ESTIMATION OF BIOAVAILABLE HEAVY METALS IN WATER ENVIRONMENTS IN BANGKOK NEIGHBORHOOD

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การประเมินโลหะหนักที่มีผลต่อสิ่งมีชีวิตในแหล่งน้ำตามธรรมชาติหรือแหล่งน้ำบริเวณใกล้เคียงกับกรุงเทพมหานคร

นางสาว พิมลพรรณ หาญศึก

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ดร.เยน เยน อัง, 108 หน้า.

เนื่องจากอนินทรีย์โลหะหนักในแหล่งน้ำตามธรรมชาติมีบางส่วนที่เป็นเลบาย(เลบายคือส่วนหนึ่งที่มีขนาดเล็กของอนินทรีย์โลหะหนักและสามารถที่จะผ่านเข้าสู่สิ่งมีชีวิตได้ง่ายและส่งผลกระทบต่อสิ่งมีชีวิต) ดังนั้นงานวิจัยนี้จึงทำการศึกษาอนินทรีย์โลหะหนัก5ชนิดดังต่อไปนี้ นิเกิล คอปเปอร์ ซิงค์ แคดเมียม และ ตะกั่ว ทั้งในแหล่งน้ำเจ้าพระยาซึ่งทำการเก็บตัวอย่างจำนวน 1 ครั้ง จากปากแม่น้ำเป็นระยะทาง29-83กิโลเมตร และแหล่งน้ำโดยรอบเขตนิคมอุตสาหกรรม จำนวน 3ครั้ง ทั้งหมด10 จุดเก็บตัวอย่าง ได้แก่ 1.น้ำดิบจากแม่น้ำเจ้าพระยาสำหรับใช้ในโรงงาน 2.น้ำที่บำบัดแล้วใช้แจกจ่ายในเขตนิคมอุตสาหกรรม 3.น้ำใต้ดินในเขตชุมชนที่อยู่รอบนอกนิคมอุตสาหกรรม 4.น้ำเสียเข้าสู่ระบบ 5.น้ำเสียที่บำบัดแล้วจากระบบบำบัดน้ำเสีย 6.บ่อผึ่งที่รองรับน้ำที่ออกจากระบบบำบัดน้ำเสีย 7.คลองซึ่งรองรับน้ำที่ออกจากระบบบำบัดน้ำเสีย 3จุด และ 8.บึงขนาดใหญ่ภายในเขตนิคมอุตสาหกรรม จากนั้นจะใช้โปรแกรมวิสชัวมินเทกคำนวนหาค่าความเข้มข้นของธาตุอนินทรีย์โลหะหนัก พบว่าค่าเฉลี่ยความเข้มข้นของธาตุอนินทรีย์โลหะหนัก นิเกิล คอปเปอร์ ซิงค์ แคดเมียม และตะกั่วในแหล่งน้ำเจ้าพระยาเท่ากับ 71.8± 12.1 ไมโครกรัม/ลิตร, 3.38± 7.02 ไมโครกรัม/ลิตร, 75.8± 61.6 ไมโครกรัม/ลิตร , 7.18± 1.86 ไมโครกรัม/ลิตร, 6.71 ±6.14 ไมโครกรัม/ลิตร ซึ่งคิดเป็น 96± 1.8 %, 7.3±14 % (เมื่อไม่ได้นำค่า 1.3±0.87 %มาคำนวณ), 99±0.64 %, 74 ± 9% and 3.8 ± 2.5 % ของค่าความเข้มข้นธาตุโลหะหนักที่ละลายได้ตามลำดับ ผลการวิเคราะห์ในจุดเก็บตัวอย่างทั้ง10จุดพบว่า 1.น้ำที่บำบัดแล้วจะมีค่าความเข้มข้นของธาตุโลหะหนักที่ละลายได้บางตัวในระดับที่สูง เนื่องมาจากการลดลงของค่าพีเอชในระหว่างกระบวนการบำบัดน้ำเสียของโรงงาน 2.ค่าความเข้มข้นของธาตุโลหะหนักที่ละลายได้ในน้ำเสียมีความแตกต่างกันไม่มาก ระหว่างน้ำเสียที่ถูกบำบัดแล้วหลังจากกระบวนการแอคติเวตเตดสลัดจ์และบ่อผึ่งที่รองรับน้ำที่ออกจากระบบบำบัดน้ำเสีย ซึ่งมีความสอดคล้องกับงานวิจัยที่ผ่านมา 3.น้ำใต้ดินที่ใกล้เขตนิคมอุตสาหกรรม โดยปกติจะแสดงค่าความเข้มข้นของธาตุโลหะหนักที่ละลายได้ในระดับที่ต่ำ แต่กลับพบว่าซิงค์และแคดเมียมมีค่าความเข้มข้นของธาตุโลหะหนักที่ละลายได้ในระดับที่สูง แตกต่างกันในแต่ละครั้งของการเก็บตัวอย่าง 4.คลองซึ่งรองรับน้ำที่ออกจากระบบบำบัดน้ำเสียแสดงค่าความเข้มข้นของธาตุโลหะหนักที่ละลายได้ในบางระดับและแตกต่างกันไม่มากเมื่อเทียบกับบึงขนาดใหญ่ภายในเขตนิคมอุตสาหกรรมรวมถึงค่าพีเอชและเปอร์เซ็นต์เลบายในบางกรณีด้วย ซึ่งอาจชี้ให้เห็นว่ามีแหล่งกำเนิดของธาตุโลหะหนักที่แตกต่างกัน ในการประเมินความเข้มข้นของเลบายด้วยโปรแกรมวิชชัวมินเทกเมื่อเปรียบเทียบกับการประเมินความเข้มข้นของเลบายด้วยเครื่องมือเอมพอลพบว่ามีความแตกต่างกันในบางเหตุผล เช่น โลหะหนักบางชนิดมีค่าเลบายที่สูงหรือต่ำแตกต่างกันไป

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The concentrations of dissolved metals in the Chao Phraya River in the stretch between 83 and 29 km away from the river mouth, and some water environment around an industrial estate situated in Bangkok suburb were measured and labile species, self-defined as unbalanced inorganic species were calculated using Visual MINTEQ Ver. 3. The Chao Phraya River sampling was carried out one time, and three time samplings were carried out for the industrial estate. The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in 5 samples collected from the Chao Phraya River in the stretch between 83 and 29 km away from the river mouth were, 71.8± 12.1µg/L, 3.38± 7.02µg/L, 75.8± 61.6µg/L, 7.18± 1.86µg/L, 6.71 ±6.14µg/L, which constitutes 96± 1.8 %, 7.3±14 %(when a value of a site was exclude, 1.3±0.87 %), 99±0.64 %,74 ± 9% and 3.8 ± 2.5 % of the dissolved metals, respectively, are found to be labile. The water environments around the industrial estate included raw water from the Chao Phraya River for uses in the estate, treated water for distribution in estate, groundwater in community outside the industrial estate, influent to WWTP (combined from industries and domestic sources within the estate), treated wastewater effluent from WWTP, polishing pond effluent of WWTP, effluent-receiving canal water at 3 points, and the lake water within the industrial estate zone. The dissolved concentrations of Ni, Cu, Cd, Zn and Pb varied from ND to a few hundreds ug/L. Remarkable findings in industrial estate samples are as follows: Treated water showed higher dissolved concentrations of some metals due to decrease in pH during treatment facilities, dissolved concentrations of metals in treated wastewater after activated sludge process and polishing pond treatment did not seem to differ much with those of influent stream which flowed into WWTP, which is in accordance with the previous studies, Groundwater near the estate normally showed low dissolved metals; high Zn and Cd were found in different sampling though,The canal water that received WWTP's effluent showed some level of dissolved metals; the lake inside the estate compound showed a bit different metals levels, pH and % labilities in some cases, indicating that the source of metals might be different, Zinc showed highest labilities in all samples, which indicated that the environmental settings in all sites favored forming inorganic species. Lowest labilities were found in Cu and Pb, uniformed and moderately high labilities are found in Ni despite difference in sampling sites, and labilities of Cd varied to an extent. The estimated labile concentrations were compared with those measured using a speciation device called Empore$^{TM.}$ The results were found to be different for some reasons.

Field of Study: Environmental Management Student's Signature:.................................
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LIST OF ABBREVIATIONS

˚C	degree Celsius
µ	micron
Ag	Silver
Al^{+3}	Aluminum (III) ion
As	Arsenic
Ca	Calcium
Ca^{2+}	Calcium ion
Cd	Cadmium
cm	centimeter
Co	Cobalt
Cr	Chromium
Cr^{6+}	Chromium (VI) ion
Cu	Copper
Cu^{2+}	Copper (II) ion
$CuSO_4$	Copper sulfate
$Cu(OH)_2$	Copper hydroxide
DI	deionized
Fe^{2+}	Iron ion
Fig.	Figure
g	gram
Ga	Gallium
H^+	Hydrogen ion
HCl	Hydrochloric acid
Hg	Mercury
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
L	liter
Kg	kilogram
Mg	milligram

Mg^{2+}	Magnesium ion
min	minute
mol	mole
Mn	Manganese
MW	molecular weigh
N_2	Nitrogen
Na	Sodium
Na^{+}	Sodium ion
NaOH	Sodium hydroxide
NH_2	Amine group
NH_3^{+}	Ammonium
Ni	Nickel
nm	nanometer
m	mass
Pb	lead
R^2	correlation coefficient
Si^{4+}	Silicon ion
SiO_4	Silicon tetra oxide
USA	United States of America
Zn	Zinc
Zn^{2+}	Zinc (II) ion

CHAPTER I

INTRODUCTION

1.1 Introduction

The Chao Phraya River, the most important waterway for the people of central Thailand, is a source of water for domestic use, agriculture, industry, electricity generation, navigation and leisure activity. The Chao Phraya River Basin covers approximately 35% of Thailand's land mass, is home to 40% of the country's population, employs 78% of its work force, and generates 66% of its Gross Domestic Product (GDP). The total population of the Chao Phraya basin was 23.0 million inhabitants in 1996 (UNESCO report 1).

A study by Thailand Environmental Institute for the pollution Control Department of the Ministry of Science, Technology and the Environment in 1997 reviewed the water quality data for the Central River Basin, which had been routinely monitored by the National Environmental Board (NEB), the pollution control Department (PCD) and the Ministry of Public Health (MOPH) they found that the Chao Phraya River have the big problem of organic and bacterial pollution that might be affect to many species of aquatic life. Furthermore, water pollution is caused by the discharge of agricultural wastes (pesticides, fertilizers, poultry/piggery farm effluent.), sewer outlets and industries. It has an adverse impact on domestic uses along waterways, on human health, aquatic fauna, flora and on several agricultural activities. Organic load, with subsequent low levels of dissolved oxygen in the water is mostly caused by domestic waste and by wastewater discharged from prawn, duck and pig farm (UNESCO report2). A monitoring of three indicators, biochemical oxygen demand (BOD), dissolved oxygen (DO) and total coliform bacteria (TCB), revealed that the water quality of Chao Praya river has decreased severely, its mean that DO, BOD and TCB values did not meet the standard of water quality of Thailand (Haapala, 2002) especially at the lower part of the river. Moreover, there are many studies on the water quality of the main rivers in Thailand, such as Chao Praya, Tha Chin, Bang Prakong and Mae Klong River (Simachaya, et al., 2000). Three independent estimates of hazardous waste production in Thailand were carried out in the 1980s (CIDA 1984; ADB 1987; US TDP 1988) from Lohwongwatana et al., 1990.

The most hazardous among the process of the chemical industries for example Cd, Cr, Cu, Ni, As, Pb and Zn, are discharged in to the environmental water which the discharge of large amounts of metal-contaminated wastewater. In Thailand, the Ministry of Industry (MOI), through its Industrial Works Department (IWD) has been engaged in activities for the control of industrial pollution for almost two decades (Lohwongwatana et al., 1990). Although the IWD has succeeded in controlling industrial pollutant discharges especially from medium and large-scale factories, the treatment is limited to organic wastewaters and some toxic wastes, preventing the dumping of hazardous sludge or solid wastes on land or in insecure dumping sites (Lohwongwatana et al., 1990). In addition, a number of small electroplating factories which are scattered in commercial or residential areas, do not have enough knowledge to operate their treatment plants properly and many of their solid residues containing toxic wastes are disposed of along with household refuse or without proper disposal facilities (Lohwongwatana et al., 1990). As a result, hazardous pollutants are being accumulated in our environment and are being concentrated in fish and aquatic plants to the extent that these may become dangerous for human consumption (Lohwongwatana et al., 1990). Heavy metals can be absorbed by living organisms (Barakat, 2010). Heavy metal contamination in the Chao Phraya River has been studied long time ago. Polprasart (1979) reported the metal contamination in river water and sediment, while Hungspreugs and Yuangtong (1983) reported the metal pollution in the upper gulf of Thailand closed to the Chao Phraya River. Kunachava et al. (2009) determined the perfluorinate compounds (PFCs), Sirivithayapakorn et al. (2010) determined the phthalate esters and Kruawal et al. (2005) quantified heavy metals, surfactants, pesticides, disinfection by products and volatile organic carbons (VOCs).

The industries are known polluters of water environment. There are 30 industrial estates in Thailand and each is equipped with a Central Effluent Treatment Plant (CETP) (Visvanathan and Shapkota, 2005). The total effluent treatment capacity is more than 300,000m^3/day in addition to individual treatment units of some of the industries (Visvanathan and Shapkota, 2005). The number of factories in existence in Thailand was about 100,000 in 1988 (Lohwongwatana et al., 1990). There are 83 wastewater treatment plants (WWTP) in Thailand with a total capacity of treating 2.84 million m^3 of wastewater per day (UNEP, 2001).

Water pollution problems for industry have been considerably reduced, especially from those discharging wastewater containing significant BOD loads (Lohwongwatana et al., 1990). There are still some small scale backyard family-type industries located amongst commercial or residential areas which do not regularly operate treatment plants, and there is still no municipal sewage treatment facility (Lohwongwatana et al., 1990). As a result, two major rivers, the Chao Phraya and the Thachin are badly polluted with a very low level of dissolved oxygen concentration (DO=1.0 mg/l or less) (Lohwongwatana et al., 1990). During last three decades, the assumptions that metal bioavailability - the portion of the total amount of metal that is available for assimilation into biota - is greatly affected by species distribution and that it is the labile metals species rather than the total metal concentrations, that play role in ecotoxicity, have grown (Sunda and Grillard, 1976). Metals in the aquatic environment are distributed as simple inorganic complexes, complexes with organic matter, and metals adsorbed onto suspended matter and particulate bound; among many reactions of metals, free ions are known to be the most toxic (Sunda and Grillard, 1976; Florence and Batley, 1980; Buffle, 1981; Gavis, 1983; Florence, 1983).

There are a lot of methods to predict bioavailable portion of metals. Labile metals will be analyzed off-site using solid phase extraction (SPE) cartridges, which extract the metals labile enough to dissociate while passing the chelate disc in the catridge are trapped, eluted and analyzed. The dialysis membrane/bag/tubing that mimic the cell membrane, which count metals that diffuse passing through it are taken as labile, thus, bioavailable, are also widely applied for metals species studied (Morrison, 1987). In addition, on-site measurement devices such as diffusive gradient in thin films (DGT) count the time average metal fluxes that diffuse into the filter membrane within a know period of time, are widely applied for assessing heavy metal species in surface water (Buzier et al., 2008; Davidson and Zhang, 1994; Aung et al., 2008). Moreover, equilibrium models such as Windermere Humic Aqueous Model (WHAM), MINEQUL and MINTEQ that predict the metal species in surface water are often used (Butler et al., 2008). Electrochemical analysis, such as stripping voltammetry techniques, is also widely being used for determination of labile metal concentration (Chaminda et al., 2008), while Drora (1987) measured the concentrations and distribution of free and bound zinc, cadmium, lead and copper of a treatment plant by Anodic Stripping Voltammetry (ASV).

Determining metal species in grab samples is a difficult task to perform because sampling schemes followed storage of water may alter the species distribution because of contamination, aggregation, and oxidation of metals, even in the short period of time spend in transport and storage (Laxen and Chandler, 1982; Tercier and Buffle, 1993; Buffle and Leppard, 1995). Rigorous samples handling and storage protocols could rarely be free from artifacts of sampling.

This study focused on the heavy metals viz., Ni, Cu, Cd, Zn and Pb, in samples collected in the downstream of Chao Phraya River (Excluding the seawater intruded river mouth) and 10 sites of surface waters around an industrial estate zone in Bangkok Neighborhood; these were raw water for the water treatment plant from Chao Phraya River; treated water by water treatment plant (Tap water); ground water (from the school near by community); influent to the wastewater treatment plant; treated effluent before the polishing pond; effluent water after the polishing pond, point; mixing point at the canal; canal water after the discharging (downstream); and the lake water beside the industrial zone and canal water after the discharge (downstream). The labile metal fraction were predicted using the surface water speciation model called Vistual MINTEQ. The predicted results were validated using Empore^{TM} SPE disk. In Thailand, like all the regulations among the nations around the world, the current regulations on heavy metal in water environment were focused on total metal concentrations. However, in the near future the integrated water management may likely to be incorporate the information on metal bioavailability; the current study would serve as a preparatory step for it.

1.2 Objectives

The objective of this study was to estimate the amount of labile species, which were assumed as bioavailable due to their small size, the ability to dissociate easily and high mobility, in several water environments around Bangkok neighborhood using a speciation device and an equilibrium model.

1.3 Hypothesis

1. The labile concentrations, a fraction of the total dissolved concentrations of the selected set of surface waters may differ from one metal to another depending on the water quality and the important environmental parameters such as dissolved organic matter, major cations and anions.
2. Although equilibrium models were designed for natural surface waters, they can also were applied for other surface waters such as wastewater treatment plant (WWTP) effluent receiving waters.

1.4 Scopes of the Study

1. This research was focused on the heavy metals viz., Ni, Cu, Zn, Cd and Pb collected in the downstream of Chao Phraya River, within Bangkok Metropolitan area (excluding the seawater intruded river mouth) and surface water environments around an industrial estate viz., raw water intake from Chao Phraya river before water treatment, treated river water for industrial use, influent to wastewater treatment plant, treated effluent of wastewater treatment plant, polishing pond effluent wastewater treatment plant, effluent recipient canal at mixing point with effluent discharge, downstream, further downstream and groundwater nearby village.
2. The sampling frequency of Chao Phraya River was one time sampling in dry season and the surface water environments around an industrial estate were three time sampling in, September, October and November, 2010, respectively.

3. The analyses of water samples were done after filtration with 0.45µm pore size PTFE membrane filter to separate suspended particles.
4. Major Cations (Ag, Al, B, Ba, Bi, Ca, Co, Cr, Fe, In, K, Li, Mg, Mn, Na, Si, Sr, Tl) including heavy metals of interest (Ni, Cu, Cd, Pb, Zn) were analyzed using by Inductively Coupled Plasma Optical Emission Spectrometer (ICPOES), major anions (F, Cl, NO_2, Br, NO_3, PO_4, SO_4) were measured using Ion Chromatography analyzer, total organic carbon (TOC) was measured using TOC analyzer.
5. The metal species were predicted using the equilibrium model called Vistual MINTEQ.
6. The predicted results were validated using Empore ^{TM} chelating disk.
7. Statistical analysis was done by SPSS program.

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Background

2.1.1 Ecotoxicity of Heavy metals

Pollution caused by heavy metals is now a worldwide phenomenon. Among the many heavy metals, lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), and copper (Cu) are of most concern. The last three metals are essential trace metals in animal and human nutrition, however they are toxic at high doses, while some heavy metals such as Cd and Pb that can be toxic even at trace levels. In addition, heavy metals can be very toxic in form of ion or charged species forms because they are soluble in water and may be readily absorbed enter living organisms such as cell copper content and copper induced growth rate inhibition to phytoplankton and it can be toxic to at least some species of planktonic algae at concentration as low concentrations as e.g. 1 ppb. (Davey, 1973) (Sunda and Grillard, 1976 and Steemaun Nielsen and Wium-Anderson, 1970). After absorption, these metals can bind to cellular components for example structural proteins, enzymes, and nucleic acids, and obstruct with their functioning. Heavy metals are known to be persistent (non-biodegradable) and bio-cumulative pollutants. In humans, some of these metals, even in small amounts, can cause severe physiological and health effects (Wayne and Ming-Ho, 2004). Metals in the aquatic environment are distributed as simple inorganic complexes, complexes with organic matter, and metals adsorbed onto suspended matter and particulate bound; among them, free ions are known to be the most toxic (Sunda and Grillard, 1976; Florence and Batley, 1980; Buffle, 1981; Gavis, 1983; Florence, 1983). Table 2.1 shows the maximum contaminant level (MCL) standards for the most hazardous heavy metals established by USEPA.

Table 2.1 The maximum contaminant level (MCL) standards for the most hazardous heavy metals established by USEPA (Babel and Kurniawan, 2003)

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

This included limits on the types and concentration of heavy metals that may was presented in the discharged wastewater industrial (Barakat, 2010).

2.1.2 Ni

At temperature between 18 and 25˚C, solubilities of nickel compound were less than 1 g/l for nickel hydroxide, nickel mono sulfide, and nickel oxide; 1 to 100 g/l for nickel chloride, nickel nitrate, and nickel sulphate (U.S. EPA, 1980). Highly toxic nickel carbonyl is soluble in water to the extent of less than 1 g/l at 9.8˚C (International Agency for Research on Cancer (IARC, 1976). Nickel is most likely to occur in natural waters as a divalent cation and has geochemical behavior similar to that of cobalt (U.S. EPA, 1980). Nickel is probably strongly sorbed to iron and manganese oxides (Hem, 1975), although nickel oxides, hydroxides and carbonates are probably common in natural water, especially those of high pH (U.S. EPA, 1980). For total recoverable nickel the criterion (in µg/l) to protect freshwater aquatic life as derived using the Guideline is the numerical value given by $e^{(0.76[\ln\ (\text{hardness})]+1.06)}$ as a-24 average, and the concentration (in ug/l) should not exceed the numerical value given by $e^{(0.76[\ln\ (\text{hardness})]+4.02)}$ at any time. For example, at hardnesses of 50, 100, and 200 mg/l as $CaCO_3$ the criteria are 59, 96 and 160 ug/l, respectively, as 24-hour averages, and the concentration should not exceed 1100, 1800 and 3100 ug/l, respectively any time. For total recoverable nickel the criterion to protect salt water aquatic life as derived using the Guideline is 7.1µg/l as 24-hour average, and the concentration should not exceed 140µg/l at any time (U.S. EPA, 1980). For the protection of human health from the toxic properties of nickel ingested through water and contaminated aquatic organisms, the ambient water criterion is determined to be 13.4µg/l (U.S. EPA, 1980). For the protection of human health from the toxic properties of nickel ingested through contaminated aquatic organisms alone, the ambient water criterion is determined to be 100µg/l (U.S. EPA, 1980).

2.1.3 Cu

Copper is moderately soluble in water and binds easily to sediments and organic matter (U.S. EPA, 2007). The most bioavailable and therefore must toxic form of copper is the cupric ion (Cu^{2+}) (U.S. EPA, 2007). Copper is a micronutrient for both plants and animals at low concentrations and is recognized as essential to all plants and animals (Kapustka et al., 2004). Fish and crustaceans are 10 to 100 times more sensitive to the toxic effects of copper than are mammals. Algae, especially blue-green algae species, are 1,000 times more sensitive to the toxic effects of copper than are mammals, as several researchers, including Forstner and Wittman (1979), Hodson (1979) and Wright and Welbourn (2002), have demonstrated. This is an exception to the general principle that aquatic animals are more sensitive than aquatic plants to the toxic effect of metals (Frances, 2009). Naturally occurring concentrations of copper have been reported from 0.03 to 0.23:g/L in surface seawaters and from 0.20 to 30:g/L in freshwater systems (Bowen, 1985). Copper concentrations in locations receiving anthropogenic inputs can vary anywhere from levels that approach natural background to 100:g/L or more (e.g., Lopez and Lee, 1977; Nriagu, 1979; Hem, 1989) and have in some cases been reported in the 200,000:g/L range in mining areas (Davis and Ashenberg, 1989; Robins et al., 1997). The toxicity of a chemical to an aquatic organism requires the transfer of the chemical from the external environment to biochemical receptors on or in the organism at which the toxic effects are elicited. Often, this transfer is not simply proportional to the total chemical concentration in the environment, but varies according to attributes of the organism, chemical, and exposure environment so that the chemical is more or less "bioavailable" (U.S. EPA, 2007). Definitions of bioavailability vary markedly (e.g., National Research Council, 2003) and are often specific to certain situations, but a useful generic definition is the relative facility with which a chemical is transferred from the environment to a specified location in an organism of interest. Copper toxicity has been reported to vary markedly due to various physicochemical characteristics of the exposure water (e.g., either laboratory or field), including temperature, dissolved organic compounds, suspended particles, pH, and various inorganic cations and anions, including those composing hardness and alkalinity (see reviews by Sprague, 1968; Hunt, 1987; Campbell, 1995; Allen and Hansen, 1996; Paquin et al., 2002). Many of these physicochemical factors affect copper speciation, and their effects on copper toxicity therefore could be due to effects on copper bioavailability (U.S. EPA, 2007). That bioavailability is an important factor is evident from uptake of copper by aquatic organisms being reduced by various organic compounds and inorganic ligands known to complex copper (Muramoto, 1980; Buckley et al., 1984; Playle et al., 1993 a,b; MacRae et al., 1999). The effects of physicochemical factors on copper toxicity are diverse and the specific chemistry of the exposure water will determine whether or not there are appreciable effects on copper speciation and a resulting strong relationship of toxicity to free copper (U.S. EPA, 2007). Usually copper toxicity is reduced by increased water hardness (reviews by Sprague, 1968; Hunt, 1987; Campbell, 1995; Allen and Hansen, 1996; Paquin et al., 2002), which is composed of cations (primarily calcium and magnesium) that do not directly interact with copper in solution so as to reduce bioavailability (U.S. EPA, 2007).

