# OCCURRENCE AND FATE OF BISPHENOL A IN SOME MUNICIPAL WASTEWATER TREATMENT PLANTS IN BANGKOK, THAILAND

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OCCURRENCE AND FATE OF BISPHENOL A IN SOME MUNICIPAL WASTEWATER TREATMENT PLANTS IN BANGKOK, THAILAND

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ABSTRACT

Bisphenol A (BPA), implicated in endocrine disruption, is used in the primary production of polycarbonate plastics and epoxy resins, which are used in the plastics industry. Because of its large scale production and widespread usage, BPA is released into the environment through air, land, and water during manufacturing, processing, and leaching from end-of-life treatment. The concern over BPA has grown over the last few years; however, there is still much debate over the potential harmful effects of BPA. Because most of the current WWTPs are not designed to treat emerging contaminants such as BPA, they can escape into the aquatic environments. This study aimed at investigating the occurrence and fate of BPA in the selected municipal wastewater treatment plants (MWWTPs) in the Bangkok region.

Based on the results of three sampling events, The WWTPs influent and effluents BPA concentrations ranged between 128.5 ng/L and 606.0 ng/L; and 38.7 ng/L and 270.5 ng/L, respectively. Even though these WWTPs are not designed to remove BPA from wastewater, the effluent BPA concentrations of most of the five WWTPs in three sampling events were lower than the influent levels. TK had the highest removal efficiency in October 2013 (80.4%) and December 2013 (90.7%) and the second highest in February 2014 (69.2%). DD had the highest removal efficiency in February 2014. The treatment process employed at TK and DD were vertical loop reactor activated sludge process and activated sludge with nutrients removal, respectively. Thus, these processes seem to be good for BPA degradation. Many of the adverse effects that BPA has on human health were studied over the past several decades. Arguments exist regarding what concentrations of BPA are dangerous to humans or wildlife, but it is clear that BPA poses potential risks and several countries have considered regulating it. However, there is no environmental policy in Thailand to control the levels of BPA residues in aquatic environments at present. Currently, the only regulation is to control BPA content used in food packaging (the maximum allowed level of BPA, including phenol and p-t-butylphenol, is 500 mg/kg in polycarbonate plastic containers and 2.5 $mg/dm^3$ for the BPA leached from various types of polycarbonate food containers). Also, BPA has been banned in the production of cosmetics. Until now, there are no standards for endocrine disrupting compounds residues including BPA in WWTPs' effluents and surface water in Thailand. Hence, there is a critical need for regulations for emerging endocrine disrupting compounds residues in aquatic environments Thailand.

KEY WORDS: BISPHENOL A/ WASTEWATER/ WWTP/ BANGKOK/ HPLC

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การเกิดและการเปลี่ยนแปลงของสารบิสฟีนอล เอ ในโรงควบคุมคุณภาพน้ำในจังหวัดกรุงเทพมหานคร
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บทคัดย่อ

สารบิสฟีนอล เอ เป็นสารที่จัดอยู่ในกลุ่มสารรบกวนการทำงานของต่อมไร้ท่อ ถูกนำ มาใช้เป็นสารตั้งต้นในการผลิตพลาสติกโพลีคาร์บอเนต และอีพ็อกซี่เรซินที่ใช้ในอุตสาหกรรมพลาสติก เนื่องจากมีการผลิตและมีการใช้งานพลาสติกที่ผลิตจากสารนี้อย่างกว้างขวาง สารบิสฟีนอล เอ จึงถูกปลดปล่อยลงสู่สิ่งแวดล้อมและปนเปื้อนสู่ อากาศ ดิน และน้ำ ในระหว่างขั้นตอนการผลิต และจากการชะละลายจากการบำบัดในขั้นตอนสุดท้าย ในช่วงที่ผ่านมาพบว่าการเกิดความตระหนักถึงผลเสียของจากการ ได้รับบิสฟีนอล เอ จากผลิตภัณฑ์ที่มีสารชนิดนี้เป็นองค์ประกอบเพิ่มสูงขึ้น อย่างไรก็ตามยังคงมีการตั้งคำถามเกี่ยวกับความปลอดภัยสำหรับการใช้สารชนิดนี้ว่ามีผลร้ายแรงต่อมนุษย์หรือไม่ เนื่องจากในปัจจุบันโรงควบคุมคุณภาพน้ำยังไม่มีกระบวนการที่ใช้ในการกำจัดสารประเภทนี้ ทำให้บิสฟีนอล เอ สามารถหลุดรอดจากการกำจัดและปนเปื้อนลงในแหล่งน้ำได้ งานวิจัยนี้มีวัตถุประสงค์หลักเพื่อศึกษาการเกิดและการเปลี่ยนแปลงของสารบิสฟีนอล เอ ในโรงควบคุมคุณภาพน้ำในเขตกรุงเทพมหานคร

ผลจากการศึกษาตัวอย่างน้ำเสียจากโรงควบคุมคุณภาพน้ำกรุงเทพมหานคร ก่อนบำบัด และหลังบำบัด พบว่ามีบิสฟีนอล เอ ปนเปื้อนในน้ำอยู่ 128.5 - 606.0 นาโนกรัมต่อลิตร และ38.7 - 270.5 นาโนกรัมต่อ1ลิตร ตามลำดับ แม้ว่าโรงควบคุมคุณภาพน้ำที่ทำการศึกษายังไม่มีวิธีการกำจัดสารชนิดนี้ในการบำบัดน้ำเสีย จากข้อมูลที่ศึกษา พบว่าโรงควบคุมคุณภาพน้ำทุ่งครุมีประสิทธิภาพในการกำจัดสารบิสฟีนอล เอ สูงที่สุดของการเก็บตัวอย่างในเดือนธันวาคม พ.ศ.2556 เท่ากับ 90.7% รองลงมาในเดือนตุลาคมเท่ากับ80.4% และโรงควบคุมคุณภาพน้ำดินแดงมีประสิทธิภาพในการกำจัดสารบิสฟีนอล เอ สูงที่สุดของการเก็บตัวอย่างในเดือนกุมภาพันธ์ พ.ศ.2557 เท่ากับ 69.2% เมื่อศึกษาถึงระบบการบำบัดน้ำเสียของโรงควบคุมคุณภาพน้ำทุ่งครุและดินแดง พบว่าเป็นระบบบำบัดน้ำเสียแบบตะกอนเร่งชนิดวีแอลอาร์ และระบบบำบัดแบบตะกอนเร่งที่สามารถกำจัดสารอาหารตามลำดับ ดังนั้น จึงสรุปได้ว่าระบบการบำบัดน้ำเสียทั้งสองระบบนี้อาจจะเป็นระบบที่มีความเหมาะสมในการกำจัดสารบิสฟีนอล เอ

ปัจจุบันประเทศไทยยังไม่มีกฎหมายหรือข้อกำหนดในการควบคุมปริมาณสารบิสฟีนอล เอ ในทรัพยากรน้ำ มีเพียงประกาศของกระทรวงสาธารณสุข เรื่องการกำหนดคุณภาพหรือมาตรฐานของภาชนะบรรจุที่ทำจากพลาสติก ว่าสามารถพบสารบิสฟีนอล เอ ในปริมาณที่ไม่เกิน 500 มิลลิกรัมต่อ1กิโลกรัม และการแพร่กระจายไม่เกิน 2.5 มิลลิกรัมต่อ 1 ลูกบาศก์เดซิเมตรของสารละลายในในพลาสติกโพลีคาร์บอเนต และมีการการประกาศให้สารบิสฟีนอล เอ เป็นวัตถุที่ห้ามใช้เป็นส่วนผสมในการผลิตเครื่องสำอาง และเนื่องจากยังไม่มีมาตรฐานควบคุมคุณภาพน้ำเกี่ยวกับสารรบกวนการทำงานของต่อมไร้ท่อ ทำให้สารเหล่านี้สามารถปนเปื้อนในแหล่งน้ำและอาจก่อให้เกิดอันตรายต่อมนุษย์ได้ จึงเป็นเรื่องที่สำคัญที่ควรเร่งให้มีการกำหนดมาตรฐานเกี่ยวกับสารที่รบกวนการทำงานของต่อมไร้ท่อในมาตรฐานการควบคุมคุณภาพแหล่งน้ำในประเทศไทย

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# LIST OF ABBREVIATIONS

**Abbreviations and symbols**

| | |
|---|---|
| % | Percent |
| $^{o}$C | Degree (s) Celsius |
| µg | Microgram (s) |
| µg/L | Microgram (s) per Liter |
| µm | Micrometer (s) |
| $^{14}$C | Carbon-14 |
| ADHD | Attention deficit hyperactivity disorder |
| ANOVA | Analysis of variance |
| Apr | April |
| BADGE | Bisphenol A diglycidyl ether |
| B.E. | Buddhist Era |
| BFDGE | Bisphenol F diglycidyl ether |
| BMA | Bangkok Metropolitan Administration |
| BNR | Biological Nutrient Removal |
| $BOD_5$ | 5 day Biochemical Oxygen Demand |
| BPA | Bisphenol A |
| BPF | Bisphenol F |
| CAS | Continuous Activated Sludge |
| CAS-No. | Chemical Abstract Service Number |
| CC | Chatu Chak WWTP |
| circa | around, about |
| CN | Chong Non Si WWTP |
| COD | Chemical Oxygen Demand |
| CWA | Clean Water Act |
| DBD | Dielectric Barrier Discharge |
| DD | Din Daeng WWTP |

# LIST OF ABBREVIATIONS (cont.)

**Abbreviations and symbols**

| | |
|---|---|
| Dec | December |
| DES | Diethylstilbestrol |
| DI | Deionized Water |
| DO | Dissolved Oxygen |
| EC | Electrical Conductivity |
| EC50 | Half Maximal Effective Concentration |
| EDCs | Endocrine Disrupting Chemicals |
| Eff. | Effluents |
| EFSA | European Food Safety Authority |
| EINECS-No | European Inventory Of Existing Commercial Chemical Substances Number |
| EPA | Environmental Protection Agency |
| ER | Estrogen Receptor |
| ERTC | Environmental Research and Training Center |
| et al. | Et alii, and others |
| EU | European Union |
| FDA | Food and Drug Administration |
| Feb | February |
| GAC | Granular Activated Carbon |
| GF/B | Glass Microfiber Filter with pore size 1.0 μm |
| g/mol | Gram (s) per mole |
| h | Hour (s) |
| HLB | lipophilic divinylbenzene with hydrophilic N-vinylpyrrolidone polymer |
| HPLC | High Performance Liquid Chromatography |
| Inf. | Influents |
| $kg/m^3$ | Kilogram (s) per cubic meter |

# LIST OF ABBREVIATIONS (cont.)

**Abbreviations and symbols**

| | |
|---|---|
| km | Kilometer (s) |
| $km^2$ | Square kilometer (s) |
| kHz | Kilohertz (s) |
| kPa | Kilopascal (s) |
| $kW/m^2$ | Kilowatt (s) per square meter |
| L | Liter (s) |
| LC | Liquid Chromatography |
| LC50 | Lethal Concentration 50 |
| LC50/ EC50 | Acute Effect Concentration |
| LDL | Lowest Detection Limit |
| LOD | Limit of Detection |
| Log $K_{ow}$ | Octanol-water partition coefficient |
| Log $K_{aw}$ | Air-water partition coefficient |
| Log $K_{oa}$ | Octanol–air partition coefficient |
| LOQ | Limit of Quantification |
| $m^2$ | Square meter (s) |
| $m^3/d$ | Cubic meter (s) per day |
| MBR | Membrane Bioreactor |
| MF | Microfiltration |
| mg | Milligram (s) |
| $mg/dm^3$ | Milligram (s) per cubic decimeter |
| mg/kg bw/day | Milligram (s) per kilogram of body weight |
| mg/L | Milligram (s) per Liter |
| min | minute (s) |
| mL | Milliliter (s) |
| ml/min | Milliliter (s) per minute |
| mm | Millimeter (s) |

# LIST OF ABBREVIATIONS (cont.)

**Abbreviations and symbols**

| | |
|---|---|
| mM | Millimolar (s) |
| MWWTP | Municipal Wastewater Treatment Plant |
| NCI | National Cancer Institute |
| ND | Not Detected |
| ng/L | Nanogram (s) per Liter |
| ng/ml | Nanogram (s) per mililiter |
| NK | Nong Khaem WWTP |
| nm | Nanometer (s) |
| NOM | Natural Organic Matter |
| NP | Nonylphenol |
| NPI | National Pollutant Inventory |
| NTP | National Toxicology Program |
| Oct | October |
| OECD | Organization for Economic Co-operation and Development |
| PC | Polycarbonate |
| PCD | Pollution Control Department |
| pKa | Alkaline pH value |
| ppb | Part (s) per Billion |
| ppm | Part (s) per Million |
| PR | Progesterone Receptor |
| PRTR | Pollutant Release and Transfer Register |
| PVC | Polyvinyl chloride |
| RE | Removal Efficiency |
| REACH | Registration, Evaluation, Authorization and Restriction of Chemicals |
| RK | Rattanakosin WWTP |
| rpm | Round (s) per minute |

# LIST OF ABBREVIATIONS (cont.)

**Abbreviations and symbols**

| | |
|---|---|
| RSDr | Relative Standard Deviation of Repeatability |
| Samp.point | Sampling Point |
| SCAS | Semi-continuous Activated Sludge |
| SDB-L | Styrene-Divinylbenzene Polymer |
| S/N | Signal-to-Noise Ratio |
| SP | Si Phraya WWTP |
| SPE | Solid-phase extraction |
| SRT | Solids Residence Time |
| SVHC | Substance of Very High Concern |
| TDS | Total Dissolved Solids |
| Temp | Temperature |
| TK | Thungkru WWTP |
| TOC | Total Organic Carbon |
| TRI | Toxic Release Inventory |
| TS | Total Solids |
| TSCA | Toxic Substance Control Act |
| TSS | Total Suspended Solids |
| UNECE | United Nations Economic Commission for Europe |
| U.S. | United States |
| U.S. EPA | United States Environmental Protection Agency |
| UV/Vis | Ultraviolet–Visible |
| WWTP | Wastewater Treatment Plant |

# CHAPTER I
# INTRODUCTION

## 1.1 Statement of the Problem

Many chemical and microbial constituents that have not historically been considered as contaminants are present in the environment on a global scale. These emerging contaminants are commonly derived from municipal, agricultural, and industrial wastewater sources and pathways (U.S. Geological Survey, 2012). Recently, the natural environment has been changing by the chemical contaminants released during human activities. These substances such as heavy metals, pharmaceuticals, pesticides, herbicides, etc, not only cause harmful effects on the environment but also on human health. Many of the thousands of anthropogenic chemicals currently released into the environment are endocrine-disrupting compounds. These are defined as exogenous chemicals or chemical mixtures that impact endocrine system structure or function and cause adverse effects (Flint et al., 2012).

Chemicals implicated in endocrine disruption include biocides, industrial compounds, surfactants, and plasticizers including Bisphenol A (BPA). BPA is a monomer used by the plastics industry to manufacture a host of consumer products and industrial resins. Because of its large scale production and widespread usages, BPA is released into the environment through air, land, and water during manufacturing, processing, and leaching from end-of-life's treatment. As a chemical that has found widespread use for more than fifty years, BPA is now being tested extensively for its potential to cause biological harm to humans via contact with products made from BPA. While it is generally agreed that this potential is negligible, there is a lingering questions whether BPA might induce elicit toxic responses in humans and other mammals that consume certain levels of BPA orally through drinking water (Crain et al., 2007; Flint et al., 2012; Santhi et al., 2012).

## 1.2 Background Information

Bisphenol A (BPA) is an organic compound containing two equivalent phenol groups that was first synthesized in 1891. In the 1930's, it was discovered that BPA has estrogenic properties, however its use as a synthetic estrogen was abandoned in favor of diethylstilbestrol (DES), which was determined to have more potent effects. DES was prescribed to women to help with difficult pregnancies, but it was discovered after it had been given to millions of women over 30 years, that DES was a carcinogen and could lead to reproductive defects in girls born to mothers taking DES. This raised the concern that a chemical with similar structure and properties such as BPA could have similar toxic effects. (Erler and Novak, 2010)

In the 1940's, BPA began to be used as a hardening agent in the production of plastics. BPA is found in a number of different plastics, including widely used polycarbonate plastic and the plastics used to make baby bottles. It is also used in dental sealants and fillings, CDs/DVDs, and various household electronic appliances. The epoxy resins that are used in canned food and beverage linings contain BPA. The widespread use of BPA has led it to be one of the most produced chemicals in the world, at 2 million metric tons a year (Lang et al., 2008). The increased production and prevalent use has made BPA a ubiquitous chemical in the environment. The world population is directly and chronically exposed to BPA through consumption due to its use in food and beverage packaging and storage containers, with exposure increased due to the fact that BPA leaches from plastics when exposed to heat or acidic environments (Le et al., 2008; Vandenberg et al., 2007).

Many of the adverse effects that BPA has on human health were first accidentally discovered about 2 decades ago. In 1993, it was revealed that BPA leached from autoclaved polycarbonate flasks, leading to increased proliferation of breast cancer cells (Vandenberg et al., 2007). Exposure to BPA due to damaged polycarbonate cages led to disruption of meiosis in the oocyte of control female mice (Hunt et al., 2003). A study with laboratory tests of the BPA effects on blood serum and found that BPA had a higher binding affinity in serum than estradiol, indicating greater estrogenic bioactivity (Nagel et al., 1997). Furthermore, exposing pregnant mice to small amounts of BPA (2μg/kg/day) resulted in significantly larger prostates

in male offspring compared to controls. This dose was 25,000 times lower than the toxic threshold set by the EPA (U.S. EPA, 2012).

The concern over BPA has grown over the last few years; however, there is still much debate over the potential effects of BPA exposure. One issue is the lack of consistency in findings, and a number of studies contradict one another. Perhaps some of the dispute can be traced to the chemical companies that have an interest in protecting their multi-billion dollar industry. Over 90% of independently funded studies have found that BPA exposure at biologically relevant doses result in adverse health effects. However, every industry-funded study has found that BPA has no effect on human health (vom Saal and Myers, 2008).

While chemical companies are trying to protect their own interest, there are legitimate debates and differences of opinions over data interpretation and the potential toxicity of BPA. For decades, a traditional toxicological approach was taken to study the effects of BPA. Extremely high doses of BPA were found to have adverse effects such as organ failure and cancer, but doses below a certain threshold were safe. There is now evidence that low doses, well below the threshold, have a completely different set of effects, which can effect development and metabolism. Proponents of BPA still dispute these findings, saying that the doses used in many of these studies (micromolar range) are still higher than environmentally relevant doses (low nanomolar range) (Ben-Jonathan et al., 2009).

Most studies lack a linear dose-dependent curve of BPA effects, making it difficult to extrapolate the action of BPA. While the debate remains open, it is clear that BPA can act as an endocrine disruptor that can possibly disrupt a number of metabolic processes.

In 2005, the Ministry of Public Health, Thailand amended the regulation for the qualities or standard for containers made from plastic. In addition to the requirements given in the Notification of the Ministry of Public Health No. 111 B.E. 2531 (1988), the newly established standard (maximum allowed level) for BPA (included phenol and p-t-butylphenol) for containers made from plastic is 500 mg/kg (Ministry of Public Health, Thailand, 2005).

This study aimed at investigating the occurrence and fate of BPA in seven municipal wastewater treatment plants (MWWTPs) in Bangkok region.

## 1.3 Objectives

The overall objective of this study was to investigate the situation of occurrence of Bisphenol A (BPA) in the selected municipal wastewater treatment plants in Bangkok region. The specific objectives of this study include:

1.3.1 To investigate the occurrence and levels of Bisphenol A (BPA) residues in the selected wastewater treatment plants in Bangkok area.

1.3.2 To evaluate the degradation of BPA correlated to the treatment process employed in the selected wastewater treatment plants.

1.3.3 To study Thai policy regarding the control of BPA residues in aquatic environments and to give recommendation for the development of Bisphenol A (BPA) standard in wastewater effluents in Thailand.

## 1.4 Scope of the Study

The scope in this study included the following:

1.4.1 Grab samples were collected from the influents and effluents of the selected wastewater treatment plants (WWTPs) Bangkok, Thailand.

1.4.2 All the samples obtained were prepared by filtration and solid phase extraction in Environmental Engineering Laboratory, Faculty of Engineering at Mahidol University. The extracted samples were brought to Environmental Research and Training Centre (ERTC), Environmental Quality Promotion Department, Ministry of Natural Resources and Environment for HPLC analyses.

1.4.3 Laboratory analyses to determine the concentration of Bisphenol A (BPA) in the samples were carried out by using high performance liquid chromatography (HPLC)

1.4.4 Other parameters analysed included: $BOD_5$, suspended solids, DO, Temperature and pH. These were measured in Environmental Engineering Laboratory, Faculty of Engineering at Mahidol University.

1.4.5 Information and data were obtained about the Thai policy regarding the control of BPA residues in aquatic environments.

1.4.6 Recommendations were provided based on the results from this study to contribute in the development of Bisphenol A (BPA) standard in wastewater effluents in Thailand

## 1.5 Limitations of the Study

Due to the cost factor of expensive analyses for BPA analysis and the practical limitation (e.g. time required for preparation and analysis of samples), the number of WWTPs in this study was reduced.

# CHAPTER II
# LITERATURE REVIEW

## 2.1 What is the Bisphenol A (BPA) ?

Bisphenol A (BPA) (CAS No. 80-05-7) is an organic compound with the chemical formula $(CH_3)_2C(C_6H_4OH)_2$. The structure consists of two phenol rings jointed by two methyl functional groups (Fig. 2.1). BPA is used in the primary production of polycarbonate plastics and epoxy resins used to make hard and clear plastic in the industrial applications. It can be found in many consumer products such as returnable beverage bottles, infant feeding bottles, tableware (plates and mugs) and storage containers.

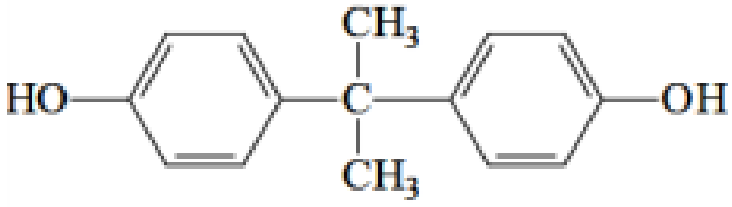



**Figure 2.1**: Chemical structure of Bisphenol A (Cao, 2010)

## 2.2 Physicochemical Properties of Bisphenol A

Bisphenol A (BPA) is a colorless solid and usually occurs as flakes or a powder. It is soluble in organic solvents such as acetic acid, ethanol, benzene and diethyl ether, but poorly soluble in water. The purity of BPA is stated as being 99 - 99.8%, depending on the manufacturer. Impurities typically include phenol (< 0.06 %) , ortho and para isomers of Bisphenol A (< 0.2 %) and water (< 0.2 %). The physico – chemical properties of BPA are summarized in Table 2.1 (Cao, 2010; European Communities, 2010).

**Table 2.1** Physio–chemical properties of BPA

| Property | Values |
|---|---|
| Chemical Abstracts Service registry number (CAS-No.) | 80-05-7 |
| European Inventory of Existing Commercial chemical Substances number (EINECS-No) | 201-245-8 |
| Other names | 4,4'-dihydroxy-2,2-diphenylpropane<br>2,2-bis(4-hydroxyphenyl)propane<br>4,4'-isopropylidenediphenol |
| Molecular weight | 228.29 g/mol |
| Molecular formula | $C_{15}H_{16}O_2$ |
| Physical state at normal temperature and pressure | White solid flakes or powder with a mild phenolic odour |
| Melting point | 155 - 157°C at atmospheric pressure |
| Boiling point | circa 360°C with decomposition at atmospheric pressure |
| Relative density | 1.1-1.2 kg/$m^3$ at 25°C |
| Vapor pressure | $5.3x10^{-9}$ kPa at 25°C |
| Solubility in water | 300 mg/l used at normal temperature |
| Partition coefficient (Log $K_{ow}$) | 3.40 |
| Partition coefficient (Log $K_{aw}$) | -9.01 |
| Partition coefficient (Log $K_{oa}$) | 12.41 |
| Flash point | circa 207°C |
| Autoflammability | circa 532°C |
| Oxidizing properties | Not an oxidizing agent |

Source: Cao, 2010; European Communities, 2010

## 2.3 Production and Application of BPA

Bisphenol A (BPA) is one of the highest production volume chemicals in the world. Global BPA production capacity was about 5,160 kilotons in 2008 (U.S. EPA, 2012). Dow Chemical and Bayer AG produce the bulk of BPA in the world. These two companies reportedly had a global BPA capacity of about 311 and 580 kilotons, respectively in 2008. Several U.S. companies have already started to remove BPA from its food packaging, also package all or part of their product in BPA-free containers (Agrawal and Suman, 2011; Clarke, 2012). BPA is mainly used as an intermediate in the production of polycarbonate (PC) (71.1%) and epoxy resins (25.0%). PCs are used to manufacture a wide variety of products such as optical media (CDs, DVDs, etc.), electrical, electronic parts, etc. Epoxy resins are also used in electrical and electronic parts. Minor uses include as an intermediate for phenoplast resins (plastics based on phenolic resins), unsaturated polyester resin, alkyloxylated Bisphenol-A, polyols/polyurethanes and modified polyamides, for can coatings, thermal paper, tyre and brake fluid manufacture, and in PVC production and processing (Bailey and Hoekstra, 2010; European Communities, 2010; Pirard et al., 2012; Umweltbundesamt, 2010). However, PC and epoxy resins represent the major applications for BPA. Examples of consumer products containing BPA are shown in Table 2.2 (PC/BPA-group-PlasticsEurope, 2007).

## 2.4 Contamination of BPA in Environment

BPA can be distributed in environment through many ways. Releases of Bisphenol A may occur during production, processing, use or disposal of the substance or products containing, and then contaminate in water, atmosphere and soil.

### 2.4.1 In aquatic environment

Over the past 10 years, the emphasis on environmental monitoring has shifted from "legacy pollutants" (for example, several persistent organic pollutants) to many new chemicals being discovered in the environment. The term "chemicals of emerging concern" characterizes the emerging awareness of the presence in the environment of many chemicals used by society and the concern over the risk that

**Table 2.2** Examples of consumer products containing BPA

| **Polycarbonate Plastics (71.1% of use)** | **Epoxy Resins (25% of use)** |
|---|---|
| 1) Optical Media (Compact discs, CDs, DVDs, etc.) | 1) Marine and protective coatings (Sea containers, water ballast tanks, gas pipes, etc.) |
| 2) Electrical and electronics (TVs, telephones, computers, plugs, etc.) | 2) Powder coatings (Pipes, valves, office furniture, etc.) |
| 3) Construction (Greenhouse glazing, roof lights, Cover for solar panels, etc.) | 3) Electrical and electronics (Printed circuit boards and potting/ encapsulation parts) |
| 4) Automotive (headlamp lenses, interior light cover, etc.) | 4) Civil engineering (Flooring, coating secondary containment walls, etc.) |
| 5) Bottles and packaging (Reusable water bottles, unbreakable baby bottles, food containers, etc.) | 5) Can and coil coatings (Food and drink cans, food trays, collapsible tubes such as toothpaste and cream, mobile homes, etc.) |
| 6) Medical and healthcare (Blood oxygenators, breastpumps, etc.) | 6) Automotive coatings (Waterborne primers for cars, buses, railcars) |
| 7) Others (Helmets, safety goggles, sun glasses, etc.) | 7) Composites (Rackets, snowboard, windmill blades, etc.) |
| | 8) Adhesives (Structural adhesives for buildings and construction, adhesives for cars, boats, aircraft) |
| | 9) Photocure (Printing inks, wood coating, etc.) |

Source: PC/BPA-group-PlasticsEurope (2007)

these chemicals may pose to humans and ecosystems (Daughton, 2001; as cited in Melcer and Klecka, 2011). Discharges from MWWTPs have been identified as significant contributors of these microconstituents to surface waters. As a result, WWTP operators are seeking additional methods for removing these substances from wastewater treatment systems.

Although it is often stated that wastewater treatment systems were not designed to remove microconstituents, recent work has shown that such facilities provide effective treatment (Drewes et al., 2006, 2009; Stephenson and Oppenheimer, 2007; as cited in Melcer and Klecka, 2011). In addition, methods for enhancing the performance of existing systems, such as advanced oxidation or use of granulated activated carbon, are being explored. Therefore, current facilities need more information on how various microconstituents are removed by wastewater treatment processes and whether there are opportunities to optimize and enhance their treatment. This information could potentially reduce the need for additional tertiary treatment processes (Melcer and Klecka, 2011).

The aquatic environment has been identified as the main compartment in which BPA may be found (Cousins et al., 2002; as cited in Melcer and Klecka, 2011). Extensive monitoring has been conducted over the past 10 years, and measurements of BPA in various environmental media have been reported (Melcer and Klecka, 2011).

The solubility of BPA in water ranges from 525.65 – 1314.12 μmol/l (120 - 300 μg/ml) (Staples et al., 1998). BPA can be found in wastewater from factories that produce it because it is not completely removed during wastewater treatment. This wastewater containing BPA can be a source of contamination of the aquatic environment (Fürhacker et al., 2000; Kang et al., 2006; Staples et al., 1998). Bacteria in river water can degrade BPA under aerobic conditions but not anaerobic conditions. BPA was degraded according to an increase of bacterial counts. A half-life for BPA degradation was between 3 and 4 days (Kang et al., 2004). Moreover, Kang and Kondo found that BPA in seawater than in river water can continue for longer time with no degradation and the possibility of BPA contamination on a marine organism can be higher than that on freshwater organism (Kang and Kondo, 2005).

