EFFECTS OF WASTEWATER COMPONENTS TO PFOS AND PFOA MEASUREMENT EFFICIENCY BY METHOD OF SOLID PHASE EXTRACTION COUPLE WITH LC-MS/MS

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ABSTRACT

This research aims to study the effects of wastewater components, which were total organic carbon (TOC), total Kjeldalh nitrogen (TKN), and total dissolved solids (TDS), on the measurement technique of Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) by using synthetic and real industrial wastewater and by investigating the occurrence and removal efficiency of PFOS and PFOA in industrial wastewater. In the study on synthetic wastewater, TKN and TDS decreased the recovery ratio of measurement for both PFOS and PFOA. In the study on real industrial wastewater, negative correlations between PFOS, PFOA and TKN, TDS were found at a high concentration of PFOS and at a low concentration of PFOA. PFOS and PFOA were detected in wastewater from air conditioning, coating, electronics, glass, food, plastics and textile industries in the range of <LOQ – 997.56 ng/L and <LOQ – 6,355.66 ng/L, respectively. Moreover, high concentrations of PFOS and PFOA were found in the central wastewater treatment plants at an average of 329.91 ng/L and 185.66 ng/L, respectively. The concentrations of PFOS and PFOA in the treated wastewater were higher than in the influent. This indicated that the conventional wastewater treatment processes such as activated sludge process and sequencing batch reactor process were ineffective at removing PFOS and PFOA.

KEY WORDS: PFOS / PFOA / INDUSTRIAL WASTEWATER / SOLID PHASE EXTRACTION / LC-MS/MS

111 pages

ผลกระทบจากองค์ประกอบของน้ำเสียต่อประสิทธิภาพการตรวจวัด PFOS และ PFOA ด้วยวิธีการสกัดโดยใช้ของแข็งเป็นตัวดูดซับ (SPE) ผนวกกับเทคนิคการแยกชนิดและวิเคราะห์สารด้วยการวัดน้ำหนักโมเลกุลของสาร (LC-MS/MS)

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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยฉบับนี้ เพื่อศึกษาผลกระทบจากองค์ประกอบของน้ำเสีย ได้แก่ ค่าปริมาณอินทรีย์คาร์บอนทั้งหมด ค่าอินทรีย์ไนโตรเจนทั้งหมด และค่าของแข็งละลายทั้งหมด ต่อประสิทธิภาพการตรวจวัด PFOS และ PFOA โดยศึกษาจากน้ำเสียสังเคราะห์และน้ำเสียจริง และศึกษาการปนเปื้อนของ PFOS และ PFOA จากน้ำเสียอุตสาหกรรม รวมทั้งประสิทธิภาพการกำจัดของระบบบำบัดน้ำเสียส่วนกลางในเขตอุตสาหกรรม การศึกษาในน้ำเสียสังเคราะห์พบว่า ค่าอินทรีย์ไนโตรเจนทั้งหมด และค่าของแข็งละลายทั้งหมดมีผลทำให้ประสิทธิภาพการตรวจวัดปริมาณ PFOS และ PFOA ลดลง ส่วนการศึกษาในน้ำเสียอุตสาหกรรมพบว่า ค่าสหสัมพันธ์ระหว่างค่าอินทรีย์ไนโตรเจนทั้งหมดและค่าของแข็งละลายทั้งหมดกับปริมาณ PFOS และ PFOA มีค่าเป็นลบเมื่อ PFOS มีค่าความเข้มข้นสูง และ PFOA มีค่าความเข้มข้นต่ำ อุตสาหกรรมเครื่องปรับอากาศ เคลือบผิววัสดุ อิเล็คทรอนิกส์ กระจก อาหาร พลาสติกและสิ่งทอ ตรวจพบค่าการปนเปื้อน PFOS ในช่วง <LOQ ถึง 997.56 ng/L และ PFOA ในช่วง <LOQ ถึง 6,355.66 ng/L โดยตรวจพบค่าการปนเปื้อนของ PFOS และ PFOA จากน้ำเสียที่ผ่านกระบวนการบำบัดหรือน้ำทิ้ง สูงกว่าน้ำเสียก่อนผ่านกระบวนการบำบัด ซึ่งมีค่าเฉลี่ยของ PFOS ที่ 329.91 ng/L และ PFOA ที่ 185.66 ng/L แสดงให้เห็นว่า ระบบบำบัดน้ำเสียแบบดั้งเดิม เช่น ระบบเติมอากาศและระบบเอสบีอาร์ไม่มีประสิทธิภาพเพียงพอต่อการกำจัด PFOS และ PFOA

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CHAPTER I
INTRODUCTION

1.1 Background

Over the past few decades, The World's dramatic economic growth has produced new environmental challenges to the industrialize society. The developed and developing countries now face problems with air and water pollution issues, as we have more development that means the pollution will be increasing also. Water pollution is one of the most visible and persistent signs of our impact on the natural world. Deteriorated water quality is a consequence of wastewater discharge from various sources such as communities, agricultural and industrial areas. Many new pollutants such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are contaminated to our environment, although the hazard assessment of PFOS and PFOA have been established and improved for many years.

PFOS and PFOA are in a group of Perfluorinated compounds (PFCs) which are a family of fluorine-containing chemicals with unique properties to make materials stain and stick resistant. PFCs are heat stable, extremely resistant to degradation and environmental breakdown, and repel both water and oil (Dinglasan-Panlilio & Mabury, 2006, Lehmler, 2005, OECD, 2002). These properties are exploited in their numerous different applications, which include the manufacture of non-stick coatings for kitchenware, stain and water repellent treatments for carpets, furniture and clothing, paper coatings, surfactants, pesticide formulations, fire-fighting foams, cleaning products, floor polishes, shampoo and food packaging materials. Due to their resistance to photolysis, hydrolysis and biological breakdown (biodegradation), PFCs persist in the environment for long periods of time (years, decades).

The unique physical properties of perfluorinated chemicals that make them such good waterproofers and stain repellents mean that they can do not accumulate in fat, like many other persistent bioaccumulative chemicals, but in protein. This does not mean however, that they are more easily eliminated, and PFCs such as PFOS can therefore build up to high levels in our bodies and wildlife. The half-life of PFOS in human is in the region of 8.67 years and the level of PFCs in our bodies may never be completely removed over our lifetimes (Burris *et al.*, 2002).

PFOS, PFOA and other PFCs have been measured in human blood from countries across Europe, Asia and the USA (Yeung *et al.*, 2006). PFCs have also been found in umbilical cord blood. Studies of archived human blood samples have also shown increasing levels of PFCs (PFOS, PFOA) over time. PFCs, including PFOS and PFOA have also been found in human breast milk, although they do not seem to accumulate to the same extent as in serum, perhaps due to a preference for binding to protein rather than lipid (Jones *et al.*, 2003). Estimates of the half-lives of PFOS and PFOA in serum vary, but are reported to be in the region of 4-8 years (Lehmler, 2005, OECD, 2002, US EPA, 2003).

Recently, at its fourth meeting in May 2009, the Conference of the Parties (COP), by decisions SC-4/10 to SC-4/18, adopted amendments to Annexes A (elimination), B (restriction) and C (unintentional production) of the Stockholm Convention to list nine chemicals as persistent organic pollutants. Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F) were listed under Annex B with acceptable purposes and specific exemptions (decision SC-4/17) (Stockholm Convention on persistent organic pollutants (POPs), 2011).

1.2 Statement of problem

Direct emission or accidental escape of PFCs including PFOS and PFOA to the environment can occur during their manufacture and application to consumer articles (Stock *et al.*, 2004). An important source of PFCs into the environment is thought to be the discharge of wastewater from sewage treatment works, as the cleaning and care of surface-treated products (from clothing to carpets) by consumers and use in industrial processes are believed to release these compounds to municipal wastewater treatment systems (Higgins *et al.*, 2005). Effluents of municipal WWTPs were suspected as one important source of PFCs in water environment (Qiu, 2007).

The analytical method of PFCs has been developed for many years which purposed to improve the efficiency of measurement accuracy. Especially, the low concentration level of PFCs in water and wastewater sample which was analyzed in a unit of ng/L. Hence, the measurement technique is very important for PFCs analysis. To determine the efficiency of analytical method, internal standard or external standard was applied for the measurement processes and reported as a recovery ratio.

PFCs have been detected in surface waters - lakes (Boulanger *et al.*, 2004) and oceans (So *et al.*, 2004, Yamashita *et al.*, 2005) with the high recoveries more than 80% (So *et al.*, 2004) but for the wastewater found that the recoveries were variable in the range from 40-110%. The different of PFCs recovery from wastewater and surface water have been suspected in many researches. Characteristic of wastewater has more complicated composition than surface water such as organic compound, inorganic compound and element material, are known as matrix components. Nowadays, many researchers had been developed the analytical method for PFCs and this study was focused on the main constituents of wastewater, which was the organic contents (i.e. Carbon, Nitrogen and Total Dissolved Solid). And to get the constant concentration for each constituent, the synthetic wastewater was used in this experiment.

1.3 Objectives of the study wastewater components

1) To study effects of wastewater components to the measurement efficiency by method of solid phase extraction and LC-MS/MS by using synthetic wastewater.

2) To study the relation of wastewater components and measurement efficiency by method of solid phase extraction and LC-MS/MS in the real industrial wastewater.

3) To investigate the contamination of PFOS and PFOA in selected industrial wastewater and central wastewater treatment plant of industrial estates.

1.4 Scope of the study

This study was evaluated the dissolved PFOS and PFOA in synthetic wastewater and selected real industrial wastewater. The synthetic wastewater was varied on the main compositions such as carbon, nitrogen and total dissolved solid.

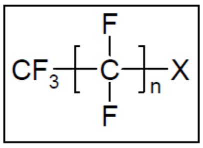
The real industrial wastewater was collected from central wastewater treatment plant and effluent pipe from selected industries. The analysis of dissolved PFOS and PFOA concentrations in samples were done by LC-MS/MS.

CHAPTER II
LITERATURE REVIEW

2.1 General review of PFOS and PFOA

2.1.1 Characteristic of PFOS and PFOA

Polyfluorinated alkylated substances (R-X) are compounds consisting of a hydrophobic alkyl chain, R, of varying length (typically C4 to C16) and a hydrophilic end group, X. The hydrophobic part may be fully $[R=F(CF_2)_n^-]$ or partially fluorinated. When fully fluorinated the molecules are also called perfluorinated substances. Their general structure is given in Figure 2.1.



$$CF_3 \left[-\overset{F}{\underset{F}{C}}- \right]_n X$$

Figure 2.1 General structure of perfluorinated alkylated substances (EFSA, 2008)

The hydrophilic end group can be neutral, or positively or negatively charged. The resulting compounds are non-ionic, cationic or anionic surface active agents due to their amphiphilic character. Examples of anionic end groups are the sulfonates ($-SO_3^-$), which include Perfluorooctane sulfonate (PFOS), the carboxylates ($-COO^-$) which include Perfluorooctanoic acid (PFOA), and the phosphates ($-OPO_3^-$). In cationic Perfluoroalkylated substances (PFAS), the fluorinated hydrophobic part is attached to e.g. a quaternary ammonium group. Examples of neutral end groups X are: -OH, $-SO_3NH_2$. Both PFOS and PFOA are perfluorinated compounds and appear to be highly persistent, because of the strong covalent C-F bond.

2.1.1.1 PFOS

Chemical name: Perfluorooctane sulfonate (PFOS)

Molecular formula: $C_8F_{17}SO_3^-$

The chemical structure of the potassium salt of PFOS is shown in Figure 2.2. The physical and chemical properties of the potassium salt of PFOS are listed in Table 2.1.

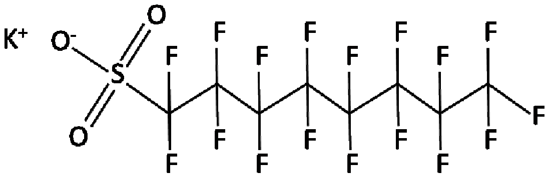


Figure 2.2 Structural formula of PFOS as its potassium salt (EFSA, 2008)

Table 2.1 Physical and chemical properties of PFOS potassium salt (OECD, 2002).