2.1.4 Cd

Cadmium is toxic to aquatic life at concentrations only slightly higher (U.S. EPA, 2001). It occurs mainly as a component of mineral in the earth's crust at an average concentration of 0.18 ppm (Babich and Stotzky, 1978). In the natural freshwaters, cadmium sometime occurs at concentrations of less than 0.1µg/L, but environments impacts by man, concentrations can be several microorganisms per liter or greater (Abbasi and Soni, 1986; Allen, 1994; Annune et al., 1994; Flick et al., 1971; Friberg et al., 1971; Henriksen and Wright, 1978; Nilsson, 1970 and Spry and Wiener, 1991). Cadmium can enter the environment from various anthropogenic sources, such as by-products from zinc refining, coal combustion, mine waste, electroplating processes, ion and steel production, pigments, fertilizers and pesticides (Hutton, 1983; Pickering and Gast, 1972). The impact of cadmium on aquatic organisms depends on variety of possible chemical forms of cadmium (Callahan et al., 1979). Fresh and salt waters, particulate matter and dissolved organic material may bind a substantial portion of the cadmium, and under these conditions cadmium may not be available due to this binding (Callahan et al., 1979 and Kramer et al., 1997). Because of the variety of cadmium (Callahan et al., 1979) and lack of definitive information about their relative toxicities, no available analytical measurement is known to be ideal for expessing aquatic life criteria for cadmium (U.S. EPA, 2001). Previous aquatic life criteria for cadmium (U.S. EPA, 1980) were expressed in term of total recoverable cadmium (U.S. EPA, 1983a), but this measurement is probably too rigorous in some situations (U.S. EPA, 1985) has also expressed cadmium criteria as acid-soluble cadmium in the past, but now recommends use of dissolved metal concentrations (operationally defined as the metal in solution that passes through a 0.45μm membrane filter) to set and measure compliance with water quality standards (Prothro, 1993; U.S. EPA 1993, 1994a). Whenever appropriate, a national criterion may be replaced by a site specific criterion (U.S. EPA, 1994a), which may include not only site-specific criterion concentrations (U.S. EPA, 1994b), but also site-specific durations of averaging periods and site specific frequencies of allowed exceedences (U.S. EPA, 1991). Hardness of water quality parameters is often thought of as having a major effect on the toxicity of cadmium, although the observed effect may be due to one or more of a number of usually interrelate ions, such as hydroxide, carbonate, calcium, and magnesium. Development of the "biotic ligand model" (BLM- formerly the "gill model") in recent years has attempted to better account for the bioavailability of metals to aquatic life (U.S. EPA, 2001).

2.1.5 Zn

Zinc is a bluish-white metal which dissolves readily in strong acids (U.S. EPA, 1980). Its principal uses include electroplating and the production of alloys (U.S. EPA, 1980). Zinc is never found free in nature, but occurs as the sulfide, oxide, or carbonate (U.S. EPA, 1980). Compounds of zinc with the common ligands of surface waters are soluble in neutral and acidic solutions, so that zinc is readily transported in most natural waters and is one of the most mobile of the heavy metals (U.S. EPA, 1980). Zinc forms complexes with a variety of organic and inorganic ligands, but these compounds are sufficiently soluble to prevent their becoming a limiting factor for the solubility of the small concentrations of zinc found in most aquatic environments (U.S. EPA, 1980). Most of the zinc introduced into the aquatic environment is partitioned into the sediments by sorption, precipitation and formation (U.S. EPA, 1980). For total recoverable zinc the criterion to protect freshwater aquatic life as derived using the Guidelines is 47μg/l as a 24-hour average (U.S. EPA, 1980). For total recoverable zinc the criterion to protect saltwater aquatic life as derived using the Guidelines is 58μg/l as a 24-hour average and the concentration should not exceed 170μg/l at any time (U.S. EPA, 1980). Using available organoleptic data, for controlling undesirable taste and odor quality of ambient water, the estimated level is 5 mg/l. (U.S. EPA, 1980). It should be recognized that organoleptic data as a basis for establishing a water quality criteria have limitations and have no demonstrated relationship to potential adverse human health effects (U.S. EPA, 1980).

2.1.6 Pb

Lead is used in electroplating, metallurgy, and the manufacture of construction materials, radiation protective devices, plastics, and electronics equipment (U.S. EPA, 1980). Although neither metallic lead nor the common lead minerals are classified as soluble in water, they can both be solubilized by some acids; in contrast, some of the lead compounds produced industrially are considered water soluble (U.S. EPA, 1980). Natural lead compounds are not usually mobile in normal ground or surface water because the lead leached from ores becomes adsorbed by ferric hydroxide or tends to combine with carbonate or sulfate ions to form insoluble compounds (Hem, 1976). The solubility of lead compounds in water depends heavily on pH and ranges from about 10,000,000μg/l of lead at pH 5.5 to 1μg/l at pH 9.0 (Hem and Durum, 1973). Lead does reach the aquatic environment through precipitation, fallout of lead dust, street runoff, and both industrial and municipal wastewater discharges (U.S. EPA, 1976). Inorganic lead compounds are most stable in the plus two valence state, while organolead compounds are more stable in the plus four states (Standen, 1967). The available data for total recoverable lead indicate that acute and chronic toxicity to saltwater aquatic life occur at concentrations as low as 668 and 25 μg/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested. The ambient water quality criterion for lead is recommended to be identical to the existing water standard which is 50μg/l (U.S. EPA, 1980).

2.2 Water Quality Standards in surface water and Industrial Effluent Standard in Thailand

Water Quality Standards in the surface water and Industrial Effluent Standard in Thailand title are as follows:

Table 2.2 Surface Water Quality Standard in Thailand (Adapted from PCD-Thailand, 2535)

Surface Water Quality Standard		
Heavy Metals Parameters	**Units**	**Standard Values**
Zinc (Zn)	mg/l	1.0
Cadmium (Cd)	mg/l	0.005* 0.05**
Chromium Hexavalent	mg/l	0.05
Lead (Pb)	mg/l	0.05
Total Mercury (Total Hg)	mg/l	0.002
Arsenic (As)	mg/l	0.01
Cupper (Cu)	mg/l	0.1
Nickle (Ni)	mg/l	0.1

*when water hardness not more than 100 mg/l as CaCO3
**when water hardness more than 100 mg/l

Table 2.3 Industrial Effluent Standard in Thailand (Adapted from PCD-Thailand, 2535)

Industrial Effluent Standards		
Heavy Metals Parameters	**Units**	**Standard Values**
1. Zinc (Zn)	mg/l	5.0
2. Chromium (Hexavalent)	mg/l	0.25
3. Chromium (Trivalent)	mg/l	0.75
4. Copper (Cu)	mg/l	2.0
5. Cadmium (Cd)	mg/l	0.03
6. Barium (Ba)	mg/l	1.0
7. Lead (Pb)	mg/l	0.2
8. Nickel (Ni)	mg/l	1.0
9. Manganese (Mn)	mg/l	5.0
10. Arsenic (As)	mg/l	0.25

2.3 Chao Phraya River

Chao Phraya River is the water source that originated in the mountainous region of northern of the country. There are four major rivers namely, the Ping, Wang, Yom, and Nan Rivers. The four upstream minor flow southward to meet at Nakhon Sawan and form to the Chao Phraya River. The river flows southward through a large alluvial plain, called the delta area, splitting in to four chanels: the Tha Chin, the Noi, the lop Buri, and the Chao Phraya Rivers (UNESCO report2)

The Chao Phraya River drains an area of about 177000 km^2, including Bangkok (the most heavily populated and industrialized city in Thailand). Flow rates average greater than 1000 m^3 s^{-1}, High flows (>3000m^3/s) occur from August to October. Low flows (about 100 m^3/s) from January to May are accompanied by a distinct salt water intrusion (salinity > 0.1%) extending up to 44 km. inland (Hungspreugs et al., 1989). Figure 2.1 shows the the basin map of Chao Phraya River in Thailand (AFDEC, 2002).

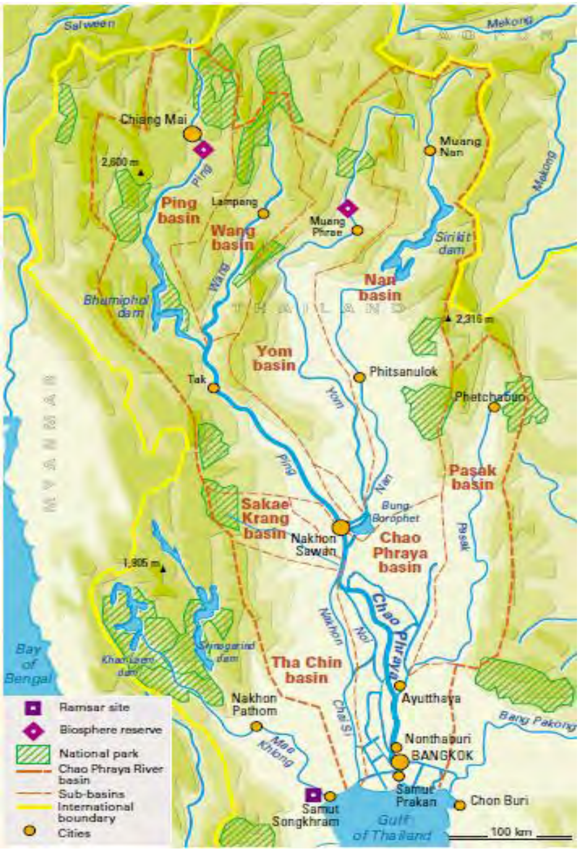

Figure 2.1 The basin map of Chao Phraya River in Thailand.

Sources: World Water Assessment Program (WWAP) by AFDEC, 2002

2.4 Industrial Estates in Bangkok Neighborhood

Industrial Estate Authority of Thailand (2009) reported water consumption of industrial estate around the country, an aggregate of 550,000 cubic meters. of water was consumed a day: 11% was the pipeline water, distributed by the Metropolitan Water Authority and the Provincial Water Authority while 1% was the underground water and another 88% was raw water. Figure 2.2 shows cluster of industrial estates in Ayutthaya area. (NECTEC)

Figure 2.2 Cluster of industrial estates in Ayutthaya area

Sources: NECTEC

We selected an industrial estate in Bangkok neighborhood as a study site. This industrial estate has electronic factories, food processing factories, garment factories and so on in the area around 75 rai. The plant has been operating since 1989 with activated sludge and combine sewer system. The catchment area is about 1900rai which that surrounding canals. The capacity of the plant is 18,000m^3/day. The wastewater was released in to the main drainage system, not exceed a BOD factor of 500 mg/l.

The Industrial Estate Authority of Thailand sold some water in industrial estates an average of 270,000 cm. a day. The loss of water was approximately at 2%. About 43,000 cm. of wastewater flew into the central wastewater treatment a day (Source: Annual Report of I-EA-T, 2009). Fig 2.3 shows the water consumption by industrial estate around the country, Thailand (I-EA-T, 2009).

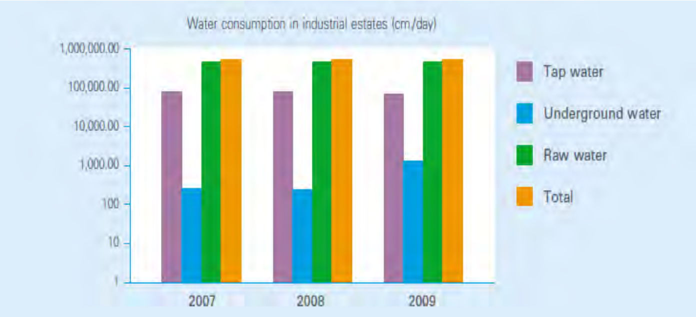

Figure 2.3 Water consumption by industrial estate around the country, Thailand

Source: Annual Report of Industrial Estate Authority of Thailand (I-EA-T), 2009

Due to the recent rapid increase of population and industrial activities, led to impact with the aquatic environment of Thailand (Hungspreugs et al., 1989 and Molle, 2002). The things that can be cause of water pollution is discharged directly or indirectly of domestic and industrial wastes from Bangkok into the river without any treatment process. Domestic sewage is estimated that responsible for over 60% of the total BOD_5 loading, with industrial effluents about 30% of total BOD_5 loading and 30% of remainder is surface and runoff. The current status of municipal wastewater facilities in Thailand from the table 2.4 is showed that the central regional has the highest of capacity which might be related with the water pollution in the Chao Phraya River. High BOD_5 values, bacterial contamination, dissolved oxygen decreasing (Onodern, 1985 and UNESCO report2) are the effect of aquatic environment that occur. Moreover, the lower of the river also show very high coliform and ammonia levels (Silpipat and Chanpongsang, 1981). Thus the Chao Phraya River was the major rivers that cause aquatic pollution (Hungspreugs et al., 1989). Table 2.4 shows status of Municipal Wastewater Facilities in Thailand.

Table 2.4 The Current Status of Municipal Wastewater Facilities in Thailand (Pollution Control Department of Thailand)

Regional/Area	Number of WWTP					Total Capacity (m^3/day)
	Constructed	Capacity (m^3/d)	Under Construction		Total WWTP	
			New	Capacity (m^3/d)		
Northern	14	200,309	3	52,600	17	252,909
Northeastern	17	302,016	2	55,550	19	357,566
Central	27	1,248600	1	24,000	29	1,797,600
Southern	13	305,300	5	94,700	18	400,000
Eastern	15	291,400	1	1,570	16	292,970
Total	**86**	**2,310,428**	**12**	**265,617**	**99**	**3,101,045**

2.5 Heavy metal species in aquatic environment

Herbert E. Allen (1980) proposed trace metals in environmental water that can be free ion and combine chemical form. Speciation of heavy metals were developed into organic and inorganic forms (Florence, T.M. and Batley, G.E., 1977). Florence (1977) has show that, in freshwaters, copper is predominately associated with organic colloidal matter, lead is divided between inorganic and organic forms, cadmium is present as the free ion, and zinc is present in both ionic and colloidal inorganic forms. Biological availability and toxicity of a trace metal, depend on its spicy forms (Barber, 1973 and Research group for atomic spectrometry, 1996). Sunda and Guillard (1976) found that, in highly chelated media of seawater, the total copper concentration is not concern about cupric ion activity. Other studied also suggest that free metal ions are the toxicant chemical species (Gachter et al., 1973; Davey et al., 1973; Davies et al., 1976; Andrew et al., 1977; Sunda et al., 1978; Anderson and Morel, 1978 and Anderson and Morel, 1978). In addition, many of researcher suggested that the more complex of metal, the lower toxic of total metal concentration (Pagenkopf et al., 1974 and Steemaun Nielsen and Wium-Anderson)

Dissolved organic matter, measured as dissolved organic carbon (DOC), is an important component of aquatic ecosystems and of the global carbon cycle (Porcal et al., 2009). That is to say, due to three decade found that DOC concentration have increased in rivers of Europe and North America (Porcal et al., 2009). DOC concentration changing is caused biological, chemical, and photochemical reaction impact (Porcal et al., 2009). For example, the interaction of trace metals with DOC may be significantly altered by climate change as organically complexed metals such as Cu, Fe and Al are released during photo-oxidation of DOC (Porcal et al., 2009).

2.6 Metal speciation

Speciation concerns the identification and quantitation of specific forms of an element (Research group for atomic spectrometry, 1996). As different forms of an element may exhibit differing toxicities and mobilities in the environment, it is clearly of importance to be able to distinguish between the individual species present in a particular sample (Research group for atomic spectrometry, 1996).

2.6.1 Equilibrium species concentration

Reaction of chemical species with waters are called hydrolysis reactions (Jensen, 2003). Figure 2.4 illustrates the complexity in aquatic system due to hydrolysis. Inputs of chemical species (from aqueous discharges, runoff, atmospheric deposition, dissolution from the atmosphere, and dissolution from sediments) react with water to form hydrolysis products (Jensen, 2003).

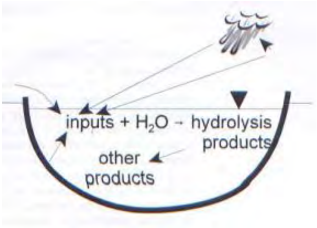

Figure 2.4 Complexity of Aquatic System

Source: A Problem- Solving Approach to Aquatic Chemistry (James, 2003)

The hydrolysis product and input chemicals react further to increase the complexity of aquatic systems (Jensen, 2003) The importance of *individual chemical species*; the concentrations of individual chemical species is important in analyzing many environment problems (Jensen, 2003). Many environmental regulations are base on total concentrations of classes of compounds rather than on the concentrations of individual species. A prime example is the transition metals (such as mercury, copper, zinc, cadmium, ion, and lead) in which toxicity varies among the hydrolysis products. Since hydrolysis product vary in their physical, chemical, and biochemical properties, the design and operation of treatment processes depend on quantitative models for the concentration of the individual species (Jensen, 2003). For example, the addition of gaseous chlorine to wastewater for disinfection result in the formation of many chemical species (including HOCl, OCl^-, NH_2Cl and $NHCl_2$), each of which differs in its ability to inactivate (i.e., kill) microorganisms (Jensen, 2003).

Individual species vary greatly in how readily they cross cell membranes or cell walls and are assimilated by aquatic biota (Jensen, 2003). Thus understanding the cycling of trace nutrients in the aquatic environment (and human kind's impact on nutrient cycling) requires knowledge of the concentrations of individual chemical species (Jensen, 2003).

As an example of the importance of the concentrations of the individual chemical species, consider the soup created when copper sulfate crystals, $CuSO_4$(s), are added to the reservoir for algae control (Jensen, 2003). The $CuSO_4$(s) dissolves in water to form a copper-containing ion (called aqua cupric ion) and sulfate (Jensen, 2003). The structure of the aquo cupric ion usually is abbreviated as number of hydrolysis products, including $CuOH^+$, $Cu(OH_2)^{2-}$ (Jensen, 2003). Under certain chemical conditions, copper may precipitate as CuO(s) As you spread the copper sulfate from the back of a boat, carbon dioxide in the atmosphere is equilibrating with the reservoir water to form its own hydrolysis products (Jensen, 2003). The hydrolysis products of carbon dioxide are H_2CO_3, HCO_3^-. The aquo cupric ion will react to some extent with the hydrolysis products of carbon dioxide to form $CuCO_3$ (aq), $Cu(CO_3)_2^{2-}$, and perhaps even solids containing copper and carbonate ($CO^{2-}{}_3$) (Jensen, 2003). By adding one copper compound to a natural water body, you may be face with accounting for as many as ten copper containing species even in a relatively simple chemical model (Jensen, 2003). The process of relating a dose to a required concentration of an individual chemical species is illustrated in Figure 2.5 (Jensen, 2003).

There are two reasons for focusing on equilibrium (Jensen, 2003). Reason is that many of the chemical reaction are fast. For example, the reaction of H^+ and OH^- to form water occurs on the time scale of 10^{-5} s at natural water conditions (Morgan and stone, 1985). Reason is that equilibrium models give insight into chemical systems, even when kinetics are known to be important (Jensen, 2003). Thus, the focus on equilibrium is somewhat constraining but not overly restrictive (Jensen, 2003).

The two most important master variable in water are pH and pe (Jensen, 2003). Water is a unique substance (Jensen, 2003). The unique properties of water stem from the large differences between the affinity of oxygen and hydrogen for electrons (Jensen, 2003). The ions form molecules (called complexes) with water (Jensen, 2003). Water is adapted at hydrating both cation and anions that water has both a partially positive pole on H and partially negative pole on O (Jensen, 2003). Water is said to be very polar, contain atoms or groups exhibiting different charges (or partial charges) (Jensen, 2003). The equilibrium concept provide an important insight of predicting speciation, fate and transport and ultimately biological effects of toxic metals and offer advantages.

2.7 Method of determining labile metal species

The development of speciation methods for separating metal fractions may provided some estimation of bioavailable species (Florence, 1983).

2.7.1 Equilibrium models

2.7.1.1 Visual MINTEQ

Visual MINTEQ version 3.0, beta version released and modified in 2010. It is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, sorption etc. for natural waters, which is originally built on USEPA's MINTEQA 2 software by Kungliga Tekniska högskolan (KTH) Royal Institue of Technology, Sweden. The entries of the equilibrium model, Vistual MINTEQ includes major cations, major anions, dissolved organic matter, pH and temperature. The inorganic species especially charged species and free ions, due to their smaller size compared to organometalic complexes, are taken as labile. Even the stable inorganic complexes, since they are in equilibrium with charged species, are readily dissociated when the free ions are uptaken by microorganism to maintain the equilibrium.

2.7.1.2 Windermere Humic Aqueous Model (WHAM)

WHAM 6 revised version was issued in 2002. It is an equilibrium chemical speciation model for natural water (Tipping and Hurley, 1992 and Tipping, 1998). It focuses on metal complexation with humic and fulvic acids in natural waters. Humic ion-binding model V is incorporated in to WHAM alongside a model for inorganic speciation (Bryan et al., 2000). Using input variables taken from simple measurements on natural water such as major cations, dissolve organic carbon (DOC), and pH., WHAM can be used to predict speciation in natural system (Bryan et al., 2000). DOC and the proportion of DOC which behave as isolated humic substance (HS) is an important input into the model (Bryan et al., 2000).

2.7.2 Voltammetry

Voltmetry is a type of electro analytical methods used in analytical chemistry and various industrial processes (Kissinger and William, 1996). In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied (Kissinger and William, 1996). Anodic stripping voltammetry is a voltammetric method for quantitative determination of specific ionic species (source: Wikipedia, the free encyclopedia 2010). Very sensitive and reproducible (RSD<5%) method for trace metal ion analysis in aqueous media (Wikipedia, the free encyclopedia 2010). The current is measured during stripping step (Wikipedia, the free encyclopedia 2010). Concentration limits of detection for many metals are in the low ppb to high pptrang (S/N=3) and this compares favorably with AAS or ICP analysis/ approximately 12-15 metal ions can be analyzed for by this method (Zoski, 2007). Voltammetry is highly suitable to distinguish the different oxidation stages of metal ions or differentiate between free and bound metal ions (Metrohm, 2010). This allows statements to be made about the biological availability and toxicity of heavy metals and makes voltammetry an essential tool for environmental analysis (Metrohm, 2010).

ASV analysis corresponds to the concentration of the metal species available to the electrode within the timescale of the electrochemical method and includes inorganic and weak organic complexes of metals (Stumm and Morgan, 1996) this fraction is usually termed electrochemically available (Lena et al., 2002). Metals are considered bioavailable if they are present as simple ions, or bound in weak or lipid soluble complexes (Morrison et al., 1989). Bioavailability is affected by complexation with humic substances (Morrison et al., 1989).

The total concentrations of the heavy metals as determined by the ASV, after digestion are present in Table 2.5 from the wastewater and effluents use for this study were taken from the the Beer Sheva, Israel, domestic wastewater treatment plant (Drora et al.,1987).

Table 2.5 Total amounts of cations in the various stages of the wastewater treatment as determined by the Anodic Stripping Voltammetry (ASV) (Drora et al.,1987)

	Concentration (µg l^{-1})							
	Zn^{2+}		**Cd^{2+}**		**Pb^{2+}**		**Cu^{2+}**	
	µg l^{-1}	**% removed**	**µg l^{-1}**	**% removed**	**µg l^{-1}**	**% removed**	**µg l^{-1}**	**% removed**
Raw sewage	224.2 (57.2)	0	2.0 (0.75)	0	53.5 (33.3)	0	34.3 (18.8)	0
Settling pond	171.6 (41.0)	24	1.9 (1.5)	5	43.0 (33.3)	20	59.7 (56.4)	
Anaerobic pond	175.4 (16.0)	22	4.3 (3.3)		38.6 (5.9)	28	29.1 (26.4)	15
Aerobic /facultative pond	203.7 (62.4)	9	2.98 (2.2)		25.3 (2.3)	53	24.1 (16.1)	30
Reservoir	130.0 (44.8)	42	1.1 (0.9)	45	31.7 (5.9)	41	24.2 15.4	30
Local tap water	92.2 (23.8)		0.3 (5)		1.3 (1.7)		6.6 (2.9)	

Values in parentheses represent standard deviation.

2.7.3 Solid phase Extraction kits

Solid-phase extraction (SPE) continues to be the leading technique for the extraction of pollutants from aquatic systems, and recent developments in this field are mainly related to the use of new sorbent materials (Soledad and Dolores, 2009). Labile metals are measured off-site using solid phase extraction (SPE) cartridges, which extract the metals labile enough to dissociate while passing the chelate disc in the cartridge are trapped, eluted and analyzed.

2.7.4 Chemcatcher passive samples

In active methods, sampling and sample preparation typically account for 70–90% of analysis time (Namiesnik et al. 2002). A water sample is widely analyzed directly on site or in the laboratory, following the correction of a grab, bottle sampler of water at a time (Huang, 2006). In case of the pollutants have only at trace level large, volume of water sample is needed (Huang, 2006). The frequency of sampling should be raised, when pollutants in that place vary over time in order to obtain more reliable analysis data (Huang, 2006). Passive methods have shown much promise as tools for measuring aqueous concentrations of a wide range of priority pollutants (Gorecki et al. 2002, Vrana et al. 2005) because passive sampling methods usually simplify sample pretreatment and very easy to implement (Huang, 2006). Moreover, passive method overcome time and labor constraints. Figure 2.6 show the principle of metal uptake by the passive sample (Huang, 2006).