### 2.4.2 In atmosphere

Human exposure to Bisphenol A is widespread and usually comes through food and beverages. One can also be exposed to BPA through air, dust, and water (U.S. National Library of Medicine, 2012). Little is known about its distribution and transport in the atmosphere. BPA can be released into the atmosphere via industrial production with a rate of some 100 t $year^{-1}$ (Fu and Kawamura, 2010; Staples et al.,

1998). According to a recent study, the widespread use of PC polymers means that there is a lot of polycarbonate waste that must be properly disposed of. A variety of recycling methods have been proposed but the majority of polycarbonate waste still ends up either in landfills or incinerators. Disposal of PC by incineration also leads to BPA as one of the major products, that either as a gas or soot residue, finds its way to nature (Sala et al., 2010). It is possible that humans may gain exposure to BPA through the air and by absorption through the skin. These routes of exposure have not received much attention to date; however, there are data to suggest that absorption of BPA through the skin is possible (Biedermann et al., 2010; Zalko et al., 2011).

### 2.4.3 In soil

BPA released to the environment can reach the soil from the application of sewage sludge from wastewater treatment plants that receive wastewaters containing BPA, or from leachate from uncontrolled landfills. The biodegradability of BPA has been investigated in various studies. However, there is only little information about the occurrence and fate of BPA in soil. Based on the results of one such study, $^{14}C$-BPA was dissipated rapidly and not detectable in soil extracts following 3 days of incubation. A dissipation half-life of less than 3 days was estimated (Fent et al., 2003).

## 2.5 Harmful Effects of BPA on Human Health

Endocrine disruptors cause adverse health effects in humans and wildlife subsequent to changes in endocrine function. BPA is among the chemicals identified as a potential endocrine disruptor based on its estrogenic properties (Carlisle et al., 2009). The toxicity of BPA has been a fairly controversial subject for a while. Industry groups have been fairly adamant about its safety, while many environmental groups suggest it is causing adverse health effects in humans (Anonymous, 2011). The toxicology of BPA has been extensively studied over the past several decades. BPA was much less toxic to microorganisms than algae, invertebrates or fish. From the several studies, BPA seems to be fairly non-toxic to bacteria and may even stimulate bacterial growth at higher concentrations. An acute effect concentration

(LC50/ EC50) of BPA lies in the range ~1 to 10 mg/L for aquatic organisms. Little information is available on the effects of BPA on terrestrial organisms. Hanze (1994) reported that BPA exerts no phytotoxic effects, but seems to kill fungi effectively (Nordic Council of Ministers, 1996; Staple et al., 1998).

Following the accidental revelation of harmful effects of BPA on human health around 1993, much research has been carried out to gain more knowledge about this. Interestingly, some studies have focused on the potential of BPA to act as an estrogen. The structure and function of BPA are similar to the hormone estradiol (Figure 2.2) with the ability to bind to and activate the same estrogen receptor as the natural hormone (Polycarbonate/BPA Global Group, 2013; Rubin, 2011).

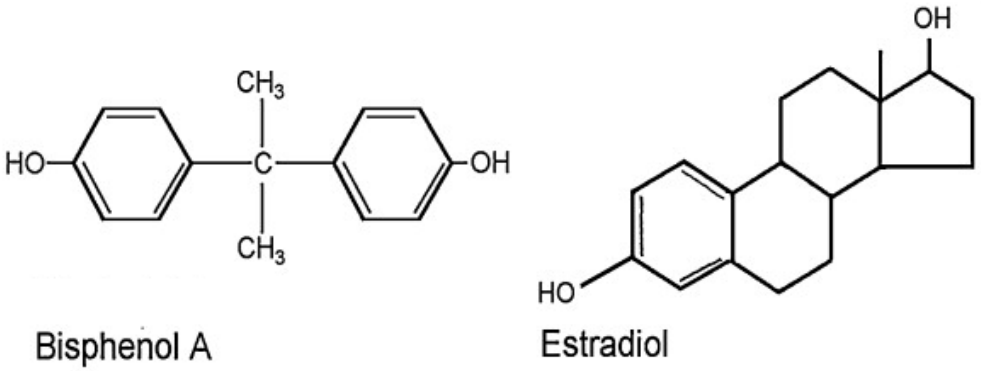



**Figure 2.2** Chemical structure of Bisphenol A and Estradiol (Rubin, 2011)

Only three studies associating BPA exposure with reproductive and developmental outcomes in humans were reported in literature. In a study of 77 women, higher serum BPA was found in women with a history of recurrent miscarriage than in controls (Sugiura-Ogasawara et al., 2005; as cited in Carlisle et al., 2009). In another study (Takeuchi et al., 2004; as cited in Carlisle et al., 2009) 19 women with polycystic ovary syndrome and 7 obese women were found to have higher serum BPA than 19 controls. Additionally, significant correlations were found between serum androgen measures and serum BPA. Another report from the same group (Takeuchi and Tsutsumi, 2002; as cited in Carlisle et al., 2009) found higher serum BPA in males than in either normal women or women with polycystic ovary syndrome and confirmed the correlation with testosterone across groups. A third study found lower concentrations of serum BPA in women with "complex endometrial hyperplasia with malignant potential" as compared to controls with normal

endometrium or with "simple endometrial hyperplasia of a benign nature" (Hiroi et al., 2004; as cited in Carlisle et al., 2009). Once again these are associations and not sure how this will be linked with marine based outcomes. (as cited in Carlisle et al., 2009).

**Health Hazard and Toxicity of BPA to Humans and Laboratory Animals**

Some of harmful effects of BPA on humans and laboratory animals include the following (Carlisle et al., 2009):

**Reproductive and Developmental Effects:** The major concern about health effects from exposure to BPA relates to its estrogen-like activity. Estrogens are a group of steroid compounds which function as the primary female sex hormone. Sex hormones influence sexual differentiation, and altered levels of the hormones can have serious effects. Studies in laboratory animals exposed during development (i.e., *in utero* or as immature animals) provide evidence of BPA's effects on the reproductive system, including:

- Altered mating behavior, maternal behavior, and sex-differentiated emotional and cognitive behavior
- Enhancement or stimulation of breast growth in female animals
- Stimulation of prostate growth in male animals

There is some evidence that BPA has effects on the reproductive ability of adult laboratory animals. Effects on the reproductive system have been observed in adult female and male rodents (Carlisle et al., 2009).

**Cancer:** In the early 1930s, it was recognized by Charles Edward Dodds (the British chemist) that BPA could be used as an artificial estrogen (Erler et al., 2010). At that time BPA was used for enhancing growth of cattle and poultry and was used for estrogen replacement for women. However, BPA was only briefly used as an estrogen replacement and then was replaced by diethylstilbestrol (DES) (BCUK, 2012). Both BPA and DES have estrogen-like chemical structure (Figure 2.3).

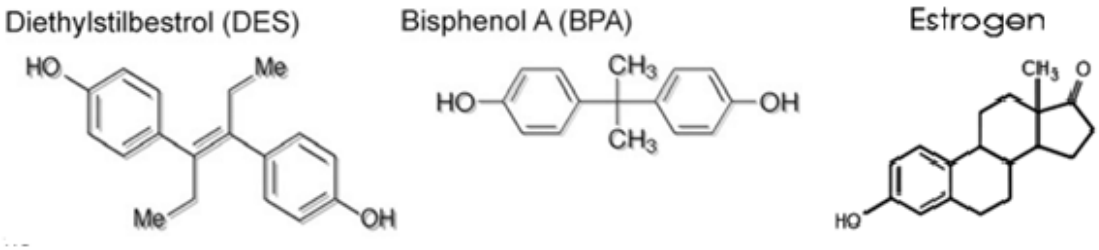



**Figure 2.3** Structures of Bisphenol A (BPA), Diethylstilbestrol (DES) and Estrogen (Doherty et al., 2010; Nunley et al., 2011)

It was later discovered that DES exposure was associated with many reproductive problems, and caused increased risk of certain cancers and pre-cancerous conditions. Because BPA structure and properties were similar to DES, it was feared that BPA could have similar effects **(**Doherty et al., 2010; Nunley et al., 2011**)**. However, no substantial evidence was found regarding BPA causing cancer in humans. Also, there is limited information on its potential to cause cancer in animals. One long-term animal study did not find convincing evidence that BPA caused cancer in rats or mice. However, there are some animal studies to suggest further research is needed (Carlisle et al., 2009).

**Obesity:** Information of BPA's influence on human obesity is sparse. In animal and cell studies, BPA was found to influence multiple processes related to obesity.

**Effects on the thyroid:** While evidence from animal and cell studies indicates that BPA can affect the thyroid, conflicting findings have been reported. No information was found for any effects of BPA on the human thyroid.

**Immune system effects:** BPA has also been shown to affect the immune system of experimental animals, diminishing its ability to mount a protective response against infections.

**Nervous system effects:** Animal and cell studies show that BPA can affect brain development in areas linked with learning, memory and a variety of behavioral traits. There is concern that BPA might be a factor in the development of human neurological disorders such as attention-deficit hyperactivity disorder (ADHD) and memory loss, but there is no information on these effects in humans.

## 2.6 Environmental Fate of BPA

Several articles and risk assessments have summarized the environmental behavior of BPA. Biodegradation is expected to be the dominant mechanism for removal of BPA from aquatic and terrestrial environments. Biodegradation of BPA has been extensively studied using several test systems. These tests range from screening tests, which assess the ready and inherent degradability, to simulation tests for surface waters, soils, and wastewater treatment systems, which are designed to examine degradation in the laboratory under conditions that closely simulate the fate of a chemical in the environment. Further, microorganisms with the ability to use BPA as a carbon source for growth have been isolated and described, and the pathways for metabolism by microorganisms have been characterized (Melcer and Klecka, 2011).

### 2.6.1 Wastewater Treatment: Laboratory and Pilot-Scale Investigations

Laboratory-scale investigations are useful because they offer the opportunity of evaluating different operating conditions in simulated secondary wastewater treatment systems in a controlled environment. Turner and Watkinson (1986) studied the biodegradation of BPA using a modified semi-continuous activated sludge (SCAS) procedure by using microorganisms were obtained from a MWWTP. The removal of BPA was 87 to 95% (after 24 to 30 days) as measured by changes in dissolved organic carbon concentration. Based on these results, the authors classified BPA as inherently biodegradable. The biodegradation of BPA has been examined in other studies designed to simulate wastewater treatment systems. Matsui et al. (1988) studied the biodegradability of BPA using activated sludge from an industrial wastewater treatment plant by monitoring changes in chemical oxygen demand (COD) concentrations. The removal efficiency of BPA was 72% based on COD. Furun et al. (1990) also reported extensive biodegradation in activated sludge studies conducted using microorganisms from a petrochemical plant. Removal efficiencies reached 99.7% after two weeks of incubation (Melcer and Klecka, 2011).

Hansveit and Aalderink (2001) examined the fate of $^{14}$C-labeled BPA in an activated sludge simulation test. The $^{14}$C-BPA was fed to the continuous flow reactor

system at a concentration of 1 mg/L, and removal of radiolabeled BPA was measured in the influent, effluent, wasted sludge, and exhaust air. The recovery of dosed radioactivity was 95 to 99%. Biodegradation was the dominant removal mechanism (63.8% mineralization of $^{14}$C-BPA), with 18% removal attributed to adsorption onto biosolids or incorporation into biomass. The overall BPA removal efficiency was 99.1% (98.5-99.4%). Chen et al. (2008) carried out laboratory-scale comparisons of BPA treatment in continuous activated sludge (CAS) and membrane bioreactor (MBR) systems. Consequently, there was no significant difference in performance between the two systems. Lee et al. (2008) compared the removal efficiencies of various treatment technologies, including MBR, nanofiltration, and reverse osmosis for the removal of BPA and other compounds. High removal efficiencies were observed for the MBR system when operated in biological nutrient removal (BNR) mode at solids residence time (SRT) of 20 days; BPA concentrations were reduced from 90 to 6 ng/L. No additional improvement in BPA removal was observed when the effluent from the MBR was treated by either nanofiltration or reverse osmosis (Chen et al., 2008; Lee et al., 2008; Melcer and Klecka, 2011).

These laboratory and pilot investigations show that BPA is biodegradable in activated sludge systems that are operated over a range of SRT. Biodegradation has been shown to be the dominant removal mechanism, although some losses may occur because of adsorption onto biomass (Melcer and Klecka, 2011).

### 2.6.2 Wastewater Treatment: Full-Scale Facilities

Wastewater treatment plants use a range of processes in both liquids and solids treatment trains. These processes use different mechanisms of microconstituent removal, and the effectiveness of the various unit operations are related to the physical, chemical, and biological properties of the substances. BPA removal efficiencies varied widely and depended on the type of facility. Based on an analysis of influent, effluent, and biosolids samples from six WWTPs in Greece, Stasinakis et al. (2008) showed that 72 ±10% of influent BPA was transformed or removed, 1.5 ±4% was adsorbed to biomass, and 13 ±7% was found in the final effluent. These results were based on three separate sampling events at six activated sludge systems, all of which implemented either nitrification or BNR and were operated at SRT ranging from 8 to

25 days. BPA concentrations ranged from less than 0.14 to 2.14 μg/L (median 0.68 μg/L) in the influents and from less than 0.14 to 1.10 μg/L (median 0.07 μg/L) in the effluents. It may be inferred that approximately 87% overall removal was observed in these plants (Melcer and Klecka, 2011; Stasinakis et al., 2008).

Other studies have examined the removal of BPA by WWTPs in WWTPs, Europe. For example, Weltin et al. (2002) studied in Germany. Influent BPA concentrations ranging from 0.15 to 7.22 μg/L (median 2.26 μg/L) were reduced to 0.03 to 2.5 μg/L (median 0.49 μg/L) in the effluents. Similar results were reported by Ballesteros-Gómez et al. (2007) in WWTPs, Spain. Bisphenol A concentrations ranged from 0.96 to 1.6 μg/L in the influent and from 0.26 to 0.36 μg/L in the effluent. Overall BPA removal efficiencies were reported to be greater than 75% (Ballesteros-Gómez et al., 2007; Weltin et al., 2002).

## 2.7 BPA Removal Methods

Nowadays, there is a special interest in decontaminating Bisphenol A from polluted waters, and several processes have been developed to degrade Bisphenol A. Most of the studied methods involve photocatalytic degradation or biodegradation. These processes do not achieve the mineralization, and in the case of biological processes, a sludge is discharged, creating another problem worse than the degradation itself. As a new alternative to these methods, the use of sonochemical reactions has been proven to be efficient for the degradation of organic compounds in waters, as can be found in several studies regarding phenol degradation, dyestuffs degradation and chlorinated compounds degradation. One study reported that BPA (0.50mM) was completely degraded after 10, 3 and 2 h of ultrasonic irradiation at a frequency of 404 kHz, and intensities of 3.5, 9.0 and 12.9kW/$m^2$, respectively. Experiments with different ultrasonic intensities were carried out to determine the efficiency of BPA degradation in solution. High intensities generated the best total organic carbon (TOC) reductions and a faster degradation of BPA (Inoue et al., 2008).

Many researches have shown that low-pressure membrane such as microfiltration and ultrafiltration had a good performance for endocrine disrupting chemicals (EDCs) removal, which can be attributed to adsorption mechanism.

However, so far only a few studies on microfiltration (MF) of BPA removal in drinking water treatment have been done. Bing-zhi et al. (2010) investigated the method for removal BPA from drinking water by hollow fiber microfiltration (MF). This study was focused on the effect of various factors on BPA removal efficiency in MF filtration with respect to BPA initial concentration, pH, ionic strength and organic matter. Adsorption plays a significant role in BPA removal in MF filtration. The results showed that MF could remove BPA effectively. A higher removal was obtained at the beginning of the filtration, and the removal efficiency decreased to around 20% when the membrane became saturated due to adsorption of BPA onto the MF membrane. As pH of solution approached to pKa (9.6–11.3) of BPA, BPA removal efficiency dropped significantly. The effect of ionic strength on BPA removal was negligible. The presence of natural organic matter (NOM) demonstrated no observable impact on BPA removal. After filtration, the backwash could recover removal efficiency effectively (Bing-zhi et al., 2010).

The allowable levels of persistent organic pollutants such as BPA are very low, and they are hard to remove completely. Granular activated carbon (GAC) is used as an efficient and versatile adsorbent in decontamination processes because of its high surface area and adsorption capacity, developed porous structure and special surface reactivity. However, the adsorption by GAC is not the final step for pollutant disposal, resulting only in the transition of the toxic organic substances from the liquid or gas phase to the solid phase. Thus, it would not only be uneconomical but would also bring environmental secondary pollution if spent GAC is not effectively treated (Tang et al., 2012). At present, dielectric barrier discharge (DBD) techniques have been extensively used in environmental protection.

In a recent study, an integrated granular activated carbon (GAC) preconcentration and dielectric barrier discharge (DBD) plasma degradation process was proposed for treatment of Bisphenol A (BPA) wastewater. Firstly, BPA in water was adsorbed onto GAC, and then the BPA was decomposed and GAC was regenerated simultaneously by DBD plasma. The adsorption characteristics of BPA on GAC were studied by batch kinetics. The effects of pulse voltage, pulse repetitive rate, treatment time and air flow rate were investigated. Experimental results indicated that increasing pulse voltage, pulse repetitive rate, treatment time and air flow rate

could enhance the degradation of BPA. The Fourier transform infrared spectroscopy analysis proved the removal of BPA on GAC after DBD treatment. The analysis of texture of GAC samples showed that the specific surface area and pore volume of GAC decreased after DBD regeneration. Furthermore, all adsorption equilibrium isotherms fitted the Langmuir model fairly well, which demonstrated that DBD plasma did not appear to modify the adsorption process but to shift the equilibrium toward lower adsorption concentrations (Tang et al., 2012).

## 2.8 Previous Studies

In the late 1970s, due to the increasing popularity surrounding BPA containing products, a carcinogenesis study was conducted by the National Toxicology Program (NTP) of the U.S. National Cancer Institute (NCI) to test the safety of BPA. The report stated that the evidence around carcinogenicity effects were not convincing. However, the NTP reported reproductive toxicity of BPA (Legislative Counsel of California, 2011). In 1993, BPA leaching from autoclaved polycarbonate flasks was reported for the first time. This leaching led to disruption of meiosis in the oocyte of control female mice and increased risk of breast cancer cells. This case renewed the attention to its estrogenicity (Vandenberg et al., 2007).

Many studies have been reported in literature during the past 10 years showing harmful effects of BPA on lab animals, including cancer, obesity, diabetes, reproductive failures and neurological disorders. In 2008, Canadian health officials began steps to declare BPA a toxin and to have it banned from use in baby bottles and tableware for children. Several manufacturers - including Nalgene, Wal-Mart, Toys "R" Us and CVS pharmacies - announced plans to phase out use of the chemical in children's products (Austen, 2007). In September 2008, the U. S. National Toxicology Program, an advisory board to the FDA and Environmental Protection Agency, released its report expressing some concern for how BPA affects the prostate and neural development of fetuses, infants and children. It also expressed concern about the chemical's effect on breast tissue and early puberty. Results of another study, published in the Journal of the American Medical Association, tied BPA to heart

disease in humans. Lawmakers started to call for a ban of the chemical in children's products (Le et al., 2008).

Several studies have reported the BPA occurrences in the wastewater effluents and receiving waters worldwide. Median effluent concentrations of 0.14, 0.15, and 0.03 μg/l were observed in Canada (Lee and Peart, 2000), Germany (Körner et al., 1998) and Japan (Nasu et al., 2001) respectively (as cited in 54-Johnson and Jürgens, 2003). Industrial effluents around Toronto had a median value of 11 μg/l (Lee and Peart , 2000). BPA concentrations in the effluent of paper production (mean 41 μg/l), metal/wood production (17 μg/l), and the chemical industry (18 μg/l) have been reported (Fürhacker et al., 2000). In the surveys of river systems in Japan (Tanaka et al., 2000) and Germany (Fromme et al., 2002), the majority of samples were below 0.1 μg/l with only one sample above 1 μg/l. An analysis of sewage sludge extracts taken from 18 treatment works in Canada gave a median concentration of 1.1 mg/kg (Lee and Peart, 2000). High concentrations of BPA of 25–146 μg/l have been found in waste dump water and compost water (Fromme et al., 2002) (as cited in Johnson and Jürgens, 2003).

Reported concentrations in domestic sewage effluent are typically below 1.5 μg/l. Based on the reported potency of BPA and receiving water dilution, this should not give rise to concern. However, significantly higher concentrations (often 10s of μg/l) were observed in the effluent emanating from some specific industries which could lead to locally elevated sediment concentrations (Johnson and Jürgens, 2003). Around October 2008, the U.S. FDA's Science Board found out that the FDA had ignored hundreds of studies on BPA and advised the agency to reopen its investigation of the chemical. A study reported that even low levels of BPA can interfere with chemotherapy for breast cancer patients.

Canada has just become the first country in the world to regulate Bisphenol A (BPA) as a toxic substance, adopting a precautionary approach and recognizing that the compound may be harmful to human and environmental health (Saxe, 2010).

The comparative review of some of the past studies on BPA is summarized in Table 2.3

**Table 2.3** An overview of some of the past studies on BPA

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 1998 | Staples, C. A., Dom, P. B., Klecka, G. M., O'Block, S. T., and Harris, L. R. | A review of the environmental fate, effects, and exposures of Bisphenol A | BPA may be released into the environment through its use and handling, and permitted discharge. BPA is moderately soluble about 120 to 300 mg/L at pH 7, may adsorb to sediment, has low volatility, and is not persistent based on its rapid biodegradation in acclimated wastewater treatment plants and receiving waters (half-lives 2.5 to 4 days). BPA is slightly to moderately toxic and has low potential for bioaccumulation in aquatic organisms. Surface water concentrations are at least one to several orders of magnitude lower than chronic effects, with most levels nondetected. |
| 1999 | Bergeron, R.M., Thompson, T.B., Leonard, L.S., Pluta, L. and Gaido, K.W. | Estrogenicity of Bisphenol A in a human endometrial carcinoma cell line | The ability of BPA to affect human estrogen receptor (ER) binding, expression of progesterone receptor (PR) mRNA and protein, and cell proliferation has been measured in the human endometrial cell line,ECC-1. Although less potent than 17β-estradiol, BPA was able to bind to the human uterine ER. The results of this study provide evidence that two ER agonists can act differentially in vitro to affect the expression of genes involved in regulating cellular growth and development, though the human risk potential remains to be determined. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2000 | Fürhacker, M., Scharf, S. and Weber, H. | Bisphenol A: emissions from point sources | In this study, industrial emitters and communal waste waters were monitored simultaneously. The samples were taken over periods of one week at nine sample sites (in a town in Lower Austria). The results showed that the concentrations and fluxes were variable. The paper industry was the major BPA contributor to the influent of the waste water treatment plant. |
| 2001 | Tsutsumi, Y., Haneda, T. and Nishida, T. | Removal of estrogenic activities of Bisphenol A and nonylphenol by oxidative enzymes from lignin-degrading basidiomycetes | Tsutsumi et al. (2001) studied removal of estrogenic activities of BPA and nonylphenol (NP) by using manganese peroxidase (MnP) and laccase. These enzymes completely removed the estrogenic activity of BPA and NP within 12 hours. This is the first report dealing with the enzymatic removal of estrogenic activities of BPA and NP. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2002 | Fromme, H., Kuchler, T., Otto, T., Pilz, K., Muller, J. and Wenzel, A. | Occurrence of phthalates and Bisphenol A and F in the environment | This study measured phthalates and BPA and BPF in 116 surface-water samples from various rivers, lakes and channels in Germany and compared the result with available ecotoxicological effect data. The concentrations of BPF were lower than BPA in all environmental media. Very high concentrations of BPA and phthalates were confirmed in waste dump water and compost water samples as well as in the liquid manure samples. |
| 2003 | Fent, G., Hein, W. J., Moendel, M. J. and Kubiak, R. | Fate of $^{14}$C-Bisphenol A in soils | BPA released to the environment can reach the soil from the other sources containing BPA. There is a few data about BPA in soil. Therefore, laboratory soil degradation and batch adsorption studies with $^{14}$C-BPA in different types soil to established procedures commonly used in the assessment of the fate of pesticides in soils. From the degradation study, the result shown that $^{14}$C-BPA was dissipated rapidly and not detectable in soil extracts following 3 days of incubation. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2004 | Lee, J.-M., Kim, M.-S. and Kim, B.-W. | Photodegradation of Bisphenol-A with $TiO_2$ immobilized on the glass tubes including the UV light lamps | Lee et al. studied photodegradation of BPA by using immobilized $TiO_2$ particles as a photocatalyst, where the titanium sol-solution synthesized by a sol–gel method was used as the binder for the immobilization. Apparent rate constant of the first order increased with increasing $TiO_2$-coating time from 1 to 3, however, decreased over 4-coating time. Rate constant (K) increased with increasing the UV light intensity, which was related with the number of inserted UV lamps. Rate constant (K) increased as the pH value shifted from basic to acidic regions. |
| 2005 | Kang, J.-H. and Kondo, F. | Bisphenol A degradation in seawater is different from that in river water | Kang and Kondo studied a relationship between changes of bacterial counts and BPA degradation in seawater under aerobic or anaerobic conditions, and at temperatures of 4, 25, and 35 $^{o}$C. The results showed that there was no relationship between BPA degradation and the change of bacterial counts in seawater. In river water, the more bacterial counts increased, the more the level of BPA decreased under aerobic conditions. Half-lives for BPA degradation at 25 and 35 $^{o}$C were 4 and 3 d, respectively. BPA can continue for longer time with no degradation in seawater than in river water and the possibility of BPA contamination on a marine organism can be higher than that on freshwater organism. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2006 | Kang, J.-H., Kondo, F. and Katayama, Y. | Importance of control of enzymatic degradation for determination of Bisphenol A from fruits and vegetables | The purpose of this study was to develop an analytical method for determination of BPA from fruits and vegetables. Recovery results in the samples spiked with a 10 ng/ml BPA were lower than those in the samples with a 50 ng/ml BPA. The low recovery results were caused by BPA degradation by enzymes. To prevent BPA degradation by enzymes is very important to detect BPA from fruit and vegetable samples because the BPA degradation may lead to wrong results. The prevention of BPA degradation by enzymes is simply possible by the pH control. |
| 2007 | Ballesteros-Gómez, A., Ruiz, F.-J., Rubio, S. and Pérez-Bendito, D. | Determination of Bisphenols A and F and their diglycidyl ethers in wastewater and river water by coacervative extraction and liquid chromatography–fluorimetry | BPA, BPF and their corresponding diglycidyl ethers (BADGE and BFDGE) in wastewater and river water were determined by coacervative extraction and liquid chromatography–fluorimetry. The method was successfully applied to the determination of the target pollutants in raw and treated sewage from four mechanical-biological treatment plants and three rivers. These substances were presented in wastewater influents at concentrations in the range 0.96 to 1.6 μg/L. The biological treatment at the WWTPs studied reduced BPA and BPF concentrations in a percentage above 75%, while diglycidyl ethers were not detected in most of the effluents investigated. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2008 | Inoue, M., Masuda, Y., Okada, F., Sakurai, A., Takahashi, I. and Sakakibara, M. | Degradation of Bisphenol A using sonochemical reactions | The use of sonochemical reactions has been proven to be efficient for the degradation of organic compounds in waters, as can be found in various studies regarding the degradation of phenol, dyestuffs and chlorinated compounds. The results from the BPA removal (0.50 mM) in aqueous solution using sonochemical degradation with different ultrasonic intensities was completely degraded after 10, 3 and 2 h of ultrasonic irradiation at a frequency of 404 kHz and intensities of 3.5, 9.0 and 12.9 $kW/m^2$, respectively. From the result showed that high intensities generated the best TOC reductions and a faster degradation of BPA |
| 2009 | Li, R., Chen, G.-Z., Tam, N.F.Y., Luan, T.-G., Shin, P.K.S., Cheung, S.G. and Liu, Y. | Toxicity of Bisphenol A and its bioaccumulation and removal by a marine microalga *Stephanodiscus hantzschii* | *Stephanodiscus hantzschii* had high removal capability at low BPA concentrations as BPA was bioaccumulated and biodegraded by cells. Toxicity experiments showed that the 96-h $EC_{50}$ of BPA was 8.65±0.26 mg/L, and the cell number and chlorophyll *a* content of *S. hantzschii* decreased significantly with increases in BPA at concentrations higher than 3.00 mg/L. From this study, *S. hantzschii* was a tolerant isolate that could be used to remove BPA from contaminated waters. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2010 | Bing-zhi, D., Hua-qiang, C., Lin, W., Sheng-ji, X. and Nai-yun, G. | The removal of Bisphenol A by hollow fiber microfiltration membrane | In this study was focused on the effect of various factors on BPA removal efficiency in MF filtration with respect to BPA initial concentration, pH, ionic strength and organic matter. The results showed that MF could remove BPA effectively. A higher removal was obtained at the beginning of the filtration, dropped significantly when pH of solution approached to pKa (9.6-11.3) and the removal efficiency decreased to around 20% when the membrane became saturated due to adsorption. In addition the effect of backwash on removal efficiency recovery was conducted to investigate because of during 50 min of filtration the removal efficiency of BPA decreased from 99% to 27% and found that after backwashing, removal restored to 70%. It indicated that the backwash could recover BPA removal efficiency effectively. |
| 2011 | Zalko, D., Jacques, C., Duplan, H., Bruel, S. and Perdu, E. | Viable skin efficiently absorbs and metabolizes Bisphenol A | The results showed that BPA is readily absorbed and metabolized by the skin. The trans-dermal route is expected to contribute substantially to BPA exposure in human, when direct contact with BPA (free monomer) occurs. Thermal paper can be a direct source for free BPA. Whether the extensive use of thermal paper raises concerns regarding human health is a question that was not under the scope of the present study, and which remains to be investigated. |

**Table 2.3** An overview of some of the past studies on BPA (cont.)

| Date | Authors | Title | Summary of the work |
|---|---|---|---|
| 2012 | Tang, S., Lu, N., Li, J. and Wu, Y. | Removal of Bisphenol A in water using an integrated granular activated carbon preconcentration and dielectric barrier discharge degradation treatment | BPA in water was adsorbed onto a granular activated carbon (GAC), and then the BPA was decomposed and GAC was regenerated simultaneously by dielectric barrier discharge (DBD) plasma. The results showed that increasing pulse voltage, pulse repetitive rate, treatment time and air flow rate could enhance the degradation of BPA. At pulse voltage of 27 kV, about 87% of BPA was removed within 50 min of treatment, while approximately 65, 73, and 82% of BPA could be degraded at pulse voltages of 15, 19, and 23 kV within the same time, respectively. BPA degradation and GAC regeneration could be simultaneously realized by DBD process. |

## 2.9 Policies for BPA Regulation Worldwide

Argument exists regarding what concentrations of BPA are dangerous to humans or wildlife, but it is clear that BPA poses potential risks and several countries have considered regulating it. Most proposed regulation addresses human exposure through food contact materials and packaging, but several nations have assessed the risk of environmental exposure to BPA. Although nearly one-third and one-quarter of global BPA production occurs in the US and the European Union, respectively (ICIS, 2008), BPA released into the environment is not strongly regulated in either location (National Institute of Health, 2008).

