uOttawa

L'Université canadienne
Canada's university

FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTOCTORALES

uOttawa

L'Université canadienne
Canada's university

FACULTY OF GRADUATE AND POSDOCTORAL STUDIES

Heyuan Zhang

AUTEUR DE LA THÈSE / AUTHOR OF THESIS

M.A.Sc. (Environmental Engineering)

GRADE / DEGREE

Department of Chemical Engineering

FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Fate of Mercury in Wastewater, Sludge and Gaseous Streams at ROPEC

TITRE DE LA THÈSE / TITLE OF THESIS

Jason Zhang

DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

Kevin Kennedy

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

EXAMINATEURS (EXAMINATRICES) DE LA THÈSE / THESIS EXAMINERS

Ronald Droste

Banu Ormeci

Gary W. Slater

LE DOYEN DE LA FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTDOCTORALES /
DEAN OF THE FACULTY OF GRADUATE AND POSTDOCORAL STUDIES

Fate of Mercury in Wastewater, Sludge and Gaseous Streams at ROPEC

by

Heyuan Zhang

A thesis

submitted under the supervision of

Dr. Kevin Kennedy, Dr. Wayne Parker and Dr. David Lean

in partial fulfillment of

the requirements for the degree of

Master of Applied Science

in

Environmental Engineering

Department of Chemical Engineering

University of Ottawa

Ottawa, Canada

K1N 6N5

October 30, 2005

Your file Votre référence
ISBN: 0-494-14978-7
Our file Notre référence
ISBN: 0-494-14978-7

ACKNOWLEDGEMENTS

During the work on my master degree, I was very fortunate to work with a lot of great people and have received all kinds of invaluable help from them. Here I would like to take this chance to give them my sincere appreciation.

First of all, I would like to express my deep gratitude to my supervisors Prof. Kevin Kennedy, Prof. Wayne Parker and Prof. David Lean for their guide and support. Their profound knowledge and abundant experience in environmental engineering and chemistry impressed me very much. I enjoyed the fruitful discussions with them. I benefited from their help on thesis and report writing and presentation skills. Secondly I would like to thank Dr. Nelson for his guide and support while conducting gaseous sampling at ROPEC and great appreciation of training and work in Dr. Leans lab. I greatly appreciate Mr. Gary Robidoux, Ms. Shanshan Lu, and other technologists of ROPEC who helped to provide the total mercury sampling for liquid and sludge samples collection for this project.

I would like to thank my wife and daughter for their love and support. They undertook too much work that I should do without any complaining during the last three years.

Last but not the least thanks must go to my parents for their selfless love and understanding. I feel indebted that I haven't seen them in the past three years, who are far away from me and suffer my long time absence, but always provide encouragement and moral support.

ABSTRACT

A study on the investigation of the fate of mercury in a secondary wastewater treatment plant has been carried out by combination of field scale sampling and computer modeling simulation at Robert O. Pickard Environmental Centre (ROPEC). Over 200 wastewater, sludge and solid samples and over 680 gaseous and biogas samples were collected from various points throughout the plant and analyzed for total mercury in July, August, December 2003, and March, April, May, June 2004. An approximated mass balance on mercury was performed around each unit process based on the data collected in the field sampling and the facility operation. Partitioning coefficients (K_p), the critical parameters, in primary and secondary treatment processes that will be employed in subsequent modeling of TOXCHEM$^+$ to predict the fate of total mercury in wastewater, sludge and gaseous streams were also calculated.

The results of this study indicated that only approximately 24 ± 9% of the total mercury load entering the plant portioned into the anaerobically digested sludge (CAKE), 65 ± 18% of the total mercury discharged to Ottawa River, and less than 0.002% of the total mercury excited in the form of biogas and total gaseous mercury (TGM) volatilization to atmosphere. The removal efficiency of total mercury within facility is about 35 ± 18%, based on the percent of mercury leaving in the final effluent compared to total inputs. The approximate total mercury-loading rate to the Ottawa River at ROPEC is approximately 191 ± 116 g/d. The comparison between the predictions run with TOXCHEM$^+$ and observed data collected from field sampling suggests that the models such as TOXCHEM$^+$ could be employed as an useful tool to evaluate and predict the fate of mercury at ROPEC after further calibration and verification.

Keywords: Fate, mercury, wastewater, sludge, solid, mass balance, modeling.

TABLE OF CONTENTS

ACRONYMS

BOD	Biological oxygen demand
CAKE	Dewatered biosolids cake
CSTR	Completely mixed continuous flow stirred tank reactor
CVAAS	Cold vapor atomic absorption spectroscopy
CVAFS	Cold vapor atomic fluorescence spectrophotometry
DC	Dewatering centrate
DIG	Digester mixed liquor
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DMHg	Dimethylmercury
U.S. EPA	U.S. Environmental Protection Agency
FE	Final effluent
MDL	Method detection limits
MeHg	Methylmercury
MLSS	Mixed liquor suspended solids
MMHg	Monomethylmercury
MOE	Ministry of the Environment
MWTP	Municipal wastewater treatment plant
PE	Primary effluent
QA	Quality assurance
QC	Quality control
RAS	Returned activated sludge
RAW	Raw sludge
ROPEC	Robert O Pickard Environmental Centre
RS	Raw sewage
SRT	Sludge retention time
SS	Suspended solids
TC	Thickening centrate
TGM	Total gaseous mercury

THg	Total mercury
TSS	Total suspended solids
TWAS	Thickening waste activated sludge
VSS	Volatile suspended solids
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 Introduction

1.1 Background

Since the early 1970s there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. Mercury is one of the most toxic metals found in the environment. The monomethylated form of mercury (CH_3Hg^+, commonly referred to as methylmercury and abbreviated as MeHg) is at least 10 times more toxic to aquatic biota than inorganic forms (e.g., $HgCl_2$) (Environment Canada, 2003). Methylmercury is of special concern not only because of its greater toxicity, but also because it biomagnifies in the food chain of the aquatic ecosystem.

Mercury occurs naturally, but approximately 50% of the mercury entering ecosystems is contributed by anthropogenic emissions and discharges (Environment Canada, 2003). In recent years, mercury emissions have decreased in many countries and North America due to legislation, improved cleaning technology and altered industrial activities. The recommended Canadian Environmental Quality Guidelines for mercury (water, sediment, tissue, and soil) have been tightened since 2003. For example, the recommended Canadian Water Quality Guidelines for inorganic mercury in freshwater has been adjusted from the previous value of 100 ng Hg/L to 26 ng Hg/L (Environment Canada, 2003).

A significant part of the anthropogenic mercury emissions ends up in wastewater. Major urban inputs to sewage water include household effluents, drainage water, business effluents (e.g. dental uses, laboratory uses, etc.), atmospheric deposition, and traffic related emissions transported with storm water into the sewage system (US EPA, 1986). Municipal wastewater treatment plants (MWTPs) are expected to control the

discharge of heavy metals including mercury to the environment. However, traditional biological wastewater treatment systems are mainly designed for removal of organic matter by aerated activated sludge, hence removal of heavy metals including mercury in these systems may be regarded as a side-benefit (Karvelas *et al.*, 2003).

Mercury discharges from wastewater treatment plants may present a significant contribution to the entire amount of mercury entering the environment. Currently the fate of mercury in wastewater is still not clearly understood, as it may be discharged to the environment through air emissions, wastewater final effluents entering receiving water bodies or from the disposal of wastewater sludge on land.

The concentration of mercury in the discharge from the Robert O. Pickard Environmental Centre, Ottawa, Ontario (ROPEC) is monitored monthly. Historically the concentrations of mercury have either been below the detection limit of the analytical method or detected but at very low concentrations. Only very rarely is mercury detected at higher concentrations. However, on these occasions very high loadings to the Ottawa River are reported because of the high flows that are discharged. Mercury is regularly detected in the biosolids that are discharged at the plant. The data would suggest that mercury tends to be associated with the wastewater solids.

The major objectives of this study were to obtain an improved understanding of the fate of mercury in the secondary treatment processes at ROPEC, and to quantify mercury emissions. An improved understanding of this behaviour will allow the city to identify the fate of mercury once it enters ROPEC and to make improved estimates of loading to the Ottawa River.

1.2 Scope of investigation

In order to meet these objectives, a combination of field scale sampling and computer modeling was carried out. From 2003 to 2004, approximately 890 samples, made up of a combination of plant influent, primary clarifier effluent, aeration basin effluent, secondary clarifier effluents, primary sludge, secondary sludge and digester effluent, aeration basin off-gas and digester biogas were taken and analyzed to investigate the loading of total mercury in different streams at ROPEC.

These samples were analyzed for total mercury in the soluble form and mercury associated with the solid phase. It is recognized that the concentrations of mercury in the wastewater stream are often below the detection limits of the analytical methods employed for regular analysis of ROPEC samples. Hence, in order to obtain data at low concentrations, advanced analytical equipment, (SP-3D Mercury Analyzer, Cold Vapour Atomic Absorption method (CVAA)), from Dr. Lean's laboratory, University of Ottawa where method detection limits (MDL, 2 ng/L) are generally much (100×) lower was employed. Some measure of mercury speciation (elemental mercury, oxidized mercury and methylmercury) was also made. In addition the samples were characterized with respect to suspended solids, volatile suspended solids, pH and other wastewater and gas characteristics that were believed to impact on the behaviour of mercury. Mass balances on mercury were performed around each unit process at ROPEC.

Based on the data collected, the tendency for mercury to partition between liquid and solids was evaluated. This facilitated the estimation of liquid-solid partitioning coefficients that would be employed in subsequent modeling exercises. The data collected in this portion were employed to determine whether the metals sub-model in the TOXCHEM$^+$ fate model could be employed for mercury. Once configured and calibrated,

a thorough sensitivity analysis was also performed to evaluate the impact of wastewater treatment plant variables on the fate of mercury at ROPEC.

CHAPTER 2 Background and Literature Review

2.1 Physical and Chemical Properties

Elemental mercury (Hg^0, atomic number 80) is a silver-white liquid metal at room temperature, has a molecular weight of 200.59, and belongs to group IIb of the periodic table of elements. Hg^0 has a low melting point (-39°C) and high boiling point (356.9°C at 101.32 KPa). Hg^0 is very volatile (vapour pressure 0.16 Pa at 20°C) and is more likely to be discovered in the atmosphere than in water. Mercury can be methylated in the environment (Environment Canada, 2003). Table 2.1 summarizes the related physical and chemical properties of mercury.

Theoretically mercury can exist in three valence states: elemental (Hg^0/Hg (0)), mercurous (Hg^+/Hg (I)), and mercuric (Hg^{2+}/Hg (II)). Hence, it can make up both inorganic and organic compounds. Although natural waters tend to be saturated with Hg^0, it is still not easily soluble in water as compared to the high water solubility of Hg^{2+} ($HgCl_2$). As shown in Table 2.1, the water solubility of Hg^0 (25-30 μg/L) is much smaller than that of Hg^{2+} ($HgCl_2$, 69 g/L). In water, the mercurous state (Hg^+) of mercury exists as a doubly charged binuclear ion (dimer), Hg_2^{2+}. Hg^+ most generally combines with inorganic molecules (Environment Canada, 2003). The chemical compounds of the mercuric ion (Hg^{2+}) are very stable and much more abundant than those of Hg^+ in the environment (Environment Canada, 2003). Although mercuric chloride ($HgCl_2$) can predominate when chloride salts are plentiful, compared to bonds formed with other inorganic anions, the mercuric cation (Hg^{2+}) creates a relatively weaker covalent bond with chloride (Alberta Environmental Protection, 1992). $HgCl_2$ is more likely to be associated with sediments since the partition coefficient between sediment and water, log

$K_{sediment}$ = 3.4 to 4.1 for Hg^{2+} (Hurley *et al.*, 1994). Macleod *et al.* (2005) also reported a log $K_{sediment}$ of 5 for Hg^{2+}, 3.7 for MeHg and 4.3 for Hg^0 in the San Francisco Bay area.

Table 2.1 Related physical and chemical properties of mercury

Property*	Mercuric mercury ($HgCl_2$)	Methyl mercury (CH_3Hg^+)	Elemental mercury (Hg^0)
Atomic number	--	--	80
Molecular Weight	271.5	215.63	200.59
Boiling point	--	$Hg(CH_3)_2$: 92°C/98.66 Kpa [4]	356.9°C/101.32 Kpa [1]
Density (spec.gravity)	5.4 [4]	$Hg(CH_3)_2$: 3.1874[4]	13.534 g/cm^3 at 25°C [4]
Melting point	--	CH_3ClHg: 170°C [4]	-38.87°C
Bioconcentration factor (BCF) for fish (Fathead minnows)	5,000 [13]	81,670 [14]	--
K_{oc} (organic carbon)	NA	DOC increases solubility [6]	NA
Log $K_{sediment}$	5 [15]; 3.4 - 4.1 [3]	3.7 [15]; 2.9-3.2 (reduced by DOC in water) [6]	4.3 [15]
Log $K_{susp.particulates}$	6 [15]; 5.35 [2]; 4.8 - 4.9 [10];	4.7 [15]; 5.73 [2];	4.5 [15]
Log K_{ow}**	3.3 [12]	1.7 [7] - 2.54 [5]	0.62 [7]
Vapour pressure, Pa	1.87 X 10^{-2} at 34°C [4]	1.13 at 20°C MeHgCl[11]	0.16 at 20°C [11] 2 X 10^{-3} at 25°C[10]
Water Solubility	69 g/L [4]	1 µg/L [8];	25 - 30 µg/L [9]

* Source: Environment Canada (2003). With the exception of molecular weight, most of these properties are dependent on pH, temperature, carbon content and other characteristics, and are given as general values only. NA: not available. ** K refers to a partition coefficient of a substance between indicated phase: water (Hg concentrations in each medium). K_{ow} = octanol/water partition coefficient; $K_{susp.particulates}$ = suspended particle/water; $K_{sediment}$ = sediment/water, K_{oc} = organic carbon/water, DOC = dissolved organic carbon.

(1) (Alberta Environmental Protection, 1992); (2) (Hurley *et al.*, 1989); (3) (Hurley *et al.*, 1994); (4) (Royal Society of Chemistry, 1994); (5) (Halbach, 1985); (6) (Miskimmin, 1991); (7) (Major and Rosenblatt, 1991); (8) (Eisler, 1987); (9) (Krenkel, 1974); (10) (Hurley *et al.*, 1995); (11) (World Health Organization, 1990); (12) (Mason *et al.*, 1995) (13) (Snarski and Olson, 1982a); (14) (Olson *et al.*, 1975); (15) (Macleod *et al.* 2005).

The hydroxyl anion has a higher affinity for Hg^{2+} when there is no organic complexing agents and will predominate in most freshwaters except when the pH is low, or the chloride concentration is high. Under reducing conditions, Hg^{2+} can easily develop stable, largely covalent bonds with sulphide (including thiols) and selenides (Jackson, 1998).

Mercuric mercury (Hg^{2+}) can be converted through abiotic and biotic processes to create alkylmercury compounds: monomethylmercury [CH_3Hg^+](MMHg or MeHg), dimethlymercury [$(CH_3)_2Hg$](DMHg), and aryl compounds [e.g., phenyl-mercury]. Monomethylmercury is normally called methylmercury and abbreviated as MeHg. It is quite volatile with a vapour pressure of 1.13 Pa at 20°C that is higher than that of Hg^0 (vapour pressure 0.16 Pa at 20°C) and Hg^{2+} ($HgCl_2$, vapour pressure 1.87×10^{-2} Pa at 34°C). Dimethylmercury, on the other hand is a very volatile organic compound and tends not to bioaccumulate (Environment Canada, 2003).

Monomethylmercury is the most toxicologically relevant form of mercury, as it can be transported across cell membranes. MeHg has a chemical affinity for sulphydryl (-SH) groups in body tissue proteins and results in toxicity to and bioaccumulation in biota. Table 2.1 shows that MeHg can be bioaccumulated easily in aquatic bio-systems with a bioconcentration factor (BCF) of 81,670 for fish (BCF referred to the ratio of mercury concentration in fish to mercury concentration in water) (Environment Canada, 2003). MeHg also has a log K_{ow} partition coefficient of 1.7 - 2.5, which indicates that MeHg compounds only have a medium affinity for fats in the body. Elemental mercury (Hg^0), on the other hand has a log K_{ow} of 0.62 and accumulation in lipids is unlikely to be significant (Environment Canada, 2003). The Log $K_{susp.particulates}$ of 5.73 for MeHg and 5.35 for Hg^{2+} also indicate that both MeHg and Hg^{2+} have a strong association with

suspended particulates in natural water bodies (Hurley *et al.*, 1989). Macleod *et al.* (2005) also reported a Log $K_{susp.particulates}$ of 6 for Hg^{2+}, 4.7 for MeHg and 4.5 for Hg^0 in the San Francisco Bay area.

2.2 Mercury in the Environment

Mercury is released from a variety of natural and anthropogenic sources, and can be transported in the atmosphere for a long distance then deposited in watersheds via precipitation. The majority of mercury in air, perhaps 95% or 100% (Iverfeldt, 1995), is in vapour form as elemental mercury, but mercury in an oxidation state Hg^{2+} or Hg^{+} is the dominant form when it is deposited from the atmosphere with dry or wet fallout.

The major anthropogenic sources of mercury in Canada include the following industrial sectors: metal smelting, coal-burning power plants, municipal waste incineration, sewage and hospital waste incineration, coal and other fossil fuel combustion, cement manufacturing, and mercury waste in landfills or storage. Other sources include removal and disposal of dental amalgams, use and disposal of mercury containing lamps (Environment Canada, 2003), and leakage from laboratory and electrical equipment, and consumer products such as latex paint (Lindqvist *et al.*, 1991).

Mercury concentrations in air and precipitation vary with the geographic location, and they are significantly higher close to the anthropogenic or natural sources. Glass *et al.* (1990) reported that mercury concentrations in air and in the rainfall at Duluth, Minnesota were in the range of 1 to 6 ng/m^3, and approximately 22 ng/L, respectively. Samples of rainwater taken in the early 1990s at the Experimental lakes Areas of northwestern Ontario averaged from 3.8 to 5.3 ng Hg/L, and from 0.017 to 0.049 ng MeHg/L (< 1% of total mercury).

Table 2.2 shows worldwide emissions of mercury in 1983, including natural and anthropogenic sources to the atmosphere, soil and water were 6,060, 10,200, and 4,600 tonne/a, respectively (Environment Canada, 2003). The anthropogenic component has reduced as use of mercury has decreased, but it is generally accepted that anthropogenic sources account for at least half of the worldwide emissions. A recent study of worldwide mercury emissions to the atmosphere reported total anthropogenic sources in the range of 2,000 to 4,000 tonne/a, and natural source emissions in the range of 2,200 to 4,000 tonne/a (Pirrone *et al.*, 2001). Table 2.2 shows that the major sources of mercury to water include coal combustion (41%), manufacturing processes (26%), atmospheric fallout (20%), and domestic wastewater (7%). Mierle (1990) reported that more than half (57%) of the mercury in a small lake in the Canadian Shield, came directly from wet atmospheric deposition, and it was also found that melting snow during spring runoff accounted for an extra 13% or more to the water body.

A large portion of the mercury deposited on land is associated with the humus-rich upper layers. Once within the soil, mercury can be transported with runoff to surface waters in association with movement of dissolved humus material. Mercury deposited in soil helps to equalize the atmospheric flux of mercury by reconversion of Hg^{2+} back to the elemental form (Hg^0) by soil microbes followed by volatilization from the soil to the atmosphere (Lindqvist *et al.*, 1991). Mercury that is present in the aqueous environment is largely sorbed to particles, including suspended solids and sediments (Ferrara *et al.*, 1991; Hurley *et al.*, 1991). It is most likely that the mercury present in solution is complexed with humic substances as Hg^{2+} (Allard and Arsenie, 1991; Lindqvist *et al.*, 1991). Low concentrations of dissolved Hg^0 also exist, which contribute to volatilization

Table 2.2 Estimates of worldwide emissions (tonne/a) of mercury to the atmosphere, water and soil in 1983

Source category	Atmosphere		Water		Soil * *	
	Min.	Max.	Min.	Max.	Min.	Max.
Coal combustion	650	3,500	0	3,600	370	4,800
Non-ferrous metal production	45	220	0	40	0	80
Refuse incineration						
Municipal	140	2,100	NA	--	NA	--
Sewage sludge	15	60				
Wastewater (domestic)	no relevance	--	0	600	10	800
Wood combustion	60	300	NA	--	NA	--
Metal mining	Insignificant input	--	0	150	NA	--
Urban refuse	NA		NA	--	0	260
Wastage - commercial prod.	NA	--	NA	--	550	820
Manufacturing processes	NA	--	20	2,300	NA	--
Atmospheric fall-out	no relevance		220	1,800	630	4,300
Phosphate fertilizer production and use	insignificant input	--	NA	--	NA	--
Agricultural Waste	NA		NA		0	1,700
Logging and other wood wastes	NA	--	NA	--	0	2,200
Mine tailings	NA		NA		550	2,800
Smelter slags and wastes	NA	--	NA	--	50	280
Dumping of sewage sludge	no relevance	--	10	310	no relevance	--
Anthropogenic total inputs	910	6,200	250	8,800	2,200	18,100
Median	3,560		4,600		10,200	
Natural source totals	100	4,900	NA	--	NA	--
Median	2,500		--		--	
Grand totals	1,010	11,100	250	8,800	2,200	18,100
(Median)	6,060		4,600		10,200	

*Source: Environment Canada, 2003

(Anthropogenic values from Nriagu and Pacyna, 1988; Natural values from Nriagu, 1989)

NA: not available.*Insignificant contributions to the atmosphere from: oil combustion, zinc-cadmium production, secondary non-ferrous production, steel and iron manufacturing, cement production, and mobile sources. ** Landfills included.

from natural water bodies (Lindqvist *et al.*, 1991). Only Hg^{2+} and MeHg significantly partition to solids, and only Hg^0 volatilizes to any significant extent. Hg^{2+} appears to be most available for methylation, and methylmercury appears most ready to biomagnify (Mason *et al.*, 1995).

The organometallic species methylmercury is known to be the most toxic form of mercury that can be bio-accumulated in the food chain. 95% of the mercury in fish tissue is methylated and fish, through direct uptake from water, can accumulate methylmercury (Goldstone *et al.*, 1990; Matilainen *et al.*, 1991). Mercury methylation is generally accepted to be a biological process carried out by microorganisms. Methylation has been shown to occur in various environments (Bisogni and Lawrence, 1975; Matilainen *et al.*, 1991), but methylation seems to generally progress in the top-layer of sediments of natural waters, where microorganisms are the most active (Matilainen *et al.*, 1991). The concentration of methylmercury in a system relies on the relative rates of methylation and demethylation. Goldstone *et al.* (1990) reported that the most important factors are likely to be the amount of organic material, pH, redox potential and temperature, which affect methylation to varying degrees, and no methylation can occur without the presence of bioavailable mercury (Hg^{2+}).

Biological processes are thought to be the dominant pathway of conversion of inorganic and organic forms of Hg^{2+} to the elemental form (Hg^0) (Bisogni and Lawrence, 1975; Lindqvist el al., 1991). Mercury can be volatilized back to the atmosphere by this reversible transformation to the elemental state, thus finishing the whole cycle needed for redistribution of mercury throughout the environment (Allard and Arsenie, 1991).

Babiarz and Andren (1992) reported that total mercury concentrations in selected Wisconsin surface waters ranged from 0.7 to 8.9 ng/L in rivers and 0.3 to 2.9 ng/L in

lakes. In this study, they found that a significant correlation existed between mercury concentrations and total suspended particulate matter. Previous research has indicated that most of the mercury is associated with particles that settle from the water column of lakes and settle into the deeper sediments (Swain *et al.*, 1992).

2.3 Mercury in Municipal Wastewater Treatment Plants

Municipal wastewater treatment plants (MWTPs) represent the focal point for collecting industrial, commercial and domestic liquid wastes. Wastewater treatment plants are generally designed for biochemical oxygen demand (BOD) and suspended solids (SS) removal, but they also have to remove heavy metals and organic pollutants. Although much research has been done on the behaviour of mercury in natural waters, (and it can be used in the wastewater field), relatively little work has been performed to characterize its behaviour in wastewater. In general, the mechanisms for removal of mercury from a wastewater stream are not thoroughly understood. Therefore it would be helpful to understand how mercury behaves in wastewater treatment and to completely understand the physical, chemical and biological interactions that may affect its removal.

In wastewater treatment processes, mercury is likely to behave in a similar way to its behavior in natural waters. Mercury can exist in three states: Hg^0, Hg^+ and Hg^{2+}, and inter-conversion also may occur in a wastewater system. Elemental mercury can be stripped off as off-gas at any stage of treatment which is open to the atmosphere such as primary and secondary clarification and particularly in aerated grit chambers and mixed liquor aeration basins (bio-oxidation) that use air. Lindqvist *et al.* (1991) reported that mercury concentrations in air coming from a wastewater treatment plant at Rya,

Goteborg, Sweden, were in the range of 4 to 6 ng/m^3. Additionally, mercury could be removed in the biogas produced during anaerobic digestion of sludge.

Goldstone *et al.* (1990) reported that mercury was volatilized as mercaptide and elemental mercury to account for mercury loss during activated sludge treatment. However, data from a full-scale municipal treatment plant indicated that volatilization of elemental mercury was insignificant.

In the primary clarifier, mercury adsorbed to and precipitated with settleable solids through adsorption and complexation mechanisms will be removed in the settled raw sludge (primary sludge). Approximately 30 to 60% of the influent mercury has been reported to be removed during primary sedimentation (Goldstone *et al.*, 1990). Balogh and Liang (1995) concluded that approximately 80% of total mercury could be removed in the primary clarification treatment process. In many plants, primary sludge undergoes further treatment in either an aerobic or anaerobic digester to stabilize the solids and produce biosolids for final disposal.

In the mixed liquor aeration basin or other aerated biological units, bacteria, protozoa, and other microorganisms reproduce and efficiently transform dissolved organic matter (DOM) and colloidal particles. Microbial biomass forms flocculent biological material, which can be separated from the aqueous phase in the secondary clarifier, and finally, will be removed as waste activated sludge (WAS) or secondary sludge. At this stage, bacteria may inter-convert inorganic Hg^{2+}, MeHg and Hg^0, additionally elemental mercury also can be stripped at this stage by aeration (Mugan, 1996). The volatility of mercury species has been reported to follow the order: Dimethylmercury (DMHg) > Hg^0 > $HgCl_2$ (Earle *et al.* 2000).

Goldstone *et al.* (1990) reported that the majority of research has found that higher mercury removal efficiency (> 95%) occurred during activated sludge treatment than during primary sedimentation (> 50 ~ 75%). They also reported that physical-chemical adsorption of soluble mercury to activated sludge contributed to the mercury removals.

A variety of solids digestion and handling processes are used at municipal facilities. Bacterial action in these processes will likely produce additional inter-conversions. Elemental mercury produced may be stripped off from solution by gas-mixing systems (in the case of anaerobic digesters) or forced aeration. In anaerobic environments, mercury can exist as a highly insoluble precipitate HgS (log K_{sp} = –52.8, Högfeldt, 1982). However, under low Eh (Redox ≤0.5V) and high pH (pH>8) conditions, it can be converted to the more soluble HgS_2^{-2} and Hg^{2+}. Hg^{2+} can be reduced to Hg^0 or methylated to form monomethylmercury (MMHg) (Earle *et al.*, 2000).

Anaerobic microorganisms have been shown to be able to methylate mercury to form MMHg or DMHg. Factors, such as mercury concentration and pH of the system affect the formation of MMHg or DMHg. MMHg exists at lower pH conditions and higher Hg^0 concentrations while DMHg forms at higher pHs in the presence of H_2S or lower Hg^0 concentrations (Earle *et al.*, 2000; Watras *et al.*, 1995). Because methylation and demethylation co-occur, under anaerobic digester conditions some microorganisms can detoxify MeHg to Hg^0 by reduction to produce CH_4 (Mason *et al.*, 1995). Sommar *et al.* (1999) reported that the DMHg and elemental mercury Hg^0 concentrations in digester gas at Goteborg, Sweden, were in the range of 54.5 to 92.5 ng/m^3 for DMHg, and 64.5 to 87.5 ng/m^3 for Hg^0, respectively.

Chemical processes are commonly used at many municipal treatment plants. Chlorination is extensively utilized for effluent disinfection; unfortunately, there were no reports on the effects of chlorine disinfection on mercury removal. On the other hand, chemicals such as alum or ferric chloride that are used to precipitate phosphorus can be expected to improve mercury removal (Mugan, 1996).

Balogh and Liang (1995) examined the mercury pathways in a MWTP. They conducted a nine-week sampling and analysis program at a large municipal wastewater treatment plant to characterize the fate of mercury entering the plant. Mercury removal in primary treatment averaged 79%, and the average mercury removal across the entire plant was approximately 96%. Mercury loadings on the secondary (activated sludge) treatment process were elevated to near plant influent levels due to the recycle of spent scrubber water from sewage sludge incinerator emissions control equipment. This internal recycle of spent incinerator scrubber water resulted in elevated mercury loadings to the incinerators, and effectively reduced the mercury control efficiency of the emissions control equipment to near zero. Measurements indicated that approximately 95% of the mercury mass entering the plant was discharged to the atmosphere via sludge incinerator emissions. Their results indicate that municipal wastewater treatment facilities can remove mercury from wastewater quite effectively. However, where wastewater sludge was incinerated, almost the entire mass of mercury removed from the wastewater can be discharged to the atmosphere.

Environment Canada (2001) carried out a mercury-sampling program to quantify the mercury present in three typical wastewater treatment plants and one landfill in 2000. Over 180 gas, wastewater, sludge and biosolids samples were collected and analyzed for total mercury. A representative group of 15 samples were also analyzed for methyl

mercury. An ultra-clean sample collection and analysis method was employed. An approximated mass balance was constructed for each plant using the data collected. Samples taken at all three plants indicated that greater than 90% of the total mercury loading to the secondary MWTPs were removed and became associated with the primary solids and biosolids, and less than 0.02% of the total mercury exited in the form of biogas with an average concentration of 75.7 ng/m^3, and a range of 22.1 to 235 ng/m^3 (n = 10). Low methyl mercury concentrations in waste activated sludge (WAS) with an average concentration of 9.5 ng/L, and a range of 3.72 to 18.6 ng/L (n = 7) indicated that methylation of mercury at each plant did not widely occur.

Gilmour and Bloom (1995) reported on the effects of a MWTP derived mercury source on treatment plant operations and biosolids quality. They studied the total mercury (THg) and methylmercury (MeHg) effects in a MWTP in which elemental mercury (Hg^0) was used as a seal in 3 trickling filter center columns. Each seal contained several hundred kilograms of Hg. The seals had leaked repeatedly over time, prompting replacement of the mercury seals with mechanical seals. A mass balance conducted three times while the seals were in place showed that the plant acted as a net source of both mercury and MeHg during routine operation. The average amount of mercury released in the sludge and effluent were 157 g mercury/day and 0.4 g MeHg/day, respectively. Of this total, 138 g mercury and 0.3 g MeHg were in excess of the influent wastewater component, and were contributed by the MWTP itself. Approximately 95% of the total mercury was released in the sludge with only 6 to 7 g mercury/day released to the receiving water body. However, on average, about 70% of the MeHg leaving the plant was released to the river. Effluent MeHg concentrations were 4-6 ng/L.

Goldstone *et al.* (1990) studied the biotransformations of mercury during wastewater treatment. They observed the *in situ* methylation of mercury, especially in the presence of bacterial solids. In their study, no detectable MeHg was found in the raw sewage and settled sewage effluents and all MeHg was detected in the returned activated sludge samples, which meant that MeHg was produced by in situ biological methylation. A further filtration and centrifugation study confirmed that almost all the MeHg in the returned activated sludge was associated with biosolids. Environment Canada (2001) also reported that methylation of mercury was found in the presence of biosolids and anaerobic digestion. Methyl mercury was found in dewatering sludge cake with a mean concentration of 3.0 ng/g, and a range of 0.16 to 3.54 ng/g and may be one of the major sites where methylation occurred.

Sommar *et al.* (1999) identified and quantified volatile mercury compounds evolved from the digestion of municipal sludge. Volatile elemental mercury and methylmercury were detected in the off-gas of anaerobic digesters with concentration in the range of 50 -110 ng/m^3.

Bodaly *et al.* (1998) studied the effect of wastewater treatment on total and methyl mercury concentrations in effluents, and their contribution to concentrations in the receiving water bodies. The concentrations of total mercury and MeHg in unfiltered samples of untreated and treated domestic sewage from three treatment facilities and receiving river water within the City of Winnipeg were determined. The concentrations of mercury in the Red and Assiniboine rivers ranged from 3 to 31 ng/L. Total mercury was associated with the suspended sediment concentrations in the rivers. The concentrations of MeHg in these rivers were 0.2 to 0.3 ng/L. Total mercury concentrations in raw sewage ranged from 2 to 150 ng/L. The average mercury removal

efficiency was around 88% for the entire treatment process. MeHg concentrations in the raw sewage were 0.5 to 4.3 ng/L. However, after treatment at two treatment facilities, MeHg was greatly reduced to 0.1 to 0.4 ng/L. Most treated sewage had MeHg concentrations that were similar to levels in the receiving rivers. However, one of the facilities was discharging higher concentrations of MeHg, up to 2 ng/L to the Assiniboine River.

The behavior and removal of heavy metals and mercury during activated sludge wastewater treatment processes has been discussed previously (Chipasa 2003; Nelson *et al.*, 1981; Balogh and Liang (1995); Environment Canada (2001); Gilmour and Bloom (1995); Goldstone *et al.* (1990); Sommar *et al.* (1999); Bodaly *et al.* (1998)). Mercury has an affinity for both inorganic and organic particulates, and hence soluble mercury can be removed during the wastewater treatment process by adsorption to activated sludge (Goldstone *et al.*, 1990; Mugan, 1996; Wang and Huang, 2002). Higher mercury removal efficiencies during activated sludge treatment than during primary clarification have been reported by a majority of the authors (Lester, 1983; Goldstone *et al.*, 1990; Balogh and Liang, 1995; Gilmour and Bloom, 1995; Environment Canada, 2001). A sewage treatment plant can be viewed as a simplified system where pH and redox potential are maintained relatively constant, and many factors affecting the fate of mercury and other heavy metals have been reported (Patterson and Kodukula, 1984; Sterritt and Lesster, 1981; Wang *et al.*, 1999, 2003). These studies at both bench-scale and field scale indicated that in the activated sludge treatment process, mercury removal was affected by DOM, activated sludge retention time, pH, suspended solids and initial influent contaminants concentration.