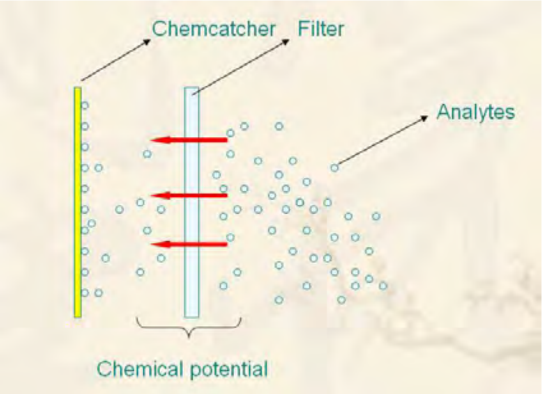

Figure 2.5 The uptake principle of passive sampler (Huang, 2006)

The principle of passive sampling is based on free flow (according to the Fick's first law of diffusion) of analyze molecules from the sampled medium to a collecting medium (Huang, 2006). Diffusion driving forces and separation mechanisms depend on the different chemical potentials of trapped and nontrapped (remaining in the sample) analyzes (Huang, 2006). The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane, as shown in Figure 3.4.5 (Huang, 2006). No extra energy is needed during sampling proceeds rather than the chemical potential difference (Gorecki et al, 2002 and Vrana et al, 2005). This chemical potential difference drives analyzes from aqueous phase (high in concentration) to receiving membrane (low in concentration) (Huang, 2006). When the analyze concentration is higher in aqueous phase then in the receiving phase, the analyze molecules will be passively transported though the permeable filter and trapped on the surface of suitable medium known as receiving reference phase or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent (Vrana et al, 2005). In additional, the labile fractions of metal ions from experiments show very good consistency with theoretical calculations (Huang, 2006).

2.7.4.1 Diffusion gradient in thin films (DGT)

DGT method is a passive sampling technique that measures the *in situ concentration* of labile metal species through preconcentrated metal masses collected during the exposure period in nature waters (Davison and Zhang, 1994). In the last 10 years, studies of the DGT method have been performed on freshwater; rivers (Denney et al., 1999; Sangi et al., 2002; Garofalo et al., 2004; Aung et al., 2007 and Meylen et al., 2004), lakes (Odzak et al., 2002 and Gimpel et al., 2003), seawater (Munksgaard and Parry, 2003; Dunn et al., 2003 and Forsberg et al., 2006), and wastewater (Buzier et al., 2006). These studies have evaluated DGT as an efficient tool for measuring in situ metal speciation, except in lakes with ionic strength less than 0.4mmol/L, and as a potential monitoring tool for routine measurements.

2.7.4.2 Dialysis membrane⁄tubing⁄bag

Dialysis speciation technique assesses to bioavailable metal species by in corporating a metal chelating resin contained within a dialysis membrane (Morrison, 1987). A major direction studies is based on the ability of chelating resins to remove metals by a process which imitates metal uptake at the cell surface (Florence, 1982 and Batley, 1983). The ability of a metal is determined not only by the species present, but also by the uptake processes at the organism/environmental interface (Luoma, 1983). This interface is usually a biological membrane and the transport of metal species across the biological membrane may not be directly comparable to resin kinetics; in fact membrane-limited metal transport is a slow process (Turner, 1984). Dialysis with receiving resins should be particularly suitable for long sampling where sporadic flushes of metal are experienced (Morrison, 1987). These features may be missed by conventional sampling procedures, but are not missed by the continuously monitoring (Morrison, 1987). The method is designed for the determination of bioavailable metal uptake rate in stormwater and other wastewaters. Dialysis with receiving resins may also prove to be suitable for measurements in natural freshwater, estuarine and marine environments (Morrison, 1987).

2.8 Literature Review

Polprasert (1982) studied heavy metals pollution in the Chao Phraya River estuary basing on the theoretical investigation of heavy metals DDT and PCBs in the upper gulf of Thailand (Phase I). There are 12 sampling stations from the river mouth to 138.5 km upstream. The accumulation of Cd, Cu, Cr, and Pb in water in the river mouth vicinity was significantly high; the downstream stations samplers contained higher concentration of Cd, Cu, Cr, and Pb than those of the upstream stations. The mean of Cd, Cu and Pb concentrations at the river mouth stations were 66.0±89.9, 43.8±21.9, and 187.±59.5μg/l of Cd, Cu and Pb respectively. They were also higher than those reported by Menasveta (1979), who found only 0.3-0.6, 2.3-5.5, and 4.7-16.2 μg/l, respectively for the same of sampling points. This study suggested that metal concentrations at the river mouth stations exceeded the stream standard for tropical country. Polprasert (1982) agreed with Apichatvullop (1976) who proposed that the relatively high concentrations of heavy metals which may have been due to one or more of the following reasons: movement of pollutants from upstream; waste water discharges from the Bangkok Metropolis and industrial estates south of Bangkok; and the physical characteristics of the estuary and tidal movements that tend to stagnate water in this area.

Aung et al. (2008) determined the labile species of Ni, Cu, Zn, Cd, and Pb in the Tama River in Tokyo, Japan by using on-site measurement devices such as diffusive gradients in thin films (DGT) under dry and wet weather, between August and October, 2006. They used two types of diffusive gradients in thin films (DGT), which DGT-RT for measuring labile inorganic and DGT-APA for total (inorganic and organic) labile species, then compared with the dissolved metal concentrations (filtered using a membrane of 0.5 μm pore size). Their results showed that 38±5% (RG) and 45±8% (APA) for Ni and 45±22% (RG) and 53±23% (APA) for Zn are labile, thus, bioavailable, while Cu was assumed to be in stable complexed forms. Their work indicated that rains brought considerably higher loads of metals in dissolved form, and DGT measurements indicated that labile metal loads also increased. The researchers compared DGT measurements with the WHAM 6 speciation model and found to be similar to the model computed results.

Buzier et al. (2008) evaluated the total metal entering wastewater treatment plant (WWTP) and reaching the river system.

Their result showed that WWTPs greatly reduce total metal concentrations but reduce labile metal concentration only slightly.

Bubb and Lester (1995) investigated the behaviour and fate of Cu, Cd, Pb, Fe and Mn in surface water and sediments of the River Ivel, Bedfordshire, UK have been investigated to assess if sewage effluent discharges affect metal partitioning and availability within the receiving environment. Increases in both metal concentrations and complexation capacity were evident immediately downstream of STW outfalls, the degree of enrichment being dependent upon the amount of dilution received. Changes induced by sewage treatment work (STW) effluent release were generally in accordance with conservative mixing of the freshwater and effluent streams but scour of the bottom deposits below Letchworth STW increased particulate loads of both Fe and Mn and stimulated a 2 fold increase in soluble Mn over conservative mixing predictions. Evidence implies that a pH reduction to 7.5 rather than organic complexation solubilized Mn from "exchangeable" sites on bottom sediments.

Gagnon and Saulnier (2003) determined The environmental impacts of municipal wastewater discharges on receiving waters are numerous and inputs of contaminants such as metals can cause toxicity to organisms in receiving waters. The effluents generated by the treatment plant of the city of Montreal, Canada, the largest such facility in the St. Lawrence Valley, was investigated to determine the environmental fate of trace metals in the receiving waters. Total and extractable metal concentrations were determined and physico-chemical parameters were measured to characterize the receiving waters and evaluate their influence on the fate and behaviour of metals released from the urban effluent. Their results showed that particulate metals near the effluent discharge point are highly reactive and their distribution seems to be significantly influenced by the abundance of HCl-reactive iron and manganese, which act as trace-metal carriers. The partitioning of metals between dissolved and particulate phases varies along the effluent dispersion plume and therefore could strongly influence the exposure routes for aquatic organisms that are exposed to the various contaminants released from the effluent. Partitioning of dissolved and particulate metals varies along a dispersion plume and could influence toxicity to aquatic biota.

CHAPTER III

METHODOLOGY

3.1 Material

All working standards were prepared with deionized water with a resistance of 18.1 MΩ cm. All acids, used for metal analysis will be of analytical grade.

3.1.1 Chemicals

Chemicals to be used in this study are listed in Table 3.1

Table 3.1 Chemical List

Chemical	Supplier/Grade
ICP multi element standard solution 1000 mg/l	Merck/Analytical Grade
Si standard	Carlo Erba/ For analysis
Standard Reference Material®1643e	NIST / Analytical Grade
Potassium hydrogen phthalate ($C_8H_5KO_0$)	Carlo Erba/ For analysis
Sodium hydrogen carbonate ($NaHCO_3$)	Nacalai Lesque/ For certainty
Sodium carbonate (Na_2CO_3)	
Nitric acid 65%	Carlo Erba/ For analysis
in 2% nitric acid	

3.1.2 Glassware

Plastics and glasswares were soaked with 1%HNO3, at least, overnight and rinsed well with deionized water three times prior to use.

3.1.3 Instruments

These instruments to be used in this study are described in Table 3.2

Table 3.2 Instruments List

Instruments	Model
ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) Varian, Australia	Vista MPX Axial
TOC	Shimadzu, TOV-VCPH
pH meter : USA	HACH sesion4 pH ISE meter S/N 030700000425
Ion Chromatography	Dionex 1996-2001 version 6.70

3.2 Methods

3.2.1 Field Investigation

3.2.1.1 Chao Phraya River

The samples to be analyzed in this study were taken from 5 points in the downstream of the Chao Phraya River; the point that were 83km, 58km, 48km, 42 km, 29 km away from the river mouth, respectively. Figure 3.1 was drawn based on data published by Pollution Control Department of Thailand. The data were obtained from the samplers collected at monitoring stations along the Chao Phraya River. Since fluctuations were observed between stations CH_6 and $CH_{15,}$ these stations were selected as sampling points in this study. Grab samples were taken using a stainless steel cup connected with a string. The samples were stored in a cooler box and immediately transported to the laboratory. Filtration was conducted after reaching back to laboratory using 0.45µm PTFE membrane filter and then filtered samples were stored at 4˚C until analysis.

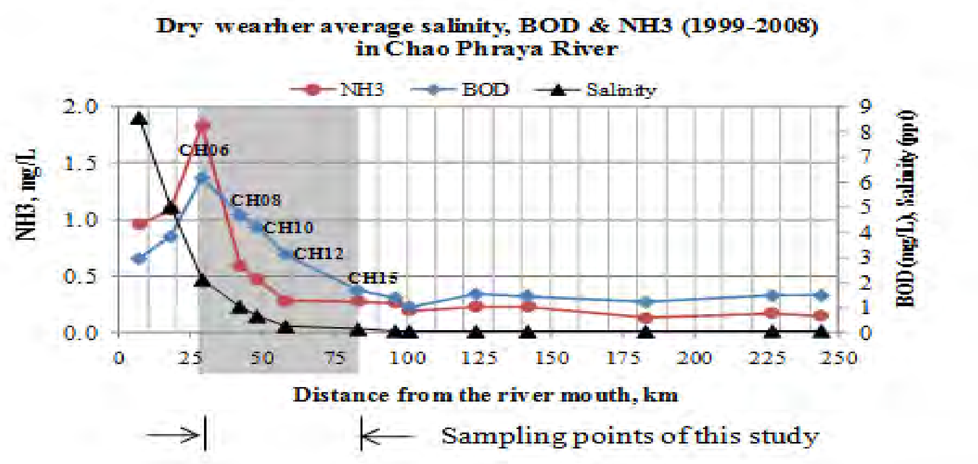

Figure 3.1 The locations of Sampling points in this study: CH_x are monitoring stations along the Chao Phraya River

Sources: Pollution Control Department, Thailand

3.2.1.2 Water environment around an industrial estate

Ten of surface waters around an industrial estate have been selected. These are:

point 1: Raw water for the water treatment plant from Chao Phraya River,

point 2: Treated water by water treatment plant (Tap water),

point 3: Ground water (from the school nearby community),

point 4: Influent to the wastewater treatment plant,

point 5: Treated effluent before the polishing pond,

point 6 : Effluent water after the polishing pond,

point 7 : Mixing point at the Canal,

point 8 : Canal water after the discharging,

point 9 : The lake water beside in the industrial zone,

point10 : Canal water after the discharging (downstream).

The technique of water sampling around an industrial estate was the same as the Chao Phraya River , the samples were stored in a cooler box with ice and immediately transport to the laboratory. Filtration was conducted after reaching back to laboratory using 0.45µm pore size PTFE membrane filter and then filtered samples and stored at 4˚C until analysis. Figure 3.2 was showed the locations of Sampling points surrounding the Bang Pa-In wastewater treatment plant.

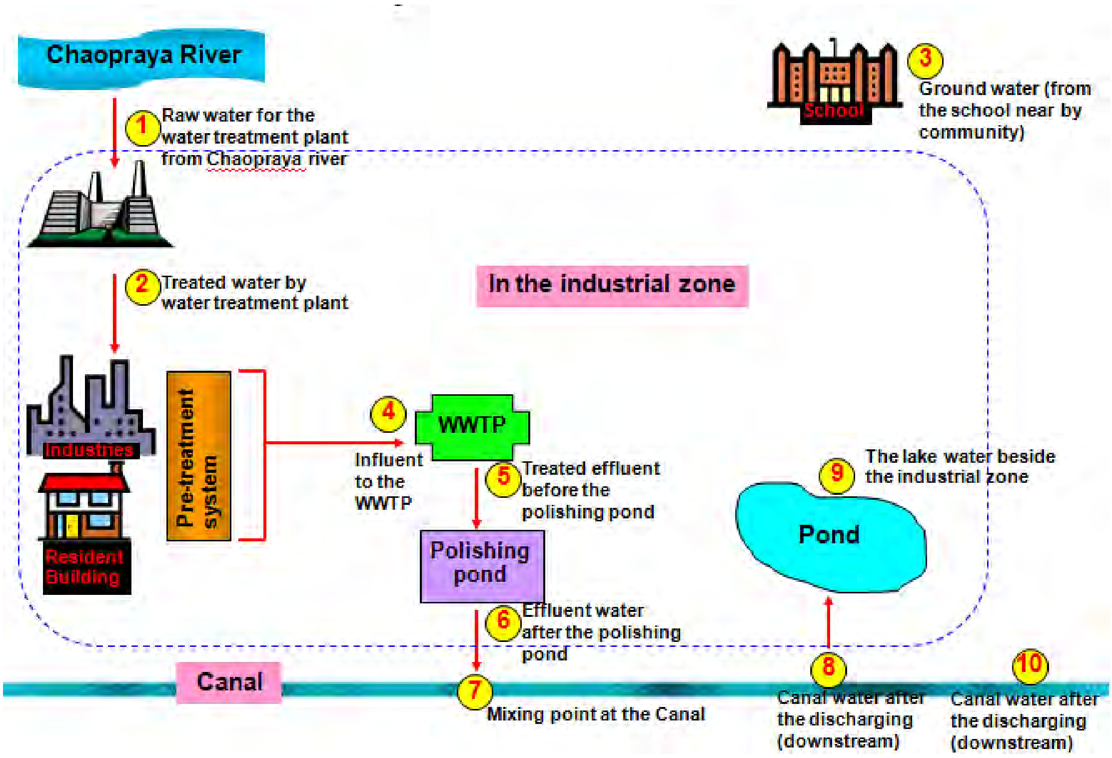

Figure 3.2 The locations of Sampling points surrounding the Bang Pa-In wastewater treatment plant: The total stations of collecting water sample are 10 stations

Source : Environmental Research and Training Centre, 2010

3.3 Sample Preparation and Analysis

The river water samples were filtered through 0.45µm pore size membrane filters immediately after getting back to laboratory. A portion of it was acidified to pH 2.0 with nitric acid and subjected to ICP analysis. Unacidified portion was subjected for TOC and anions analyses and Empore^{TM} SPE measurements. In addition, Filtered samples was kept in a refrigerator at 4˚c for Empore analysis.

The sample bottles and glasswares were soaked by nitric acid in the 2% acid for at least 12 hrs, followed by cleaning with distilled water for 3 times before using in order to avoid precipitation of metal hydroxide or adsorption to container wall.

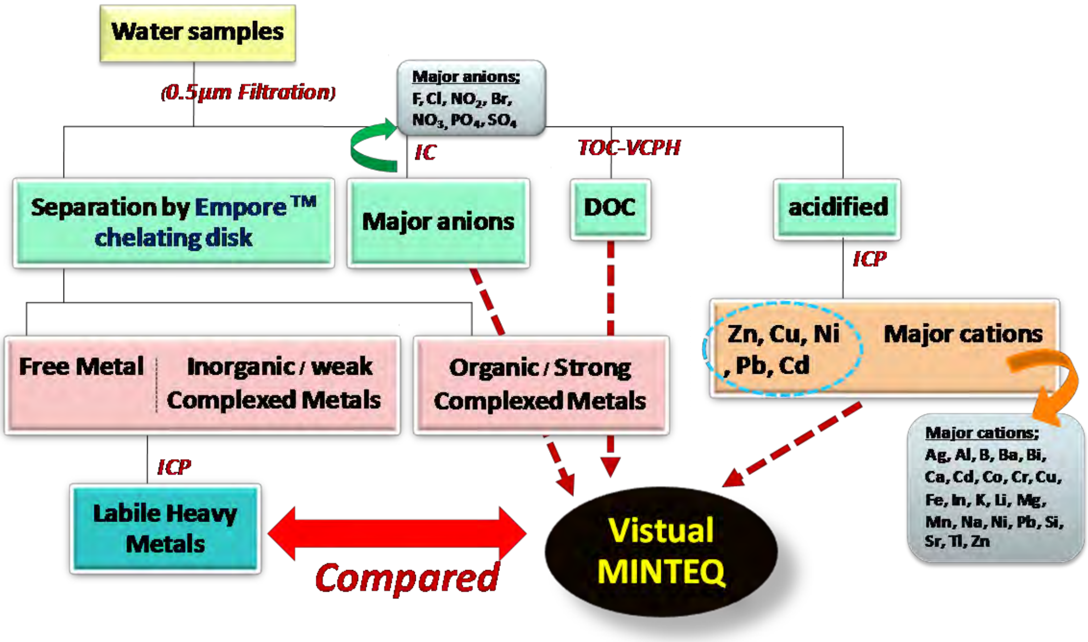

Figure 3.3 Analytical Methods of Heavy Metals in Aquatic Samples

3.3.1 Major cations and heavy metals measurement

In order to analyze major cations (Ag, Al, B, Ba, Bi, Ca, Co, Cr, Fe, In, K, Li, Mg, Mn, Na, Si, Sr, Tl) and heavy metals of interest (Cu, Ni, Zn, Pb, Cd) in the water samples, a portion of water samples were filtered through 0.45µm PTFE filter to separate suspended particles. The water samples were acidified prior to analysis by addition of 1% (v/v) of nitric acid according to the German standard procedure DIN 38406. Metals and minerals were measured using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The ICP-OES measurements were programmed to measure in 3 replicates to each sample.

3.3.2 Method Validation

The Standard Reference Material (SRM 1643e) by NIST intended primarily for use in evaluating methods use in the determination of trace elements in fresh water, SRM 1643e was used for method validation and accuracy check.

3.3.3 Major anions measurement

Major anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were measured using Ion Chromatography analyzer. Working reference solutions were prepared by serial dilution of a certified reference anion solution from Dionex (fluoride 100 mg/l, chloride 250 mg/l, nitrite1000 mg/l, bromide 1000 mg/l, nitrate 500 mg/l, phosphate 1000 mg/l, sulfate 500 mg/l) with de-ionized water in ratios. All reagents were of analytical reagent grade unless otherwise specified. Separations were performed with 9.0mmol/l sodium carbonate as the eluent. The experimental procedure involved choice of column type, eluent concentration and flow rate, reagent concentration and flow rate, dilution ratio and integration parameters. Most of these parameters were selected based upon literature references, personal experience and the Dionex operator manuals (Zeyrek, et al., 2009).

3.3.4 Total organic compound measurement

Total organic carbon (TOC) was a measure of the carbon content of dissolved and undissolved organic matter present in the water. TOC was analyzed according to the European standard procedure EN 1484 using a TOC analyzer (Shimadzu, TOV-VCPH). In this method, the inorganic carbon present in a water sample was removed by acidification and subsequent stripping with nitrogen. The organic compounds then undergo catalytical oxidation to carbon dioxide which was stripped and detected by infrared spectroscopy. TOC measurements were programmed to measure in 3 replicates to each sample according to the European standard procedure DIN EN 1484.

- Potassium hydrogen phthalate, stock solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 1.0625 g of potassium hydrogen phthalate ($C_8H_5KO_0$) (dried for 2 hrs at a temperature between 105º C and l20º C, Desicator > 2hrs), and made up to volume with water.
- Sodium bicarbonate, stock solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 1.35 g of Sodium bicarbonate ($NaHCO_3$) (dried for 1 hr at a temperature between 280º C and 290º C, Desicator > 2hrs), and made up to volume with water.
- Sodium carbonate, stock solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 2.21 g of Sodium carbonate (Na_2CO_3) (dried for 2 hrs at a temperature between 280º C and 290º C, Desicator > 2hrs), and made up to volume with water.

3.4 Empore$^{\text{TM}}$ chelating disk (General Guidelines for Applications, 1996)

Labile metal concentration of the prefiltered sample were determined by Empore$^{\text{TM}}$ chelating disk cartridge provides a mechanism to remove labile metal from solutions by simply passing the solution through the porous membrane. The Empore$^{\text{TM}}$ cartridge contains chelating disk, consists of a polymer support (cross-linked polystyrenedivinylbenzene) functionalized by bonding at the nitrogen atoms to iminodiacetic acid groups (Figure 3.3).

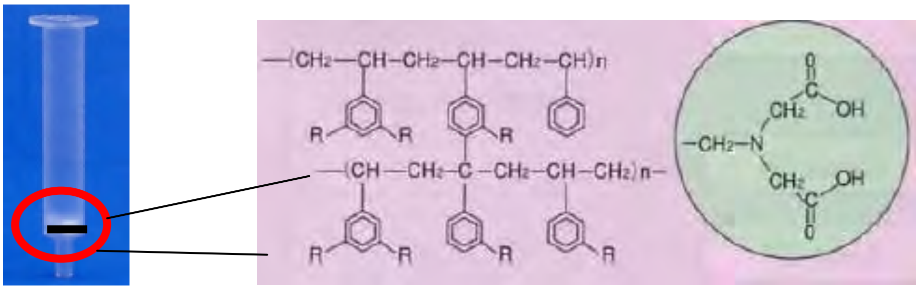

Figure 3.4 Empore$^{\text{TM}}$ chelating disk cartridge and its polymer functionalized by bonding at the nitrogen atoms to iminodiacetic acid groups.

Figure 3.5 Vacuum manifold used with chelating disk cartridge

A vacuum manifold was used with chelating disk cartridge to draw liquids through the cartridge (Figure 3.4). First the cartridge was washed by passing 5mL of HNO_3 (3M) followed by Milli-Q water. Then the chelating disk was preconditioned with CH_3COONH_4 (adjusted to pH 5.5) for optimum condition as recommended by the manufacturer. After conditioning, samples (generally 15mL of sample) was passed through the cartridge with suction pressure 50.8 kPa. When the samples were passing through the chelating disk, labile metals including free metal ions and weak complexes was obtained by the chelate. The chelated metals in the resin was eluted by two step; first 2mL and then 1mL (altogether 3 mL), with 3M HNO_3 and the eluted metal concentration was determined by ICP-MS. Three set of Milli-Q samples were also subjected to same procedure to represent labile blank.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Accuracy and Precision

The Standard Reference Material (SRM 1643e) by NIST was applied to validate the method of metal analyses throughout this study. The certified results and the results of the measurements in this study were shown in Table 4.1

Table 4.1 Results of Ni, Cu, Zn, Cd and Pb in freshwater standard reference material (SRM 1643e) analyzed in this study vs. certified values.

Sample	**Certified Values (µg/l)**	**Analyzed Result Concentration (µg/l)**			
		1st	**2nd**	**3nd**	**Average**
Ni (n=3)	62.4±0.69	66.0	62.8	54.8	61.2±6.00
Cu (n=3)	22.7±0.31	48.3	22.2	14.8	30.0±20.0
Zn (n=3)	78.5±2.20	82.7	72.3	95.9	80.0±10.0
Cd (n=3)	6.57±0.07	6.25	6.10	6.27	10.0±4.00
Pb (n=3)	19.63±0.21	6.22	18.0	15.7	13.0±6.00

4.2 Total dissolved and labile metals in Chao Phraya River

Total dissolved concentrations of of metals at five sampling points in Chao Phraya River were measured and labile species were calculated. All the total dissolved metals and minerals were determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ 3. The instrumental detection limits of the metals in ICPOES were: Cu = 0.11 µg/L, Ni = 0.10 µg/L, Pb = 0.08 µg/L, Zn = 0.003 µg/L and Cd = 0.01 µg/L. The total dissolved, inorganic labile and % labile metal concentration were displayed in Table 4.2. The concentrations of Ni, Cu, Zn, and Pb in water samples were above the detection limits, except Pb in the sampling point CH12

Table 4.2 The total dissolved, labile concentrations of metals and % lability at five sampling points in Chao Phraya River.