### 2.9.1 US Chemical Policy

BPA is one of a burgeoning class of chemicals that do not fit well into the current US chemical regulatory structure. The import of BPA into the US is regulated

under any specific US chemical policy. When a chemical like BPA reaches the environment via effluents, runoff, or other means, it falls under the jurisdiction of the US EPA, which receives its regulatory authority in part from the Clean Water Act and the Toxic Substance Control Act (Flint et al, 2012).

The main objective of the Clean Water Act (CWA), initiated in 1972, was to control the most toxic and high-volume industrial point-source polluters in the nation and the second was to trigger badly needed updates in municipal sewage treatment. When implementing the CWA, the US EPA did not prioritize low-volume or low-toxicity pollutants, although the law allows for such regulation. The wording of the CWA can make adding a chemical to the list of priority pollutants quite cumbersome. For each chemical and type of emitter, this process requires a battery of studies to determine the "best available technology" for chemical removal and to establish effluent standards. It is possible that the CWA could be used to regulate BPA discharged into natural systems, but the law might be more effective if it were revised to streamline regulatory processes (Flint et al, 2012).

The Toxic Substance Control Act of 1976 (TSCA) regulates the introduction of new or already existing chemicals. In 2010, the US EPA released a report acknowledging the large amounts of BPA released into the environment (US Food and Drug Administration, 2010). The report states that while there is uncertainty in the interpretation of low-dose effects of BPA, environmental concentrations of BPA may pose some threat to aquatic organisms. The US Food and Drug Administration has also changed its rating of BPA from "generally considered safe" to a chemical of "some concern," indicating that US regulatory agencies are concerned about potential effects of BPA on humans (Flint et al, 2012).

### 2.9.2 European Union Chemical Policy

The European Union (EU) has a fundamentally different philosophy on chemical regulation based on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) policies of 2007. REACH is often considered to be the EU equivalent to TSCA and is intended to manage chemicals of concern to human and environmental health that are manufactured in or imported into the EU. For substances manufactured or imported in quantities greater than 10,000 kg per year,

like BPA, a more intensive chemical safety assessment must be conducted. To date, BPA has not been considered a "Substance of Very High Concern" (SVHC) under REACH because it has not been shown to be "toxic, carcinogenic, persistent or bioaccumulative". Chemicals can be considered a SVHC if they are proven to be endocrine disruptors, but BPA did not meet REACH criteria for this classification (Flint et al, 2012).

### 2.9.3 Canada Regulation

Canada is currently the only country regulating environmental fates of BPA. In 2008, the Canadian government formally declared BPA to be a hazardous substance and listed it among chemicals considered toxic to human health and the environment. In 2010, Canada increased controls on BPA and in the same year, new regulations were proposed requiring facilities to develop and implement plans limiting environmental releases of BPA. The new regulatory proposal was based on concerns about the persistence, degradation rates, and release volumes of BPA. In a 2009 risk assessment, Canada proposed a limit of 1.75 μg/L for industrial effluents from manufacturers and users of BPA. Thus Canada became the first country to consider regulation of BPA specifically intended to reduce the exposure of wildlife and ecosystems (Flint et al, 2012).

Many countries that have deemed BPA safe at current levels in past risk assessments are reviewing evidence and updating studies, and several are calling for a new risk assessment from the European Commission (vom Saal and Hughes, 2005). Concerned parties point out that the US assessment of BPA is based on research that is now decades old and that the risk assessment conducted under REACH may have involved conflicts of interest associated with industry-funded research (vom Saal and Hughes, 2005). Japan, another major producer of BPA, is currently reviewing the results of a 2005 risk assessment declaring that the chemical is safe at current levels (Japan National Institute of Advanced Industrial Science and Technology, 2007). The US EPA is considering new regulation and additional testing of BPA, with some action expected in 2012 (US Environmental Protection Agency, 2011). Canada remains the only country that has proposed restrictions on BPA that are not directly related to food contact materials.

### 2.9.4 Pollutant Release and Transfer Register

Pollutant Release and Transfer Registers (PRTRs) are systems to collect and disseminate information on environmental releases and transfers of toxic chemicals from industrial and other facilities. They were established in several countries after the 1984 Bhopal Disaster, and the 1992 United Nations Conference on Environment and Development in Rio de Janeiro, which affirmed the "right-to-know" of communities and workers about toxics chemicals and other substances of concern.

A PRTR is a national or regional environmental database or inventory of hazardous chemical substances and other pollutants released to air, water and soil, and transferred off-site for treatment or disposal (OECD, 2013). About 30 countries around the world already report emissions and transfers of chemicals to air, water and soil through their PRTRs and about 14 countries are in the process of designing their own PRTR system such as USA-Toxic Release Inventory (TRI), Australia-National Pollutant Inventory (NPI), Japan (Japan PRTR), etc (PCD, 2011; PRTR:Learn Training and Knowledge Sharing Platform, 2013).

The PRTR is a system that (i) requires businesses handling chemical substances potentially hazardous to the environment to estimate the amounts of chemical substances released and transferred in waste, and to report the data to their local governments, and that (ii) the national government then compiles data submitted and makes the results public. The basic structure of the PRTR system is shown in Fig. 2.4. PRTR aims to establish the common background of risk communication among the government, the business operators and the public by providing data about releases of chemical substances to the environment. These data also help the business operators to manage their own amount of releases. In consequence, it can contribute to reduce the environmental risks from chemical substances (Ministry of the Environment Government of Japan, 2008).

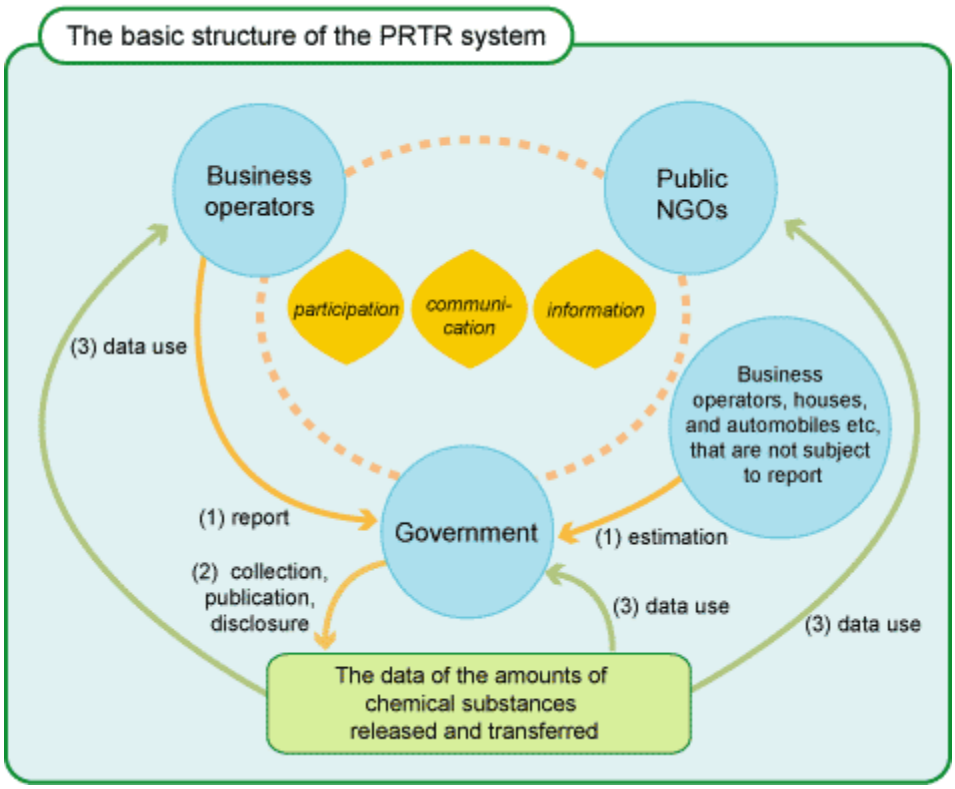



**Figure 2.4** The basic structure of the PRTR system (Ministry of the Environment, Japan, 2008)

# CHAPTER III
# MATERIALS AND METHODS

## 3.1 Site Selection and Sampling

At present, there are total of seven municipal wastewater treatment plants operated by Bangkok Metropolitan Administration (BMA) in and around Bangkok, Thailand. All seven full-scale WWTTPs selected for this study are: Si Phraya (SP), Rattanakosin (RK), Chong Non Si (CN), Din Daeng (DD), Nong Khaem (NK), Thungkru (TK) and Chatu Chak (CC).

Locations of the WWTPs are shown in Fig. 3.1. The basic information, characteristics, and operating conditions of these plants are presented in Table 3.1 and Table 3.2.


**Figure 3.1** The seven selected wastewater treatment plants (WWTPs) Bangkok, Thailand (Banjongproo, 2011)

**Table 3.1** The basic information of seven wastewater treatment plants (WWTPs)

| WWTPs | Service Area ($km^2$) | Pipe length (km) | Population served (persons) | Capacity ($m^3/d$) | Treatment Area ($m^2$) | Outfall point | Treatment Process |
|---|---|---|---|---|---|---|---|
| Si Phraya | 2.7 | 2.3 | 120,000 | 30,000 | 2,800 | Chaophraya River | Contact Stabilization Activated Sludge |
| Rattana-kosin | 4.1 | 16.3 | 76,000 | 40,000 | 6,683 | Klong Banglampoo | Two-Stage Activated Sludge |
| Chong Non Si | 28.5 | 51 | 580,000 | 200,000 | 32,000 | Chaophraya River | Cyclic Activated Sludge System |
| Din daeng | 37 | 64 | 1,080,000 | 350,000 | 27,200 | Bueng Makkasan | Activated Sludge with Nutrients Removal |
| Nong Khaem | 44 | 46 | 520,000 | 157,000 | 86,400 | Klong Ratchaburana | Vertical Loop Reactor Activated Sludge |
| Thungkru | 42 | 26 | 177,000 | 65,000 | 14,400 | Klong Ban Jak | Vertical Loop Reactor Activated Sludge |
| Chatu Chak | 33.4 | 28 | 432,500 | 150,000 | 11,200 | Klong Bang Sue | Cyclic Activated Sludge System |
| **Total** | **191.7** | **233.6** | | **992,000** | **180,683** | | |

Source: Water Quality Management Office, BMA, 2008

**Table 3.2** The wastewater quality parameters of seven treatment plants (annual mean)

| Parameters | | Si Phraya | Rattana kosin | Chong Non Si | Din daeng | Nong Khaem | Thung kru | Chatu Chak |
|---|---|---|---|---|---|---|---|---|
| Design Flow ($m^3$/d) | | 15,551.58 | 22,439.83 | 163,093.87 | 189,056.92 | 128,460.08 | 58,627.50 | 145,461.33 |
| BOD (mg/L) | Inf | 53.85 | 54.72 | 39.12 | 36.57 | 31.48 | 24.51 | 32.91 |
| | Eff | 5.81 | 8.91 | 5.57 | 4.18 | 6.05 | 3.70 | 4.18 |
| COD (mg/L) | Inf | 106.95 | 102.32 | 76.71 | 83.17 | - | 66.78 | 76.64 |
| | Eff | 19.08 | 37.32 | 22.24 | 19.26 | - | - | 20.77 |
| SS (mg/L) | Inf | 107.24 | 51.17 | 52.39 | 43.48 | 64.52 | 49.37 | 61.84 |
| | Eff | 6.81 | 16.92 | 7.87 | 11.64 | 9.50 | 7.09 | 3.90 |
| T – P (mg/L) | Inf | 1.15 | - | 1.94 | 1.54 | 1.24 | 1.36 | 2.55 |
| | Eff | 0.96 | - | 1.11 | 1.06 | 0.40 | 0.57 | 1.04 |
| TKN (mg/L) | Inf | 9.43 | 8.61 | 10.63 | - | 9.82 | 9.42 | 14.42 |
| | Eff | 3.26 | 2.92 | 2.26 | - | 2.66 | 1.45 | 3.27 |
| T – N (mg/L) | Inf | 9.92 | 8.69 | 11.10 | 15.12 | 10.68 | 9.45 | 13.45 |
| | Eff | 8.68 | 6.32 | 8.25 | 6.44 | 6.40 | 5.46 | 7.90 |
| pH | Inf | 7.04 | 6.57 | 7.43 | 7.24 | 6.92 | 7.39 | 7.28 |
| | Eff | 7.22 | 6.16 | 7.45 | 7.19 | 7.36 | 7.45 | 7.35 |
| DO (mg/L) | Eff | 3.91 | 5.48 | 6.29 | 6.84 | 5.75 | 7.11 | 7.16 |

Note: Inf. = Influents, Eff. = Effluents, BOD = biochemical oxygen demand, COD = chemical oxygen demand SS = suspended solids, T-P = total phosphorus, TKN = total kjeldahl nitrogen, T-N = total nitrogen, DO = dissolved oxygen, - = no data

Source: Average data from Water Quality Management Office, BMA, 2012

**Sampling Points in WWTPs**

The schematics diagrams of these treatment plants and the locations of the sampling points - ① : influent, ② : effluent, are shown in Fig. 3.2.

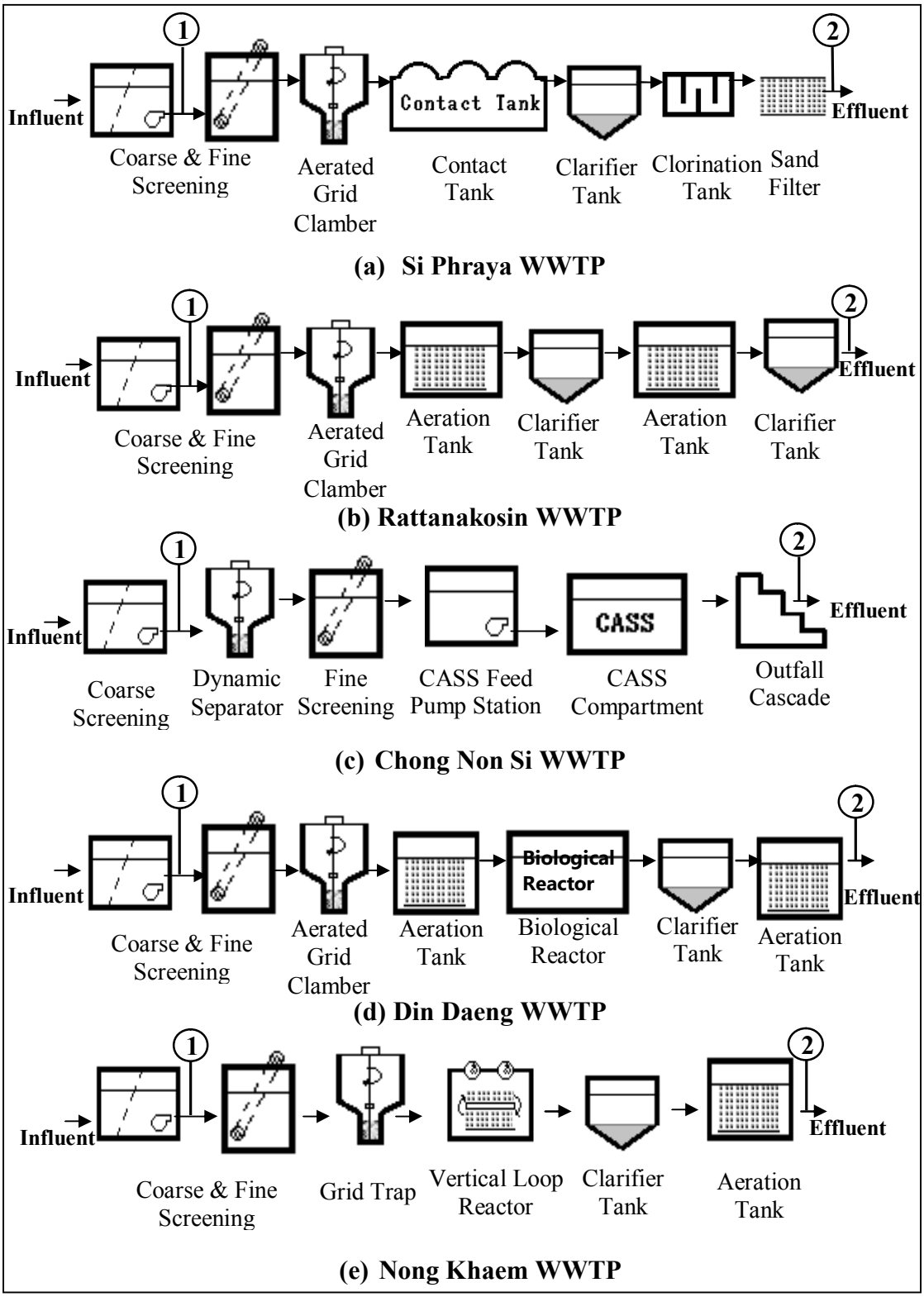



**Figure 3.2** Schematic diagrams of all WWTPs and the sampling points

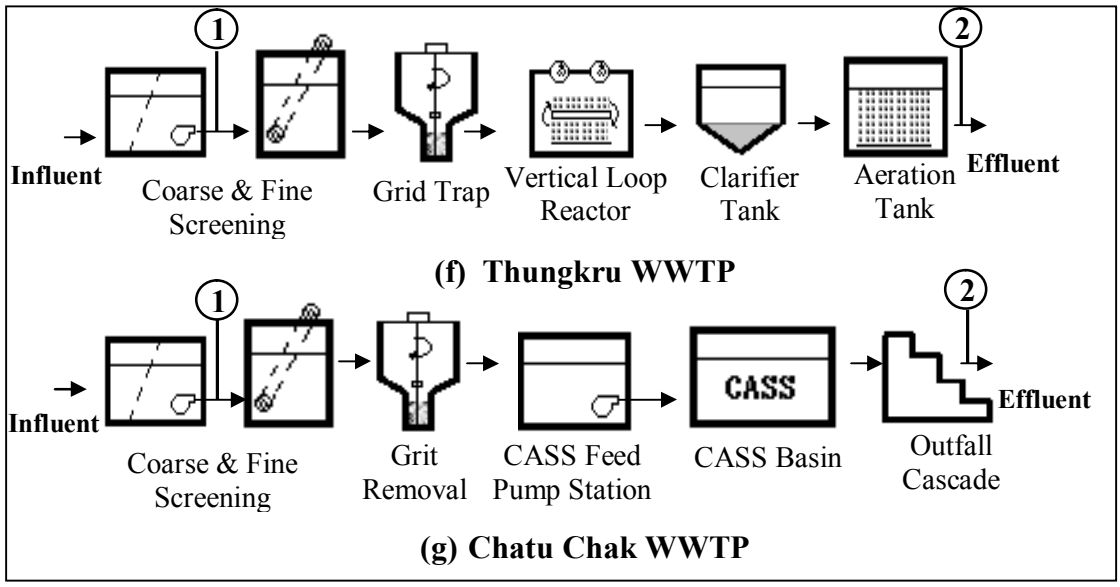



**Figure 3.2** Schematic diagrams of all WWTPs and the sampling points (cont.)

## 3.2 Sampling plan

Grab samples were collected in four separate events (April 2013, October 2013, December 2013, and February 2014). For BPA measurement, amber glass bottles (500 ml) were used for sampling that were pre-rinsed several times in the laboratory with DI water, methanol and Milli-Q water, and were rinsed again with ambient water on site. Plastic bottles (1.5 L) were used for measuring other parameters. Samples were immediately placed on ice and brought to the laboratory within 8 h, and stored in a cold room (4 $^{o}$C) until analysis. Analyses were carried out and completed within a week after the sampling. The overall sampling plan is shown in Table 3.3.

## 3.3 Experimental Analyses

Experimental analysis was consisting of two parts:

1) Solid phase extraction (SPE) of water and wastewater samples
2) Determination of BPA in extracted samples by HPLC

**Table 3.3** Sampling Plan

| Sampling Events | Date | WWTPs | Sampling Location | No. of Samples | No. of Replication | No. of Analysis |
|---|---|---|---|---|---|---|
| April 2013 | 23 – 26 April, 2013 | SP, RK, CN, DD, NK, TK and CC | Influent and Effluent | 42 | 3 | 126 |
| October 2013 | 8 – 9 October, 2013 | RK, CN, DD, NK, and TK | Influent and Effluent | 30 | 3 | 90 |
| December 2013 | 19 – 20 December, 2013 | RK, CN, DD, NK, and TK | Influent and Effluent | 30 | 3 | 90 |
| February 2014 | 26 – 27 February, 2014 | RK, CN, DD, NK, and TK | Influent and Effluent | 30 | 3 | 90 |
| **Total** | | | | **132** | **12** | **396** |

### 3.3.1 Solid phase extraction (SPE)

Solid phase extraction (SPE) is a process used to separate compounds dissolved or suspended in a liquid. SPE was used to concentrate and purify samples for analysis. SPE provided the sample clean-up, recovery, and concentration necessary for accurate quantitative analysis. This technique can be very effective, even when the solutes are present at extremely dilute concentration.

**Samples Preparation**

Samples (500 ml) were first filtered with glass microfiber filter papers (Whatman, GF/B, 1.0 μm, Adelaide Co., Thailand). Solid-phase extraction (SPE) was done by using vacuum manifolds coupled with 6 $cm^3$, 500 mg, OASIS HLB cartridges (Waters-Millford, MA, USA) to concentrate the samples. The cartridges were conditioned with 10 mL of acetone, 10 mL of methanol, and 10 mL of Mili-Q water (+1% formic acid) in sequence. The flow rate of the equipment was maintained at

approximately 3 mL/min. The cartridge washing was done twice with 6 mL of Mili-Q water at 5 min interval. Subsequently, the cartridges were allowed to dry under vacuum suction for 45 min. To extract BPA, the cartridges were rinsed with 2 mL of methanol (+1% formic acid) three time at 5 min intervals. A total of 6 ml of eluted fractions were collected in brown glass tubes and then evaporated under nitrogen gas. The dried residues were dissolved in 0.5 mL of methanol and transferred to amber vials for HPLC analysis. Concentrated samples (25 µL) from the above procedure were injected into the HPLC for BPA measurement (Hu, Chen, Tao, and Kekred, 2007). The steps of the whole process are shown in Fig 3.3.

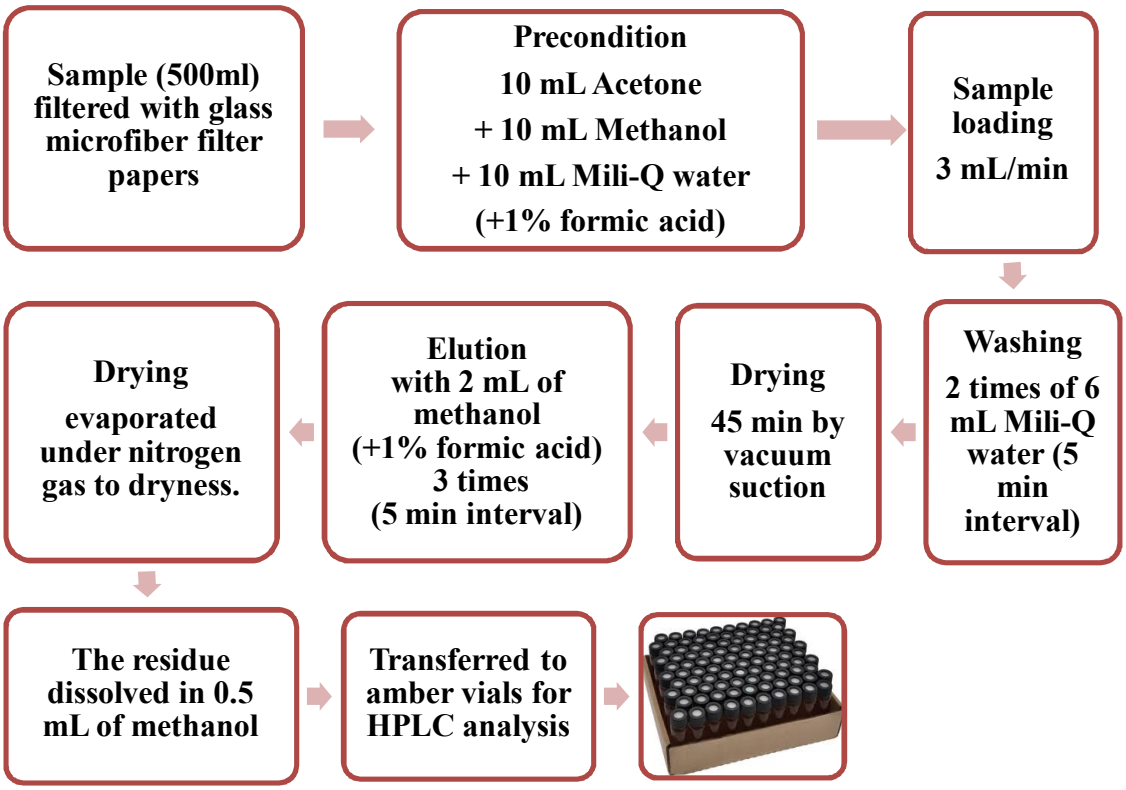



**Figure 3.3** Samples Preparation for BPA analysis

### 3.3.2 High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) is an analytical technique in which a liquid mobile phase transports a sample through a column containing a liquid in stationary phase. The interaction of the sample with the stationary phase selectively retains individual compounds and permits separation of

sample components. Detection of the separated sample compounds is achieved mainly though the use of absorbance detectors for organic compounds and through conductivity and electrochemical detectors for metal and inorganic components. HPLC has maximum efficiency at low flow rate because of typically slow diffusion rates between liquid phases.

Bisphenol A ($C_{15}H_{16}O_2$) was used as internal standard. The standard was dissolved in ethanol and diluted to final stock solution of 50 mg/L. Stock solution was prepared just before use, but when necessary was kept in the air-tight amber glass bottle and stored in a freezer.

In this study, all wastewater samples were analyzed using HPLC performed on a Shimadzu model LC-20AB equipped with a Shimadzu model SPD-20A UV/Vis detector, a Shimadzu model RF-20A fluorescence detector, and a C18 reversed-phase column (Luna 5µ, 250 mm × 4.6 mm, phenomenex, U.S.A). The Shimadzu model equipment (Shimadzu Corporation, Japan) consist of a communication bus module, a column oven and an auto sampler. The column oven temperature was held at 30$^{o}$C, fluorescence detection was carried out using 228 nm as the excitation and 313 nm as the emission wavelengths. UV/VIS detection was carried out using 221 nm. Details of the analytical operating conditions for HPLC are summarized in Table 3.4.

The mobile phase which is a solvent is contained in a bottle. A high pressure pump is needed to deliver the mobile phase at a certain flow rate apparently in milliliters per minute. Also, an injector known as auto-sampler passes samples into a constant moving mobile phase stream that moves the sample into the HPLC column. The stationary phase is a chromatographic material packed in a column and it is needed to effectively carry out the sample separation. Furthermore, a detector helps to visualize the separated sample bands eluting the HPLC column and the mobile phase leaves the detector which is collected by waste system.

**Table 3.4** Analytical operating conditions for HPLC

| Parameters | Operating Condition | |
|---|---|---|
| | **UV/Vis detector** | **Fluorescence detector** |
| LC Column | C18 column (Luna 5µ, 250 mm × 4.6 mm, phenomenex, U.S.A) | C18 column (Luna 5µ, 250 mm × 4.6 mm, phenomenex, U.S.A) |
| Mobile phase | A: Acetonitrile 60%<br>B: Water 40% | A: Acetonitrile 60%<br>B: Water 40% |
| Solvent reservoir | Isocratic | Isocratic |
| Wavelength | 221 nm | 228 nm (excitation wavelength)<br>313 nm (emission wavelength) |
| Flow (ml/min) | 1.0 | 1.0 |
| Run time (min) | 7 | 7 |
| Injection volume | 25 µl | 25 µl |
| Column temperature | 30 $^{o}$C | 30 $^{o}$C |


**Figure 3.4** High Performance Liquid Chromatography (HPLC) equipped with UV/Vis detector and fluorescence detector, Shimizu, Japan

However, the detector is connected to a data collection system that stores the electrical signal that produces the chromatogram on its screen. The end results are seen as chromatogram appearing as peaks of various heights depending on the concentration of the sample constituents (Fig. 3.5) (Waters Corporation, 2010; as cited in Gilala, 2010).