Wang and Huang (2002) studied the interactions of heavy metals including Hg^{2+} with secondary activated sludge particulates using sludge samples collected from four full-scale MWTPs. Results showed that Hg^{2+} was very absorbable and the uptake by secondary sludge was significantly affected by pH and high concentration of DOM. The percentage of Hg^{2+} uptake increased with increasing pH because pH influenced the chemical speciation of mercury and their distribution between biosolids and solution phase. DOM can form complexes with heavy metals including mercury, thus the presence of high concentration of DOM will affect mercury uptake. However, the effect of DOM on mercury uptake was not significant because the concentration of DOM is low in neutral and low pH conditions.

Nelson *et al.* (1981) studied the factors affecting the fate of heavy metals in the activated sludge process by batch-reactor experiment. They studied the effect of biological solids retention time (SRT) on heavy metal adsorption. Metal affinity for the bacterial solids increased as biological SRT increased from 1 to 5 days in laboratory reactors fed a soluble substrate. It was also reported that most metal removal followed a pattern of accumulation of mixed liquor suspended solids (MLSS) as SRT increased, which indicted this metal was strongly associated with the biomass, and the maximum removal efficiencies for most metals occurred at SRT is of 9 to 12 days (Sterritt and Lester, 1981).

2.4 Analytical Techniques for Mercury in Wastewater and Sludge

Over the past few years, the methods of analysis for low concentrations of total mercury and methylmercury have been reported (Lee, 2002; Jones *et al.*, 1995; Bloom, 1989; Watras *et al.*, 1995; Cai *et al.*, 1996; Pichet *et al.*, 1999). Historically the analytical

techniques were unable to quantify total mercury and organic mercury at low part-per-billion (ng/L) or part-per-trillion (pg/L) levels and hence EPA Methods 1631, 245.7and 7473 were developed to meet these ultra-low level mercury monitoring requirements by GC/CVAFS (gas chromatograph with cold vapour atomic fluorescence detector) or GC/CVAA (gas chromatograph with cold vapour atomic absorption).

EPA Method 7473 was designed for measuring total mercury in solids, aqueous samples, and digested solutions in both the laboratory and field environments by thermal decomposition, amalgamation and atomic absorption spectrophotometry. An oxygenated decomposition combustion tube at 700°C is used to release mercury from solid and aqueous samples in the instrument. The sample is thermally and chemically decomposed within the decomposition combustion tube. Flowing oxygen carries the decomposition products to the catalytic section of the combustion tube where oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through an atomic absorption spectrophotometer detector and it is measured at 253.7 nm as a function of mercury concentration. Total mercury in soils, sediments, bottom deposits, and sludge type materials as well as in aqueous wastes and ground waters can be measured without sample pre-treatment using this method. Alternatively, this method can be used for the measurement of total mercury from total decomposition sample preparation methods, such as Method 3052, or for detection of extracted or leached mercury compounds or species from methods such as the SW-846 3000 series methods.

The typical working range for the AAS (atomic absorption spectrophotometric) method is 0.05 - 600 ng (< 2 ng/L) (Salvato and Pirola 1996; U.S. EPA 1997). The instrument detection limit for this method is 0.01 ng for total mercury (1-2 ng/L). However, it was less sensitive than Method 1631 described below.

Before the year 2000, total mercury in various samples was determined using the less sensitive EPA analytical Method 245.1 (manual) or 245.2 (automated). Both Method 245. 1 and 245.2 use potassium permanganate digestion, stannous chloride reduction, and direct flameless AA detection. The sample is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for two hours at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by conventional cold vapor atomic absorption spectrometry. The sensitivity of Method 245.1 and 245.2 was 0.2 μg/L and yielded very few detectable or quantifiable concentrations in MWTP effluents. Sample contamination also was a major issue.

EPA Methods 1631 and 245.7 are both suitable for determination of part-per-trillion level mercury in samples ranging from seawater to wastewater effluent. Method 1631 specifies digestion using bromine monochloride. The sample is treated with hydroxylamine hydrochloride and then reduced by the addition of stannous chloride. The sample is placed into a bubbler and purged with an inert carrier gas. The eluted mercury is captured on a gold-coated cartridge. This first stage cartridge is then thermally desorbed onto a second, analytical gold cartridge. The second cartridge is then thermally desorbed into an atomic fluorescence detector. Both Method 245.7 and 1631 use similar digestion, and chemistry. Digestion is performed using bromine monochloride. Hydroxylamine hydrochloride is then used to neutralize the BrCl. Final reduction is done

with stannous chloride. Gold preconcentration is not used in Method 245.7. A permeation dryer is used to remove water vapor from the sample before sending the carrier gas directly to a CVAF detector. Both methods require clean sampling techniques and a clean environment in which to digest and run the samples.

The method ranges and method detection limit (MDL) for Methods 1631 and 245.7 are 0.5 to 100 ng/L, 5.0 to 100 ng/L; 0.2 ng/L and 1.7 ng/L, respectively. Both methods 1631 and 245.7 are capable of generating quantifiable values where previously "less than" values had to be used. Method 1631 is used for low and sub-part-per-trillion levels analysis and the cost of ultra-clean analysis for Method 1631 is approximately twice that of Method 245.7, as the QA/QC requirements become more stringent and repeated sampling and analysis resulted in analysis cost increasing (Lee, 2002; U.S. EPA, 1996).

Table 2.3 Summary of applications of analytical methods for total mercury

Application	Methods	Method range	MDL	Reference
Ambient In-Stream Monitoring	EPA Method 1631E (Ultra Clean)	0.5-100 ng/L with CVAAS; 0.001-0.06 ng/L with CVAFS	0.2 ng/L with CVAAS; 0.1 ng/L with CVAFS	Bloom, 1989; Watras *et al.*, 1995
NPDES Monitoring	EPA Method 245.7 (Clean Techniques)	5.0-100 ng/L	1.7 ng/L	Lee, 2002
Environmental Monitoring (soil, sediment, sludge, aqueous waste, and ground water	EPA Method 7473 (Clean Techniques)	0.05-600 ng (<50 ng/L) with CVAAS	0.01 ng Hg (10 ng/L) at 1 mL aqueous sample size	Salvato and Pirola, 1996
Biosolids, Selected Effluents	EPA Methods 245.1 or 245.2 (No Special Requirements)	0.2-10 μg/L for Method 245.1, 0.2-20 μg/L for Method 245.2	0.2 μg/ L	Lee, 2002

Note: NPDES (National Pollutant Discharge Elimination System)

Total mercury and MeHg were determined using a cryogenic gas chromatograph with a highly sensitive cold vapour atomic fluorescence detector (CVAFS) by Bloom (1989), Jones *et al.* (1995) and Watras *et al.* (1995). The detection limits for total mercury ranged from 0.001 to 0.06 ng/L, from 0.001 to 0.02 ng Hg/L for MeHg, and from 0.004 to 0.02 ng Hg/L for Hg^0 (Watras *et al.*, 1995). Pichet *et al.* (1999) also reported that they used modified versions of CVAAS and CVAFS to reach the detection limits down to 0.1 ng/L for total mercury and 1 pg/L for MeHg. The summary of current analytical techniques for total mercury is listed in Table 2.3. Based on the reviews of current analytical techniques, from Table 2.3, in this study, EPA Method 7473 (Clean Techniques) with CVAAS was applied for determination of total mercury in wastewater, sludge, biosolids and biogas samples collected during the July 2003 - June 2004 sampling period at ROPEC.

2.5 Models to Predict the Fate of Mercury in MWTPs

2.5.1 Literature Review on Mercury Modeling

Metals are among the most frequently detected contaminants in municipal wastewater (Monteith, 1993). Metals discharged in treated wastewater streams can be toxic to aquatic biota and can be potential hazards to the receiving water body. Additionally, metals accumulated in wastewater sludge may restrict disposal options for the produced sludge. Regulatory authorities in North America have implemented legislation to reduce the emissions of metals in both liquid and solid effluents (U.S. Clean-water Act, 1987; Ontario Municipal-Industrial Strategy for Abatement, 2002; Provincial Nutrient Management Act, 2002). Because control of liquid and solid effluent quality is complicated and in order to reduce the cost of implementing regulations,

reliable models that can be used to predict the behaviour of metals in wastewater treatment plants are needed.

Models developed to describe the fate of heavy metals in municipal wastewater treatment plant unit processes, can be employed by treatment operators and regulators to predict the effects of variable input loadings of toxic trace contaminants on effluent quality and residual sludge quality. Based on discharged effluent or sludge, models can also be utilized to determine allowable headwork concentrations.

The literature contains numerous models for soluble chemical speciation calculations in various media. Adsorption models and empirical models have been developed to predict the speciation and distribution of metals between the soluble and biosolids phases in activated sludge wastewater treatment environment. Equilibrium chemical principles including soluble complexation and surface adsorption reactions were used to calculate the distribution of metals in activated sludge (Nelson *et al.*, 1981; Patterson and Kodukula, 1984; Fukushi *et al.*, 1996; Wang *et al.*, 1999). More recently, adsorption on the solid phase has been included in speciation models to allow calculation of the distribution between soluble and particulate (adsorbed) phases. This was developed to quantify the metal uptake by sludge particulates as affected by pH and DOM (Wang *et al.*, 2000; 2003; Wang and Huang; 2002). In order to calculate the speciation and distribution of heavy metals including Hg^{2+} in wastewater treatment plants, the adsorption constants of heavy metals for activated sludge particulates were calculated. The predicted heavy metal distribution results were then verified using the measured metal distribution data from field samples (Wang *et al.*, 2003). The model was developed to calculate metal distribution as a function of pH to analyze the behavior of heavy metals in aeration tank mixed liquors based on the adsorption constants and the field pH and SS

conditions. The metal distribution in mixed liquor samples can be calculated by (Wang *et al.*, 1999; 2000; 2003):

$$R = \frac{K_H K_S \Gamma_m SS}{K_H K_S \Gamma_m SS + [H^+] + K_H} \tag{2.1}$$

where:

R = the ratio of adsorbed metal to the total metal;

Γ_m = sludge site density (1.7×10^{-3} mol/g-SS for activated sludge);

K_H = acidity constant of sludge sites for the secondary sludge ($10^{-6.1}$ mol/L);

K_S = stability constant of metal-sludge complex (L/mol);

SS = suspended solids concentration (g/L).

The studies showed that 1) heavy metal uptake by sludge particulates is a physical-chemical process that is not related to the sludge viability (Fukushi *et al.*, 1996; Wang *et al.*, 1999); 2) metal uptake by activated sludge is significantly affected by pH and high concentrations of dissolved organic matter (DOM) (Nelson *et al.*, 1981; Tien and Huang, 1987; 1991; Wang *et al.*, 1999); and 3) in neutral and low pH conditions, the DOM effects on metal uptake is not significant (Wang *et al.*, 1999).

Compared with adsorption models (Nelson *et al.*, 1981; Patterson and Kodukula, 1984; Wang *et al.*, 1999), the mechanistic model, termed TOXCHEM$^+$ (Monteith *et al.*, 1993; Parker *et al.*, 1994), was a significant improvement over earlier models to predict the fate of heavy metals including mercury in MWTPs. TOXCHEM$^+$ had adsorption and heavy metal precipitation in its models. This fate model was employed in the present study and will be described in detail below.

2.5.2 TOXCHEM$^+$

TOXCHEM$^+$, a commercial software, was developed by Enviromega Ltd. to simulate the fate of toxic organics and heavy metals in wastewater sewer systems and treatment plants (Enviromega, 1996; Monteith *et al.*, 1993; and Parker *et al.*, 1994). The model includes both steady state and dynamic models to simulate operation of a conventional activated sludge plant, incorporating grit removal, primary clarification, aeration, and secondary clarification unit processes. The schematic diagram of the fate of heavy metals in MWPT is illustrated in Figure 2.1. The definitions of terms describe each of the terms used in subsequent equations, and detailed modeling equations were listed in Appendix A.

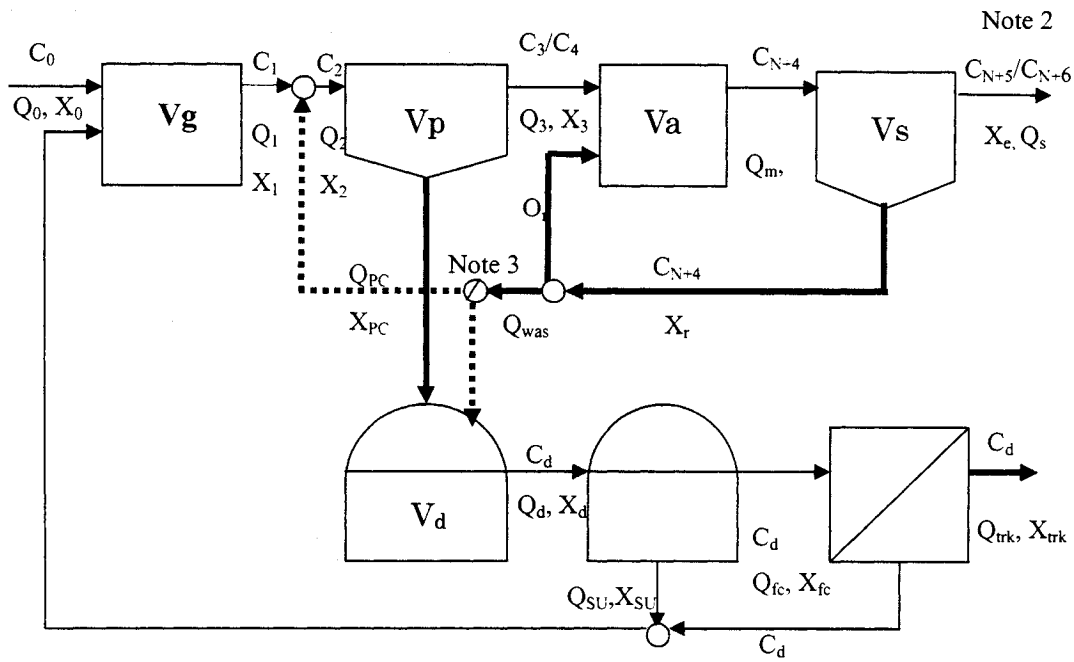


Figure 2.1 Schematic diagram of the fate of heavy metals in MWPTs

Note 1: C_3/C_4 are the contaminant concentrations before/after the weir in the primary clarifier.

Note 2: C_{N+5}/C_{N+6} are the contaminant concentrations before/after the weir in the secondary clarifier.

Note 3: The waste activated sludge can be wasted directly to the digester or mixed with the grit chamber effluent prior to being wasted with the primary waste sludge.

The removal mechanisms for trace heavy metals include: (1) metals sorbed to biological solids and (2) metal precipitates. The mathematical basis for the hazardous heavy metals process simulation is based on mass balances of the contaminants around each unit process. In the current version of TOXCHEM$^+$, equalization basins, channels, trickling filters, rotating bio-contactors, anaerobic digestion, sludge dewatering and centrifuges, have been modeled to help predict the behaviour of trace metals in more complex MWTPs.

For all metals including mercury the biological rate constants are always assumed to be zero. A sensitivity analysis feature is incorporated into the program to allow the user to investigate the impact of design and operating conditions and the contaminants physical/chemical properties on removal by various MWTP unit process and mechanisms.

Unfortunately no parameter values exist for mercury in the model's database. Parameters for mercury in wastewater treatment processes can be obtained by conducting full-scale sampling, to obtain the critical parameters, K_{p1}, the primary solids partitioning sorption coefficient of the metals sorbed onto volatile suspended solid particles and K_{p2}, the partitioning sorption coefficient of the metals sorbed onto volatile suspended biological solids, respectively, which are needed to run this software model. By incorporating these parameters with full-scale treatment plant operating data, a particular MWTP can be modeled. The method for determination of mercury partitioning sorption coefficient K_{p1}, and K_{p2} values will be discussed in detail in Chapter 4.

Inputs to the TOXCHEM$^+$ model include influent wastewater flow rate, influent metal concentration, dimensions of individual process units, plant operating conditions (for instance, mixed liquor suspended solids concentration), and raw wastewater, primary

sludge, and secondary effluent suspended solids concentrations. The model then predicts metals concentrations in primary sludge, return activated sludge, waste activated sludge, and secondary settler effluent, based on mass balance calculations and removals through precipitation and sorption. Volatilization of metals is not incorporated in the model. The steady state model accounts for removal by sorption of soluble metals onto settleable solids and precipitation of the metals into a settleable form. TOXCHEM$^+$ simulates sorption of metals to bio-solids and the precipitation of metals based on the solubility of the metal in the influent, effluent and digester effluent. The model assumes separate sorption partitioning and solubility coefficients for the primary and activated sludge systems. Additionally, anaerobic digestion will also have a specific solubility coefficient. All other processes (i.e. chemical addition) in the TOXCHEM$^+$ model are assumed to have no effect on the sorption or solubility of the metal. In the case where multiple streams are mixed before entering a process, the model calculates new partitioning sorption and solubility coefficients for the mixed stream based on a mass flow-weighted basis. A new metal liquid concentration will then be calculated based on this value. If the liquid concentration is above the newly calculated solubility level then the metal will form a precipitate. Once a precipitate is formed TOXCHEM$^+$ assumes that the precipitate will not re-dissolve. Three major mass balances employed in TOXCHEM$^+$ to simulate the fate and transport of mercury in MWTPs are described as below.

2.5.2.1 Influent Mass Balance

The influent total mercury concentration is partitioned into soluble, sorbed and precipitate fractions by initially calculating the influent mercury concentration based on Eq.2.2:

$$C_{Test} = \frac{C_0}{(1 + K_{P1} X_0)} \tag{2.2}$$

where,

C_{Test} = current influent soluble concentration of total mercury, µg/L
C_0 = influent total mercury concentration (total soluble, sorbed and precipitate), µg/L
K_{P1} = primary solids sorption coefficient, L/g
X_0 = influent volatile suspended solids concentration, g/L

If C_{Test} is greater than the mercury's primary solubility limit, the soluble concentration is set to the influent solubility and the concentration of mercury present as precipitate is calculated as Eq. 2.3:

$$C_{P0} = C_0 - (1 + K_{P1} X_0) C_{soli} \tag{2.3}$$

where,

C_{P0} = concentration of the mercury precipitate, µg/L
C_{soli} = solubility limit of the mercury, µg/L

If C_{Test} is less than the mercury's primary solubility limit then the concentration of mercury present as precipitate (C_{P0}) is zero and the soluble concentration (C_{soli}) is equal to C_{Test}. The total mercury concentration at any point in the treatment process is calculated as the sum of the soluble, sorbed and precipitate fractions.

Assumptions associated with modeling the fate of mercury in the unit processes are as follow:

- The aeration basin is a series of equal-volume CSTRs.
- Sludge wasting occurs only from the clarifiers.
- The soluble mercury concentration in the activated sludge waste and recycle streams is equal to the secondary clarifier-influent soluble mercury concentration.
- The soluble mercury concentration in the primary sludge waste stream is equal to the primary clarifier-influent soluble mercury concentration.
- The equilibrium-sorbed mercury concentration is a first-order function of the liquid-phase mercury concentration.
- Sorption is reversible.
- Sorption and desorption occur instantaneously.
- Precipitates in the primary clarifier are removed to the same extent as TSS.
- Precipitates in the secondary clarifier are concentrated in the same ratio as the biomass.

2.5.2.2 Biological Processes Mass Balance

The effluent leaving a biological process is considered to have a different characteristic (sorption and solubility) from the influent to the process. For example, the influent of biological process is equal to the primary effluent, therefore the sorption partitioning coefficient of total mercury in the primary effluent (K_{p1}), is different from the sorption partitioning coefficient of total mercury sorbed onto the biological solids (K_{p2}) in the effluent leaving the biological process. Thus, to calculate the total mercury concentrations leaving a biological process the following equations are used:

$$C^*_{Test} = \frac{C^*_0}{(1 + K_{P2} X_b)} \tag{2.4}$$

where,

C^*_{Test} = biological process effluent liquid concentration of total mercury, µg/L
K_{P2} = sorption coefficient of the total mercury to biological solids, L/g
X_b = concentration of volatile suspended solids in the biological process, g/L
C^*_0 = biological process influent total mercury concentration (total liquid, sorbed and precipitate), µg/L

If C^*_{Test} is greater than the solubility of the total mercury in the secondary effluent, then the following equations are used:

$$C_P = C^*_{P0} + C^*_{Test} - C_{sole} \tag{2.5}$$

$$C_{out} = C_{sole}\left(1 + K_{P2} X_b\right) \tag{2.6}$$

where,

C_P = precipitate concentration of total mercury leaving the biological process, μg/L
C^*_{P0} = precipitate concentration of total mercury entering the biological process, μg/L
C_{sole} = solubility of the mercury in the effluent of the biological process, μg/L
C_{out} = effluent liquid concentration of the total mercury including the sorbed fraction, μg/L

If C^*_{Test} is less than or equal to the C_{sole}, then the value for C_P is set equal to the value of C^*_{p0}, and C_{out} is set equal to C^*_{Test}.

For each stream leaving a biological process a value for mercury solubility and mercury sorption will be calculated when leaving the process. For biological processes the value of K_P for the stream is set equal to K_{P2} and the value of C_S is set equal to C_{sole}.

2.5.2.3 Digester Processes Mass Balance

The effluent leaving an anaerobic digester is also considered to have a different solubility value than the influent to the process. To calculate the total mercury concentrations leaving a biological process the following equations are used:

$$C'_{Test} = \frac{C_0^*}{(1 + K_P X_d)} \tag{2.7}$$

where,

C'_{Test} = concentration of total mercury leaving an anaerobic digester, μg/L
C_0^* = concentration of the total mercury in the influent to the biological process, μg/L
K_P = sorption coefficient of the total mercury in the influent stream, L/g
X_d = concentration of volatile suspended solids in the anaerobic digester process, g/L

If C'_{Test} is greater than the solubility of the metal in digester effluent, then the following equations are used:

$$C'_p = C^*_{P0} + C'_{Test} - C_{sold} \tag{2.8}$$

$$C'_{out} = C_{sold}(1 + K_P X_d) \tag{2.9}$$

where,

C'_P = precipitate concentration leaving the anaerobic digester process, μg/L
C'_{p0} = precipitate concentration entering the anaerobic digester process, μg/L
C_{sold} = solubility of mercury in the effluent from the digester process, μg/L
C'_{out} = effluent liquid concentration of the total mercury including the sorbed fraction, μg/L

If C'_{Test} is less than or equal to the C_{sold}, then the value for C'_p is set equal to the value of C_{P0} and C'_{out} is set equal to C'_{Test}.

For each stream leaving an anaerobic digester a value for mercury solubility will be calculated. The sorption coefficient is considered to remain constant through the anaerobic digester process. For the anaerobic digester process the value of C'_p in the stream is set to C_{sold}.

2.5.2.4 Stream Mixing

TOXCHEM$^+$ modifies the value for K_P and C_S for total mercury modeling whenever multiple streams are combined into a unit process. The model assumes that the new value of K_P and C_S will be based on a flow-weighted average of the value in the streams that are combined together. An example of a mixing of two streams is shown in the equation below:

$$K'_P = \frac{K'_{P1}Q_2 + K'_{P2}Q_2}{Q_1 Q_2} \tag{2.10}$$

where,

K'_P = new sorption coefficient of the mixed stream, L/g,
K'_{P1} = sorption coefficient of the first stream, L/g,
Q_1 = flow of the first stream, m^3/day,
K'_{P2} = sorption coefficient of the second stream, L/g,
Q_2 = flow rate of the second stream, m^3/day.

The same technique is used for calculating new values for C_S.

Despite extensive laboratory and field studies over the past the decade, little advance has been made in the modeling to predict mercury fate and transport in MWTPs. No mathematical model has been developed to simulate and predict the fate and behaviour of mercury as a function of sorption, complexation, precipitation and volatilization during the municipal wastewater treatment process. The theoretical model based on chemical reactions among heavy metal, activated sludge particulates and DOM, only simulated mercury sorption on the activated sludge particulates and complexation with DOM to predict the mercury distribution in mixed liquor and mercury removal under various pH conditions (Wang *et al.*, 2002; 2003). However, the mechanisms of precipitation and volatilization were not considered in this sorption model. They used a

batch equilibrium method for mercury uptake studies, and the experiment was conducted in multi-metal systems. The mercury sorption constant was obtained from uptake experiments using activated sludge samples collected from four full-scale municipal wastewater treatment plants at different SS concentrations. Because the adsorption constants determined using different activated sludge samples had the same order of magnitude, therefore the normalized adsorption constant (log Ks) of Hg^{2+} for activated sludge particulates was set to 6.6. On the basis of the normalized adsorption constant and the field pH and SS conditions, the distribution of Hg^{2+} in mixed liquor samples was calculated by Eq.2.1.

Comparing with the above sorption model, TOXCHEM$^+$ used three mass balance equations, metal adsorption constants in primary and secondary treatment processes and solubility limits to calculate the fate of total mercury in the entire municipal wastewater treatment plant. The adsorption constants and solubility limits could also be obtained by many batch equilibrium experiments. Similar to Wang (2003), the mechanism of volatilization of elemental mercury and MeHg was not accounted for in TOXCHEM$^+$. However, it was reported that mercury volatilization in the natural environment was modelled by MERC4, which was developed by EPA for use with the EPA's WASP4 (Water Quality Analysis Program, recently upgraded to WASP6) water quality modeling system. The MERC model is a generalized mercury transport, speciation, and kinetics model. It was developed for application to a variety of natural sites experiencing mercury contamination including ponds, streams, lakes, and estuaries. Mercury volatilization can be modeled as a Fickian diffusion process using the two-layer film model and assuming that resistance to transfer is predominantly in the liquid phase. The flux, J_{vol}, of elemental

mercury from the water column to the atmosphere due to diffusive exchange was given by:

$$J_{vol} = K_v([Hg^0]_s - [Hg^0]) \quad (2.11)$$

where:

J_{vol} = the flux of elemental mercury from the water column to the atmosphere, ($\mu g/m^2 day$);

K_v = coefficient of overall mass transfer for elemental mercury;

$[Hg^0]_s$ = saturation concentration of Hg^0 with respect to background atmospheric concentrations, ($\mu g/m^3$);

$[Hg^0]$ = concentration of elemental mercury in the water column, and calculated by:

$$[Hg^0]_s = \frac{[Hg^0]_g}{H_e} \quad (2.12)$$

where:

$[Hg^0]_g$ = the background concentration of atmospheric elemental mercury, ($\mu g/m^3$);

H_e = the dimensionless Henry's Law coefficient for elemental mercury.

It was reported that the vapour pressure of elemental mercury was strongly dependent upon temperature, and it vaporized readily under ambient conditions. Its saturation vapour pressure was 14 mg/m^3 at 20°C (Bale, 2000).

It was also reported that two approaches, Flux Chamber Method and Micrometeorological Method, had been applied for measuring mercury volatilization rate (flux) over air- water surfaces to quantify the mercury volatilisation from a water body to the atmosphere (Schroeder, 1995; Boudala *et al.*, 2000). In this study, the Flux Chamber Method was applied for measuring the total gaseous mercury released from the secondary clarifiers to quantify the total mercury loading in the gaseous streams at ROPEC.

Summary: On the basis of extensive literature review above, it is important and feasible to conduct investigations on the fate and transport of total mercury in wastewater, sludge and gaseous streams at ROPEC through the approaches of complementing a full-scale field sampling program, performing mass balances around each process unit and establishing mercury models using TOXCHEM$^+$ to simulate and predict the fate of mercury in differing ways: sorption, complexation, precipitation and volatilization in the entire municipal wastewater treatment unit processes.

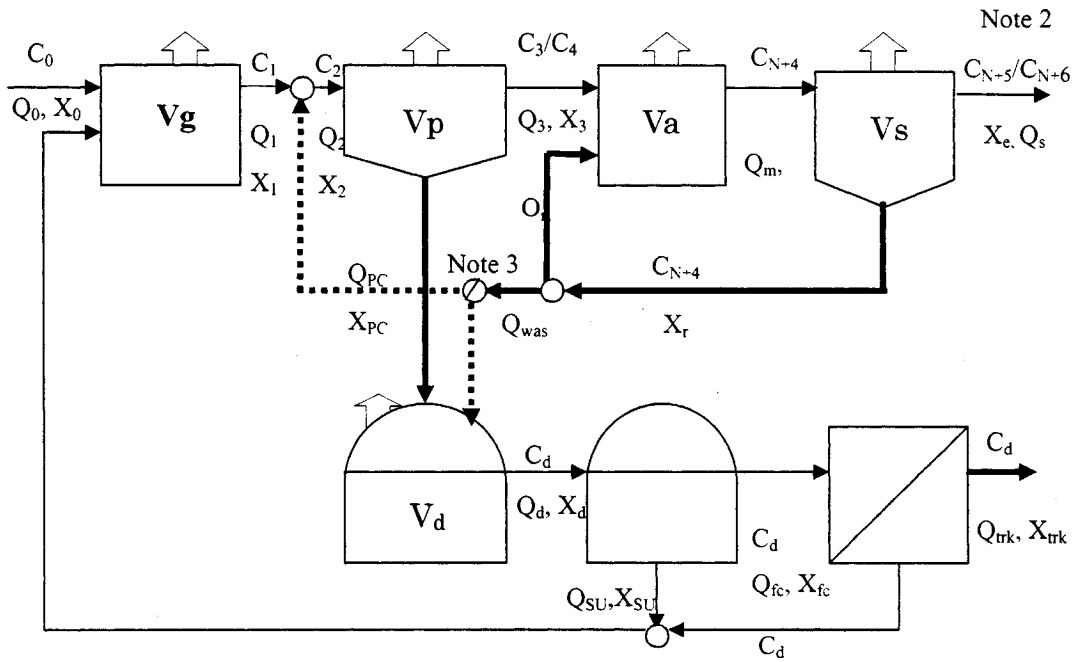


Figure 2.2 Schematic diagram of conceptual mercury model for predicting the fate and transport of mercury in MWPTs

Note 1: C_3/C_4 are the contaminant concentrations before/after the weir in the primary clarifier.

Note 2: C_{N+5}/C_{N+6} are the contaminant concentrations before/after the weir in the secondary clarifier.

Note 3: The waste activated sludge can be wasted directly to the digester or mixed with the grit chamber effluent prior to being wasted with the primary waste sludge.

⇧: Volatilization mercury stream; ⟶: Wastewater streams; ⟹: Sludge streams.

Currently, the low level sensitive analytical techniques for total mercury provide ultra clean techniques of MDL down to 0.2 ng/L. This low level detection will avoid the difficulties associated with non-detectable contaminations. Based on the mercury modeling review, a mercury conceptual model can be established for simulating the fate and transport of mercury in the ROPEC wastewater treatment plant. As illustrated in Figure 2.2, the differences between a conceptual model of the fate of the different species of mercury in MWTPs and TOXCHEM$^+$ are mercury volatilization in grit chamber, primary clarifiers, aeration basins and secondary clarifiers, which should be included in the TOXCHEM$^+$ to identify and quantify the mercury volatilization. If mercury volatilization were insignificant, the current version of TOXCHEM$^+$ could be employed as an appropriate tool to help simulate the fate of mercury in municipal wastewater treatment plants.

CHAPTER 3 Experimental Materials and Methods

Introduction

Up to late 1980s, the detection limit of mercury in water samples was very high (0.1 μg/L) due to poor sampling and poor analytical techniques (Driscoll *et al.*, 1994). At present the detection limit of mercury in water samples has been improved by combining both sampling and handling techniques and methods of mercury analysis i.e. cold vapor atomic fluorescence spectrophotometry (CVAFS), detection limits 0.001 ng/L and cold vapor atomic absorption spectroscopy (CVAAS), detection limits 0.1 ng/L. For methylmercury determination, the detection limits could be as low as 1 pg/L in water samples using CVAFS (Pichet *et al.*, 1999)

In the present study, the "clean hands-dirty hands" method of sample collection was combined with low detection limit CVAAS for a full-scale sampling program at the Robert O Pickard Environmental Centre (ROPEC). The analysis of the wastewater and sludge samples from ROPEC was performed from July 2003 up to June 2004. Total mercury (THg) mass balances for the primary, the secondary and the entire treatment process were performed and the partitioning sorption coefficients for total mercury between the dissolved and the particulate phase of the wastewater for the primary clarification and activated sludge treatment processes (K_{p1} and K_{p2}) were also determined. This data were used to simulate the ROPEC treatment process and establish the baseline for predicting the fate of mercury in wastewater, sludge and gaseous streams at ROPEC using TOXCHEM$^+$.

3.1 Description of Facility and Operation Data

ROPEC serves the urban Municipality of Ottawa-Carleton with a population of more than 780,000 people. The facility is designed to treat an average daily flow of 545,000 m^3/d with a maximum peak daily flow of 1,362,500 m^3/d (Gore & Storrie Limited, 1994). The plant is designed to remove suspended solids, carbonaceous biochemical oxygen demand (BOD) and phosphorus compounds, and its effluent is disinfected with chlorine prior to discharge to the Ottawa River. Biogas produced during anaerobic digestion of primary and secondary wastewater sludge is used to supplement plant energy needs. The ROPEC plant operation data, which have been applied in the modeling simulation, are summarized in Table 3.1. The average effluent criteria used in

Table 3.1 Summary of ROPEC wastewater treatment plant characteristics

Parameter	
Wastewater flow rate (m^3/d)*	420,000
Influent total suspended solids concentration (mg/L)*	215
Grit chamber surface area (m^2)	4,750 (Units = 10)
Grit chamber depth (m)	5.3
Primary clarifier surface area (m^2)	11,780 (Units =15)
Primary clarifier depth (m)	3.4
Suspended solids removal in primary clarifier (%)*	65
Aeration basin volume (m^3)	92,160 (Units = 8)
Aeration basin depth (m)	7.4
SRT (Sludge retention time) (day)*	5
Mixed-liquor suspended solids concentration (mg/L)*	1,200
Return activated sludge suspended solids concentration (mg/L)*	5,000
Secondary clarifier surface area (m^2)	38,430 (Units =16)
Secondary clarifier depth (m)	4
Final effluent suspended solids concentration, (mg/L) *	<10-15

* This value is total average value during sampling period.

the design of the secondary treatment facilities were more conservative than the Ontario Ministry of the Environment (MOE) regulations. The compliance criteria for MOE are shown in Table 3.2. These differences between design and compliance criteria help to ensure that the ROPEC effluent meets the MOE requirements.