Stations	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
CH6	**Ni**	64.6	61.1	95
	Cu	2.75	1.45x10-3	0.10
	Zn	9.55	6.40	67
	Cd	184	183	99
	Pb	140	3.04	2
CH8	**Ni**	68.0	64.5	95
	Cu	23.1	0.48	2
	Zn	12.7	9.13	72
	Cd	66.6	65.6	99
	Pb	70.0	1.58	2
CH10	**Ni**	77.2	72.4	94
	Cu	24.4	0.38	2
	Zn	12.3	8.40	68
	Cd	45.0	43.9	98
	Pb	218	6.92	3
CH12	**Ni**	70.5	69.4	98
	Cu	50.9	15.9	31
	Zn	8.61	7.59	88
	Cd	57.4	56.7	99
	Pb	ND	ND	-
CH15	**Ni**	95.1	92.0	97
	Cu	7.68	0.11	1
	Zn	5.77	4.40	76
	Cd	29.8	29.3	99
	Pb	206	15.3	7
Average	**Ni**	62.6±12.1	71.9±12.1	96±2
	Cu	18.1±18.8	3.38±7.02	1±1
	Zn	63.9±61.8	75.8±61.6	99±1
	Cd	8.16±2.85	7.18±1.86	74±9
	Pb	127±68.1	6.71±6.14	4±2

ND*=Non Detectable

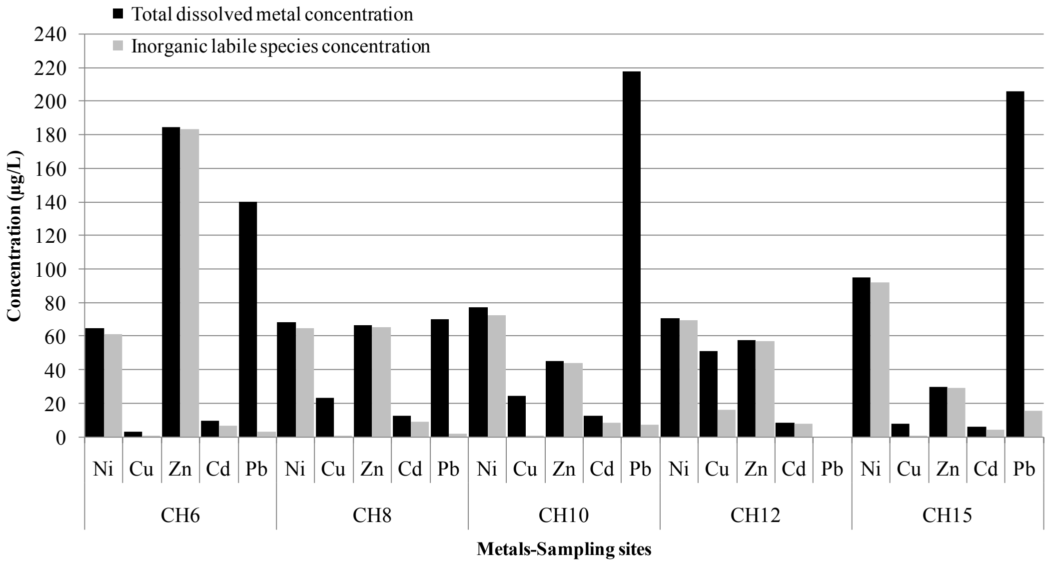

Figure 4.1 The total dissolved and inorganic labile species concentrations of metals at five sampling points in Chao Phraya River (one time sampling in dry season).

Polprasert (1982) reported dissolved metals concentrations along the Chao Phraya River. Lower concentrations were found in upstream and highest concentration in the samples collected near river mouth. Those dissolved metals concentrations were: Cd between ND – 121 µg/L, Cu between ND – 68.7 µg/L, Pb between ND – 263 µg/L and Zn between 11.2 – 178 µg/L.

The results of this study showed that the relatively lower concentrations compared to Polprasert's in the certain metals such as Cu and Ni might be due to the more stringent regulation on industrial discharges and the more attention of authorities and public given to river sustainability and environment in recent times. Polprasart (1982) reported the relatively higher concentrations of Cd, Cu, Cr and Pb at the vicinity of the Chao Phraya River mouth compared to upstream sampling points and refered the assumption of Apichatvullop (1976) that the accumulation of heavy metals might be due to movement of pollutants from upstream, wastewater discharges from the Metro Bangkok, and the physical characteristics of the estuary and tidal movements that tend to stagnate water at the vicinity of the river mouth.

All dissolved metals and minirals determined by ICPOES at each sampling points were found to be significantly correlated (*p*<0.01) each other; *r* = 0.90 for CH15/CH12, *r* = 0.92 for CH15/CH10, *r* = 0.86 for CH15/CH8, 0.86 for CH15/CH16. It was expected that metals of the same or similar sources track one another, if those sources were primarily responsible for the concentrations found in the samples.

Lead concentration of lower than detection limit at CH12 sampling point had affected the species distribution at it, and the most pronounced effect was observed in case of Cu species; an increase in inorganic Cu species was observed in CH12. The percentages of calculated inorganic species from 5 sampling points are as described in Table 4.2. The several previous research findings indicated the Cu's affinity to organic matter and the high stability of these organo-copper complexes. It could be assumed that Cu tended to form complexes with anions when competing Pb ions were absent, thus, 31% of total dissolved Cu are in the inorganic form, while the rest of 69% was complexed with organic matter at CH12 sampling point. From the calculated species, most of the dissolved Ni and Zn tend to be in the form of inorganic forms, whereas inorganic species of Cu and Pb are found to be less than 10%. The affinity of Cu to organic ligands is noted (Tipping and Hurley, 1992); that might be the reason that most of the dissolved Cu might be in the form of organocopper complexes. The same conclusion can be drawn for Pb; the environmental conditions at the sampling period might favor the formation organolead complexes.

Aung et al (2008) showed that there was a reasonable agreement between the computed inorganic species of Zn and Ni using WHAM 6, an equilibrium model designed for surface waters which has basically similar concept with Vistual MINTEQ, and those determined using DGT-RG, which claimed to take only inorganic labile metals. In this study, though we did not compare with the other method, the reasonable species concentrations were obtained and the findings were in accordance with the previous findings, though the major anions were literature values. Since some anions (such as sulphate, though they could be in trace amounts) might be missing from our dataset applied for model calculations, the species distribution could be deviated from the actual situation. However, total inorganic species concentrations, the summed values of the inorganic species, in this study would not be wrong because dissolved organic carbon concentrations were self-measured and Vistual MINTEQ predicted the inorganic species from the pool of the elements remained uncomplexed with organic matter.

In Thailand, surface water standards concentrations were: 0.1 mg/L for Ni, 0.1 mg/L for Cu, 1.0 mg/L for Zn, 0.005 mg/L for Cd and 0.05 mg/L for Pb. Mostly, the total concentrations of Surface Water Quality Standards were applied as the total dissolved concentrations in this study, even the dissolved concentration Cd at all and Pb at three sampling points in this study, exceeded the standards. Due to their toxicity, the risk to aquatic life is alarming, if no bioaccessibility is not taken into account.

4.3 Dissolved Organic Carbon at Chao Phraya River

The increasing trend of organic carbon concentration from the graph below was observed (DOC at CH15 = 2.21 mg/L, at CH12 = 1.37 mg/L, at CH10 = 4.36 mg/L, at CH8 = 3.63 mg/L and at CH6 = 5.67 mg/L, respectively) indicating the growing organic matter pollution when the river approaches to the river mouth.

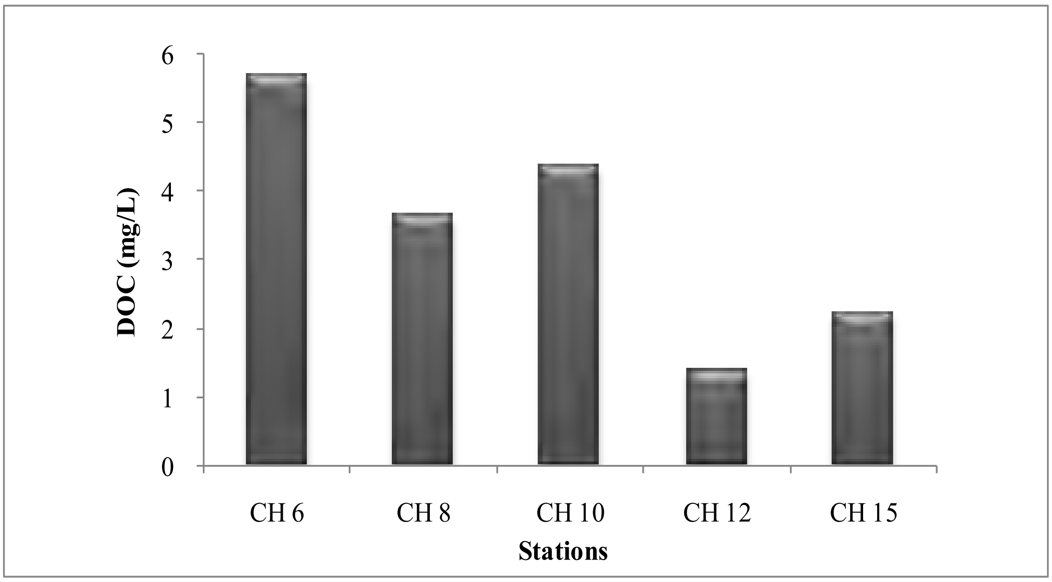

Figure 4.2 The dissolved organic carbon concentrations at 5 sampling sites along Chao Phraya River**.**

The correlation coefficients of 5 sampling points in Chao Phraya River were calculated between the concentrations of DOC and %labile metals concentrations. The result showed that DOC was negatively correlated with %lability of Ni, Cu, Cd and Pb that mean the two variables are changed in the reverse direction, the higher the DOC, the lower the % labile concentrations, which is in accordance with the theoretical findings.

4.4 Total dissolved and labile concentrations of metals in water environments within and around an industrial estate

4.4.1 The total dissolved, labile concentrations of metals and % lability at site 1, raw water from the Chao Phraya River

Table 4.3, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 1, raw water from Chao Phraya River for the water treatment plant before distribution.

Table 4.3 The total dissolved, labile metals concentrations and % lability at site 1, raw water from Chao Phraya River for the water treatment plant for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 1	**September**	**Ni**	32.5	17.0	52
		Cu	2.80	$1.08\text{x}10^{-5}$	<0.001
		Zn	21.8	17.4	80
		Cd	ND	ND	-
		Pb	8.10	$2.47\text{x}10^{-3}$	0.0305
	October	**Ni**	35.1	23.1	66
		Cu	1.97	$3.62\text{x}10^{-6}$	<0.001
		Zn	34.9	29.8	85
		Cd	0.07	$2.82\text{x}10^{-3}$	4
		Pb	9.96	$3.40\text{x}10^{-3}$	0.0342

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Stations	**Months**	**Metals**	**Total dissolved (µg/L)**	**Labile (µg/L)**	**% labile concentrations**
	November	**Ni**	24.9	13.8	55
		Cu	0.95	4.42x10^{-7}	<0.001
		Zn	72.7	61.7	8
		Cd	7.52	1.17	16
		Pb	ND	ND	
	Average	**Ni**	30.8±5.31	18.0±4.77	58±7
		Cu	1.91±0.93	4.94x10^{-6} ±5.32x10^{-6}	<0.001
		Zn	43.2±26.4	36.3±22.9	83±3
		Cd	2.54±4.31	0.59	7.02±7.49
		Pb	6.06±5.23	2.94x10^{-3}	0.0229±0.0165

Graphically, the average concentrations in site 1 can be described as in Fig 4.3.

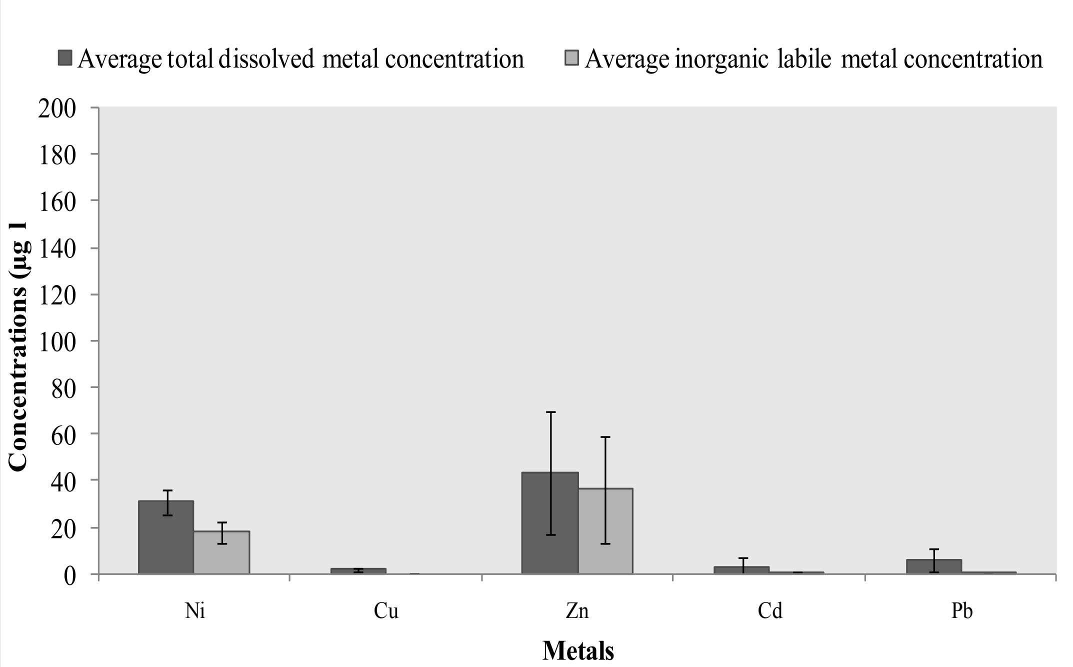


Figure 4.3 The total dissolved and labile concentrations of metals at site 1, raw water for the water treatment plant from Chao Phraya River for three time samplings.

4.4.2 The total dissolved, labile concentrations of metals and % lability at site 2, treated water for distribution in the estate (collected from distribution tap)

Table 4.4 described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 2, treated water by from distribution tap.

Table 4.4 The total dissolved, labile concentrations of metals and % lability at site 2, for distribution in the estate (collected from distribution tap) for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 2	**September**	**Ni**	23.4	19.9	85
		Cu	ND	ND	-
		Zn	37.0	35.8	97
		Cd	23.0	14.0	61
		Pb	ND	ND	-
	October	**Ni**	29.9	19.0	64
		Cu	3.02	4.76×10^{-5}	0.00157
		Zn	162	136	84
		Cd	13.9	3.69	27
		Pb	3.08	1.27×10^{-3}	0.0412
	November	**Ni**	23.2	8.02	35
		Cu	ND	ND	-
		Zn	ND	ND	-
		Cd	ND	ND	-
		Pb	15.5	3.57×10^{-3}	0.0230
	Average	**Ni**	25.5±3.80	15.7±6.63	61±25
		Cu	1.09±1.67	4.76×10^{-5}	<0.001
		Zn	66.6±84.2	57.7±70.4	80±19
		Cd	12.3±11.6	8.85	29±31
		Pb	6.23±8.16	2.42×10^{-3}	0.0372±0.0127

ND*=Non Detectable

Graphically, the average concentrations in site 2 can be described as in Fig 4.4.

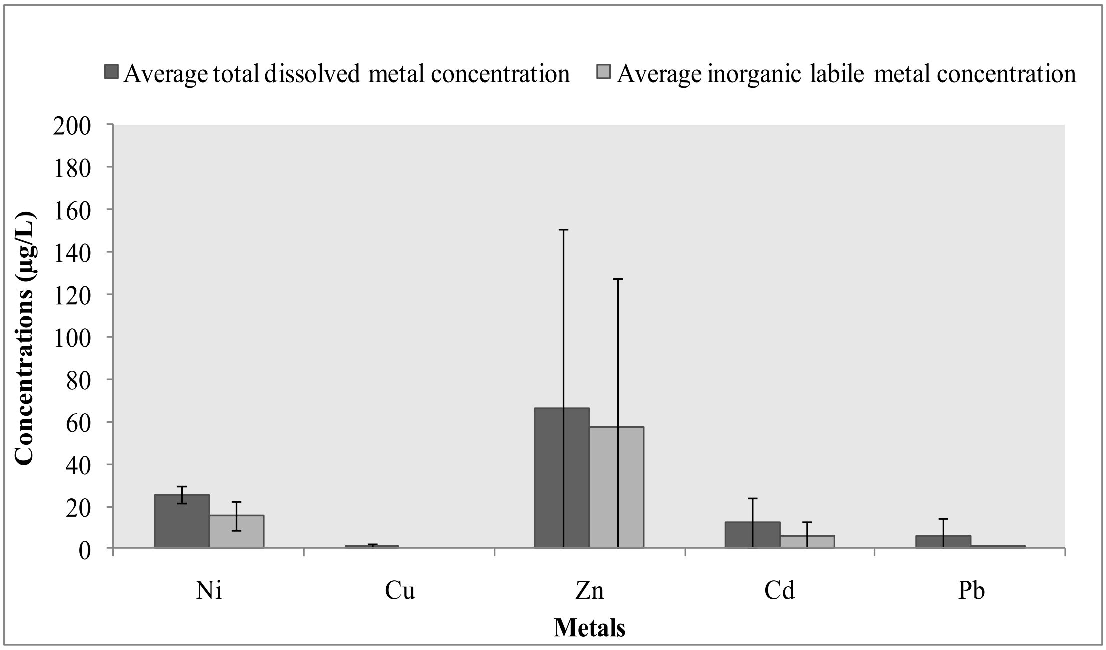


Figure 4.4 The total dissolved and labile concentrations of metals at site 2, treated water by water treatment plant (Tap water) for three time samplings.

4.4.3 The total dissolved, labile concentrations of metals and % lability at site 3, the groundwater from community distribution

Table 4.5, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 3, ground water (from the school nearby community).

Table 4.5 The total dissolved, labile concentrations of metals and % lability of at site 3, the groundwater from community distribution (from the tap of a school nearby) for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 3	**September**	**Ni**	41.7	16.9	41
		Cu	0.10	$1.19\text{x}10^{-10}$	<0.001
		Zn	6.82	5.23	77
		Cd	3.56	0.23	6
		Pb	2.59	$1.31\text{x}10^{-4}$	0.00506
	October	**Ni**	47.3	14.8	31
		Cu	0.46	$1.67\text{x}10^{-9}$	<0.001
		Zn	ND	ND	-
		Cd	ND	ND	-
		Pb	ND	ND	-
	November	**Ni**	40.7	14.0	34
		Cu	0.33	$1.09\text{x}10^{-9}$	<0.001
		Zn	45.3	34.9	77
		Cd	7.74	0.47	6
		Pb	1.91	$5.72\text{x}10^{-5}$	0.00300
	Average	**Ni**	43.2±3.54	15.3±1.51	35±5
		Cu	0.30±0.18	$9.60\text{x}10^{-10}$ $\pm 7.84\text{x}10^{-10}$	<0.001
		Zn	17.8±24.0	20.1	74±5
		Cd	3.78±3.86	0.35	4±3
		Pb	1.54±1.28	$9.41\text{x}10^{-5}$	0.00290 ±0.00220

ND*=Non Detectable

Graphically, the average concentrations in site 3 can be described as in Fig 4.5.

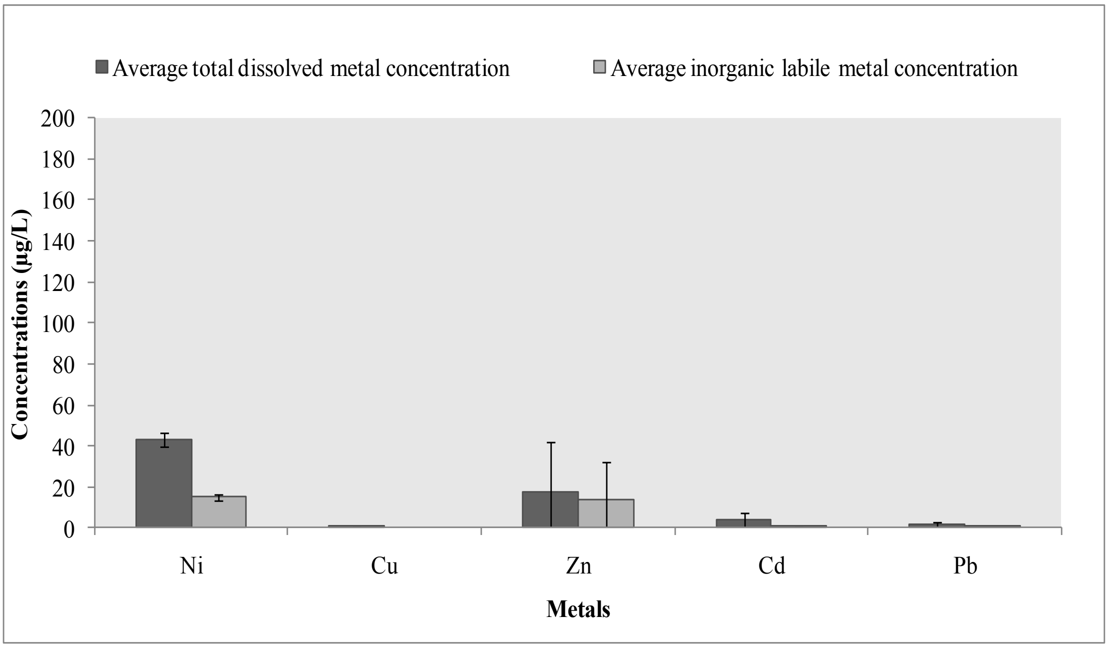


Figure 4.5 The total dissolved and labile metals concentrations at site 3, ground water (from the school nearby community) for three time samplings.

4.4.4 The total dissolved, labile concentrations of metals and % lability at site 4, influent to the wastewater treatment plant (WWTP)

Table 4.6, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 4, influent to WWTP.

Table 4.6 The total dissolved, labile concentrations of metals and % lability at site 4, influent to WWTP for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 4	**September**	**Ni**	35.5	21.7	61
		Cu	6.66	4.93x10^{-5}	<0.001
		Zn	15.7	13.9	89
		Cd	33.3	8.39	25
		Pb	ND	ND	-
	October	**Ni**	36.3	15.9	44
		Cu	5.14	9.42x10^{-5}	0.00183
		Zn	37.2	30.0	80
		Cd	1.19	0.03	3
		Pb	9.23	1.19x10^{-3}	0.0128
	November	**Ni**	33.6	12.6	38
		Cu	8.31	6.01x10^{-6}	<0.001
		Zn	12.7	10.0	78
		Cd	28.9	3.66	13
		Pb	ND	ND	-
	Average	**Ni**	35.1±1.37	16.7±4.59	48±12
		Cu	6.70±1.59	4.98x10^{-5} ±4.41x10^{-5}	<0.001
		Zn	21.9±13.4	17.9±10.6	83±5
		Cd	21.1±17.4	4.03±4.19	13±11
		Pb	3.15±5.27	1.19x10^{-3}	0.00579 ±0.00629

ND*=Non Detectable

Graphically, the average concentrations in site 4 can be described as in Fig 4.6.

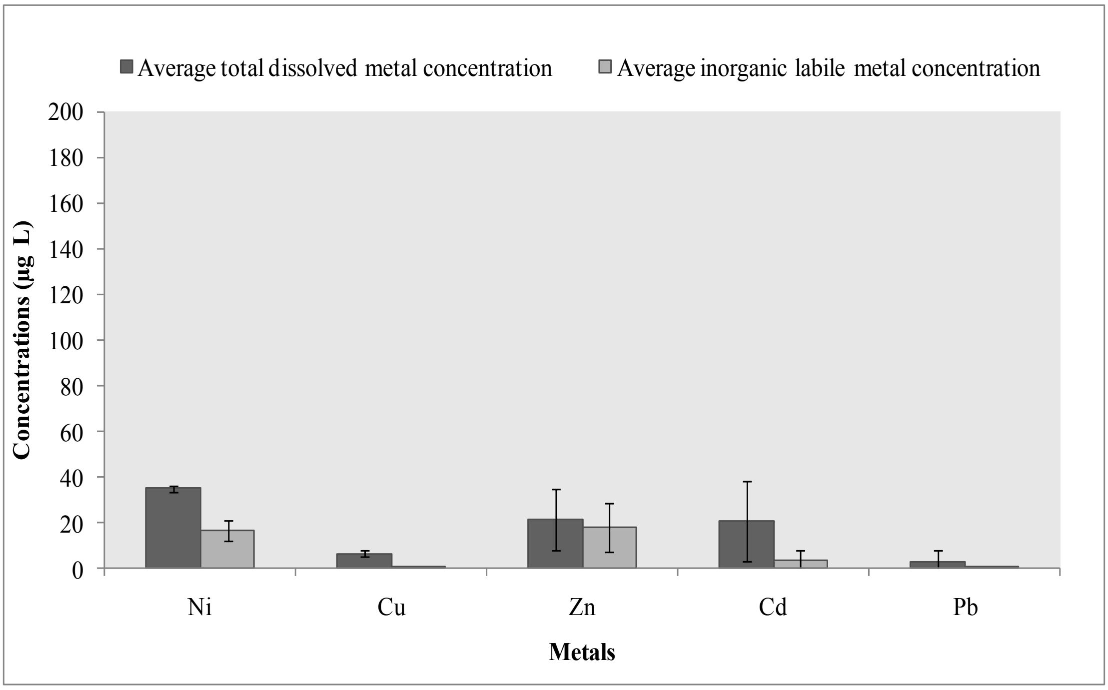


Figure 4.6 The total dissolved and labile concentrations of metals at site 4, influent to WWTP for three time samplings.

4.4.5 The total dissolved, labile concentrations of metals and % lability at site 5, effluent from WWTP

Table 4.7, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, in at site 5, treated effluent before the polishing pond.