Property	Value
Appearance at normal temperature and pressure	White powder, White-pale yellow, crystals or crystalline powder
Molecular formula	$C_8F_{17}KO_3S$
Molecular weight	538.22 g/mol
Vapor Pressure	3.31×10^{-4} Pa (20 °C)
Water solubility in pure water	519 mg/L (20 ± 0,5°C)
	680 mg/L (24 - 25°C)
Melting point	> 400 °C
Boiling point	Not measurable
Log K_{OW}	Not measurable
Log K_{OC} [a)]	2.57
Log K_D [a)]	0.30-1.04
	0.87-1.55
Air-water partition coefficient	$< 2 \times 10^{-6}$
Henry's Law Constant (calculated)	3.05×10^{-9} atm. m^3/mol pure water
pKa	-3.3 (calculated value for acid)

[a)] Data refer to the anion rather than to the salt

PFOS is a fully fluorinated anion, which is commonly used as a salt (potassium, sodium, ammonium) or incorporated into larger polymers. The schematic structure of perfluoroalkane sulfonate substances is given in Figure 2.3.

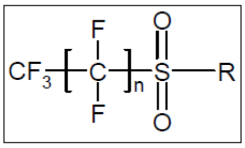


Figure 2.3 Schematic structure of perfluoroalkane sulfonates (EFSA, 2008)

R is equal to any given functional group such as OH, NH_2, etc. For PFOS-related substances, n = 7.

2.1.1.2 PFOA

Chemical name: Perfluorooctanoic acid (PFOA)

Molecular formula: $C_8HF_{15}O_2$

PFOA is a completely fluorinated organic acid. The free acid is expected to completely dissociate in water, leaving the anionic carboxylate in the water and the perfluoroalkyl chain on the surface. At pH 4, about 6% of the molecules will be undissociated. In aqueous solutions, individual molecules of PFOA anion loosely associate on the water surface and partition between the air/water interface (U.S. EPA, 2005).

The dissociated acid has a negligible vapor pressure, high water solubility, and moderate sorption to solids. Based on these properties, accumulation in surface waters is expected (Prevedouros *et al.*, 2006). The chemical structure of PFOA is presented in Figure 2.4.

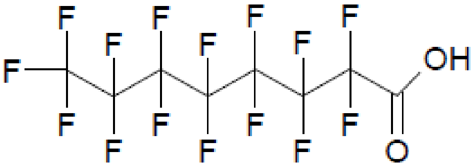


Figure 2.4 Chemical structure of PFOA (EFSA, 2008)

Table 2.2 Physical and chemical properties of PFOA (U.S. EPA, 2005).

Property	Value
Appearance at normal temperature and pressure	White powder or waxy white solid, crystals or mass
Molecular formula	$CF_3(CF_2)_6COOH$
Molecular weight	414.07 g/mol
Vapor Pressure	0.1 kPa (20 ºC)
	10 mm Hg (25 ºC)
	4.2 Pa (25ºC)
	(APFO: 0.0081 Pa at 20ºC)
Water solubility in pure water	3.4 g/L
	4.1 g/L (22 ºC)
	9.5 g/L (25 ºC)
Melting point	45-50 ºC
Boiling point	189-192 ºC (736 mm Hg)
Log K_{OW}	Not measurable
Log K_{OC}	2.06
Log K_D	-0.22-0.55 a)
	-0.39-0.94 soils
	1.10-1.57 sludge
Air-water partition coefficient	Not available
Henry's Law Constant (calculated)	Cannot be estimated b)
pKa	2.5, 2 to 3

a) As free acid unless otherwise stated

b) The vapor pressure of the pure solid is sufficient to sustain mg/kg concentrations of vapor in the atmosphere, but in practice this is unlikely as PFOA will dissociate in aqueous media thereby reducing its vapor pressure above aqueous solutions. For this reason the Henry's Law constant cannot be estimated from the vapor pressure and solubility.

PFOA can enter the environment from direct and indirect sources. Direct sources include the manufacture and use of PFOA, whereas indirect sources are reaction impurities or (bio) degradation of related compounds (Prevedouros *et al.*, 2006). Indirect sources mentioned in the literature include *N*-EtFOSE, *N*-methyl perfluorooctane-sulfonamidoethanol (*N*MeFOSE), perfluorosulfonamides, and fluorotelomer raw materials (Prevedouros *et al.*, 2006). The transformation pathways include biodegradation (Wang *et al.*, 2005a and b), reaction with OHx, ozonolysis (Ellis & Mabury, 2003; Ellis *et al.*, 2004; Vesine *et al.*, 2000).

From the data presented in Tables 2.1 and 2.2, it can be concluded that both PFOS and PFOA dissolve readily in water, with PFOA having the highest aqueous solubility. In water at environmentally relevant pH values (pH = 3 - 8), PFOS will occur in an entirely dissociated (ionised) form, whereas about 6% of PFOA molecules be protonated at pH 4 (at pH 7, only 3 - 6 in 100,000 molecules of PFOA are protonated, with the remaining being dissociated).

2.1.2 Synthesis of PFOS and PFOA

Two major processes exist for production of Perfluoroalkylated substances (PFAS), as follow Simons Electro-Chemical Fluorination (ECF), and Telomerisation (TM) (Hekster *et al.*, 2003). In the ECF process, organic feed stocks are dispersed in liquid anhydrous hydrogen fluoride, and an electric current is passed through the solution, leading to the replacement of all of the hydrogen atoms in the molecule with fluorine atoms. In the telomerisation process, tetrafluoroethylene is reacted with Pentafluoroethyl iodide (IF_5) to produce fluorinated alkyl iodide with linear, even numbered alkyl chain lengths, so called fluorotelomers.

2.1.2.1 PFOS

Perfluorooctane sulfonate is manufactured by the ECF process (see Figure 2.5). The starting feedstock for this process is 1-octanesulfonyl fluoride, and the initial product is perfluorooctanesulfonyl fluoride (POSF). This product is sold commercially to some extent, but is mainly used as an intermediate in the production of other substances. The simplest of these is PFOS itself, produced by hydrolysis of POSF. The various salts are then produced from this.

The majority of POSF is reacted first with either methylamine or ethylamine to give *N*methyl- or *N*-ethyl perfluorooctane sulfonamide, respectively. These intermediates can be used to make various amides, oxazolidinones, silanes, carboxylates and alkoxylates which are available commercially.

The sulfonamide derivatives can react with ethyl carbonate to form either *N*-MeFOSE and *N*EtFOSE. These then form the basis of adipates, phosphate esters, fatty acid esters, urethanes, copolymers and acrylates as commercialised products. The majority of the POSF-related products were from this group of products (OECD, 2002, 2005a and b).

It should be noted that the secondary reactions producing the various products are single or sequential batch reactions, and do not necessarily lead to pure products. There may be varying amounts of fluorochemical residuals (unreacted or partially reacted starting materials or intermediate products) carried forward into the final product. These residues are present at around 1% or less in the final commercial products (OECD, 2002).

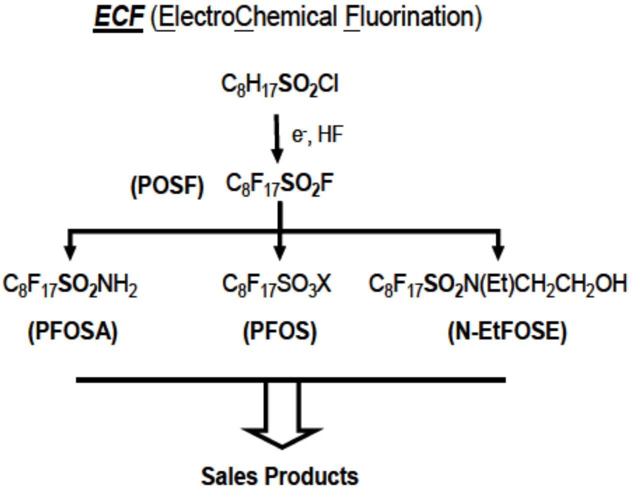


Figure 2.5 Electrochemical fluorination (ECF) process schematic.

The production (3M Company, 2000a and b), use, distribution and environmental releases (3M Company, 1999) of PFOS and POSF-based substances has been well documented by the major global producer, who terminated manufacture in 2002, and by global regulatory agencies (OECD, 2002; Brooke *et al.*, 2004). PFOS is the major impurity in, as well as the primary degradation product of POSF-based products. PFOS is chemically and biologically stable and not expected to degrade in the environment.

2.1.2.2 PFOA

Commercial Manufacturing Processes: Ammonium Perfluorooctanoate (APFO) $F(CF_2)_7COONH_4$

- Electrochemical Fluorination (ECF): $H(CH_2)_7COF + e^- + HF$ (Branched & Linear Isomers)
- Perfluorooctyl Iodide Oxidation: $F(CF_2)_8I + [O]$ (Linear Isomers Only)

Perfluorooctanoate was first manufactured in 1947 by the electrochemical fluorination process and has been used for over fifty years. The ammonium salt is the most widely produced form used as an essential surfactant for the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE).

The largest historic production sites for ammonium salt of perfluorooctanoate (APFO) were in the U.S. and Belgium, the next largest in Italy and small scale producers in Japan. The remaining 10-20% of APFO was manufactured from about 1975 to the present by direct oxidation of perfluorooctyl iodide (Grottenmuller *et al.,* 2002) at one site in Germany and at least one site in Japan. Solid APFO was used in making fluoropolymers (e.g. Fluorad™ FC-143). An aqueous solution (e.g. Fluorad™ FC-118) has been used in recent years because solid APFO readily sublimes and proved difficult to handle. Additional production, use and disposal of limited research quantities of perfluorocarboxylic acid (PFCA) has taken place in numerous academic and industrial locations worldwide over the past fifty years as indicated by patents and papers in the scientific literature. In 1999, global annual APFO production was approximately 260 tonnes (FMG, 2002). Perfluorooctanoate emissions from the largest ECF production plant, located in the U.S., were reported to be approximately 20 tonnes (5-10% of total annual production) in 2000, roughly 5% discharged to air and 95% to water (3M Company, 2000b). During 1951-2004 the estimated industry-wide global emissions from APFO manufacture were 400 - 700 tonnes (Prevedouros *et al.*, 2006). By 2002, the principal worldwide APFO manufacturer by the ECF process discontinued external sales and ceased production leaving only a number of relatively small producers in Europe and in Asia (OECD, 2004). New APFO production capacity based on >99% pure perfluorooctyl iodide commenced in the U.S. in late 2002 with reported annual releases of approximately 50 kilograms per year to air (DuPont, 2005). With the termination of U.S. ECF-based manufacture, current and future U.S. releases from APFO manufacture have been dramatically reduced from many tonnes per year to kilograms per year. As a result, global APFO manufacturing emissions decreased from about 45 tonnes in 1999 to about 15 tonnes in 2004 and to an expected 7 tonnes in 2006 (FMG, 2002). Recently, a number of global companies who manufacture or use PFOA have committed to a voluntary stewardship program to reduce manufacturing emissions and product content (U.S. EPA, 2006). The 3M company, a major world producer of PFOS, using the ECF process, with manufacturing plants in North America and Europe, announced the termination of the ECF production process by May 2002. This decision was probably based partially on findings of Perfluoroalkylated substances in occupationally exposed persons and in the environment (e.g., in terrestrial, estuarine and Arctic ecosystems) (Hoff *et al.*, 2003, 2004; Martin *et al.*, 2004a). As a result, the telomerisation based production has increased.

2.1.3 Use of the compounds

Perfluoroalkylated substances (PFAS) have found numerous applications, including textile, carpet and leather treatment (water and dirt proofing), surfactants, fire fighting foams and paper grease proofing treatments. The PFAS products found hitherto in the environment are known to be possible end products resulting from ECF, but recently more information has become available suggesting that Telomerisation (TM) building blocks or end products may also be precursors of PFAS in the environment.