Table 3.2 Differences between design effluent criteria at ROPEC and the MOE requirements

Parameter (mg/L)	Design Criteria (mg/L)	Compliance Criteria (mg/L)
BOD	15	25
SS	15	25
TP	1	1

Data examined from 2001 show that the plant provides high quality effluent exceeding government guidelines greater than 95% of the time.

3.2 Sampling Methods

The sampling for total mercury in wastewater, sludge, biosolids and gaseous streams was carried out, from July 2, 2003 to June 24, 2004 at ROPEC. The sampling plan is illustrated in detail in Table 3.3. The site plan and sampling locations are illustrated in Fig.3.1. A process schematic of the liquid treatment at ROPEC is shown in Fig. 3.2.

Table 3.3 Sampling plan for total mercury in wastewater, sludge and gaseous streams

Sampling Location	Sample Matrix	Sampling Method	Sampling Device	Sample Characterized for	Analytical Method Used
Raw Sewage (RS)	Wastewater	Composite sampling (Auto, 30 min/each)	500 mL polyethylene bottle	Total Hg, TSS, VSS, pH	EPA Method 7473, CVAAS
Primary Effluent (PE)	Wastewater	Composite sampling (Auto, 30 min/each)	500 mL polyethylene bottle	Total Hg, TSS,VSS, pH	EPA Method 7473, CVAAS
Raw Sludge (RAW) (Primary Sludge)	Sludge	Composite sampling (Manual, 4 time/day)	500 mL polyethylene bottle	Total Hg, TS, VS, pH	EPA Method 7473, CVAAS
Mixed Liquor SS (MLSS)	Wastewater	Composite sampling (Auto, 30 min/each)	500 mL polyethylene bottle	Total Hg, TSS, VSS, pH	EPA Method 7473, CVAAS
Waste Activated Sludge (WAS)	Sludge	Composite sampling (Manual, 4 time/day)	500 mL polyethylene bottle	Total Hg, TS, VS, pH	EPA Method 7473, CVAAS
Thickening Waste Activated Sludge (TWAS)	Sludge	Composite sampling (Manual, 4 time/day)	500 mL polyethylene bottle	Total Hg, TS, VS, pH	EPA Method 7473, CVAAS
Thickener Centrate (TC)	Wastewater	Composite sampling (Auto, 30 min/each)	500 mL polyethylene bottle	Total Hg, TSS, VSS, pH	EPA Method 7473, CVAAS
Digester Mixed Liquor (DIG01/02)	Sludge	Grab sampling (Manual, 1 time/day)	500 mL polyethylene bottle	Total Hg, TS, VS, pH	EPA Method 7473, CVAAS
Dewatering Centrate (DC)	Wastewater	Composite sampling (Manual, 4 time/day)	500 mL polyethylene bottle	Total Hg, TSS, VSS, pH	EPA Method 7473, CVAAS
Dewatered Sludge (CAKE)	Biosolid Sludge	Grab sampling (Manual, 1 time/day)	500 mL polyethylene bottle	Total Hg, TS, pH,	EPA Method 7473, CVAAS
Final Effluent (FE)	Treated Wastewater	Composite sampling (Auto, 30 min/each)	500 mL polyethylene bottle	Total Hg, TSS, pH	EPA Method 7473, CVAAS
Primary Clarifier	Off-gas	Composite sampling	Auto sampling	Total Gaseous Mercury (TGM)	CVAFS (Tekran 2537A)
Aeration Basin	Off-gas	Composite sampling	Auto sampling	Total Gaseous Mercury (TGM)	CVAFS (Tekran 2537A)
Secondary Clarifier	Off-gas	Composite sampling	Flux chamber	Total Gaseous Mercury (TGM)	CVAFS (Tekran 2537A)
Anaerobic Digester	Bio-gas	Grab sampling (Manual)	20 L Teflon bag	Total Hg	CVAAS

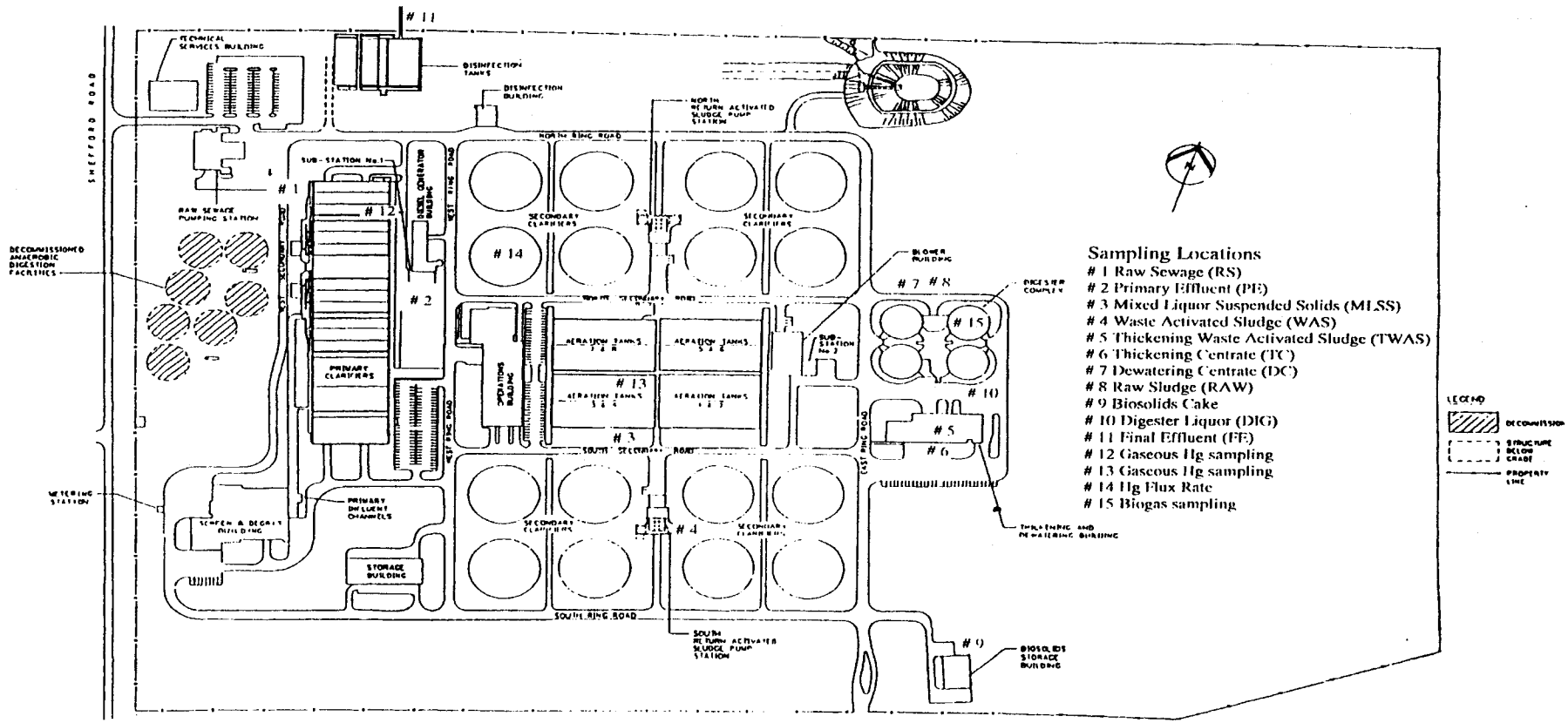


Figure 3.1 Site plan and sampling locations at ROPEC

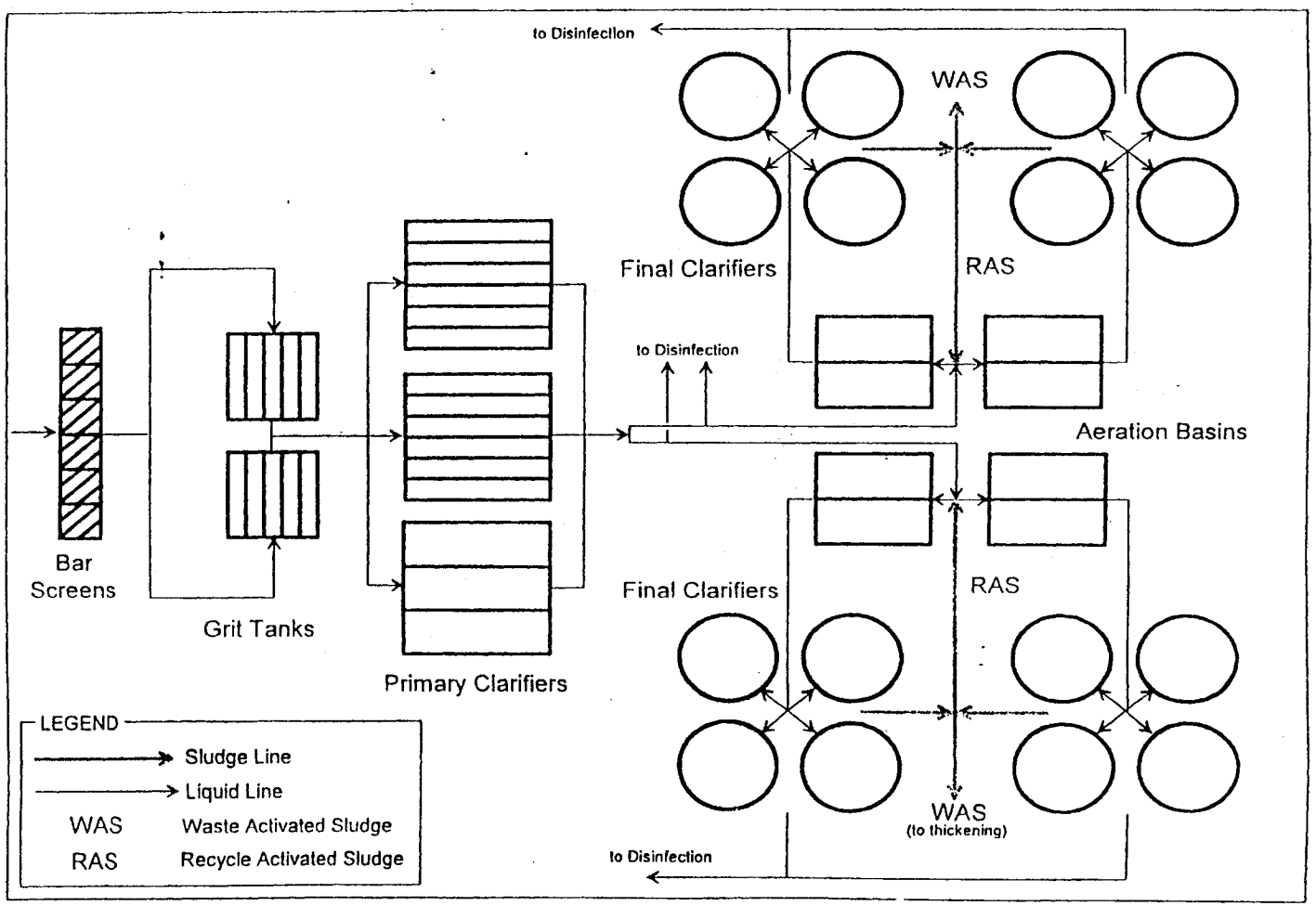


Figure 3.2 A process schematic of the liquid treatment at ROPEC

In order to reduce sample variability, a defined sampling plan was used for collecting samples from wastewater, sludge, biogas and biosolids.

3.2.1 Wastewater, Sludge and Solids Sample Collection

In the present study, the "clean hands-dirty hands" method of sample collection for trace mercury was conducted based on St. Louis *et al.* (1994). Samples were collected in 500 mL polyethylene bottles, which were cleaned with hot HNO_3. The cleaned bottles were filled with 1% ACS grade HCl and stored in new polyethylene zip bags until used for sampling (St. Louis *et al.*, 1994).

Samples collected in bottles were stored in a refrigerator overnight at 10°C. The unfiltered samples were transported to the analytical laboratory in a cooler for immediate analysis. Otherwise, samples were frozen at -18°C until being analyzed.

3.2.2 Biogas and Gaseous Sample Collection

Samples for total gaseous mercury (elemental mercury and methylmercury) in the atmosphere of the primary clarifier and aeration basin, were collected 70 cm above from the liquid surface and were analyzed with a Tekran 2537A ultra- trace mercury analysis system (detection limit < 10 pg/m^3). For secondary clarifiers, the flux chamber method was used for measuring the mercury flux fate from the water surface using a rectangular floating Teflon flux chamber, which was placed on top of the water surface of the clarifier (surface area of 0.12 m^2, dimension of 0.2 m × 0.2 m × 0.6 m). The airflow rate in the flux chamber was 0.6 m^3/h (Carpi and Lindberg, 1998; Boudala *et al.*, 2000, O'Driscoll *et al.*, 2003), and the outlet was analyzed with the Tekran 2537A

system. The details of the flux chamber method were as follows (Schroeder, 1995; Boudala *et al.*, 1999):

With the flux chamber situated on top of the water surface, the mass flow rate of mercury, R_o (in ng/min) can be calculated by:

$$R_o = R_i + R_s \quad (3.1)$$

where,

R_i= the rate at which gaseous mercury enters the chamber (in ambient air) through the inlet ports;

R_s = the rate at which mercury is emitted from (or deposited to) the water surface.

The rate of release (or uptake) of mercury at the environmental surface being investigated, R_s, is calculated by rearranging Eq. 3.1, so that:

$$R_s = R_o - R_i \quad (3.2)$$

R_o and R_i could be addressed by measuring mercury concentration at chamber outlet and inlet respectively, then times the ratio of air flow to surface area of liquid open to chamber. It is important to note that R_s can assume either a positive value (corresponding to an emission of mercury), or a negative value (corresponding to a deposition of mercury). All gaseous samples were taken from July 27 to August 1, 2003. The total gaseous mercury sampling set-ups are shown in Figs. 3.3 – 3.5A. The illustrations of the flux chamber with Tekran 2537A mercury vapor analyzer system are shown in Fig. 3.5B.

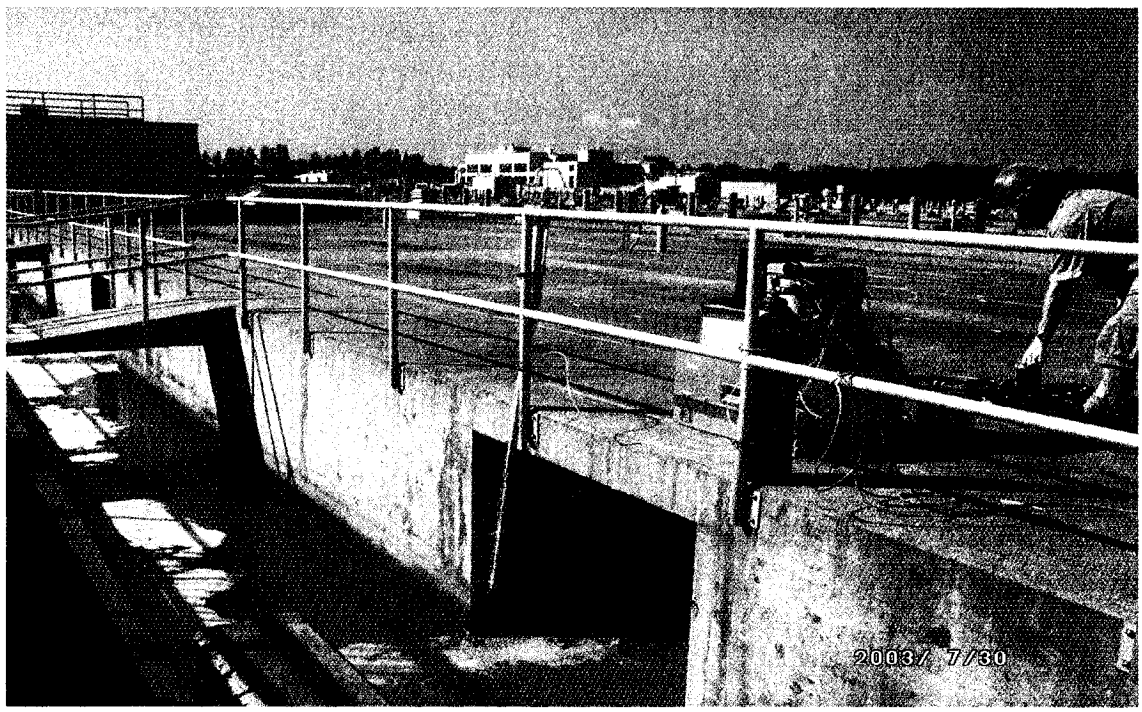


Figure 3.3 Total gaseous mercury sampling set-up over primary clarifier (# 1) at ROPEC

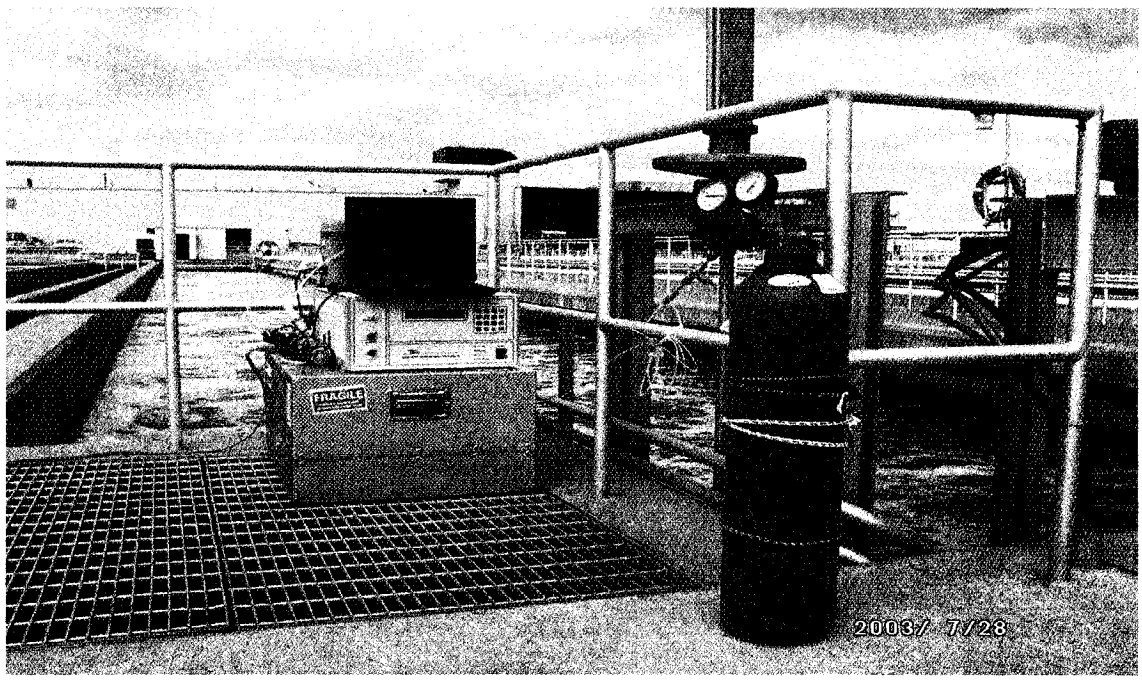


Figure 3.4 Total gaseous mercury sampling set-up over aeration basin (# 4) at ROPEC

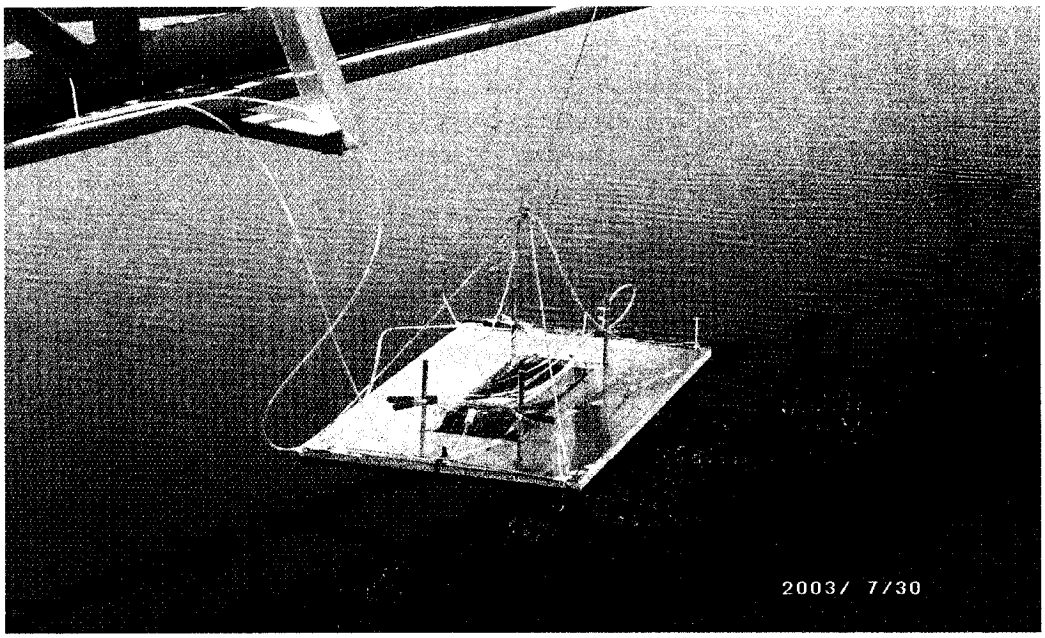


Figure 3.5A Water to air mercury flux rate measuring set-up over secondary clarifier (# 2) at ROPEC

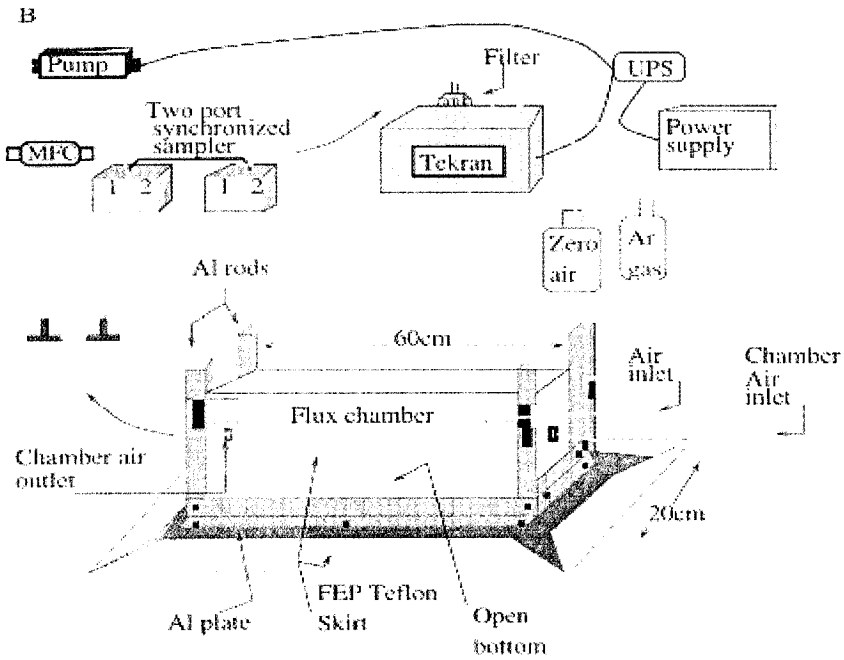


Figure 3.5B Illustration of the experimental set-up of the dynamic flux chamber with Tekran 2537A mercury vapor analyzer system (MFC: mass flow controller)
Source: Boudala et al., 2000

3.3 Analytical Methods

3.3.1 Total Mercury in Liquid and Solid Samples

Analyses for total mercury in wastewater, sludge and biosolids samples were performed with an SP-3D Mercury Analyzer. The SP-3D is an automatic mercury analyzer based on thermal decomposition, dual-step gold amalgamation and detection via CVAA at 253.7 nm to measure the quantity of mercury contained in any sample matrices (solid, liquid or gas). Samples can be analyzed with high sensitivity and precision without any pre-treatment procedure. The analysis is sensitive to 0.01 ng mercury and in liquid hydrocarbons, the detection limit can be 0.002 μg/L (parts per billion). Compared with other CVAA instruments, the SP-3D Mercury Analyzer (Figure 3.6) has the following features:

- Requires no compressed gases for operation, producing its own zero-grade carrier gas internally.
- No sample digestion required with combustion configuration.
- Capable of analyzing any sample type (solid, liquid, and gas matrices) without any pre-treatment procedure.
- Sensitivity down to 0.01 ng mercury, the detection limits can be 2 ng/L.

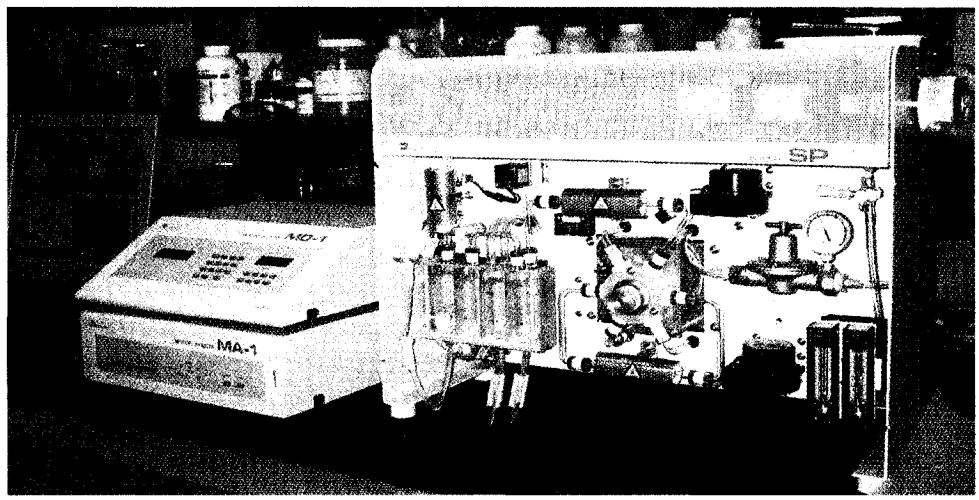
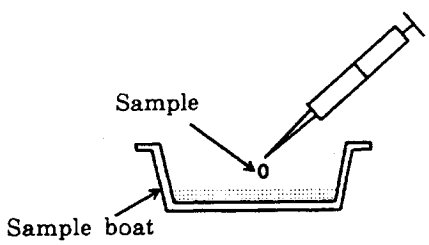


Figure 3.6 SP-3D Mercury Analyzer

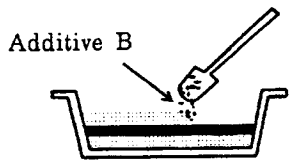
Procedure Modifications

Wastewater samples underwent pre-treatment which consisted of applying ultrasonication to 100 mL of sample for 30 min for homogenizing. After homogenizing, 100 μL of liquid sample was taken by micropipette to accurately load the ceramic holder (i.e. sample boat), and then covered with additive B (active alumna) and additive M (50% sodium carbonate and 50% calcium hydroxide). The additive application for liquid samples is illustrated in Fig 3.7. The sample boat was then put into the heating furnace of the SP-3D unit. The combustion tube was tightly covered prior to starting the machine. Upon combustion at 700°C, mercury was collected and converted as gold-amalgam on a gold sand trap in the mercury collector.

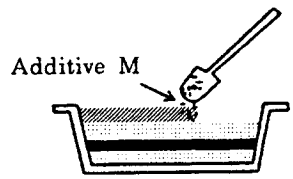


Spread a layer of additive B on the bottom of the sample boat. With the micropipette, measure the liquid sample amount and drop it onto the layer of additive B.

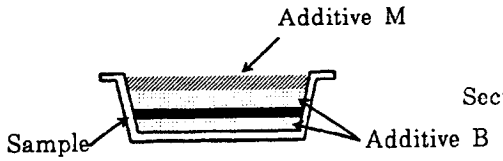
Note: Use almost care not to smear the wall of the boat with the sample.



Put a layer of additive B over the sample.



Finally, cover the layer of additive B with a layer of additive M.



Sectional view of a finished sample boat.

Figure 3.7 Additive application for liquid samples: B+S+B+M

The SP-3D utilizes "dual-step" amalgamation before the carrier gas (pure air) transfers the mercury to the CVAAS detector for detection at 253.7nm. After liberating the mercury, the mercury collector was cooled to recover its normal function for repetitive use. Buffer of 1 N KOH solution was used for liquid, sludge and solid sample determination to absorb halogenic ions (e.g. Cl^- and Br^-) and sulfide to minimize acid/moisture effects on the gold-coated sand, which caused interference with the determination of total mercury.

Freeze drying was used to homogenize the sludge and biosolids samples to avoid mercury loss during the conventional thermal drying process. Less than 50 mg of freeze dried sludge or biosolids sample was accurately weighed, then set into the sample boat on a layer of additive M' (100% sodium carbonate powder, Na_2CO_3). The sample boat was then completely filled with additive M'. A view of final sample is shown in Fig 3.8.

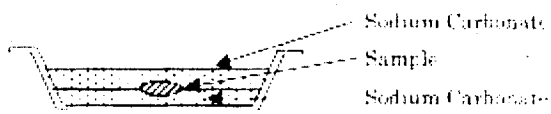


Figure 3.8 Additive application for biosolids CAKE samples: M'+ S + M'

Quality Assurance/Quality Control (QA/QC)

Mercury standard solution samples were determined before and after each 5 samples were measured to ensure the SP-3D Mercury Analyzer was in good working condition during sample determination. Reference material of sediment (MESS-2) from the Canadian National Research Council was used as a standard during total mercury determination. The QA/QC results obtained in this study were all within the limits

recommended by the reference material data sheets. The average recovery for analysis of all samples was > 95%. Additionally, on April 2004, five freeze dried sludge samples (WAS, TWAS, DIG01, RAW and CAKE) collected on December 21, 2003 were sent to Nippon Instruments Corporation (NIC) (Osaka, Japan) in duplicate for inter lab comparison for total mercury determination. The results of this study were in agreement with NIC's results and provide additional confidence in the analysis (see Appendix C, NIC analytical report).

To verify results, some biosolid samples and a portion of the sludge samples taken in duplicate were also sent to Accutest Lab (Ottawa, Ontario). Mercury samples sent to Accutest Lab were divided into two streams for analytical analysis; one stream for wastewater samples and another one for solid samples. At the Accutest lab solid samples were digested for 3 hours using a mixture of potassium permanganate, sulphuric acid, nitric acid and potassium persulphate at 95°C. The excess permanganate was then reacted with hydroxylamine hydrochloride. Mercury was then reduced with stannous chloride and measured using a Varian atomic absorption spectrometer 400 CETAC as per Standard Method 3112 (Standard Methods for the Examination of Water and Wastewater (APHA 1989)). The detection limit for this method is 10 μg/L. Liquid samples were also sent to the Accutest Lab for verification; however, almost all of the liquid samples sent to Accutest were not detectable, due to the higher method detection limits of Standard Method 3112 for liquid samples (0.1 μg/L).

3.3.2 Total Mercury in Gaseous Samples

Total gaseous mercury (TGM) analysis at the aeration basins, primary clarifier and over the secondary clarifier with flux chamber (O'Driscoll *et al.* 2003; Carpi and

Lindberg 1997, 1998; Kim and Lindberg 1995) was performed with a Tekran 2537A automatic analyser. In brief, the analytical train of this apparatus is based on amalgamation of mercury onto a pure gold surface followed by thermodesorption and analysis by CVAFS at 253.7 nm. The dual cartridge design of the Tekran 2537A allowed alternate sampling and desorption, resulting in continuous measurements of mercury in the air stream. Particulate matter in the air was removed by a 47 mm diameter Teflon filter (0.45 μm). Near real-time measurements of ambient mercury concentrations to <10 pg/m^3 are achievable with the instrument (Schroeder *et al.* 2002).

A QC protocol in the laboratory, including overall control of the sampling analysis trains was applied before and after field experimentation. No contamination of the mercury analyser was expected because it was an automated device working within a closed and clean environment. However, the Tekran analyser was recalibrated after the experimentations and was found to be within 2% of the pre-campaign calibration (Schroeder *et al.* 2002; O'Driscoll *et al.* 2003).

Biogas samples at room temperature were also analyzed with the SP-3D analyzer.

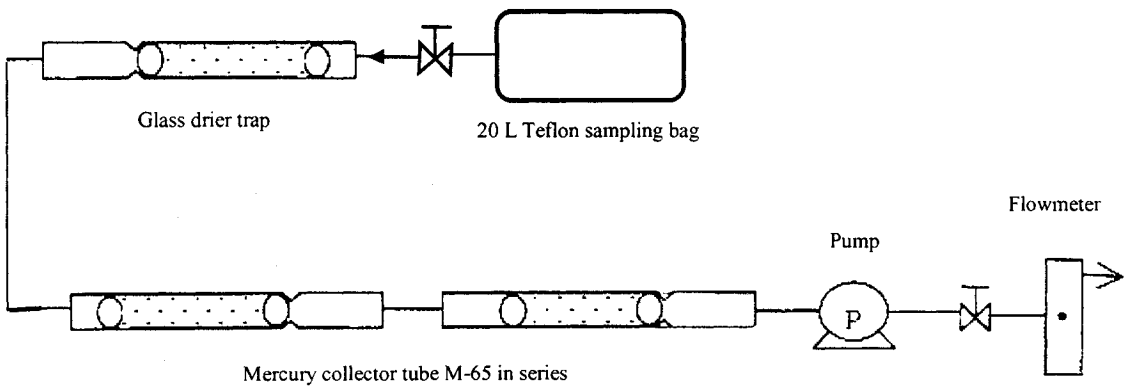


Figure 3.9 Simplified biogas sampling train

Biogas samples at ROPEC were collected in a 20 L Teflon bag and then were pulled through a glass drier trap and two glass gold traps (i.e. mercury collector tube M-65), which had been preheated at 700°C for 1 hour to reduce the blank of the gold trap. Biogas samples were drawn in by an air sampling pump operating at 300 mL/min to accurately record the volume of biogas drawn through the gold traps (Fig 3.9). The two glass gold traps were then loaded into the sample boat shown in Fig 3.10 and placed in the combustion tube of the SP-3D Mercury Analyzer to quantify the total mercury.