Table 4.7 The total dissolved, labile concentrations of metals and % lability at site 5, treated effluent (before the polishing pond) for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 5	**September**	**Ni**	40.2	23.5	59
		Cu	33.7	2.26×10^{-3}	0.00671
		Zn	52.6	46.9	89
		Cd	35.3	8.19	23
		Pb	7.18	1.31×10^{-3}	0.0182
	October	**Ni**	47.9	24.2	51
		Cu	9.45	2.37×10^{-5}	<0.001
		Zn	169	149	88
		Cd	25.7	3.98	16
		Pb	9.46	1.01×10^{-3}	0.0106
	November	**Ni**	37.6	12.6	34
		Cu	9.57	5.22×10^{-5}	<0.001
		Zn	118	106	90
		Cd	10.8	1.56	14
		Pb	8.71	0.09	1.03
	Average	**Ni**	41.9±5.34	20.1±6.51	48±13
		Cu	17.6±14.0	7.79×10^{-4} $\pm1.28\times10^{-3}$	0.00250 ±0.00322
		Zn	113±58.4	101±51.2	89±1
		Cd	23.9±12.3	4.58±3.36	18±5
		Pb	8.45±1.16	0.03±0.05	0.354 ±0.588

Graphically, the average concentrations in site 5 can be described as in Fig 4.7.

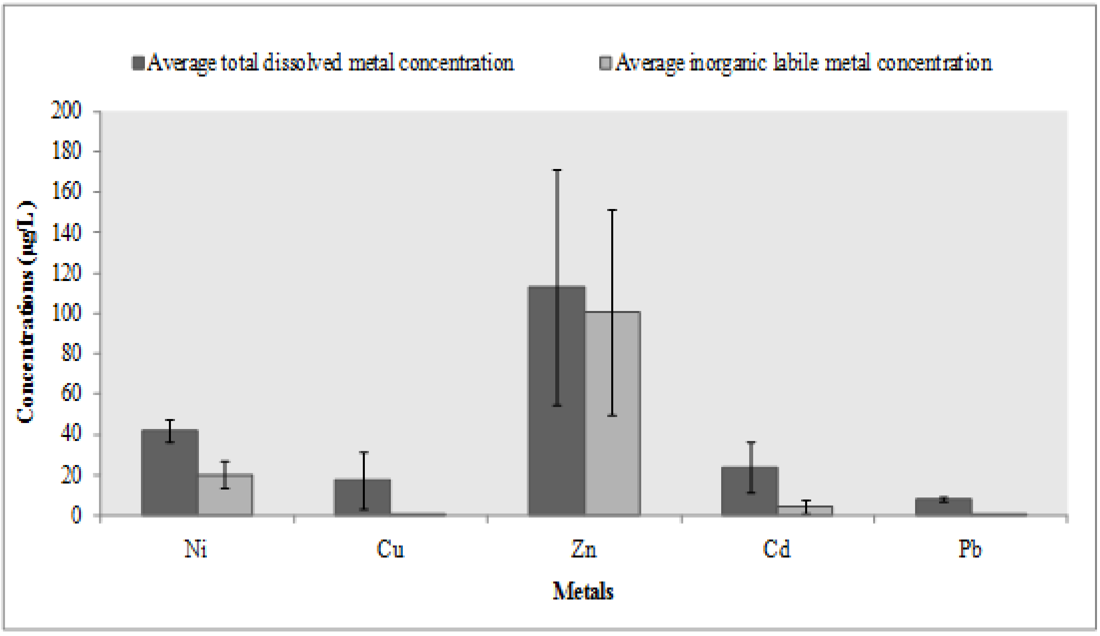


Figure 4.7 The total dissolved and labile concentrations of metals at site 5, treated effluent (before the polishing pond) for three time samplings.

4.4.6 The total dissolved, labile concentrations of metals and % lability at site 6, effluent from polishing pond of WWTP

Table 4.8, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 6, from polishing pond of WWTP.

Table 4.8 The total dissolved, labile concentrations of metals and % lability at site 6, from polishing pond of WWTP for three time samplings.

Stations	**Months**	**Metals**	**Total dissolved (µg/L)**	**Labile (µg/L)**	**% labile concentrations**
Site 6	**September**	**Ni**	32.1	20.0	62
		Cu	37.7	0.01	0.0161
		Zn	84.3	77.9	92
		Cd	13.5	3.50	26
		Pb	0.25	1.55×10^{-5}	0.00610
	October	**Ni**	49.7	26.3	53
		Cu	10.2	3.60×10^{-5}	<0.001
		Zn	160	142	87
		Cd	4.83	0.41	9
		Pb	ND	ND	-
	November	**Ni**	43.1	22.9	53
		Cu	24.2	4.18×10^{-4}	0.00173
		Zn	137	121	88
		Cd	27.2	4.88	18
		Pb	3.02	2.33×10^{-4}	0.00773
	Average	**Ni**	41.7±8.87	23.1±3.14	56±5
		Cu	24.0±13.8	2.18×10^{-3} $\pm 3.38 \times 10^{-3}$	0.00606 ±0.00774
		Zn	127±38.7	114±32.5	90±2
		Cd	15.2±11.3	2.93±2.29	18±9
		Pb	1.13±1.64	1.24×10^{-4}	0.00496 ±0.00347

ND*=Non Detectable

Graphically, the average concentrations in site 6 can be described as in Fig 4.8.

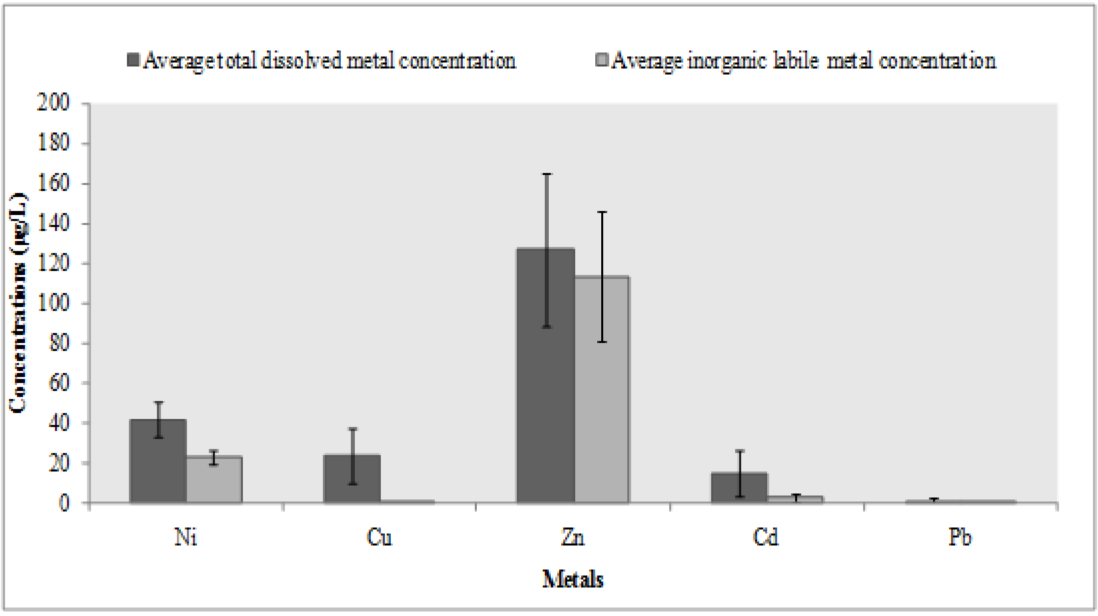


Figure 4.8 The total dissolved and labile concentrations of metals at site 6, from polishing pond of WWTP for three time samplings.

4.4.7 The total dissolved, labile concentrations of metals and % lability at site 7, the point where treated effluent discharged into the canal (the mixing point)

Table 4.9, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 7, mixing point in the canal.

Table 4.9 The total dissolved, labile concentrations of metals and % lability at site 7, mixing point in the canal for three time samplings.

Stations	**Months**	**Metals**	**Total dissolved (µg/L)**	**Labile (µg/L)**	**% labile concentrations**
Site 7	**September**	**Ni**	18.6	10.2	55
		Cu	3.89	2.61×10^{-5}	<0.001
		Zn	47.8	0.02	0.05
		Cd	20.9	5.77	28
		Pb	ND	ND	-
	October	**Ni**	56.5	32.6	58
		Cu	10.8	4.86×10^{-5}	<0.001
		Zn	105	43.0	41
		Cd	38.7	8.35	22
		Pb	1.74	1.09×10^{-4}	0.00628
	November	**Ni**	41.4	21.6	52
		Cu	17.9	1.65×10^{-4}	<0.001
		Zn	145	127	88
		Cd	12.2	1.63	13
		Pb	10.2	1.29×10^{-3}	0.0126
	Average	**Ni**	38.8±19.1	21.5±11.2	55±3
		Cu	10.9±6.98	9.16×10^{-5} $\pm 9.46 \times 10^{-5}$	<0.001
		Zn	99.3±48.6	56.8±64.7	43±44
		Cd	23.9±13.5	5.25±3.39	21±7
		Pb	4.03±5.43	7.00×10^{-4}	0.00787 ±0.00427

ND*=Non Detectable

Graphically, the average concentrations in site 7 can be described as in Fig 4.9.

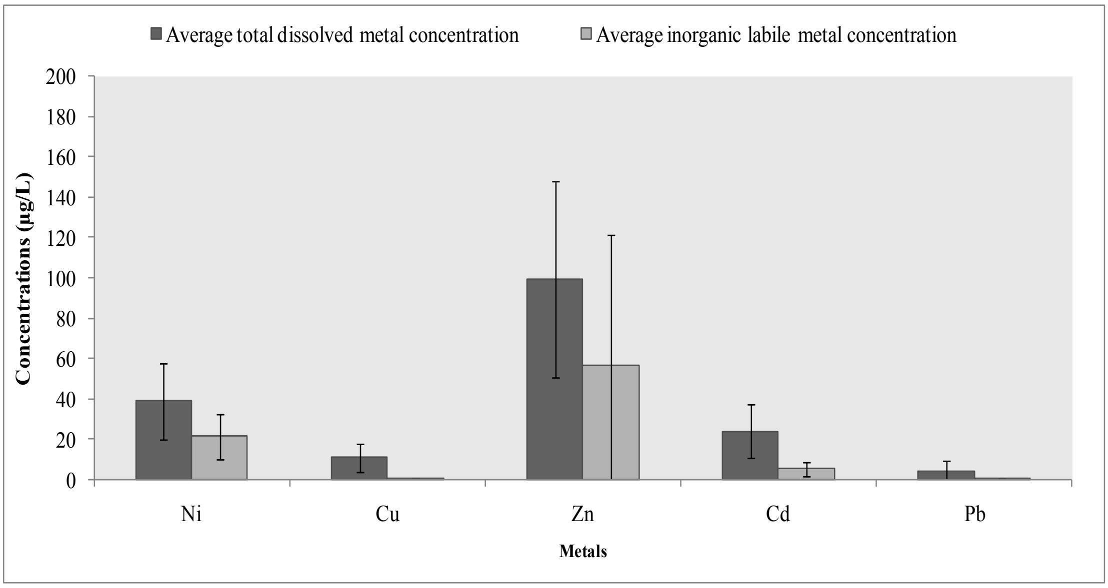


Figure 4.9 The total dissolved and labile concentrations of metals at site 7, mixing point in the canal for three time samplings.

4.4.8 The total dissolved, labile concentrations of metals and % lability at site 8, downstream of mixing point in the canal

Table 4.10, described all the total dissolved metals and minerals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 8, canal water after the discharging.

Table 4.10 The total dissolved, labile concentrations of metals and % lability at site 8, downstream of mixing point in the canal for three time samplings.

Stations	Months	Metals	Total dissolved (µg/L)	Labile (µg/L)	% labile concentrations
Site 8	**September**	**Ni**	20.4	8.50	42
		Cu	2.29	7.72 $\times10^{-7}$	<0.001
		Zn	47.9	39.0	82
		Cd	8.13	1.24	15
		Pb	ND	ND	-
	October	**Ni**	28.5	14.8	52
		Cu	1.06	2.68×10^{-7}	<0.001
		Zn	ND	ND	-
		Cd	ND	ND	-
		Pb	ND	ND	-
	November	**Ni**	37.4	18.0	48
		Cu	1.91	1.75×10^{-7}	<0.001
		Zn	82.0	72.7	89
		Cd	25.9	4.74	18
		Pb	ND	ND	-
	Average	**Ni**	28.7±8.54	13.8±4.84	47±5
		Cu	1.75±0.63	2.72×10^{-6} $\pm4.33\times10^{-6}$	<0.001
		Zn	43.7±40.5	37.6±35.9	83±6
		Cd	11.4±13.2	1.99±2.46	12±9
		Pb	0.11±0.00	ND	0.00181

ND*=Non Detectable

Graphically, the average concentrations in site 8 can be described as in Fig 4.10.

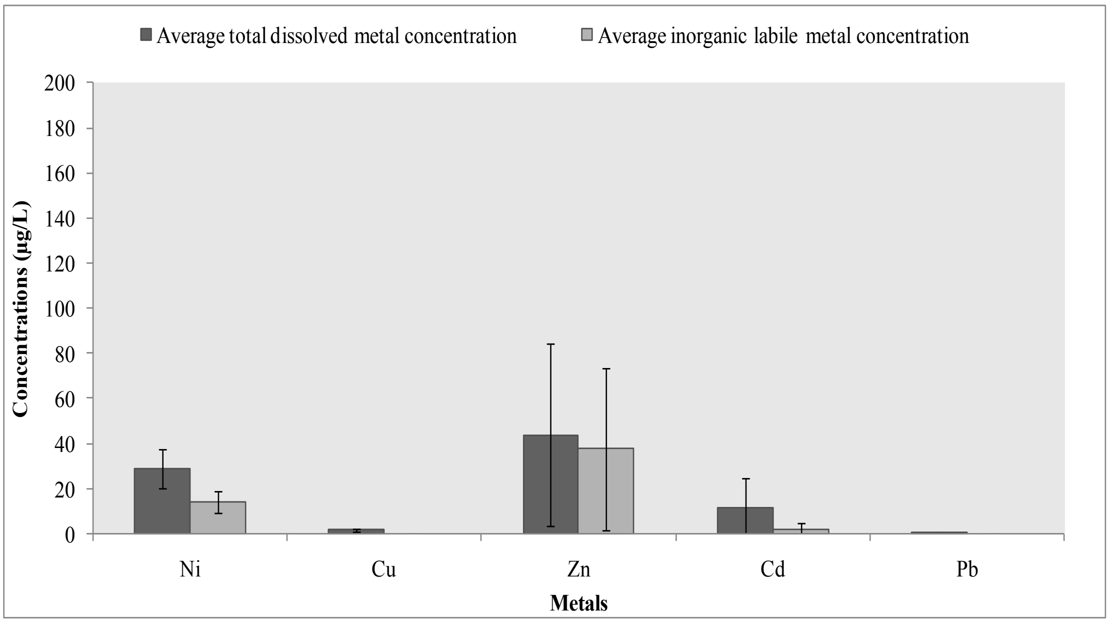


Figure 4.10 The total dissolved and labile concentrations of metals at site 8, downstream of mixing point in the canal for three time sampling.

4.4.9 The total dissolved, labile concentrations of metals and % lability at site 9, lake water beside the industrial zone in the industrial estate

Table 4.11, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 9, the lake water beside the industrial zone.

Table 4.11 The total dissolved, labile concentrations of metals and % lability at site 9, the lake water beside the industrial zone for three time samplings.

Stations	**Months**	**Metals**	**Total dissolved (µg/L)**	**Labile (µg/L)**	**% labile concentrations**
Site 9	**September**	**Ni**	27.3	4.30	15
		Cu	2.45	4.27×10^{-8}	<0.001
		Zn	105	26.6	25
		Cd	17.7	2.26	13
		Pb	4.66	2.59×10^{-4}	0.00556
	October	**Ni**	33.2	19.3	58
		Cu	0.94	4.27×10^{-8}	<0.001
		Zn	ND	ND	-
		Cd	19.7	4.35	22
		Pb	ND	ND	-
	November	**Ni**	31.6	9.92	31
		Cu	1.24	1.48×10^{-8}	<0.001
		Zn	95.7	58.3	61
		Cd	ND	ND	-
		Pb	12.8	1.08×10^{-3}	0.00847
	Average	**Ni**	30.7±3.04	11.2±7.56	35±21
		Cu	1.54±0.80	3.34×10^{-8} $\pm 1.61 \times 10^{-8}$	<0.001
		Zn	67.3±57.4	42.5	58±31
		Cd	12.5±10.8	3.31	12±11
		Pb	5.84±6.40	6.70×10^{-4}	0.00550 ±0.00300

ND*=Non Detectable

Graphically, the average concentrations in site 9 can be described as in Fig 4.11.

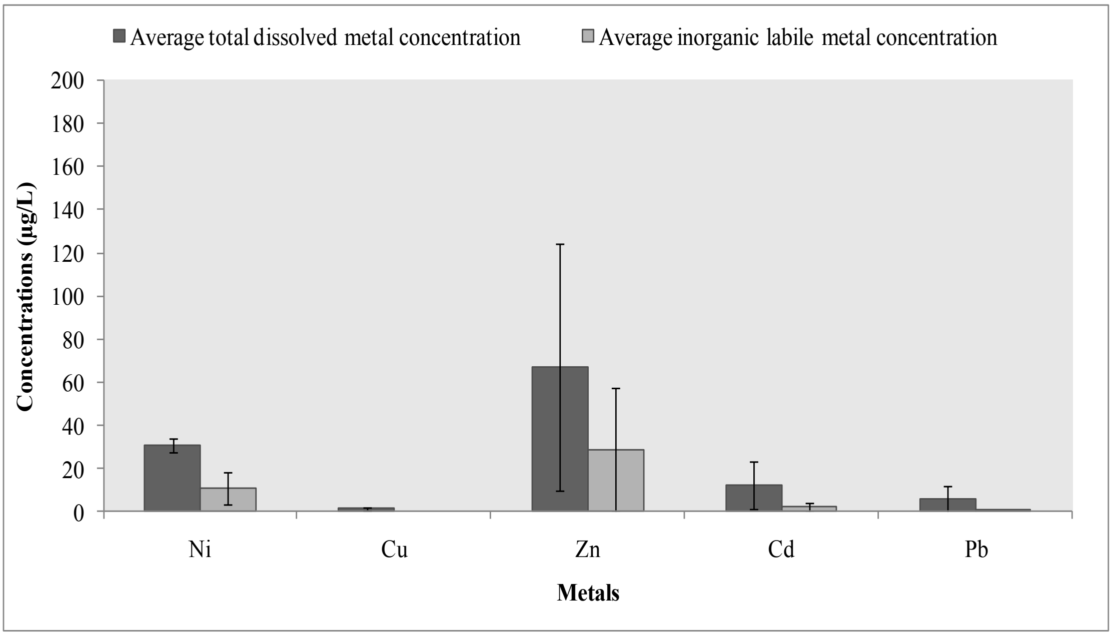


Figure 4.11 The total dissolved and labile concentrations of metals at site 9, the lake water beside the industrial zone for three time samplings.

4.4.10 The total dissolved, labile concentrations of metals and % lability at site 10 downstream far away from mixing point in the canal

Table 4.12, described all the total dissolved metals determined by ICPOES and computed inorganic species concentrations using Visual MINTEQ V.3, at site 10, downstream far away from mixing point in the canal.

Table 4.12 The total dissolved, labile concentrations of metals and % lability at site 10, downstream far away from mixing point in the canal for three time samplings.

Stations	**Months**	**Metals**	**Total dissolved (µg/L)**	**Labile (µg/L)**	**% labile concentrations**
Site 10	**September**	**Ni**	39.8	22.3	56
		Cu	36.1	$1.92\text{x}10^{-3}$	0.00532
		Zn	120	107	89
		Cd	ND	ND	-
		Pb	ND	ND	-
	October	**Ni**	25.4	15.2	60
		Cu	2.83	$3.35\text{x}10^{-6}$	<0.001
		Zn	ND	ND	-
		Cd	ND	ND	-
		Pb	ND	ND	-
	November	**Ni**	42.1	13.3	32
		Cu	2.81	$8.47\text{x}10^{-8}$	<0.001
		Zn	92.1	63.6	69
		Cd	30.9	5.03	16
		Pb	ND	ND	-
	Average	**Ni**	35.7±9.07	16.9±4.73	49±15
		Cu	13.9±19.2	$6.41\text{x}10^{-4}$ $\pm1.11\text{x}10^{-3}$	0.00181 ±0.00264
		Zn	71.24±62.2	85.3	82±11
		Cd	10.3±17.8	5.03	6±9
		Pb	0.11±0.00	ND	0.00194 ±0.00107

ND*=Non Detectable

Graphically, the average concentrations in site 10 can be described as in Fig 4.12.

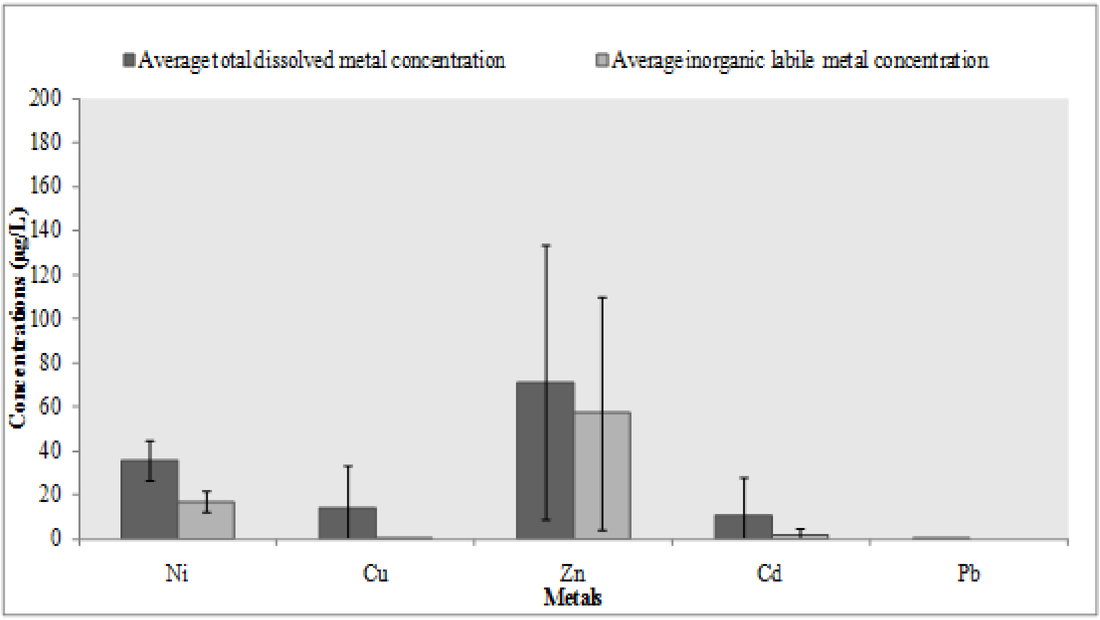
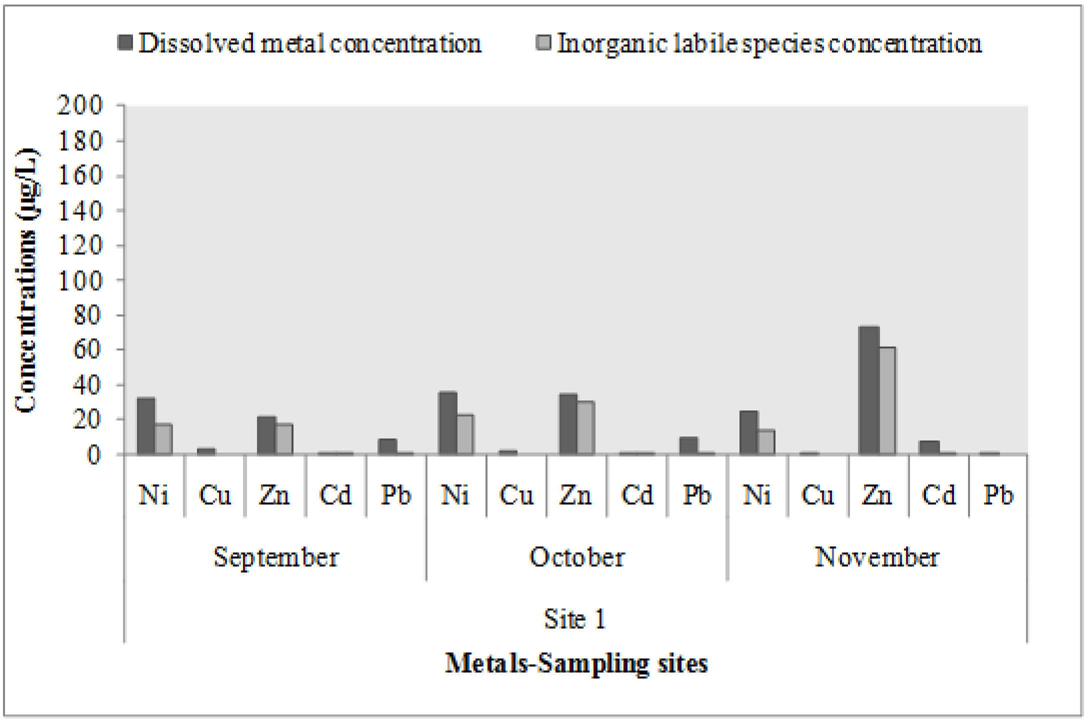


Figure 4.12 The total dissolved and labile concentrations of metals at site 10, downstream far away from mixing point in the canal for three time samplings.

