharmaceutical by Industry Indonesian Ministry of the Environment

****

Parameter	Process to make formula (mg/l)	Formulation (Mixing) (mg/l)
1. BOD $_5$	100	75
2. COD	300	150
3. TSS	100	75
4. Total-N	30	-
5. Phenol	1.0	-
4. pH	6.0 - 9.0	

****

Appendix D-8: Standard Quality of Liquid Waste for Paint Industry by Indonesian Ministry of the Environment

Parameter	Max. Conconcentration (mg/l)	Max.poll. load (gr/m^2)
1. BOD	100	80
2. TSS	60	48
3. Cadmium (Cd)	0.10	0.08
4. Mercury (Hg)	0.015	0.012
5. Lead (Pb)	0.40	0.42
6. Copper (Cu)	1.0	0.80
7. Hexavalent Cr^6	0.25	0.20
8. Titanium (Ti)	0.5	0.4
9. Zinc (Zn)	1.5	1.2
10. Phenol	0.25	0.20
11. Oil and fat	15	12
12. pH	6.0 - 9.0	
Max. flow rate (debit)	0.8 L per L water base of paint product Zero discharge for solvent base	

Appendix E-1 : Water Quality Parameters in Banjir Kanal Barat River

****

Location	Temp (° C)	pH	Susp solid (mg/l)	DO (mg/l)	BOD (mg/l)	COD (mg/l)
1	26.6	8.6	86	8.01	1.71	37.44
2	27	8.9	80	8	1.9	12.67
3	30	9.4	73	9.07	1.41	15.55
4	30.4	9.4	85	9.17	2.41	13.25
5	30.2	9	77	8.36	2.81	22.47
6	30	9.1	84	7.35	2.79	23.62
7	29	8.3	96	7.32	2.34	17.86
8	29	7.8	93	5.83	5.16	5.14
9	29.2	8	724	2.89	1.85	1.84
10	29.4	7.8	921	16.71	32.26	31.11
Mean	29.1	8.6	231.9	8.27	5.46	18.1
Stdev	1.3	0.6	314.8	3.49	9.47	11

****

Appendix E-2: Water quality parameters in Babon River, Semarang, Indonesia

****

Location	Temp (o C)	pH	Susp solid (mg/l)	DO (mg/l)	BOD (mg/l)	COD (mg/l)
1	26.2	8.6	165	5.28	0.87	32.4
2	29	8.9	59	7.06	0.95	26.49
3	28.4	8	64	4.21	1.11	11.52
4	30.4	8.7	101	4.85	2.28	25.35
5	29.8	8	91	4.62	1.5	47.81
6	30	7.3	69	4.61	1.15	25.35
7	29.2	8	9,070	0	36.59	339.88
8	29.4	8.2	13,675	0	69.9	455.1
9	29	7.8	6,500	0	184.7	426.29
10	29	7.6	6,738	3.79	5.1	541.51
Mean	29	8.1	3653	3.4	30.4	193.3
Stdev	1.2	0.5	1576	0.8	18.6	69.1

****

Appendix F-1: Water Clarity and Surface Water Velocity data in Banjir Kanal Barat River

****

Location	Time	Water Clarity (cm)	Velocity(m/sec)
1. BKB 1	9.30	31	0.31
2. BKB 2	10.17	35	1.25
3. BKB 3	11.45	32	0.71
4. BKB 4	12.40	20	0.40
5. BKB 5	13.40	27	0.33
6. BKB 6	14.35	28	0.23
7. BKB 7	15.00	25	0.11
8. BKB 8	15.35	30	0.13
9. BKB 9	16.15	38	change direction
10.BKB 10	17.00	50	change direction

****

Appendix F-2 : Water clarity and Surface Water Velocity data in Babon River

****

Location	Time	Water clarity (cm)	Velocity(m/sec)
1. BR 1	09.12	17	0.32
2. BR 2	10.05	50	0.20
3. BR 3	10.45	40	0.33
4. BR 4	12.15	50	0.30
5. BR 5	3.30	35	0.08
6. BR 6	14.30	50	0.11
7. BR 7	14.55	23	0.15
8. BR 8	15.25	15	0.20
9. BR 9	16.15	25	0.08
10. BR 10	17.00	50	0.15