Perfluorinated substances with long carbon chains, including PFOS, are both lipid-repellent and water-repellent. Therefore, the PFOS-related substances are used as surface-active agents in different applications. The extreme persistence of these substances makes them suitable for high temperature applications and for applications in contact with strong acids or bases. It is the very strong carbon-fluorine bindings that cause the persistence of perfluorinated substances.

2.1.4 Regulations and guidance levels of PFOS and PFOA

In October 2005, the Department for Environment, Food and Rural Affairs (Defra) announced its intention to move forward with national action to restrict the use and marketing of PFOS and substances that degrade to it. The European Union have subsequently published plans to restrict the marketing and use of PFOS. The UK Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) in 2005, after consideration of the mammalian toxicity of ingested PFOS, decided on a No Observed Adverse Effect Level (NOAEL) of 0.1 mg/kg body weight/day to derive a provisional Tolerable Daily Intake (TDI) value of 1 μg/kg body weight/day. This in turn has led to consideration of what level of PFOS in drinking water is unlikely to be harmful to human health (Atkinson *et al.*, 2008). A summary of the guidance levels is given in Table 2.3 .

On receipt of an initial toxicological assessment of PFOS by the Health Protection Agency (HPA) early in 2006, the value of 3 μg/l (microgrammes per litre) was provided by the Drinking Water Inspectorate to water companies as reflecting the best available evidence on which a water company could base its judgement of wholesomeness (Atkinson *et al.*, 2008).

In early 2007 the HPA provided further advice on both PFOS and PFOA. This revised advice included consideration of the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) statement on provisional Total Daily Intake (TDI) for PFOS and PFOA, and the Food Standards Agency's work on UK dietary intakes of fluorinated chemicals. Due to the complexity of the issue and uncertainties involved, the Inspectorate also sought further advice from an independent toxicological consultant (Atkinson *et al.*, 2008).

The European Union plan to introduce an imminent, although not total, ban on PFOS (EU, 2006). Uses at concentrations >0.005%, in semi-finished products at levels >0.1% and in textiles and coated materials at 1 μg/m^2 will be banned. The exemptions are reported to include its use in anti-reflective coatings for photolithography and hydraulic fluids, however, safer alternatives are to be introduced as and when they become available. Member States are required to implement the ban from mid-2008. However, any PFOS containing fire-fighting foams in existence at this time will still be permitted for use until the end of June 2011 (Atkinson *et al.*, 2008).

Table 2.3 Drinking water inspectorate (DWI) guidance levels for PFOS and PFOA (Atkinson *et al.*,2008)

Item	**Regulatory requirement**	**Guidance value (concentration)**	**Minimum action to be taken**
Perfluorooctane sulphonate (PFOS)			
Tier 1	Regulation 10 (Sampling: further provisions)	> 0.3 µg/l	• consult with local health professionals; • monitor levels in drinking water
Tier 2	Regulation 4(2) (Wholesomeness)	> 1.0 µg/l	As tier 1 plus: • put in place measures to reduce concentrations to below 1.0µg/l as soon as is practicable.
Tier 3*	Water Undertakers Information Direction 2004 (Notification of events)	> 9.0 µg/l	As tier 2 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days.
* Note - notification to the Inspectorate under the Information Direction may also be triggered at lower levels due to Tier 1 or Tier 2 activities			
Perfluorooctanoic acid (PFOA)			
Tier 1	Regulation 10 (Sampling: further provisions)	> 0.3 µg/l	• consult with local health professionals; • monitor levels in drinking water.
Tier 2	Regulation 4(2) (Wholesomeness)	> 10.0 µg/l	As tier 1 plus: • put in place measures to reduce concentrations to below 10.0µg/l as soon as is practicable.
Tier 3*	Water Undertakers Information Direction 2004 (Notification of events)	> 90.0 µg/l	As tier 2 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days.
* Note - notification to the Inspectorate under the Information Direction may also be triggered at lower levels due to Tier 1 or Tier 2 activities			

Following the explosion and fire at the Buncefield oil depot in December 2005, there was large-scale use of fire-fighting foams and it was found that some of these foams contained PFOS, although the exact extent of the use of PFOS is unclear. This use has further highlighted the potential hazard of PFOS compounds to drinking water sources. There is also a concern that the replacement of PFOS compounds, with those based on PFOA or perfluorinated compounds that may break down to PFOA, may also increase the potential exposure to PFOA (Atkinson *et al.*,2008).

At the present time, neither PFOS nor PFOA are regulated by means of a standard, nor are there specific parameters for the purpose of routine monitoring of drinking water under the Water Supply (Water Quality) Regulations 2000 (2001 in Wales). However, the presence (if any) of PFOS, PFOA and related substances in drinking water is regulated in England and Wales through the catch-all requirement for drinking water to be wholesome, meaning that it may not contain any substance at a level which would constitute a potential danger to human health.

As such, water companies are required to monitor for the presence of such compounds where there is considered to be a risk of them impacting on treated water quality. Thus the extent of data available on PFOS, PFOA and associated compounds in drinking water and its sources is limited to specific incidents where these compounds have been detected in raw waters and further investigations have been carried out to ensure no impact on treated drinking water.

2.1.5 Toxicity and carcinogenicity

2.1.5.1 Toxicity and carcinogenicity of PFOS

PFOS has been shown to cause moderate toxicity in rats. Numerous studies done on the exposure of rats and primates to PFOS have shown that it is toxic to the liver. Adverse signs in 90 day rat studies include increase in liver enzymes, hepatic vacuolization and hepatocellular hypertrophy, gastrointestinal effects, hematological abnormalities, weight loss, and convulsions. Adverse effects in Rhesus Monkey studies include anorexia, emesis, diarrhea, hypoactivity, convulsions, atrophy of the salivary glands, thymus and the pancreas, marked decreases in serum cholesterol, and lipid depletion in the adrenals. The potential carcinogenicity of PFOS was examined in a dietary 2 year bioassay in rats, where a significant increase in the incidence of hepatocellular (liver) adenomas in both males and females at the highest PFOS dose occurred. This study also found that female rats had a significant increase in combined hepatocellular adenomas and carcinomas. The study also found that there was a significant increase in follicular cell adenomas and combined thyroid follicular cell adenomas and carcinomas in the male rats at high PFOS doses (OECD, 2002).

In a mortality study of 3M workers at the 3M Decatur, Alabama plant, which spanned a 30 year period, there was a statistically significant association between PFOS levels in workers blood and bladder cancer. Statistical analysis of the mortality data indicated that workers who were employed in high exposure jobs were 13 times more likely to die of bladder cancer than the general population of Alabama. The study concluded that bladder cancer is a potentially significant yet uncertain endpoint in the analysis of risks from PFOS-related substances. To evaluate morbidity outcomes an “episode of care” analysis was completed for 3M employees who had worked at the 3M Decatur, Alabama plant during 1993 and 1998. Increased incidences of cancer and non-malignant growths were not found to be of significance and no mortality risks were reported for most of the cancer types. However, the analysis found an increased risk of episodes of neoplasms of the male reproductive system, as well as an increase in the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract. Risk ratios were highest in employees with the highest and longest exposures to fluorochemicals (Olsen *et al*., 2001).

Postnatal deaths and other developmental effects were reported in offspring in a 2-generation reproductive toxicity study of rats exposed to low doses of PFOS. Prenatal developmental effects were also reported in toxicity studies done with rats and rabbits at slightly higher dose levels. During the high dose studies significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed (OECD, 2002). No data were found regarding the effects of PFOS on soil-dwelling or sediment-dwelling species.

PFOS has been tested on two species of bird, the Mallard duck, *Anas platyrhynchos*, and the Northern Bobwhite quail, *Colinus virginianus.*

A lowest acute dietary LC50 value of 220 mg/kg of food was determined in the test with the quail, while a lowest NOEC of 37 mg/kg of food for effects on body weight was obtained in the test with the duck (United Nations Environment Programme (UNEP), 2006).

2.1.5.2 Toxicity and carcinogenicity of PFOA

The EPA Office of Pollution Prevention and Toxics has been investigating the toxicity of PFOA. PFOA is used extensively in coated (Teflon) cookware and other similar products. Most of the toxicity studies have been conducted with the ammonium salt of PFOA. Epidemiological studies on the effects of PFOA in humans have been conducted on workers. A retrospective mortality study demonstrated a statistically significant association between prostate cancer mortality and employment duration in a PFOA manufacturing plant. However, an update to this study did not find a significant association. A study which examined hormone levels in workers reported an increase in estradiol levels in workers with the highest PFOA serum levels. Cholesterol and triglyceride levels were positively associated with PFOA exposures. A statistically significant positive association was reported for PFOA and T3 (thyroid hormone) levels in workers but not for any other thyroid hormones (U.S. EPA, 2005).

Studies have shown that PFOA readily crosses the placenta and is present in the breast milk of rats. Distribution studies have shown that PFOA is distributed primarily to the serum, liver, and kidney (U.S. EPA, 2005). Repeat dose studies in rats and mice demonstrate that the liver is the primary target organ. Chronic dietary exposures to PFOA (ammonium salt) for 90 days resulted in significant increases in liver weight and hepatocellular hypertrophy in female rats at 1000 ppm and in male rats at doses as low as 100 ppm. Chronic dietary exposure of rats to 300 ppm of PFOA (ammonium salt) for 2 years resulted in increased liver weight, hepatocellular hypertrophy, hematological effects, and testicular masses in males; and reductions in body weight and hematological effects in females (U.S. EPA, 2005). The carcinogenic potential of PFOA has been investigated in two dietary carcinogenic studies in rats. Under conditions of these studies there is some evidence that PFOA is carcinogenic, inducing liver tumors, Leydig cell tumors (LCT), and pancreatic acinar cell tumors (PACT) in male rats. There is sufficient evidence to indicate that PFOA is a peroxisome proliferator-activated receptor (PPARα) agonist and that the liver carcinogenicity (and toxicity) of PFOA is mediated by binding to the PPARα in the liver. A mode of action analysis has demonstrated that the hepatic effects are due to PPARα agonism, and that this mode of action is unlikely to occur in humans. The LCT and PACT induced in the rat by PFOA probably do not represent a significant cancer hazard for humans because of quantitative differences in the expressions of receptors and of other toxic dynamic differences between the rat and human. Based on no adequate human studies and uncertain relevance of the tumors from the rat studies, the EPA in its January 2005 summary stated that PFOA may be best described as "suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential". (U.S. EPA, 2005). In February 2006, however, the EPA Science Advisory Board recommended to EPA that PFOA is a "likely carcinogen" based on its assessment of available studies".

2.2 Methods of analysis

Analytical method for the determination of PFOS and PFOA or related compounds have developed for many year, but the currently method that usually used to evaluate the concentration of PFCs is solid phase extraction (SPE) couple with liquid chromatography–tandem mass spectrometry (LC-MS/MS)

Liquid chromatography (LC) has been used with several conventional detectors for the separation of Perfluoroalkylated substances (PFAS). These include a conductimetric detection (Hori *et al.*, 2004) and fluorescence detection (LC-FLU). The latter can only be employed after derivatisation (e.g. with 3-bromoacetyl-7-methoxycoumarin) because of the general absence of fluorophores in PFAS (Ohya *et al.*, 1998).

The development of LC–electrospray ionisation (ESI) mass spectrometry (MS) and LC tandem MS has enabled substantial improvements of the analytical chemistry of the PFAS. LC-MS and in particular LC-MS/MS can be considered the current standard for analysis of anionic perfluorinated surfactants (European Food Safety Authority (EFSA), 2008). LC with single quadrupole MS, though a sensitive technique, requires more thorough clean up of the sample in order to remove interferences, because of its inherent lower selectivity. The majority of reports in the literature employed LC-ESI MS/MS as the analytical method.