4.5 Discussion on specific sites

4.5.1 Site 1 and Site 2

The dissolved and labile concentrations of metats at site 1, raw water, and site 2, treated water were descsribed at each sampling were described in Figure 4.13.



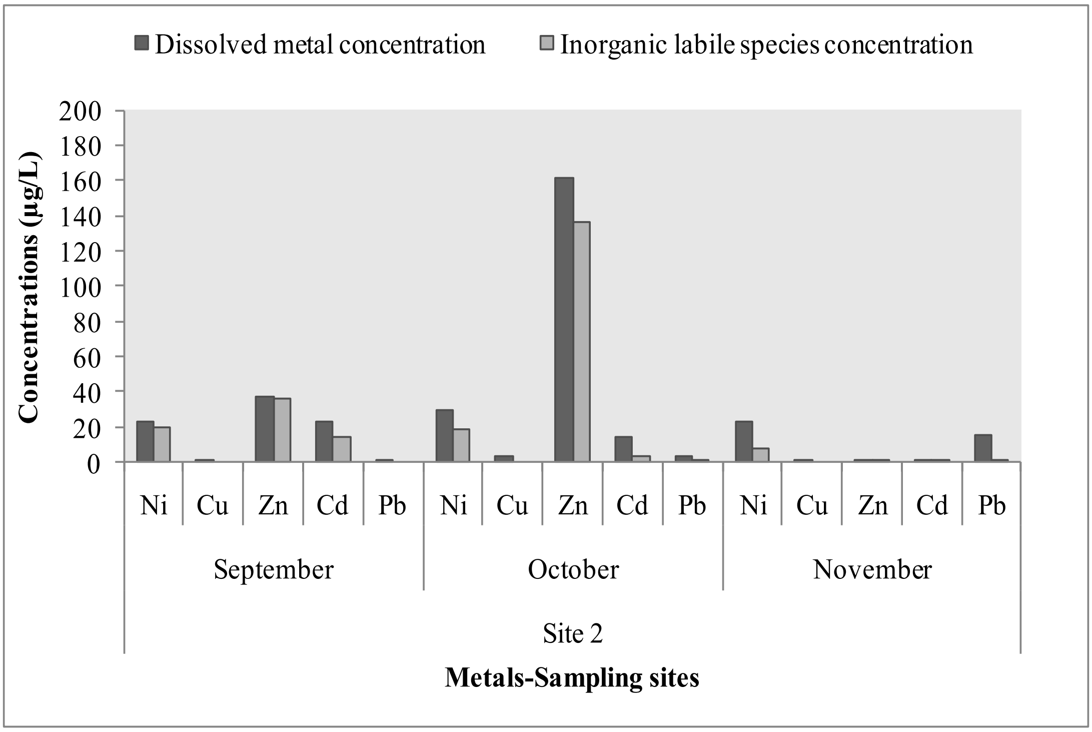


Figure 4.13 The dissolved and labile concentrations of metats at site 1, raw water, and site 2, treated water.

Higher dissolved metals in treated water for distribution within industrial estate collected at site 2 were observed compared to raw water of Chao Phraya River collected at site1; dissolved Zn at site 2 during September sampling and dissolved Cd, Cu, and Zn in October sampling were higher than those in site1. The probable reason is that a drop in pH measured at site 2 compared to that of site 1, raw water, in September and October sampling (7.07→6.64 in September and 7.32→6.69 in October) might have caused higher metals concentrations in treated water. Some treatment process in water treatment plant might drop a few unit of pH of raw water, which might dissolve insoluble metals forms causing more dissolved metals in treated water. However, it is difficult to make conclusions on one-time grab samples; it is necessary to take composite or time-average samples in order to draw effective conclusion.

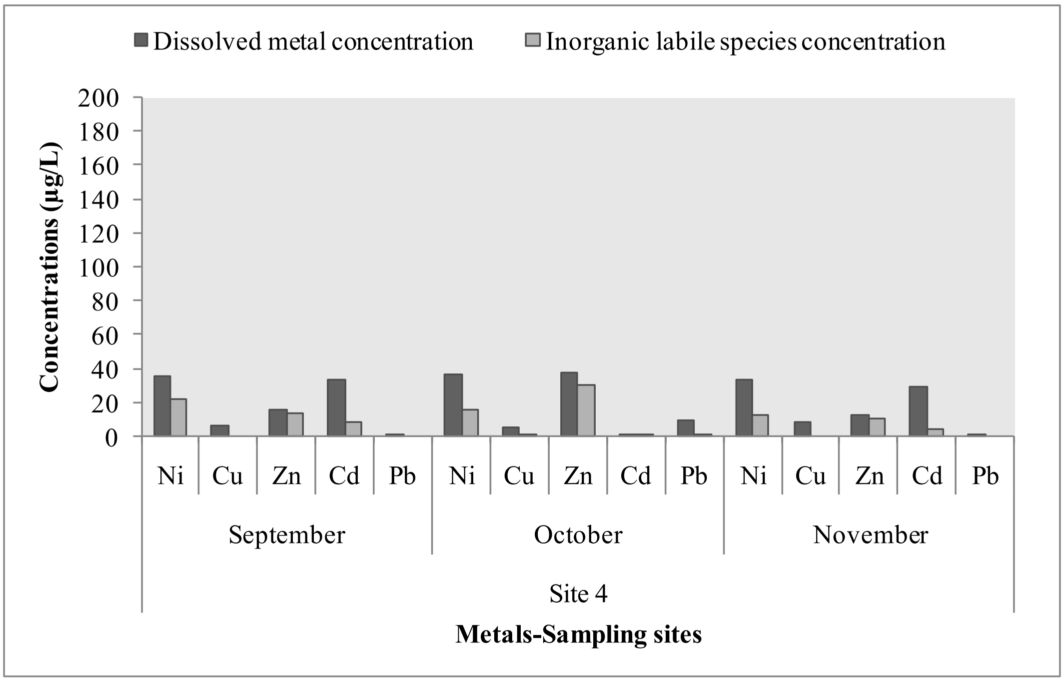
In Thailand, Surface Water Quality Standards concentrations were: 0.1 mg/L for Ni, 0.1 mg/L for Cu, 1.0 mg/L for Zn, 0.005 mg/L for Cd and 0.05 mg/L for Pb. In fact, the total concentrations were applied in any water quality standards. The dissolved concentrations of metals determined in this study are only a fraction of total concentrations, The comparisons were made to emphasize the fact that when dissolved concentrations exceed the Standard values, there is a high probability that total concentrations may exceed the Standards. In this study, at site1, raw water for the water treatment plant from Chao Phraya River,even the dissolved concentration Cd concentrations in November sampling, exceeded the Surface Water Quality Standard.

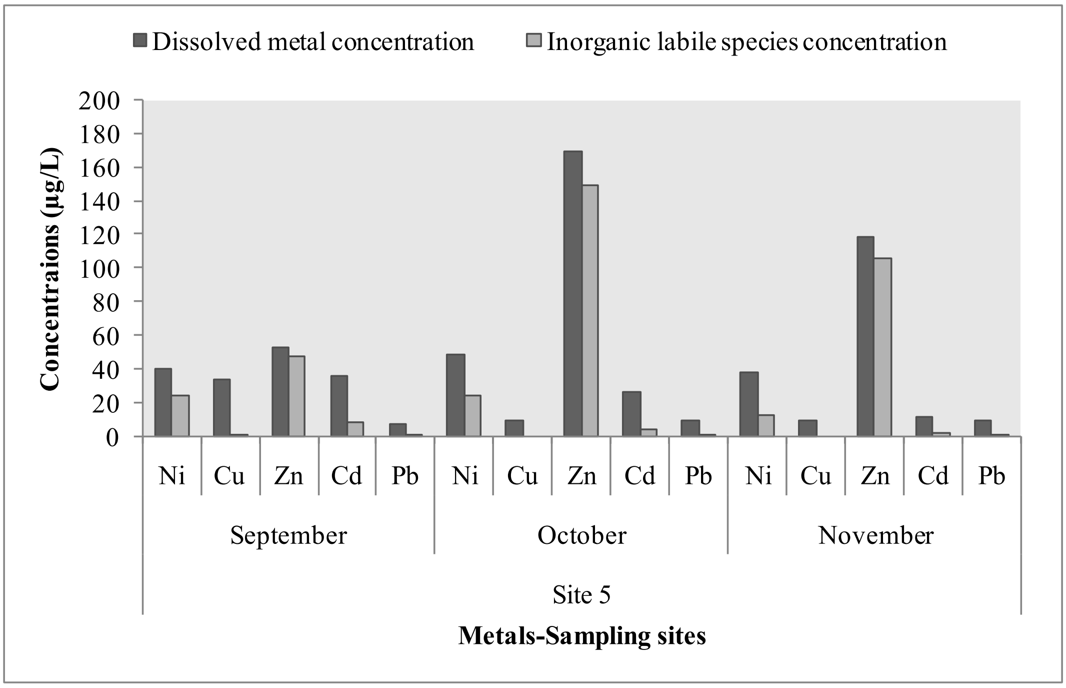
The Water Quality Standard of Metropolitan Waterworks Authority (WHO's guidelines) and Pollution Control Department (PCD), Thailand were: 0.02 mg/L for Ni (PCD, Thailand), 0.1 mg/L for Cu, 3 mg/L for Zn, 0.05 mg/L for Cd and 0.01 mg/L for Pb (WHO's guidelines). At site 2, treated water (Tap water), even the dissolved concentrations Ni at all and Pb at November samplings of this study, exceeded the standards.

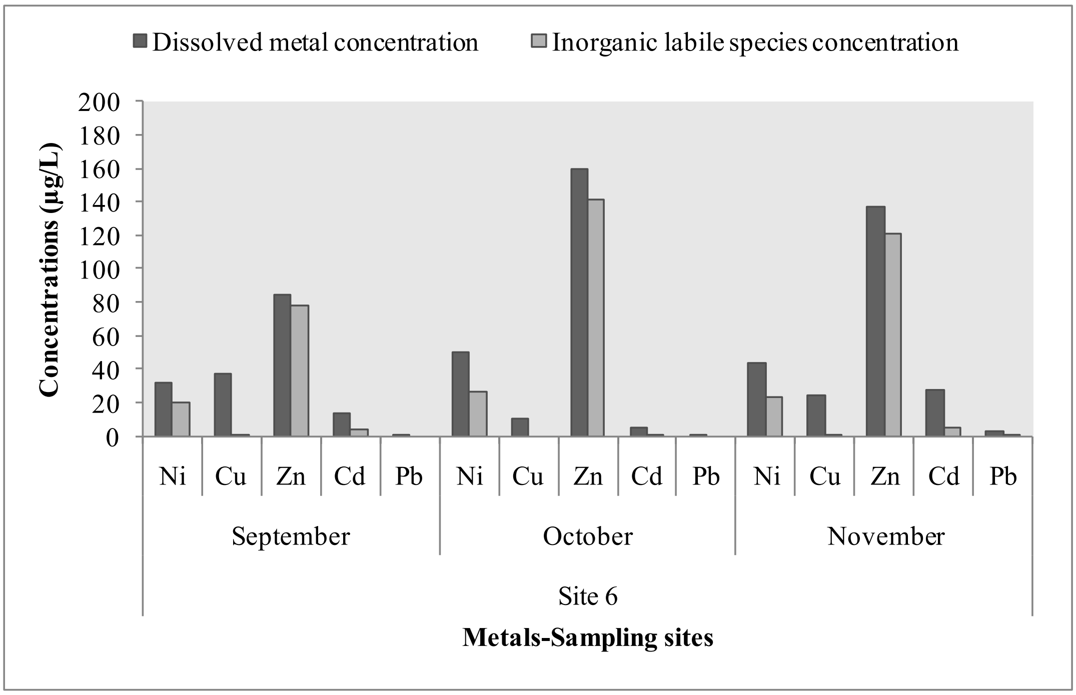
4.5.2 Site 4, site 5, site 6, and site 7

The dissolved and labile concentrations of metats at site 4, influent of

WWTP, site 5, treated wastewater before poshing pond, site 6, treated wastewater after poshing pond, and site 7, the point where treated effluent discharged into the canal (the mixing point) at each sampling were described in Figure 4.14.







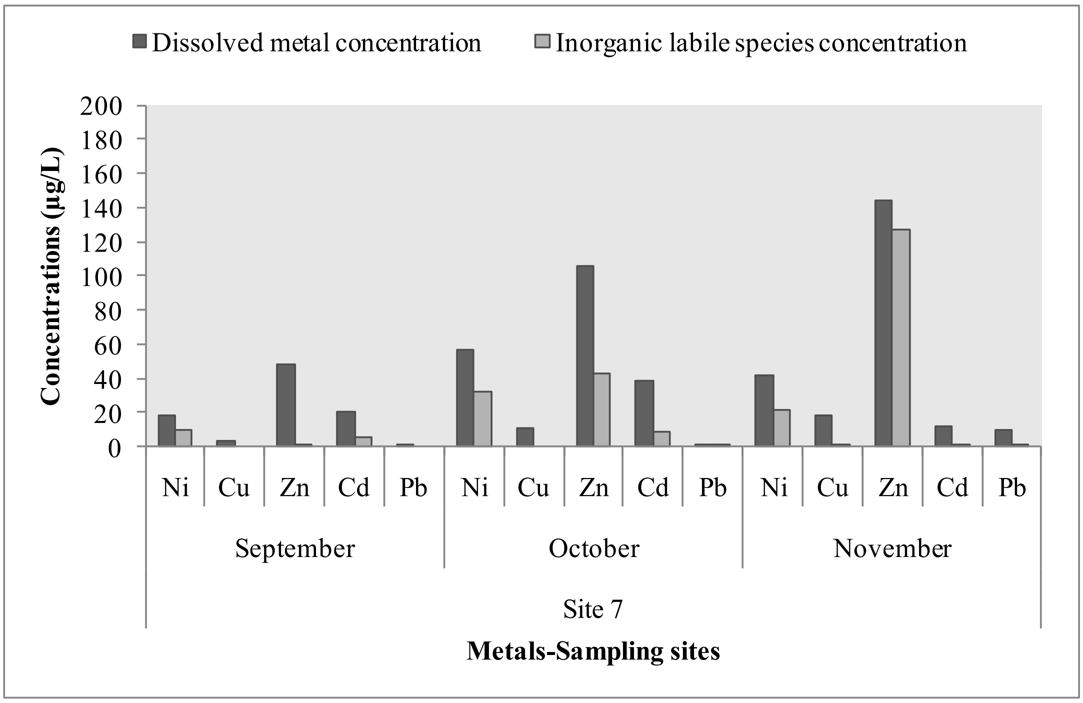


Figure 4.14 The dissolved and labile concentrations of metats at site 4, influent of WWTP, site 5, treated wastewater before poshing pond, site 6, treated wastewater after poshing pond, and site 7, the point where treated effluent discharged into the canal (the mixing point).

In all three samplings, the metal concentrations in effluent samples were higher than those in influent. In fact, WWTPs are not designed to reduce metal concentrations, but to reduce BOD or COD, thus, may not necessarily reduce metal concentrations. The WWTP in this study, dissolved organic carbon concentration in influent were found to be reduced in effluent and polishing pond. Organic carbon content after discharging into canal at site 7 may not be much different, however, the type of it, which affects much on metal speciation, may differ due to involvement of natural carbon of plant origin in canal; this is not involved in the scope of this study. Similar consideration can be made judging on one-time grab samples; composite or time-average samples should be taken in order to understand the removal scenario.

The Industrial Effluent Standard Concentrations in Thailand were: 1 mg/L for Ni, 2 mg/L for Cu, 5 mg/L for Zn, 0.03 mg/L for Cd and 0.2 mg/L for Pb. At site 5, treated effluent before the polishing pond at September sampling, even the dissolved concentrations Cd, exceeded standard. However, at site 6, effluent water after the polishing pond, also when compared with the Industrial Effluent Standard, the concentrations of dissolved metals were lower than the standard values at all three samplings.

4.5.3 Site 3

The dissolved and labile concentrations of metats at site 3, the groundwater from community distribution, were described in Figure 4.15.

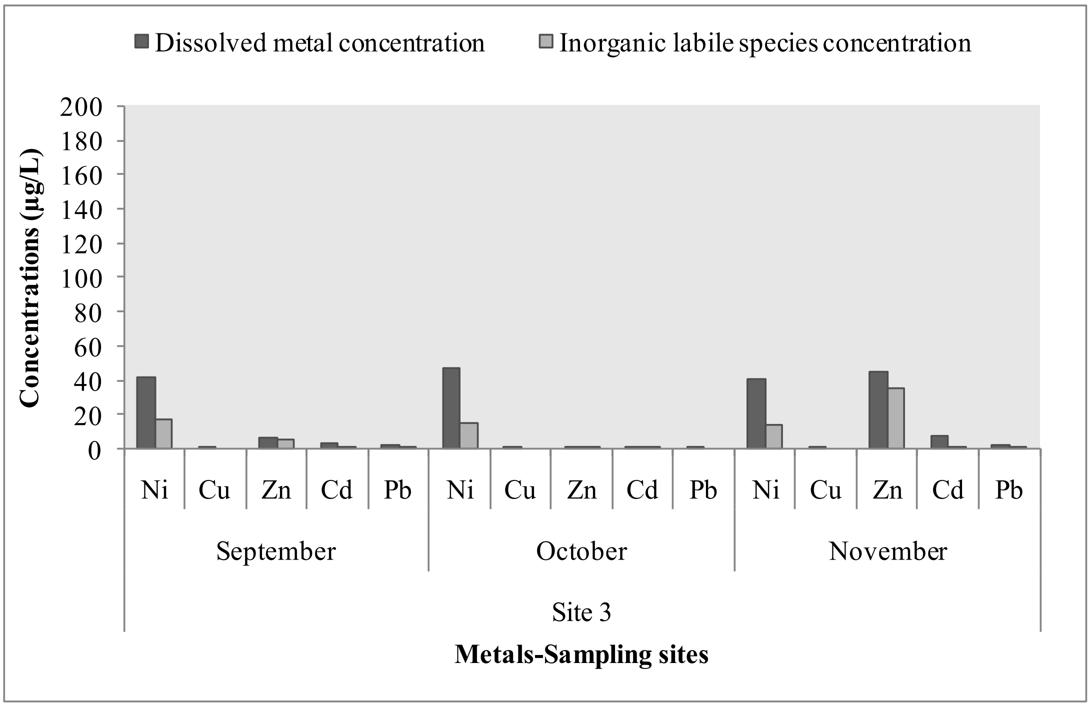


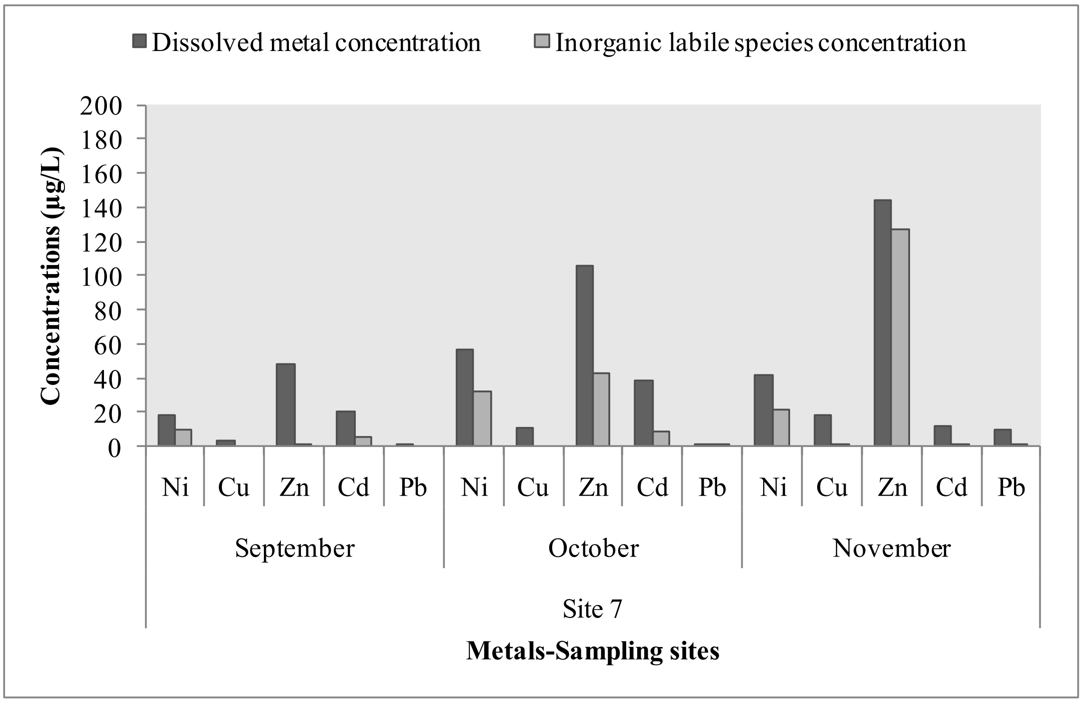
Figure 4.15 The dissolved and labile concentrations of metats at site 3, the groundwater from community distribution.

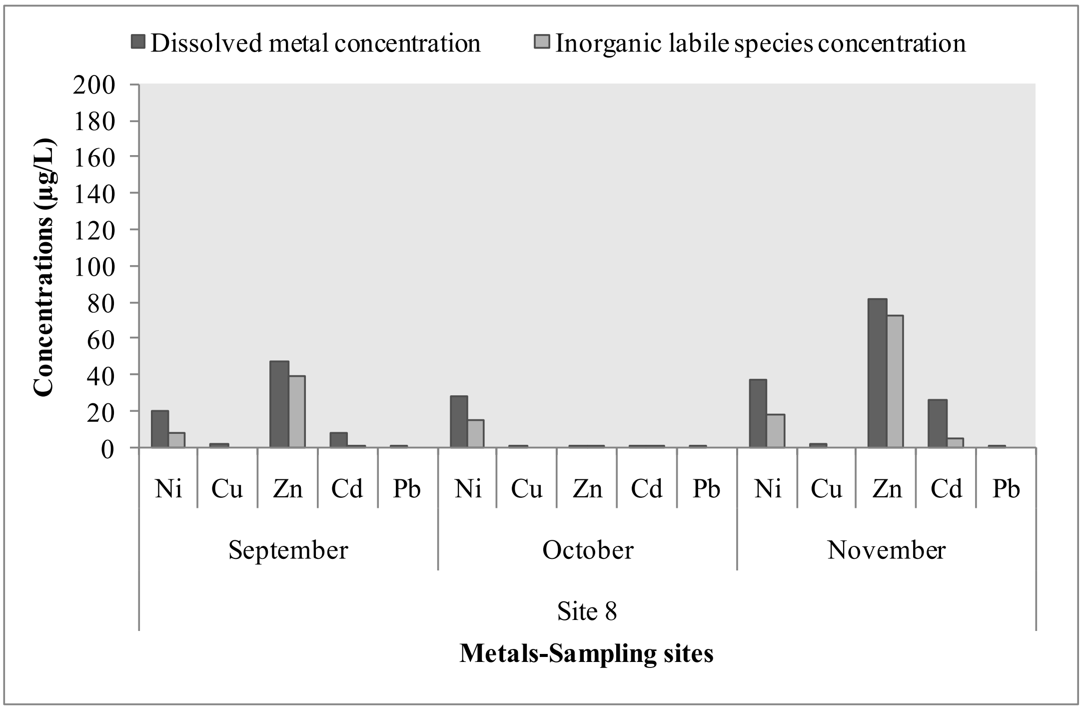
Extremely low dissolved concentrations of metals were expected for site 3, since it is the groundwater for the community distribution source. Compared to other sites, very low dissolved Cu (ND-0.46 µg/L) and Cd (ND-3.56 µg/L) were observed in samples collected at site3, in all samplings. Very low dissolved Zn (ND in October and 6.82 µg/L in September) and very low dissolved Pb (ND in October and November, 2.59 µg/L in September) were found too. Dissolved Ni concentrations at site3 were comparable to influent or effluent of WWTP, which might indicate the existence of a contamination source of Ni around the area. Even though Ni concentrations were comparable to those in other sites, relatively lower labilities in groundwater were observed, which might indicated that the Ni source is different from that in the influent/effluent of WWTP. In fact, visual MINTEQ is designed for surface water, however, it was assumed as valid to use for groundwater at site 3 because the water samples were collected from the distribution tap in community. When groundwater passes through the tap, it is in contact with atmosphere and in equilibrium with atmospheric CO_2; it might be in the same condition as the surface water. Regarding the lower labilities of groundwater Ni should be confirmed by other speciation devices.