****

Appendix G-1: Heavy metals concentration in the water column of Banjir Kanal Barat River/Garang River

Location	Pb (mg/l)	Cu (mg/l)	Cr (mg/l)	Cd (mg/l)
1.	0.08	nd	0.06	nd
2.	0.03	nd	0.06	nd
3.	nd	nd	nd	nd
4	0.03	nd	0.06	nd
5	0.03	nd	nd	nd
6	0.08	0.02	nd	nd
7	0.11	0.01	nd	nd
8	0.08	0.01	nd	nd
9	0.03	nd	nd	nd
10	0.03	nd	nd	nd

nd = not detected

Appendix G-2: Heavy metals concentration in the water column of Babon River

Location	Pb (mg/l)	Cu (mg/l)	Cr (mg/l)	Cd (mg/l)
1	nd	nd	nd	nd
2	0.03	nd	nd	nd
3	0.08	0.01	nd	nd
4	0.08	0.01	nd	nd
5	0.03	0.01	nd	nd
6	0.03	0.01	nd	nd
7	0.19	0.02	0.11	nd
8	0.36	0.02	0.06	nd
9	0.26	0.02	0.06	nd
10	0.21	0.02	0.06	nd

nd = not detected

Appendix H-1 : Trace/Heavy Metals content (Strong Acid Digestion) in Banjir Kanal Barat River Sediments, Semarang, Indonesia

****

Location	Ni	Cu	Mn	Zn	Pb
************	************	************	************	************	************
1	36.5	176.9	1708.4	296.4	0.79
2	33	51.5	719.4	85	0.77
3	27.6	79	1093.6	304.1	0.76
4	29.9	92.3	858.5	135.1	0.81
5	49.9	78.4	2199	469.5	0.83
6	35.9	57.9	815.4	268.2	0.74
7	47.6	52.7	1389.3	408.2	0.79
8	31.6	81.8	917.7	161.6	3.82
9	58.2	67.7	1210.8	572.5	0.88
10	31.1	40	817.8	88.4	0.76
Mean	**38.13**	**77.8**	**1173**	**278.9**	**1.09**
Stdev	**10.20**	**38.4**	**473**	**166.2**	**0.96**

****

Appendix H-2: Trace/Heavy Metals content (Strong Acid Digestion) in Babon River Sediment Semarang, Indonesia

****

Location	Ni	Cu	Mn	Zn	Pb
************	************	************	************	************	************
1	30.4	56.6	1708.6	156.6	17.78
2	23.3	71.7	792.7	350.5	26.79
3	27	35.3	753.9	83	19.53
4	29.7	51.2	525.7	193.9	13.7
5	31.1	57.3	846.4	131.5	16.69
6	25.7	41	815.6	92.4	16.55
7	16.6	23.6	440.9	54.8	10.83
8	14	18.1	418.1	45.5	8.26
9	22.7	50.1	673.6	73.9	16.87
10	22.4	40.8	643.7	70.7	14.77
Mean	**24.3**	**44.6**	**762**	**125.3**	**16.2**
Stdev	**5.7**	**16.2**	**366**	**92.1**	**5.0**

****

Appendix J-1 : Heavy metal content (Weak Acid Digestion) in Banjir Kanal Barat River

* * *

Location	Pb (mg/l)	Cu (mg/l)	Cr (mg/l)	Cd (mg/l)
1	5.9	19.4	7.0	0.05
2	13.1	22.8	181.1	0.05
3	6.4	24.3	8.6	0.06
4	8.6	28.9	2.9	0.03
5	8.9	22.4	7.4	0.05
6	10.9	24.2	7.6	0.05
7	7.2	16.6	7.9	0.08
8	9.2	53.6	7.5	0.06
9	9.2	19.0	7.4	0.05
10	11.1	21.0	76.9	0.05
Mean	9.1	31.4	25.2	0.05
Stdev	2.2	57.0	10.5	0.01