Currently quadrupole-time-of-flight (Q-TOF) MS analyzers have a lower sensitivity than triple quadrupole MS/MS systems, but seem to be suitable instruments for the identification of PFAS in the environment (Hansen *et al.*, 2001; Martin *et al.*, 2004b). Berger *et al.* (2004) compared three different mass spectrometric techniques coupled to LC, follow by ion trap MS, triple quadrupole MS and high resolution TOF. For all instruments ESI was the best suited interface for analysis of PFAS. Ion trap MS was best suited for qualitative purposes and identification of branched isomers. Triple quadrupole MS-MS appeared to be the method of choice for quantitative analysis of telomer alcohols, having a limit of detection (LOD) in the low picogram range, and with typical detection limits for other PFAS of 10 to 100 pg. TOFMS appeared to be the optimum quantitative method for PFAS, combining high selectivity with high sensitivity (2 to 10 pg).

2.2.1 Analysis in biological samples and food

Currently three methods of analysis are used most often for the determination of anionic PFAS in biological samples, all involving detection by LC-MS/MS. The method used most often is the ion pairing extraction method introduced by Ylinen and co-workers in 1985 and modified by Hansen *et al.* (2001). This method is flexible and reported recoveries are generally good (70-120%). It can be used for a wide range of matrices, including egg, liver, muscle and other biological tissues. However, the method is quite time consuming and matrix-matched calibration standards are not routinely employed, i.e. matrix-induced ionisation disturbances in the ion source of the mass spectrometer are usually not accounted for (Berger & Haukås, 2005).

2.2.2 Analysis in water and wastewater

The analytical methods applied to water samples generally employ C_{18}-SPE, either with or without ion pairing or acidification, followed by LC-MS/MS (de Voogt & Sáez, 2006). LC with single quadrupole MS has also been used successfully for the determination of PFAS employing styrenedivinylbenzene polymethacrylate cartridges for the SPE, and reported limits of detection (LOD) of 0.1 ng/L (Saito *et al.,* 2003; Harada *et al*., 2003).

Researched by So (2006), the joint cooperation between Japan and Hong Kong targeted the development of new methods for the analysis of PFCs in various matrices at low concentrations, and the subsequent monitoring of PFCs in different environmental matrices and human population in Asian countries. An accurate and reliable analysis of PFCs has been impeded by the problems of procedural blanks and the lack of well-developed analytical methods. In the present study, the concentrations of PFCs in various laboratory equipment and parts of the analytical instruments were measured, and subsequent modifications were made to reduce the blank levels as necessary. New methods were also developed for the analysis of PFCs in water samples, mussel and oyster tissues, and human breast milk samples. Coastal and open ocean water samples were extracted by solid phase extraction (SPE) employing hydrophilic-lipophilic balance (HLB) cartridge. This method allows the measurement of perfluorooctane sulfonamide (PFOSA), perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS) and perfluorobutane sulfonate (PFBS), 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (THPFOS), perfluorononanoic acid (PFNA) and perfluorooctanoic acid (PFOA) at pg/L levels. A combination of alkaline digestion and SPE was developed for the extraction of PFCs from soft tissues of mussels and oysters. This method is rapid and robust with acceptable recoveries for most of the target analytes. However, trace levels of certain PFCs in the procedural blanks restricted the applicability of this method to highly-contaminated samples. New extraction method by SPE employing weak-anion exchange (WAX) cartridge was developed for the analysis of human breast milk. The achievement of low limits of quantifications (LOQs) for various PFCs makes this new method suitable for the analysis of milk samples with comparatively low PFC concentrations.

Studied by Qiu (2007) found that fifteen kinds of PFCs were included in the report, consisting of twelve kinds of perfluorocarboxylic acids (PFCAs) with 4~18 carbons and three kinds of perfluoroalkyl sulfonates (PFASs) with 4~8 carbons. An integral procedure was developed to pretreat wastewater samples. LC-ESI-MS/MS was applied to quantify all PFCs in trace level. Pretreatment methods were optimized between C_{18} and WAX-SPE processes for aqueous samples, and between ion-pair extraction (IPE), Alkaline digestion-Weak anion exchange (AD-WAX) and Accelerated solvent extraction-Weak anion exchange (ASE-WAX) processes for particulate samples. WAX-SPE showed better performance on samples with very high organics concentrations, and C_{18}-SPE performed better for long-chained PFCs. ASE-WAX was proposed as the optimum method to pretreat particulate samples because of the simple and time saving operations. 9H-perfluorononanoic acid (9H-PFNA) was used as internal standard to estimate matrix effect in wastewater.

LC-MS and LC-MS/MS were the most common analytical technique for quantification of PFOS and PFOA. GC-MS and GC-MS/MS and ^{19}F NMR (Moody, 1999) were rarely used in measurement of PFOS and PFOA. In order to quantify the trace levels of PFOS and PFOA (ng/L orders), water concentration (extraction) is needed. Direct measurement without concentration by ^{19}F NMR and ES-MS, have been demonstrated for PFOS (Moody *et al.*, 2001), however, the detection limits were relatively high, at 3-10 μg/L. The most common used method of extraction is solid phase extraction (SPE) which normally apply reversed phase cartridge. Reversed phase separations involve a polar or moderately polar matrix (mobile phase) and a nonpolar stationary phase. The analyte of interest is typically mid-to nonpolar. Retention of organic analytes from polar solutions (e.g. water) onto SPE material is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the SPE material surface. These nonpolar-polar attractive forces are van der Waals forces or dispersion forces. To elute an adsorbed compound form a reserved phase, SPE tube or disk, a non-polar solvent was apply to disrupt the forces that bind the compound to the packing (Lien, 2007). Summaries methods for analysis of PFOS and PFOA in environmental water shown in the Table 2.4

SPE is four-step process as shown in Figure 2.6. The SPE process provides samples that are in solution, free of interfering matrix components, and concentrated enough for detection. Steps include: (1) condition the SPE tube or disk, (2) add the sample, (3) wash the packing, (4) elute the compounds of interest. In reversed phase type silicas and nonpolar adsorption media usually are conditioned with a water-miscible organic solvent such as methanol, followed by water or an aqueous buffer. Methanol moistens surface of the sorbent and penetrates bonded alkyl phases, allowing water to wet the silica surface efficiently (Lien, 2007).

Table 2.4 Summaries methods for analysis of PFOS and PFOA in environmental water (Lien, 2007).

HPLC	
Instrument	Ultra Microprotein Analyzer
Column	Agilent Zorbax XDB D-18 (2.1×150 mm, 5mm)
Mobile phase	A: 10 mM CH_3COONH_4/H_2O; B: CH_3CN
Gradient application	1→2 min: A:B = 45.55 2→8 min: A: 45%→5%; B: 55→95 8→8.5 min: A:B = 5:95 8.5→9 min: A: 5→45; B: 95→55 9→15 min: A:B = 45:55
Flow rate	0.2 mL/min
Oven temperature	30°C
Injection volume	10 mL
MS	
Instrument	TSQ 7000 (ThermoQuest, USA)
Ionization	Electronspay ionization
Polarity mode	Negative
Sheath gas	N_2 (70 psi)
Auxilary gas	N_2 (10 mL/min)
Spray voltage	4200 V
Electron multiplier	1500 V
Capillary temperature	175°C
SIM mode	PFOS: 499 (m/z); PFOA 413 (m/z)
Instrumental detection limits	0.3 pg
The limits of quantifications	PFOS: 0.05 ng/L (for concentration factor of 1000) PFOA: 0.10 ng/L (for concentration factor of 1000)

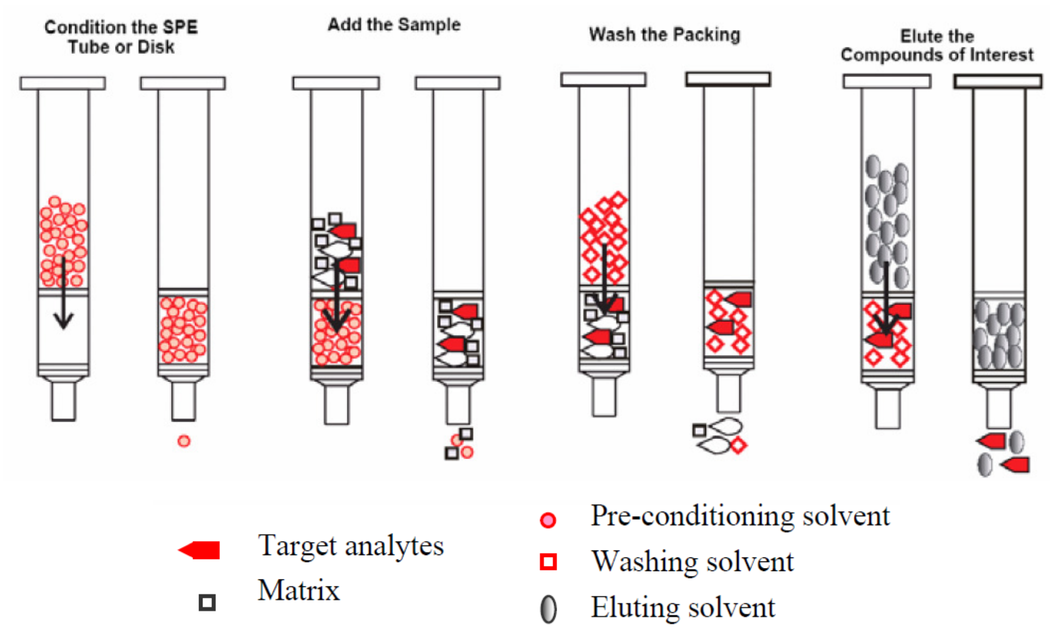


Figure 2.6 Steps in Solid-phase extraction (SPE) for water concentrations (Lien, 2007)

2.2.3 Matrix effects to measurement method in wastewater

In wastewater samples, ionization of PFCs were often suppressed because of the strong background organics (de Voogt & Saez, 2006; Sinclair & Kannan, 2006). A simple method to estimate ionization suppression was to compare different responses of the internal standard (Matuszewski, *et al.*, 1998). Furthermore, a method based on the responses to spiked external standards in different matrix was developed to estimate solid phase extraction (SPE) efficiency and matrix effect simultaneously (Matuszewski, *et al.*, 2003). Although it can estimate matrix effect on each analyte, much systematic variance would be introduced by considering the high RSD value for LC-MS/MS analysis (13±6%). Therefore, method based on internal standard was adapted to estimate ionization suppression by matrix effect from wastewater samples (Qiu, 2007).

Hydrogen substituted perfluorocarboxylates (PFCA) were applied as internal standard for PFCs analysis, including 9H-perfluorononanoic acid (9H-PFNA) (Risha, *et al.*, 2005), 7H-perfluoroheptanoic acid (7H-PFHpA) and 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (TH-PFOS) (Hansen, *et al.*, 2001; Kärrman, *et al.*, 2004;

Harada, *et al.*, 2005). After SPE process, internal standard was spiked into the elution before LC-MS/MS analysis.

Wastewater sample contains aqueous phase and particulate phase. In aqueous phase, PFCs are homogenously distributed as anions because of their lower p*Ka* values (Swedish Chemicals Inspectorate (KemI) and Swedish EPA, 2004). The main purpose of aqueous sample pretreatment was to improve extraction efficiency and to reduce interferences in matrix. C_{18} and WAX cartridge were applied in SPE process to optimize pretreatment procedure for aqueous wastewater samples (Qiu, 2007).

Matrix in environmental sample hindered analytical quality of LC-MS/MS and was impossible to eliminate completely from the sample. Oasis WAX (mixed mode Weak Anion-eXchange) cartridge was specially designed by Waters Company to selectively extract strong hydrophobic acid from various matrices. WAX sorbent contains hydrophobic structure like C_{18} sorbent and weak ionized part like anion-exchanged resin. WAX sorbent performs adsorption and ion exchange in parallel, which combines merits of both C_{18} cartridge and ion exchange cartridge. Given the application of orthogonal extraction in reverse phase adsorption and ion exchange mechanisms, WAX cartridge can clean up the matrix (Young & Tran, 2006) and satisfy the analysis of strong matrix samples such as wastewater and activated sludge (Taniyasu *et al.*, 2005).