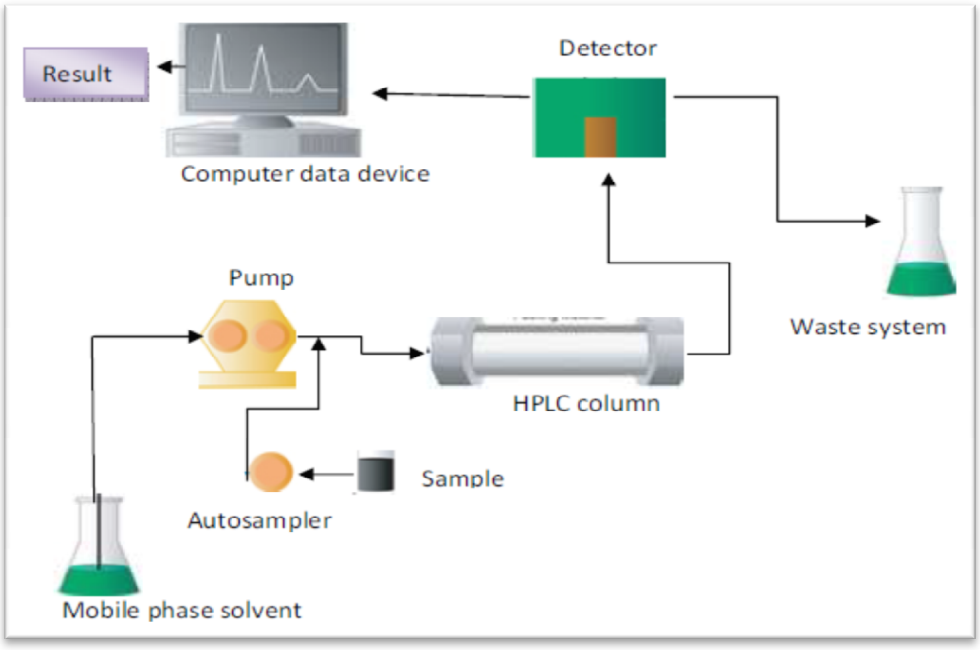



**Figure 3.5** Operation of HPLC system copyright by Waters Corporation 2010 (Gilala, 2010)

## 3.4 BPA Removal Efficiency Calculation

BPA removal efficiency (R.E.) is the ability of WWTPs to reduce the concentration of BPA in wastewater though the treatment process. The % R.E. was calculated as following;

$$\text{BPA removal efficiency (\%)} = \frac{(C_i - C_f)}{C_i} \text{x } 100$$

Where; $C_i$ is the initial BPA concentration (ng/L)

$C_f$ is the final BPA concentration (ng/L)

## 3.5 BPA Analysis Method

Wastewater samples were collected from influents and effluents of the selected wastewater treatment plants (WWTPs) during the four sampling events (April 2013, October 2013, December2013, and February 2014). Conventional parameter measurement and sample preparation were carried out in Environmental Engineering Laboratory, Faculty of Engineering, Mahidol University after each sampling event.

In April 2013, all samples (500 ml) were first transferred to micro-centrifuge tubes and centrifuged at a speed of 10,000 rpm for 5 min to eliminate suspended particulates. The supernatants were filtered with syringe filter (cellulose acetate, pore size 0.2 μm, diameter 13 mm, Chromtech, U.S.A.) and then transferred to amber vials for HPLC analysis. The HPLC (1100, Agilent, USA) equipped with UV/Vis detector were used at Tropical Medicine Laboratory, Faculty of Tropical Medicine, Mahidol University. The steps of the whole process are shown in Fig 3.6.

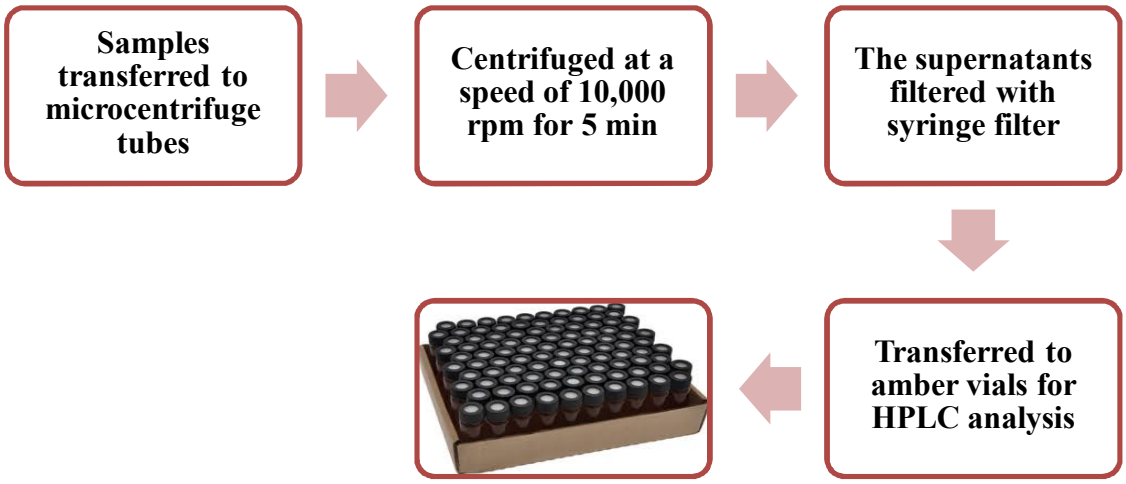



**Figure 3.6:** The former steps of the whole process of BPA analysis

The calibration curve was obtained from the standard BPA solution concentration 2, 5, 10, 15, 20, 25, 30, 35, and 40 mg/L, as shown in Fig 3.7. The BPA concentrations in all samples were to be obtained by using the regression equation of the calibration curve (y=72.279x). However, BPA was not detected in any sample during this sampling. This could be due to the reason that the concentrations in the samples were lower than the lowest detection limit (LDL) of the equipment (2 mg/L).

Therefore, it appeared that BPA levels in all the WWTPs' influents and effluents were lower than 2 mg/L. Another possible reason of no detection could have been due to the fact that solid phase extraction (SPE) was not carried out to concentrate the samples before the HPLC analyses. Moreover, HPLC/UV-VIS technique might not be appropriate for this study as the sensitivity of UV detection is lower than the fluorescence detection.

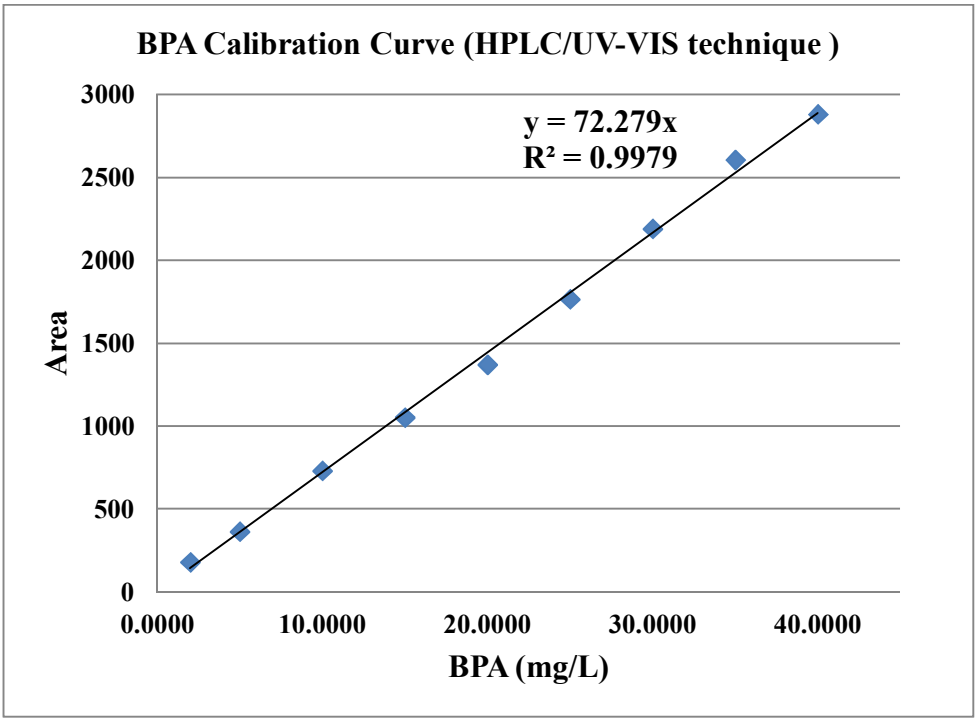



**Figure 3.7** BPA Calibration Curve (HPLC/UV-VIS technique)

Subsequently, alternative methods of BPA analysis were tried out at the laboratory facilities of Environmental Research and Training Centre (ERTC), Environmental Quality Promotion Department, Ministry of Natural Resources and Environment, by using the HPLC equipped with UV/Vis detector and fluorescence detector (Shimadzu Corporation, Japan).

On 20 August 2013, BPA in the standard solutions at 6 different concentrations (0.01, 0.05, 0.1, 0.5, 1.0, and 2.0 mg/L) could be detected by this equipment. Hence, the lowest detection limit (LDL) of the equipment was found to be 0.01 mg/L (10 ppb). Additionally, another technique was also tried following the EPA

method 528 by doing SPE with Strata Styrene-Divinylbenzene Polymer (SDB-L) cartridges prior to HPLC analysis of the standard solutions with the 6 above mentioned concentrations. However, this method did not give results. It might have been due to some error during the SPE steps.

In September, 2013, the SPE method of Hu et al. (2007) was applied to use for samples preparation (Fig. 3.3). The Oasis HLB (lipophilic divinylbenzene with hydrophilic N-vinylpyrrolidone polymer) cartridges could be used for the extraction of BPA from wastewater samples. Following this SPE method, the BPA in extracted samples are 1000 times higher than the actual concentration.

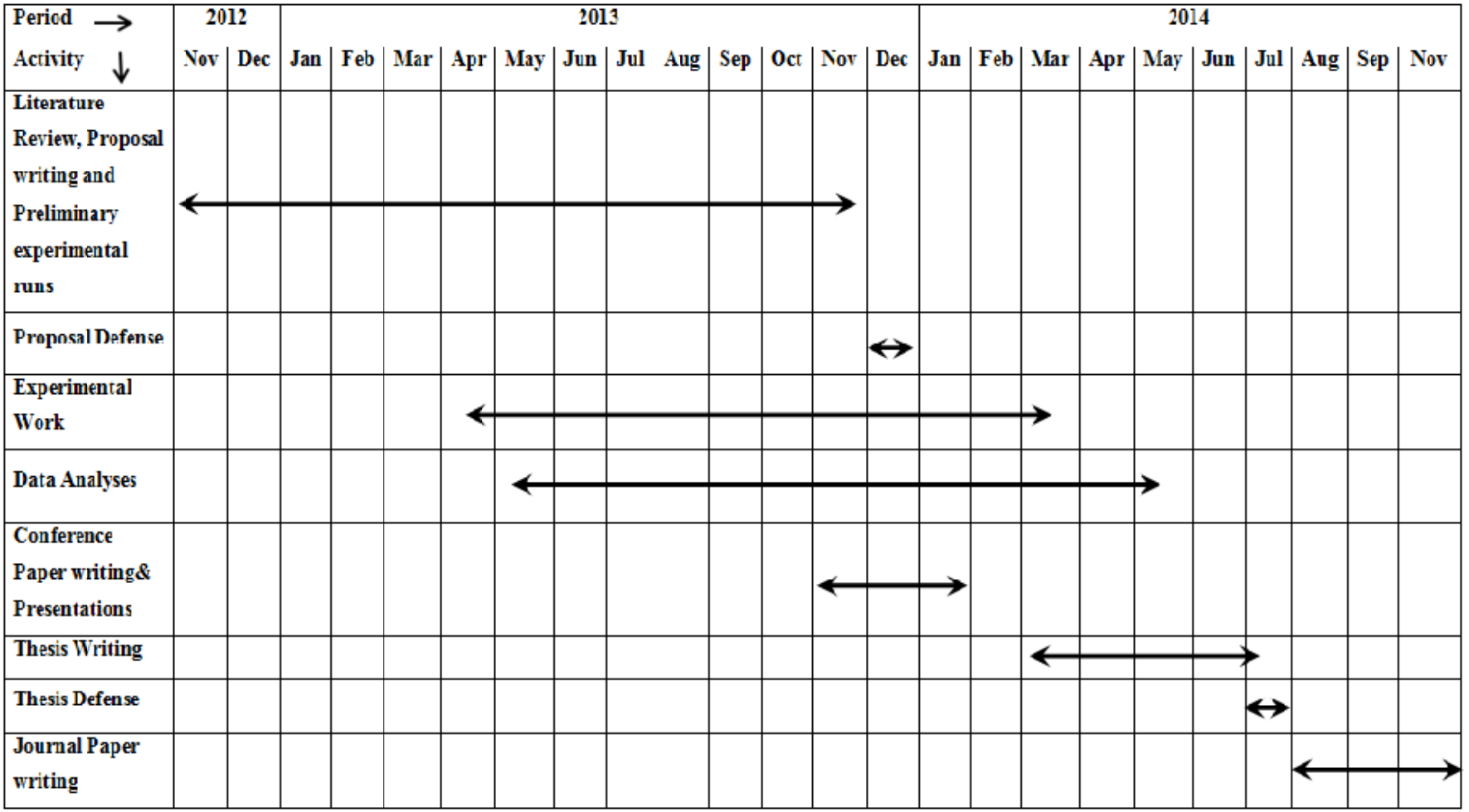
The prepared samples during the last three sampling events (October 2013, December2013, and February 2014) were brought to Environmental Research and Training Centre (ERTC), Environmental Quality Promotion Department, Ministry of Natural Resources and Environment for HPLC analyses.

## 3.6 Investigations on the Environmental Policy and Regulations for BPA in Aquatic Environments in Thailand

Investigations on the environmental policy and regulations for BPA in aquatic environments in Thailand were carried out through search on the websites of the various ministries e.g. Ministry of Public Health. Evaluation of the level of awareness and concern about the risk associated with BPA in the environment was also done through research in Thai media and news. Interestingly, many people living in Thailand especially the mothers of newly born babies are quite aware about the hazard of BPA leaching from the plastic containers and baby milk bottles. Currently, the only regulation found about BPA in Thailand was for its usage in food packaging plastic materials and food containers.

The overall study plan is shown in Table 3.5.

**Table 3.5** Study Plan



# CHAPTER IV
# RESULT AND DISCUSSIONS

## 4.1 Sampling Events for Detection of Bisphenol A and Conventional Parameters Measurements

Overall four sampling events were carried out between April 2013 and February 2014 to collect samples from the influents and the effluents of the selected wastewater treatment plants (WWTPs) in Bangkok region operated under Bangkok Metropolitan Administration (BMA) (Figure 4.1). The results of all sampling events are presented in the following sections.

### 4.1.1 First Sampling Event in April 2013

The first sampling of influents and effluents from the seven wastewater treatment plants (WWTPs) : Si Phraya (SP), Rattanakosin (RK), Chong Non Si (CN), Din Daeng (DD), Nong Khaem (NK), Thungkru (TK) and Chatu Chak (CC), was carried out during 23-26 April 2013. Subsequently, all samples were prepared for the analyses. Some conventional parameters (temperature, DO, TS, TDS, TSS, COD and $BOD_5$) were determined at the Environmental Engineering Laboratory of Faculty of Engineering. Measurements of Bisphenol A (BPA) concentrations in the samples were carried out at the laboratory of Faculty of Tropical Medicine, Mahidol University by using HPLC/UV-VIS (1100, Agilent, USA).

**Conventional Parameters in WWTPs in Bangkok in April 2013**

The concentrations of the six conventional parameters (DO, TS, TDS, TSS, COD and $BOD_5$) in the influents and the effluents of the seven WWTPs are shown in the Table 4.1 and Figures 4.2-4.7.

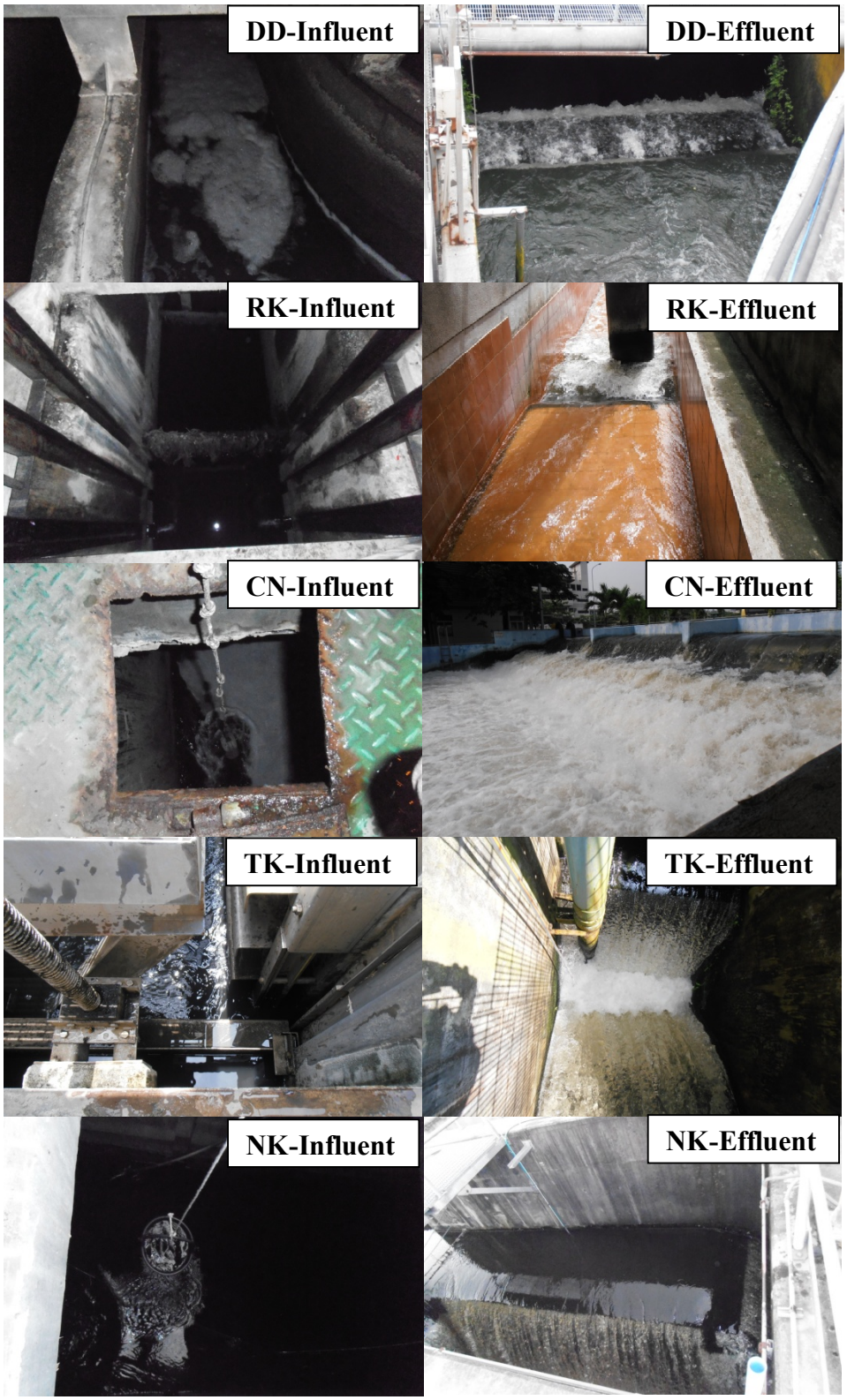



**Fig 4.1** Sampling points in seven WWTPs, Bangkok, Thailand

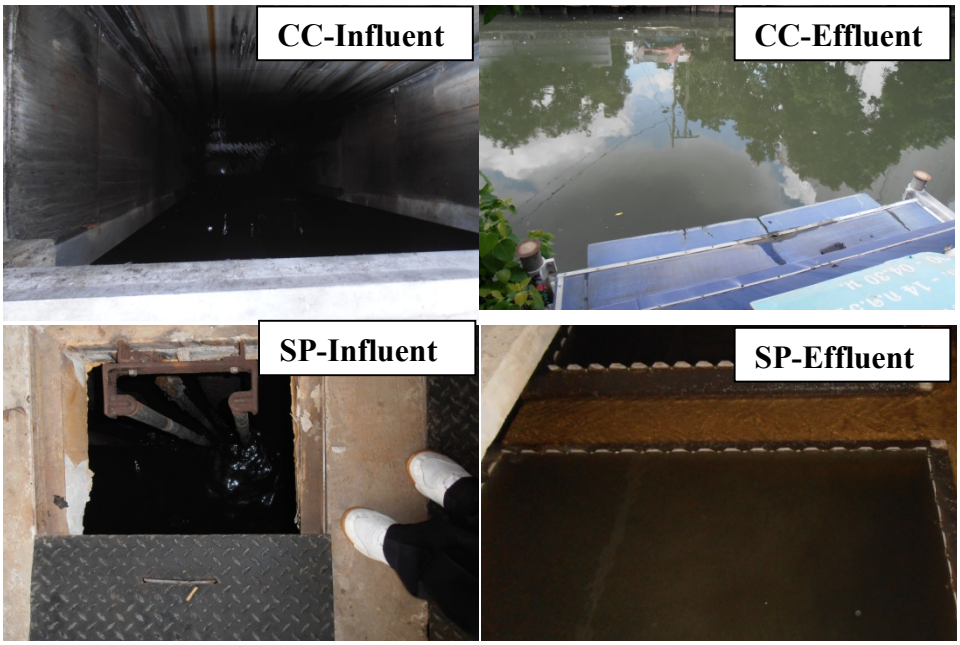



**Fig 4.1** Sampling points in seven WWTPs, Bangkok, Thailand (cont.)

Influent TS, TSS and TDS concentrations of the seven WWTPs ranged between 336.22 mg/L (NK) and 1,592.44 mg/L (CN); 8.13 mg/L (CN) and 116.93 mg/L (RK); and 340.27 mg/L (NK) and 1,468.53 mg/L (CN), respectively. All seven plants had higher dissolved solids (TDS) than suspend solids (TSS) in the influents. Influent DO levels of the all the plants had similar range varying between 1.00 mg/L (NK) and 4.40 mg/L (CN) with an average of about 3.07 mg/L. Influent $BOD_5$ and COD concentrations ranged between 29.1 mg/L (CN) and 73.2 mg/L (RK), and 54.3 mg/L (NK) and 126.70 mg/L (DD), respectively. RK had the highest influent concentrations of TSS and $BOD_5$ and the second highest levels of TS (1,543.11 mg/L) and TDS (1,052.53 mg/L). However, the difference between TS and TDS concentrations of RK and CN (having highest levels) was not significant. RK had second lowest DO levels (2.60 mg/L). Based on the influents concentrations of the six parameters in the seven WWTPs, it appeared that RK's influent quality was poorer than the other plants.

Effluent TS, TSS and TDS concentrations of the seven WWTPs ranged between 276.44 mg/L (NK) and 1,261.56 mg/L (RK); 3.87 mg/L (CN) and 15.60 mg/L (RK); and 318.13 mg/L (NK) and 1,066.53 mg/L (CN), respectively. Effluent DO levels of the all the plants also had similar range varying between 2.10 mg/L (SP)

and 7.24 mg/L (TK) with an average of about 5.19 mg/L. Effluent $BOD_5$ and COD concentrations ranged between 4.5 mg/L (DD and CC) and 8.1 mg/L (RK), and 18.10

**Table 4.1** Concentration of conventional parameters and BPA levels in seven WWTPs in Bangkok region in April 2013

| WWTPs | Samp. Point | Temp ($^oC$) | DO (mg/L) | TS (mg/L) | TDS (mg/L) | TSS (mg/L) | $BOD_5$ (mg/L) | COD (mg/L) | BPA (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | Inf. | 30.9 | 3.8 | 581.33 | 438.93 | 25.20 | 42.2 | 126.70 | ND |
| **DD** | Eff. | 31.0 | 6.1 | 472.89 | 412.27 | 6.00 | 4.5 | 81.45 | ND |
| | RE (%) | - | - | 18.65 | 6.07 | 76.19 | 89.3 | 35.71 | - |
| | Inf. | 30.8 | 2.6 | 1543.11 | 1314.53 | 116.93 | 73.2 | 108.60 | ND |
| **RK** | Eff. | 30.9 | 6.2 | 1261.56 | 1052.53 | 15.60 | 8.1 | 72.40 | ND |
| | RE (%) | - | - | 18.25 | 19.93 | 86.66 | 88.9 | 33.33 | - |
| | Inf. | 30.7 | 4.4 | 1592.44 | 1468.53 | 8.13 | 29.1 | 72.40 | ND |
| **CN** | Eff. | 30.7 | 5.6 | 1173.11 | 1066.53 | 3.87 | 5.5 | 24.13 | ND |
| | RE (%) | - | - | 26.33 | 27.37 | 52.40 | 81.1 | 66.67 | - |
| | Inf. | 30.2 | 3.6 | 998.00 | 901.20 | 23.60 | 30.2 | 90.50 | ND |
| **TK** | Eff. | 29.6 | 7.2 | 914.89 | 720.27 | 14.27 | 4.9 | 36.20 | ND |
| | RE (%) | - | - | 8.33 | 20.08 | 39.53 | 83.8 | 60.00 | - |
| | Inf. | 31.1 | 1.0 | 336.22 | 340.27 | 18.00 | 42.0 | 54.30 | ND |
| **NK** | Eff. | 31.0 | 3.0 | 276.44 | 318.13 | 8.67 | 6.0 | 18.10 | ND |
| | RE (%) | - | - | 17.78 | 6.51 | 51.83 | 85.7 | 66.67 | - |
| | Inf. | 24.5 | 3.1 | 527.78 | 477.33 | 27.07 | 40.2 | 120.66 | ND |
| **CC** | Eff. | 26.8 | 6.1 | 489.78 | 444.40 | 10.53 | 4.5 | 36.20 | ND |
| | RE (%) | - | - | 7.20 | 6.90 | 61.10 | 88.8 | 70.00 | - |
| | Inf. | 32.1 | 3.0 | 1017.11 | 866.80 | 18.67 | 51.0 | 72.40 | ND |
| **SP** | Eff. | 30.8 | 2.1 | 978.00 | 847.87 | 7.47 | 5.0 | 54.30 | ND |
| | RE (%) | - | - | 3.85 | 2.18 | 59.99 | 90.2 | 25.00 | - |

Note: Samp.point = Sampling Point, Inf. = Influents, Eff. = Effluents, Temp = Temperature, DO = dissolved oxygen, $BOD_5$ = 5 day biochemical oxygen demand, COD = chemical oxygen demand, TS = total solids, TDS = total dissolved solids, TSS = total suspended solids, TK = Thungkru, NK= Nong Khaem, RK = Rattanakosin, SP = Si Phraya, DD = Din Daeng, CC = Chatuchak, CN = Chong Non Si, Inf. = influent, Eff. = effluent, ND = not detected, RE = Removal Efficiency.