* * *

Appendix J-2: Heavy metal content (Weak Acid Digestion) in Babon River

* * *

Location	Pb (mg/l)	Cu (mg/l)	Cr(mg/l)	Cd (mg/l)
1	10.6	21.9	6.23	0.10
2	10.7	23.4	7.34	0.08
3	12.1	24.1	8.12	0.15
4	11.3	18.6	5.39	0.18
5	11.3	19.9	6.27	0.10
6	12.1	23.8	8.87	0.07
7	9.3	21.3	16.57	0.08
8	12.0	21.2	165.59	0.07
9	12.2	24.7	75.86	0.07
10	10.7	22.4	79.07	0.08
Mean	11.2	22.1	37.9	0.1
Stdev	0.94	1.9	53.4	0.04

* * *

Appendix K : Trace/ Heavy Metals Content (X-Ray Fluorescence) in Banjir Kanal Barat and Babon Rivers

* * *

ID code	Pb	Cu	Cr	Cd	Ni	Mn	Zn	Fe
KB3	< 50	< 50	8.0	< 50	< 50	200.0	< 50	6,900
KB4	< 50	< 50	11.0	< 50	5.4	250.0	11.0	9,700
KB7	< 50	< 50	12.0	< 50	< 50	160.0	< 50	7,700
BKB6	< 50	< 50	12.0	< 50	5.7	240.0	20.0	11,400
BKB7	< 50	< 50	23.0	< 50	14.0	330.0	22.0	21,800
BKB9	< 50	< 50	24.0	< 50	16.0	340.0	20.0	26,900

* * *

Appendix I-1: Organic matter and Organic Carbon content in Banjir Kanal Barat River

****

Location	% LOI (Loss on ignition)	Organic Carbon (%)
1	4.97	1.0
2	7.91	3.5
3	6.64	1.9
4	7.75	2.2
5	8.38	1.2
6	10.01	5.9
7	4.85	1.0
8	6.27	3.8
9	2.62	0.5
10	15.69	1.8
Mean	**7.46**	**2.3**
Stdev	**1.08**	**1.7**

****

Appendix I-2: Organic matter (LOI) and Organic Carbon content in Babon River

****

Location	% LOI (Loss on ignition)	Organic Carbon (%)
1	6.52	0.0
2	4.96	1.3
3	8.66	0.9
4	12.58	0.1
5	8.77	0.5
6	22.21	1.8
7	13.37	1.4
8	15.13	9.0
9	19.10	19.0
10	16.25	6.0
Mean	**12.46**	**4.0**
Stdev	**5.57**	**6.02**

****

Appendix L-1: Granulometric content (%) of Surface Sediment of Banjir Kanal Barat River

****

	Granulometric content (%) of various sediment fractions in Mesh #					
Study site	70	100	120	140	325	400
1	88.97	4.43	3.03	1.17	2.59	0.80
2	86.8	2.2	2.9	6.85	0.09	0.20
3	94.28	0.07	1.12	2.23	1.67	0.07
4	89.65	1.65	2.67	4.08	1.85	0.01
5	68.35	12.7	8.5	5.51	4.56	0.47
6	82.72	5.6	8.01	3.5	0.16	0.00
7	72.17	10.38	7.59	5.95	3.83	0.61
8	90.72	2.69	1.57	3.37	1.42	0.20
9	46.49	19.62	15.55	12.76	5.26	0.30
10	46.78	9.9	9.75	22.49	10.19	0.80
Mean	76.9	6.92	6.07	6.79	3.16	0.35
Stdev	17.83	6.13	4.61	6.38	3.02	0.30