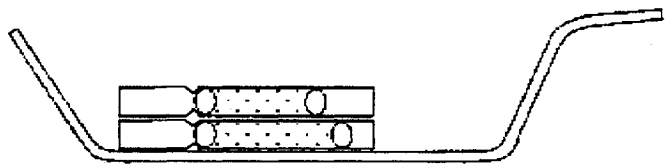


Figure 3.10 Mercury collector tubes M-65 in a sample boat

3.3.3 Analysis of Conventional Parameters TSS, VSS and pH

Conventional MWTP parameters TSS, VSS and pH in wastewater and sludge samples were determined by employing methods from Standard Methods for the Examination of Water and Wastewater (APHA, 1989). The TSS and VSS concentration were analyzed gravimetrically. An Orion general-purpose pH electrode (Orion No. 910500) was used to measure pH values.

Chapter 4 Results and Discussion

4.1 Fate of Total Mercury within a MWTP

4.1.1 Total Mercury Concentrations in Wastewater, Sludge and Gaseous Streams

In the present study, over 195 wastewater, sludge, dewatered biosolids and biogas samples were collected and analyzed for total mercury and 677 gaseous samples were auto-sampled and analyzed in situ during the sampling period of July 02, 2003 to June 24, 2004 at the ROPEC municipal wastewater treatment plant.

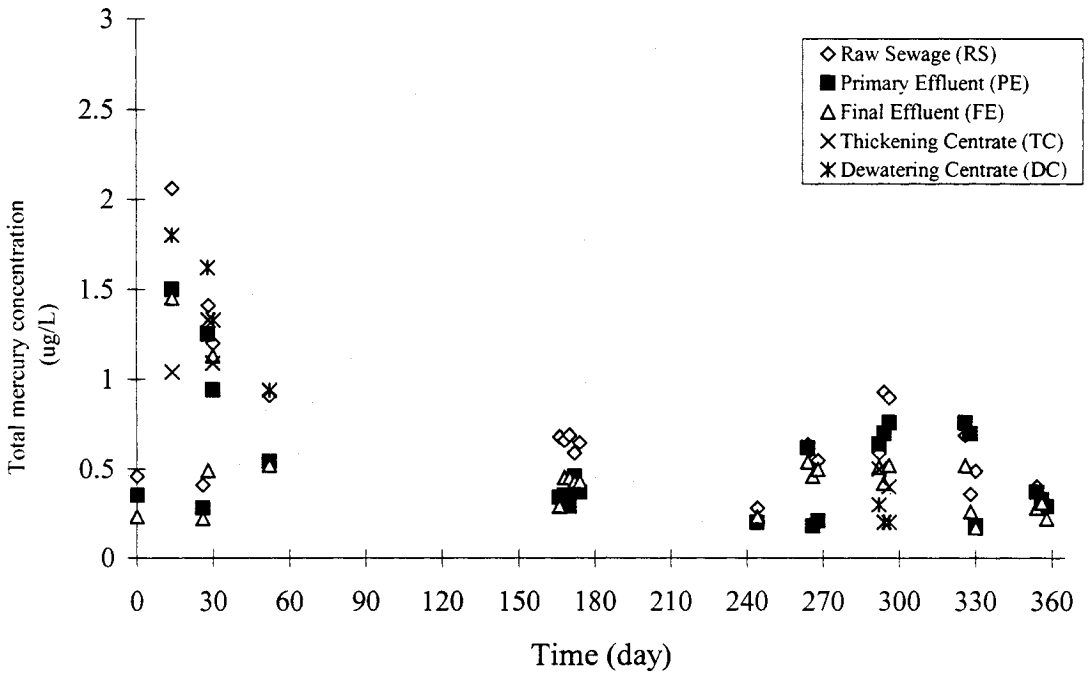


Figure 4.1 Measured total mercury concentrations in various wastewater streams at different sampling time (starting from July 02, 2003)

4.1.1.1 Total Mercury in Wastewater Samples

The total mercury concentrations in the wastewater streams are shown in Fig. 4.1, which shows the total mercury concentration in raw sewage had the highest concentration

of 2.06 μg/L on July 14, 2003 (day 14), and then decreased to an average concentration around 0.69 μg/L.

Fig. 4.1 also indicates that high total mercury concentrations occurred during the spring and summer time period, and lower total mercury concentrations occurred during the winter season (days 150 ~ 240). Therefore, there were high total mercury loadings to the ROPEC plant during the summer time due to some unknown reasons. Similarly, Fig. 4.1 also shows the highest total mercury concentrations in other liquid streams i.e. PE, FE, TC and DC, followed a similar profile to the raw influent (high total mercury concentration in the summer and spring period and lower total mercury concentration in the winter). The results showed that the overall average concentration of total mercury with standard deviations of all samples was: 0.69 ± 0.40, 0.53 ± 0.34, 0.46 ± 0.29, 0.76 ± 0.45, and 0.91 ± 0.69 μg/L in RS, PE, FE, TC and DC, respectively.

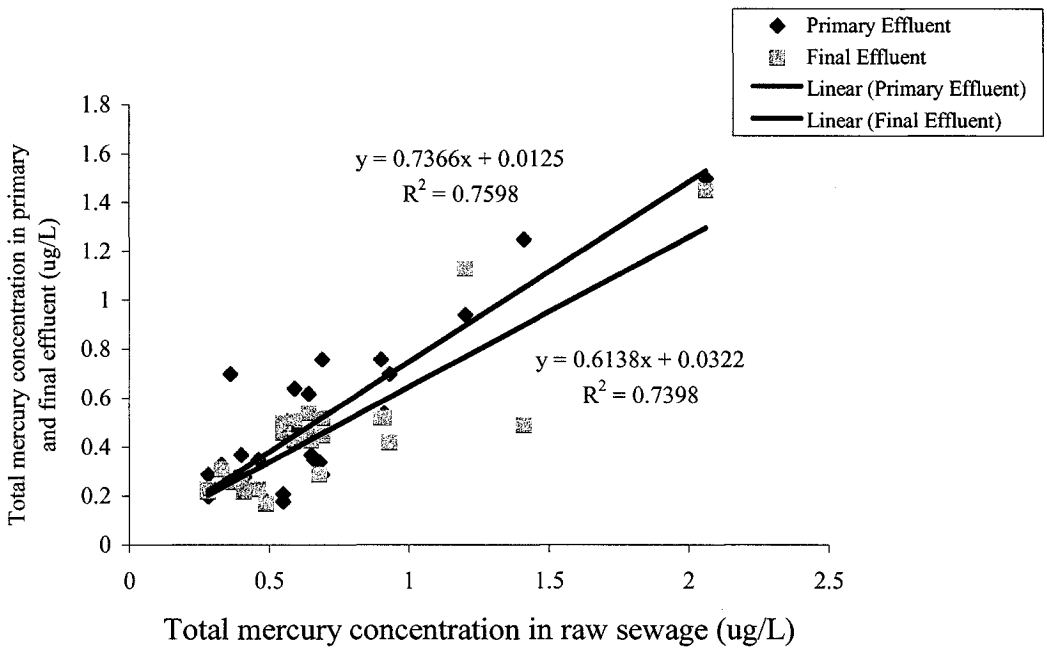


Figure 4.2 Correlations of total mercury concentrations between raw sewage and primary effluent, and final effluent

The correlations of total mercury concentrations between raw sewage and primary effluent, and final effluent are presented in Fig. 4.2. Fig. 4.2 indicates the total mercury concentrations in PE and FE were correlated with the total mercury concentration in RS

(R^2 = 0.76 for the primary effluent, and R^2 = 0.74 for the final effluent), and supports the data collected by Chipasa, (2003).

In the present study, the mean concentration of total mercury in the final effluent, 0.46 μg/L, was higher than ROPEC's historical monitoring data from 2002 (most values were not detectable, less than 0.1 μg/L). The discrepancy might be due to the different analytical approach they used (Method 3112, AAS, MDL = 0.1 μg/L). Other reasons may be: 1) When the Method 3112 was employed at low concentration, especially close to the method detection limits, the error would be increased and the results may not be reliable. 2) During their sample pre-treatment, the samples were digested with Aqua Regia at 95°C for 2 hours. In this case, at very low total mercury concentration, loss of total mercury would take place and it might account for a large portion of the total mercury in the sample.

4.1.1.2 Speciation of Mercury in Wastewater Streams

The speciation of total mercury in the wastewater stream raw sewage and final

Table 4.1 Speciation of total mercury in wastewater samples

Sample ID	Concentration (μg/L)	Sample ID	Concentration (μg/L)	Soluble Fraction
FE (DEC15UF)	1.86	FE (DEC15F)	1.12	0.60
FE (DEC17UF)	1.50	FE (DEC17F)	1.32	0.88
FE (DEC19UF)	1.66	FE (DEC19F)	1.09	0.66
FE (DEC21UF)	1.26	FE (DEC21F)	1.09	0.87
FE (DEC23UF)	1.32	FE (DEC23F)	1.64	n/a
Average	1.52		1.25	0.75
Standard Deviation	0.25		0.24	0.14
RS (DEC17UF)	1.50	RS (DEC17F)	0.64	0.43
RS (DEC19UF)	1.25	RS (DEC19F)	0.80	0.64
RS (DEC21UF)	1.63	RS (DEC21F)	0.68	0.42
RS (DEC23UF)	1.44	RS (DEC23F)	0.55	0.38
Average	1.46		0.67	0.47
Standard Deviation	0.16		0.10	0.12

Note: 1) UF: unfiltered, F: filtered. 2) FE: final effluent, RS: raw sewage. 3) n/a: not available. 4) Measuring date: 02/02/2004.

effluent samples was conducted on February 02, 2004. In this procedure 500 mL of wastewater sample was split into two equal volumes. One of the volumes was filtered through 0.45 μm Whatman glass fibre membrane filter paper. The samples were then analyzed by CVAAS and a SP-3D Mercury Analyzer. The distributions of total mercury between the dissolved and the particulate phases of wastewater are presented in Table 4.1. Table 4.1 indicates the soluble fraction of total mercury in the final effluent with standard deviation of all samples and in the raw sewage was about 75% ± 14, and 47% ± 12%, respectively. That meant that approximately 75% of total mercury that remained in the final effluent was in the soluble state, while 47% of total mercury in the raw sewage was in the soluble phase.

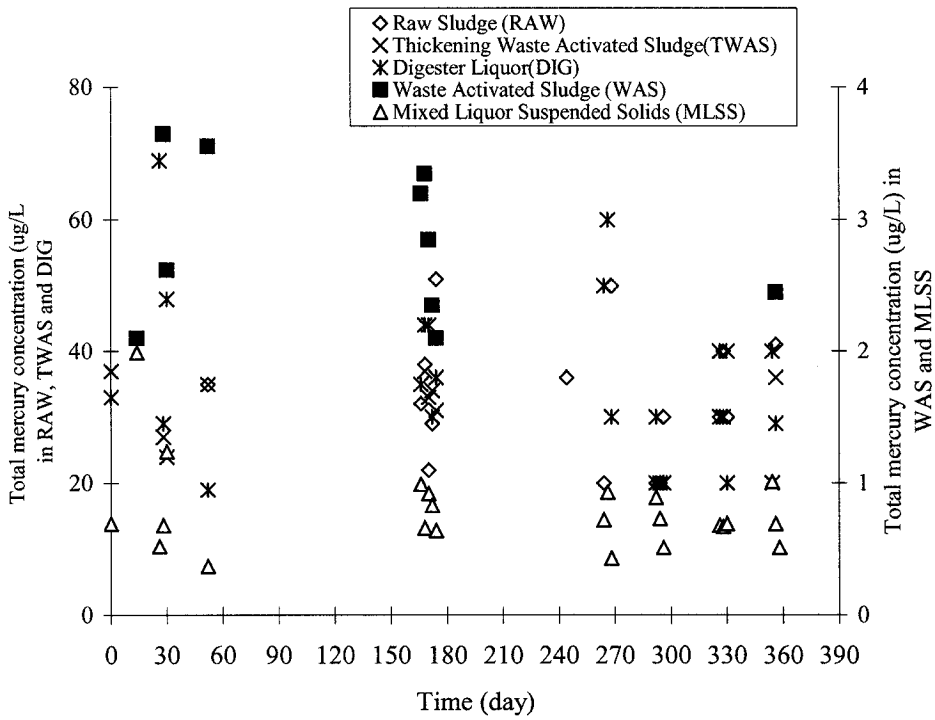


Figure 4.3 Measured total mercury concentrations in various sludge stream samples (starting from July 02, 2003)

4.1.1.3 Total Mercury in Sludge and Biosolids Samples

The total mercury concentrations in the sludge streams (RAW, MLSS, WAS, TWAS and DIG) and dewatered biosolids (CAKE) at the different sampling times are

illustrated in Figs. 4.3 and 4.4, respectively. Fig. 4.3 shows that the highest total mercury concentration in the sludge streams occurred during the summer time (16 days, and then decreased to a lower concentration.

The variation of total mercury in the wastewater stream MLSS was minimal. The concentrations ranged between 0.50 and 1.00 μg/L. The highest concentration of total mercury in the MLSS was measured in the sample collected on July 16, 2003.

Based upon the data shown in Fig. 4.3 the total mercury mean concentrations in RAW, MLSS, WAS, TWAS and DIG were estimated as: 33.00 ± 8.00, 0.78 ± 0.33, 2.82 ± 0.37, 30.00 ± 7.00 and 36.00 ± 13.00 μg/L, respectively.

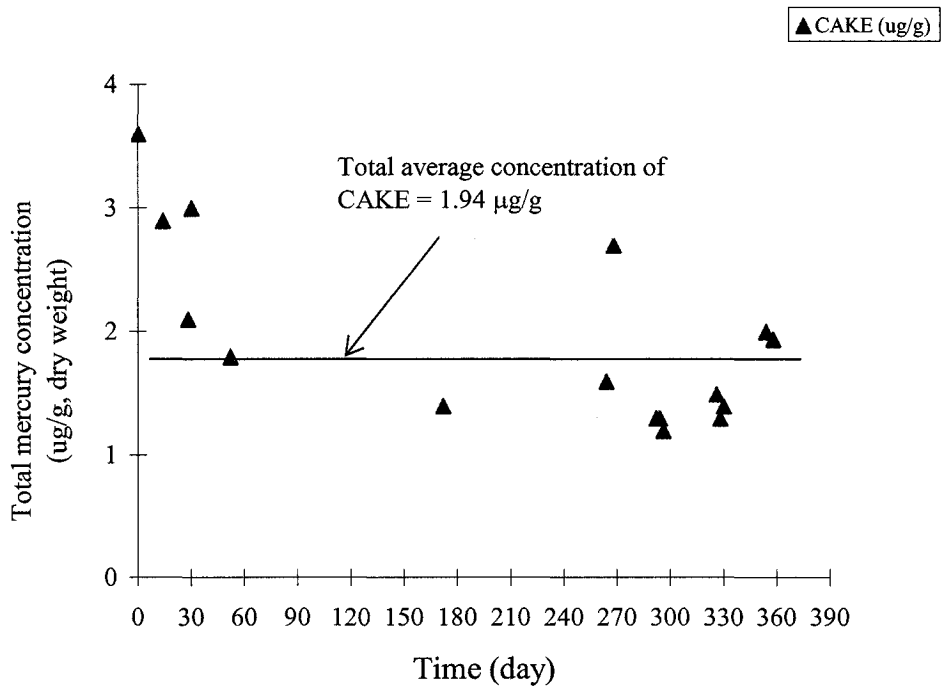


Figure 4.4 Measured total mercury concentrations in dewatered biosolids CAKE samples (30% Solids) (starting from July 02, 2003)

Fig. 4.4 shows the total mercury concentration in CAKE samples. Fig. 4.4 indicates the total mercury concentration was in the range of 1.20 to 3.60 μg/g (30% TS, dry weight). The highest concentration of total mercury was measured on July 2003 (0-30 days). The average total mercury concentration in all the CAKE samples was 1.94 ± 0.73

μg/g, (30% TS, dry weight), which was in agreement with a previous study 1.37 to 2.84 μg/g (14% to 29% TS, dry weight) (Environment Canada, 2001).

Quality Assurance/Quality Control (QA/QC)

Five replicate samples of WAS, DIG01, RAW, TWAS and biosolids CAKE were collected on December 21, 2003 and sent to the NIC laboratory to have an inter lab comparison measurement for total mercury between the laboratories at the University of Ottawa and NIC. The results of the intercomparison for total mercury in the sludge samples between two laboratories are shown in Table 4.2. Table 4.2 shows that variability of total mercury concentration in the sludge samples was small with the relative difference between the two laboratories in the range of 8 ≈ 12%. The analytical results for total mercury from NIC are listed in the Appendix C.

Table 4.2 Comparison of total mercury in sludge samples between two laboratories

Sample	Total Mercury Concentration (μg/g)		
	University of Ottawa	NIC	Relative Error %
WAS (TS 0.5%)	0.44 ± 0.09*	0.39	11
CAKE (TS 30%)	1.37 ± 0.26	1.38 ± 0.20*	-1
DIG01 (TS 2.6%)	1.25 ± 0.18	1.17 ± 0.12	6
RAW SLUDGE (TS 4.5%)	0.74 ± 0.13	0.65 ± 0.13	12
TWAS (TS 6%)	0.49 ± 0.05	0.53 ± 0.09	-8

*Standard deviation of replicate analyses

4.1.1.4 Total Mercury in Gaseous Samples

The mean concentration of total gaseous mercury (TGM) in the biogas collected from anaerobic digester #1 was 175.70 ± 5.25 ng/m^3. This is consistent with the results of a previous study (Sommar *et al.*, 1999) in which it was reported that the concentration of total mercury detected in the biogas was in the range of 109 to 175 ng/m^3. The ratio of TGM in the biogas to the total mercury concentration in the DIG samples showed that TGM in biogas was approximately 10 times greater than the elemental mercury saturation vapor pressure 14 mg/m^3 at 20°C (Bale, 2000). The concentration of TGM in the biogas was about 100 times higher than that concentration in typical ambient air (Sommar *et al.*,

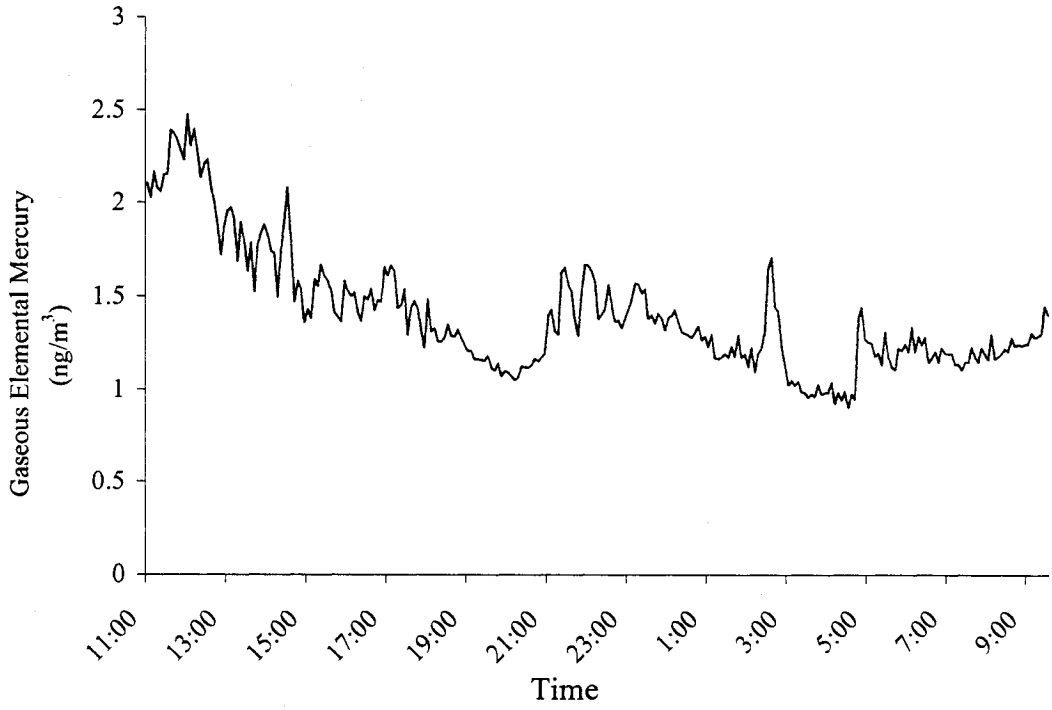


Figure 4.5 Variations of total gaseous mercury concentration over primary clarifiers

1999; Boudala *et al.*, 2000). Hence it may be identified as one of the sources of gaseous mercury to the atmosphere.

The secondary clarifiers have a surface that is similar to the water surface in lake, and hence the flux chamber method was used to measure the volatilization rate (flux rate) of total gaseous mercury from secondary clarifier to the air. The total mercury flux from water to air over the secondary clarifiers could be calculated by using following equation (which is based on the Eq.3.2):

$$\text{Flux } (ng/m^2/h) = Q\,(Fc - Fa)/SA \qquad (4.1)$$

where,
Q = chamber air flow (0.6 m^3/h)
Fc = mercury concentration at chamber outlet (ng/m^3)
Fa = mercury concentration at chamber inlet (ng/m^3)
SA = surface area of liquid open to chamber (0.12 m^2)

On substituting SA = 0.12 m^2, Q = 0.6 m^3/h, the total average chamber blank value of 0.12 $ng/m^2/h$ and the values of Fc and Fa obtained from the readings of the Tekran 2537A mercury vapor analyzer system, the mean flux was 0.89 ± 1.01 $ng/m^2/h$ (146 samples). Flux measurements over secondary clarifiers were similar to the data measured over pristine freshwater lakes, with diurnal cycles observed over clarifiers similar to what has been observed in freshwater lakes (Boudala *et al.*, 2000).

The mercury flux over the secondary clarifier with a strong diurnal cycle was consistent with the results of previous researchers in which mercury fluxes over the open water surfaces (e.g. lakes) were most strongly correlated with solar radiation, although the flux was also significantly correlated with water temperature, air temperature, DOC concentration in water, and negatively correlated with relative humidity (Schroeder *et al.*,

Figure 4.6 Variations of total gaseous mercury concentration over aeration basins

1989; Xiao *et al.*, 1991; Poissant and Casimir, 1998, Boudala *et al.*, 2000). The measured average mercury concentration in ambient air in the present study was 1.23 ± 0.07 ng/m^3 (N = 16 samples).

The concentrations of TGM over primary clarifiers, aeration basins and water to air total mercury volatilization over secondary clarifier are shown in Figs.4.5, 4.6 and 4.7, respectively. The concentrations measured in the atmosphere over the surface of the primary clarifiers and aeration basins suggested low levels of mercury volatilization to the atmosphere (i.e. data similar to ambient air).

TGM concentration in ambient air has been reported to be 1.7 ± 0.2 ng/m^3 (Sommar *et al.*, 1999). Glass *et al.* (1990) also determined the mercury levels in ambient air at Duluth, Minnesota and reported in the range of 1 to 6 ng/m^3. The measured mean TGM concentration of 1.23 ± 0.07 ng/m^3 in the present study is consistent with previous studies (Glass *et al.*, 1990; Sommar *et al.*, 1999). The concentration of TGM, which emanated from treatment units of primary clarifiers, aeration basins and secondary clarifiers at ROPEC also were similar to the ambient air concentration.

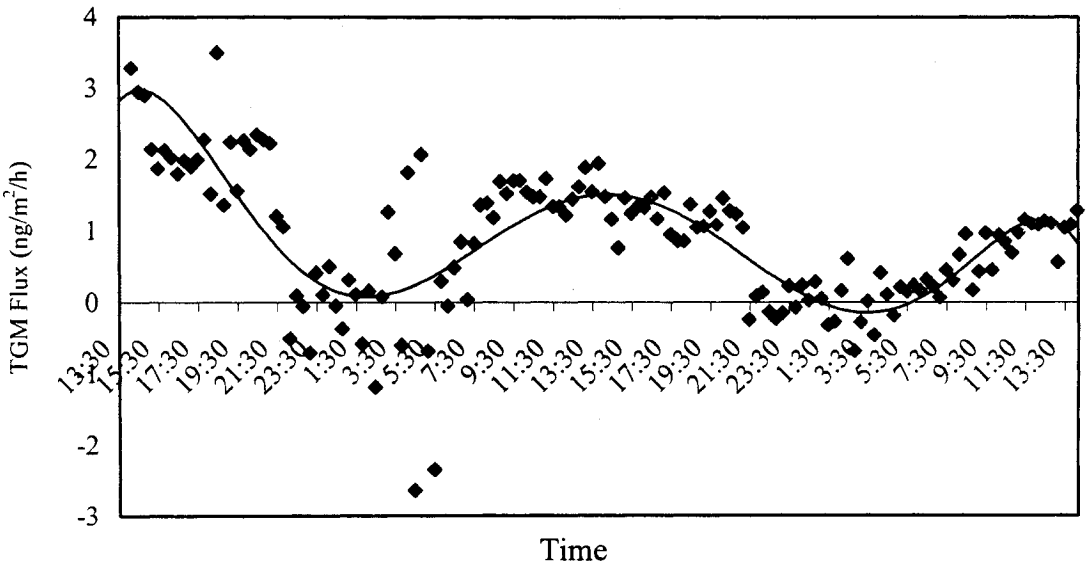


Figure 4.7 Mercury flux over secondary clarifiers

A summary of the total mercury concentration in the wastewater, sludge and gaseous stream samples with standard deviations is listed in Table 4.3. Table 4.3 shows that the total mercury concentration in the wastewater streams in the order:

RS>DC>TC>PE>FE. Thus it seems that the total mercury concentration in the liquid streams decreased after primary clarification and activated sludge treatment.

Table 4.3 Summary of total mercury concentrations measured at ROPEC

Sampling location	Total average measured concentration*	Number of samples	Range of results
Raw Sewage (RS)	0.69 ± 0.40 μg/L	24	0.28 ~ 2.06 μg/L
Raw Sludge (RAW) (TS 4.4%)	33.00 ± 8.00 μg/L	16	20.00 ~ 51.00 μg/L
Waste Activated Sludge (WAS) (TS 0.5%)	2.82 ± 0.37 μg/L	10	2.10 ~ 3.65 μg/L
Final Effluent (FE)	0.46 ± 0.29 μg/L	24	0.17 ~ 1.45 μg/L
Dewatered biosolids (CAKE) (Dry Weight, TS 30%)	1.94 ± 0.73 μg/g	15	1.20 ~ 3.60 μg/g
TGM in biogas from anaerobic digester	175.70 ± 5.25 ng/m^3	6	170.30 ~ 182.90 ng/m^3
TGM volatilization from secondary clarifier	0.89 ± 1.01 $ng/m^2/h$	146	
Gaseous elemental mercury from primary clarifier	1.39 ± 0.20 ng/m^3	261	
Gaseous elemental mercury from aeration basins	1.41 ± 0.32 ng/m^3	270	
Mixed Liquor Suspended Solids (MLSS)	0.78 ± 0.33 μg/L	23	0.37 ~ 1.99 μg/L
Primary Effluent (PE)	0.52 ± 0.34 μg/L	24	0.18 ~ 1.50 μg/L
Thickening Centrate (TC)	0.76 ± 0.45 μg/L	6	0.20 ~ 1.33 μg/L
Dewatering Centrate (DC)	0.91 ± 0.69 μg/L	7	0.20 ~ 1.80 μg/L
Thickening Waste Activated Sludge (TWAS) (TS 5.4%)	30.00 ± 7.00 μg/L	17	20.00 ~ 40.00 μg/L
Digester Liquor (Dig01/02) (TS 2.3%)	36.00 ± 13.00 μg/L	21	19.00 ~ 69.00 μg/L

* Value is expressed by total average with standard deviation of all samples.

It also shows that the total mercury concentrations in the sludge streams suggested that the mercury was strongly associated with the solids. Comparing the total mercury concentration and total solids concentration in WAS with those of in RAW, TWAS and DIG, correspondingly, the ratio of total mercury concentration WAS/RAW, WAS/TWAS and WAS/DIG remained the same at a ratio equal to 0.1. However, the ratios of total

solids in WAS/RAW and WAS/TWAS have the same ratio approximately equal to 0.1. These results strongly suggest that total mercury is associated with the solids particulates in the wastewater treatment process units. It indicated that the total mercury concentrations in the sludge streams were proportionally increased along with the increasing of total solids concentration in the corresponding sludge stream.

4.1.2 Total Mercury Removal Efficiency around Treatment Units

Total mercury mass balances across the primary clarification, activated sludge treatment unit process and across the entire facility were calculated on the basis of the measured concentrations of total mercury in the wastewater and sludge streams, the concentration of suspended solids and corresponding flow data obtained from the plant operation records. Mass balance calculations were performed separately for each sampling day and 24 sampling day data points in total were employed to carry out the mass balance calculation based upon Eqs. 4.2, 4.3 and 4.4.

Total mercury mass balance across the primary clarification process was performed based on Eq. 4.2. Eq. 4.2 was used to estimate the total mercury removal efficiency in the liquid phase of the primary effluent. The mass balance affected determination of total mercury recovery on a mass basis.

$$Q_{in,RS} \times C_{in,RS} = Q_{out,PE} \times C_{out,PE} + Q_{out,RAW} \times C_{out,RAW} \quad (4.2)$$

where,

$Q_{in,\,RS}$ = flow rate of raw sewage influent, m^3/d
$C_{in,\,RS}$ = total mercury concentration of raw sewage influent, μg/L
$Q_{out,\,PE}$ = flow rate of primary clarifier effluent, m^3/d
$C_{out,\,PE}$ = total mercury concentration of primary clarifier effluent, μg/L
$Q_{out,\,RAW}$ = flow rate of raw sludge effluent from primary clarifier, m^3/d
$C_{out,\,RAW}$ = total mercury concentration of raw sludge effluent from primary clarifier, μg/L

A total mercury mass balance across the activated sludge treatment process was carried out based on Eq. 4.3. Similar to Eq. 4.2, Eq. 4.3 was used to estimate the total mercury removal efficiency in the liquid phase of the final effluent across the activated sludge treatment process. The mass balance also affected the determination of the total mercury recovery on a mass basis.

$$Q_{in,PE} \times C_{in,PE} = Q_{out,WAS} \times C_{out,WAS} + Q_{out,FE} \times C_{out,FE} \quad (4.3)$$

where,

$Q_{in,\,PE}$ = flow rate of primary clarifier effluent, m^3/d
$C_{in,\,PE}$ = total mercury concentration of primary clarifier effluent, μg/L
$Q_{out,\,WAS}$ = flow rate of waste activated sludge, m^3/d
$C_{out,\,WAS}$ = total mercury concentration of waste activated sludge, μg/L
$Q_{out,\,FE}$ = flow rate of final effluent from secondary clarifier, m^3/d
$C_{out,\,FE}$ = total mercury concentration of final effluent from secondary clarifier, μg/L

Total mercury mass balance across the entire facility treatment processes was estimated according to Eq. 4.4. Similar to Eq. 4.2 and Eq. 4.3, Eq. 4.4 was used to estimate the total mercury removal efficiency in the liquid phase of the final effluent across the entire plant. The mass balance affected the determination of the total mercury recovery on a mass basis.

$$Q_{in,RS} \times C_{in,RS} = Q_{out,FE} \times C_{out,FE} + Yield_{CAKE} \times C_{CAKE} \quad (4.4)$$

where,

$Yield_{\,CAKE}$ = yield of biosolids, tonne/d
C_{CAKE} = total mercury concentration of biosolids, μg/kg

Total mercury removal efficiency for primary clarification, activated sludge treatment unit process and entire facility treatment unit processes were calculated by the following equations:

Percentage removal of total mercury in primary clarifier

= 1 – total mercury in primary effluent / total inputs of total mercury

$$= (1 - \frac{Q_{PE} \times C_{PE}}{Q_{in,RS} \times C_{in,RS}}) \times 100\% \quad (4.5)$$

Percentage removal of total mercury in activated sludge treatment unit

= 1 – total mercury in final effluent / total mercury in primary effluent

$$= (1 - \frac{Q_{FE} \times C_{FE}}{Q_{PE} \times C_{PE}}) \times 100\% \quad (4.6)$$

Percentage removal of total mercury within the whole facility

= 1 – total mercury in final effluent / total inputs of total mercury

$$= (1 - \frac{Q_{FE} \times C_{FE}}{Q_{in,RS} \times C_{in,RS}}) \times 100\% \quad (4.7)$$

The calculated removal efficiencies were on the basis of the wastewater stream. In theory, there should be good agreement between the input and output loadings for total mercury as it cannot be degraded and settle out in the sludge or remain in the wastewater stream. The ratio of ((In–Out)/In) × 100 equals the percentage loss or gain of total mercury. A positive value means loss and a negative value means a gain of total mercury respectively. The detailed calculation sheets for the total mercury mass balance and removal efficiency around each treatment unit are displayed in Tables 4.4, 4.5 and 4.6.

Table 4.4 shows the total mercury mass balances as well as removal efficiencies of total mercury, TSS and VSS around the primary clarification treatment process. As seen in Table 4.4, the mass balance was generally satisfactory for total mercury in the primary clarification treatment with closures between –34 and +50%. The losses or gains might be attributed to relative mismatching of influent and effluent samples. It also indicates that the best total mercury removal efficiency of 67% was observed on March 24, 2004 corresponding to removal of 54% of TSS and 57% of VSS. The mean total mercury removal efficiency with standard deviation of all samples was 27 ± 23% with an average of 42% of TSS removal efficiency and an average of 43% of VSS removal efficiency.