In case of WWTP influent and primary effluent with very high DOC concentrations (30~60 mg/L), 100 mL sample was introduced to WAX cartridge. In case of wastewater in lower DOC concentrations, 250 mL sample was loaded. Before SPE process, pH of sample was adjusted to be less than 3 by 1~2 mL of 10% formic acid, in order to ionize WAX sorbent to be positive charged completely during SPE process (Qiu, 2007).

Process recovery (PR) of C_{18}-SPE process varied in 0.1~0.9 and PR of WAX-SPE process were in range of 0.2 ~ 1.2. Average values of PR for each PFC in the two SPE processes were both equal to 0.6. Figure 2.7 showed correlations of PR of PFCs to their carbon chain lengths. WAX cartridge showed better performances for short-chained PFCs like perfluorocarboxylates (PFCA) (4~9) and perfluoroalkyl sulfonate (PFAS)(4,6), and C_{18} cartridge performed better for long-chained PFCs.

One possible explanation was that long-chained PFCs had higher pK*a* values and might not be completely dissociated under pH3 in WAX-SPE process (Qiu, 2007).

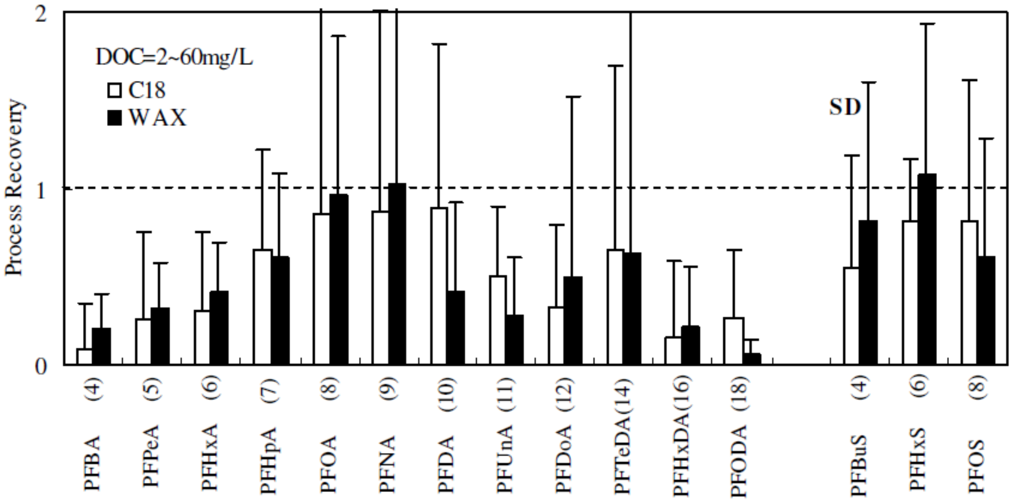


Figure 2.7 Process recoveries of C18 and WAX-SPE for wastewater samples (*n*=40) (Qiu, 2007)

Although WAX-SPE can clean up strong organic matrix, interference cannot be eliminated completely, so that analysis of short-chained PFCs by WAX-SPE process was still suffered from the early elution. Long-chained PFCs were reported to be easily adsorbed onto surface of containers in PP or PE materials (van Leeuwen & de Boer, 2007), which might resulted in poor recoveries of long-chained PFCs by both SPE methods. As a brief summary, C18 and SPE cartridge showed satisfied quality to analyze some PFCs like PFCA (7~11) and all PFAS. C18 cartridge had advantages to concentrate long-chained PFCs, and WAX cartridge performed better in short-chained PFCs.

Figure 2.8 shows process recovery (PR) of each PFC in wastewater samples with different DOC concentrations. The samples shown in the figure were pretreated by C18-SPE process. Wastewater samples can be classified into three catalogues according to their DOC concentrations. Influent and primary effluent samples, represented by DOC-H in range of 26~60 mg/L, had highest DOC concentrations in all aqueous samples from WWTPs. Samples from activated sludge process, as shown by DOC-M in range of 4~6 mg/L, were typical effluents of WWTPs. DOC-L in range of

2~4 mg/L included samples of effluent from advanced treatment facilities like ozonation and biological activated carbon filtration (Qiu, 2007).

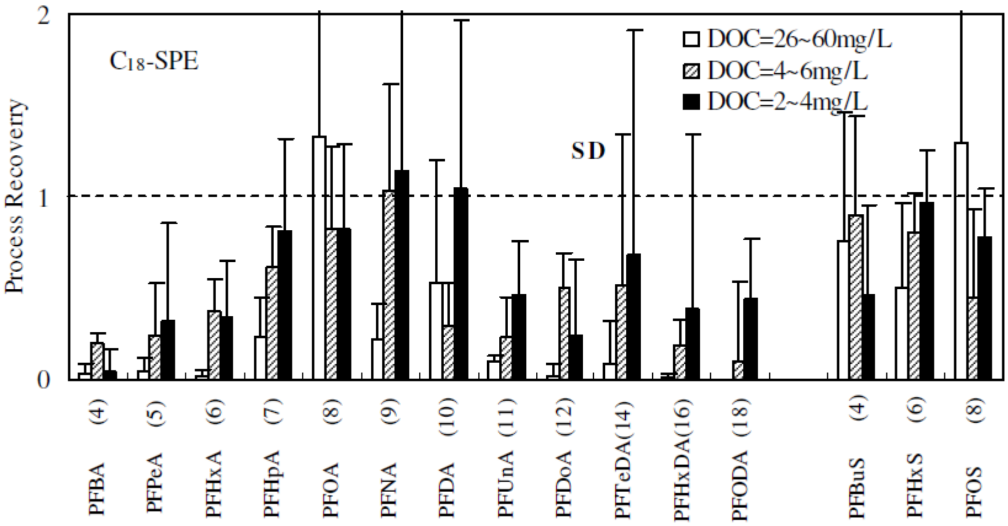


Figure 2.8 Influence of DOC on process recoveries for PFCs analysis (*n*=5) (Qiu, 2007)

Process recoveries of DOC-H samples varied from 0.2 to 0.8, with the highest value for PFOA. For each PFC, PR of DOC-H was smaller than those of either DOC-M or DOC-L. Average value of PR for each PFC in DOC-H samples was calculated to be 0.38±0.2, which implied unsatisfied performance of current analysis. PR of DOC-M samples varied in range of 0.3~1.7 and the average value of PR was 0.81±0.5. PR of DOC-L samples varied in range of 0.2~1.8 and the average value of PR was 0.94±0.7. With the decreasing of DOC concentration, analytical quality was increased based on the average values of PR in wastewater samples (Qiu, 2007).

2.3 Industrial wastewater characteristic and composition

Industrial wastewaters are effluents from such processing or manufacturing. Examples of industrial wastewaters include those arising from chemical, pharmaceutical, electrochemical, electronics, petrochemical, and food processing industries. Industrial wastewaters have very varied compositions depending on the type of industry and materials processed. Some of these wastewaters can be organically very strong, easily biodegradable, largely inorganic, or potentially inhibitory. This means TSS, BOD_5 and COD values may be in the tens of thousands mg/L. Because of these very high organic concentrations, industrial wastewaters may also be severely nutrients deficient. A significant factor influencing the flow pattern of industrial wastewater would be the shift nature of work at factories. These shifts may be 8 h or 12 h shifts and there can be up to three shifts per day. These shifts may mean that there can be more than the two peaks in flow seen in sewage and there may be no flow for parts of the day. Factories may operate five to seven days per week. A consequence of this can be the possibility of zero flow on days when a factory is not operating. In contrast to the narrower band of variation in the characteristics of domestic sewage within a community, industrial wastewaters can have very different characteristics even for wastewaters from a single type of industry but from different locations. The cause of these differences has much to do with the operating procedures adopted at each site and the raw materials used therein. To further complicate matters, wastewater characteristics within a factory can also vary with time because it may practice campaign manufacturing, or it may practice slug discharges on top of its usual discharges. Apart from these events which occur on a regular basis, there would be spillages and dumping which may occur within the factory infrequently but can have very adverse impacts on the performance of the wastewater treatment plant. Consequently it would be prudent to assess an industrial wastewater, as well as its pretreatment and treatment requirements very carefully and not immediately assume that its wastewater characteristics and treatment requirements are similar to a previously encountered example. It would also be prudent to acquire some understanding of the nature of the factory's operations.

In the last decade, the emergence of industrial pollution has been identified as a trend in the coastal areas of Southern China, Vietnam, Kampuchea, and Thailand. The effects pollutants have on the water environment can be summarized in the following broad categories:

a) Physical effects: These include impact on clarity of the water and interference to oxygen dissolution. Water clarity is affected by turbidity which may be caused by inorganic (Fixed Suspended Solids or FSS) and/or organic particulates suspended in the water (Volatile Suspended Solids or VSS). Turbidity reduces light penetration and photosynthesis while the attendant loss in clarity, and also affect the food gathering capacity of aquatic animals because these may not be able to see their prey. Settleable particulates may accumulate on plant foliage and bed of the waterbody forming sludge layers which would eventually smother benthic organisms. In contrast to the settleable material, particulates lighter than water eventually float to the surface and form a scum layer and interfere with the passage of light and oxygen dissolution. Many industrial wastewaters contain oil and grease (O&G) and can have temperatures substantially above ambient temperatures. These raise the temperatures of the receiving water and reduce the solubility of oxygen.

b) Oxidation and residual dissolved oxygen: as a result of biological or chemical processes induced by the presence of organic or inorganic substances which exert an oxygen demand (i.e. as indicated by the BOD or COD), exceeded this capacity then the dissolved oxygen (DO) levels would decline. A manifestation of such conditions would be the presence of malodours released by facultative and anaerobic organisms. The depletion of free oxygen would affect the survival of aerobic organisms. The elevated temperatures can affect metabolic rates positively but elevated temperatures also reduce the solubility of oxygen in water. This would mean increasing demand for oxygen while its availability declines. Because of the impact of DO levels on aquatic life, much importance has been placed on determining the BOD value of a discharge. Typical BOD_5 limits set are values such as 20 and 50 mg/L.

c) Inhibition or toxicity and persistence: These effects may be caused by organic or inorganic substances and can be acute or chronic, examples of these include the pesticides and heavy metals. Many industrial wastewaters do contain such potentially inhibitory or toxic substances. The presence of such substances in an ecosystem may bias a population towards members of the community which are more tolerant to the substances while eliminating those which are less tolerant and resulting in a loss of biodiversity. For similar reasons, an awareness of the impact such substances have on biological systems is not only relevant in terms of protection of the environment but is of no less importance in terms of their impact on the biological systems used to treat industrial wastewaters. Even successful treatment of such a wastewater may not necessarily mean that the potability of water in a receiving waterbody would not be affected. Apart from the organic pollutants which are potentially inhibitory or toxic, there are resistant to biological degradation. Such persistent compounds can be bio-accumulated in organisms resulting in concentrations in tissues being significantly higher than concentrations in the environment and thereby making these organisms unsuitable as prey/food for organisms (including Man) higher up the food chain. While some organic compounds may be persistent, metals are practically non-degradable in the environment.

d) Eutrophication: Nitrogenous and phosphorous compounds discharge into receiving waterbodies may alter their fertility. Enhanced fertility can lead to excessive plant growth and include algal growth. The subsequent impact of such growth on a waterbody can include increased turbidity, oxygen depletion, and toxicity issues. Algal growth in unpolluted waterbodies is usually limited because the water is nutrient limiting. While nutrients would include marco-nutrients and micro-nutrients are required only in very small quantities, the focus in concerns over eutrophication would be on phosphorous and nitrogen as quantities of the other nutrients in the natural environment are often inherently adequate. In freshwaters the limiting nutrient is usually phosphorous while in estuarine and marine waters it would be nitrogen. Treatment of industrial wastewater (or domestic sewage for that matter) can then target the removal of either phosphorous or nitrogen, depending on the receiving waterbody, to ensure that the nutrient limiting condition is maintained. When the nutrient limiting condition is no longer present in the waterbody, and when other conditions such as ambient temperature are appropriate, excessive algal growth or algal blooms (e.g. the red tide) may occur. Algal blooms may affect the productivity of the fisheries in the locale.

e) Pathogenic effects: Pathogens are disease-causing organisms and an infection occurs when these organisms gain entry into a host (e.g. man or an animal) and multiply therein. These pathogens include bacteria, viruses, protozoa, and helminthes. Industrial wastewaters are not typically associated with this category of effects. The exception to this is wastewaters associated with the sectors in the agro-industry dealing with animals. The concern would be the presence of such organisms in the wastewater which is discharged into a receiving waterbody and diseases.