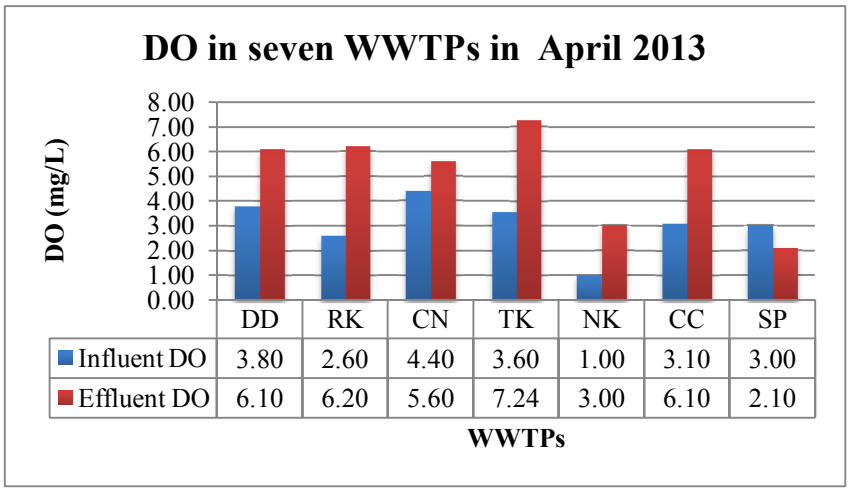



**Fig. 4.2** Average DO concentrations in seven WWTPs in Bangkok in April 2013

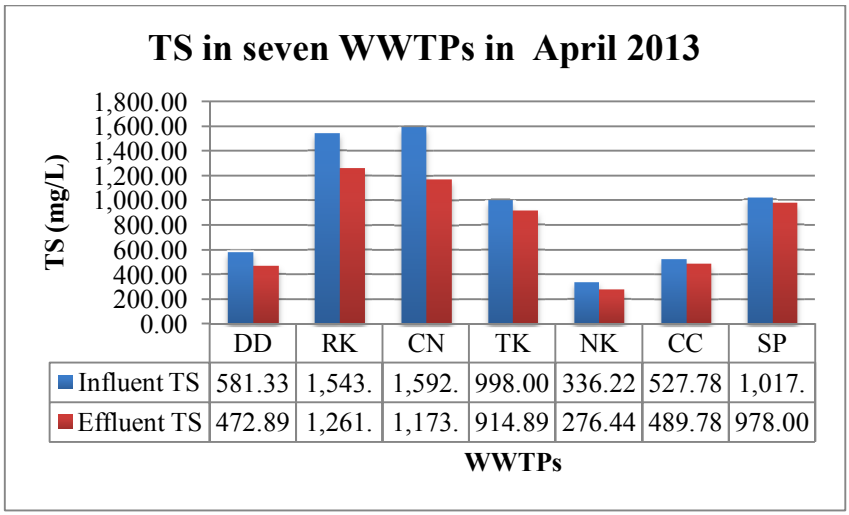



**Fig. 4.3** Average TS concentrations in seven WWTPs in Bangkok in April 2013

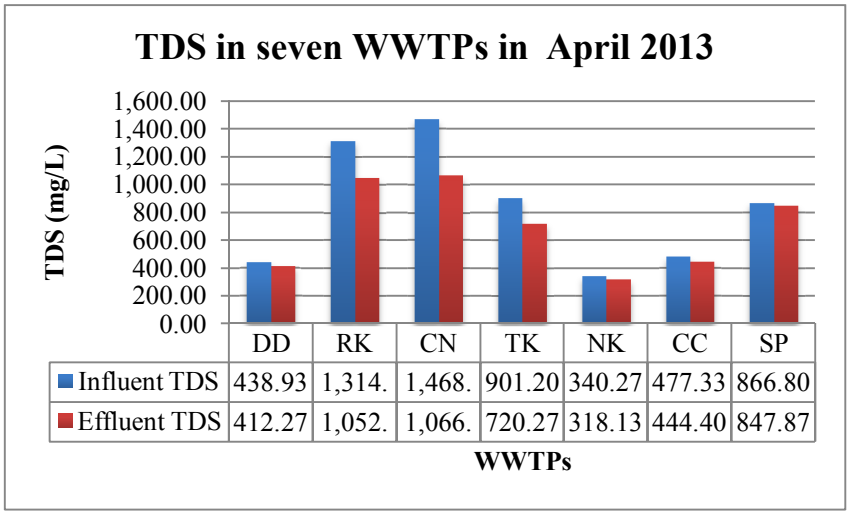



**Fig. 4.4** Average TDS concentrations in seven WWTPs in Bangkok in April, 2013

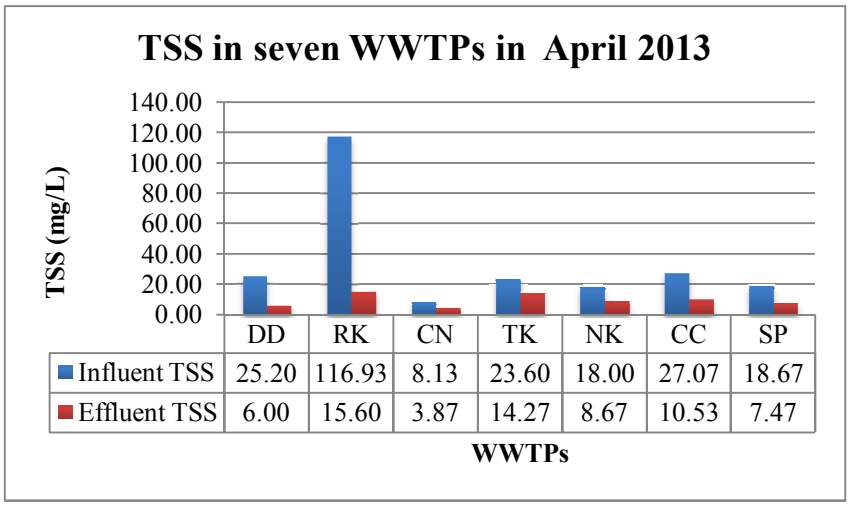



**Fig. 4.5** Average TSS concentrations in seven WWTPs in Bangkok in April 2013

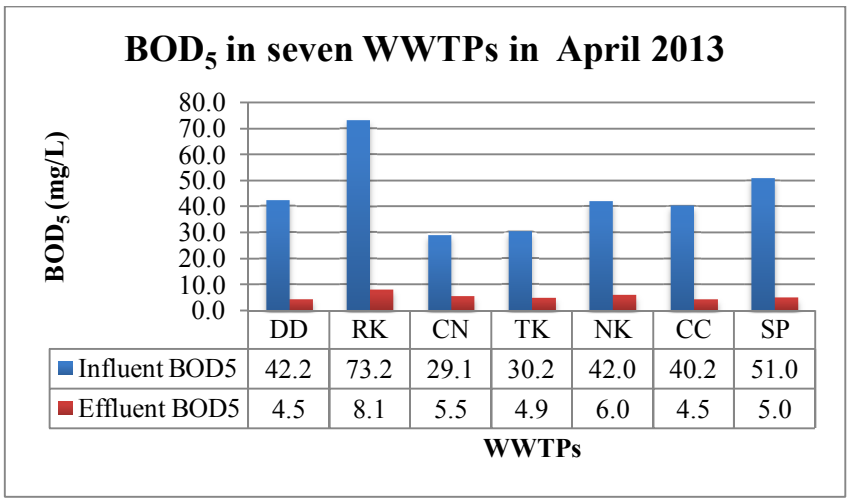



**Fig. 4.6** Average $BOD_5$ concentrations in seven WWTPs in Bangkok in April 2013

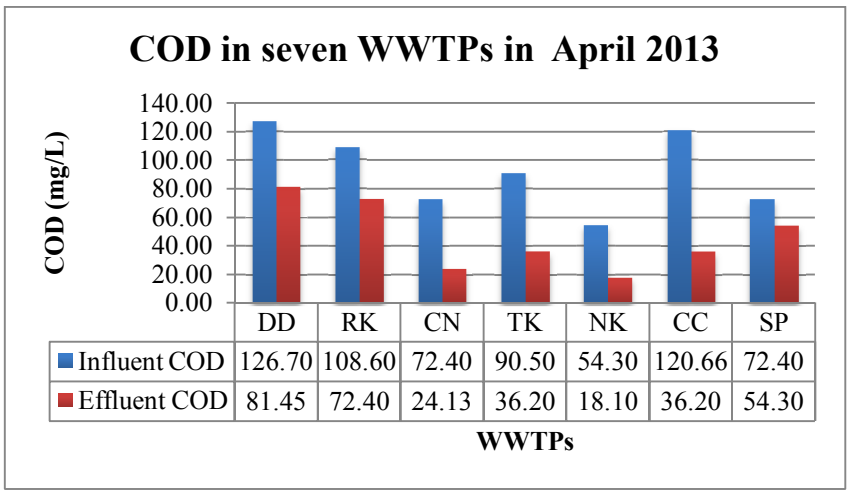



**Fig. 4.7** Average COD concentrations in seven WWTPs in Bangkok in April 2013

mg/L (NK) and 81.45 mg/L (DD), respectively. Thus, effluent $BOD_5$ concentrations were low (≤ 8 mg/L) as compared to COD levels.

Similar to the influents, RK also had the highest effluent concentrations of TSS and $BOD_5$, and the second highest levels of TDS. It also had the second highest levels of COD. However, the difference between TDS and COD concentrations of RK and DD (having highest levels) was not significant. The lowest levels of TDS, TS, and COD in the effluents were found at NK. CN had the lowest concentrations of TSS. Based on the effluents concentrations of the six parameters in the seven plants, it appeared that RK's effluent quality was poorer than the other plants and the best effluent quality was appeared at NK. All of the measured conventional parameters in the effluents were within the domestic wastewater effluents' standards of Thailand.

Removal efficiencies of the seven WWTPs ranged between 3.8% and 26.3% for TS; 39.5% and 86.7% for TSS; 2.2% and 27.4% for TDS; 81.1% and 90.2% for $BOD_5$; and 25.0% and 70.0% for COD (Figure 4.8-4.9).

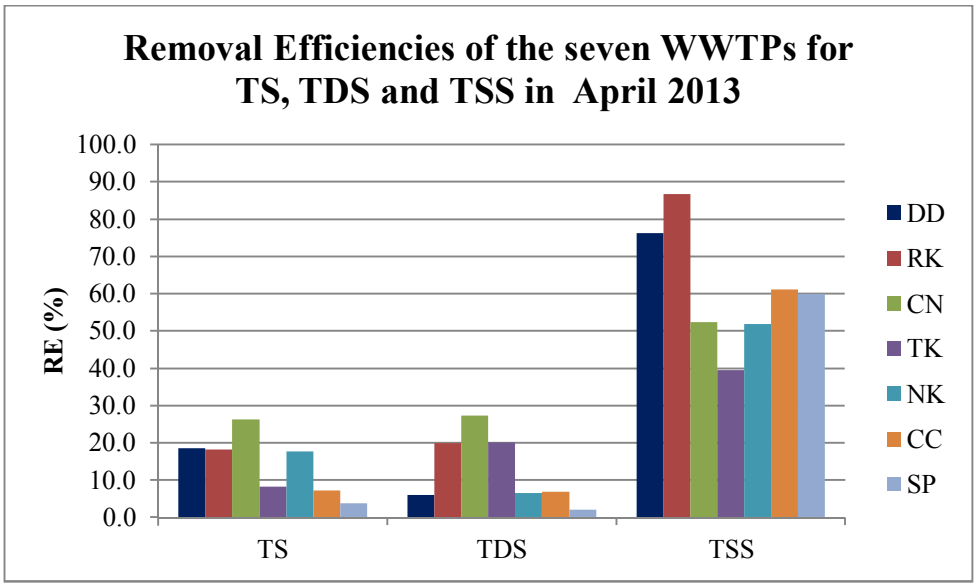



**Fig 4.8** Removal Efficiencies of the seven WWTPs for TS, TDS, TSS in April 2013

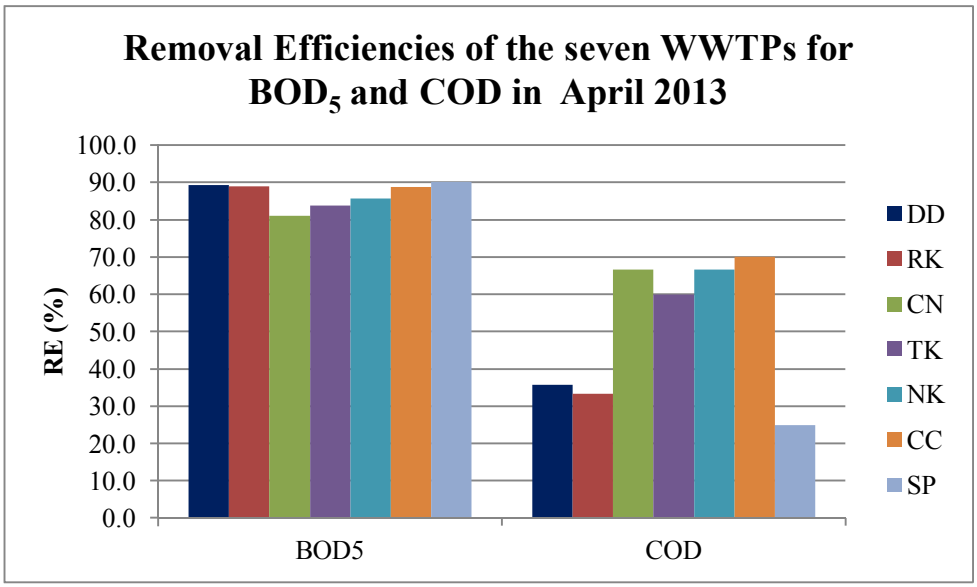



**Fig 4.9** Removal Efficiencies of the seven WWTPs for$BOD_5$ and COD in April 2013

SP had the highest $BOD_5$ removal efficiency (90.2%) while RK, CC, and CN were also very near, having about 89% $BOD_5$ removal. Even the lowest $BOD_5$ removal efficiency (TK) was more than 80%. Interestingly, even though RK's influent and effluent qualities were the worst (based on the measured parameters' concentrations), it had the highest removal efficiency for TSS (86.7%) and the third highest removal efficiency for $BOD_5$ (88.9%). Efficiency of all the seven WWTPs for TDS removal was lower than 30% (and therefore TS removal efficiency was also low).

**Bisphenol A Concentrations in Seven WWTPs in Bangkok in April 2013**

Investigation on BPA concentrations in the influents and the effluents samples was carried out by using High Performance Liquid Chromatography (HPLC) equipped with UV detector (wavelength 221 nm). Method validation was performed by obtaining calibration curve for the prepared standards with the concentrations in the range between 2 and 40 mg/L. The correlation coefficient ($R^2$) was found to be 0.9979 (Figure 4.10). However, BPA was not detected in any sample during this sampling. This could be due to the reason that the concentrations in the samples were lower than the lowest detection limit (LDL) of the equipment (2 mg/L). Therefore, it

appeared that BPA levels in all the WWTPs' influents and effluents were lower than 2 mg/L. Another possible reason of no detection could have been due to the fact that solid phase extraction (SPE) was not carried out to concentrate the samples before the HPLC analyses. Moreover, HPLC/UV-VIS technique might not be appropriate for this study as the sensitivity of UV detection is lower than the fluorescence detection.

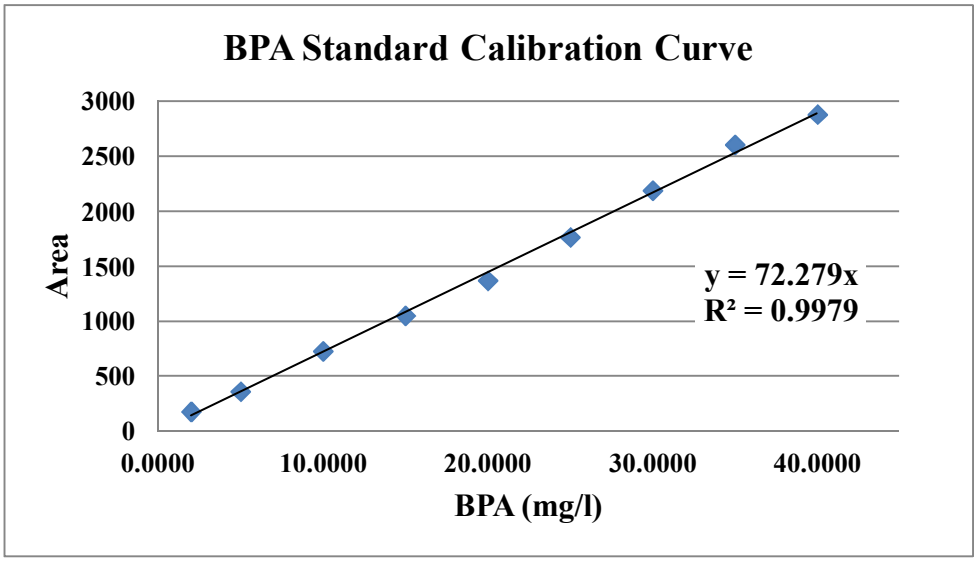



**Fig. 4.10** BPA standard calibration curve by using HPLC/UV-VIS technique

Subsequently, an alternative method of BPA determination was employed during the three more sampling events between October 2013 and February 2014, by doing the solid phase extraction (SPE) and using HPLC equipped with fluorescence detector.

After the first sampling event (April 2013), only five out of seven full-scale WWTTPs in Bangkok region were selected for the further investigations: Rattanakosin (RK), Chong Non Si (CN), Din Daeng (DD), Nong Khaem (NK), and Thungkru (TK). Wastewater samples were collected from influents and effluents of these plants during the three more sampling events during October and December 2013, and February 2014. The results of these three samplings events are presented in the following sections.

### 4.1.2 Second Sampling Event in October 2013

The influents and effluents samples from the five selected WWTPs were analyzed by using HPLC equipped with UV/Vis detector and fluorescence detector after solid phase extraction (SPE) to determine BPA concentrations and removal efficiency of the WWTPs.

**Concentrations of the Conventional Parameters in five WWTPs in Bangkok region in October 2013**

The concentrations of the conventional parameters in the influents and effluents of the five WWTPs in Bangkok during October 2013 sampling event are summarized in Table 4.2 and the Figures 4.11-4.16**.**

Influent TS, TSS and TDS concentrations of the five WWTPs ranged between 340.44 mg/L (RK) and 511.78 mg/L (NK); 5.07 mg/L (TK) and 53.87 mg/L (NK); and 308.53 mg/L (RK) and 484.40 mg/L (NK), respectively. Unlike April 2013 sampling event, NK had the highest TS and TDS levels while RK had the lowest levels. Influent EC levels ranged between 539 µS/cm (RK) and 782 µS/cm (NK). Influent DO levels of the all the plants had similar range varying between 3.10 mg/L (NK) and 6.50 mg/L (DD) with an average of about 5.02 mg/L. Similar to April 2013, NK had the lowest influent DO level. Influent $BOD_5$ concentrations ranged between 37.0 mg/L (TK) and 67.0 mg/L (NK). The influent $BOD_5$ concentrations in four of the five WWTPs (except RK) were higher than in April 2013. NK had the highest influent concentrations of the five measured parameters (EC, TS, TDS, TSS, and $BOD_5$) and the lowest DO levels. Based on the influent concentrations of the six parameters in the five WWTPs in October 2013, unlike in April 2013, NK's influent quality appeared to be poorer than the other plants.

**Table 4.2** Concentrations of the conventional parameters in five WWTPs in Bangkok in October 2013

| WWTPs | Samp. Point | Temp ($^0$C) | DO (mg/L) | pH | EC (µS/cm) | TS (mg/L) | TDS (mg/L) | TSS (mg/L) | $BOD_5$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | Inf. | 28.5 | 6.5 | 7.39 | 577 | 346.22 | 343.87 | 20.20 | 51.0 |
| **DD** | Eff. | 28.3 | 8.9 | 7.41 | 455 | 321.56 | 294.93 | 8.53 | 3.8 |
| | RE (%) | - | - | - | - | 7.1 | 14.2 | 57.8 | 92.5 |
| | Inf. | 29.1 | 3.8 | 7.47 | 539 | 340.44 | 308.53 | 14.80 | 61.0 |
| **RK** | Eff. | 28.8 | 8.6 | 7.38 | 393 | 314.00 | 302.80 | 11.07 | 1.1 |
| | RE (%) | - | - | - | - | 7.8 | 1.9 | 25.2 | 98.2 |
| | Inf. | 28.3 | 6.0 | 7.30 | 704 | 479.56 | 347.87 | 15.20 | 45.0 |
| **CN** | Eff. | 28.3 | 7.2 | 7.19 | 567 | 434.67 | 327.73 | 13.20 | 8.4 |
| | RE (%) | - | - | - | - | 9.4 | 5.8 | 13.2 | 81.3 |
| | Inf. | 28.8 | 5.7 | 7.29 | 729 | 382.44 | 427.33 | 5.07 | 37.0 |
| **TK** | Eff. | 29.3 | 8.6 | 7.46 | 668 | 369.56 | 410.80 | 4.40 | 1.6 |
| | RE (%) | - | - | - | - | 3.4 | 3.9 | 13.2 | 95.7 |
| | Inf. | 28.5 | 3.1 | 7.16 | 782 | 511.78 | 484.40 | 53.87 | 67.0 |
| **NK** | Eff. | 29 | 6.6 | 7.28 | 720 | 448.67 | 379.73 | 3.47 | 4.6 |
| | RE (%) | - | - | - | - | 12.3 | 21.6 | 93.6 | 93.1 |

Note: Samp. Point = Sampling Point, Inf. = Influents, Eff. = Effluents, Temp = Temperature, DO = dissolved oxygen, EC = electrical conductivity, $BOD_5$ = 5 day biochemical oxygen demand, TS = total solids, TDS = total dissolved solids, TSS = total suspended solids, TK = Thungkru, NK= Nong Khaem, RK = Rattanakosin, DD = Din Daeng, CN = Chong Non Si, Inf. = influent, Eff. = effluent, ND = not detected, RE = Removal Efficiency.

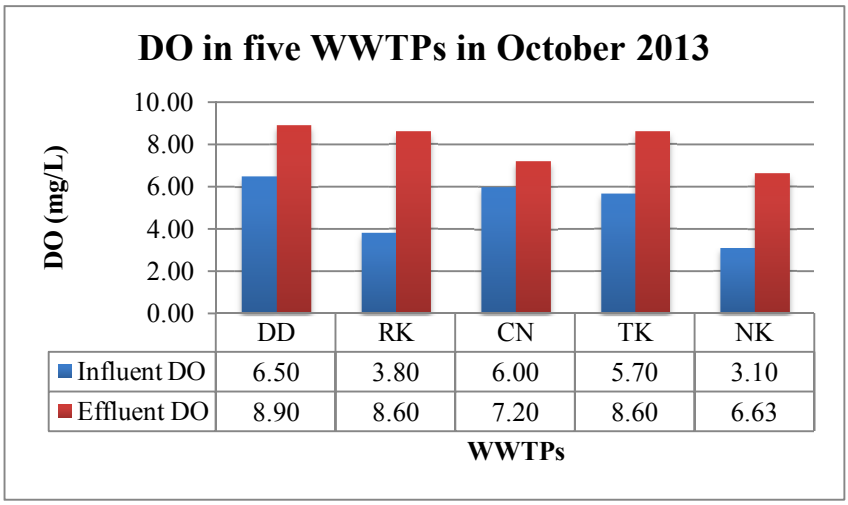



**Fig. 4.11** Average levels of DO in five WWTPs in Bangkok in October 2013

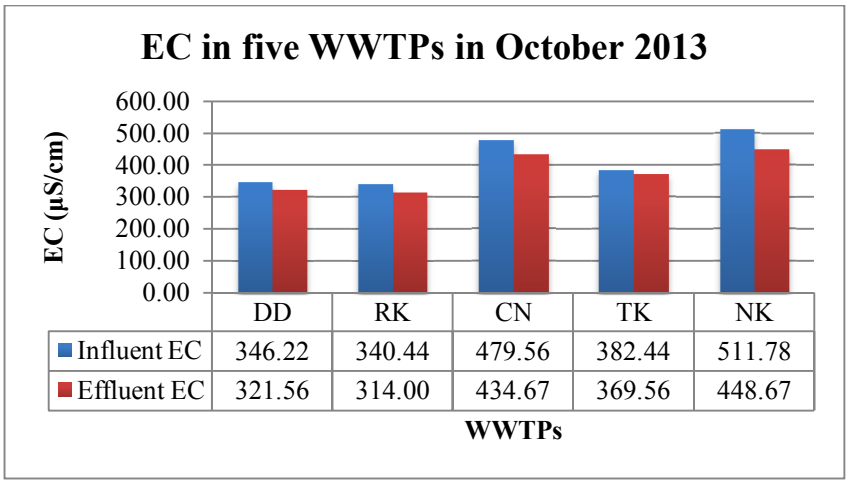



**Fig. 4.12** Average EC levels in five WWTPs in Bangkok in October 2013

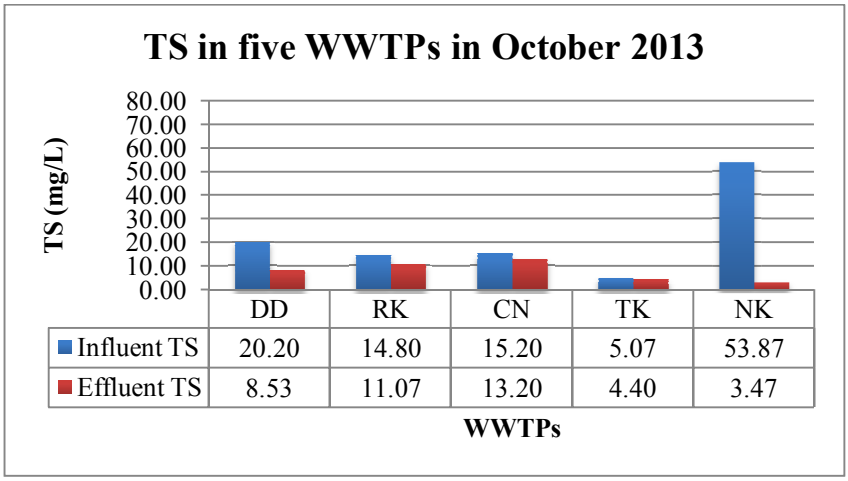



**Fig. 4.13** Average TS concentrations in five WWTPs in Bangkok in October 2013

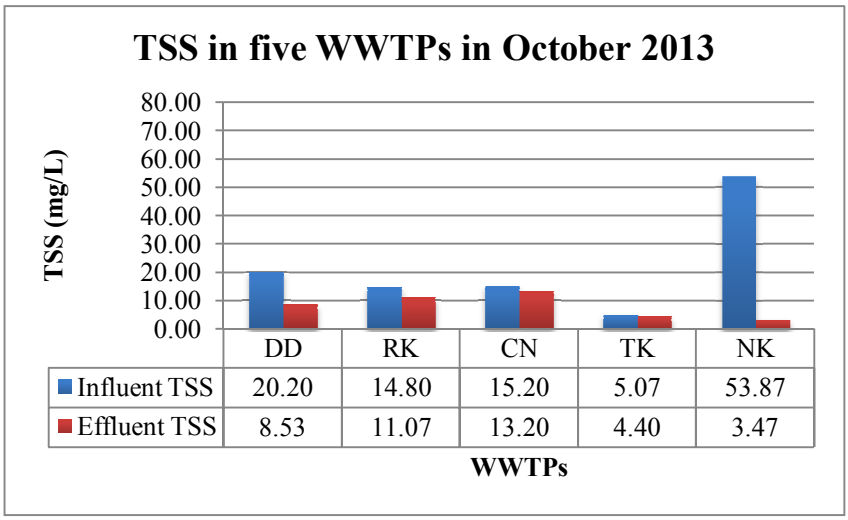



**Fig. 4.14** Average TSS concentrations in five WWTPs in Bangkok in October 2013

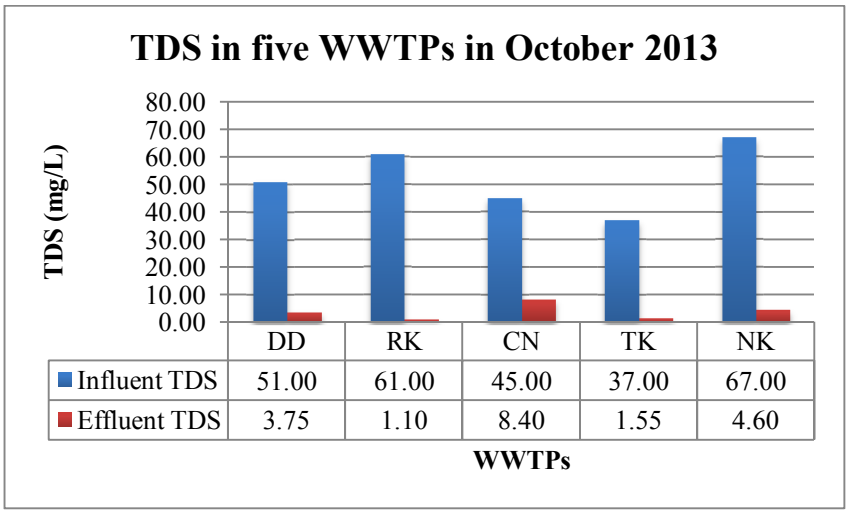



**Fig. 4.15** Average TDS concentrations in five WWTPs in Bangkok in October 2013

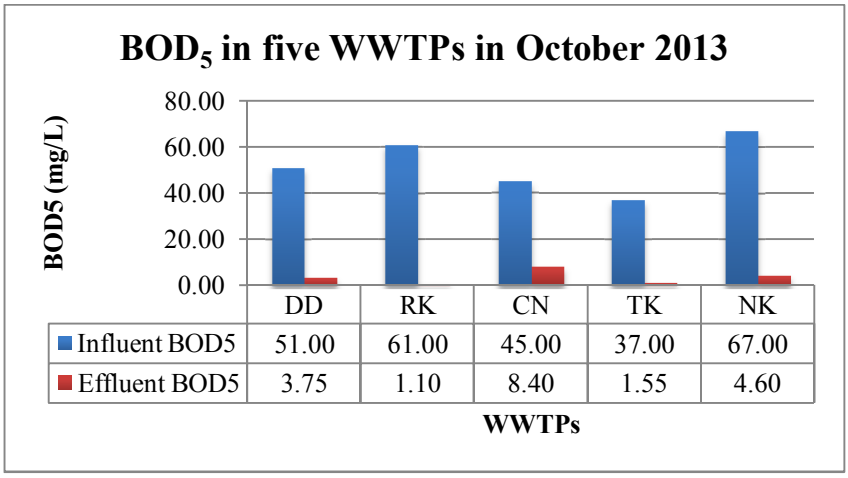



**Fig. 4.16** Average $BOD_5$ concentrations in five WWTPs in Bangkok in October 2013

Unlike in April 2013, when RK had the highest influent concentrations of EC, TS, TSS, TDS, and $BOD_5$, highest influent levels of these parameters were found to be at NK during October 2013 sampling. It could be due to fact that NK also receives the sludge of all the seven WWTPs operated under Bangkok Metropolitan Administration (BMA). In addition, solid waste from the surrounding municipal area is collected at the Nong Khaem Solid Waste Disposal Center before sending to landfill. The runoff from this facility, which is not very far from the location of NK, is also received and treated along with the influent wastewater at NK. Therefore, all of the measured influent water quality parameters of NK were at highest levels in October 2013 which happened to be the rainy season.

Effluent TS, TSS and TDS concentrations of the five WWTPs ranged between 314.00 mg/L (RK) and 448.67 mg/L (NK); 3.47 mg/L (NK) and 13.20 mg/L (CN); and 294.93 mg/L (DD) and 410.80 mg/L (TK), respectively. Unlike April 2013 sampling event, NK had the highest TS levels while RK had the lowest levels. Moreover, CN which had the lowest effluent TSS levels in April 2013 had the highest TSS concentration in this sampling event. Effluent EC levels ranged between 393 μS/cm (RK) and 720 μS/cm (NK). Effluent DO levels of the all the plants had also similar range varying between 6.63 mg/L (NK) and 8.90 mg/L (DD) with an average of about 7.99 mg/L. Similar to April 2013, NK also had the lowest effluent DO level. Effluent $BOD_5$ concentrations ranged between 1.1 mg/L (RK) and 8.4 mg/L (CN). During October 2013 sampling, RK had the lowest $BOD_5$ level.

The temperature and pH of the influents and effluents of all WWTPs were not significantly different. The average values of temperature and pH were 28.7$^{o}$C (1.5 $^{o}$C lower than in April 2013) and 6.80, respectively. The lowest levels of EC and TS in the effluents were found at RK and the second lowest levels of EC, TS and TDS were found at DD. However, the difference between these concentrations of RK and DD was not significant. NK had the lowest level of TSS while RK had the lowest effluent concentration of $BOD_5$. NK had the highest effluent concentrations of EC and TS. CN had the highest effluent concentrations of TSS and $BOD_5$, and the second highest levels of TS. However, the difference between TDS concentrations of CN and TK was not significant. Based on the effluents concentrations of the six parameters in

the five plants, it appeared that CN's effluent quality was poorer than the other plants. The best effluent quality was at RK.

The highest effluent levels of EC and TS were found to be in NK. However, the percent removal of TS, TSS, TDS, and $BOD_5$ of NK were higher than the other WWTPs. Although, both NK and TK use the Vertical Loop Reactor Activated Sludge for the treatment system, NK has the higher capacity and the larger treatment area and also the higher removal efficiency than TK.

Removal efficiencies of five WWTPs ranged between 7.1% and 12.3% for TS; 13.2% and 93.6% for TSS; 1.9% and 21.6% for TDS; and between 81.3% and 98.2% for $BOD_5$ (Figure 4.17). RK and CN had the highest and lowest $BOD_5$ removal efficiency, respectively. However, the $BOD_5$ removal efficiency of DD (92.5%), TK (95.7%), and NK (93.1%) were also high. Moreover, the TSS removal efficiency of almost all the plants (except NK) was lower than in April 2013. On the other hand, the $BOD_5$ removal efficiency of almost all the plants (except CN) appeared to be higher than in April 2013. Interestingly, even though NK's influents qualities were found to be the worst during this sampling event, it had the highest removal efficiency for TS, TSS and TDS among the five plants.