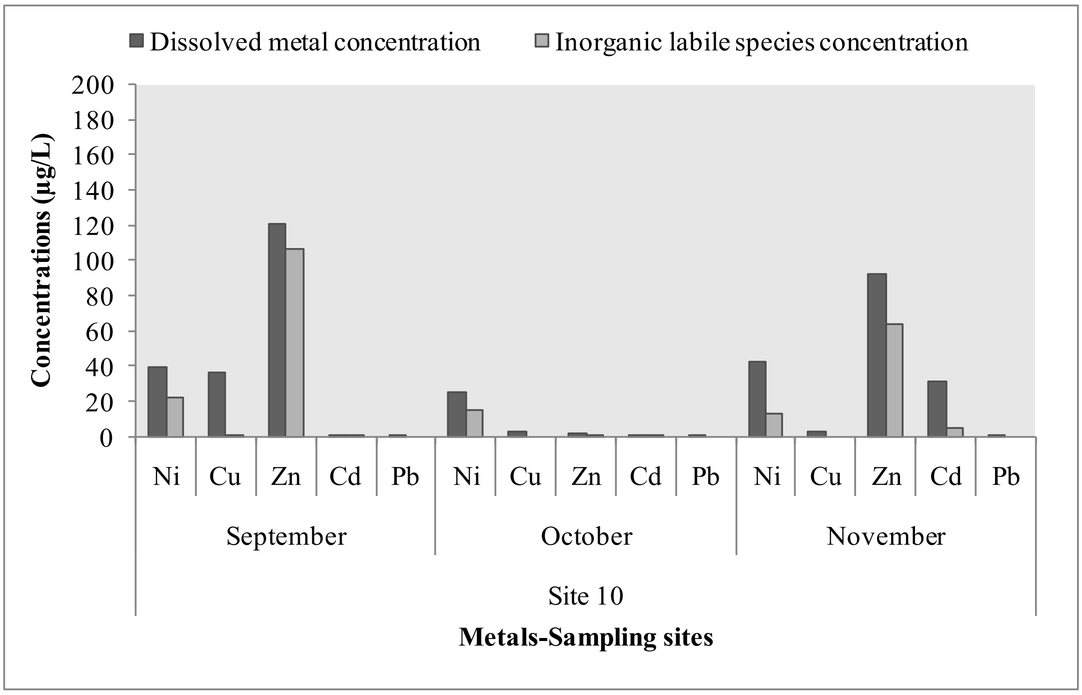
The Groundwater Quality Standard concentrations (reference) were less than 0.02mg/L for Ni, less than 1.0 mg/L for Cu less than 5 mg/L for Zn, less than 0.003 mg/L for Cd and less than 0.01 mg/L for Pb. Ni concentrations at all sampling and Cd at September and November samplings of this study, even the dissolved concentrations, exceeded the standards.

4.5.4 Site 7, site 8, site 10 and site 9

The total dissolved and labile concentrations of metals at site 7, the mixing point of WWTP in canal, site 8, downstream after mixing point, site 10, downstream after mixing point, and site 9, lake water beside industrial zone were described in Figure 4. 16




Dissolved metal concentration
Inorganic labile species concentration
Concentrations (µg/L)
200
180
160
140
120
100
80
60
40
20
0
Ni
Cu
Zn
Cd
Pb
September
October
November
Site 8
Metals-Sampling sites


Dissolved metal concentration
Inorganic labile species concentration
Concentrations (µg/L)
200
180
160
140
120
100
80
60
40
20
0
Ni
Cu
Zn
Cd
Pb
September
October
November
Site 10
Metals-Sampling sites

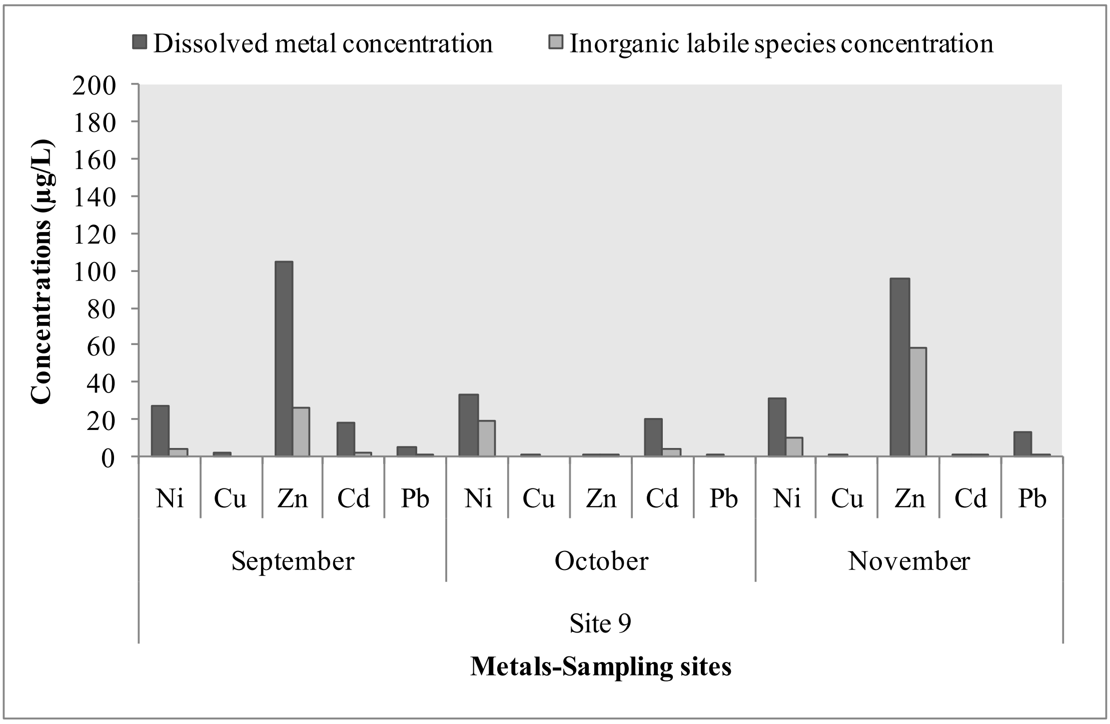


Figure 4.16 The total dissolved and labile concentrations of metals at site 7, the mixing point of WWTP in canal, site 8, downstream after mixing point, site 10, downstream after mixing point, and site 9, lake water beside industrial zone.

Since they are the outdoor sites, and sites 7, 8, and 10 receive the effluent of WWTP, it was expected that metal concentrations and speciation scenario would be different. However, no much difference was found in calculated speciation profile. Being an outdoor site, due to a heavy rain during October sampling, thus, very low dissolved Zn, Pb and Cd were observed in these sites, Ni and Cu dissolved concentrations did not differ from those of other two samplings.

Site 9, the lake within industrial estate but not very close to industrial zone, is assumed as the unique surface water site in current sampling scheme. There is no visible discharge of any point source of wastewater or effluent from WWT, yet comparably high dissolved metals with effluent receiving waters, sometimes higher than them, were observed. The reason could be the non point sources around it; being the parking area around the lake and road run-off could be the contributors of dissolved metals and minerals. Remarkable finding is that pH of site 9 was the highest among other surface waters in this study (8.96 in September and 8.47 in November sampling, respectively); the reason must be cumulative minerals dissolved in lake water over times since the lake seem to have limited flow. Lower pH in October sampling (7.50) indicated dilution due to rain.

In Thailand, Surface Water Standards concentrations were: 0.1 mg/L for Ni, 0.1 mg/L for Cu, 1.0 mg/L for Zn, 0.005 mg/L for Cd and 0.05 mg/L for Pb (reference). At site7, the mixing point of effluent with canal water, even the dissolved concentration of Cd at all samplings exceeded the standard. Other sampling site, downstream after the mixing point (site 8), Cd at September and November sampling exceeded the standard. In addition, Cd in the lake water (site 9), even the dissolved concentrations exceeded the standard at September and October sampling. Moreover, at site 10, downstream far away from the mixing point, even the dissolved concentrations Cd at November sampling exceeded the standard.

4.6 Overview of metals

4.6.1 Ni in all sites

Throughout the samplings for 3 times, least variation was observed for Ni concentrations. Remarkable fact is that groundwater Ni concentrations at site 3 were found to be higher than raw water samples collected at site 1. Variation in labilities (%) did not differ much, though relatively lower labilities (35± 5) were found in samples taken in site 3 in all samplings and site 9, lake within the industrial estate, in September and November sampling (15% for September and 31% for November sampling) respectively.

4.6.2 Cu in all sites

Highest dissolved Cu concentrations were associated with influent or effluent, polishing pond effluent of the WWTP in the industrial estate and mixing point of polishing pond effluent and canal water. From this finding, it can be assumed that there might be a point source of dissolved Cu which flows into the influent of WWTP; it seems to persist to the effluent stream, polishing pond effluent until the polishing pond effluent is discharged into the canal. A high concentration of Cu was found in site 10, downstream far away from the mixing point of WWTP in September sampling.

All the samples showed very low %lability of Cu. Since lability in this study is the percent of unbalanced inorganic species over total dissolved species concentration, low %labilty of Cu mean Cu inorganic species were very low and almost all the dissolved Cu might be organic form. The affinity of Cu to organic matter and stability of organo-copper complexes (Bubb et al., 1991) might have caused low %lability of Cu.

4.6.3 Zn in all sites

Highest dissolved Zn concentrations, concentrations higher than 100 µg/L were found in site 5, 6 and 7 the effluent stream, polishing pond effluent until the polishing pond effluent is discharged into the canal in October and November samplings and relatively higher compared to raw water in September sampling, indicating possible the domestic sources. Over 100 µg/L Zn concentration were also found in the treated water for distribution at site 2 in September sampling for unknown reasons, also during September sampling, Zn concentration higher than 100 µg/L were found in the samples taken in site 9, which could be cumulated minerals in lake, and at site 10, which could be residual discharged Zn or fecal contamination. Among all metals, Zn showed the highest lability indicating that most of the Zn are inorganic forms. Reduced labilities of Zn were observed in site 9, the lake; this is expected as other sources might contribute minerals and metals in lake.

4.6.4 Cd in all sites

Highest dissolved Cd concentrations were found in the samples taken at site4 and site5, the influent and the effluent of WWTPs in September sampling, at site5 and site7, the effluent of WWTP and the point where WWTP's polishing pond discharge and the canal mix in October sampling and at site4 and site6, the influent to WWTP and the WWTP's polishing pond discharge in November sampling. These results indicate that there is a source (sources) of Cd in the influent stream to WWTP, and the flow of it might be intermittent fashion, suggesting a likely industrial source. The dissolved Cd seems to persist after discharge in canal, dissolved Cd of downstream in canal are somewhat high, except in october sampling which was conducted during heavy rain. Lake water samples taken in September and October showed high dissolved Cd, this might indicate the cumulated Cd due to limited flow in the lake. Labilities of Cd barely exceeded 25%.

4.6.5 Pb in all sites

High dissolved Pb were found in sample taken in WWTP effluent in September sampling, influent and effluent of WWTP in October, and effluent and the point where WWTP's polishing pond discharge and the canal mix in November. Similar conclusion for Cd can be made that there might be a resource (sources) of Pb in the influent stream to WWTP, more likely an industrial source (sources). Highest dissolved Pb were found in site1, raw water sample taken from the Chao P hraya River in October sampling, and at site2, treated water for distribution in November sampling. The possible reason for high Pb in October sampling can be the contribution of non-point sources caused by weather conditions, though the reason for latter cannot be given. Lake water samples taken in September and November showed high dissolved Pb, indicating existence of cumulated Pb. Labilities of Pb rarely exceed 1% of the dissolved Pb, indicating that the environmental setting of the sampling sites in this study did not favor the formation of inorganic species of Pb.

4.7 Dissolved organic carbon in water environment within and around an industrial estate

DOC concentrations were measured 10 sampling sites in water environment within and around an industrial estate for three time samplings were descsribed in Figure 4.17. In other studies dealing with DOC in WWTPs, concentrations in untreated wastewater were found to be 72 mg/L (Katsoyiannis and Samara, 2007), 82 mg/L (Dignac et al. 2000), 60 mg/L (Escals et al.,2003), 59 mg/L (Ueda and Hata,

1999) and 11.1 mg/L(Ahn and Song 1999). The DOC results of this study at WWTP influent (site 4) were: 41.7 mg/L, 67.6 mg/L and 50.4 mg/L in September, October and November sampling, respectively. These DOCs decreased in water after treatment, 39.7 mg/L, 52.2 mg/L and 39.7 in treated effluent before the polishing pond (site5), 31.6 mg/L, 51.5 mg/L and 42.7 mg/L in effluent water after the polishing pond (site6), in September, October and November sampling, respectively, indicating the degradation of biodegradable-DOC occuring. In literature, DOC values of treated wastewater were found 19 mg/L (Katsoyiannis and Samara, 2007), 3.7 mg/L (Ueda and Hata, 1999) and 22 mg/L (Escalas et al., 2003).

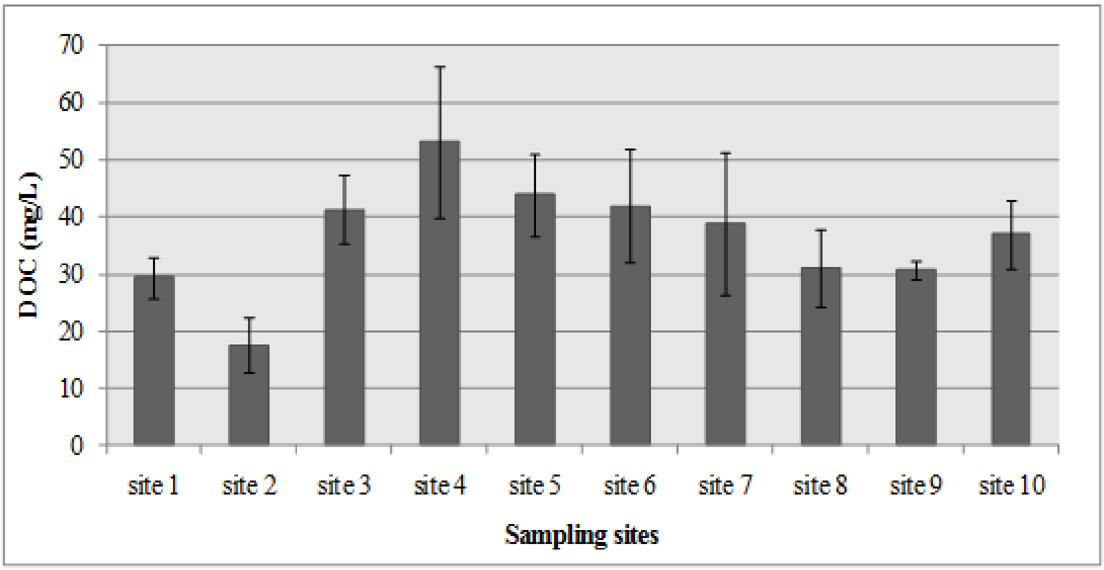


Figure 4.17 The average dissolved organic carbon concentrations of 10 sampling sites in water environment within and around an industrial estate 3 time samplings**.**

The negative correlations between labile metals with DOC were expected; the Higher the DOC concentration, the more complexations may take place, thus the lower labile species concentrations. Strong negative correlations in this study might indicate the interactions between these metals and organic matters at certain sites and at certain environmental setting.

4.8 Comparison of Empore^{TM} and Vistual MINTEQ

The figure 4.18 shows the labile concentrations of metals calculated using visual MINTEQ and those measured using a speciation device called Empore™. The comparison was done on all the samples collected from site 1 to site 10 in November samplings. The calculated labile Ni and Zn concentrations were much higher, Cd slightly higher, in all sites than the values determined using Empore™. The calculated labile Cu and Pb, as well as Empore™ values were very low, indicating most of the species of them are in complex forms. Different values of Cd, Ni and Zn determined by two methods would be the difference in nature of organic matters, which may differ the complex formation capacity assumed in the model and the organic matter found in the samples of this study, or simply instrumental measurement errors. The other reason for the difference in results estimated by two methods can be speciation changes during storage, sample handling and Empore™ procedures, which was an important common source of error which were shown in Fig 4.18.

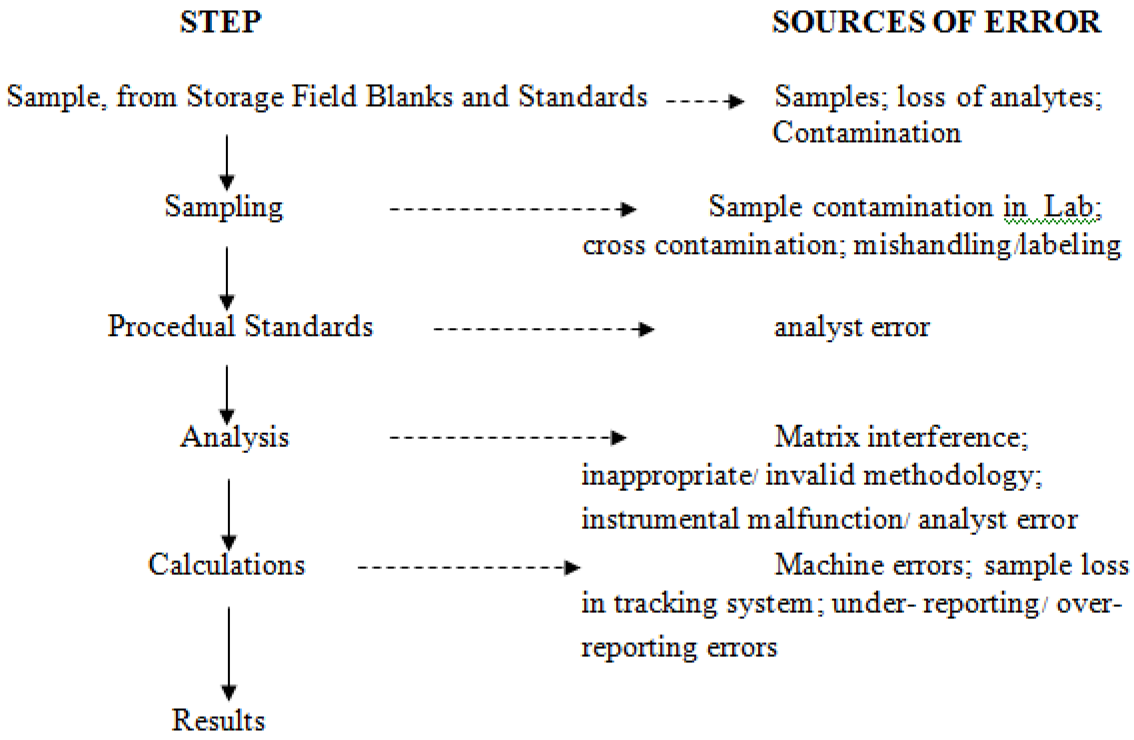


Fig 4.18 Step in water sample analysis and source error.

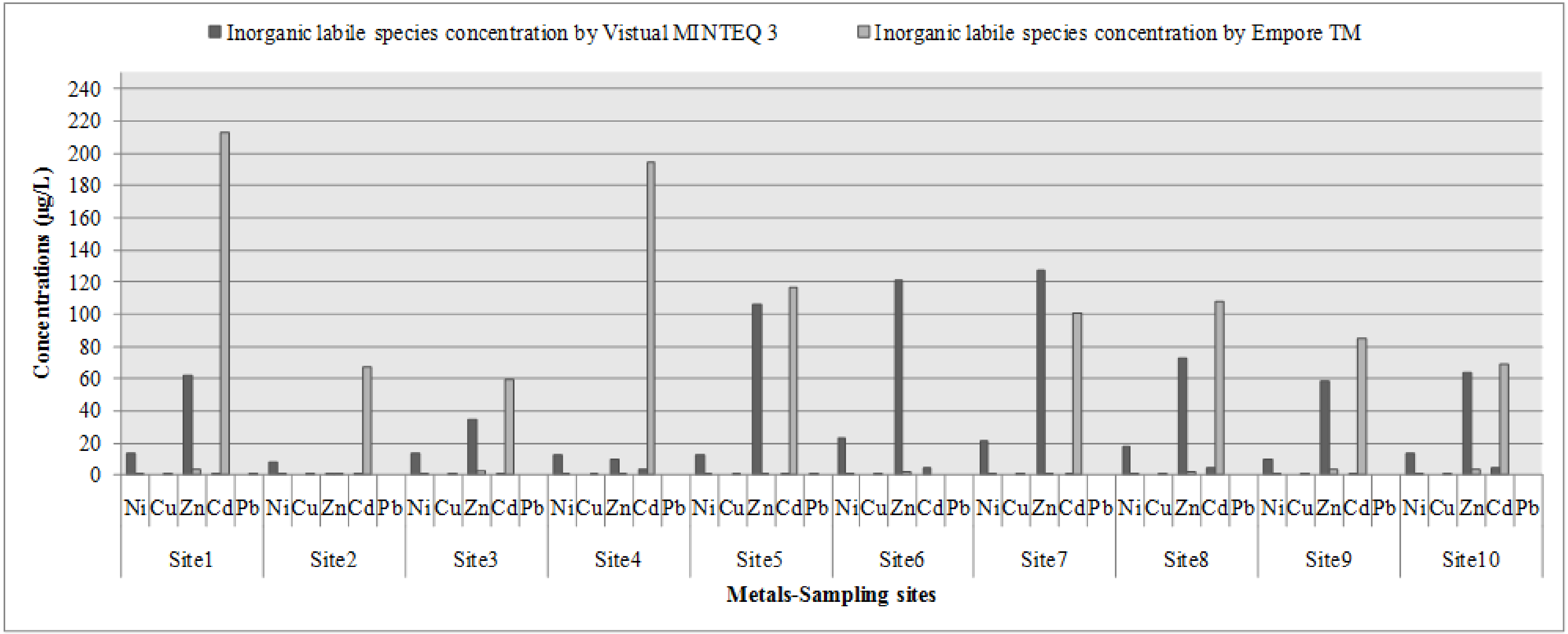


Figure 4. 18 The comparison of labile metals calculated using visual MINTEQ and Empore™ speciation devices.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in 5 samples collected from the Chao Phraya River in the stretch between 83 and 29 km away from the river mouth were, 71.8± 12.1 µg/L, 3.38± 7.02 µg/L, 75.8± 61.6 µg/L, 7.18± 1.86 µg/L, 6.71± 6.14 µg/L. The labilities (%) were 96± 1.8%, 7.3± 14% (when a value of a site was exclude, 1.3± 0.87%), 99± 0.64%, 74± 9% and 3.8± 2.5%, respectively. Compared to the work of Ponprasert (1979), the average concentrations of this study were found to be lower. This might be due to the more stringent regulations on industrial discharges and the more attention of the authorities and public given to river sustainability and environment in recent times.

2. Concentrations of metals in ten samples collected in and around an industrial estate varied in three sampling carried out in September, October and November.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 1 were, 18.0± 4.77 µg/L, 4.94x10^{-6}± 5.32x10^{-6} µg/L, 36.3± 22.9 µg/L, 0.39± 0.67 µg/L and 1.96x10^{-3}±1.75x10^{-3} µg/L. The labilities (%) were 58± 7%, <0.001± <0.001%, 83± 3, 7.02± 7.49 and 0.02± 0.02%, respectively.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 2 were, 15.7± 6.63 µg/L, 1.59x10^{-5}± 2.74x10^{-5} µg/L, 57.7± 70.4 µg/L, 5.9± 7.26 µg/L and 1.63x10^{-3}±1.78x10^{-3} µg/L. The labilities (%) were 61± 25%, 0.001± 0.001%, 80± 19%, 29± 31% and 0.04± 0.01%, respectively.

-The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 3 were, 15.3± 1.51 µg/L, $9.60x10^{-10}$± $7.84x10^{-10}$ µg/L, 13.7± 18.5 µg/L, 0.23± 0.23 µg/L and $6.30x10^{-5}$±$6.53x10^{-5}$ µg/L. The labilities (%) were 35± 5%, <0.001± <0.001%, 74± 5%, 4± 3% and 0.003± 0.002% of the dissolved metals, respectively, are found to be labile.

-The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 4 were, 16.7± 4.59 µg/L, $4.98x10^{-5}$± $4.41x10^{-5}$ µg/L, 17.9± 10.6 µg/L, 4.03±4.19 µg/L and $3.98x10^{-4}$±$6.86x10^{-4}$ µg/L. The labilities (%) were 48± 12%, 0.001± 0.001%, 83± 5%, 13±11% and 0.006± 0.006% of the dissolved metals, respectively, are found to be labile.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 5 were, 20.1± 6.51 µg/L, $7.79x10^{-4}$± $1.28x10^{-3}$ µg/L, 101± 51.2 µg/L, 4.58±3.36 µg/L and 0.03±0.05 µg/L. The labilities (%) were 48± 13%, 0.003± 0.003%, 89± 1%, 18± 5% and 0.35± 1% of the dissolved metals, respectively, are found to be labile.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 6 were, 23.1± 3.14 µg/L, $2.18x10^{-3}$± $3.38x10^{-3}$ µg/L, 114± 32.5 µg/L, 2.93± 2.29 µg/L and $8.33x10^{-5}$± $1.30x10^{-4}$ µg/L. The labilities (%) were 56± 5%, 0.01± 0.01%, 90± 2%, 18± 9% and 0.005±0.003%, respectively.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 7 were, 21.5± 11.2 µg/L, $9.16x10^{-5}$± $9.46x10^{-5}$ µg/L, 56.8± 64.7 µg/L, 5.25±3.39 µg/L and $4.71x10^{-4}$±$7.18x10^{-4}$ µg/L. The labilities (%) were 55± 3%, 0.001± <0.001%, 43± 44%, 21± 7% and 0.01± 0.004%, respectively.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 8 were, 13.8± 4.84 µg/L, $2.72x10^{-6}$± $4.33x10^{-6}$ µg/L, 37.6± 35.9 µg/L, 1.99± 2.46 µg/L and $2.04x10^{-7}$±$7.88x10^{-7}$ µg/L. The labilities (%) were 47± 5%, <0.001± <0.001%, 83± 6%, 12± 9% and 0.002±0.001%, respectively.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 9 were, 11.2± 7.56 µg/L, $3.34\text{x}10^{-8}$± $1.61\text{x}10^{-8}$ µg/L, 28.7± 28.7 µg/L, 2.20± 2.17 µg/L and $4.47\text{x}10^{-4}$±$5.63\text{x}10^{-4}$ µg/L. The labilities (%) were 35± 21%, <0.001± <0.001%, 58± 31%, 12± 11% and 0.01±0.003%, respectively.