2.3.1 Nature and characteristics of industrial wastewater

The following table (Table 2.5) gives a comparison between the typical range of biochemical oxygen demand (BOD) and total suspended solid (TSS) load for industrial and municipal domestic wastewater and Table 2.6 gives a comparison in concentration values.

Table 2.5 Typical range of BOD and TSS load

Origin of waste	BOD (kg/ton product)	TSS (kg/ton product)
Domestic sewage	0.025 (kg/day/person)	0.022 (kg/day/person)
Dairy industry	5.3	2.2
Yeast industry	125	18.7
Starch & glucose industry	13.4	9.7
Fruits & vegetable canning industry	12.5	4.3
Textile industry	30 – 314	55 – 196
Pulp & paper industry	4 – 130	11.5 – 26
Beverage industry	2.5 – 220	1.3 – 257
Tannery industry	48 - 86	85 - 155

Table 2.6 Typical range of concentration values for wastewater

Origin of waste	pH	TSS mg/L	BOD mg/L	COD mg/L	TDS mg/L	O&G mg/L
Domestic Sewage	7	220	250	500	500	-
Dairy Industry	4	12,150	14,000	21,100	19,000	320
Yeast Industry	5.3	540	2,100	3,400	3,500	9
Fruits & Vegetable Canning	5.5	2,200	800	1,400	1,270	94
Textile Industry	6.5	1,800	840	1,500	17,000	155
Pulp & Paper Industry	8	1,640	360	2,300	1,980	-
Beverage Industry	9	760	620	1,150	1,290	-
Tannery Industry	10	2,600	2,370	4,950	8,500	115
Fish Canning	11	565	890	2,350	8,218	290

The important contaminants of concern in wastewater treatment are listed in the Table 2.7. Secondary treatment standards for wastewater are concerned with the removal of biodegradable organics, suspended solids, and pathogens. Many of the more stringent standards that have been developed recently deal with the removal of nutrients and priority pollutants. When wastewater is to be reused, standards normally include requirements for the removal of refractory organics, heavy metals, and in some cases dissolved inorganic salts.

Table 2.7 Important contaminants of concern in industrial wastewater treatment

Contaminants	Reason for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Nutrients	Both nitrogen and phosphate, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Priority pollutants	Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of these compounds are found in wastewater.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metals	Heavy metals are usually discharged to wastewater from commercial and industrial activities and have to be removed if the wastewater is to be reused.
Dissolved inorganics	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.

2.3.1.1 Physical characteristics

The most important physical characteristic of wastewater is total solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Other important physical characteristics include odor, temperature, color, and turbidity.

a) Total solids

Analytically the total solids content of a wastewater is defined as all the matter that remains as residue upon evaporation at 103 to 105 °C. Matter that has a significant vapor pressure at this temperature is lost during evaporation & is not defined as a solid. Settable solids are those solids that will settle to the bottom of a cone-shaped container (called an Imhoff cone) in a 60-minute period.

Settable solids, expressed as mL/L, are an approximate measure of the quantity of sludge that will be removed by primary sedimentation. Total solids, or residue upon evaporation, can be further classified as non-filterable (suspended) or filterable by passing a known volume of liquid through a filter.

The filterable-solids fraction consists of colloidal and dissolved solids. The colloidal fraction consists of the particulate matter with an approximate size range of from 0.001 to 1 µm. The dissolved solids consist of both organic & inorganic molecules and ions that are present in true solution in water. The colloidal fraction cannot be removed by settling. Generally, biological oxidation or coagulation, followed by sedimentation, is required to remove these particles from suspension.

The suspended solids are found in considerable quantity in many industrial wastewater, such as cannery and paper-mill effluents. They are screened and/or settled out at the treatment plant. Solids removed by settling and separated from wash water are called *sludge*, which may be pumped to drying beds or filtered for extraction of additional water (dewatering).

Each of the categories of solids may be further classified on the basis of their volatility at 550^{o}C. The organic fraction will oxidize and will be driven off as gas at this temperature, and the inorganic fraction remains behind as ash. Thus the terms "Volatile suspended solids" and "Fixed suspended solids" refer to the organic and inorganic (or mineral) content of the suspended solids, respectively. The volatile-solids analysis is applied most commonly to wastewater sludge to measure their biological stability.

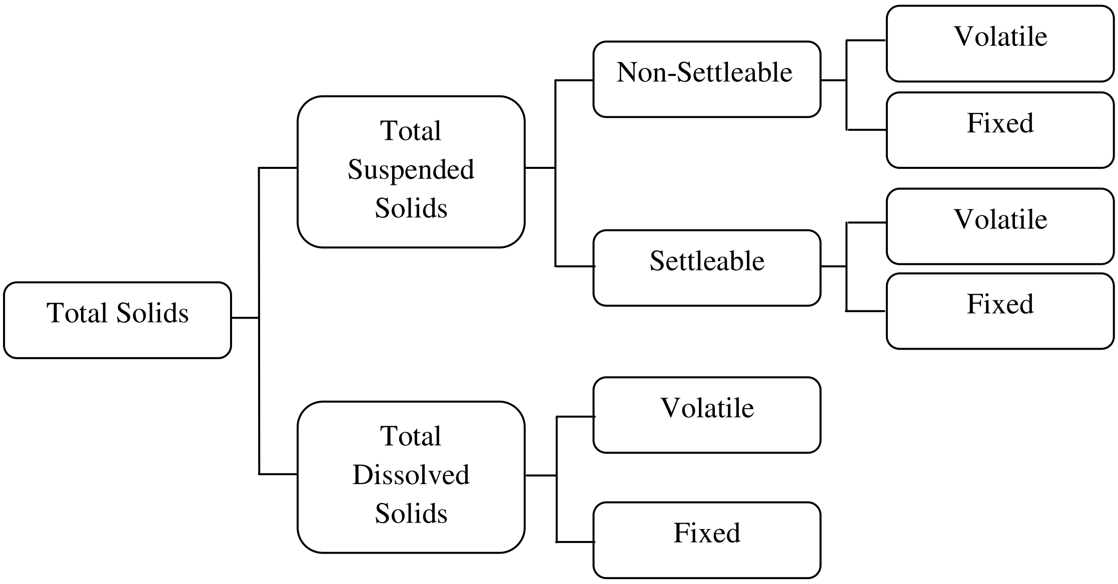


Figure 2.9 Classification of Total Solids

b) Odors

Odors are usually caused by gases produced by the decomposition of organic matter or by substances added to the wastewater. Industrial wastewater may contain either odorous compounds or compounds that produce odor during the process of wastewater treatment.

c) Temperature

The temperature of water is a very important parameter because of its effect on chemical reactions and reaction rates, aquatic life, and the suitability of the water for beneficial uses. Increased temperature, for example, can cause a change in the species of fish that can exist in the receiving water body. Industrial establishments that use surface water for cooling-water purposes are particularly concerned with the temperature of the intake water.

In addition, oxygen is less soluble in warm water than in cold water. The increase in the rate of biochemical reactions that accompanies an increase in temperature, combined with the decrease in the quantity of oxygen present in surface waters, can often cause serious depletions in dissolved oxygen concentration in the summer months. When significantly large quantities of heated water are discharged to natural receiving water, these effects are magnified. It should also be realized that a sudden change in temperature can result in a high rate of mortality of aquatic life. Moreover, abnormally high temperatures can foster the growth of undesirable water plants and wastewater fungus.

d) Color

Color of industrial wastewater varies according to the type of industry. Knowledge of the character and measurement of color is essential. Since most colored matter is in a dissolved state, it is not altered by conventional primary devices, although secondary treatment units, such as activated sludge and trickling filters, remove a certain percentage of some types of colored matter. Sometimes color matters need chemical oxidation procedures for removal.

e) Turbidity

Turbidity, a measure of the light-transmitting properties of water, is another test used to indicate the quality of wastewater discharges and natural waters with respect to colloidal and residual suspended matter. In general, there is no relationship between turbidity and the concentration of suspended solids in untreated wastewater.

2.3.1.2 Chemical characteristics

a) Organic matter

Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. Other important elements, such as sulfur, phosphorus, and iron, may also be present. Also, industrial wastewater may contain small quantities of a large number of different synthetic organic molecules ranging from simple to extremely complex in structure. Typical examples include surfactants, organic priority pollutants, volatile organic compounds and agricultural pesticides as shown in Table 2.7. The presence of these substances has complicated industrial wastewater treatment because many of them either cannot be or are very slowly decomposed biologically.

Fats, oils, and grease

Fats are among the more stable of organic compounds and are not easily decomposed by bacteria. Kerosene, lubricating oils reach the sewer from workshops and garages, for the most part they float on the wastewater, although a portion is carried into the sludge on settling solids. To an even greater extent than fats, oils, and soaps, the mineral oils tend to coat surfaces causing maintenance problems. If grease is not removed before discharge of the wastewater, it can interfere with the biological life in the surface waters and create unsightly floating matter and films. The oil and grease (O & G) is a very important test used to determine the hydrocarbon content of industrial wastewaters. O&G tests include free O&G and emulsified O&G measures. These tests will determine the type of treatment required. Free O&G can be removed by flotation & skimming using gravity oil separator (GOS). However, emulsified oil is removed by Dissolved Air Flotation system after chemical de-emulsification of oil. In any case, O&G have to be removed prior biological treatment as they will clog the flow distributing devices and air nozzles.

Surfactants

Surfactants are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in surface waters into which the wastewater effluent is discharged. Surfactants tend to collect at the air-water interface. During aeration of wastewater, these compounds collect on the surface of the air bubbles and thus create very stable foam.

Phenols

Phenols and other organic compounds are also important constituents of water. Phenols cause taste problems in drinking water, particularly when the water is chlorinated. They are produced primarily by industrial operations and find their way to surface waters via industrial wastewater discharges. Phenols can be biologically oxidized at concentrations up to 500 mg/liter.

Volatile organic compounds (VOCs)

Organic compounds that have a boiling pointless than < 100°C and/or a vapor pressure > 1 mm Hg at 25°C are generally considered to be volatile organic compounds (VOCs). The release of these compounds in sewers and at treatment plants is of particular concern with respect to the health of collection system and treatment plant workers.

Pesticides and agricultural chemicals

Trace organic compounds, such as pesticides, herbicides, and other agricultural chemicals, are toxic to most life forms and therefore can be significant contaminants of surface waters.

b) Inorganic matter

Several inorganic components of wastewater are important in establishing and controlling wastewater quality. Industrial wastewater has to be treated for removal of the inorganic constituents that are added in the use cycle. Concentrations of inorganic constituents also are increased by the natural evaporation process, which removes some of surface water and leaves the inorganic substance in the wastewater.

pH

The hydrogen-ion concentration is an important quality parameter of wastewater. The concentration range suitable for the existence of most biological life is quite narrow and critical. Wastewater with an adverse concentration of hydrogen ion is difficult to treat by biological means, and if the concentration is not altered before discharge, the wastewater effluent may alter the concentration in the natural waters.