****

Appendix L-2 : Granulometric content (%) of Surface Sediment of Babon River

****

	Granulometric content (%)of various sediment fractions in Mesh #					
Study site	70	100	120	140	325	400
1	82.28	7.53	3.01	3.38	3.13	0.7
2	82.23	4.52	3.35	5.81	2.97	0.13
3	40.78	15.68	10.41	15.56	16.19	1.38
4	73.88	8.94	4.76	7.51	4.62	0.3
5	90.27	3.26	1.65	2.26	2.26	0.1
6	56	7.2	9.33	14.4	12	1.07
7	54.74	9.98	8.65	8.55	16.47	1.6
8	54.1	17.46	7.44	10.31	0.1	0.48
9	57.47	10.52	7.77	9.94	13.72	0.58
10	73.25	4.46	3.12	5.7	11.34	1.7
Mean	66.5	8.95	5.95	8.34	8.28	0.80
Stdev	16.01	4.7	3.12	4.36	6.27	0.60

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Appendix M : Background concentration of metals in the freshwater environment

Type of material	Cu	Co	Zn	Fe	Mn	Ni	Cr
Fresh waters							
Fresh waters in general[3]	1.8	0.05	0.5	< 30	< 5	0.3	0.5
River waters [1]	1		10	55	6	0.3	0.5
Various rocks,soils & sediments							
Rocks and sediments[3]	4-250	0.1-74	16-165		390-6700		11-90
Lake sediments[1]	13		68			29	72
Soils[2]	20	8	50	38000			100

Note: These data are only presented as a guide: there are very wide ranges of metal concentrations in uncontaminated water, sediments, and/or soils. These values are expressed in $\mu g\ g^{-1}$ (ppm) for soils and sediments, and $\mu g\ l^{-1}$ (ppb).

[1] Salomons and Forstner, 1984 ; [2] Driver and Tukahirwa, 1990 ; [3] Forstner and Wittmann, 1981).

Appendix N : Several guidelines of Sediment Quality

Metals	US EPA Region 5 ($\mu g.kg^{-1}$) [1]			Wisconsin Dept. of [2]	Ontario Ministry of Environment [3]		
	Non polluted	Moderately poll.	Heavily poll.	Nat. Res. Sed Quality Criteria	No effect level	Lowest effect level	Limit of tolerance level
Pb	< 40	40-60	> 60	50	23.0	31.0	250.0
Zn	< 90	90-200	> 200	100	65.0	110.0	800.0
Fe	< 17,000	17,000-25,000	> 25,000	-	2.0*	3.0*	4.0*
Ni	< 20	20 - 50	> 50	100	15.0	31.0	90.0
Mn	< 300	300-500	> 500	-	400.0	457.0	1110.0
Cd	-	-	> 6	1	0.6	1.0	10.0
Cr	< 25	25 - 75	> 75	100	22.0	31.0	111.0
Cu	< 25	25 - 50	> 50	100	15.0	25.0	114.0

Source :

[1] Anon. (1977a) in Giesy and Hoke, 1990. All concentrations as $\mu g.kg^{-1}$, dry weight

[2] Sullivan et al..(1985) in Giesy and Hoke, 1990. All concentrations as $\mu g.g^{-1}$, dry weight

[3] Persaud et.al.(1989) in Giesy and Hoke, 1990. All concentrations as $\mu g.g^{-1}$, dry weight

Appendix O :. Procedures of Total Organic Content Analyses as describes in MLS-1200 MEGA Operator Manual (May 1994).

- Wet destruction method :

This method can be used for soil/ sediments with organic Carbon, ranging from 0.2-12%. Sensitivity of this method is 0.2 - 0.5 %. Because wet destruction can only oxidize ± 75% of the total carbon, in calculation, factor correction of 4/3 or 1.33 is used. Titration method which was used is automatic titration procedure. Reagents that are used are 95 - 97 % H_2SO_4 concentrate, 1 N K_2CrO_7, and 0.5 N $FeSO_4.7\ H_2O$.