- The average inorganic species concentrations of Ni, Cu, Zn, Cd and Pb in site 10 were, 16.9± 4.73 µg/L, $6.41\text{x}10^{-4}$± $1.11\text{x}10^{-3}$ µg/L, 57.1± 53.0 µg/L, 1.68± 2.90 µg/L and 0.00±$1.21\text{x}10^{-6}$ µg/L. The labilities (%) were 49± 15%, 0.002± 0.003%, 82± 11%, 6± 9% and 0.002±0.001%, respectively.

3. Remarkable findings in industrial estate samples are as follows:

- Treated water showed higher dissolved concentrations of some metals due to decrease in pH during treatment facilities.

- Dissolved concentrations of metals in treated wastewater after activated sludged process and polishing pond treatment did not seem to differ much with those of influent stream which flowed into WWTP, which is in accordance with the previous studies.

- Groundwater near the estate normally showed low dissolved metals; high Zn and Cd were found in different sampling though.

- The canal water that received WWTP's effluent showed some level of dissolved metals; the lake inside the estate compound showed a bit different metals levels, pH and % labilities in some cases, indicating that the source of metals might be different.

- Zinc showed highest labilities in all samples, which indicated that the environmental settings in all sites favored forming inorganic species. Lowest labilities were found in Cu and Pb, uniformed and moderately high labilities are found in Ni despite difference in sampling sites, and labilities of Cd varied to an extent.

4. Comparison of Empore$^{\text{TM}}$ and Vistual MINTEQ

Comparing the labile species calculated by Visual MINTEQ 3 and determined by Empore™ speciation device, the calculated labile Cu and Pb, the calculated labile Ni and Zn concentrations were much higher, Cd slightly higher, in all sites than the values determined using Empore™ . The calculated labile Cu and Pb, as well as Empore™ values were very low, indicating most of the species of them are in complex forms. Different values of Cd, Ni and Zn determined by two methods would be the difference in nature of organic matters, which may differ the complex formation capacity assumed in the model and the organic matter found in the samples of this study, *or simply instrumental measurement errors*. The other reason for the difference in results estimated by two methods can be speciation changes during storage, sample handling and Empore procedures, which was an important common source of error. More studies on speciation of metals are recommended.

5.2 Recommendations

Since rive sediments play an important role in dissolved concentrations of metals, the concentration levels of sediment in the Chao Phraya River should be studied in parallel with the speciation studies.

Industries are known polluters in terms of metal contamination in all environmental media. However, when the fact that the content of bioavailable portions/species of metals as the only threat to environment is considered, the image would be not as unpleasant as the one under the concentration of total metal levels. More speciation studies should be conducted.

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APPENDICES

APPENDIX A

Detailed Procedure for Sample Analysis

A-1 Analytical technigues:

ICP

- **Stock standard solution:** ICP – Multi Element Standard Solution at 1000 ppm
- **Working Standard Solution:** Prepared ICP – Multi Element Standard Solution

of 0.001, 0.005, 0.01, 0.02, 0.005, 0.1, 0.2, 0.05, 0.1, 0.2, 0.5, 1, 3, 5, 10, 20, 30 and 50 ppm (Adjusted Volume with 1% (v/v) HNO3)

IC

- **Stock standard solution:** Nitrite, Phosphate and Bromide Standard Solution at 1000 ppm
- **Working Standard Solution:** Prepared IC - Nitrite, Phosphate and Bromide Standard Solution of 0.01, 0.02, 0.05, 0.1, 0.5, 1, 5, 10, 20, 30 and 50 ppm (Adjusted Volume with DI)

TOC

- **Stock standard solution:** TC Standard Solution at 1000 ppm
- **Working Standard Solution:** Prepare TC - Potassium hydrogen phthalate, stock

solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 1.0625 g of potassium hydrogen phthalate ($C_8H_5KO_0$) (dried for 2 hrs at a temperature between 105° C and l20° C, Desicator > 2hrs), and make up to volume with water. TC Standard Solution of 0.00, 20.8, 35.7, 50.0, 83.3, 125, 250 ppm (Adjusted Volume with DI)

- **Stock standard solution:** IC Standard Solution at 1000 ppm
- **Working Standard Solution:** Prepare IC-- Sodium bicarbonate, stock

solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 1.35 g of Sodium bicarbonate ($NaHCO_3$) (dried for 1 hr at a temperature between 280º C and 290º C, Desicator > 2hrs), and make up to volume with water, Sodium carbonate, stock solution 1000 mg/l Dissolve in a 500 ml one-mark volumetric flask 2.21 g of Sodium carbonate (Na_2CO_3) (dried for 2 hrs at a temperature between 280º C and 290º C, Desicator > 2hrs), and make up to volume with water. IC Standard Solution of 5, 10, 35.7, 83.3, 125, 250 ppm (Adjusted Volume with DI).

Table A-1 Accuracy and Precision

Element (n=2)	**Certified Values (µg/l)**	**Analyze Result Average Concentration (µg/l)**
Aluminum	142 ± 8.60	120±40.0
Barium	544 ± 5.80	540±20.0
Bismuth	14.1± 0.15	40±20.0
Boron	158 ± 3.90	470±210
Cadmium	6.57 ± 0.07	10.0±0.12
Calcium	$300 \pm 1.10x10^3$	$8.81x10^3 \pm 6.65x10^3$
Copper	22.8 ± 0.31	40.0±20.0
Iron	98.1 ± 1.40	70.0±70.0
Lead	19.6 ±0.21	10.0±10.0
Lithium	17.4 ±1.70	10.0±10.0
Magnesium	804 ± 98	$7.96x10^3 \pm 1.80x10^2$
Manganese	39.0 ± 0.45	40.0±0.00
Nickel	62.4 ± 0.69	60.0±2.00
Potassium	$2.03x10^3 \pm 29$	$1.21x10^4 \pm 1.40x10^4$
Silver	1.06 ± 0.08	30.0±40.0
Sodium	$2.07x10^4 \pm 260$	$1.66x10^4 \pm 1.66x10^3$
Strontium	323 ± 3.6	$3.30x10^2 \pm 30.0$
Thallium	7.45 ± 0.10	70.0±100
Zinc	78.5 ± 2.20	80.0±10.0

Table A-2 Correlation analysis of %labile metal concentrations and dissolved organic carbon (DOC) concentrations of 5 sampling sites at Chao Phraya River

% labile inorganic	*r*	*p*
Ni	-0.90	0.04
Cu	-7.00	0.19
Zn	0.05	0.94
Cd	-1.00	0.00
Pb	-0.80	0.20

Table A-3 Correlation analysis of %labile metal concentrations and dissolved organic carbon (DOC) concentrations of 10 sampling sites in water environment within and around an industrial estate for three time samplings.

Stations	% labile inorganic	*r*	*p*
Site 1	**Ni**	-0.50	0.67
	Cu	1.00	0.00
	Zn	-0.50	0.67
	Cd	-1.00	0.00
	Pb	-1.00	0.00
Site 2	**Ni**	-0.50	0.67
	Cu	0.00	0.00
	Zn	-1.00	0.00
	Cd	1.00	0.00
	Pb	0.00	0.00
Site 3	**Ni**	-1.00	0.00
	Cu	1.00	0.00
	Zn	1.00	0.00
	Cd	-1.00	0.00
	Pb	-1.00	0.00

(**Continue to next page 96**)

(From previous page 95)

Stations	**% labile inorganic**	***r***	***p***
Site 4	**Ni**	-0.500	0.67
	Cu	0.87	0.33
	Zn	-0.500	0.67
	Cd	-1.00	0.00
	Pb	0.00	0.00
Site 5	**Ni**	0.00	1.00
	Cu	0.00	1.00
	Zn	-0.87	0.33
	Cd	0.00	1.00
	Pb	-0.87	0.33
Site 6	**Ni**	-1.00	0.00
	Cu	-1.00	0.00
	Zn	-0.50	0.67
	Cd	-1.00	0.00
	Pb	-1.00	0.00
Site 7	**Ni**	0.50	0.67
	Cu	1.00	0.00
	Zn	0.50	0.67
	Cd	-0.50	0.67
	Pb	-1.00	0.00
Site 8	**Ni**	0.50	0.67
	Cu	-1.00	0.00
	Zn	1.00	0.00
	Cd	1.00	0.00
	Pb	0.00	0.00

Table A-3 Correlation analysis of %labile metal concentrations and dissolved organic carbon (DOC) concentrations of 10 sampling sites in water environment within and around an industrial estate for three time samplings.

Stations	**% labile inorganic**	***r***	***P***
Site 9	**Ni**	-1.00	0.00
	Cu	-0.500	0.67
	Zn	-1.00	0.00
	Cd	-1.00	0.00
	Pb	-1.00	0.00
Site 10	**Ni**	-1.00	0.00
	Cu	0.00	1.00
	Zn	-1.00	0.00
	Cd	0.00	0.00
	Pb	0.00	0.00

A-4 Field data of Chao Phraya River

Stations	**CH6**	**CH8**	**CH10**	**CH12**	**CH15**
Distance from river mouth	29 km	42 km	48 km	58 km	83 km
Date	Jan26,10	Jan26,10	Jan26,10	Jan26,10	Jan26,10
Time	13.40	14.55	14.30	14.00	13.00
pH	7.11	7.15	7.17	7.18	7.25
Temperature ˚C	28.1	27.8	27.6	27.7	27.1
Conductivity mS/m	1510	158	62	48.4	42.1
Salinity	6.9	0.6	0.2	0.1	0.1
Turbidity	0	0	0	0	9.5
DO	3	3	2	2	4
COD	100	55	36	34	39
BOD	3.4	2.5	2.1	2.8	2.4
SS	13	5	4	5	7
NO2-N	0.4	0.4	0.4	0.4	0.4
NO3-N	1.25	2.00	1.87	2.12	2.08
NH3-N	1.98	7.62	1.12	0	0.95
Cl-	0.8	0.8	0.8	0.8	0.8
PO4-3	0.76	0.76	0.76	0.76	0.76
DOC	5.67	3.63	4.36	1.37	2.21

A-5 Field data of water environment within and around an industrial estate for three time samplings.

September:

Sample	Time	pH	temp.(°C)	Turb.(NTU)	Cond.	Sali.(ppt)
1.Raw water	10:05	7.07	30	198	60 ms/m	0.1
2.Tap water	10:25	6.64	29.7	0	29.2ms/m	0.2
3.Ground water	10:52	7.62	33.3	0.4	92.6ms/m	0.4
4.WWTP(Inf.)	11:45	7.03	31.6	186	0.148ms/m	1.1
5.WWTP(Enf.)	11:47	7.2	31.5	16.2	0.225s/m	0.7
6.PO	11:30	7.17	31.7	7.8	0.143s/m	0.7
7.CA	11:25	7.19	31.3	14.4	0.1s/m	0.5
8.LI	11:06	7.78	30.6	23.1	81.7ms/m	0.4
9.LB	11:15	8.96	32.1	15.9	93.6ms/m	0.4
10.LF	10:56	7.3	30.6	26.9	69.2ms/m	0.3

October:

Sample	Time	pH	temp.(°C)	Turb.(NTU)	Cond.	Sali.(ppt)
1.Raw water	10.30	7.32	29.6	46.2	22.6 ms/m	0.1
2.Tap water	10.11	6.96	29.8	1.8	31.3 ms/m	0.1
3.Ground water	11.00	7.87	29.8	143.8	89.1 ms/m	0.4
4.WWTP (Inf.)	12.15	6.92	31.2	39.7	0.124 s/m	0.6
5.WWTP (Enf.)	12.03	7.34	31.1	18.8	0.146 s/m	0.7
6.PO	11.54	7.28	30.5	20.1	0.148 s/m	0.7
7.CA	11.40	7.28	28.2	28.2	0.117 s/m	0.6
8.LI	11.29	7.41	30.4	13.3	0.100 s/m	0.5
9.LB	11.24	7.50	30.2	16.3	0.100 s/m	0.5
10.LF	11.12	7.38	28.5	28.1	82.3 ms/m	0.4

November:

1.Raw water	Time	pH	temp.(°C)	Turb.(NTU)	Cond.	Sali.(ppt)
2.Tap water	10.58	7.22	27.1	29.8	20 ms/m	0
3.Ground water	10.36	7.34	27.3	1.8	30.2 ms/m	0.1
4.WW(Inf.)	11.23	7.79	33.4	4.1	92.7 ms/m	0.4
5.WW(Enf.)	12.25	7.68	29.4	148.7	0.14 s/m	0.6
6.PO	12.16	7.32	29.0	11.7	0.133 s/m	0.7
7.CA	12.09	7.39	29.6	13.8	0.15 s/m	0.7
8.LI	11.58	7.40	28.5	10.3	0.15 s/m	0.7
9.LB	11.39	7.73	27.6	22.4	0.13 s/m	0.6
10.LF	11.46	8.47	27.3	15.8	0.11 s/m	0.5
1.Raw water	11.32	8.37	27.5	59.3	0.15 s/m	0.7

IC standard curve for 7 elements

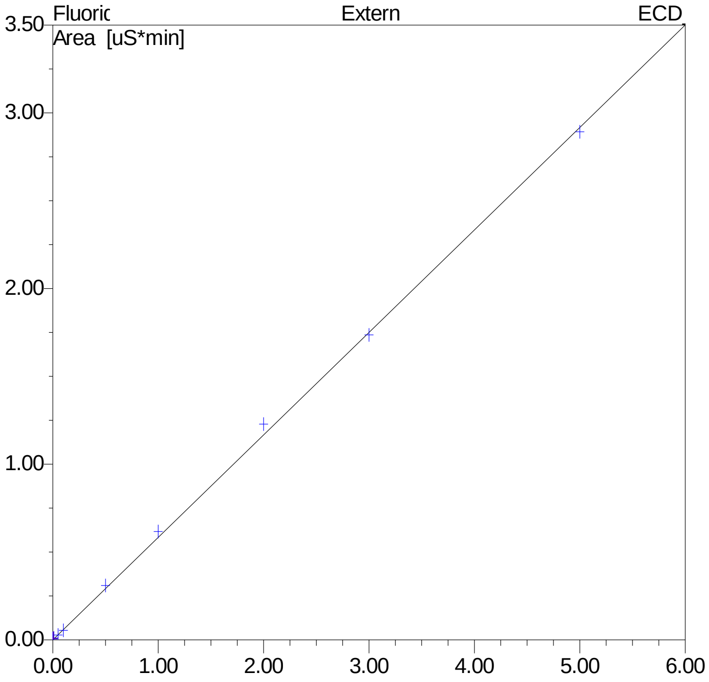

Fig. A-25 F^- standard curve

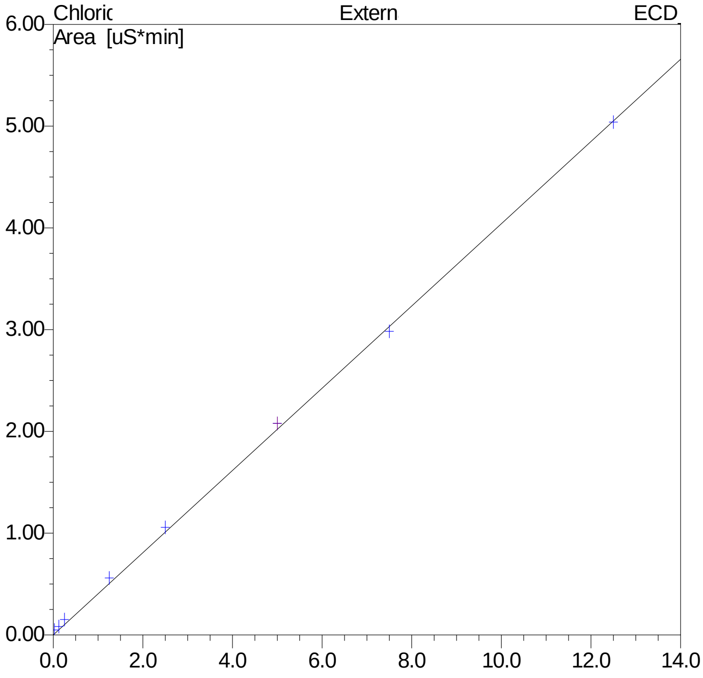

Fig. A-26 Cl^- standard curve

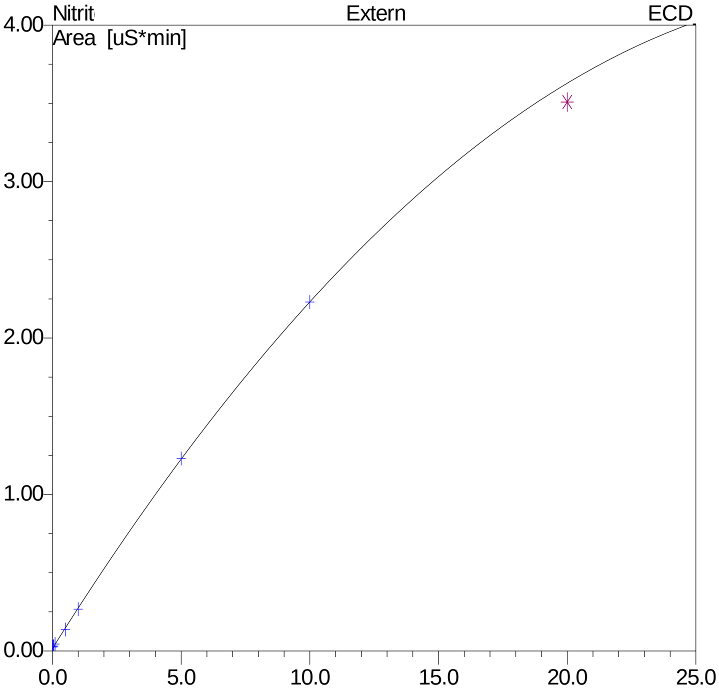

Fig. A-27 NO_2^- standard curve

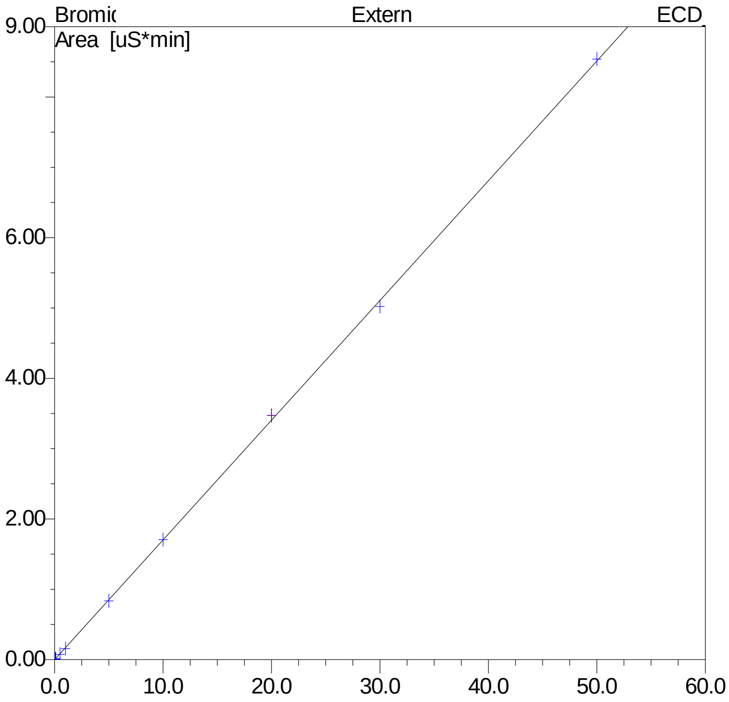

Fig. A-28 Br^- standard curve

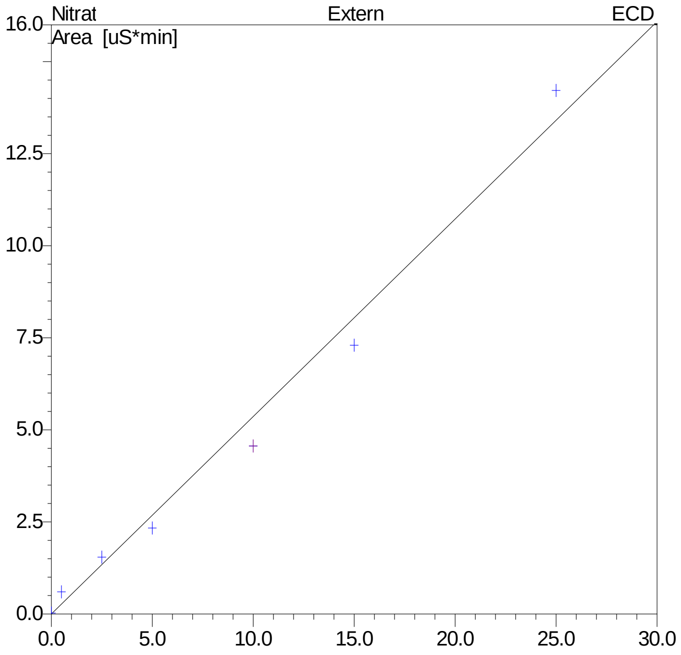

Fig. A-29 NO_3^- standard curve

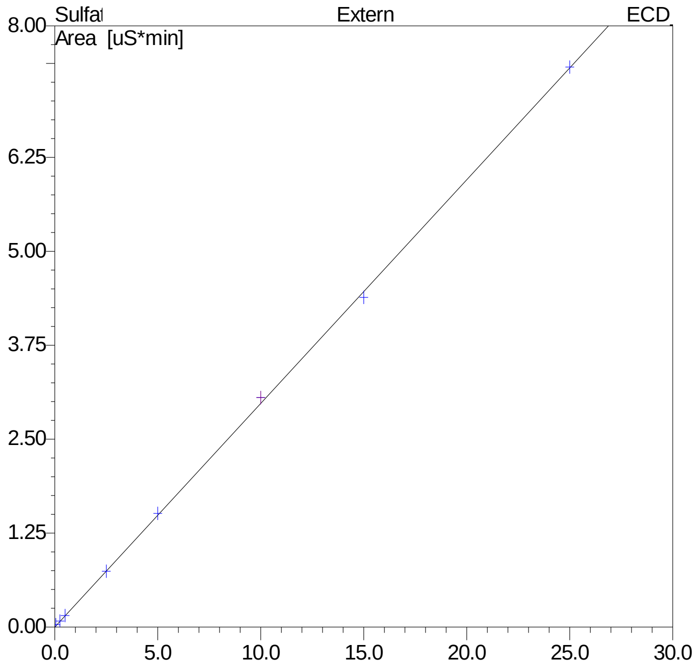

Fig. A-30 SO_4^{2-} standard curve

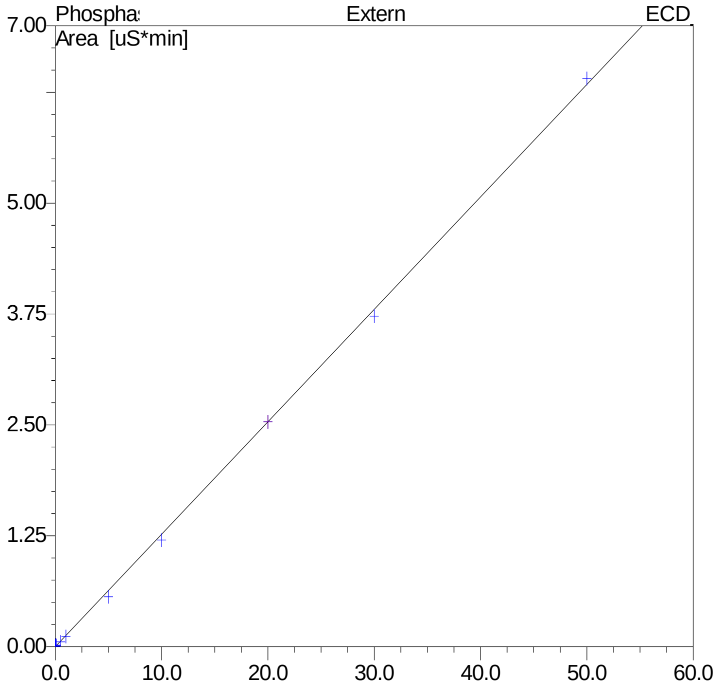

Fig. A-31 PO_4^{3-} standard curve

A-6 Dissolve Organic Carbon Values of water environment within and around an industrial estate for three time samplings (mg/L).

	September	**October**	**November**
1.Raw	33.2	29.2	26.0
2.Tap	12.1	21.0	19.8
3.Ground	35.0	46.7	42.5
4.WW(Inf.)	41.7	67.6	50.4
5.WW(Enf.)	39.7	52.2	39.7
6.PO	31.6	51.5	42.7
7.CA	24.6	48.2	43.7
8.LI	26.7	27.6	38.9
9.LB	32.3	28.9	31.0
10.LF	40.2	30.0	40.7

APPENDIX B

Paper Publication (Conference Articles)

Pimonpan Harnsuk, Nyein Nyein Aung, Tushara Chaminda G.G. and Hiroaki Furumai. **Estimation of labile heavy metals in downstream of the Chao Phraya River using equilibrium model**. Proceeding, pp 301-307, 8th South East Asia Water Environment International Symposium, October 24-27, 2010, Phuket, Thailand.

Pimonpan Harnsuk, Nyein Nyein Aung, Tushara Chaminda G.G and Hiroaki Furumai. **Speciation of Heavy Metals in Water Environment within and Around an Industrial Estate in Metro Bangkok.** 4 th International Water Association - Asia Pacific Region (IWA- ASPIRE), October, 2011, Tokyo, Japan

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- Water Science and Technology or
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- Water Practice and Technology, or
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