The average error in the mass balance was 11% of total mercury around the primary clarification process. The average daily total mercury loading in the plant influent raw swage stream was 291 g/d, and approximately 76% of the total mercury remained in the primary effluent stream. The highest total mercury loading of 863 g/d entered the plant on July 16, 2003, consequently, the highest total mercury loading to the primary effluent stream also can be observed on the same day with 27% total mercury removal efficiency associated with more than 60% TSS and VSS removal efficiency. The total mercury removal efficiency in the primary clarifier of 27 ± 23% was lower than

other studies that reported more than 50% mercury removal efficiency during primary sedimentation (Goldstone *et al.*, 1990; Balogh and Liang, 1995).

Table 4.5 shows that the average total mercury removal efficiency over all samples of activated sludge treatment process was 12% ± 28%. The mass balance on total mercury in the activated sludge treatment process showed poor closure and ranged between –74 and +57% with an average gain of –14%. The highest total mercury loading of 606 g/d with a mass balance closure of +1% to the final effluent was found on July 16, 2003 with 3% removal efficiency in the activated sludge process. The highest total mercury removal was observed on May 27, 2004 with 63% removal efficiency; however, the mass balance closure showed a 57% loss. The results for the activated sludge treatment disagree with the previous studies that indicated that total mercury was predominantly associated with solids (Goldstone *et al.*, 1990; Balogh and Liang, 1995, Wang and Huang, 2002). If this were true then the total mercury concentration in the effluent would have been much lower and the removal efficiencies would have been higher.

Table 4.6 shows the average total mercury mass balances across the entire facility. It indicates a total 35 ± 18% mercury removal efficiency along with more than 90% of TSS removal efficiency can be expected. The daily mass balance of total mercury over the whole plant ranged between –39% and +52%, with about 7% loss. Correspondingly, the highest total mercury removal efficiency of 65% occurred on May 27, 2004 with about 80% TSS removal efficiency.

The summary of total mercury mass balances with removal efficiency calculations are presented in Table 4.7. The average removal efficiencies with standard deviations over all samples for total mercury around the primary clarification, activated sludge treatment process and the entire wastewater treatment plant facility were 27 ± 23, 12 ± 28 and 35 ± 18%, respectively. Correspondingly, the TSS removal efficiencies with standard deviations overall samples in primary clarification and the entire plant were 42 ± 31 and 94 ± 5%, respectively. The results indicated approximately 65% total mercury remained in the treated effluent stream and was discharged to the receiving water body, and approximately 35% of the total mercury was associated with the solids and removed.

Table 4.4 Total mercury mass balance around primary clarification treatment process

Sampling Date	RS					RAW					PE					Primary Mass Balance	Primary Mass Balance	Primary Removal	TSS Removal	VSS Removal
	THg (µg/L)	Q (m^3/d)	Loading (g/d)	TSS (mg/L)	VSS (mg/L)	THg (µg/L)	Q (m^3/d)	Loading (g/d)	TS (%)	VS (%TS)	THg (µg/L)	Q (m^3/d)	Loading (g/d)	TSS (mg/L)	VSS (mg/L)	(g/d)	Err. %	%	%	%
07/02/03	0.46	379000	174	240	197	33*	1000	38	4.9	82	0.35	378000	132	90	70	4	5	24	63	64
07/16/03	2.06	419000	863	210	186	33*	1000	25	4.6	81	1.50	418000	627	69	60	211	24	27	67	68
07/28/03	0.41	390000	160	240	194	33*	1000	21	4.4	83	0.28	389000	109	71	56	30	11	32	70	71
07/30/03	1.41	404000	570	n/a	n/a	33*	1000	32	n/a	n/a	1.25	395000	494	n/a	n/a	44	8	13	n/a	n/a
08/01/03	1.20	382000	458	183	153	33*	1000	30	3.8	80	0.94	381000	358	80	65	70	15	22	56	58
08/23/03	0.91	351000	319	220	192	35	1000	35	5.2	76	0.54	350000	189	90	72	95	30	41	59	63
12/15/03	0.68	458000	311	200	172	32	1000	23	4.2	83	0.34	457000	155	69	55	133	40	50	66	68
12/17/03	0.66	446000	294	141	116	38	1000	33	4.3	83	0.35	445000	156	87	70	106	34	47	38	40
12/19/03	0.69	408000	282	63	52	22	1000	21	4.7	79	0.29	407000	118	81	68	142	50	58	-29	-31
12/21/03	0.59	397000	234	49	45	29	1000	37	4.4	82	0.46	396000	182	61	50	15	10	22	-24	-11
12/23/03	0.65	487000	317	n/a	94	51	1000	55	3.3	83	0.37	486000	180	n/a	n/a	81	27	43	n/a	n/a
02/03/04	0.28	505000	141	280	200	36	1000	46	4.6	72	0.20	504000	101	105	72	-6	3	29	63	64
03/22/04	0.64	408000	261	210	178	20	1000	22	4.3	83	0.62	407000	252	81	70	-13	-4	3	61	61
03/24/04	0.55	382000	210	210	171	n/a	1000	n/a	4.3	81	0.18	381000	69	96	74	n/a	n/a	67	54	57
03/26/04	0.55	379000	208	210	163	50	1000	75	4.9	74	0.21	378000	79	107	80	54	38	62	49	51
04/19/04	0.59	488000	288	220	169	20	1000	27	2.9	82	0.64	487000	311	75	55	-51	-15	-8	66	68
04/21/04	0.93	465000	432	171	140	20	1000	20	4.7	77	0.70	464000	325	71	57	87	20	25	58	59
04/23/04	0.90	483000	435	167	138	30	1000	29	4.6	79	0.76	482000	366	78	68	39	9	16	53	51
05/23/04	0.69	380000	262	80	68	30	1000	28	4.3	84	0.76	379000	288	80	68	-54	-21	-10	0	0
05/25/04	0.36	489000	176	82	64	40	1000	53	5.0	77	0.70	488000	341	82	64	n/a	n/a	n/a	0	0
05/27/04	0.49	436000	214	90	85	30	1000	45	4.1	82	0.18	434000	78	90	85	91	49	63	0	0
06/20/04	0.40	352000	141	210	168	33*	1000	34	2.9	84	0.37	351000	130	89	68	-23	-16	8	58	60
06/22/04	0.33	407000	134	169	125	41	1000	43	4.5	83	0.33	406000	134	88	61	-43	-31	0	48	51
06/24/04	0.28	385000	108	156	133	33*	1000	44	3.7	81	0.29	384000	111	91	76	-47	-34	-3	42	42
Total Avg.	0.70	420000	291	173	139	33	1000	36	4.3	80	0.53	419000	220	83	67	46	11	27	42	43
STDEV	0.40	47000	168	64	50	8	200	13	0.6	3	0.34	47000	143	12	9	69	24	23	31	30

Total mercury removal efficiency around primary clarifier % = $(1 - \frac{Q_{PE} \times C_{PE}}{Q_{in,RS} \times C_{in,RS}}) \times 100\%$,

*Total average of all samples instead of n/a.

Table 4.5 Total mercury mass balance around activated sludge treatment process

Sampling Date	PE					WAS					FE					Secondary	Secondary	Secondary
	THg (μg/L)	Q (m^3/d)	Loading (g/d)	TSS (mg/L)	VSS (mg/L)	THg (μg/L)	Q (m^3/d)	Loading (g/d)	TS (mg/L)	VS (mg/L)	THg (μg/L)	Q (m^3/d)	Loading (g/d)	TSS (mg/L)	VSS (mg/L)	Mass Balance (g/d)	Mass Balance Err. %	Removal %
07/02/03	0.35	378000	132	90	70	2.82*	5000	13	7000	5100	0.23	378000	87	10	n/a	32	24	34
07/16/03	1.50	418000	627	69	60	2.10	6000	13	4900	n/a	1.45	418000	606	5	n/a	8	1	3
07/28/03	0.28	389000	109	71	56	2.82*	6000	18	5700	n/a	0.22	389000	86	5	n/a	6	5	21
07/30/03	1.25	395000	494	n/a	n/a	3.65	6000	20	n/a	n/a	0.49	395000	193	n/a	n/a	280	57	61
08/01/03	0.94	381000	358	80	65	2.62	6000	16	n/a	4100	1.13	381000	430	6	n/a	-88	-24	-20
08/23/03	0.54	350000	189	90	72	3.56	6000	20	n/a	3500	0.52	350000	182	6	n/a	-13	-7	4
12/15/03	0.34	457000	155	69	55	3.20	8000	26	6200	4600	0.29	460000	133	8	n/a	-3	-2	15
12/17/03	0.35	445000	156	87	70	3.35	8000	26	6200	n/a	0.45	445000	200	6	n/a	-71	-45	-29
12/19/03	0.29	407000	118	81	68	2.85	8000	23	4900	n/a	0.45	407000	183	6	n/a	-88	-74	-55
12/21/03	0.46	396000	182	61	50	2.35	8000	19	4500	n/a	0.43	396000	170	5	n/a	-7	-4	7
12/23/03	0.37	486000	180	n/a	n/a	2.10	8000	17	4900	n/a	0.43	486000	209	6	n/a	-46	-26	-16
02/03/04	0.20	504000	101	105	72	2.82*	8000	22	n/a	4200	0.23	504000	116	10	n/a	-37	-37	-15
03/22/04	0.62	407000	252	81	70	2.82*	8000	22	n/a	4100	0.54	407000	220	9	n/a	10	4	13
03/24/04	0.18	381000	69	96	74	2.82*	8000	22	n/a	n/a	0.46	381000	175	10	n/a	-128	n/a	n/a
03/26/04	0.21	377000	79	107	80	2.82*	8000	23	n/a	n/a	0.50	377000	189	12	n/a	-133	n/a	n/a
04/19/04	0.64	487000	311	75	55	2.82*	8000	22	n/a	3600	0.51	486000	248	11	n/a	41	13	20
04/21/04	0.70	464000	325	71	57	2.82*	8000	22	n/a	n/a	0.42	464000	195	6	n/a	108	33	40
04/23/04	0.76	482000	366	78	68	2.82*	8000	22	n/a	n/a	0.52	482000	250	8	n/a	94	26	32
05/23/04	0.76	379000	288	80	68	2.82*	8000	21	n/a	n/a	0.52	379000	197	11	n/a	70	24	32
05/25/04	0.70	488000	341	82	64	2.82*	8000	21	n/a	7200	0.26	487000	127	18	n/a	193	57	63
05/27/04	0.18	435000	78	90	85	2.82*	8000	22	n/a	n/a	0.17	434000	74	16	n/a	-17	-22	6
06/20/04	0.37	351000	130	89	68	2.82*	7000	19	n/a	n/a	0.28	351000	98	10	n/a	13	10	24
06/22/04	0.33	406000	134	88	61	2.45	7000	16	n/a	n/a	0.31	406000	126	5	n/a	-8	-6	6
06/24/04	0.29	384000	111	91	76	2.82*	7000	19	n/a	n/a	0.22	384000	84	11	n/a	8	7	24
Total Avg.	0.53	419000	220	83	67	2.82	7000	20	6000	5000	0.46	418000	191	9		9	-14	12
STDEV	0.34	47000	143	12	9	0.37	1000	3	1000	1000	0.29	47000	116	4		93	58	28

Total mercury removal efficiency around secondary clarifier $\% = (1 - \frac{Q_{FE} \times C_{FE}}{Q_{PE} \times C_{PE}}) \times 100\%$,

*Total average of all samples instead of n/a.

Table 4.6 Total mercury mass balance across the entire facility treatment processes

Sampling	RS					CAKE					FE					Total Mass	Total Mass	Total	TSS	VSS
	THg	Q	Loading	TSS	VSS	THg	Yield	Loading	TS	VS	THg	Q	Loading	TSS	VSS	Balance	Balance	Removal	Removal	Removal
Date	(µg/L)	(m^3/d)	(g/d)	(mg/L)	(mg/L)	(ug/g)DW	(tone/d)	(g/d)	%	%	(µg/L)	(m^3/d)	(g/d)	(mg/L)	(mg/L)	(g/d)	Err. %	%	%	%
07/02/03	0.46	379000	174	240	197	3.6	124	134	30	n/a	0.23	378000	87	10	n/a	-46	-27	50	96	95
07/16/03	2.06	419000	863	210	186	2.9	124	108	30	n/a	1.45	418000	606	5	n/a	150	17	30	98	97
07/28/03	0.41	390000	160	240	194	n/a	124	n/a	30	n/a	0.22	389000	86	5	n/a	n/a	n/a	46	98	97
07/30/03	1.41	404000	570	n/a	n/a	2.1	124	78	30	n/a	0.49	395000	193	n/a	n/a	298	52	64	n/a	n/a
08/01/03	1.20	382000	458	183	153	3.0	102	92	30	n/a	1.13	381000	430	6	n/a	-64	-14	6	97	96
08/23/03	0.91	351000	319	220	192	1.8	102	55	30	n/a	0.52	350000	182	6	n/a	82	26	43	97	97
12/15/03	0.68	458000	311	200	172	n/a	113	n/a	30	n/a	0.29	457000	133	8	n/a	n/a	n/a	57	96	95
12/17/03	0.66	446000	294	141	116	n/a	113	n/a	30	n/a	0.45	445000	200	6	n/a	n/a	n/a	32	96	95
12/19/03	0.69	408000	282	63	52	n/a	113	n/a	30	n/a	0.45	407000	183	6	n/a	n/a	n/a	35	90	88
12/21/03	0.59	397000	234	49	45	1.4	113	47	30	n/a	0.43	396000	170	5	n/a	17	7	27	90	89
12/23/03	0.65	487000	317	n/a	94	n/a	113	n/a	30	n/a	0.43	486000	209	6	n/a	n/a	n/a	34	n/a	94
02/03/04	0.28	505000	141	280	200	n/a	125	n/a	30	n/a	0.23	504000	116	10	n/a	n/a	n/a	18	96	95
03/22/04	0.64	408000	261	210	178	1.6	125	60	30	n/a	0.54	407000	220	9	n/a	-18	-7	16	96	95
03/24/04	0.55	382000	210	210	171	n/a	125	n/a	30	n/a	0.46	381000	175	10	n/a	n/a	n/a	17	95	94
03/26/04	0.55	379000	208	210	163	2.7	125	101	30	n/a	0.50	377000	189	12	n/a	-82	-39	10	94	93
04/19/04	0.59	488000	288	220	169	1.3	137	53	30	n/a	0.51	486000	248	11	n/a	-14	-5	14	95	93
04/21/04	0.93	465000	432	171	140	1.3	137	53	30	n/a	0.42	464000	195	6	n/a	184	43	55	96	96
04/23/04	0.90	483000	435	167	138	1.2	137	49	30	n/a	0.52	482000	250	8	n/a	135	31	42	95	94
05/23/04	0.69	380000	262	80	68	1.5	120	54	30	n/a	0.52	379000	197	11	n/a	11	4	25	86	84
05/25/04	0.36	489000	176	82	64	1.3	120	47	30	n/a	0.26	487000	127	18	n/a	3	1	28	78	72
05/27/04	0.49	436000	214	90	85	1.4	120	50	30	n/a	0.17	434000	74	16	n/a	89	42	65	82	81
06/20/04	0.40	352000	141	210	168	2.0	120	72	30	n/a	0.28	351000	98	10	n/a	-29	-21	30	95	94
06/22/04	0.33	407000	134	169	125	n/a	120	n/a	30	n/a	0.31	406000	126	5	n/a	n/a	n/a	6	97	96
06/24/04	0.28	385000	108	156	133	n/a	120	n/a	30	n/a	0.22	384000	84	11	n/a	n/a	n/a	22	93	92
Total Avg.	0.69	420000	291	173	139	1.94	121	70			0.46	418000	191	9		48	7	35	94	92
STDEV	0.40	47000	168	64	50	0.76	9	27			0.29	47000	116	4		106	26	18	5	6

Total mercury removal efficiency across the entire facility %= $(1 - \frac{Q_{FE} \times C_{FE}}{Q_{in,RS} \times C_{in,RS}}) \times 100\%$

Table 4.7 Total mercury mass balances for the July 2003 - June 2004 sampling period at ROPEC

Sampling location	Average flow*	Measured total Hg concentration*	Average daily Hg loading (g/d)*	Hg loading as a percentage of the influent*
Raw Sewage (RS)	420,000 ± 47,000 m^3/day	0.69 ± 0.40 µg/L	291 ± 168	100%
Raw Sludge (RAW) (TS 4.4%)	1,000 ± 200 m^3/day	33.00 ± 8.00 µg/L	36 ± 13	12 ± 4%
Waste Activated Sludge (WAS) (TS 0.5%)	7,000 ± 1,000 m^3/day	2.82 ± 0.37 µg/L	20 ± 3	7 ± 1%
Primary Effluent (PE)	419,000 ± 47,000 m^3/day	0.53 ± 0.34 µg/L	220 ± 143	76 ± 34%
Final Effluent (FE)	418,000 ± 47,000 m^3/day	0.46 ± 0.29 µg/L	191 ± 116	65 ± 18%
Dewatered biosolids (CAKE) (dry weight, TS 30%)	121 ± 9 tonne/day (a)	1.94 ± 0.76 µg/g (b)	70 ± 27	24 ± 9%
TGM in biogas from anaerobic digester	31,000 m^3/day	176 ± 5 ng/m^3	5.4 ± 0.2 mg	0.002%
TGM volatilization from secondary clarifier	38,400 m^2	Flux rate=21 ng/m^2/day	0.8 mg	
% Removal of total mercury in primary clarifier based on the percent of mercury leaving in the primary effluent compared to the total inputs				27 ± 23%
% Removal of total mercury in secondary clarifier based on the percent of mercury leaving in the final effluent compared to the primary effluent				12 ± 28%
% Removal of total mercury within facility based on the percent of total mercury leaving in the final effluent compared to total inputs				35 ± 18%
% Total mercury mass balance closure = 100 - (66 + 24 + 0.002) = 10%				

* Total average with standard deviation of all samples.
(a) Value is given on a wet weight basis.
(b) Value is given on a dry weight basis.

In the present study, the total mercury removal efficiency (35%) in the entire plant treatment process was lower than that observed in other MWTP studies. Balogh and Liang (1995); Gilmour and Bloom (1995); and Mugan (1996) observed that almost all of the mercury was associated with biosolids in dewatered biosolids sludge with total

mercury removal efficiencies up to 95%, and only a very minor loading of total mercury discharged to the receiving water body.

The total mercury in the gaseous streams accounted for only 0.002% of the total input of total mercury. The results indicate that the total mercury gaseous emissions in the various wastewater treatment processes were minor, which was consistent with a previous study (Goldstone *et al.*, 1990). It has been also reported that less than 0.02% of the total mercury exited in biogas of MWTPs based on the total mercury mass balance performance across the whole treatment process at MWTPs (Environment Canada, 2001). Concomitantly, total mercury mass balance results showed that mercury loss to the atmosphere was negligible and would not affect the accuracy of the total mercury mass balance in ROPEC. The mass balance of total mercury in the entire treatment process showed good closure with an average loss of about 10%. Based on the general total mercury mass balances, the data were used to calibrate and run the TOXCHEM$^+$ model.

The reasons for the higher total mercury concentrations in the treated final effluent and the lower removal efficiencies in the present study were most likely due to the fact that approximately 75% of the total mercury that remained in the treated effluent was in the soluble state. It might not be associated so tightly with biosolids particulates and not be related to the total suspended solids concentration in the final effluent. Also as discussed before, the strongly positive correlation between total mercury concentrations in the raw sewage and the final effluent existed when the total mercury concentration was higher in the raw sewage, the removal efficiency might be expected to be lower than found by previous authors. Another likely reason might be the low mixed liquor suspended solids concentration in the present study (less than 1,000 mg/L) in aeration basins during the sampling period. It was lower than the conventional designed operation values (1,200 to 1,500 mg/L). As mixed liquor suspended solids concentration increased, the portion of mercury associated with the biosolids would increase; the content of total mercury in the dewatered biosolids sludge would be correspondingly increased, and the removal efficiency would be decreased.

4.2 Modeling Calculations and Predictions

Modeling calculations were roughly divided into three tasks. These tasks included: (1) determination of partitioning sorption coefficients K_{p1} & K_{p2}; (2) plant layout development; and (3) parameter identification.

The objective of these tasks was to develop a working simulation model that could adequately predict the performance of the treatment plant under a variety of operating conditions. The section on determination of partitioning sorption coefficients K_{p1} & K_{p2} describes how these parameters were determined; while the plant layout development describes the development of process flow schematics used for modeling purposes. The parameter identification task describes how model parameters were selected and calibrated.

4.2.1 Determination of Partitioning Sorption Coefficients K_p

In order to use the TOXCHEM$^+$ model to simulate and predict the fate of mercury within secondary wastewater treatment unit processes, it is essential to determine two major parameters, K_{p1} and K_{p2}. The partitioning coefficients for mercury in primary clarification and the activated sludge treatment unit processes are not available in the TOXCHEM$^+$ database.

It was assumed that the value of the partitioning coefficient K_{p1} in the influent, primary effluent and primary sludge streams around the primary clarifier were the same. Similarly the partitioning coefficient K_{p2} in the mixed liquor suspended solids, waste activated sludge and final effluent around the activated sludge treatment process including aeration basin and in the secondary clarifier also were equal. The soluble mercury concentration in the activated sludge waste and recycle streams was assumed to be equal to the secondary clarifier-influent soluble mercury concentration; and the soluble mercury concentration in the primary sludge waste stream was assumed to be equal to the primary clarifier-influent soluble mercury concentration. The equilibrium-sorbed mercury concentration was a first-order function of the liquid-phase mercury concentration, the sorption was reversible, and sorption and desorption occurred instantaneously.

It was also assumed that when the current liquid total mercury concentration (C_{TEST}) was less than the mercury solubility limits, no mercury precipitation occurred and the soluble total mercury concentration ($C_{Soluble}$) equal to C_{TEST}. If C_{TEST} was equal to or more than the mercury solubility limits, the sorption capacity of the biosolids would be at the maximum limit and therefore any additional mercury would precipitate and the concentration of soluble mercury ($C_{Soluble}$) would be equal to the mercury solubility limits.

Thus based upon Eqs. 2.2 and 2.4, and assumptions made above, Eqs 4.8 and 4.9 were used to determine K_{p1} and K_{p2}:

$$\frac{C_{0,RAW}}{(1+K_{P1}X_{0,RAW})} = \frac{C_{0,RS}}{(1+K_{P1}X_{0,RS})} \tag{4.8}$$

and

$$\frac{C_{0,PE}}{(1+K_{P1}X_{b,PE})} = \frac{C_{0,WAS}}{(1+K_{P2}X_{b,WAS})} \tag{4.9}$$

Employing the measured total mercury concentrations ($C_{0,RAW}$, $C_{0,RS}$, $C_{0,PE}$, and $C_{0,WAS}$) and VSS concentrations ($X_{0,RAW}$, $X_{0,RS}$, $X_{b,PE}$, and $X_{b,WAS}$) in the streams around the primary clarification and activated sludge treatment process, the partitioning sorption coefficients K_{p1} and K_{p2} were estimated for the different sampling days. The detailed calculations of the partitioning sorption coefficients K_{p1} and K_{p2} are demonstrated in Tables 4.8 and 4.9. The variations of calculated values of K_{p1} and K_{p2} are presented in Figs. 4.8 and 4.9, respectively. The calculated mean values with standard deviation overall samples were K_{p1} = 2.5 L/g ± 2.1 L/g and K_{p2} = 1.8 ± 1.2 L/g. The high variability in the estimated K_p values in primary clarification and activated sludge process made it impossible to identify any differences between these values (Parker *et al.*, 1994).

The total mercury solubility limits employed in the present study were 0.50, 0.60 and 0.05 mg/L for the influent solubility limit, effluent solubility limit and digester solubility limit, respectively (Table 4.10). These solubility limits were assumed based on the mercury chloride and mercuric acetate solubility in water. The solubility of mercuric acetate in water at 10°C is 250 g/L (Rosenblatt *et al.*, 1975) and of mercury chloride at 20°C is 69 g/L (Shiu *et al.*, 1990).

Table 4.8 Detailed calculation sheet of partitioning sorption coefficient K_{p1}

Sampling date	Raw Sewage			Raw Sludge			K_{p1} (L/g) a = b
	S_1=THg_{RS} (μg/L)	X_1=VSS_{RS} (mg/L)	$S_1/(1+K_{p1}*X_1)$ = a	S_2=THg_{RAW} (μg/L)	X_2=VSS_{RAW} (mg/L)	$S_2/(1+K_{p1}*X_2)$ = b	
07/02/03	0.46	197	$0.46/(1+K_{p1}*197)$	33.00*	41000	$33/(1+K_{p1}*41000)$	2.8
07/16/03	2.06	186	$2.06/(1+K_{p1}*186)$	33.00*	38000	$33/(1+K_{p1}*38000)$	0.4
07/28/03	0.41	194	$0.41/(1+K_{p1}*194)$	33.00*	37000	$33/(1+K_{p1}*37000)$	3.8
07/30/03	1.41	192	$1.41/(1+K_{p1}*192)$	33.00*	37000	$33/(1+K_{p1}*39000)$	0.7
08/01/03	1.20	153	$1.20/(1+K_{p1}*153)$	33.00*	31000	$33/(1+K_{p1}*31000)$	1.0
08/23/03	0.91	192	$0.91/(1+K_{p1}*192)$	35.00	40000	$35/(1+K_{p1}*40000)$	1.2
12/15/03	0.68	172	$0.68/(1+K_{p1}*172)$	32.00	36000	$32/(1+K_{p1}*36000)$	17
12/17/03	0.66	116	$0.66/(1+K_{p1}*116)$	38.00	36000	$38/(1+K_{p1}*36000)$	1.9
12/19/03	0.69	52	$0.69/(1+K_{p1}*52)$	22.00	38000	$22/(1+K_{p1}*38000)$	0.9
12/21/03	0.59	45	$0.59/(1+K_{p1}*45)$	29.00	37000	$29/(1+K_{p1}*37000)$	1.4
12/23/03	0.65	94	$0.65/(1+K_{p1}*94)$	51.00	28000	$51/(1+K_{p1}*28000)$	3.7
03/02/04	0.28	200	$0.28/(1+K_{p1}*200)$	33.00*	34000	$33/(1+K_{p1}*34000)$	n/a
03/22/04	0.64	178	$0.64/(1+K_{p1}*178)$	20.00	36000	$20/(1+K_{p1}*36000)$	1.0
03/26/04	0.55	163	$0.55/(1+K_{p1}*163)$	50.00	37000	$50/(1+K_{p1}*37000)$	4.0
04/19/04	0.59	169	$0.59/(1+K_{p1}*169)$	20.00	24000	$20/(1+K_{p1}*24000)$	1.8
04/21/04	0.93	140	$0.93/(1+K_{p1}*140)$	20.00	37000	$20/(1+K_{p1}*37000)$	0.6
04/23/04	0.90	138	$0.90/(1+K_{p1}*138)$	30.00	37000	$30/(1+K_{p1}*37000)$	1.0
05/23/04	0.69	68	$0.69/(1+K_{p1}*68)$	30.00	37000	$30/(1+K_{p1}*37000)$	1.3
05/25/04	0.36	64	$0.36/(1+K_{p1}*64)$	40.00	39000	$40/(1+K_{p1}*39000)$	3.4
05/27/04	0.49	85	$0.49/(1+K_{p1}*85)$	30.00	34000	$30/(1+K_{p1}*34000)$	2.1
06/20/04	0.40	168	$0.40/(1+K_{p1}*168)$	33.00*	25000	$33/(1+K_{p1}*25000)$	7.4
06/22/04	0.33	125	$0.33/(1+K_{p1}*125)$	41.00	38000	$41/(1+K_{p1}*38000)$	5.7
06/24/04	0.28	133	$0.28/(1+K_{p1}*133)$	33.00*	31000	$33/(1+K_{p1}*31000)$	7.8
Avg.							2.5
STDEV							2.1

*Measured total average concentration

Table 4.9 Detailed calculation sheet of partitioning sorption coefficient K_{p2}

Sampling date	PE			WAS			K_{p2} (L/g) a'= b'
	S_1=THg_{PE} (mg/L)	X_1=VSS_{PE} (mg/L)	$S_1/(1+K_{p2}*X_1)$ = a'	S_2=THg_{WAS} (mg/L)	X_2=VSS_{WAS} (mg/L)	$S_2/(1+K_{p2}*X_3)$ =b'	
02/07/2003	0.35	70	$0.35/(1+K_{p1}*70)$	2.82*	5100	$2.82/(1+K_{p2}*5100)$	1.7
16/07/2003	1.50	60	$1.50/(1+K_{p1}*60)$	2.10	3400	$2.10/(1+K_{p2}*3400)$	0.1
28/07/2003	0.28	56	$0.28/(1+K_{p1}*56)$	2.82*	3900	$2.82/(1+K_{p2}*3900)$	2.9
30/07/2003	1.25	62	$1.25/(1+K_{p1}*62)$	3.65	4100	$3.65/(1+K_{p2}*4100)$	0.5
01/08/2003	0.94	65	$0.94/(1+K_{p1}*65)$	2.62	4100	$2.62/(1+K_{p2}*4100)$	0.5
23/08/2003	0.54	72	$0.54/(1+K_{p1}*72)$	3.56	3500	$3.56/(1+K_{p2}*3500)$	1.7
15/12/2003	0.34	55	$0.34/(1+K_{p1}*55)$	3.20	4600	$3.20/(1+K_{p2}*4600)$	2.0
17/12/2003	0.35	70	$0.35/(1+K_{p1}*70)$	3.35	4700	$3.35/(1+K_{p2}*4700)$	2.2
19/12/2003	0.29	68	$0.29/(1+K_{p1}*68)$	2.85	3700	$2.85/(1+K_{p2}*3700)$	2.6
21/12/2003	0.46	50	$0.46/(1+K_{p1}*50)$	2.35	3400	$2.35/(1+K_{p2}*3400)$	1.3
23/12/2003	0.37	61	$0.37/(1+K_{p1}*61)$	2.10	3700	$2.10/(1+K_{p2}*3700)$	1.6
02/03/2004	0.20	72	$0.20/(1+K_{p1}*72)$	2.82*	4200	$2.82/(1+K_{p2}*4200)$	n/a
22/03/2004	0.62	70	$0.62/(1+K_{p1}*70)$	2.82*	4100	$2.82/(1+K_{p2}*4100)$	0.9
26/03/2004	0.21	80	$0.21(1+K_{p1}*80)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	4.2
19/04/2004	0.64	55	$0.64/(1+K_{p1}*55)$	2.82*	3600	$2.82/(1+K_{p2}*3600)$	1.1
21/04/2004	0.70	57	$0.70/(1+K_{p1}*57)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	0.8
23/04/2004	0.76	68	$0.76/(1+K_{p1}*68)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	0.7
23/05/2004	0.76	68	$0.76/(1+K_{p1}*68)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	0.8
25/05/2004	0.70	64	$0.70/(1+K_{p1}*64)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	1.0
27/05/2004	0.18	85	$0.18/(1+K_{p1}*85)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	4.4
20/06/2004	0.37	68	$0.37/(1+K_{p1}*68)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	2.7
22/06/2004	0.33	61	$0.33/(1+K_{p1}*61)$	2.45	4000*	$2.45/(1+K_{p2}*4000)$	2.3
24/06/2004	0.29	76	$0.29/(1+K_{p1}*76)$	2.82*	4000*	$2.82/(1+K_{p2}*4000)$	3.6
Avg.							1.8
STDEV							1.2

*Measured total average concentration

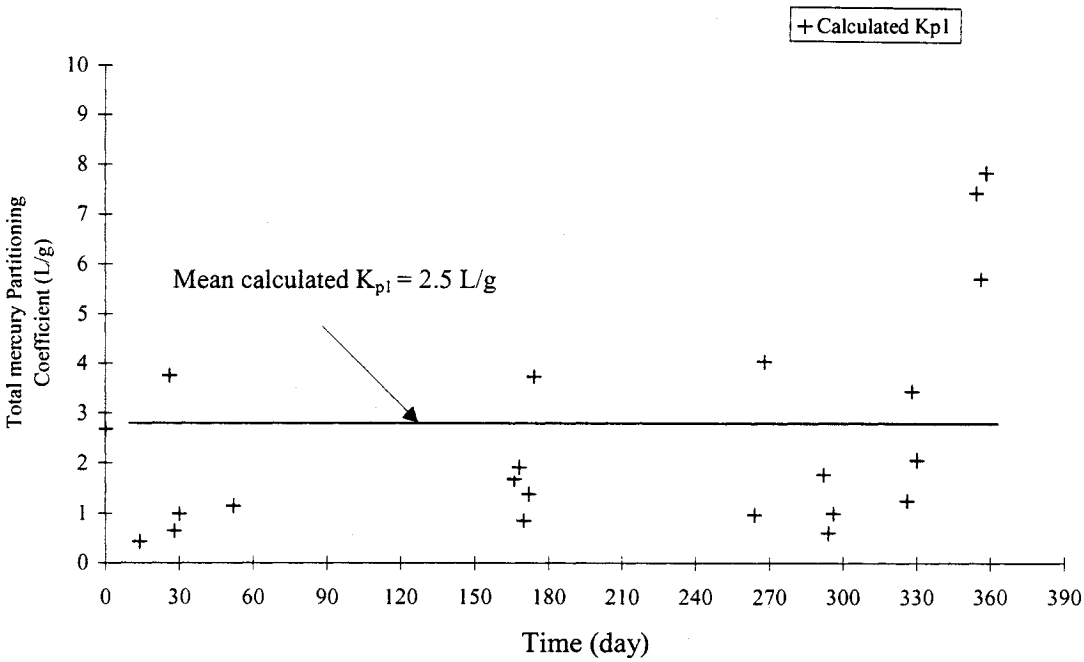


Figure 4.8 Variations of calculated total mercury K_{p1} and mean calculated K_{p1}

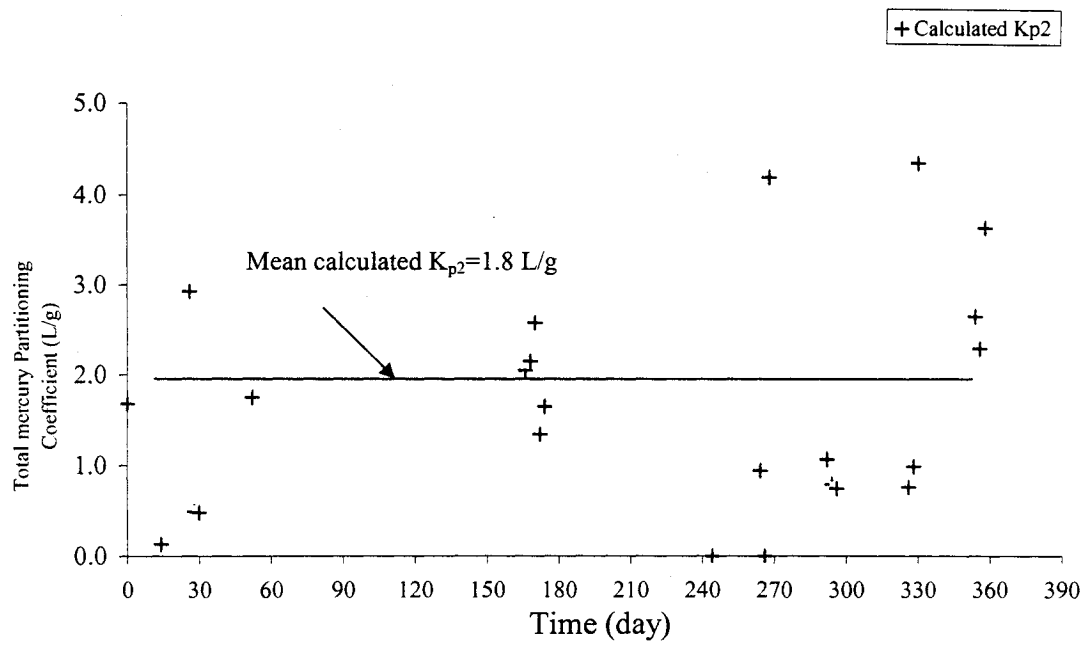


Figure 4.9 Variations of calculated total mercury K_{p2} and mean calculated K_{p2}

The measured total mercury concentrations in the wastewater and sludge streams did not exceed the assumed solubility limits. Therefore no precipitation would be observed in the primary clarification, activated sludge and anaerobic digestion treatment processes.