- Procedure

  - 1 gr of sample was put in erlenmeyer
  - 10 ml of K_2CrO_7 and 20 ml H_2SO_4 concentrated were added
  - after 30 minutes, 150 ml of aquadest was added
  - the electrode was put on this solution
  - the solution was stirred up using magnetic stirrer
  - automatic titration was turned on

- Titration system consist of :

  - Radiometer TTT85 Titrator and ABU80 Autoburett for organic-C determination
  - For electrode indicator, platina electrode was used,
    For reference indicator, Ag/AgCl electrode was used
  - Blank consists of dichromate and H_2SO_4 was titrated

- Calculation :

If A ml Fe (II) solution was added into the blank and B ml was added into the sample, the difference amount of titration as much as (A-B) is equal to dichromate that has been reducted by organic-C from tested samples.

-10 ml of 1 N $K_2Cr_2O_7$ (or 10 meq $K_2Cr_2O_7$) can oxidize 10 meq Carbon

- Equivalent weight of C (carbon) is 12 / 4 = 3 and 10 meq C equal to 30 mg of C

- Relative proportion of dichromate which can react with organic-C is equal to the value of (A-B) / A

- For 1 g sediment , C organic content which was oxidized (Co) is :

Co (mg) = 30 x {(A-B) /A}

Co (%) = 3 x {(A-B) /A}

Because $K_2Cr_2O_7$ can only oxidize 75 % of total carbon in the sample, so that in calculation, the total organic-C (C_t) is (4/3 = correction factor) :

C_t (mg) = 4/3 x 30 x {(A-B) /A}

C_t (%) = 4/3 x 3 x {(A-B) /A}

- For 1 g sediment (absolute concentration = ac) :

C_t (%) = 4 x {(A-B) /A} x {(100/(100 + ac)

Appendix P : Procedures of suspended solids measurement can be described as follows:

- ***Procedures :***

  - 100 ml of water sample was filtered
  - filtered sample was removed from the membrane filter funnel assembly, and transfered to preweighed porcelaine disk
  - this porcelaine disk was put on the oven for 103 - 105 °C drying procedure until a constant weight
  - sample were cooled in the desiccator, and weighed

- ***Calculation*** :

$$\text{mg/l total nonfiltrable residue} = \frac{(A-B) \times 1{,}000}{\text{ml sample}}$$

Total Suspended Solid is expressed as milligrams per litre on a dry-mass basis.

Appendix Q : Procedure on determination of insoluble residue (IR)

The filtered samples that contains the alumiosilicate fraction of the sedimens were run for insoluble residue. The IR have to be weighed and substracted it from the original weigh .These were done as follows :

1. Vitrocel crucibles were cleaned
2. The muffle furnace was set to 500 C and allow it to heat up to this temperature.
3. Before "cooking " the crucibles, each one was identified by some mark or number that is on them.

4. The vitrocel crucibles were placed in the oven for 1 h to oxidize grease, finger prints and to drive off water vapour. The crucibles were removed using the tongs, to an asbestos pad beside the oven and allow the crucibles to cool a little.
5. The crucibles were weighed to 4 figures.
6. A filter paper were placed with I.R. into each crucible, then put the crucibles back into the oven at 500 c for 1 hour.
7. Re-weigh each crucible and record in lab book
8. The weight of the I.R. will be the weight of the crucible and I.R. (weight from #7) minus the weight of the crucible alone (weight #5)

Appendix R : Heavy metals (in water column) analysis

Atomic Absorption flame emission spectrophotometer was applied to measure the concentration of Cu, Cr, Cd, and Pb in the Banjir Kanal Barat and Babon Rivers water. Principally, 100 ml of water samples were transfered into 250 ml beaker, and treated with 1 ml of HCl concentrate + 4 ml of HNO_3 concentrate. This solution was diluted with 100 ml H_2O and heated until it evaporate (10 - 15 ml of solution was left). After dilution with 200 ml of H_2O, this solution is ready for AAS spectropothometer (Shimadzu AA-630-12). Recalibration using standard before each run is required.