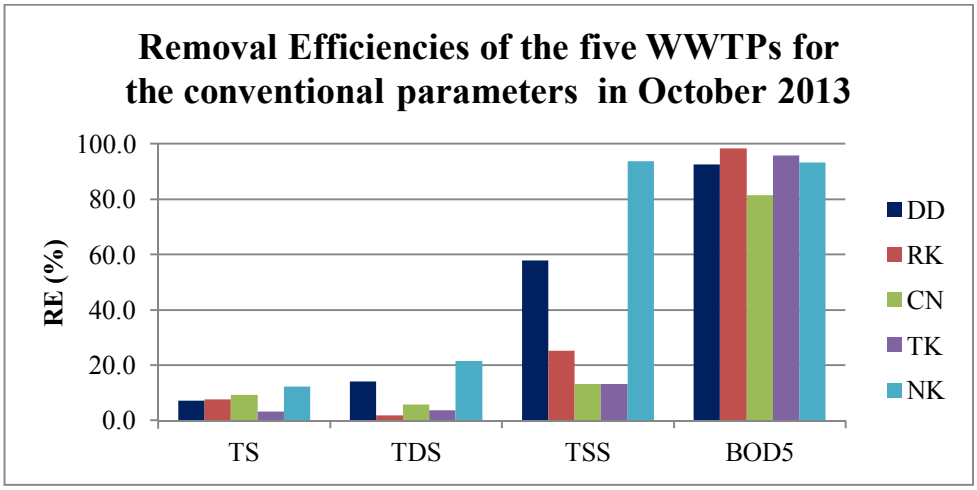



**Fig 4.17** Removal Efficiencies of the five WWTPs for the conventional parameters in October 2013

**Bisphenol A Concentrations in Five WWTPs in Bangkok in October 2013**

Investigation on BPA concentrations in the influents and the effluents samples were carried out by using HPLC equipped with a fluorescence detector at the wavelengths of 228 nm for the excitation and 313 nm for the emission. Method validation was performed by obtaining the calibration curve for the prepared standards with the concentrations in the range 10 – 5,000 µg/L. The limit of detection (LOD) and limit of quantification (LOQ) were defined as the concentrations with a signal-to-noise (S/N) ratio of 3 and 10, respectively. The observed LOD and LOQ were 1.3 and 4.2 µg/L, respectively. The correlation coefficient ($R^2$) between area under the peak of HPLC and BPA concentrations was found to be 0.9995 (Figure 4.18). Accuracy (trueness) and precision when tested at BPA concentrations 50 ng/L the percentage recovery (% recovery) was between 89.5% and 114.6%, and repeatability by relative standard deviation of repeatability (% RSDr) was 5.5%.

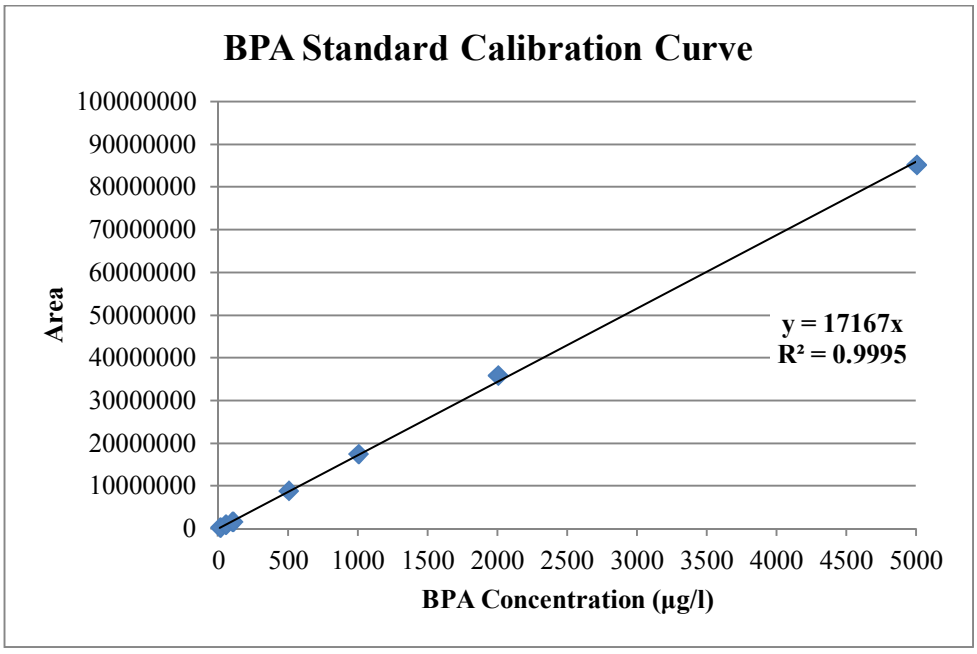
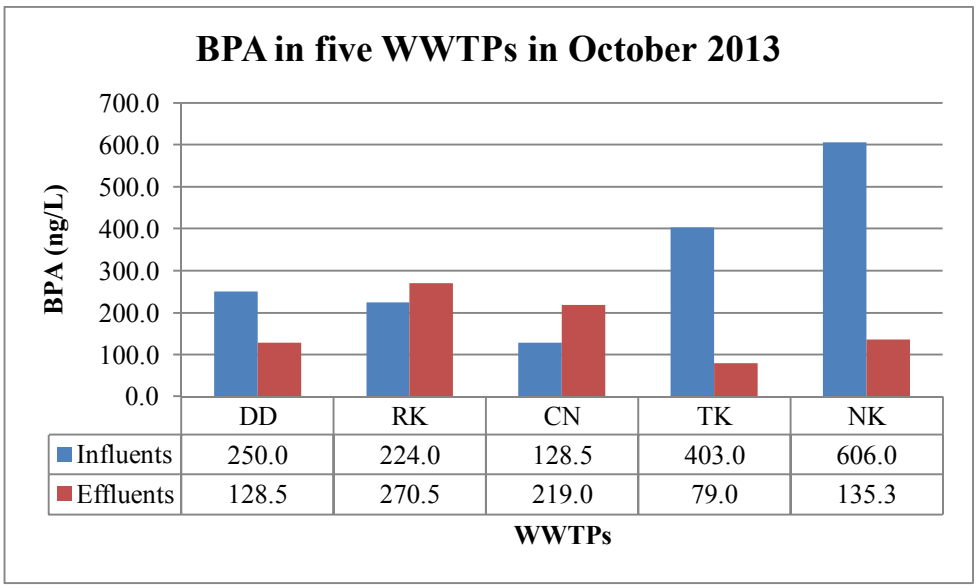



**Fig. 4.18** BPA standard calibration curve by using HPLC with fluorescence detector in October, 2013

During the October 2013 sampling, the influent BPA concentrations in the five WWTPs ranged between 128.5 ng/L (CN) and 606.0 ng/L (NK), while the

effluent BPA levels in the effluents ranged between 79.0 ng/L (TK) and 270.5 ng/L (RK) (Figure 4.19). The highest BPA influent concentration was found at NK that had the highest influent EC, TDS and TSS levels and the lowest influent DO levels. The BPA concentration appeared to be significantly correlated to influent TDS (R = 0.9209), pH (R = - 0.7327) and TSS levels (R = 0.7027), and moderately correlated to influent EC (R = 0.6405) and DO levels (R = - 0.6024). It was reported in a study (Kang and Kondo, 2005) that BPA degradation in river waters could be under aerobic conditions.




| | DD | RK | CN | TK | NK |
|---|---|---|---|---|---|
| Influents | 250.0 | 224.0 | 128.5 | 403.0 | 606.0 |
| Effluents | 128.5 | 270.5 | 219.0 | 79.0 | 135.3 |

**Fig. 4.19** Average BPA concentrations in five WWTPs in Bangkok in October 2013

The effluent BPA concentrations in DD, TK and NK were lower than the influent levels while RK and CN had effluent BPA concentrations at higher levels than the influents. The BPA concentration appeared to be significantly correlated to effluent TSS (R = 0.7982), and moderately correlated to effluent TDS (R = - 0.6620) and EC levels (R = - 0.6465). Thus, high BPA concentrations were observed in samples with low EC and TDS levels and also in the samples with high TSS.

The highest BPA removal efficiency was of TK (80.4%) followed by NK (77.7%) and DD (48.6%). The treatment process employed at TK and NK was vertical loop reactor activated sludge process. Thus, this process seems to be more effective for BPA degradation. On the other hand, BPA concentrations in the effluents

of RK and CN were higher than their influent levels. It could probably be due to the error in samples preparation/analysis as this was not observed in the 2 more sampling events following October 2013.

### 4.1.3 Third Sampling Event in December 2013

**Concentrations of the Conventional Parameters in five WWTPs in Bangkok region in December 2013**

The concentrations of the conventional parameters in the influents and effluents of the five WWTPs in Bangkok during December 2013 sampling event are summarized in Table 4.4 and the Figures 4.20-4.25.

The ranges of influent conventional parameters' concentrations of the five WWTPs were similar to October 2013, having concentrations 366.22 mg/L (RK) and 1,067.78 mg/L (CN) for TS, 6.80 mg/L (RK) and 65.73 mg/L (NK) for TSS and 279.80 mg/L (RK) and 798.27 mg/L (CN) for TDS, respectively. Similar to April 2013 sampling event, CN had the highest TS and TDS levels. RK had the lowest TS and TDS levels similar to October 2013. Moreover, all influent TS and TDS concentrations were higher than in October 2013. Similar to October 2013, NK had the highest TSS concentrations. Influent EC levels ranged between 549 μS/cm (RK) and 1,659 μS/cm (CN). Influent DO levels of the all the plants had similar range varying between 1.9 mg/L (TK) and 5.2 mg/L (CN) with an average of about 3.82 mg/L. Influent $BOD_5$ concentrations ranged between 59.0 mg/L (DD) and 109.0 mg/L (NK). The influent $BOD_5$ levels of all WWTPs were higher than in April and October 2013. Similar to October 2013, NK had the highest influent $BOD_5$ concentrations. TK had the lowest influent DO level and the second highest levels of EC, TS, TDS and $BOD_5$. Based on the influent concentrations of the six parameters in the five WWTPs in December 2013, it appeared that TK's influent quality was poorer than the other plants, while RK and NK were the ones having poorest influent quality during the first and the second sampling events, respectively.

Effluent TS, TSS and TDS concentrations of the five WWTPs ranged between 321.33 mg/L (RK) and 907.11 mg/L (CN); 2.00 mg/L (CN) and 8.80 mg/L (NK); and 279.80 mg/L (RK) and 798.27 mg/L (CN), respectively. Similar to April 2013, CN had the highest TDS levels and had the lowest TSS levels. RK had the

lowest TDS levels similar to October 2013. Effluent EC levels ranged between 524 µS/cm (RK) and 1,504 µS/cm (CN).

**Table 4.3** Concentrations of the conventional parameters in five WWTPs in Bangkok in December 2013

| WWTPs | Samp. Point | Temp ($^{o}$C) | DO (mg/L) | pH | EC (µS/cm) | TS (mg/L) | TDS (mg/L) | TSS (mg/L) | $BOD_5$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | Inf. | 26.9 | 4.8 | 7.26 | 736 | 421.33 | 416.40 | 12.20 | 59.0 |
| **DD** | Eff. | 28.1 | 6.7 | 7.40 | 674 | 394.44 | 398.67 | 4.00 | 8.9 |
| | RE (%) | - | - | - | - | 6.4 | 4.3 | 67.2 | 84.9 |
| | Inf. | 26.6 | 4.5 | 7.31 | 549 | 366.22 | 310.67 | 6.80 | 78.0 |
| **RK** | Eff. | 26.6 | 6.8 | 7.59 | 524 | 321.33 | 279.80 | 4.20 | 4.9 |
| | RE (%) | - | - | - | - | 12.3 | 9.9 | 38.2 | 93.7 |
| | Inf. | 26.3 | 5.2 | 7.28 | 1659 | 1067.78 | 955.60 | 8.40 | 70.0 |
| **CN** | Eff. | 26.3 | 5.8 | 7.09 | 1504 | 907.11 | 798.27 | 2.00 | 6.0 |
| | RE (%) | - | - | - | - | 15.0 | 16.5 | 76.2 | 91.4 |
| | Inf. | 26.4 | 1.9 | 7.27 | 1317 | 740.22 | 711.87 | 8.80 | 78.0 |
| **TK** | Eff. | 26.5 | 7.5 | 7.42 | 1057 | 662.44 | 656.00 | 8.60 | 4.7 |
| | RE (%) | - | - | - | - | 10.5 | 7.8 | 2.3 | 94.0 |
| | Inf. | 26.4 | 2.7 | 7.34 | 627 | 406.67 | 407.47 | 65.73 | 109.0 |
| **NK** | Eff. | 26.8 | 5.1 | 7.17 | 599 | 401.11 | 395.07 | 8.80 | 8.5 |
| | RE (%) | - | - | - | - | 1.4 | 3.0 | 86.6 | 92.2 |

Note: Samp. Point = Sampling Point, Inf. = Influents, Eff. = Effluents, Temp = Temperature, DO = dissolved oxygen, EC = electrical conductivity, $BOD_5$ = 5 day biochemical oxygen demand, TS = total solids, TDS = total dissolved solids, TSS = total suspended solids, TK = Thungkru, NK= Nong Khaem, RK = Rattanakosin, DD = Din Daeng, CN = Chong Non Si, Inf. = influent, Eff. = effluent, ND = not detected, RE = Removal Efficiency.

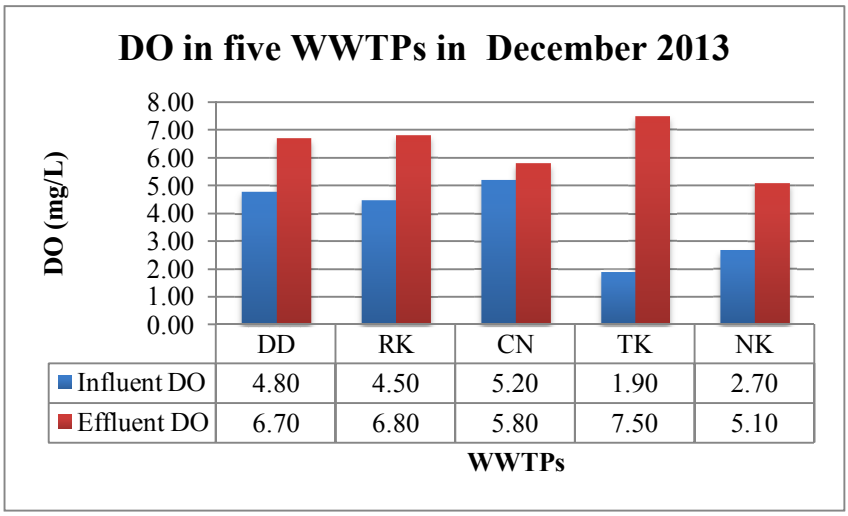



**Fig. 4.20** Average DO concentrations in five WWTPs in Bangkok in December 2013

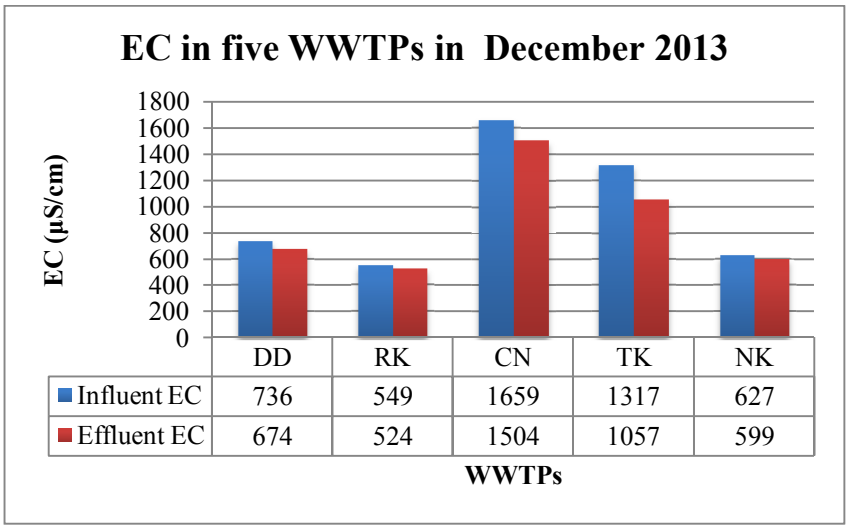



**Fig. 4.21** Average EC levels in five WWTPs in Bangkok in December 2013

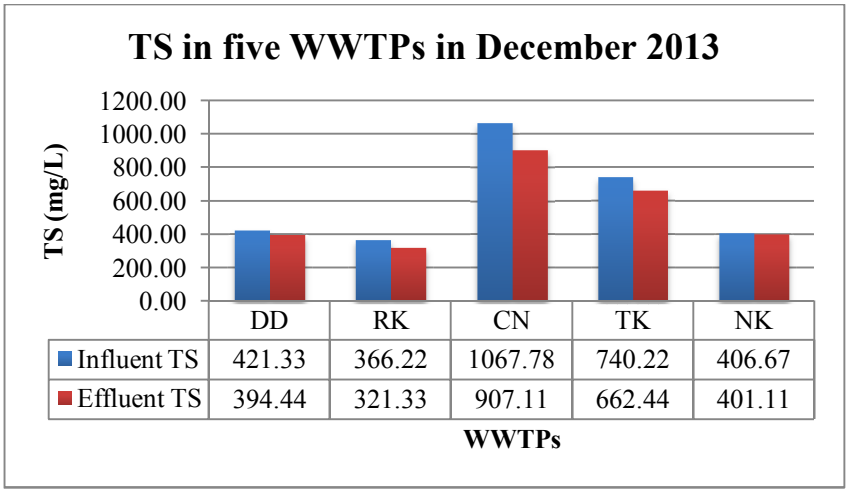



**Fig. 4.22** Average TS concentrations in five WWTPs in Bangkok in December 2013

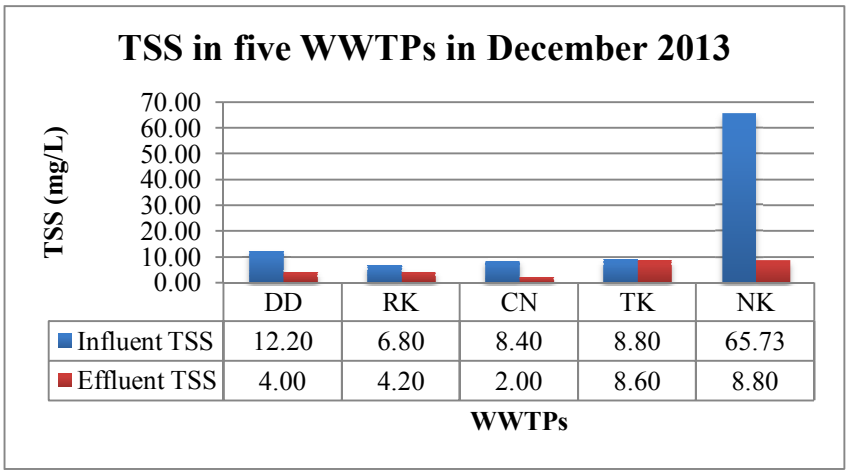



**Fig. 4.23** Average TSS concentrations in five WWTPs in Bangkok in December 2013

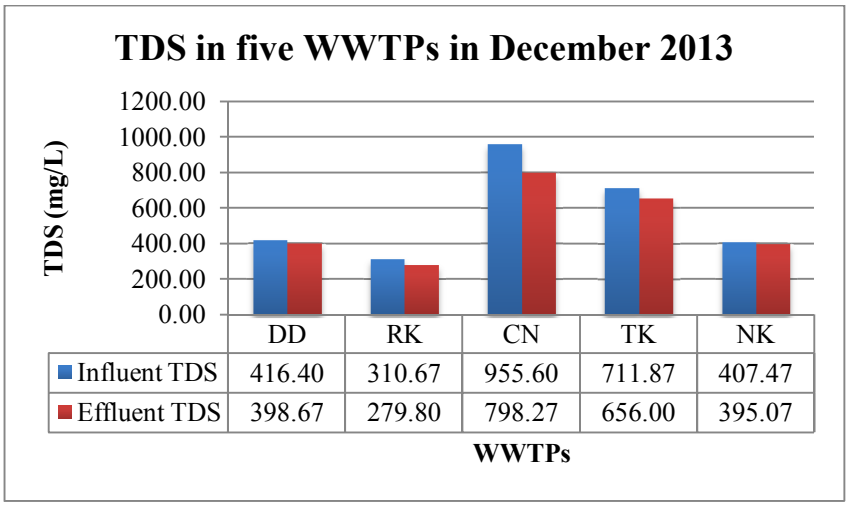



**Fig. 4.24** Average TDS concentrations in five WWTPs in Bangkok in December 2013

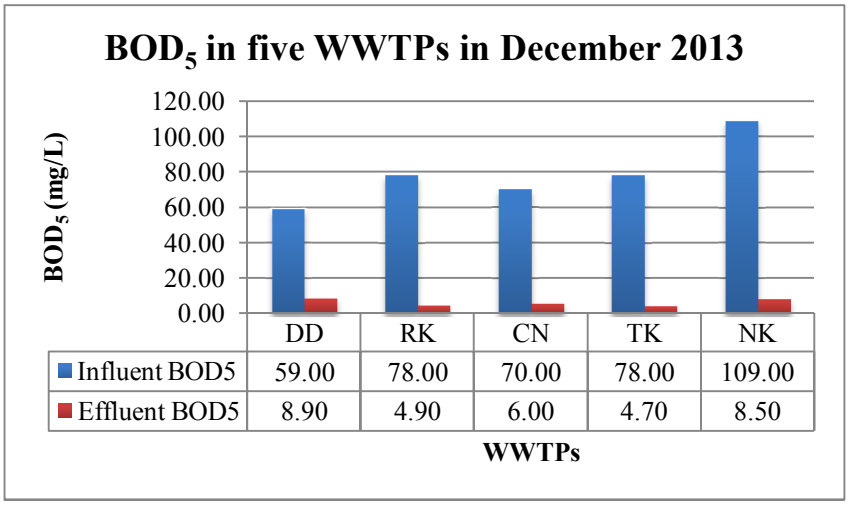



**Fig. 4.25** Average $BOD_5$ concentrations in five WWTPs in Bangkok in December 2013

Effluent DO levels of the all the plants also had similar range varying between 5.1 mg/L (NK) and 7.5 mg/L (TK) with an average of about 6.38 mg/L. Similar to April 2013, TK had the highest effluent DO level while NK had the lowest DO levels like in October 2013. Effluent $BOD_5$ concentrations ranged between 4.7 mg/L (TK) and 8.9 mg/L (DD). The temperature and pH of the influents and effluents of all WWTPs were not significantly different. The average temperature and pH were 26.7°C and 7.31, respectively. The average temperatures of the wastewater samples were slightly lower than in April and October 2013. CN had the highest effluent concentrations of EC, TS and TDS and the second lowest DO levels. The lowest levels of EC, TS and TDS in the effluents were found at RK. Based on the effluents concentrations of the six parameters in the five plants, CN's effluent quality appeared to be poorer than the other plants while RK had the best effluent quality.

Removal efficiencies of five WWTPs varied widely ranging between 1.4% and 15.0% for TS; 2.3% and 86.6% for TSS; 3.0% and 16.5% for TDS; and between 84.9% and 94.0% for $BOD_5$ (Figure 4.26). Similar to April 2013, CN had the highest removal of TS and TDS. On the other hand, NK had the highest removal of TSS like in October 2013, while this time it had the lowest removal of TS and TDS.

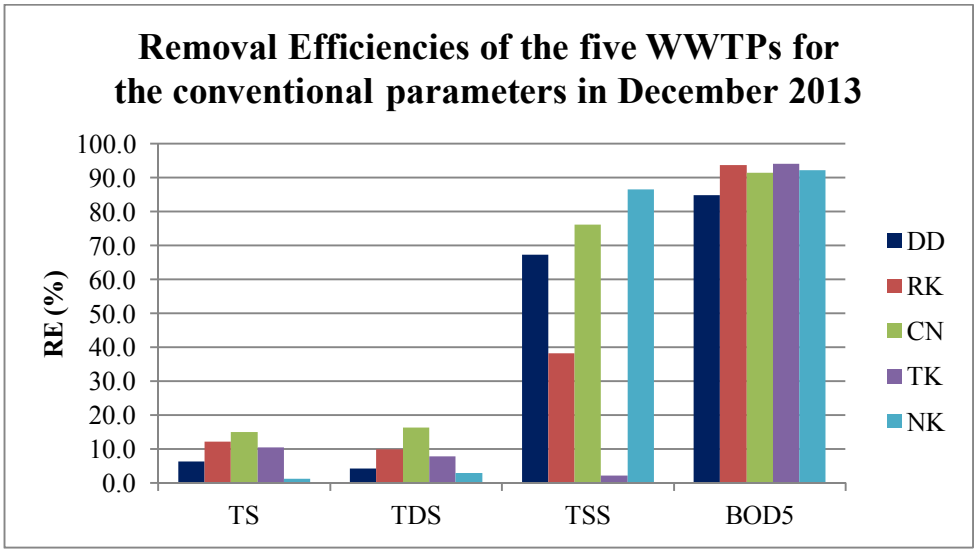



**Fig 4.26** Removal Efficiencies of the five WWTPs for the conventional parameters in December 2013

**Bisphenol A Concentrations in Five WWTPs in Bangkok in December 2013**

Method validation for the investigation on BPA concentrations in influent and effluent samples in December 2013 was performed by obtaining the calibration curve for the prepared standards with the concentrations ranging between 10 and 5,000 µg/L. The correlation coefficient ($R^2$) between area under the peak of HPLC and BPA concentrations was found to be 0.9985 (Figure 4.27).

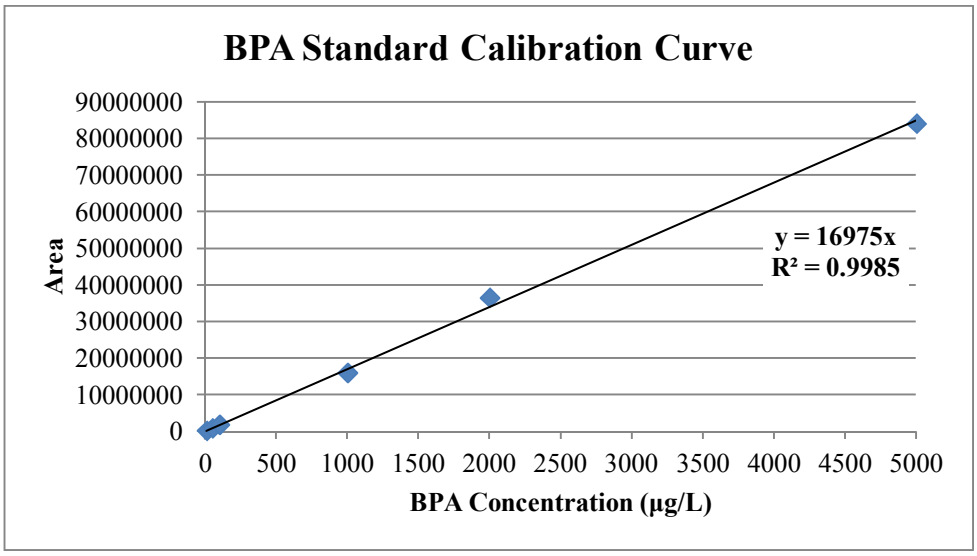



**Fig. 4.27** BPA standard calibration curve by using HPLC with fluorescence detector in December, 2013

During the December 2013 sampling, the influent BPA concentrations in the five WWTPs ranged between 247.5 ng/L (RK) and 559.3 ng/L (TK), while the effluent BPA levels ranged between 51.8 ng/L (TK) and 111.3 ng/L (RK) (Figure 4.28). The BPA concentration appeared to be moderately correlated to influent DO level (R = - 0.6983). The highest BPA influent concentration was found at TK that had the lowest influent DO levels.

The effluent BPA concentrations in all the five WWTPs were lower than the influent levels. The BPA concentration appeared to be significantly correlated to effluent TDS (R = - 0.7634), and moderately correlated to effluent TS (R = - 0.6556) and EC levels (R = - 0.6345). Thus, high BPA concentrations were observed in samples with low TDS, TS and EC levels.

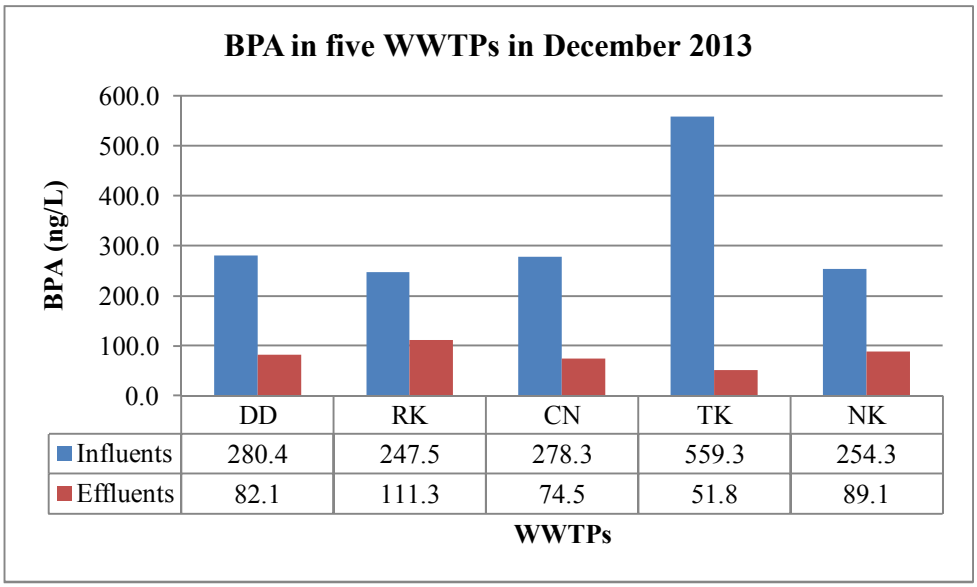



**Fig. 4.28** Average BPA concentrations in five WWTPs in Bangkok in December 2013

BPA removal efficiencies of DD, RK, CN, TK and NK were 70.7%, 55.0%, 73.2%, 90.7%, and 64.9%, respectively. Similar to October 2013, the highest BPA removal efficiency was found at TK. Hence, the treatment process of TK (vertical loop reactor activated sludge process) seems to be the best for BPA removal.