Table 4.10 Model parameters K_{p1}, K_{p2} and solubility limits applied in the present study

Parameter	Calculated Hg	Adjusted Hg
Influent K_{p1} (L/g)	2.5 ± 2.1[a]	6.4 ± 5.4
Effluent K_{p2} (L/g)	1.8 ± 1.2[a]	0.5 ± 0.3
Influent solubility (mg/L)	n/a	0.50[b]
Effluent solubility (mg/L)	n/a	0.60[b]
Digester solubility (mg/L)	n/a	0.05[b]

[a] Values are expressed as the total average with standard deviation of all samples.
[b] Assumed solubility limits.

4.2.2 Plant Layout Development

Based on the wastewater treatment unit processes at ROPEC, a simplified model simulating ROPEC using the commercial software, TOXCHEM$^+$, was established for predicting and quantitating the fate of total mercury across the entire treatment facility. A process layout is shown in Fig. 4.10.

In this simple plant layout, the fate of total mercury was simulated in four unit operations: (1) one primary clarifier object to represent the entire primary clarifier surface area for primary clarification; (2) one aeration basin object to represent the entire aeration basin volume for aeration; (3) one secondary clarifier object to represent the entire secondary clarifier surface area for secondary clarification; and (4) one anaerobic digester object to represent the entire anaerobic digester volume for anaerobic digestion.

Two removal mechanisms were considered: (1) mercury sorbed to biological solids and (2) mercury precipitates. However, due to the assumed solubility limits employed in this study were so high that they would have no impact on data and there were no precipitation occurred. The fate of total mercury in gaseous streams from primary clarifiers, aeration basins, secondary clarifiers and anaerobic digesters were not simulated by the model, and the minor stream from sludge dewatering centrate to plant influent was also neglected due to the low flow rate (~ 1,500 m^3/d, 0.32% of the total flow, Hydromantis Inc., 1994) and low total mercury concentration (0.91 ± 0.69 μg/L).

The flow rate and the total mercury concentration of plant influent (raw sewage) were equal to the flow rate and concentration of the primary clarifier influent.

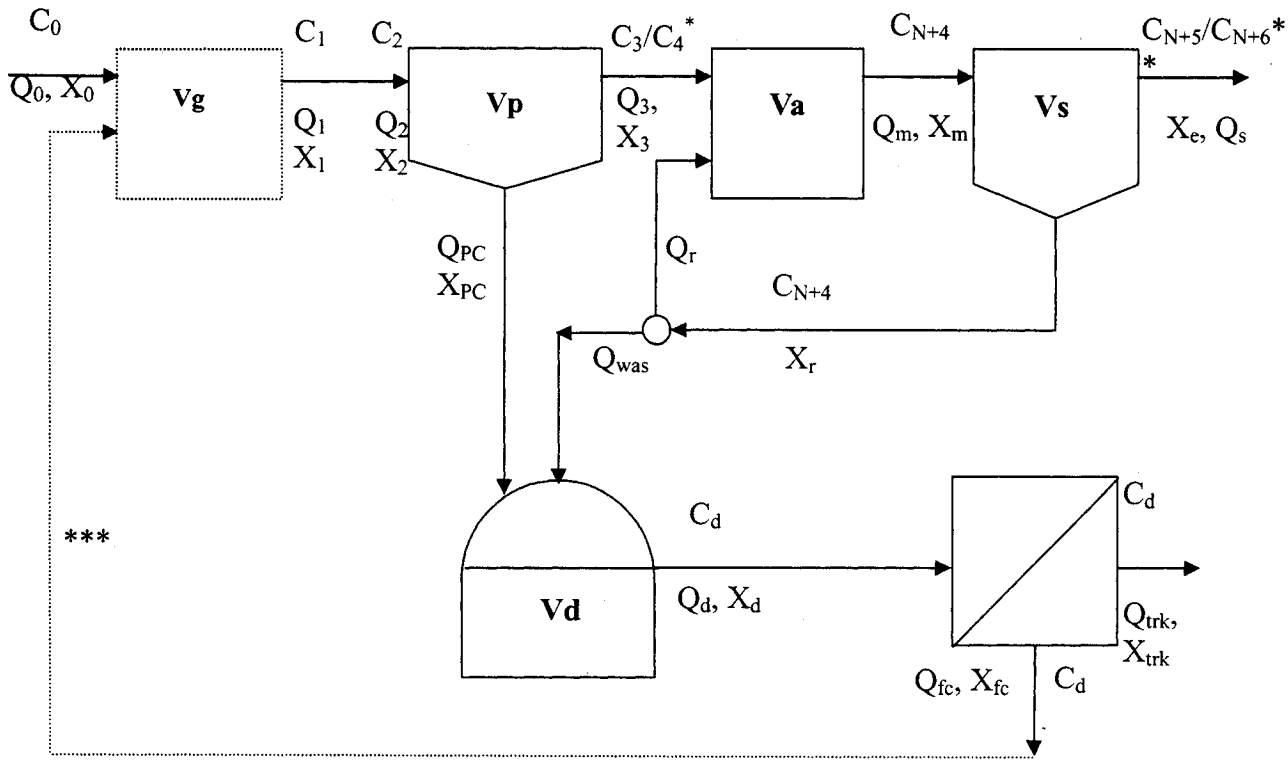


Figure 4.10 A simplified schematic plant layout for predicting fate of total mercury at ROPEC

Note: *C_3/C_4 is the contaminant concentrations before/after the weir in the primary clarifier
**C_{N+5}/C_{N+6} are the contaminant concentrations before/after the weir in the secondary clarifier
***Minor stream from sludge dewatering centrate not included

The main disadvantage of the simple model is that it does not allow the effects of the flow imbalances or disproportionately loaded processes, to be modeled. The non-balanced splits would affect the loading and removal efficiency of total mercury in each sub-stream. To sample each sub-stream (i.e. 15 primary clarifiers), the cost and time also make this was an impossible task. However, if all processes had a reasonably proportionate load (e.g., all 8 aeration basins have the same influent flow and concentration), then modeling it as a single object is completely acceptable.

4.2.3 Parameter Identification and Adjustment

After the plant layout was developed, the model was populated with appropriate data. Three methods were used to develop the model parameter set, each of which was used to varying degrees in this study: (1) direct measurement or knowledge of the parameter (e.g. total mercury concentration, VSS and TSS in wastewater, sludge and gaseous streams); (2) adjustment of the parameter such that model output matches known plant performance (e.g. partitioning sorption coefficients K_{p1} and K_{p2}); and (3) default data derived from the literature or similar studies (e.g. total mercury solubility values in influent, effluent and anaerobic digester).

4.2.3.1 Basic Physical and Operational Data

All model parameters within TOXCHEM$^+$ were initially populated with default data for all treatment units. These data describe each treatment process unit physical characteristics, such as surface area and depth. Some of these data were changed for subsequent simulations to reflect changes in operation, such as influent flow rate or out of service tanks.

Primary Clarifier

The primary clarifier object in the simple layout actually represented 15 parallel rectangular settling basins. The total surface area of these basins was initially entered as 11,780 m^2. The average depth of the primary clarifier basins was entered as 3.29 m. The basins actually vary in depth along the length of the basins, and different basins have different dimensions. When simulations were performed, it will be important to change the surface area to reflect any basins out of service. Changing the surface load would impact on the primary sludge removal efficiency and amount of sludge predominant.

Aeration Basin

The total volume of all eight aeration basins is 92,170 m^3. This value was entered into the aeration basin object that represents the eight aeration basins in the simple layout. Another key physical characteristic is to select the effective number of complete-mix reactors in series used to model the plug-flow tanks. A total of six reactors were used to

model each tank. It was based on one previous study at ROPEC (Hydromantics Inc, 1994), in which they reported that six reactors in series was chosen since there are six aeration grids within each aeration tank, which allows each reactor to represent a section of the tank with independent air flow control.

Operational data for the aeration basin object was the total air flow, and the air flow distribution to the six tanks in series. Total air flow was 864,000 m^3/d, and it was distributed 25% to each of the first two reactors, and 12.5% to each of the four remaining reactors. This distribution was not actual air flow distribution, but it was chosen to approximate tapered aeration within the aeration basins.

It was possible that aeration could result in stripping of mercury into the atmosphere. This could be of one concern at drop structure and in the aeration basin where oxygen was added for biological activated sludge and mixing. Gaseous emanation could be observed at primary clarifier (column condition) and aeration basin when air striping may occur.

Secondary Clarifier

One secondary clarifier object was used in the simple layout to represent the 16 secondary clarifiers. The total surface area is 38,430 m^2. The secondary clarifier object was given water depths of 4.6 m at the centre and 4.05 m at the outside.

The main operational data for the secondary clarifiers are recycling rate and wasting rate. The effective recycle fraction, which is the total recycle flow rate divided by the total treated flow rate, is 60%. The wasting rate for the waste activated sludge was 4,500 m^3/d.

4.2.3.2 Determining Influent Flow Rate and Concentration

Influent flows and concentrations (total mercury, VSS and TSS) changed depending on the case being modeled. Influent water quality (VSS and TSS) was based on the daily average composite samples for each sampling date.

To be perfectly correct the four influent streams should be included in the model: (1) raw influent from the collection system; (2) hauled sewage and septage that were pumped into a holding tank and released into the plant headworks; (3) centrate from the

dewatering of digested sludge; and (4) centrate from the thickening of waste activated sludge.

The raw influent from the collection system was automatically recorded based on the measured influent flow that reflected the period being modeled. The other three sources, which have a relatively minor impact on the total influent load, were assumed to be constant for all subsequent analyses. Since plant influent data is actually measured downstream of the confluence of these three sources, influent flow data could be adjusted to reflect the likely values for the raw sewage exclusive of the other three sources. When flow rate and composition data was available, it was possible to adjust these values in the models if necessary.

4.2.3.3 Steady-State Calibration and Evaluation

The steady state calibration in the present study included two steps: (1) parameter adjustment such that the predicted results matched available performance data; and (2) evaluation, which verified the parameters identified and set in the first step could be used to predict plant performance and fate of total mercury under variable conditions, and comparing of these predictions to actually measured data based on the total average data over the sampling period from July 2003 to June 2004.

The following section will be focus on the following two topics: (1) input of case specific parameters and (2) parameter adjustment.

Case Specific Parameters

Case specific parameters refer to data that were changed for each simulation scenario to reflect the operational conditions at the plant. These parameters included influent flow rate, VSS, TSS, MLSS, total mercury concentration, and the number of in service treatment units (i.e. number of aeration basins, primary clarifiers, etc.).

Parameter Adjustment

The steady-state calibration resulted in three parameters being adjusted: (1) partitioning sorption coefficients K_{p1} and K_{p2}, and (2) sludge retention time (SRT).

In order to match the total mercury concentration in the primary and final effluent, based on the simple plant layout, the partitioning sorption coefficients K_{p1} and K_{p2} for total mercury were adjusted with a low factor and a high factor from their mean calculated values with a standard deviation of all samples: $K_{p1} = 2.5 \pm 2.1$ L/g and $K_{p2} = 1.8 \pm 1.2$ L/g to a new value of $K_{p1} = 6.4$ L/g and $K_{p2} = 0.5$ L/g.

The partitioning sorption coefficients of $K_{p1} = 2.5$ L/g and $K_{p2} = 1.8$ L/g were employed in the database of TOXCHEM$^+$ to obtain the predicted total mercury concentration in the primary effluent and the final effluent. The simulation was based on the simple plant layout and under steady state using total average concentration of all sampling days (influent flow rate, influent TSS, influent total Hg concentration and MLSS) to run the TOXCHEM$^+$ model.

Considering the difference of the mechanism of sorption between the primary clarification and the activated sludge treatment process, the partitioning sorption coefficient K_{p1} was adjusted to compare the predicted total mercury concentration in the primary effluent with the measured mean concentration in the primary effluent. The K_{p1} values were varied within the range of 1.5 ~ 6.4 L/g, which was obtained by changing the estimated $K_{p1} = 2.5$ L/g with a low factor of 0.6 and high factor of 4.3. Similarly, the partitioning sorption coefficient K_{p2} was adjusted to compare the predicted total mercury concentration in the final effluent with the measured mean concentration in the final effluent. The K_{p2} values varied within the range of 0.9 ~ 3.6 L/g with a low factor of 0.5 and a high factor of 2.

The results indicated when that with $K_{p1} = 6.4$ L/g and $K_{p2} = 0.90$ L/g, the predicted total mercury concentration in the primary effluent matched the measured value, the relative error for $K_{p1} = 6.4$ L/g between the measured and predicted values in the primary effluent was: 4%, and the relative error for $K_{p2} = 0.9$ L/g between the measured and predicted values in the final effluent was: 11%. However, the predicted total mercury concentration in the final effluent still overestimated the measured total mercury concentration in the final effluent. When the TOXCHEM$^+$ model was run with a new K_{p2} value of 0.5 L/g and $K_{p1} = 6.4$ L/g, the best fit of the predicted total mercury concentration with the measured values in the primary effluent (relative error was 4%) and final effluent (relative error was 1%) was obtained.

Further verification of the K_p values was performed by picking two typical days, (December 15, 2003 and August 01, 2003) which represented the winter and summer scenarios and then comparing the predicted total mercury concentrations using various K_p values with the measured total mercury concentrations in the primary and final effluents. Three sets of K_p values were employed, the first set was the calculated K_p values that were based on the actual measured data, the second set was the mean calculated K_p values with K_{p1} = 2.5 L/g and K_{p2} = 1.8 L/g, and the third set was the adjusted K_p values with K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g. The results of comparison are listed in Table 4. 11.

Table 4.11 Comparison of total mercury concentration between the measured and predicted concentration using various K_p values

Summer time August 01, 2003	Predicted total mercury concentration (μg/L)			Measured total mercury concentration (μg/L)
	K_{p1} = 6.4, K_{p2} = 0.5 (L/g)	K_{p1} = 2.5, K_{p2} = 1.8 (L/g)	K_{p1} = 1.0, K_{p2} = 0.5 (L/g)	
Primary Effluent	0.91	1.05	1.13	0.94
Relative error%	3	12	20	
Final Effluent	0.84	0.71	1.00	1.13
Relative error%	26	37	12	
Raw Sewage				1.20
Winter time December 21, 2003	Predicted total mercury concentration (μg/L)			Measured total mercury concentration (μg/L)
	K_{p1} = 6.4, K_{p2} = 0.5 (L/g)	K_{p1} = 2.5, K_{p2} = 1.8 (L/g)	K_{p1} = 1.4, K_{p2} = 1.3 (L/g)	
Primary Effluent	0.55	0.57	0.58	0.46
Relative error%	2	5	17	
Final Effluent	0.47	0.31	0.36	0.43
Relative error%	9	28	16	
Raw Sewage				0.59

Table 4.11 shows that using the adjusted K_p values to predict the total mercury concentration in the primary and final effluent fitted the measured total mercury concentrations well for both days. For the selected sampling day in the winter, the relative errors between the measured and predicted values in the primary effluent were: 2, 5 and 17% for K_{p1} = 6.4 and K_{p2} = 0.5 (L/g), K_{p1} = 2.5 and K_{p2} = 1.8 (L/g), and K_{p1} = 1.4 and K_{p2} = 1.3 (L/g), respectively. Similarly, the relative errors between the measured and predicted values in the final effluent were: 9, 28 and 16% for K_{p1} = 6.4 and K_{p2} = 0.5 (L/g), K_{p1} = 2.5 and K_{p2} = 1.8 (L/g), and K_{p1} = 1.4 and K_{p2} =1.3 (L/g), respectively.

Table 4.11 also shows that the relative errors between the measured and predicted values in the primary effluent for the selected sampling day in the summer were: 3, 12 and 20 for K_{p1} = 6.4 and K_{p2} = 0.5 (L/g), K_{p1} = 2.5 and K_{p2} = 1.8 (L/g) and K_{p1} = 1.0 K_{p2} = 0.5 (L/g), respectively. Similarly, the relative errors between the measured and predicted values in the final effluent were: 26, 37 and 12 for K_{p1} = 6.4 and K_{p2} = 0.5 (L/g), K_{p1} = 2.5 and K_{p2} = 1.8 (L/g), and K_{p1} = 1.0 and K_{p2} = 0.5 (L/g), respectively. The results suggest that using the adjusted K_{p1} = 6.4 and K_{p2} = 0.5 (L/g) to run TOXCHEM$^+$ was better than the other two sets of K_p values and the predicted values fitted the measured values.

The adjusted partitioning sorption coefficient in the primary clarifier K_{p1} = 6.4 L/g is agreed with the previous studies that were within the range of 4.8 ~ 6.0 L/g in natural water (Hurley *et al.*, 1989; 1995; Macleod *et al.*, 2005). The results suggest that the partitioning sorption coefficient values of K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g can be employed in the parameter database of TOXCHEM$^+$ to predict the fate of total mercury in the ROPEC municipal wastewater treatment plant.

It was also found that temperature had a seasonally effect on the effluent sorption coefficient K_{p2} and total mercury removal efficiency. The K_{p2} declined from 1.9 L/g (average value of 5 sampling days in winter) to 1.2 L/g (average value of 5 sampling days in summer). The total mercury removal efficiency increased approximately 10% from 37% (average value of 5 sampling days in winter) to 47% (average value of 5 sampling days in summer).

The results also indicated that total mercury removal efficiency was positively correlated with total mercury concentration in influent. The removal efficiency increased from 25% (average value of 6 sampling days at 0.34 μg/L) to 40% (average value of 6 sampling days at 1.24 μg/L). While the K_{p1} and K_{p2} was decreased from 5.6 to 0.80 L/g and 2.5 to 0.70 L/g, respectively.

Another operational parameter that was adjusted was the SRT. The SRT increased from initial value of 5 days to a new value within the range of 5 to 12 days as reported by Sterritt and Lester, (1981). Sterritt and Lester reported that SRT could affect metal sorption. Adjustment of SRT increased the total mercury removal efficiency from the current 35% up to more than 85 ~ 95% as reported in the literature.

4.3 Predicted Total Mercury Concentration in Primary and Final Effluent

A simplified model using TOXCHEM$^+$ to simulate the ROPEC scenario (Fig. 4.11) was established to predict the fate of total mercury across the entire treatment facility. The facility parameters and plant operating data were summarized in Table 3.1 and listed in detail in Appendix B-1, B-2 and B-3. The K_{p1} and K_{p2} values and assumed solubility limits in the primary clarifier, secondary clarifier and anaerobic digester derived from the literature were presented in Table 4.10. All parameters were substituted into the TOXCHEM$^+$ model to predict the total mercury concentration in the final effluent.

Two sets of partitioning sorption coefficients K_{p1} and K_{p2} were employed in TOXCHEM$^+$ to predict the total mercury concentration in the final effluent. The first set of partitioning sorption coefficients with standard deviation of all samples was K_{p1} = 2.5 ± 2.1 L/g and K_{p2} = 1.8 ± 1.2 L/g, which were calculated from the estimation of partitioning sorption coefficients in Section 4.2.1. The second set of partitioning sorption coefficients was the adjusted K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g. The K_p values were substituted into TOXCHEM$^+$ to predict the total mercury concentration in the primary effluent and the final effluent, and the results were compared with the measured total mercury concentrations in the primary and final effluents, respectively. The observed and predicted total mercury concentrations in the primary effluent and the final effluent are shown in Figs. 4.12 and 4.13, respectively.

Fig. 4.12 shows that both sets of predicted total mercury concentrations fitted the pattern of measured total mercury concentrations in the primary effluent. However, both sets of predicted total mercury concentrations overestimated the measured values generally. Furthermore, it seems that predictions the adjusted K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g (relative error was 4%) were closer to the measured values.

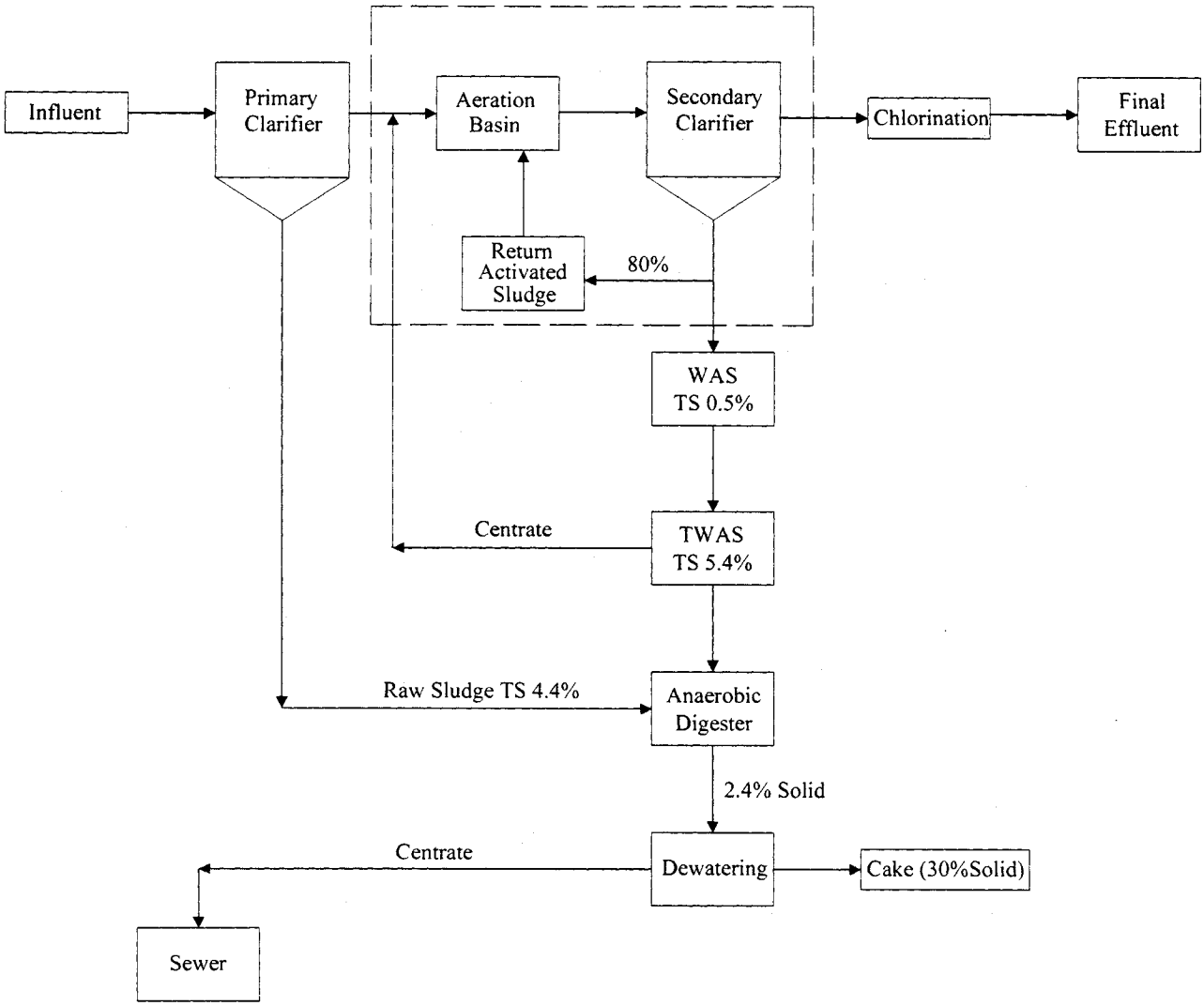


Figure 4.11 A simplified model to predict fate of total mercury across the entire treatment facility at ROPEC using TOXCHEM^{+}

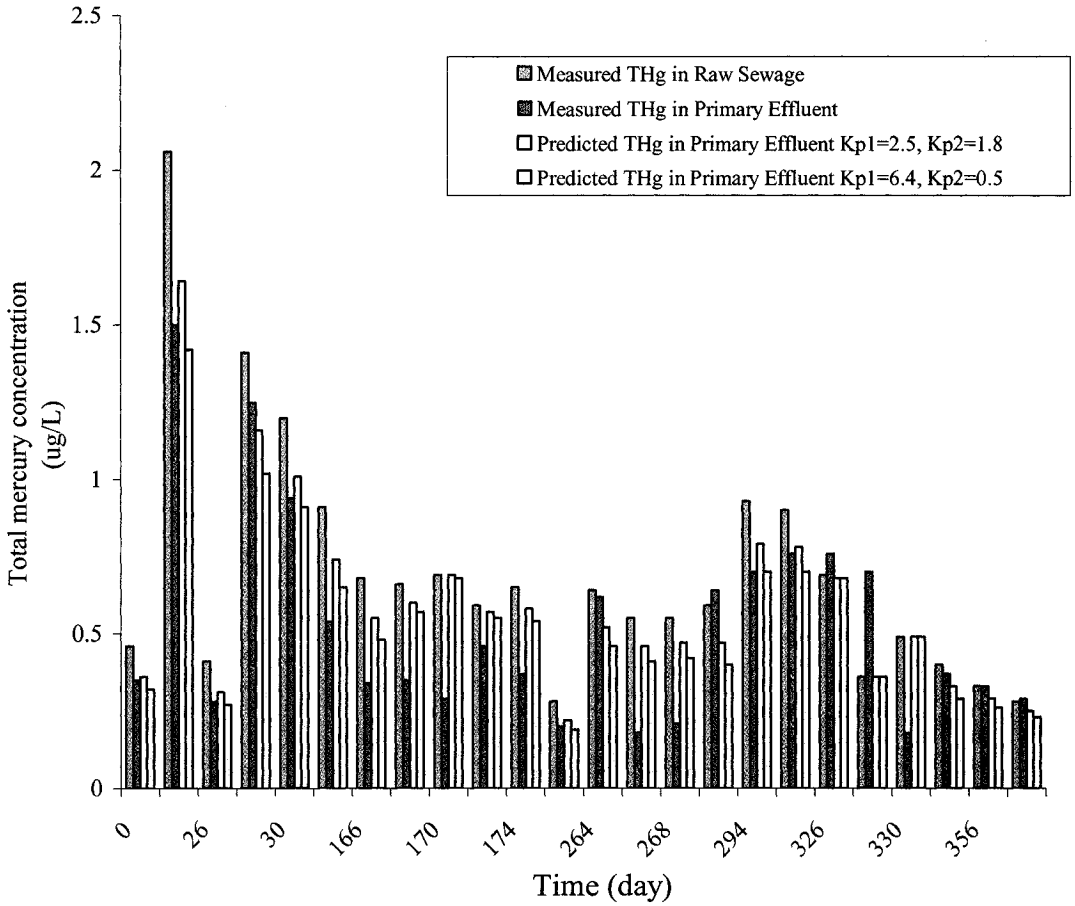


Figure 4.12 Comparison of total mercury concentration in the primary effluent between predicted and measured values

Fig. 4.13 presents the predicted total mercury concentrations using the calculated K_p values and the adjusted K_p values. From Fig. 4.13, it can be seen that the predicted values also fitted the pattern of the measured total mercury concentrations in the final effluent well. However, both sets of predicted total mercury concentrations underestimated the measured values generally. Fig. 4.13 indicates that using the adjusted K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g (relative error was 1%) fitted the measured values better than using K_{p1} = 2.5 L/g and K_{p2} = 1.8 L/g (relative error was 22%).

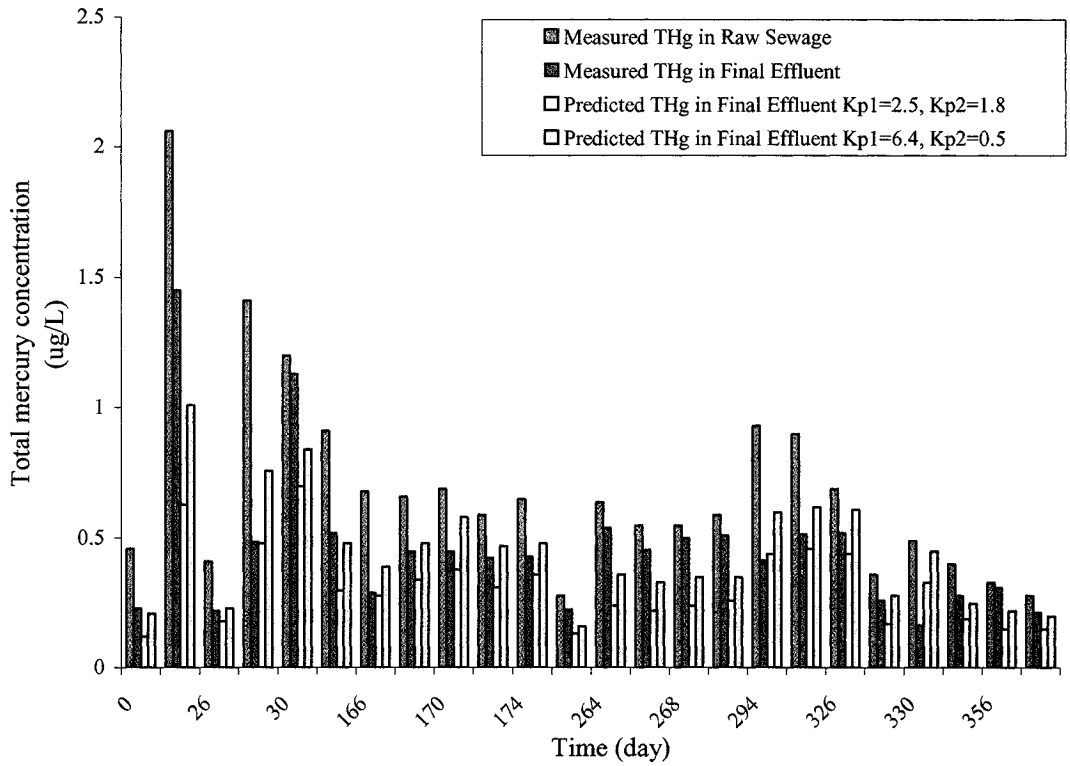


Figure 4.13 Comparison of total mercury concentration in the final effluent between predicted and measured values

The results suggest that the adjusted K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g can be substituted into the TOXCHEM$^+$ model to predict the fate of the total mercury in the primary and final effluent at the ROPEC municipal wastewater treatment plant. The discrepancy illustrates the problem of comparing the results of steady-state analysis to data that are the average of a dynamic process.

4.4 Sensitivity Analysis of the Model

Based on the simple plant layout, which was developed for simulating the fate of total mercury at ROPEC illustrated in Fig. 4.10, a sensitivity analysis was performed at steady-state to examine the impact of the input parameters on the final outputs of the TOXCHEM$^+$ model. In the present study, the outputs of the sensitivity analysis were

given by the percentage of the fate of total mercury in the sludge and the effluent stream vs. the sensitivity parameter.

When the sensitivity analysis was conducted, the average data over the sampling period was employed. This indicated the influent TSS concentration, primary effluent TSS concentration, MLSS concentration, influent sorption coefficient K_{p1} and effluent sorption coefficient K_{p2} that selected was based on the measured total average value.