Alkalinity

Alkalinity in wastewater results from the presence of the hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Borates, silicates, phosphates, and similar compounds can also contribute to the alkalinity. The alkalinity in wastewater helps to resist changes in pH caused by the addition of acids. The concentration of alkalinity in wastewater is important where chemical treatment is to be used, in biological nutrient removal, and where ammonia is to be removed by air stripping.

Nitrogen

Because nitrogen is an essential building block in the synthesis of protein, nitrogen data will be required to evaluate the treatability of wastewater by biological processes. Insufficient nitrogen can necessitate the addition of nitrogen to make the wastewater treatable. Where control of algal growth in the receiving water is necessary to protect beneficial uses, removal or reduction of nitrogen in wastewaters prior to discharge may be desirable. The total nitrogen, as a commonly used parameter, consists of many numerous compounds such as; NH_3, NH_4-N, NO_3-N, NO_2-N, urea, organic-N (amines, amino acids, etc.).

Phosphorus

Phosphorus is also essential to the growth of algae and other biological organisms. The organically bound phosphorus is an important constituent of industrial wastewater and sludge.

Sulfur

Sulfate is reduced biologically under anaerobic conditions to sulfide, which in turn can combine with hydrogen to form hydrogen sulfide (H_2S). Hydrogen sulfide released to the atmosphere above the wastewater in sewers that are not flowing full tends to accumulate at the crown of the pipe. The accumulated H_2S can then be oxidized biologically to sulfuric acid, which is corrosive to steel pipes and equipment.

Toxic Inorganic Compounds

Because of their toxicity, certain cations are of great importance in the treatment and disposal of wastewater. Many of these compounds are classified as priority pollutants. Copper, lead, silver, chromium, arsenic, and boron are toxic in varying degrees to microorganisms and therefore must be taken into consideration in the design of a biological treatment plant. Many plants have been upset by the introduction of these ions to the extent that the microorganisms were killed and treatment ceased. Other toxic cations include potassium and ammonium at 4,000 mg/L. Some toxic anions, including cyanides and chromates, are also present in industrial wastewater. These are found particularly in metal-plating wastewater and should be removed by pretreatment at the site of the industry rather than be mixed with the municipal wastewater. Fluoride, another toxic anion, is found commonly in wastewater from electronics manufacturing facilities. Organic compounds present in some industrial wastewater are also toxic.

Heavy Metals

Trace quantities of many metals, such as nickel (Ni), manganese (Mn), lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), copper (Cu), iron (Fe), and mercury (Hg) are important constituents of some industrial wastewaters.

The presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water because of their toxicity; therefore, it is frequently desirable to measure and control the concentration of these substances.

Table 2.8 Industrial effluent standards

Parameters	Standard Values	Method for Examination
pH value	5.5-9.0	pH Meter
Temperature	not more than 40°C	Thermometer during the sampling
Total Dissolved Solids (TDS)	- not more than 3,000 mg/L depending on receiving water or type of industry under consideration of PCC but not exceed 5,000 mg/L - not more than 5,000 mg/L exceed TDS of receiving water having salinity of more than 2,000 mg/L or TDS of sea if discharge to sea	Dry Evaporation 103-105 °C, 1 hour
Suspended solids (SS)	not more than 50 mg/L depending on receiving water or type of industry or wastewater treatment system under consideration of PCC but not exceed 150 mg/L	Glass Fiber Filter Disc
Color and Odor	not objectionable	Not specified
Sulphide as H_2S	not more than 1.0 mg/L	Titrate
Cyanide as HCN	not more than 0.2 mg/L	Distillation and Pyridine Barbituric Acid Method
Fat, Oil & Grease (FOG)	not more than 5.0 mg/L depending of receiving water or type of industry under consideration of PCC but not exceed 15.0 mg/L	Sovent Extraction by Weight
Formaldehyde	not more than 1.0 mg/L	Spectrophotometry
Phenols	not more than 1.0 mg/L	Distillation and 4-Aminoantipyrine Method
Free Chlorine	not more than 1.0 mg/L	lodometric Method
Pesticides	not detectable	Gas-Chromatography

Table 2.8 Industrial effluent standards (Cont.)

Parameters	Standard Values	Method for Examination
Biochemical Oxygen Demand (BOD)	not more than 20 mg/L depending on receiving water or type of industry under consideration of PCC but not exceed 60 mg/L	-Azide Modification at 20 °C , 5 days
Total Kjedahl Nitrogen (TKN)	not more than 100 mg/L depending on receiving water or type of industry under consideration of PCC but not exceed 200 mg/L	Kjeldahl
Chemical Oxygen Demand (COD)	not more than 120 mg/L depending on receiving water of type of industry under consideration of PCC but not exceed 400 mg/L	Potassium Dichromate Digestion
Heavy metals		
- Zinc (Zn)	not more than 5.0 mg/L	Atomic Absorption Spectro Photometry; Direct Aspiration or Plasma Emission Spectroscopy ; Inductively Coupled Plama : ICP
- Chromium (Hexavalent)	not more than 0.25 mg/L	
- Chromium (Trivalent)	not more than 0.75 mg/L	
- Copper (Cu)	not more than 2.0 mg/L	
- Cadmium (Cd)	not more than 0.03 mg/L	
- Barium (Ba)	not more than 1.0 mg/L	
- Lead (Pb)	not more than 0.2 mg/L	
- Nickel (Ni)	not more than 1.0 mg/L	
- Manganese (Mn)	not more than 5.0 mg/L	
- Arsenic (As)	not more than 0.25 mg/L	Atomic Absorption Spectrophotometry; Hydride Generation, or Plasma Emission Spectroscopy; Inductively Coupled Plasma : ICP
- Selenium (Se)	not more than 0.02 mg/L	
- Mercury (Hg)	not more than 0.005 mg/L	Atomic Absorption Cold Vapour Techique

Source: Notification the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gazette, Vol. 113 Part 13 D, dated February 13, B.E.2539 (1996)

2.3.1.3 Biological characteristics

Some industries have certain pathogenic organisms like slaughterhouses others have molds and fungi as starch and yeast factories. Biological tests on wastewater determine whether pathogenic organisms are present by testing for certain indicator organisms. Biological information is needed to assess the degree of treatment of the wastewater before its discharge to the environment. Total nitrogen is a commonly used parameter that includes a number of parameters, NH_3, NH_4-N, NO_3-N, NO_2-N, urea, organic N such as amines, amino acids, proteins, etc. and process chemicals. The presence of these compounds depends on the production. The parameters setting the standards for the discharge of industrial wastewater effluents are outlined in Table 2.8.

Most industries produce some wet waste although recent trends in the developed world have been to minimize such production or recycle such waste within the production process. However, many industries remain dependent on processes that produce wastewaters. Industrial wastewater generated from many sources;

1) Agricultural waste

Agricultural wastewater treatment relates to the treatment of wastewaters produced in the course of agricultural activities. As agriculture is a highly intensified industry in many parts of the world, the range of wastewaters requiring treatment can encompass at least the following: Animals wastes - both liquid and solid, Silage liquor, Pesticide run off and surpluses, Milking parlour wastes including milk, Slaughtering waste, Vegetable washing water, and Fire water

2) Iron and steel industry

The production of iron from its ores involves powerful reduction reactions in blast furnaces. Cooling waters are inevitably contaminated with products especially ammonia and cyanide. The conversion of iron or steel into sheet, wire or rods requires hot and cold mechanical transformation stages frequently employing water as a lubricant and coolant. Contaminants include hydraulic oils, tallow and particulate solids. Many steel industry wastewaters are contaminated by hydraulic oil also known as *soluble oil*

All metal industrial wastewater includes Electroplating, Electroless plating, Anodizing, Coating (including *phosphating or chromating* metal parts prior to application of a finish coating), Chemical etching and milling, and Printed circuit board manufacture, discharges to a publicly owned treatment works (POTW) are subject to the general regulations found in Title 40 of the Code of Federal Regulations (CFR), Part 403.5. These regulations prohibit wastewater discharges that include any pollutant which may pass through or cause interference with the POTW treatment process. Wastewater pollutants that create an explosion hazard, corrosive structural damage, obstructions to flow, excessive heat, and toxic gases are also prohibited as shown in Table 2.9.

Additional restrictions on wastewater pH levels and the amount of oil/grease and total suspended solids allowed in the discharge will likely be established by the local POTW.

3) Mines and quarries

The principal waste-waters associated with mines and quarries are slurries of rock particles in water. These arise from rainfall washing exposed surfaces and haul roads and also from rock washing and grading processes. Volumes of water can be very high, especially rainfall related arisings on large sites. Wastewater from metal mines and ore recovery plants are inevitably contaminated by the minerals present in the native rock formations. Following crushing and extraction of the desirable materials, undesirable materials may become contaminated in the wastewater. For metal mines, this can include unwanted metals such as zinc and other materials such as arsenic. Extraction of high value metals such as gold and silver may generate slimes containing very fine particles in where physical removal of contaminants becomes particularly difficult.

4) Food industry

Wastewater generated from agricultural and food operations have distinctive characteristics that set it apart from common municipal wastewater managed by public or private wastewater treatment plants throughout the world: it is biodegradable and nontoxic, but that has high concentrations of biochemical oxygen demand (BOD) and suspended solids (SS). The constituents of food and agriculture wastewater are often complex to predict due to the differences in BOD and pH in effluents from vegetable, fruit, and meat products and due to the seasonal nature of food processing and post-harvesting.

Processing of food from raw materials requires large volumes of high grade water. Vegetable washing generates waters with high loads of particulate matter and some dissolved organics. It may also contain surfactants.

Table 2.9 Pretreatment standards for existing sources (PSES)

Pollutant or Pollutant Property	Single Day – Maximum Milligrams per liter (mg/l)
Total Cadmium	0.69 (0.11[*])
Total Chromium	2.77
Total Copper	3.38
Total Lead	0.69
Total Nickel	3.98
Total Silver	0.43
Total Zinc	2.61
Total Cyanide	1.20
Total Toxic Organics (TTO)	2.13

[*] PSNS for cadmium. PSNS for all other parameters are the same as those listed for PSES.

5) Complex organic chemicals industry

A range of industries manufacture or use complex organic chemicals. These include pesticides, Pharmaceuticals, paints and dyes, petro-chemicals, detergents, plastics etc. Waste waters can be contaminated by feed-stock materials, by-products, product material in soluble or particulate form , washing and cleaning agents, solvents and added value products such as plasticisers.

In most industries, wastewater effluents result from the following water uses:

- sanitary wastewater (from washing, drinking and personal hygiene);
- cooling (from disposing of excess heat to the environment);
- cleaning (including wastewater from cleaning and maintenance of industrial areas); and

- process wastewater (including both water used for making and washing products and for removal and transport of waste and by-products).

The wastewater at existing facilities will be analyzed to determine the characteristics and constituents as required in Table 2.10. Excluding the large volumes of cooling water discharged by the electric power industry, the wastewater production from urban areas is about evenly divided between industrial and municipal sources. Therefore, the use of water by industry can significantly affect the water quality of receiving waters.

The level of wastewater loading from industrial sources varies markedly with the water quality objectives enforced by the regulatory agencies. There are many possible in-plant changes, process modifications and water-saving measures through which industrial wastewater loads can be significantly reduced.

Industrial wastewater effluents are usually highly variable, with quantity and quality variations brought about by bath discharges, operation start-ups and shut-downs, working-hour distribution and so on. A long-term detailed survey is usually necessary before a conclusion on the pollution impact from an industry can be reached.