### 4.1.4 Fourth Sampling Event in February 2014

**Concentrations of the Conventional Parameters in five WWTPs in Bangkok region in February 2014**

The concentrations of the conventional parameters in the influents and effluents of the five WWTPs in Bangkok during February 2014 sampling event are summarized in Table 4.4 and the Figures 4.29-4.34**.**

**Table 4.4** Concentrations of the conventional parameters in five WWTPs in Bangkok in February 2014

| WWTPs | Samp. Point | Temp ($^{o}$C) | DO (mg/L) | pH | EC (µS/cm) | TS (mg/L) | TDS (mg/L) | TSS (mg/L) | $BOD_5$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | Inf. | 28.1 | 5.2 | 7.45 | 2184 | 1316.00 | 1164.27 | 21.40 | 75.00 |
| **DD** | Eff. | 28.7 | 5.7 | 7.34 | 2060 | 1156.00 | 1094.00 | 7.00 | 11.40 |
| | RE (%) | - | - | - | - | 12.2 | 6.0 | 67.3 | 84.8 |
| | Inf. | 28.0 | 2.0 | 7.16 | 3999* | 7032.22 | 6203.60 | 39.60 | 61.00 |
| **RK** | Eff. | 28.0 | 6.5 | 7.47 | 3999* | 5255.78 | 4559.07 | 33.60 | 5.70 |
| | RE (%) | - | - | - | - | 25.3 | 26.5 | 15.2 | 90.7 |
| | Inf. | 28.9 | 6.1 | 7.35 | 3999* | 9585.11 | 8124.93 | 50.00 | 33.00 |
| **CN** | Eff. | 27.9 | 6.5 | 6.91 | 3999* | 9565.00 | 7830.13 | 47.60 | 6.20 |
| | RE (%) | - | - | - | - | 0.2 | 3.6 | 4.8 | 81.2 |
| | Inf. | 28.4 | 2.2 | 7.23 | 3999* | 3637.33 | 3200.67 | 28.20 | 43.00 |
| **TK** | Eff. | 28.3 | 7.3 | 7.28 | 3999* | 3529.78 | 3071.33 | 17.40 | 5.80 |
| | RE (%) | - | - | - | - | 3.0 | 4.0 | 38.3 | 86.5 |
| | Inf. | 28.7 | 2.3 | 7.14 | 835 | 537.11 | 443.87 | 11.20 | 53.00 |
| **NK** | Eff. | 28.3 | 4.2 | 7.19 | 822 | 496.89 | 435.33 | 2.60 | 9.50 |
| | RE (%) | - | - | - | - | 7.5 | 1.9 | 76.8 | 82.1 |

Note: Samp. Point = Sampling Point, Inf. = Influents, Eff. = Effluents, Temp = Temperature, DO = dissolved oxygen, EC = electrical conductivity, $BOD_5$ = 5 day biochemical oxygen demand, TS = total solids, TDS = total dissolved solids, TSS = total suspended solids, TK = Thungkru, NK= Nong Khaem, RK = Rattanakosin, DD = Din Daeng, CN = Chong Non Si, Inf. = influent, Eff. = effluent, ND = not detected, RE = Removal Efficiency, *= the highest detection of EC meter.

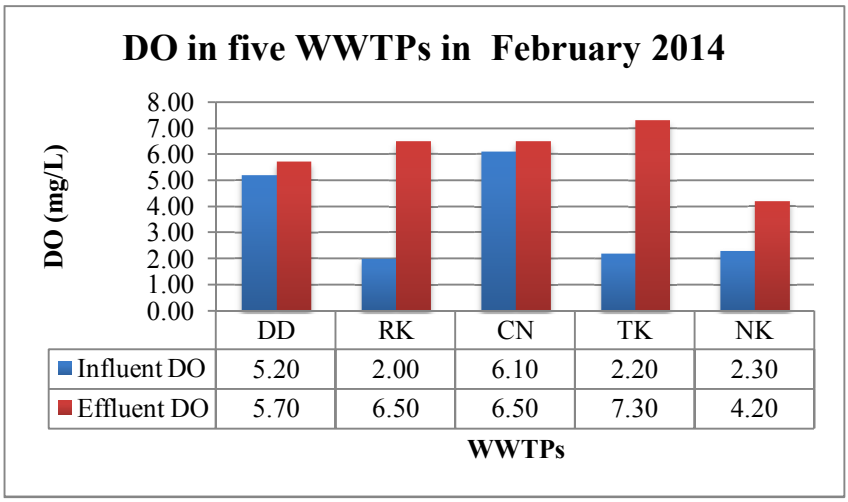



**Fig. 4.29** Average DO concentrations in five WWTPs in Bangkok in February 2014

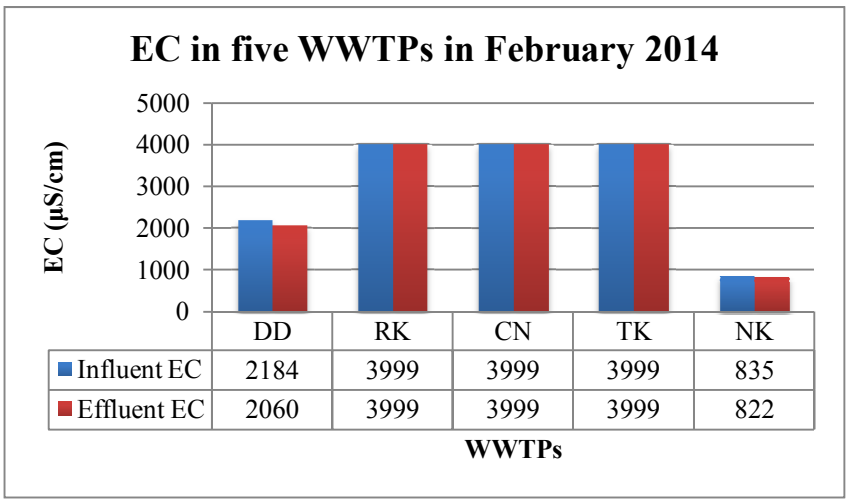



**Fig. 4.30** Average EC levels in five WWTPs in Bangkok in February 2014

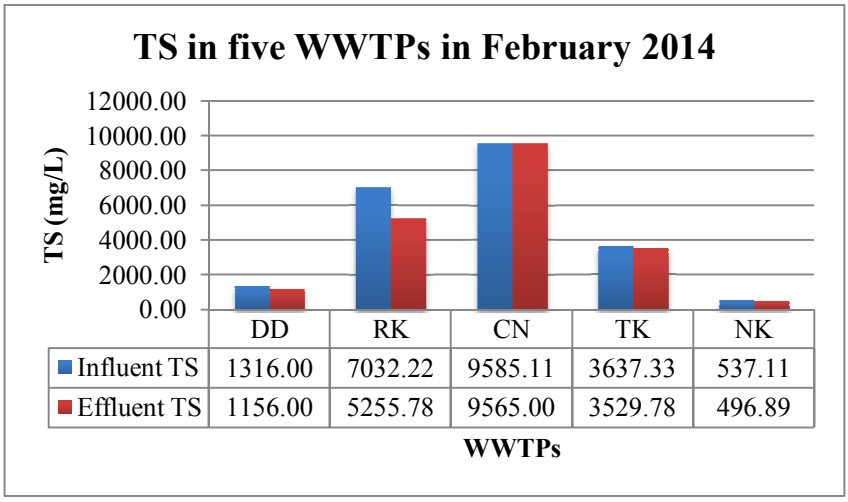



**Fig. 4.31** Average TS concentrations in five WWTPs in Bangkok in February 2014

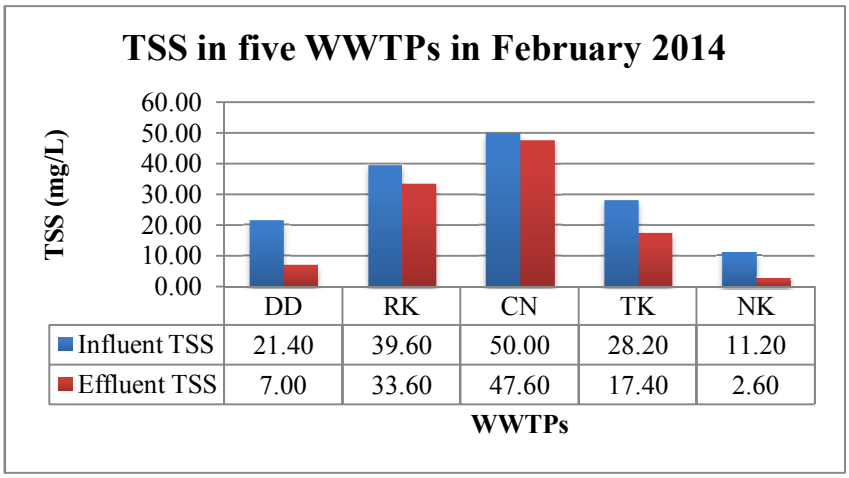



**Fig. 4.32** Average TSS concentrations in five WWTPs in Bangkok in February 2014

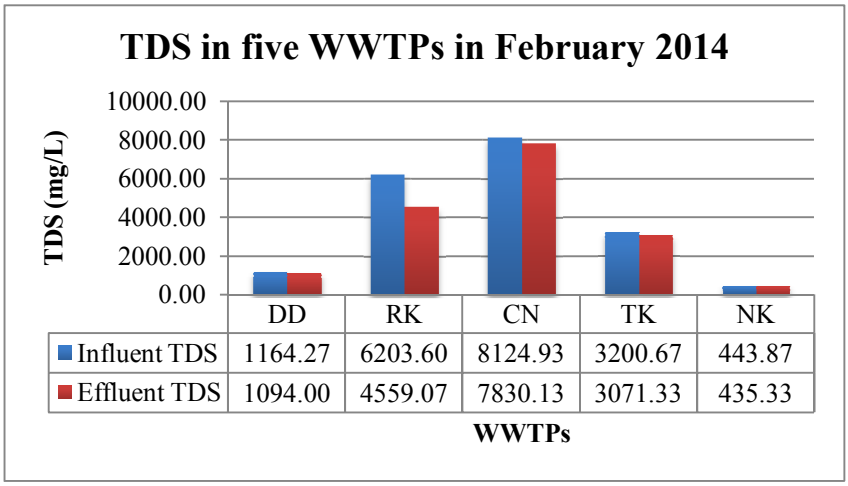



**Fig. 4.33** Average TDS concentrations in five WWTPs in Bangkok in February 2014

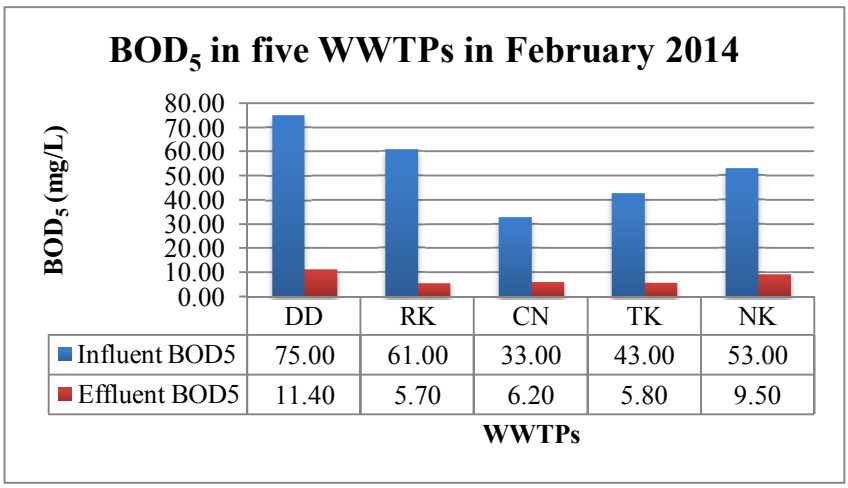



**Fig. 4.34** Average $BOD_5$ concentrations in five WWTPs in Bangkok in February 2014

Influent TS, TSS and TDS concentrations of the five WWTPs ranged between 9,585.11 mg/L (CN) and 537.11 mg/L (NK); 11.20 mg/L (NK) and 50.00 mg/L (CN); and 443.87 mg/L (NK) and 8,124.93 mg/L (CN), respectively. Influent TS and TDS levels of CN were similar to April and December 2013. It was observed that TS, TSS and TDS were highest in this sampling event (≥ 10 times higher than in April, October and December 2013). Influent EC levels ranged between 835 μS/cm (NK) and more than 3,999 μS/cm (RK, CN, and TK). Because of the maximum limit EC meter and the high solid concentrations in this sampling event, the highest EC level could not be determined. Influent DO levels of the all the plants had similar range varying between 2.0 mg/L (RK) and 6.1 mg/L (CN) with an average of about 3.0 mg/L. Similar to April and December 2013, CN had the highest influent DO level. Influent $BOD_5$ concentrations ranged between 33.0 mg/L (CN) and 75.0 mg/L (NK). CN had the highest influent concentrations of the five measured parameters (TS, TDS, TSS, and DO) and the high of EC level. Based on the influent concentrations of the six parameters in the five WWTPs in February 2013, CN's influent quality was found to be poorer than the other plants. Hence, it appeared that the WWTP with the poorest influent quality was always a different one in four sampling events.

Effluent TS, TSS and TDS concentrations of the five WWTPs ranged between 496.89 mg/L (NK) and 9,565.00 mg/L (CN); 2.60 mg/L (NK) and 47.60 mg/L (CN); and 435.33 mg/L (NK) and 7,830.13 mg/L (CN), respectively. Effluent EC levels ranged between 822 μS/cm (NK) and more than 3,999 μS/cm (RK, CN, and TK). Similar to the influents, the highest EC level could not be determined. Effluent DO levels of the all the plants had also similar range varying between 4.2 mg/L (NK) and 7.3 mg/L (TK) with an average of about 5.0 mg/L. Thus, the effluent DO levels were higher than the influent DO levels in all the plants during the four sampling events. Effluent $BOD_5$ concentrations ranged between 5.70 mg/L (RK) and 11.40 mg/L (DD). The temperature and pH in the influents and effluents of all WWTPs were not significantly different, with the average values of 28.3$^{o}$C and 7.3, respectively. The lowest levels of EC, TS, TSS and TDS in the effluents were found at NK. $BOD_5$ and DO concentrations among the five plants were not significantly different. Based on the effluents concentrations of the six parameters in the five

plants, it appeared that similar to October and December 2013, CN's effluent quality was poorer than the other plants. The best effluent quality appeared to be at NK.

Removal efficiencies of five WWTPs ranged between 0.2% and 25.3% for TS, 4.8% and 76.8% for TSS, 1.9% and 26.5% for TDS, and between 81.2% and 90.7% for $BOD_5$ (Figure 4.35).

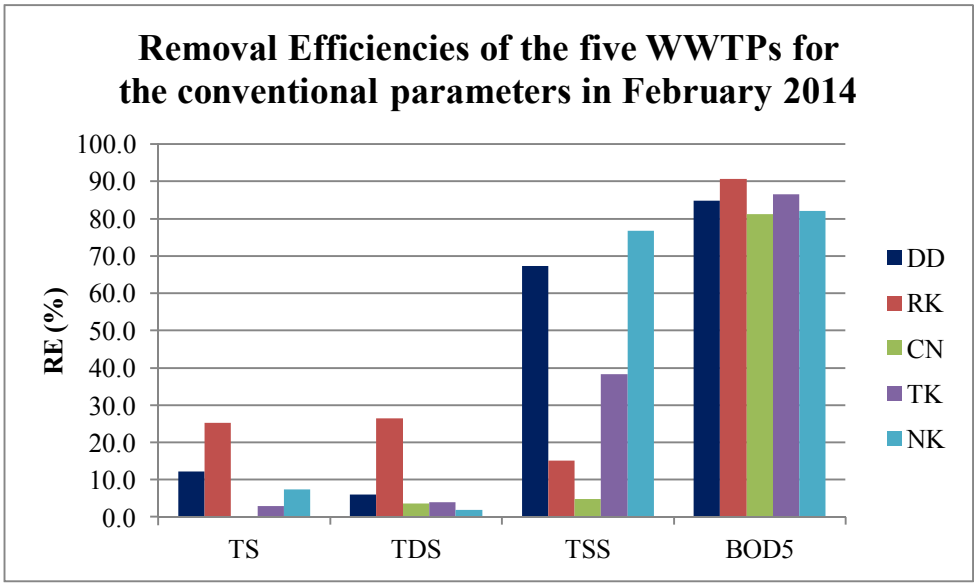



**Fig 4.35** Removal Efficiencies of the five WWTPs for the conventional parameters in February 2014

The removal efficiencies of all the conventional parameters in this event were lower than in October and December 2013. RK had the highest removal of TS, TDS and $BOD_5$ but the second lowest removal of TSS. NK had the highest TSS removal efficiency. Overall, RK's treatment process showed the highest efficiency of removal. It can be noted that, during the October and December 2013 and February 2014 sampling events, NK had the highest TSS removal while RK had the highest $BOD_5$ removal.

**Bisphenol A Concentrations in Five WWTPs in Bangkok in February 2014**

Similar to the October and December 2013 sampling events, method validation for the investigation on BPA concentrations in influent and effluent samples

in February 2014 was performed by obtaining the calibration curve for the prepared standards with the concentrations ranging between 10 and 5,000 µg/L. The correlation coefficient ($R^2$) between area under the peak of HPLC and BPA concentrations was found to be 0.9999 (Figure 4.36).

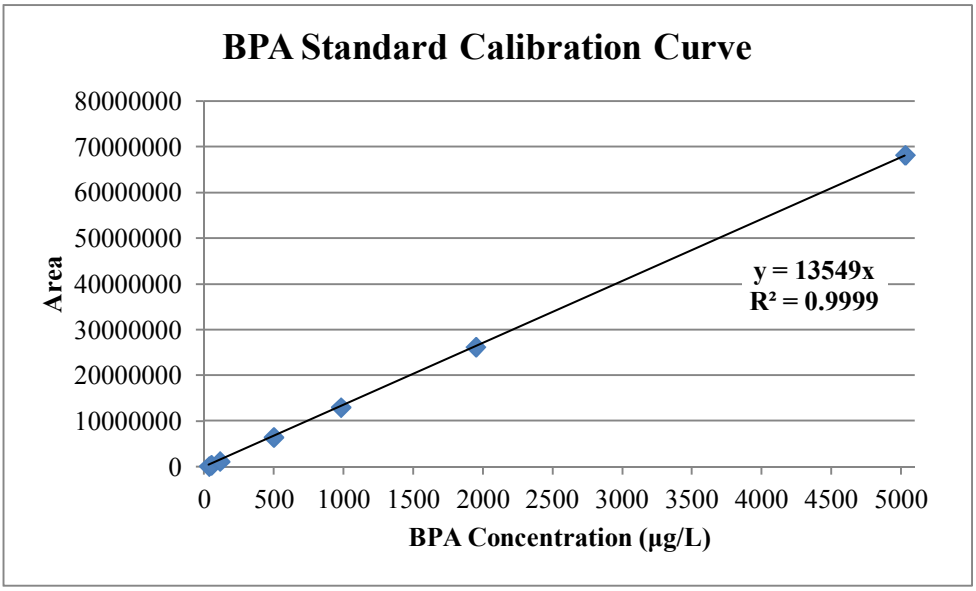



**Fig. 4.36** BPA standard calibration curve by using fluorescence detector in February, 2014

During the February 2014 sampling, the influent BPA concentrations in the five WWTPs ranged between 152.4 ng/L (CN) and 473.9 ng/L (DD), while the effluent BPA levels ranged between 38.7 ng/L (DD) and 131.9 ng/L (RK) (Figure 4.37). The BPA concentration appeared to be significantly correlated to influent EC (R = - 0.8796), TS (R = - 0.9047), TDS (R = - 0.9079), TSS (R = - 0.8771), and $BOD_5$ levels (R = 0.7445). The highest and the second highest BPA influent concentrations were found at DD (473.9 ng/L) and NK (429.5 ng/L), respectively. Thus, high BPA concentrations were observed in samples with low EC, TS, TDS and TSS levels, and with high $BOD_5$.

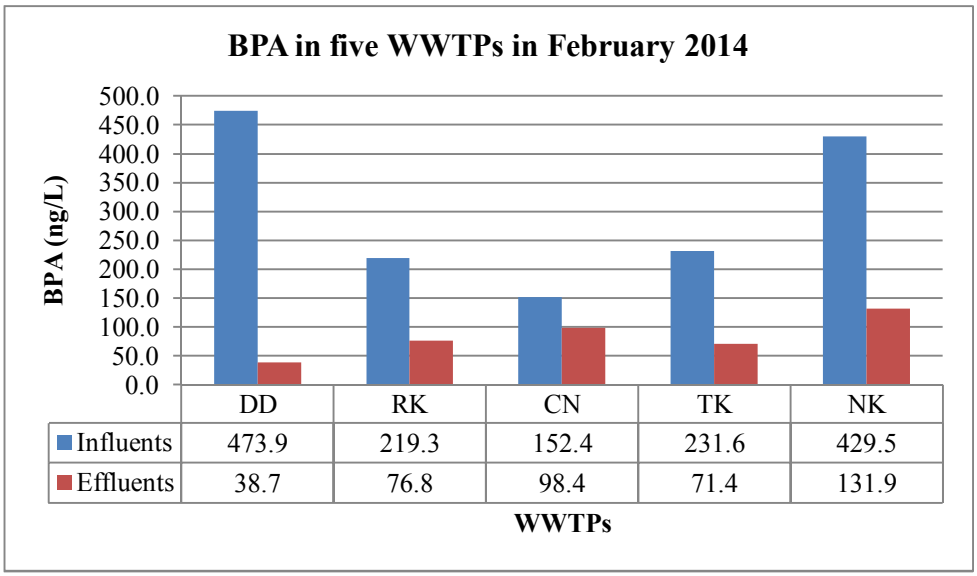



**Fig. 4.37** Average BPA concentrations in five WWTPs in Bangkok in February 2014

The effluent BPA concentrations in all the five WWTPs were lower than the influent levels. Similar to October 2013, the lowest influent BPA level was at CN. Unlike the influent conventional parameters concentrations, CN had the lowest BPA level. CN had the worst influent quality. The BPA concentration appeared to be only moderately correlated to effluent DO (R = -0.5269) and temperature (R = - 0.5061). Thus, high BPA concentrations were observed in samples with low DO and temperature.

BPA removal efficiencies of DD, RK, CN, TK and NK were 91.8%, 65.0%, 35.5%, 69.2%, and 69.3%, respectively. The highest BPA removal efficiency was found at DD. Hence, the treatment process of DD (activated Sludge with Nutrients Removal) seems to be the best for BPA removal in this event.

## 4.2 Comparison of BPA Concentrations and Removal Efficiencies in WWTPs in Bangkok during the Three Sampling Events

The concentrations of BPA in the influents and effluents of the five WWTPs in Bangkok during the three sampling events are summarized in Table 4.5 and Figures 4.38-4.39. BPA were not detected in any influent and effluent samples of the seven WWTPs in April 2013 sampling event.

**Table 4.5** BPA Concentrations in WWTPs in Bangkok during the Three Sampling Events

| WWTPs | Samples | Sampling Events | | |
|---|---|---|---|---|
| | | **Oct.** | **Dec.** | **Feb.** |
| **DD** | Inf. (ng/L) | 250.0 | 280.4 | 473.9 |
| | Eff. (ng/L) | 128.5 | 82.1 | 38.7 |
| | RE (%) | 48.6 | 70.7 | 91.8 |
| **RK** | Inf. (ng/L) | 224.0 | 247.5 | 219.3 |
| | Eff. (ng/L) | 270.5 | 111.3 | 76.8 |
| | RE (%) | - | 55.0 | 65.0 |
| **CN** | Inf. (ng/L) | 128.5 | 278.3 | 152.4 |
| | Eff. (ng/L) | 219.0 | 74.5 | 98.4 |
| | RE (%) | - | 73.2 | 35.5 |
| **TK** | Inf. (ng/L) | 403.0 | 559.3 | 231.6 |
| | Eff. (ng/L) | 79.0 | 51.8 | 71.4 |
| | RE (%) | 80.4 | 90.7 | 69.2 |
| **NK** | Inf. (ng/L) | 606.0 | 254.3 | 429.5 |
| | Eff. (ng/L) | 135.3 | 89.1 | 131.9 |
| | RE (%) | 77.7 | 64.9 | 69.3 |

Note: Sp.point = Sampling Point, TK = Thungkru, NK= Nong Khaem, RK = Rattanakosin, SP = Si Phraya, DD = Din Daeng, CC = Chatuchak, CN = Chong Non Si, Inf. = influent, Eff. = effluent, ND = not detected, * SPE was not used and BPA was detected by only using HPLC/UV-VIS (BPA values are lower than 2 mg/L).

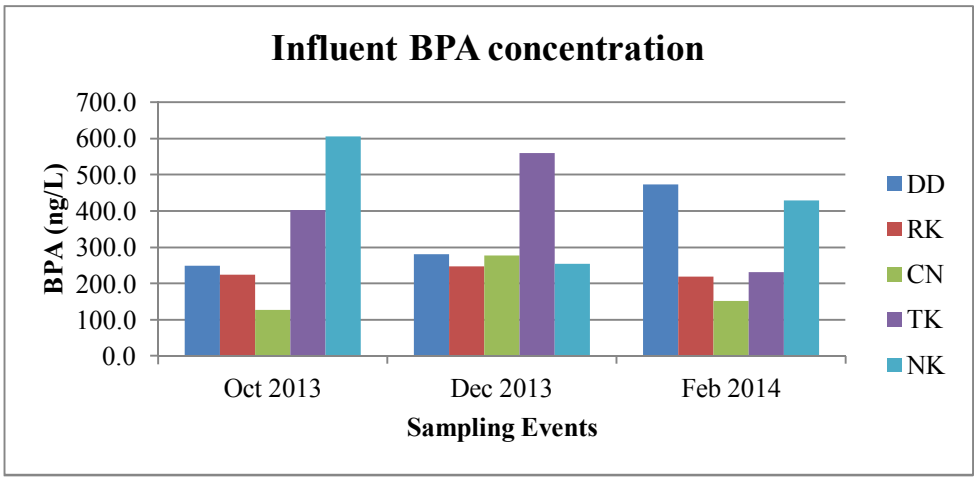



**Fig 4.38** Average influent BPA concentrations in the five WWTPs during the three sampling events

As shown in Table 4.5 and Figure 4.38, the BPA concentrations in the influents of five WWTPs during three sampling events (October and December 2013, and February 2014) ranged between 128.5 ng/L and 606.0 ng/L. During the three sampling events, WWTP having the highest influent BPA concentration was not the same.

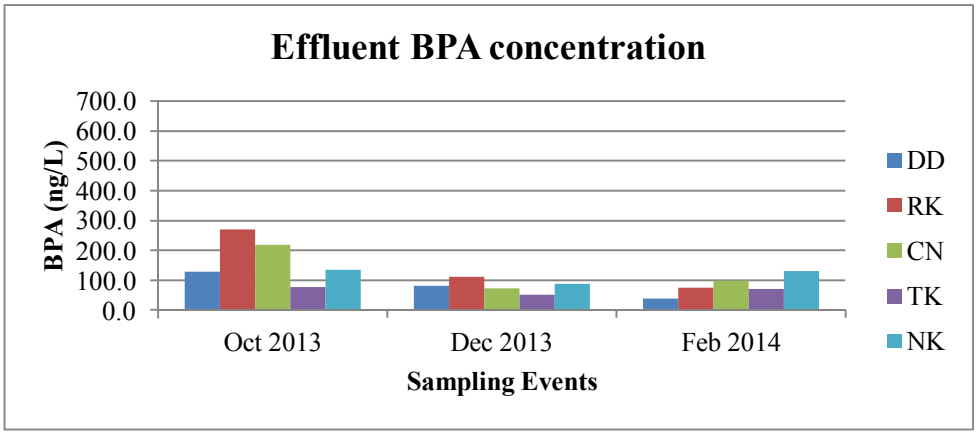



**Fig 4.39** Average effluent BPA concentrations in the five WWTPs during the three sampling events

As shown in Table 4.5 and Figure 4.39, the BPA concentrations in the effluents of five WWTPs during three sampling events (October and December 2013, and February 2014) ranged between 38.7 ng/L and 270.5 ng/L.

**BPA Removal Efficiency of the five WWTPs during three sampling events**

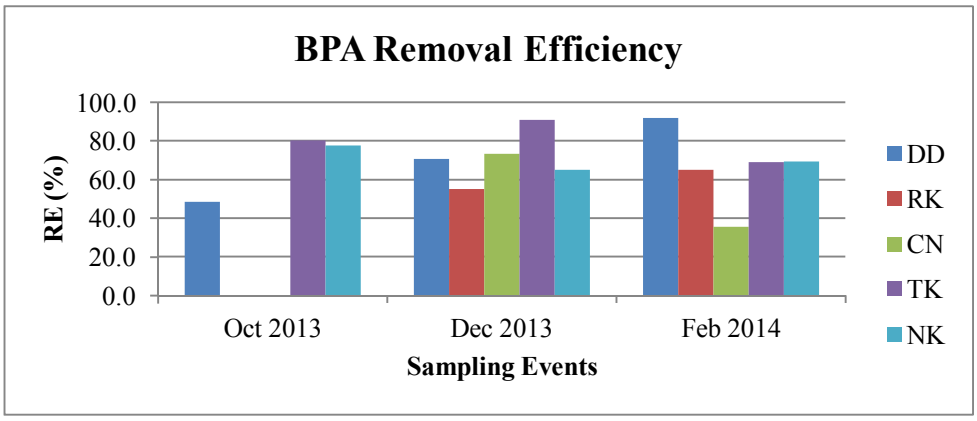



**Figure 4.40** BPA Removal Efficiency of the WWTPs during three sampling events

BPA removal efficiencies of the five WWTPs during three sampling events are shown in Fig 4.40. Even though these WWTPs are not designed to remove BPA from wastewater, the effluent BPA concentrations of most of the five WWTPs in three sampling events were lower than the influent levels. TK had the highest removal efficiency in October 2013 (80.4%) and December 2013 (90.7%) and the third highest in February 2014 (69.2%). DD had the highest removal efficiency in February 2014. The treatment process employed at TK and DD were vertical loop reactor activated sludge process and activated sludge with nutrients removal, respectively. Thus, these processes seem to be good for BPA degradation.