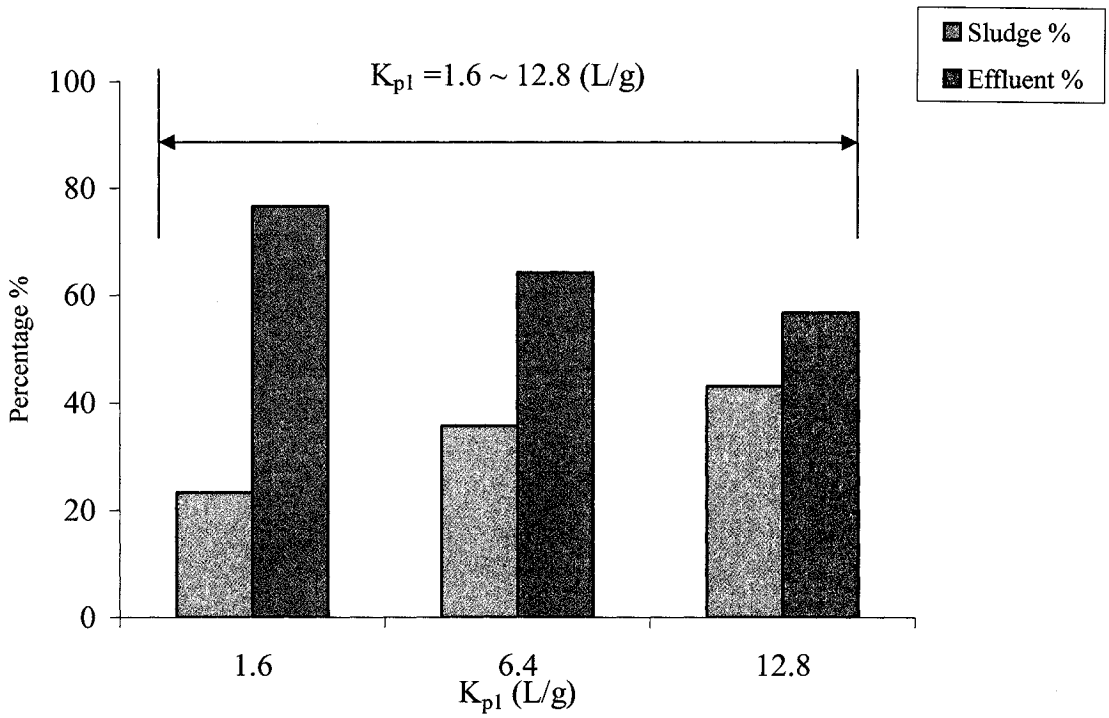


Figure 4. 14 Sensitivity analysis of parameter influent sorption (K_{p1})
K_{p2} = 0.50 L/g

The range selected for conducting the sensitivity analysis was set by changing the selected parameter value with a low factor and a high factor respectively. The mercury sensitivity analysis outputs are shown in Figs. 4.14 to 4.18.

Fig. 4.14 indicates that changing K_{p1} within a range of 1.6 to 12.8 L/g by adjusting the selected K_{p1} = 6.4 L/g with a low factor of 0.25 and a high factor of 2, on setting K_{p2} = 0.5 L/g, impacted on the total mercury distribution between liquid and sludge released from the plant. The percentage of total mercury in the sludge stream increased with an increase of the K_{p1} value. When K_{p1} was at 1.6 L/g, about 23% of total

mercury was predicted to be in the final dewatered biosolids stream. With K_{p1} at 6.4 L/g, the percentage of total mercury in the sludge stream increased to 35%. Comparing the ratio of the observed mean total mercury concentration in the primary sludge to that of the primary effluent 1.6 L/g, and about 27% of the measured total mercury removal efficiency in the primary clarifier in the field study, it suggests that the trend of the results of the sensitivity analysis for the portioning sorption coefficient K_{p1} is in agreement with the observed data in the field study.

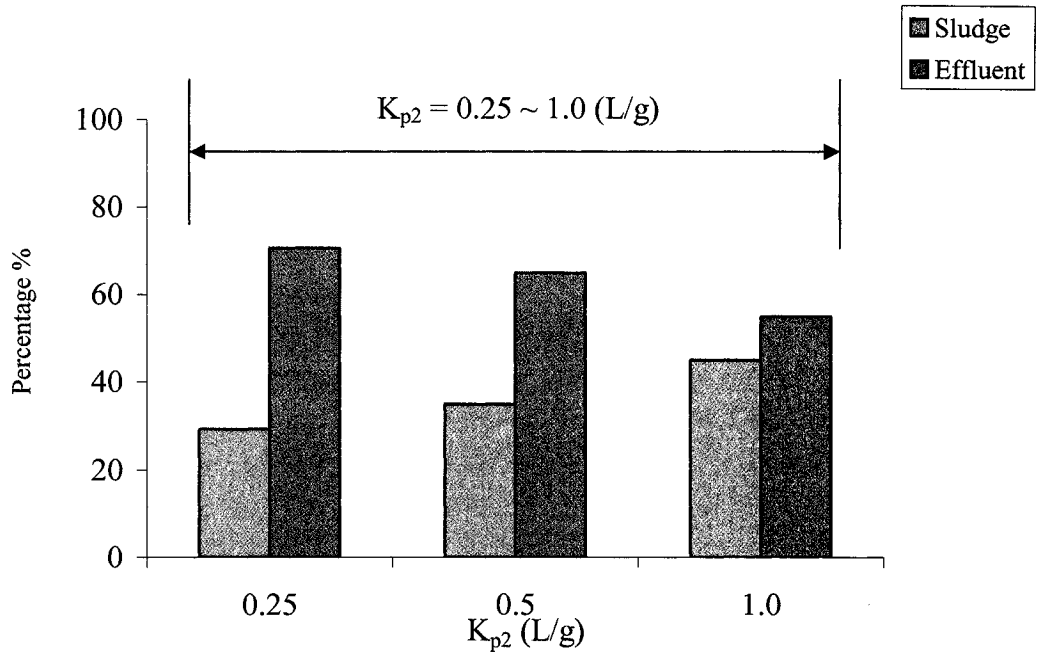


Figure 4. 15 Sensitivity analysis of parameter effluent sorption (K_{p2})
K_{p1} = 6.4 L/g

Fig. 4.15 shows the results of varying K_{p2} within the range of 0.25 to 1.0 L/g by changing the selected K_{p2} = 0.5 L/g with a low factor of 0.5 and a high factor of 2, and on setting K_{p1} = 6.4 L/g. It shows that the percentage of the total mercury in the sludge stream increased significantly, as K_{p2} increased within the above range. It is apparent that the impact on the total mercury distribution between liquid and sludge streams was greater than that observed when K_{p1} was adjusted. When K_{p2} was set at 1.0 L/g, about 45% of the total mercury was removed associated with the activated sludge solids. Comparing the ratio of the observed mean total mercury concentration in the thickening

waste activated sludge (TWAS) to that of in the thickener centrate (TC) 1.1 L/g, and the total mercury removal efficiency across the entire treatment facility 35%, it suggests that the trend of the results of the sensitivity analysis for the portioning sorption coefficient K_{p2} also fit the observed data in the field study.

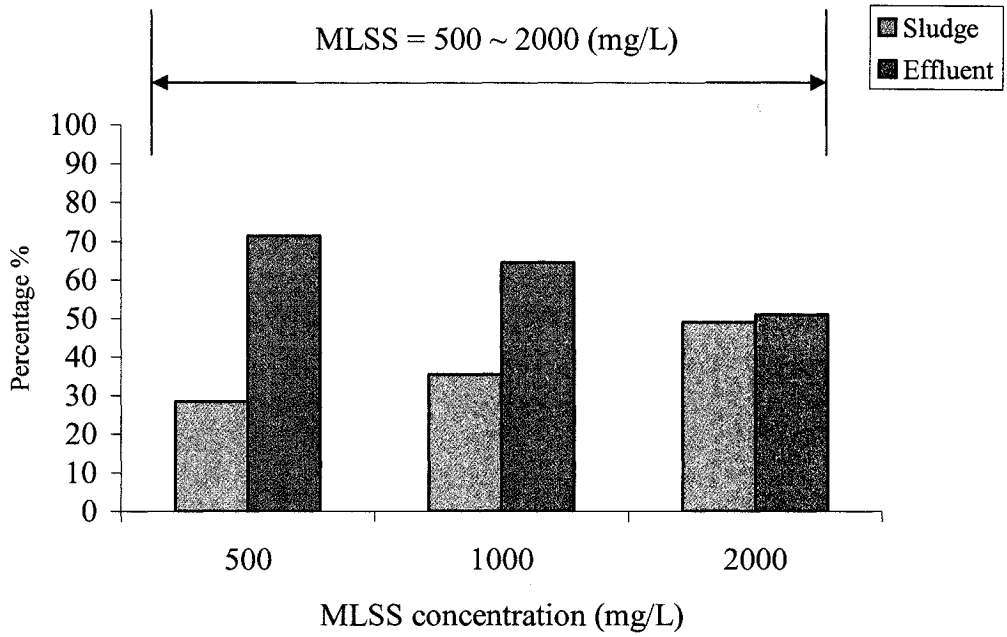


Figure 4. 16 Sensitivity analysis of parameter MLSS concentration
K_{p1} = 6.4 and K_{p2} = 0.5 (L/g)

If K_{p2} were increased to 3.6 L/g, approximately 70% of total mercury would be expected in the sludge stream. All those suggest that partitioning sorption coefficient K_{p2} is more important than the partitioning sorption coefficient K_{p1} in the MWTP treatment process and significantly affects the total mercury removal efficiency. The nature of the sludge can also be another factor that affects the partition of total mercury and the final fate of mercury at the plant.

Fig. 4.16 indicates that when increasing the mixed liquor suspended solids concentration in the activated sludge treatment process within the range of 500 to 2000 mg/L by changing the selected MLSS concentration 1000 mg/L with a low factor of 0.5 and a high factor of 2, and setting K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g, the percentage of total mercury in biosolids sludge increased from 28 to 50%.

Additionally, a high MLSS concentration has a significant effect on the fate of total mercury. It is likely expected to increase 10% of the total mercury in biosolids sludge from 38 to 50% by lifting the MLSS concentration from 1,150 to 2,000 mg/L.

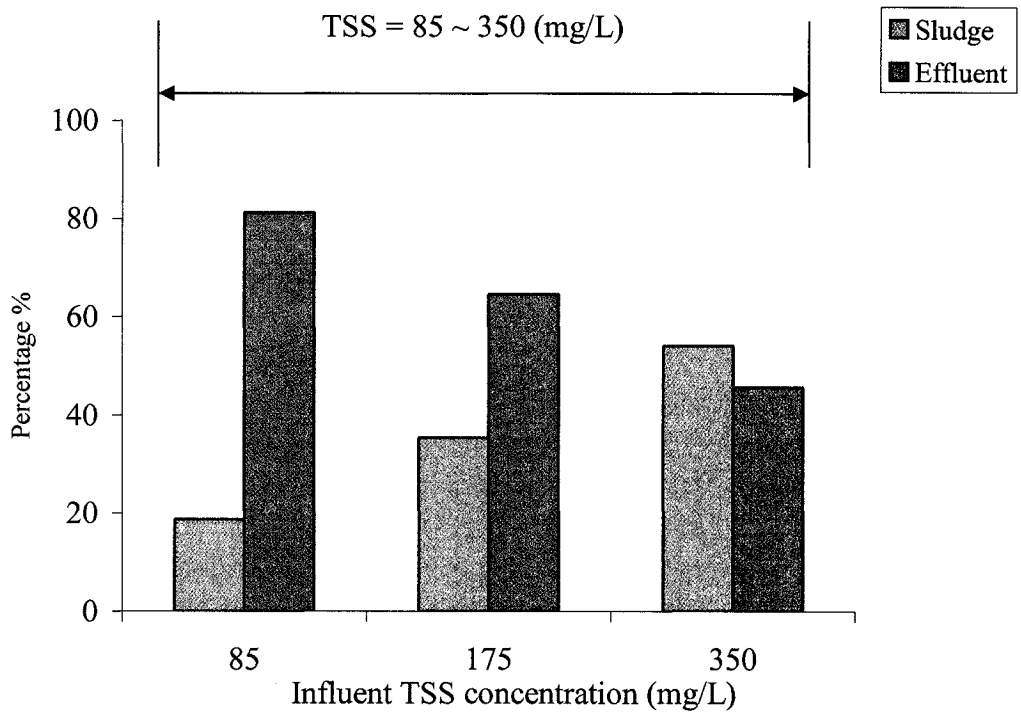


Figure 4.17 Sensitivity analysis of parameter influent TSS concentration
K_{p1} = 6.4 and K_{p2} = 0.5 (L/g)

Since the high MLSS concentration may be caused by a longer sludge retention time, which would result in a high proportion of the total mercury in the biosolids sludge.

Fig.4.17 shows the effect of varying the influent TSS concentration within the range of 85 to 350 mg/L by changing the selected influent TSS concentration of 175 mg/L with a low factor of 0.5 and a high factor of 2 and with K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g. The total mercury removal efficiency increased from 19 to 54% with the influent TSS concentration increasing within the range of 85 to 350 mg/L. That implied the total mercury content in the sludge stream was positively associated with the influent TSS concentration.

Fig. 4.18 shows the results of a sensitivity analysis that varied TSS concentration in the primary effluent within the range of 40 to 170 mg/L by changing the selected TSS concentration of 85 mg/L in the primary effluent with a low factor of 0.5 and a high factor of 2 and setting K_{p1} = 6.4 L/g and K_{p2} = 0.5 L/g. Fig. 4.18 indicates that 19 to 44% of the total mercury would be removed when the TSS concentration changes within the above range. When the TSS concentration was around 80 mg/L, the percentage of total

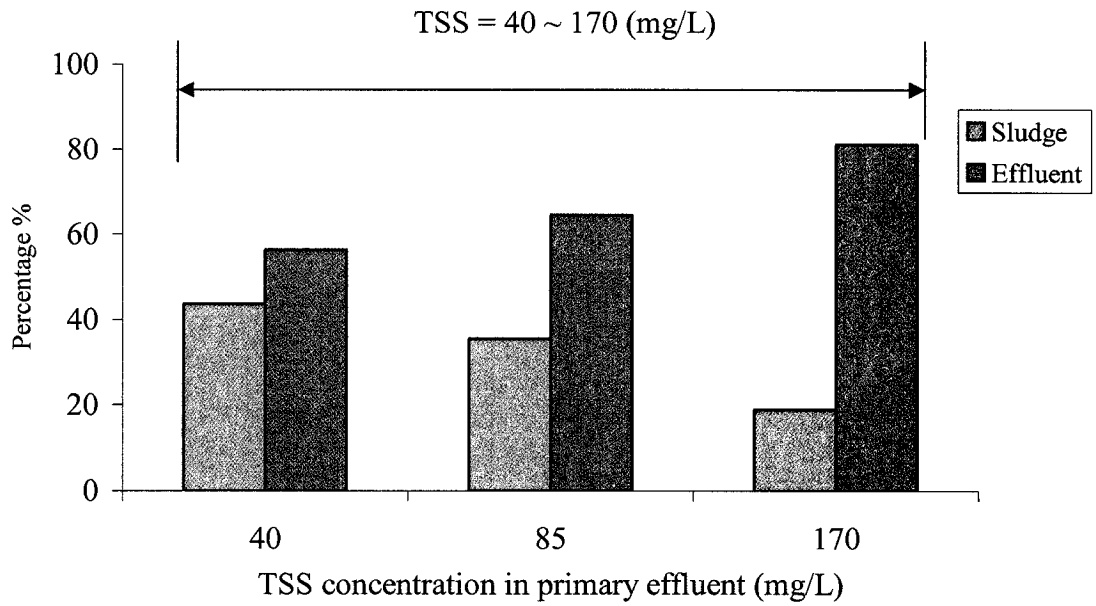


Figure 4. 18 Sensitivity analysis of parameter TSS concentration in primary effluent, K_{p1} = 6.4 and K_{p2} = 0.5 (L/g)

mercury in the primary sludge stream would be expected to be around 35%, which agreed with the measured field study data.

In this study it was found that the partitioning sorption coefficients K_{p1} and K_{p2}, TSS concentration in the influent, TSS concentration in the primary effluent and MLSS concentration were the most sensitive parameters, which affected the final outputs of the TOXCHEM$^+$ model in terms of concentration of total mercury in the primary and final effluent and hence daily total mercury loading to the receiving water body.

CHAPTER 5 Conclusions and Recommendations

5.1 Conclusions

A full-scale investigation for the fate of total mercury in wastewater, sludge and gaseous streams has been carried out at the ROPEC municipal wastewater treatment plant from July 2003 to June 2004. At same time, a modeling simulation and prediction also has been performed to evaluate the fate of total mercury within above the specific activated sludge treatment plant. In the present study, the cleaned sampling method for trace mercury and the sensitive analytical methods have been used for the wastewater, sludge and biogas sample determination by using a SP-3D Mercury Analyzer (CVAAS) and a Tekran 2537A Mercury Analyser (CVAFS) plus the flux chamber method for total gaseous mercury over the secondary clarifier.

- The mean total mercury concentration with standard deviation of all samples in the wastewater stream sample RS, PE, FE, TC and DC were 0.69 ± 0.40, 0.53 ± 0.34, 0.46 ± 0.29, 1.15 ± 1.12, and 0.91 ± 0.69 μg/L, respectively.
- The mean total mercury concentration with standard deviation of all samples in the sludge stream sample RAW, WAS, MLSS, TWAS, DIG 01/02 and dewatered biosolids sample CAKE were 33.00 ± 8.00, 2.82 ± 0.37, 0.78 ± 0.33, 30.00 ± 7.00, 36.00 ± 13.00 and 1.90 ± 0.60 μg/g, respectively.
- The mean concentration of TGM in the biogas from digester was 175.00 ± 5.25 ng/m^3. The concentration of TGM at the primary clarifier and aeration basin was 1.39 ± 0.20 and 1.41 ± 0.32 ng/m^3, respectively. The mean TGM flux over the secondary clarifiers was 0.89 ± 1.01 $ng/m^2/h$. The mercury flux over the secondary clarifier with a strong diurnal cycle was most strongly correlated with

solar radiation, water temperature, air temperature and DOC concentration in water.

- The total mercury mass balances across the primary clarification, activated sludge treatment unit process and the whole facility were performed. The total mercury removal efficiencies for the above treatment unit processes were: 27, 12 and 35%, respectively. It indicated that the pathways to the environment via mercury volatilization from the primary clarifiers, aeration basins and secondary clarifiers were insignificant.
- The partitioning sorption coefficients of K_{p1} and K_{p2} in the primary and the activated sludge treatment unit process were achieved by estimation using the measured total mercury concentration in the wastewater and sludge streams and the corresponding plant daily routine monitoring VSS data.
- A simple plant layout was established to simulate and predict the fate of total mercury within the ROPEC municipal wastewater treatment plant by using the TOXCHEM$^+$ model.
- Parameter identification and adjustment were performed by comparing the predicted total mercury concentration with the measured total mercury concentration in the primary effluent and final effluent under steady state and based on the simple plant layout.
- Sensitivity analysis was also conducted. The partitioning coefficients K_{p1} and K_{p2}, MLSS, influent TSS concentration, and primary effluent TSS concentration were identified to be the parameters affected the model predicting outputs significantly.
- It suggests that the TOXCHEM$^+$ model could be employed to predict and evaluate the fate of total mercury within the ROPEC municipal wastewater treatment plant.

5.2 Recommendations for Future Research

- Methylmercury sampling and determination in the wastewater treatment process are need to quantify the mercury methylation and de-methylation process in the activated sludge treatment process and the anaerobic digestion process.
- Further detailed studies, such as the study of partitioning sorption coefficients and the solubility limits in the wastewater treatment process are necessary for using TOXCHEM$^+$ model to predict the fate of mercury at the municipal wastewater treatment plant specifically.

REFERENCES

Alberta Environmental Protection (1992), *Mercury and its compounds in the environment: their chemistry, toxicology and human health hazards with special reference to Alberta*. Standards Research and Development Branch. Environmental Assessment Division Edmonton, AB.

Allard, B., and Arsenie, I. (1991), "Abiotic Reduction of Mercury by Humic Substances in Aquatic System-An Important Process for the Mercury Cycle", *Water, Air, Soil Poll.* (Neth.), 56: 457.

American Public Health Association (APHA) (1989), *Standard Methods for the Examination of Water and Wastewater 17th Edition*. Port City Press, Baltimore.

Bale, A.E. (2000), "Modeling Mercury Fate in Clear Lake, CA.", *J. Environ. Engin.*, 126(2): 153-163.

Balogh, S. and Liang, L. (1995), "Mercury pathways in municipal wastewater treatment plants", *Water, Air and Soil Pollution* 80: 1181 -1190.

Bisogni, j. L, and Lawrence, A. W. (1975), "Kinetics of Mercury Methylation in Aerobic and Anaerobic Aquatic Environments", *J. Water Pollut. Copurol Fed.* 47: 135.

Bloom, N. (1989), "Determination of picogram levels of methylmercury by aqueous phase methylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection", *Canadian Journal of Fisheries and Aquatic Sciences* 46: 1131-1140.

Bodaly, R., Rudd, J. and Flett, R. (1998), "Effect of urban sewage treatment on total and methyl mercury concentrations in effluents", *Biogeochemistry* 40: 279-291

Boudala, F.S., Folkins, I., Beauchamp, S., Tordon, R., Neima, J., and Johnson, B. (2000), "Mercury flux measurements over air and water in Kejimkujik National Park, Nova Scotia", *Water, Air, and Soil Pollution* 122: 183-202.

Carpi, A., Lindberg, S. E. (1997), "Sunlight-Mediated emission of elemental mercury from soil amended with municipal sewage sludge", *Environ. Sci. Technol.* 31: 2085-2091.

Carpi, A., Lindberg, S. E. (1998), "Application of a teflon™ dynamic flux chamber for quantifying soil mercury flux: tests and results over background soil", *Atmos. Environ.*32: 873-882.

Chipasa, K. B. (2003), "Accumulation and fate of selected heavy metals in a biological wastewater treatment system", *Waste Management* 23: 135-143.

Driscoll, C. T., Yan C., Schofield, C. L., Munson, R. K. and Holsapple, J. G. (1994), "The mercury cycle and fish in the Adirondack lakes", *Environ. Sci. Technol.* 28:136A-143A.

Environment Canada (2001), *Quantification of mercury concentrations and releases from landfills and wastewater treatment processes.*

Environment Canada (2003), *Canadian water quality guidelines for the protection of aquatic life: inorganic mercury and methylmercury Report No. 1-7.*

Earle, C. D. A., Rhue, R. D. and Chynoweth, D. P. (2000), "Partioning of mercury among solid, liquid and gas phases following anaerobic decomposition of a simulated waste", *Water, Air, and Soil Pollution* 121: 189-203.

Enviromega, (1996), TOXCHEM+ Version 2.0 User's Manual.

Ferrara, R., Maserti, B. E, Breder, R. (1991), "Mercury in Abiotic and Biotic Compartments of an Area Affected by a Geochemical Anornaly (Mt. Arniata, Italy)", *Water, Air, Soil Pollut.* 56: 219.

Fukushi, K., Chang, D. and Ghosh, S. (1996), "Enhanced heavy metal uptake by activated sludge cultures grown in the presence of bioplymer simulators", *Water Sci. Tech.* 34 (5-6): 267-272.

Glass, G. E, Sorensen, J. A., Schmidt, K. W., Rapp, G. R. (1990), "New source Identification of Mercury Contamination in the Great Lakes", *Environ. Sci. Technol.* 24: 1059.

Gilmour, C. C. and Bloom, N.S. (1995), "A case study of mercury and methylmercury dynamics in a Hg contaminated municipal wastewater treatment plant", *Water Air Soil Pollut.*80: 799-803.

Goldstone, M. E., Atkinson, C., Kirk, P. W. W. and Lester, J. N. (1990), "The behavior of heavy metals during wastewater treatment III. Mercury and Arsenic", *The Science of the Total Environment.* 95: 271-294.

Gore & Storrie Limited (1994), ROPEC Design and Operating Philosophy.

Hurley, J. R, Watras C. L, Bloom, N. S. (1991), "Mercury Cycling in a Northern Wisconsin Seepage Lake: The Role of Particulate Matter in Vertical Transport", *Water, Air, Soil Pollut.*56: 543.

Iverfeldt, Å., Munthe, J., Brosset, C. and Pacyna, J.M. (1995), "Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia", *Water, Air & Soil Poll.* 80, 227-233.

Jackson, T. A. (1998), *Mercury in aquatic systems. In: Metal Metabolism in Aquatic Environments*, eds. W. J. Langston and M. J. Bebianno, pp. 77-158. Chapman & Hall London.

Jones, R. D., Jacobson, M. E., Jaffe, R., West-Thomas, J., Arfstrom, C. and Alli, A (1995), "Method development and sample processing of water, soil, and tissue for the analysis of total and organic mercury by cold vapor atomic fluorescence spectrometry", *Water, Air and Soil Pollution* 80: 1285-1294.

Karvelas, M., Kassoyiannis, A and Samara, C. (2003), "Occurrence and fate of heavy metals in the wastewater treatment process", *Chemosphere* 53: 1201-1210.

Kim, K.; Lindberg, S. (1995), "Design and initial tests of a dynamic enclosure chamber for measurements of vapor-phase mercury fluxes over soils", *Water, Air, Soil Pollut. 80*: 1059-1068.

Lee, P. R. (2002), "An evaluation of low level mercury analytical techniques", WEFTEC 2002.

Lester, J. (1983), "Significance and behavior of heavy metals in wastewater treatment processes", *The Science of the Total Environment* 30: 1-44.

Liang, L., Horvat, M., and Bloom, N.S., (1994), "An improved speciation method for mercury by GC-VAFS after aqueous phase ethylation and room temperature precollection", *Talanta*. 41: 371 -379.

Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Hikanson, L., Iverfeldt, A., Meili, M. and Timm, B.(1991), "Emissions of mercury to the atmosphere", *Water, Air and Soil Pollution* 55(1/2): 23-32.

Macleod, M., Mckone, T, and Mackay, D. (2005), "Mass balance for mercury in the San Francisco Bay Area", *Environ. Sci. Technol.* 39: 6721-6729.

Mason, R. P., Reinfelder, J. R. and Morel, F. M. M. (1995), "Bioaccumulation of mercury and methylmercury", *Water Air Soil Pollut.* 80: 915-921.

Matilainen, T., Verta, Niemi, M., Uusi-Rauva, M., A. (1991), "Specific Rates of Net Methylmercury Production in Lake Sediments", *Water, Air, Soil Pollut.* 56: 595.

Mierle, G. (1990), "Aqueous inputs of mercury to Precambrian Shield lakes in Ontario", *Environ. Toxicol. Chem.* 9: 843-851.

Monteith, H. D., Bell, J. P., Thompson, D. J., Kemp, J., Yendt, C. M. and Melcer, H. (1993), "Modellingthe fate of metals in municipal water pollution control plants", *Water Environment Research* 65 (2): 129-137.

Mugan, T. (1996), "Quantification of total mercury discharges from publicly owned treatment works to Wisconsin surface waters", *Water Environ. Res.* 68 (2): 229-234.

Nelson, P. O., Chung, A. K. and Hudson, C. M. (1981), "Factors affecting the fate of heavy metals in the sludge process", *Journal WPCF* 53(8): 1323-1333.

Nielsen, J. S. and Hrudey, S. E. (1983), "Metal loadings and removal at a municipal activated sludge plant", *Water Res.* 17 (9): 1041-1052.

O'Driscoll, N. J., Beauchamp, S., Siciliano, S., Rencz, A., Lean, D.S. (2003), "Continuous analysis of dissolved gaseous mercury (DGM) and mercury flux in two freshwater lakes in Kejimkujik Park, Nova Scotia: Evaluating mercury flux models with quantitative data", *Environ. Sci. Technol.* 37:2226-2235.

Parker, W. J., Monteith, H. D., Bell, J. P., Melcer, H., and Berthouex, P. M. (1994), "Comprehensive fate model for metals in municipal wastewater treatment", *Journal of Environmental Engineering* 120 (5): 1266-1283.

Patterson, J. M. and Kodukula P. S. (1984), "Metals distributions in activated sludge systems", *Journal WPCF* 56 (5): 432-441.

Pichet, P., Morrison, K. A. Rheault, I., Tremblay, A. (1999), *Analysis of total and methylmercury in environmental samples. In: Mercury in the biogeochemical cycle: mercury in natural environments and hydroelectric reservoirs of northern Quebec,* eds. M. Lucotte, R. Schetagne, N. Therien, C. Langlois, and A. Tremblay, pp. 41-52. Springer-Verlag Berlin.

Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R. (2001), "Atmospheric mercury emissions from anthropogenic and natural sources in the Mediterranean Region", *Atmos. Environ.* 2997-3006.

Phagoo, D. and Melcer, H. (2003), "The effects of wastewater characteristics on metals portioning in activated sludge mixed liquor", Personal communication.

Poissant, L., and Casimir, A. (1998), "Water-air and soil-air exchange rate of total gaseous mercury measured at background sites", *Atmos. Environ.* **32**: 883–893.

Rosenblatt, DH et al. (1975), "Appecdix K-Aldrin / Dieldrin, *Preliminary assessment of ecological hazards and toxicology of environmental pollutants at Rocky Montain Arsenal.*"

Salvato, N. and Pirola, C, (1996), "Analysis of mercury traces by means of solid sample atomic absorption spectrometry", *Mikrochimica Acta.* Vol. 123, 63 – 71.

Scancar, J., Milacic, R., Strazar, M. and Burica, O. (2000), "Total metal concentrations and partioning of Cd, Cr, Cu, Fe, Ni and Zn in sewage sludge", *The Science of the Total Environment* 250: 9-19.

Schroeder, W.; Munthe, J.; Lindqvist, O. (1989), "Environmental measurements and results of mercury volatilization rates (Fluxes) from soil and lake surfaces", *Water, Air, Soil Pollut. 48*, 337.

Schroeder, W.H. (1995), "Environmental measurements and results of mercury volatilization rates ("fluxes") from soil and lake surfaces", *In* Proceedings of the 1995 Canadian Mercury Network Workshop. Available from http://www.cciw.ca/eman-temp/reports/publications/mercury95/ [accessed on 24/11/99].

Shui, Wy et al. (1990), *Rev Envrion Contam Toxicol* 116:15-187.

Sommar, J. Feng, X. and Lindqvist, O. (1999), "Speciation of volatile mercury species present in digester and deposit gases", *Appl. Organometal. Chem.* 13: 441-445.

Sterritt, R. M. and Lester, J. N. (1981), "The influence of sludge age on heavy metal removal in the activated sludge process", *Water Research* 15: 59-65.

St.Louis, V. L., Rudd, J., W. M., Kelly, C. A., Beaty, K. G., Bloom, N. S. and Flett, R. J. (1994), "Importance of wetlands as sources of methyl mercury to boreal forest ecosystems", *Can. J. Fish. Aquat. Sci.* 51: 1065-1076.

Struhs, D. (1996), *Mercury in Massachusetts: An Evaluation of Sources, Emissions, Impacts and Control s-Executive Summary.* Department of Environment Protection. http://www.state.ma.us/dep/files/mercunLlhqexsum.htm

Swain, E. B., Engstrom, D. R., Brigham, M. E., Henning, T. A., Brezonik, P. L. (1992), "Increasing Rates of Atmospheric Mercury Deposition in Midcontinental North America", *Science*, 257: 784.

Tien, C. T. and Huang, C. P. (1987), "Adsorption of Cu (II) onto sludge particulate surfaces", *J. Environ. Eng.* 113 (2): 285-299.

Tien, C. T. and Huang, C.P. (1991), "Formation of surface complexes between heavy metals and sludge particles". *In Heavy Metals in the Environment. Proc. Int. Conf.,* J.P, Vernet (Ed.), Amsterdam, Netherlands.

Wang, J., Huang, C. P., Allen, H. E., Poesponegoro, I, Poesponegoro, H., and Takiyama, L. R. (1999), "Effects of dissolved organic matter and pH on heavy metal uptake by sludge particulates exemplified by copper (II) and nickel (II): three-variable model", *Water Environ. Res.* 71(2): 139-47.

Wang, J., Huang, C. P. and Allen, H. E. (2003), "Modeling heavy metal uptake by sludge particulates in the presence of dissolved organic matter", *Water Research* 37: 4835-4842.

Wang, J. and Huang, C. P. (2002), "Heavy metal interactions with activated sludge particulates", *WEFTEC 2002.*

Watras, C. J., Morrison, K. A. and Host, J. S. (1995), "Concentration of mercury species in relationship to other site- specific factors in the surface waters of northern Wisconsin lakes", *Limnol.Oceanogr.* 40: 556-565.

World Health Organization (1989), *Mercury- Environmental Aspects.* World Health Organization, 86. Geneva, Switz.

Appendix A

Nomenclature for mass balance equations and modeling equations in TOXCHEM+

1 Nomenclature for mass balance equations

Concentration terms

C_{in} Total contaminant concentration in plant influent, μg/L

C_S Soluble concentration of metals in streams, μg/L

C_{Soli} Solubility limit of metals in grit chamber and primary clarifier, μg/L

C_{Sole} Solubility limit of metals in aeration basin and secondary clarifier, μg/L

C_{Sold} Solubility limit of metals in primary digester, μg/L

C_0 Liquid phase contaminant concentration in plant influent, μg/L

C_1 Liquid phase contaminant concentration in grit chamber effluent, μg/L

C_2 Liquid phase contaminant concentration in primary clarifier after mixing with WAS (if applicable), μg/L

C_3 Liquid phase contaminant concentration in primary clarifier (before weir), μg/L

C_4 Liquid phase contaminant concentration in primary clarifier effluent (after weir), μg/L

C_5 Liquid phase contaminant concentration in effluent from lst CSTR of aeration basin, μg/L

C_d Liquid phase contaminant concentration in effluent from primary digester, μg/L

C_{N+4} Liquid phase contaminant concentration in effluent from last CSTR of aeration basin, μg/L

C_{n+4} Liquid phase contaminant concentration in effluent from nth CSTR of aeration basin, μg/L

C_{n+3} Liquid phase contaminant concentration in effluent from (n-1)th CSTR of aeration basin, μg/L

C_{N+5} Liquid phase contaminant concentration in secondary clarifier (before weir), μg/L

C_{N+6} Liquid phase contaminant concentration in secondary clarifier effluent (after weir), μg/L

Note: Subscripts of metals concentrations are preceded with an S or P to indicate soluble or precipitate fractions respectively.

Flow terms

Q_0 Plant influent wastewater flow rate, m^3/h

Q_1 Wastewater flow rate after grit chamber, m^3/h

Q_2 Wastewater flow rate after sec. waste sludge mixed with grit chamber effluent, m^3/h

Q_3 Wastewater flow rate after primary clarifier, m^3/h

Q_r Return activated sludge flow rate, m^3/h

Q_d Primary digester flow rate, m^3/h

Q_{pc} Primary clarifier underflow rate, m^3/h

Q_{was} Waste activated sludge flow rate, m^3/h

Q_{su} Secondary digester supernatant return flow rate, m^3/h

Q_{fc} Sludge dewatering filtrate/centrate return flow rate, m^3/h

Q_{trk} Final sludge flow rate, m^3/h

R Recycle ratio, dimensionless

Suspended solids terms

X_0 Volatile suspended solids (VSS) concentration in plant influent, g/L

X_1 Grit chamber effluent VSS concentration, g/L

X_2 Primary clarifier influent VSS after mixing with waste activated sludge, g/L

X_3 Primary clarifier effluent VSS, g/L

X_{pc} Primary clarifier underflow VSS concentration, g/L

X_m Mixed liquor VSS (MLVSS) concentration, g/L

X_r VSS concentration in return sludge and waste activated sludge, g/L

X_e Secondary clarifier effluent VSS concentration, g/L

X_d Primary digester effluent VSS concentration, g/L

X_{su} Secondary digester supernatant VSS concentration, g/L

X_{fc} Filtrate/Centrate from sludge dewatering VSS concentration, g/L

X_{trk} Final sludge VSS concentration, g/L

R_p Fraction of solids removed by primary clarifier, dimensionless

Other parameters used in equations

K_p Sorption partition coefficient for organic chemicals or heavy metals, L/g

K_{p1} Metals sorption partitioning coefficient in grit chamber and primary clarifier, L/g

K_{p2} Metals sorption partitioning coefficient in aeration basin and secondary clarifier, L/g

t Time, h

V_g Volume of grit chamber, m^3

V_p Volume of primary clarifier, m^3

V_a Volume of each CSTR in aeration basin, m^3

V_s Volume of secondary clarifier, m^3

V_d Volume of primary digester, m^3

2 Modeling Equations

2.1 Influent Mass Balance

The influent total mercury concentration is partitioned into soluble, sorbed and precipitate fractions by initially calculating the influent mercury concentration based on Eq.1.1:

$$C_{Test} = \frac{C_0}{(1 + K_{P1} X_0)} \tag{2.1}$$

where,

C_{Test} = current influent soluble concentration of total mercury, µg/L

C_0 = influent total mercury concentration (total soluble, sorbed and precipitate), µg/L

K_{P1} = primary solids sorption coefficient, L/g

X_0 = influent volatile suspended solids concentration, g/L

If C_{Test} is greater than the mercury's primary solubility limit, the soluble concentration is set to the influent solubility and the concentration of mercury present as precipitate is calculated as Eq. 2.2:

$$C_{P0} = C_0 - (1 + K_{P1} X_0) C_{soli} \tag{2.2}$$

where,

C_{P0} = concentration of the mercury precipitate, µg/L

C_{soli} = solubility limit of the mercury, µg/L

If C_{Test} is less than the mercury's primary solubility limit then the concentration of mercury present as precipitate (C_{P0}) is zero and the soluble concentration (C_{soli}) is equal to C_{Test}. The total mercury concentration at any point in the treatment process is calculated as the sum of the soluble, sorbed and precipitate fractions.

Assumptions associated with modeling the fate of mercury in the unit processes are as follow:

- The aeration basin is a series of equal-volume CSTRs.
- Sludge wasting occurs only from the clarifiers.
- The soluble mercury concentration in the activated sludge waste and recycle streams is equal to the secondary clarifier-influent soluble mercury concentration.
- The soluble mercury concentration in the primary sludge waste stream is equal to the primary clarifier-influent soluble mercury concentration.
- The equilibrium-sorbed mercury concentration is a first-order function of the liquid-phase mercury concentration.
- Sorption is reversible.
- Sorption and desorption occur instantaneously.
- Precipitates in the primary clarifier are removed to the same extent as TSS.
- Precipitates in the secondary clarifier are concentrated in the same ratio as the biomass.

Default parameters for Kp and metal solubility (in raw screened wastewater and secondary effluent) are included in the model's database and are determined from experimental work described by Monteith *et al.* (1993); Parker *et al.* (1994); and Phagoo and Melcer (2003), the metals include Cd, Zn, Al, Cr, Cu, Ni, and Pb. Mercury was not one of the metals for which data was available from database. Metal solubility is not derived from solubility products for individual metal salts (for example, chlorides or carbonates). Rather solubility is determined experimentally from dosing experiments in

which the metal concentrations are at equilibrium, as described earlier.

2.1.1 Grit chamber

The mass balance for soluble and sorbed metal and precipitate fraction around the grit chamber is given by Eqs. 1.3 and 1.4, respectively.

Soluble and sorbed fractions:

$$Q_0(1+K_{P1}X_0)C_{S0}+(Q_{su}(1+K_{P1}X_{su})+Q_{fc}(1+K_{P1}X_{fc}))C_{Sd}-Q_1(1+K_{P1}X_1)C_{S1}=V_g(1+K_{P1}X_1)\frac{dC_{S1}}{dt} \quad (2.3)$$

where,

Q_0 = plant influent wastewater flow rate, m^3/h
Q_{su} = secondary digester supernatant return flow rate, m^3/h
Q_{fc} = sludge dewatering filtrate/centrate return flow rate, m^3/h
Q_1 = wastewater flow rate after grit chamber, m^3/h
C_{S0} = liquid phase mercury concentration in plant influent, µg/L
C_{Sd} = liquid phase mercury concentration in effluent from primary digester, µg/L
C_{S1} = liquid phase mercury concentration in grit chamber effluent, µg/L
X_{su} = secondary digester supernatant VSS concentration, g/L
X_{fc} = filtrate/Centrate from sludge dewatering VSS concentration, g/L
V_g = volume of grit chamber, m^3
t = time, h

Precipitate fraction (if applicable)

$$Q_0C_{P0}+\left(Q_{su}\left(\frac{X_{su}}{X_d}\right)+Q_{fc}\left(\frac{X_{fc}}{X_d}\right)\right)C_{Pd}-Q_1C_{P1}=V_g\frac{dC_{P1}}{d_t} \quad (2.4)$$

where,

X_d = primary digester effluent VSS concentration, g/L
C_{P1} = concentration of mercury precipitate in grit chamber effluent, µg/L
C_{Pd} = concentration of mercury precipitate in effluent from primary digester, µg/L

2.1.2 Primary clarifier

The equations used for calculating the concentration of metal leaving the primary clarifier in the liquid and sludge streams differ depending on whether waste activated sludge (WAS) is mixed with the primary sludge before sludge digestion. Both cases are presented in the following sections.

a) Primary clarifier (WAS directly to primary digester)

In this case no change to the concentrations leaving the grit chamber unit operation is required. The following assignments are performed only for convenience in the other following equations.

$$C_{S2} = C_{S1}$$

$$C_{P2} = C_{P1}$$

where,

C_{S2} = liquid phase mercury concentration in primary clarifier after mixing with WAS (if applicable), µg/L

C_{P2} = concentration of mercury precipitate in primary clarifier after mixing with WAS (if applicable), µg/L

b) Primary clarifier (WAS wasted to primary clarifier)

Initial mixing of waste activated sludge with grit chamber effluent stream.

Soluble and sorbed fraction:

$$Q_1(1+K_{P1}X_1)C_{S1} + Q_{was}(1+K_{P2}X_r)C_{Ssc} = Q_2(1+K_{P1}X_2)C_{S2} \qquad (2.5)$$

where,

Q_{was} = waste activated sludge flow rate, m^3/h

K_{P2} = mercury sorption partitioning coefficient in aeration basin and secondary clarifier, L/g

X_r = VSS concentration in return sludge and waste activated sludge, g/L

X_2 = primary clarifier influent VSS after mixing with waste activated sludge, g/L

Q_2 = wastewater flow rate after sec. waste sludge mixed with grit chamber effluent, m^3/h

C_{Ssc} = liquid phase mercury concentration in effluent from last CSTR of aeration basin, μg/L

C_{Psc} = concentration of mercury precipitate in effluent from last CSTR of aeration basin, μg/L

Precipitate fraction:

$$Q_1 C_{P1} + Q_{was} C_{Psc} = Q_2 C_{P2} \tag{2.6}$$

where,

$$Q_2 = Q_1 + Q_{was}$$

$$X_2 = \frac{(Q_1 X_1 + Q_{was} X_r)}{Q_2}$$

Based on Eqs. 2.3 – 2.6, the mass balance relationship for primary clarifier precipitate and soluble treatment are given by Eqs. 2.7 and 2.8, respectively.

Soluble fraction:

$$Q_2(1+K_{P1}X_2)C_{S2} - Q_{pc}((1+K_{P1}X_{pc})C_{s2} - Q_3(1+K_{P1}X_3)C_{S3} = V_P(1+K_{P1}X_3)\frac{dC_{S3}}{dt} \tag{2.7}$$

where,

Q_{pc} = primary clarifier underflow rate, m^3/h

X_{pc} = primary clarifier underflow VSS concentration, g/L

Q_3 = wastewater flow rate after primary clarifier, m^3/h

X_3 = primary clarifier effluent VSS, g/L

C_{S3} = liquid phase mercury concentration in primary clarifier (before weir), μg/L

V_p = volume of primary clarifier, m^3

Precipitate fraction:

$$Q_2 C_{P2} - Q_{pc}\left(\frac{X_{pc}}{X_2}\right)C_{P2} - Q_3 C_{P3} = V_p \frac{dC_{P3}}{dt} \tag{2.8}$$

where,

$$Q_{pc} = \frac{(Q_1 R_P X_1 + Q_{was} X_r)}{X_{pc}}$$

$$Q_3 = Q_2 - Q_{pc}$$

$$X_3 = (1 - R_P) X_1 \frac{Q_1}{Q_3}$$

C_{P3} = concentration of mercury precipitate in primary clarifier (before weir), µg/L
R_P = fraction of solids removed by primary clarifier, dimensionless.

2.2 Biological Processes Mass Balance

The effluent leaving a biological process is considered to have a different characteristic (sorption and solubility) from the influent to the process. To calculate the total mercury concentrations leaving a biological process the following equations are used:

$$C^*_{Test} = \frac{C^*_0}{(1 + K_{P2} X_b)} \tag{2.9}$$

where,

C^*_{Test} = biological process effluent soluble concentration of total mercury, µg/L
K_{P2} = sorption coefficient of the total mercury to biological solids, L/g
X_b = concentration of volatile suspended solids in the biological process, g/L
C^*_0 = biological process influent total mercury concentration (total soluble, sorbed and precipitate), µg/L

If C^*_{Test} is greater than the solubility of the total mercury in the secondary effluent, then the following equations are used:

$$C_P = C^*_{P0} + C^*_{Test} - C_{sole} \tag{2.10}$$

$$C_{out} = C_{sole}\left(1 + K_{P2} X_b\right) \tag{2.11}$$

where,

C_P = precipitate concentration of total mercury leaving the biological process, µg/L
C^*_{P0} = precipitate concentration of total mercury entering the biological process, µg/L
C_{sole} = solubility of the mercury in the effluent of the biological process, µg/L
C_{out} = effluent liquid concentration of the total mercury including the sorbed fraction, µg/L

If C^*_{Test} is less than or equal to the C_{sole}, then the value for C_P is set equal to the value of C^*_{p0}, and C_{out} is set equal to C^*_{Test}.

For each stream leaving a biological process a value for mercury solubility and mercury sorption will be calculated when leaving the process. For biological processes the value of K_P for the stream is set equal to K_{P2} and the value of C_S is set equal to C_{sole}.

2.2.1 Aeration Basin

Aeration basins are modeled as a user specified number of CSTRs in series. Since the volatilization at the primary weir has negligible or no effect on metals the following equivalences can be used:

$$C_{P4} = C_{P3}$$

$$C_{S4} = C_{S3}$$

where,

C_{S4} = liquid phase mercury concentration in primary clarifier effluent (after weir), µg/L
C_{P4} = concentration of mercury precipitate in primary clarifier effluent (after weir), µg/L

Soluble and sorbed fractions:

1st CSTR

$$Q_3(1+K_{P1}X_1)C_{S4}+Q_r(1+K_{P2}X_r)C_{S,n+3}-(Q_3+Q_r)(1+K_{P2}X_m)C_{S5}=V_a(1+K_{P2}X_m)\frac{dC_{S5}}{dt} \quad (2.12)$$

where,

Q_r = return activated sludge flow rate, m^3/h

$C_{S,n+3}$ = liquid phase mercury concentration in effluent from (n-1) th CSTR of aeration basin, μg/L

X_m = mixed liquor VSS (MLVSS) concentration, g/L

C_{S5} = liquid phase mercury concentration in effluent from lst CSTR of aeration basin, μg/L

V_a = volume of each CSTR in aeration basin, m^3

Subsequent CSTRs:

$$(Q_3+Q_r)(1+K_{P2}X_m)(C_{S,n+3}-C_{S,n+4})=V_a(1+K_{P2}X_m)\frac{dC_{S,n+4}}{dt} \quad (2.13)$$

where,

$C_{S,n+4}$ = liquid phase mercury concentration in effluent from n th CSTR of aeration basin, μg/L

Precipitate fraction:

1st CSTR:

1.) No precipitate formation in aeration basin ($C_{S5} < C_{sole}$)

$$Q_3\left(C_{P4}+Q_r\left(\frac{X_r}{X_m}\right)\right)C_{P,N+4}-(Q_1+Q_r)C_{P5}=V_a\frac{dC_{P5}}{dt} \quad (2.14)$$

where,

$C_{P,N+4}$ = concentration of mercury precipitate in effluent from last CSTR of aeration basin, μg/L

C_{P5} = concentration of mercury precipitate in effluent from lst CSTR of aeration basin, µg/L

2.) Precipitate formation in aeration basin ($C_{S5} \geq C_{sole}$)

$$Q_3(C_{P2}+(1+K_{p1}X_1)C_{S2})+Q_r\left(C_{P.N+4}\left(\frac{X_r}{X_m}\right)+(1+K_{P2}X_r)C_{S.N+4}\right)-(Q_3+Q_r)(C_{P5}+(1+K_{P2}X_m)C_{sole})$$
$$=V_a\frac{dC_{P5}}{dt} \qquad (2.15)$$

where,

C_{sole} = solubility limit of mercury in aeration basin and secondary clarifier, µg/L

Subsequent CSTRs:

$$(Q_3+Q_r)(C_{P,n+3}-C_{P.N+4})=V_a\frac{dC_{P.n+4}}{dt} \qquad (2.16)$$

where,

$C_{p,n+3}$ = concentration of mercury precipitate in effluent from (n-1) th CSTR of aeration basin, µg/L

$C_{P,n+4}$ = concentration of mercury precipitate in effluent from n th CSTR of aeration basin, µg/L

2.2.2 Secondary Clarifier

The bulk volume of the clarifier is modeled as a CSTR. The liquid phase total mercury concentration in the sludge waste stream is assumed to be equal to the clarifier influent liquid phase total mercury concentration.

Soluble and sorbed fractions:

$$((Q_3+Q_r)(1+X_mK_{P2})-(Q_r+Q_{was})(1+X_rK_{P2}))C_{s.N+4}-(Q_3-Q_{was})(1+X_eK_{P2})C_{S.N+5}$$

$$= V_s(1 + X_e K_{P2})\frac{dC_{S,N+5}}{dt} \tag{2.17}$$

where,

X_e = secondary clarifier effluent VSS concentration, g/L
$C_{S,N+5}$ = liquid phase mercury concentration in secondary clarifier (before weir), µg/L
V_s = volume of secondary clarifier, m^3

Precipitate fraction (If applicable):

$$(Q_3 + Q_r) - (Q_r + Q_{was})\left(\frac{X_r}{X_m}\right)C_{P,N+5} - (Q_3 - Q_{was})C_{P,N+5} = V_s\frac{dC_{P,N+5}}{dt} \tag{2.18}$$

where,

$C_{P,N+5}$ = concentration of mercury precipitate in secondary clarifier (before weir), µg/L

2.3 Digester Processes Mass Balance

The effluent leaving an anaerobic digester is also considered to have a different solubility value than the influent to the process. To calculate the total mercury concentrations leaving a biological process the following equations are used:

$$C'_{Test} = \frac{C_0^*}{(1 + K_P X_d)} \tag{2.19}$$

where,

C'_{Test} = concentration of total mercury leaving an anaerobic digester, µg/L

C_0^* = concentration of the total mercury in the influent to the biological process, µg/L

K_P = sorption coefficient of the total mercury in the influent stream, L/g
X_d = concentration of volatile suspended solids in the anaerobic digester process, g/L

If C'_{Test} is greater than the solubility of the metal in digester effluent, then the following equations are used:

$$C_p^{'} = C_{P0}^{*} + C_{Test}^{'} - C_{sold} \tag{2.20}$$

$$C_{out}^{'} = C_{sold}\left(1 + K_P X_d\right) \tag{2.21}$$

where,

$C_P^{'}$ = precipitate concentration leaving the anaerobic digester process, μg/L
$C_{p0}^{'}$ = precipitate concentration entering the anaerobic digester process, μg/L
C_{sold} = solubility of mercury in the effluent from the digester process, μg/L
$C_{out}^{'}$ = effluent liquid concentration of the total mercury including the sorbed fraction, μg/L

If C'_{Test} is less than or equal to the C_{sold}, then the value for C'_p is set equal to the value of C_{P0} and C'_{out} is set equal to C'_{Test}.

For each stream leaving an anaerobic digester a value for mercury solubility will be calculated. The sorption coefficient is considered to remain constant through the anaerobic digester process. For the anaerobic digester process the value of C'_p in the stream is set to C_{sold}.

2.3.1 Primary Digester

The equation used for calculating the concentration of mercury leaving the primary digester depends on whether the WAS is mixed with the primary sludge before digestion. The two cases are presented in the following section.

a) Primary digestion (WAS directly to digester)

The mass balance equations employed to simulate the fate of metals in primary anaerobic digestion are as follows:

Soluble and sorbed fraction:

$$Q_{pc}(1+K_{P1}X_{pc})C_{S2}+Q_{was}(1+K_{P2}X_r)C_{S,N+4}-Q_d(1+K_{P1}X_d)C_{Sd}=V_d(1+K_{P1}X_d)\frac{dC_{Sd}}{dt} \quad (2.22)$$

where,

Q_d = primary digester flow rate, m^3/h

C_{Sd} = solubility limit of mercury in primary digester, µg/L

V_d = volume of primary digester, m^3

Precipitate fraction:

i.) No formation of precipitate:

$$Q_{pc}\left(\frac{X_{pc}}{X_2}\right)C_{P2}+Q_{was}\left(\frac{X_r}{X_m}\right)C_{P,N+4}-Q_dC_{Pd}=V_d\frac{dC_{Pd}}{dt} \quad (2.23)$$

where,

C_{Pd} = concentration of mercury precipitate in primary digester, µg/L

ii.) Formation of precipitate:

$$Q_{pc}\left(C_{P2}\left(\frac{X_{pc}}{X_2}\right)+(1+K_{P1}X_{pc})C_{S2}\right)+Q_{was}\left(C_{P,N+4}\left(\frac{X_r}{X_m}\right)+(1+K_{P2}X_r)C_{S,N+4}\right)-Q_d(C_{Pd}+(1+K_{P1}X_d)C_{Sold})$$
$$=V_d\frac{dC_{Pd}}{dt} \quad (2.24)$$

where,

C_{Sold} = solubility limit of mercury in primary digester, µg/L

b) Primary digestion (WAS wasted to primary clarifier)

The mass balance equations employed to simulate the fate of metals in primary anaerobic digestion are as follows:

Soluble and sorbed fraction:

$$Q_{pc}(1+K_{P1}X_{pc})C_{S2}-Q_d(1+K_{P1}X_d)C_{Sd}=V_d(1+K_{P1}X_d)\frac{dC_{Sd}}{dt} \quad (2.25)$$

Precipitate fraction:

i.) No formation of precipitate

$$Q_d\left(C_{P2}\left(\frac{X_{pc}}{X_2}\right)-C_{Pd}\right)=V_d\frac{dC_{Pd}}{dt} \quad (2.26)$$

ii.) Formation of precipitate:

$$Q_d\left(C_{P2}\left(\frac{X_{pc}}{X_2}\right)+(1+K_{P1}X_{pc})C_{S2}-(C_{Pd}+(1+K_{P1}X_d)C_{Sold})\right)=V_d\frac{C_{Pd}}{dt} \quad (2.27)$$

2.4 Stream Mixing

TOXCHEM$^+$ modifies the value for K_P and C_S for total mercury modelingwhenever multiple streams are combined into a unit process. The model assumes that the new value of K_P and C_S will be based on a flow-weighted average of the value in the streams that are combined together. An example of a mixing of two streams is shown in the equation below:

$$K'_P=\frac{K'_{P1}Q_2+K'_{P2}Q_2}{Q_1Q_2} \quad (2.28)$$

where,

K'_P = new sorption coefficient of the mixed stream, L/g,
K'_{P1} = sorption coefficient of the first stream, L/g,
Q_1 = flow of the first stream, m^3/day,
K'_{P2} = sorption coefficient of the second stream, L/g,
Q_2 = flow rate of the second stream, m^3/day.

The same technique is used for calculating new values for C_S.

Appendix B-1 Plant operation data

	RAW SEWAGE			RAW SLUDGE			FINAL EFFLUENT		MLSS		WAS	
	Q	TSS	VSS	Q	TS	VS	Q	TSS	Q	VSS	Q	VSS
YEAR 2003	(m^3/d)	(mg/L)	(mg/L)	(m^3/d)	(%)	(% of TS)		(mg/L)		(mg/L)	(m^3/d)	(mg/L)
2-Jul	379000	240	197	1160	4.9	82	n/a	10	n/a	1460		5100
16-Jul	419000	210	186	743	4.6	81	n/a	5	n/a		6424	
28-Jul	390000	240	194	642	4.4	83	n/a	5	n/a	760	6279	3900
1-Aug	382000	183	153	909	3.8	80	n/a	6	n/a		5930	N/A
23-Aug	351000	220	192	1013	5.2	76	n/a	6	n/a		5682	N/A
15-Dec	458000	200	172	722	4.2	83	n/a	8	n/a	1175	8042	4600
17-Dec	446000	141	116	867	4.3	83	n/a	6	n/a		7785	TSS/6200
19-Dec	408000	63	52	977	4.7	79	n/a	6	n/a	1024	7971	TSS/4900
21-Dec	397000	49	45	1290	4.4	82	n/a	5	n/a	1039	7948	TSS/4500
23-Dec	487000	n/a	94	1086	3.3	83	n/a	6	n/a	850	8029	TSS/4900
YEAR 2004												
2-Mar	505000	280	200	1286	4.6	72	n/a	10	n/a	630	7757	4200
22-Mar	408000	210	178	1076	4.3	83	n/a	9	n/a	1020	7879	4100
24-Mar	382000	210	171	1132	4.3	81	n/a	10	n/a	1274	7624	n/a
26-Mar	379000	210	163	1496	4.9	74	n/a	12	n/a	1198	8243	n/a
19-Apr	488000	220	169	1364	2.9	82	n/a	11	n/a	780	7918	3600
21-Apr	465000	171	140	1016	4.7	77	n/a	6	n/a	1008	7796	n/a
23-Apr	483000	167	138	966	4.6	79	n/a	8	n/a	900	7836	n/a
23-May	380000	80	68	949	4.3	84	n/a	11	n/a	780	7561	n/a
25-May	489000	82	64	1320	5.0	77	n/a	18	n/a	1018	7541	72
27-May	43600	90	85	1488	4.1	82	n/a	16	n/a	675	7654	n/a
20-Jun	352000	210	168	1016	2.9	84	n/a	10	n/a	1008	6707	n/a
22-Jun	407000	169	125	1060	4.5	83	n/a	5	n/a	1098	6579	n/a
24-Jun	385000	156	133	1323	3.7	81	n/a	11	n/a	950	6674	n/a

TWAS			DIG01			DIG02			Total Eff. DIG	Primary Effluent		
Q	TS	VS	Q	TS	VS	Q	TS	VS	Q	Q	TSS	VSS
(m^3/d)	(%)	(% of TS)	(m^3/d)	(%)	(% of TS)	(m^3/d)	(%)	(% of TS)	(m^3/d)	(m^3/d)	(mg/L)	(mg/L)
5100	5.4	71	1605	2.6	56	231	2.5	55	1469	334000	90	70
4900	5	69	940	2.7	55	186	2.5	54	1212	360000	69	60
3900	5.4	70	777	2.7	55	138	2.5	54	1082	326000	71	56
4100	5.7	70	1422	2.6	55	288	2.3	55	1266	328000	80	65
3500	4.6	67	1485	2.6	54	363	2.8	56	966	259000	90	72
4600	4.9	71	1346	1.98	55	569	2.7	56	1293	418000	69	55
6200	5.8	72	2032	2.1	55	587	2.7	57	1295	397000	87	70
4900	5.5	72	2264	2.2	56	669	2.7	58	1479	377000	81	68
4500	5.8	72	2641	2.2	56	761	2.8	58	1692	357000	61	50
4900	5.3	71	2801	2.2	56	714	2.7	57	1605	417000	n/a	n/a
4200	5.1	69	1876	2.1	57	667	2.3	58	1798	453000	105	72
4100	5.2	70	1809	2.2	55	628	2.3	57	1723	347000	81	70
	5.1	70	1681	2.2	55	595	2.5	58	1620	n/a	96	74
	5.4	69	2300	2.2	55	933	2.5	57	2329	489000	107	80
3600	5.9	71	1888	2.3	56	707	2.3	58	1927	362000	75	55
	5.2	68	1494	2.2	56	571	2.4	57	1556	333000	71	57
	5.6	70	1487	2.3	56	564	2.4	57	1521	370000	78	68
	6.5	69	1264	2.5	57	497	2.6	58	1298	315000	80	68
4500	6.2	70	1609	2.4	55	607	2.6	57	1601	434000	82	64
	6.7	70	1765	2.4	55	666	2.8	57	1774	377000	90	85
	5.2	68	1442	2.4	55	541	2.6	57	1454	282000	89	68
	5.2	69	1559	2.4	55	574	2.6	57	1534	324000	88	61
	4.5	68	1957	2.4	55	730	2.6	56	1946	291000	91	76

Appendix B-2 Plant monthly average operation data

DATE	RAW SEWAGE Q (m^3/d)	RAW SLUDG Q (m^3/d)	WAS Q (m^3/d)	FINAL EFFLUENT Q (m^3/d)	TWAS Q (m^3/d)	DIGESTERS DIG01 (m^3/d)	DIG02 (m^3/d)	DIG03 (m^3/d)	DIG04 (m^3/d)	CAKE Yield (wet ton/day)
Jul-03	404000	963	5607	n/a	519	1304	225	536	586	124
Aug-03	383000	849	4576	n/a	395	1181	410	399	356	102
Dec-03	498000	1089	6947	n/a	534	2264	681	684	151	113
Mar-04	471000	1126	7254	n/a	613	1688	606	600	433	125
Apr-04	480000	1216	7831	n/a	580	1722	647	633	479	137
May-04	445000	1215	7526	n/a	430	1553	595	590	385	n/a

Appendix B-3 Plant in-service operation data

Year 2003	Plant flow(m^3/d)	Atk's i/s	Avg air flow (scmm)	Prim. Tanks	Sec. Clarifiers i/s	Digesters i/s
2-Jul	379000	4	1197	2 to 10,12,13	8	4
16-Jul	419000	4	1137	2 to 13	8	4
28-Jul	390000	4	1238	1 to 13	8	4
30-Jul	374000	4	1210	1 to 13	8	4
1-Aug	382000	4	1225	1 to 13	8	4
				Tanks O/S		
23-Aug	351000	4	1372	14 & 15	8	4
15-Dec	458000	8	1160	8	16	4
17-Dec	446000	8	1127	8	16	4
19-Dec	408000	8	1156	8	16	4
21-Dec	397000	8	1169	8	16	4
23-Dec	487000	8	1108	8	16	4
				Tanks O/S		
Year 2004						
2-Mar	505000	8	925	7 & 14	16	4
22-Mar	408000	8	1061	15	16	4
24-Mar	382000	8	956	none o/s	16	4
26-Mar	379000	8	893	10	16	4
19-Apr	488000	8	1000	none o/s	16	4
21-Apr	465000	8	875	none o/s	16	4
23-Apr	483000	8	951	none o/s	16	4

ZJ-839
April 25, 2004

To : University of Ottawa

Analytical Report

NIC NIPPON INSTRUMENTS CORPORATION
Head office: 4-14-4, Sendagaya, Shibuya-ku, Tokyo, Japan
TEL: +81-3-3479-6014 FAX: +81-3-3479-6166
Osaka office: 14-8, Akaoji-cho, Takatsuki-shi, Osaka, Japan
Factory: TEL: +81-72-694-5195 FAX +81-72-694-0663

1. Samples

Sludge 5 samples

2. Analyzer

Mercury / SP-3D

3. Measuring Conditions

3.1 Measuring mode

Sample heating mode	Measuring Range
Mode 2 (350℃ : 4min 700℃ : 6min)	200ng

3.2 Calibration

Calibration curve was calculated by the least square method.

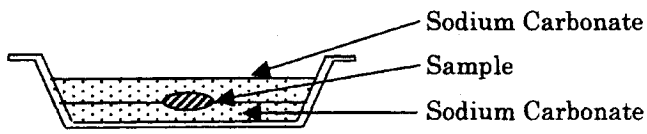
3.3 Measuring conditions

(1) Washing solution

When the samples "CAKE" and "TWAS" were measured by normal method, some spots of acid were recognized on the edge of the 1st collector tube. So the washing solution of the scrubber was changed to 2N Sodium Hydroxide (NaOH).

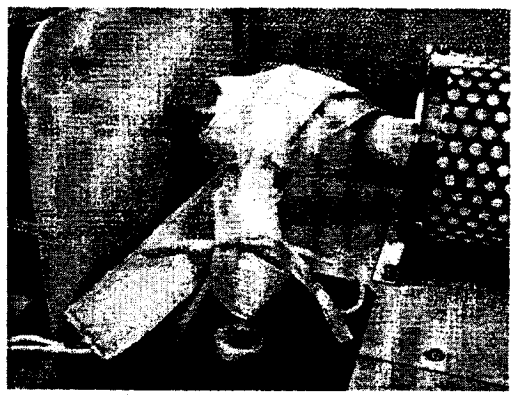
(2) Additive

To reduce the chlorine in Sample, the powder of Sodium Carbonate (Na_2CO_3) was used instead of Additive B, and M.



(3) Glass cap

To prevent the contamination of the glass cap, it was heated about 130℃ by the tape heater



(4) Confirmation of sensitivity

After measuring of each sample, the mercury standards (40ng) was measured to confirm the recovery.

4. Measuring results

Sample Name	Mercury Content (mg/kg)	C.V.(%)
DIG01	1.17	10.0 (n=3)
RAN	0.65	20.3 (n=3)
TWAS	0.53	16.2 (n=3)
CAKE	1.37	14.6 (n=3)
WAS*	0.39	

The amount of sample "WAS" was little, it was measured one time.

Analyzed by _____

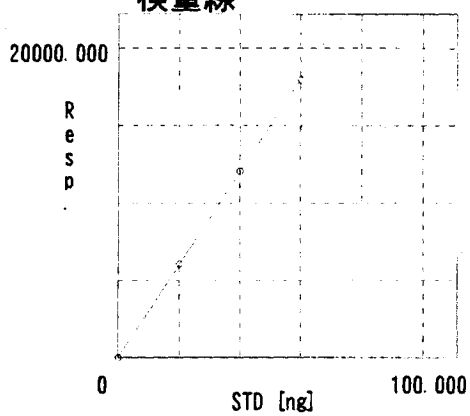
H.KOMUTA

Approved by _____ _____

K.TANIDA

タイトル： Ottawa Univ.
測定日　： 2004-04-20
測定者　： Komuta
装置名　： MD-1 + SP-3D

-検量線-



番号	標準値 [ng]	積分値
1	0.000	12.934
2	20.000	6072.217
3	40.000	12100.270
4	60.000	17950.720

y = ax + b
a = 299.2071
b = 57.8233
r = 1.0000

-測定結果-

番号	試料名 [固体試料]	標準値 [ng]	試料量 [mg]	積分値	水銀量 [ng]	濃　度 [mg/kg]
1	STD	0.000	-	12.934	-	-
2	STD	20.000	-	6072.217	-	-
3	STD	40.000	-	12100.270	-	-
4	STD	60.000	-	17950.720	-	-
5	DIG01	-	18.100	5924.583	19.608	1.08
6	DIG01	-	18.400	7236.063	23.991	1.30
7	DIG01	-	18.100	6121.470	20.266	1.12
8	40ng	-	40.000	12355.560	41.101	1.03
9	RAN	-	22.700	3541.948	11.645	0.51
10	RAN	-	21.800	4401.710	14.518	0.67
11	RAN	-	25.100	5850.918	19.361	0.77
12	40ng	-	40.000	12051.930	40.086	1.00
13	TWAS	-	19.500	3622.975	11.915	0.61
14	TWAS	-	19.800	3295.837	10.822	0.55
15	TWAS	-	19.900	2670.319	8.731	0.44
16	40ng	-	40.000	11930.030	39.679	0.99
17	CAKE	-	21.300	10087.210	33.520	1.57
18	CAKE	-	23.200	8175.830	27.132	1.17
19	CAKE	-	22.100	9198.313	30.549	1.38
20	40ng	-	40.000	12193.090	40.558	1.01
21	WAS	-	18.000	2140.824	6.962	0.39
22	40ng	-	40.000	12271.370	40.820	1.02

-統計計算結果-

番号	試料名	回数	平均値 [mg/kg]	標準偏差 [mg/kg]	CV値 [%]
1	DIG01	3	1.167	0.11719	10.04
2	40ng	5	1.010	0.01581	1.57
3	RAN	3	0.650	0.13115	20.18
4	TWAS	3	0.533	0.08622	16.18
5	CAKE	3	1.373	0.20008	14.57

-プロファイル-