## 4.3 ANOVA Analysis

Three samples each were taken from the influents and effluents of all the WWTPs and there were three replications of BPA analysis for each sample in all the sampling events. The experimental data were analyzed using two-way ANOVA with replication to find the difference due to WWTPs and the time of sampling events. A value of $P < 0.05$ was considered statistically significant. The null hypothesis was no statistically significant difference among BPA concentrations for different type of plants and sampling event timings. The results of the ANOVA analysis for influent and effluent concentrations are shown in Table 4.6 and Table 4.7, respectively.

**Influent Concentrations**

Based on the ANOVA results for influent BPA concentrations (Table A1), F = 3.87 and 7.09 for Samples (sampling events) and Columns (WWTPs), respectively. With a critical value of p = 0.05, the critical F value = 3.32 and 2.69 for Samples (sampling events) and Columns (WWTPs), respectively. Thus, F statistic of sampling events and WWTPs are higher than the F critical values. Hence, there are the differences in influent BPA concentrations between the sampling events and WWTPs' type (size, location, population served, processes, etc.). Therefore, it implies to reject the null hypothesis for influent BPA concentrations.

It can be seen that according to the ANOVA results shown above, the differences between influent BPA concentrations in the five WWTPs during three sampling events were statistically significant. However, the correlation technique could not be used because the data was not enough to evaluate the relationships between the various parameters for individual plants for each sampling event.

Based on the meteorological conditions during the three sampling events, total amount of rainfall in October 2013 was 368.5 mm while there was no rainfall in December 2013 and February 2014. In December 2013, influent BPA concentrations in four of the five WWTPs (except NK) were higher than in October 2013. One of the reasons could be that the rainfall during October 2013 diluted BPA concentrations in the influent wastewater. On the other hand, the higher influent concentration in the influent of NK during October 2013 as compared to December 2013 could possibly be explained by the fact that the Nong Khaem Solid Waste Disposal Center, where the solid waste from the surrounding municipal area is collected, is very near to NK. Thus, the runoff from this facility which may have the residual BPA is also treated together with influent wastewater at NK. Therefore, the influent BPA concentrations of NK are at highest levels, especially in rainy season. In February 2014, influent BPA concentrations in three WWTPs (RK, CN and TK) were lower than in December 2013. There was no rainfall during these two sampling events, however the average temperature of the wastewater during February 2014 (28.3 $^{o}$C) was more than 2$^{o}$C higher than in December 2013(26.7 $^{o}$C). Also, influent BPA concentrations in RK, TK and NK during February 2014 were lower than in October 2013.

Based on the population served by the five WWTPs and the average influent BPA concentrations, RK (the smallest WWTP) and TK (the second smallest plant) had the high BPA concentrations. One of the reasons could be that the people who live around these two WWTPs use the BPA containing products more than those living in other areas.

**Effluent Concentrations**

Based on the ANOVA results for effluent BPA concentrations (Table A2), F = 21.72 and 1.17 for Sample (sampling events) and Columns (WWTPs), respectively. With a critical value of p = 0.05, the critical F value = 3.32 and 2.69 for Samples (sampling events) and Columns (WWTPs), respectively. F statistic of sampling events is higher than the critical values. Hence, there is statistically significant difference in effluent BPA concentrations during the three sampling events. On the other hand, F statistic of WWTPs is smaller than the F critical value. There are no statistically significant differences between the effluent BPA concentrations of the five WWTPs. Therefore, the null hypothesis for effluent BPA concentrations is true.

The correlation technique was used to evaluate the relationships between the various parameters and BPA concentrations in the effluent for each sampling event (Table 4.7 – 4.9).

**Table 4.7** Correlation between effluent BPA concentrations and conventional parameters in October 2013

| | *DO* | *pH* | *TS* | *TDS* | *TSS* | *Temp.* | *BOD5* | *EC* | *BPA* |
|---|---|---|---|---|---|---|---|---|---|
| DO | 1 | | | | | | | | |
| pH | 0.8297 | 1 | | | | | | | |
| TS | -0.9424 | -0.7498 | 1 | | | | | | |
| TDS | -0.3205 | 0.1490 | 0.5140 | 1 | | | | | |
| TSS | 0.1318 | -0.4314 | -0.2120 | -0.7590 | 1 | | | | |
| Temp. | -0.0287 | 0.4738 | 0.0963 | 0.8276 | -0.7886 | 1 | | | |
| BOD5 | -0.6626 | -0.8860 | 0.7026 | -0.1405 | 0.4095 | -0.6270 | 1 | | |
| EC | -0.6386 | -0.1962 | 0.7959 | 0.8955 | -0.7119 | 0.5739 | 0.2313 | 1 | |
| BPA | -0.0763 | -0.4505 | -0.1564 | -0.6620 | 0.7982 | -0.4537 | 0.1498 | -0.6465 | 1 |

As shown in the Table 4.8, the correlation coefficient (R) ranged between -1.0 to +1.0. Closer is the R value to +1 or -1, the more closely are the two variables are related. The effluent BPA concentration appeared to be significantly correlated to effluent TSS (R = 0.7982), and moderately correlated to effluent EC (R = - 0.6620) and TDS levels (R = - 0.6465). It was also observed during the October 2013 sampling that samples with the high TSS concentrations and low EC and TDS levels had high BPA concentration.

**Table 4.8** Correlation between effluent BPA concentrations and conventional parameters in December 2013

| | *DO* | *pH* | *TS* | *TDS* | *TSS* | *Temp.* | *BOD5* | *EC* | *BPA* |
|---|---|---|---|---|---|---|---|---|---|
| DO | 1 | | | | | | | | |
| pH | 0.7606 | 1 | | | | | | | |
| TS | -0.0399 | -0.6173 | 1 | | | | | | |
| TDS | 0.0139 | -0.6080 | 0.9880 | 1 | | | | | |
| TSS | 0.0222 | 0.0602 | -0.2913 | -0.1810 | 1 | | | | |
| Temp. | 0.1281 | 0.2410 | -0.5170 | -0.4610 | -0.1144 | 1 | | | |
| BOD5 | -0.5635 | -0.3810 | -0.3510 | -0.3142 | 0.0516 | 0.7222 | 1 | | |
| EC | -0.0127 | -0.5915 | 0.9965 | 0.9801 | -0.3614 | -0.4707 | -0.3430 | 1 | |
| BPA | -0.3245 | 0.3168 | -0.6556 | -0.7634 | -0.3131 | 0.1126 | 0.1512 | -0.6345 | 1 |

As shown in Table 4.9, the effluent BPA concentrations appeared to be significantly correlated to effluent TDS (R = - 0.7634), and moderately correlated to effluent TS (R = - 0.6556), and EC levels (R = - 0.6345). It was also observed during the December 2013 sampling that samples with the low TDS, TS and EC levels had high BPA concentration.

**Table 4.9** Correlation between effluent BPA concentrations and conventional parameters in February 2014

| | *DO* | *pH* | *TS* | *TDS* | *TSS* | *Temp.* | *BOD5* | *EC* | *BPA* |
|---|---|---|---|---|---|---|---|---|---|
| DO | 1 | | | | | | | | |
| pH | 0.0634 | 1 | | | | | | | |
| TS | 0.5819 | -0.5482 | 1 | | | | | | |
| TDS | 0.6029 | -0.5189 | 0.9994 | 1 | | | | | |
| TSS | 0.5907 | -0.4123 | 0.9852 | 0.9892 | 1 | | | | |
| Temp. | -0.3116 | 0.3900 | -0.8196 | -0.8193 | -0.8429 | 1 | | | |
| BOD5 | -0.7056 | 0.1102 | -0.7102 | -0.7234 | -0.7366 | 0.8289 | 1 | | |
| EC | 0.9438 | -0.0368 | 0.7780 | 0.7971 | 0.8057 | -0.5890 | -0.8418 | 1 | |
| BPA | -0.4789 | -0.5875 | 0.1302 | 0.1058 | 0.0679 | -0.5042 | -0.1888 | -0.2995 | 1 |

As shown in Table 4.10, the effluent BPA concentrations during the February 2014 sampling appeared to be only moderately correlated to effluent pH (R = - 0.5875). This time it was observed that samples with the low pH had high BPA concentration.

Even though there are differences between the correlation of the various parameters and BPA concentrations in the effluent for each sampling event, it can be noted that during the three sampling events, samples with the high TSS concentration and low levels of EC, TDS, TS and pH had high BPA concentration. According to the results of correlation between effluent BPA concentrations and conventional parameters of all three samplings, it was observed that the effluent BPA concentrations were negatively correlated with EC levels.

## 4.4 Policy for BPA Regulation in Thailand

At present, there is no environmental policy in Thailand to control the levels of BPA residues in aquatic environments. However, there is regulation to control BPA content used in the food packaging. In Thailand, food packaging is regulated by the Food Act, B.E. 2522 (1979), which prohibits the production, importation, and distribution of impure, adulterated, substandard, and otherwise banned foods. Notably, the Food Act defines "impure" foods to include "food in

containers made of materials which are likely to be dangerous to health." The Thai Food and Drug Administration (FDA), a department in the Ministry of Public Health, has specific responsibility for regulating food packaging materials. This includes reviewing and granting approvals for packaging materials. Under Ministerial Notification No. 92, B.E. 2528 (1985), a variety of requirements are specified with respect to food containers. The notification requires that food containers must be clean and free of germs, not emit any heavy metals or other substances that contaminate food at levels that may be harmful to health, and not emit any color to food. Other requirements include specific standards for food containers made of plastic, and a ban on reusing certain types of food containers (Clark and Nielsen 2013).

In 2005, the Ministry of Public Health, Thailand amended the previous Regulation for the Qualities or Standard of Plastic Containers, Usage of Plastic Containers, and Prohibition of Usage of Articles as Food Containers (the Notification of the Ministry of Public Health No. 111 B.E. 2531 (1988)) to the new notification of the Ministry of Public Health No. 295 B.E. 2548 (2005). The newly established standard (maximum allowed level) for BPA (included phenol and p-t-butylphenol) is 500 mg/kg in polycarbonate plastic containers and 2.5 $mg/dm^3$ for the BPA leached from various types of polycarbonate food containers (Ministry of Public Health, Thailand, 1988 and 2005).

As shown above, the Government of Thailand tried to ban the usage of BPA in the production of plastic especially in the baby bottles. However, this has not been fully successful. On the other hand, BPA was successfully banned in the production of cosmetics. Five years ago, a new regulation came as the Notification of the Ministry of Public Health B.E. 2551 (2009). According to this regulation, BPA is no. 1170 in the list of 1242 substances which are prohibited to be the ingredients that must form part of cosmetic products except under the conditions laid down. This Notification is under the Cosmetic Act B.E. 2535 (1992). Any products found to contain prohibited substances, e.g. BPA will be banned and confiscated. Consequently, the person responsible for placing such products on the market will be charged with distribution of hazardous products (Ministry of Public Health, Thailand, 2009).

Pollutant Release and Transfer Register System (PRTR) is the system to collect and disseminate information on environmental releases and transfers of toxic chemicals from industrial and other facilities. They were established in several countries after the 1984 Bhopal Disaster, and the 1992 United Nations Conference on Environment and Development in Rio de Janeiro, which affirmed the "right-to-know" of communities and workers about toxics chemicals and other substances of concern. In many countries industrial facilities need a permit to operate processes that are causing environmental pressures. Authorities have to balance the interests of different actors when issuing such permits and will reflect this balance in the conditions and requirements put down in the permit. Companies and civilians living near to the facilities generally have quite different levels of understanding and information on the processes and the environmental impact. In a democratic context however a level playing field for all actors involved in permitting decisions is paramount to acceptance of the decisions. Against this background, the Aarhus Convention requires the parties to this convention to set up PRTRs as a tool to provide the general public this type of information UNECE (2003). Protocol on Pollutant Release and Transfer Registers. This system may also include estimates of releases from diffuse sources, such as agriculture and transport and from the end use of products.

A PRTR can be an important tool in the total environmental policy of a government encouraging reporters to reduce pollution and engendering broad public support for government environmental policies. Indeed, governments may wish to set forth long-term national environmental goals to promote sustainable development and then use PRTR as an important tool to examine objectively how well these goals are being met.

On 8 July 2010, Pollution Control Department (PCD) in cooperation with Department of Industrial Works (DIW) and Japan International Cooperation Agency (JICA) had a signing ceremony for the Record of Discussion to kick off a technical cooperation project "The Development of Basic Schemes for Pollutant Release and Transfer Register System (PRTR) in the Kingdom of Thailand". The main objective of this project is to develop a model for PRTR system in Thailand. PRTR encourages industry, business to reduce releases and transfers of waste and to adopt cleaner production techniques. In addition, PRTR provides information for governments to

develop plans for pollution prevention, control measurement and for chemicals management in a sound manner. According to this system, any companies must declare to the government if they import/export BPA as a chemical or the products containing BPA more than 1000 ton/year (PCD, 2010 and UNECE, 2014).

There are 3 concerned government organizations in Thailand, DIW, IEAT and PCD, who have joined this project. According to the signed contract of the technical cooperation, JICA was supposed to provide a technical guidance to the Thai counterparts during the 4 years (March 2011 to February 2014) pertaining to the implementation of the project. Rayong Province was chosen for launching a pilot trial, since the Maptaput Industrial Estate and the nearby area are currently known as the major sources of industrial pollution. Other sources of pollution such as agriculture and exhaust from the vehicles were also to be included in the study.

In 2012, the General Director, Department of Foreign Trade in the Ministry of Commerce, Thailand - Mr. Surasak Riangkrul issued a warning that the European Union (EU) has banned the items exported by the Thai entrepreneur because of use of BPA in those products. However, to date there is still no regulation to ban the use of BPA in the goods produced either for export purpose or for consumption within Thailand (Logistics Digest, 2012).

Wastewater effluents containing BPA can be a source of contamination of the aquatic environment of receiving water bodies leading to contaminated aquatic organisms. Fishes are at the top of the aquatic ecological food chain as well as at the top of the consumers 'food products' list. Hence, they are also at the top of the sources of BPA contamination with bioaccumulations in their bodies. Although, European Food Safety Authority (EFSA) had completed its full risk assessment of BPA in 2006 and set a Tolerable Daily Intake (TDI) of 0.05 milligrams/kilogram of body weight (mg/kg bw/day) for BPA (EFSA, 2014), there is no such limit set for BPA in Thailand yet. Thus, Thailand does not have either the policy or the regulation about BPA, not only for the packaging standard (maximum allowable limit of BPA in the packaging materials for the food items) but also for water quality standard. Hence, there is a potential risk of exceeding TDI of BPA and bioaccumulation for people living in Thailand.

**Table 4.10** History of the regulations established in Thailand during the past 35 years about the use of hazardous substances, such as BPA

| Year | Regulation | Description |
|---|---|---|
| 1979 | Food Act, B.E. 2522 (1979) | Prohibits the production, importation, and distribution of impure, adulterated, substandard, and otherwise banned foods. Notably, the Food Act defines "impure" foods to include "food in containers made of materials which are likely to be dangerous to health." |
| 1985 | Ministerial Notification No. 92, B.E. 2528 (1985) | Food containers must be clean and free of germs, not emit any heavy metals or other substances that contaminate food at levels that may be harmful to health, and not emit any color to food. |
| 1988 | Notification of the Ministry of Public Health No. 111 B.E. 2531 (1988) | “Qualities or Standards of Plastic Containers, Usage of Plastic Containers, and Prohibition of Usage of Articles as Food Containers” |
| 2005 | Notification of the Ministry of Public Health No. 295 B.E. 2548 (2005). | This notification was amended from Notification of the Ministry of Public Health No. 111 B.E. 2531 (1988). The newly established standard (maximum allowed level) for BPA (included phenol and p-t-butylphenol) is 500 mg/kg in polycarbonate plastic containers and 2.5 $mg/dm^3$ for the BPA leached from various types of polycarbonate food containers. |

**Table 4.10** History of the regulations established in Thailand during the past 35 years about the use of hazardous substances, such as BPA (cont)

| Year | Regulation | Description |
|---|---|---|
| 2009 | Notification of the Ministry of Public Health B.E. 2551 (2009). | This Notification is under the Cosmetic Act B.E. 2535 (1992). There are five listings of designated cosmetic ingredients, namely prohibited substances, specially controlled substances, controlled substances, colorants and preservatives. BPA is no. 1170 in the list of 1242 substances which are prohibited to be the ingredients that must form part of cosmetic products except under the conditions laid down. |
| 2010 | The Development of Basic Schemes for Pollutant Release and Transfer Register System (PRTR) in the Kingdom of Thailand | The main objective of this project is to develop a model for PRTR system in Thailand. According to this system, any companies must declare to the government if they import/export BPA as a chemical or the products containing BPA more than 1,000 ton/year. |

# CHAPTER V
# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Present study was aimed at investigating the situation of occurrence of Bisphenol A (BPA) in seven municipal wastewater treatment plants in Bangkok, Thailand. Samples were collected from influents and effluents of the WWTPs during the four sampling events – April, October, December 2013, and February 2014. All samples were prepared for the analyses. Some conventional parameters (temperature, DO, pH, EC, TS, TDS, TSS, COD and $BOD_5$) were determined. Measurements of Bisphenol A (BPA) concentrations in the samples were carried out by High Performance Liquid Chromatography (HPLC) with or without the solid phase extraction (SPE).

In April 2013, investigations on BPA concentrations in the influents and the effluents samples in seven WWTPs were conducted by using High Performance Liquid Chromatography (HPLC) equipped with UV detector. BPA was not detected in any sample during this sampling. This could be due to the reason that the concentrations in the samples were lower than the lowest detection limit (LDL) of the equipment (2 mg/L). Therefore, it appeared that BPA levels in all the WWTPs' influents and effluents were lower than 2 mg/L. Another possible reason of no detection could have been due to the fact that solid phase extraction (SPE) was not carried out to concentrate the samples before the HPLC analyses. Moreover, HPLC/UV-VIS technique might not be appropriate for this study as the sensitivity of UV detection is lower than the fluorescence detection.

After the first sampling event (April 2013), only five out of seven full-scale WWTTPs in Bangkok region were selected for the further investigations: Rattanakosin (RK), Chong Non Si (CN), Din Daeng (DD), Nong Khaem (NK), and Thungkru (TK). Moreover, an alternative method of BPA determination was employed during the three more sampling events between October 2013 and February

2014, by doing the solid phase extraction (SPE) and using HPLC equipped with fluorescence detector.

Based on the results of three samplings events (October, December 2013, and February 2014), The WWTPs influent and effluents BPA concentrations ranged between 128.5 ng/L and 606.0 ng/L; and 38.7 ng/L and 270.5 ng/L, respectively. In December 2013, influent BPA concentrations in four of the five WWTPs (except NK) were higher than in October 2013. One of the reasons could be that the rainfall during October 2013 diluted BPA concentrations in the influent wastewater. Based on the population served by the five WWTPs and the average influent BPA concentrations, RK (the smallest WWTP) and TK (the second smallest plant) had the high BPA concentrations. One of the reasons could be that the people who live around these two WWTPs use the BPA containing products more than those living in other areas.

Even though these WWTPs are not designed to remove BPA from wastewater, the effluent BPA concentrations of most of the five WWTPs in three sampling events were lower than the influent levels. TK had the highest removal efficiency in October 2013 (80.4%) and December 2013 (90.7%) and the second highest in February 2014 (69.2%). DD had the highest removal efficiency in February 2014. The treatment processes employed at TK and DD were vertical loop reactor activated sludge process and activated sludge with nutrients removal, respectively. Thus, these processes seem to be good for BPA degradation.

The experimental data were analyzed using two-way ANOVA with replication to find the difference due to WWTPs and the time of sampling events. The correlation technique was used to evaluate the relationships between the various parameters and BPA concentrations.

ANOVA results showed that the differences between influent BPA concentrations in the five WWTPs during three sampling events were statistically significant. However, the correlation technique could not be used because the data was not enough to evaluate the relationships between the various parameters for individual plants for each sampling event.

Based on the ANOVA results, it appeared that there were statistically significant differences in effluent BPA concentrations during the three sampling events. However, the effluent BPA concentrations of the five WWTPs were not

significantly different. Based on the correlation between effluent BPA concentrations and conventional parameters in each sampling event, it was observed that during the October 2013 investigation, samples with the high TSS concentrations and low EC and TDS levels had high BPA concentrations. On the other hand, in December 2013 sampling event, samples with the low TDS, TS and EC levels had high BPA concentrations. Subsequently, during the February 2014 investigation, samples with the low pH appeared to have high BPA concentrations.

Due to the daily use of these products, the high concentration of BPA was observed in municipal wastewater. The varying BPA concentrations are released from BPA containing products. Hence, the BPA levels in the influents depend on the WWTPs location and the season of the year. Based on the results of influent and effluent BPA concentrations, it appeared that there is a potential risk of exceeding Tolerable Daily Intake (TDI) limit of BPA and bioaccumulation for people living in Thailand.

Many of the adverse effects that BPA has on human health were studied over the past several decades. Argument exists regarding what concentrations of BPA are dangerous to humans or wildlife, but it is clear that BPA poses potential risks and several countries have considered regulating it. However, there is no environmental policy in Thailand to control the levels of BPA residues in aquatic environments at present. Currently, the only regulation is to control BPA content used in the food packaging (the maximum allowed level of BPA, including phenol and p-t-butylphenol, is 500 mg/kg in polycarbonate plastic containers and 2.5 $mg/dm^3$ for the BPA leached from various types of polycarbonate food containers). Also, BPA has been banned in the production of cosmetics.

The results of this study could be helpful in identifying the knowledge gaps and research needs on the following;

1) the occurrence and levels of BPA residues in the influents and effluents of wastewater treatment plants and receiving water in Bangkok area.

2) the degradation of BPA correlated to the treatment process employed in the five wastewater treatment plants.

3) Thai policy regarding the control of BPA residues in aquatic environments and to give recommendation for the development of Bisphenol A (BPA) standard in wastewater effluents in Thailand.

The outcome of such a study may contribute in the development of National Implementation Plan for the management and regulation of one of the very toxic industrial contaminants (BPA) in Thai aquatic environments.

## 5.2 Recommendations

- More research should be carried out to evaluate the influence of the each step in the different wastewater treatment processes employed in the wastewater treatment plants on the removal efficiencies for BPA.
- Further research work is also needed to be carried out for investigating BPA residues in the effluents from the industries manufacturing BPA containing products, metropolitan waterworks authority's drinking water treatment plants, as well as tap water.

Until now, there are no standards for endocrine disrupting compounds residues including BPA in WWTPs' effluents and surface water in Thailand. Hence, there is a critical need for regulations for emerging endocrine disrupting compounds residues in aquatic environments Thailand.

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# APPENDIX

# Results of ANOVA Analysis for influent and effluent concentrations during three sampling events

**Table A.1 Influent BPA concentrations for ANOVA analysis**

| Events | BPA concentration (µg/l) | | | | |
|---|---|---|---|---|---|
| | DD | RK | CN | TK | NK |
| Oct. | 0.235 | 0.226 | 0.129 | 0.438 | 0.606 |
| | 0.246 | 0.222 | 0.110 | 0.368 | 2.252 |
| | 0.269 | 0.549 | 0.147 | 0.403 | 1.429 |
| Dec. | 0.280 | 0.285 | 0.321 | 0.559 | 0.388 |
| | 0.337 | 0.247 | 0.272 | 0.576 | 0.214 |
| | 0.224 | 0.210 | 0.242 | 0.543 | 0.160 |
| Feb. | 0.595 | 0.264 | 0.152 | 0.232 | 0.430 |
| | 0.471 | 0.203 | 0.168 | 0.232 | 0.437 |
| | 0.355 | 0.191 | 0.137 | 0.232 | 0.422 |

**Table A.2 Effluent BPA concentrations for ANOVA analysis**

| Events | BPA concentration (µg/l) | | | | |
|---|---|---|---|---|---|
| | DD | RK | CN | TK | NK |
| Oct. | 0.126 | 0.271 | 0.230 | 0.339 | 0.133 |
| | 0.222 | 0.257 | 0.219 | 0.599 | 0.135 |
| | 0.131 | 0.284 | 0.208 | 0.079 | 0.138 |
| Dec. | 0.082 | 0.111 | 0.072 | 0.052 | 0.086 |
| | 0.091 | 0.120 | 0.077 | 0.052 | 0.089 |
| | 0.073 | 0.103 | 0.075 | 0.052 | 0.092 |
| Feb. | 0.041 | 0.077 | 0.088 | 0.068 | 0.130 |
| | 0.036 | 0.047 | 0.098 | 0.072 | 0.102 |
| | 0.039 | 0.076 | 0.109 | 0.074 | 0.134 |

**Table A.3 ANOVA: two-factor with replication result for influent BPA concentrations**

Anova: Two-Factor With Replication

| SUMMARY | DD | RK | CN | TK | NK | Total |
|---|---|---|---|---|---|---|
| *Oct.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 0.75 | 0.997 | 0.3855 | 1.209 | 4.287 | 7.6285 |
| Average | 0.25 | 0.332333 | 0.1285 | 0.403 | 1.429 | 0.508567 |
| Variance | 0.000301 | 0.035212 | 0.000342 | 0.001225 | 0.677329 | 0.337924 |
| *Dec.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 0.841305 | 0.74247 | 0.83492 | 1.67796 | 0.76294 | 4.859595 |
| Average | 0.280435 | 0.24749 | 0.278307 | 0.55932 | 0.254313 | 0.323973 |
| Variance | 0.003184 | 0.00144 | 0.001571 | 0.00027 | 0.01415 | 0.01796 |
| *Feb.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 1.42162 | 0.657865 | 0.45715 | 0.694935 | 1.28854 | 4.52011 |
| Average | 0.473873 | 0.219288 | 0.152383 | 0.231645 | 0.429513 | 0.301341 |
| Variance | 0.014469 | 0.001546 | 0.00023 | 0 | 6.37E-05 | 0.019467 |
| *Total* | | | | | | |
| Count | 9 | 9 | 9 | 9 | 9 | |
| Sum | 3.012925 | 2.397335 | 1.67757 | 3.581895 | 6.33848 | |
| Average | 0.334769 | 0.266371 | 0.186397 | 0.397988 | 0.704276 | |
| Variance | 0.015546 | 0.012146 | 0.005394 | 0.02052 | 0.47408 | |

ANOVA

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Sample | 0.387648 | 2 | 0.193824 | 3.869599 | 0.031984 | 3.31583 |
| Columns | 1.421074 | 4 | 0.355269 | 7.092753 | 0.000382 | 2.689628 |
| Interaction | 2.331184 | 8 | 0.291398 | 5.817612 | 0.000164 | 2.266163 |
| Within | 1.502668 | 30 | 0.050089 | | | |
| Total | 5.642575 | 44 | | | | |

**Table A.4 ANOVA: two-factor with replication result for effluent BPA concentrations**

Anova: Two-Factor With Replication

| SUMMARY | DD | RK | CN | TK | NK | Total |
|---|---|---|---|---|---|---|
| *Oct.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 0.479 | 0.8115 | 0.657 | 1.017 | 0.406 | 3.3705 |
| Average | 0.159667 | 0.2705 | 0.219 | 0.339 | 0.135333 | 0.2247 |
| Variance | 0.00292 | 0.000182 | 0.000121 | 0.0676 | 6.33E-06 | 0.015992 |
| *Dec.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 0.246345 | 0.33378 | 0.223575 | 0.15534 | 0.26743 | 1.22647 |
| Average | 0.082115 | 0.11126 | 0.074525 | 0.05178 | 0.089143 | 0.081765 |
| Variance | 7.79E-05 | 7.55E-05 | 6.79E-06 | 0 | 9.34E-06 | 0.000426 |
| *Feb.* | | | | | | |
| Count | 3 | 3 | 3 | 3 | 3 | 15 |
| Sum | 0.11607 | 0.200377 | 0.295053 | 0.214165 | 0.365648 | 1.191313 |
| Average | 0.03869 | 0.066792 | 0.098351 | 0.071388 | 0.121883 | 0.079421 |
| Variance | 6.38E-06 | 0.000302 | 0.000109 | 1.15E-05 | 0.000309 | 0.000972 |
| *Total* | | | | | | |
| Count | 9 | 9 | 9 | 9 | 9 | |
| Sum | 0.841415 | 1.345657 | 1.175628 | 1.386505 | 1.039078 | |
| Average | 0.093491 | 0.149517 | 0.130625 | 0.154056 | 0.115453 | |
| Variance | 0.003568 | 0.008744 | 0.004559 | 0.036215 | 0.000504 | |

ANOVA

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Sample | 0.20771 | 2 | 0.103855 | 21.7157 | 1.47E-06 | 3.31583 |
| Columns | 0.022456 | 4 | 0.005614 | 1.17389 | 0.342104 | 2.689628 |
| Interaction | 0.077536 | 8 | 0.009692 | 2.026556 | 0.077233 | 2.266163 |
| Within | 0.143475 | 30 | 0.004782 | | | |
| Total | 0.451177 | 44 | | | | |

# BIOGRAPHY


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|---|---|
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1. **I. Pookpoosa**, R. Jindal, D. Morknoy and K. Tantrakarnapa (2014). "Occurrence of Bisphenol A in Some Municipal Wastewater Treatment Plants' Effluents in Bangkok Region". International Conference on Biological, Chemical and Environmental Sciences (BCES-2014), 21 - 22, January 2014, Patong Beach, Phuket, Thailand.