Table 2.10 Characteristics of industrial wastewater

Parameter	**concentration**
pH	7.0 std units
Total solids	720 mg/L
Total volatile solids	420 mg/L
Suspended solids	200 mg/L
Settleable solids	4 ml/L
BOD	200 mg/L
Total nitrogen	30 mg/L
Ammonia nitrogen	15 mg/L
Oils and grease	100 mg/L
Phosphorus	10 mg/L
Chloride	50 mg/L

Table 2.11 Typical range of BOD and SS load for industrial and municipal wastewater [c] (EWATEC, 2002)

Origin of waste	BOD (kg/ton product)	TSS (kg/ton product)
Domestic sewage	0.025 (kg/day/person)	0.022 (kg/day/person)
Dairy industry	5.3	2.2
Yeast industry	125	18.7
Starch & glucose industry	13.4	9.7
Fruits & vegetable canning industry	12.5	4.3
Textile industry	30 - 314	55 - 196
Pulp & paper industry	4 - 130	11.5 - 26
Beverage industry	2.5 - 220	1.3 - 257
Tannery industry	48 - 86	85 - 155

c) Rapid assessment for industrial pollution

Table 2.12 Typical range of concentration values for industrial and municipal wastewater [d] (EWATEC, 2002)

Origin of waste	pH	TSS, mg/L	BOD, mg/L	COD, mg/L	TDS, mg/L	O&G, mg/L
Domestic Sewage	7	220	250	500	500	-
Dairy Industry	4	12150	14000	21100	19000	320
Yeast Industry	5.3	540	2100	3400	3500	9
Fruits & Vegetable Canning	5.5	2200	800	1400	1270	94
Textile Industry	6.5	1800	840	1500	17000	155
Pulp & Paper Industry	8	1640	360	2300	1980	-
Beverage Industry	9	760	620	1150	1290	-
Tannery Industry	10	2600	2370	4950	8500	115
Fish Canning	11	565	890	2350	8218	290

d) Previous analysis conducting in several companies.

In Table 2.11 gives a comparison between the typical range of BOD and SS. load for industrial and municipal domestic wastewater. While Table

2.12 gives a comparison of typical concentration values (pH, TSS, BOD, COD, TDS, oil and grease for different industrial effluents.

CHAPTER III
METHODOLOGY

3.1 Framework

The overall methodologies used to obtain the results were separated into two phases include;

Phase I Synthetic wastewater: study the relation of organic components (C, N, and TDS) to the measurement technique of PFOS and PFOA by using synthetic wastewater and

Phase II Real industrial wastewater: study the relation of wastewater components to the measurement technique of PFOS and PFOA and monitoring the PFOS and PFOA concentration by using real industrial wastewater.

The component of synthetic wastewater will varied on total organic carbon (TOC), total Kjeldahl nitrogen (TKN), and total dissolved solid (TDS). All of experimental runs for Phase I was spiked with PFOS and PFOA standard solution at the concentration of 5 μg/L. Industrial wastewater was directly collected from central wastewater treatment plant and discharged pipe from selected industries. The overall framework of this study shown in Figure 3.1 .

3.2 Duration and experiment site

Duration of this study was in October 2008 – March 2010 which were included: synthesis of wastewater by varying on organic component at the Laboratory of Environmental Engineering, Civil Engineering, Mahidol University, Salaya campus. The concentration of organic, inorganic compound, PFOS and PFOA were analyzed in the department of Civil and Environmental engineering, Faculty of Engineering, Mahidol University, Salaya campus. Monitoring of PFOS and PFOA concentration in real industrial wastewater samples were collected from Bang-Pa-In industrial estate and Hi-Tech estate, Ayutthaya province, Thailand.

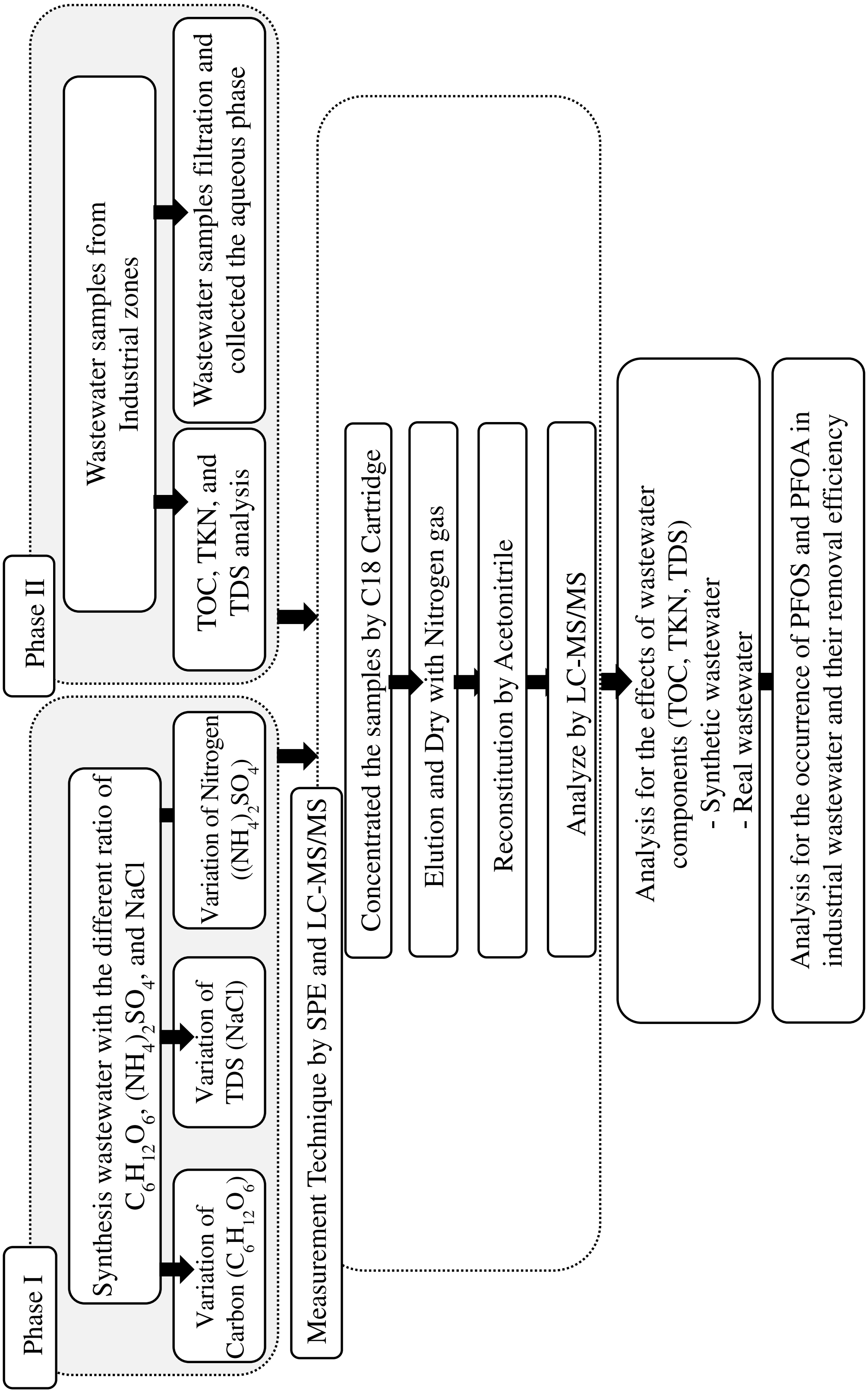


Figure 3.1 Framework of study

3.3 Synthetic wastewater

Wastewater was synthesized by varying on organic compound (Carbon, Nitrogen and Total dissolved solid) and mixing of PFOS and PFOA stock solutions with Milli-Q water to obtain synthetic wastewaters which have a concentration 5 µg/L for each chemical as shown in Table 3.1.

Table 3.1 Characteristic of the synthetic wastewater

Experimental Runs	**C source ($C_6H_{12}O_6$) (mg/L)**	**N source ($(NH_4)_2SO_4$) (mg/L)**	**TDS source (NaCl) (mg/L)**	**PFOS and PFOA (µg/L)**
1	0.0	0.0	0.0	5.0
2	50.0	0.0	0.0	
3	100.0	0.0	0.0	
4	500.0	0.0	0.0	
5	1000.0	0.0	0.0	
6	0.0	10.0	0.0	
7	0.0	50.0	0.0	
8	0.0	100.0	0.0	
9	0.0	500.0	0.0	
10	0.0	0.0	500.0	
11	0.0	0.0	1000.0	
12	0.0	0.0	3000.0	
13	0.0	0.0	5000.0	
14	500.0	100.0	0.0	
15	500.0	100.0	500.0	
16	500.0	100.0	1000.0	
17	500.0	100.0	3000.0	
18	500.0	100.0	5000.0	
19	0.0	100.0	3000.0	
20	50.0	100.0	3000.0	
21	100.0	100.0	3000.0	
22	500.0	100.0	3000.0	
23	1000.0	100.0	3000.0	
24	500.0	0.0	3000.0	
25	500.0	10.0	3000.0	
26	500.0	50.0	3000.0	
27	500.0	100.0	3000.0	
28	500.0	500.0	3000.0	

3.4 Monitoring PFOS and PFOA in industrial wastewater

3.4.1 Sampling protocol (Lien, 2007)

The monitoring of PFOS and PFOA were collected wastewater samples from industrial estate by followed to the sampling protocol (Lien, 2007).

Sampling and analysis procedure were prevented for glass and TEFLON materials because PFOS and PFOA may bind to the glass in aqueous solution and TEFLON materials may introduce interferences.

For sampling of industrial wastewater, metal bucket and funnel were used. They were rinsed with methanol and Milli-Q water to avoid cross contamination among different sampling. In order to minimize the possibility of contaminants introduction, materials attached to sample were rinsed carefully with methanol and *Milli-Q* water before being used. Disposable (polyethylene terephthalate) PET bottles with the volume of 1L to 2 L were used as sampling bottles. After filtration, samples were transfer to polypropylene (PP) or polyethylene (PE) bottles. After extraction, samples were transferred in PP vial for LC-MS/MS measurement.

At the sampling site, conductivity, pH, and temperature were simultaneously measured with the sampling process. Sample was separated into 2 parts, the first part was analyzed for PFOS, PFOA, TOC, and TDS. The second part was analyzed for TKN which was added with sulfuric acid to maintain pH of the sample below 2 . After collecting the samples, filtration was done immediately, after that followed by the SPE process and LC-MS/MS as shown in the next section.

3.4.2 Sampling location

Real industrial wastewater which used for Phase II study was collected from 2 industrial zones which were defined as IZ1 and IZ2, located in Ayutthaya province. The samples were collected from central wastewater treatment plant of industrial zone and the discharged pipe from selected industries. The details of sampling for Phase II study show in table 3.2 .

Table 3.2 Details of sampling for Phase II study

Industrial Zone	Sampling Date	Sampling points	Number of Sample
IZ1	30 September 2009	Central wastewater treatment plant	
		- CT1 : Influent of WWTP	2
		- CT2 : Aeration tank of WWTP	2
		- CT3 : Sedimentation of WWTP	2
		- CT4 : Effluent of WWTP	2
		Industries	
		- IN1 : Plastic industry	2
		- IN2 : Electronic industry	2
		- IN3 : Metal and mechanical industry	2
		- IN4 : Plastic industry	2
		- IN5 : Textile industry	2
		- IN6 : Electronic industry	2
		Total	*20*
IZ2	30 September 2009	Central wastewater treatment plant	
		- CT5 : Influent of WWTP	2
		- CT6 : Aeration of WWTP	2
		- CT7 : Sedimentation of WWTP	2
		- CT8 : Effluent of WWTP	2
		Industries	
		- IN7 : Air-conditioning industry	2
		- IN8 : Food industry	2
		- IN9 : Metal and mechanical industry	2
		- IN10 : Plastic industry	2
		- IN11 : Electronic industry	2
		Total	*18*

The study of occurrence of PFOS and PFOA in industrial wastewater was included with the existing data and previous sampling in Phase II study. The sampling of industrial wastewater was conducted in 7 industrial zones, which were defined as IZ1 - IZ7 as shown in Figure 3.2. The samplings were conducted for 12 times from August 2007 to September 2009. Totally 58 samples were collected from air-conditioning, coating, electronic, food, glass, plastic, textile industries and central wastewater treatment plant (WWTP). In the central wastewater treatment plant

(WWTP), the samples were collected from influent, aeration tank, and effluent. The details of sampling data show in Table 3.3 .

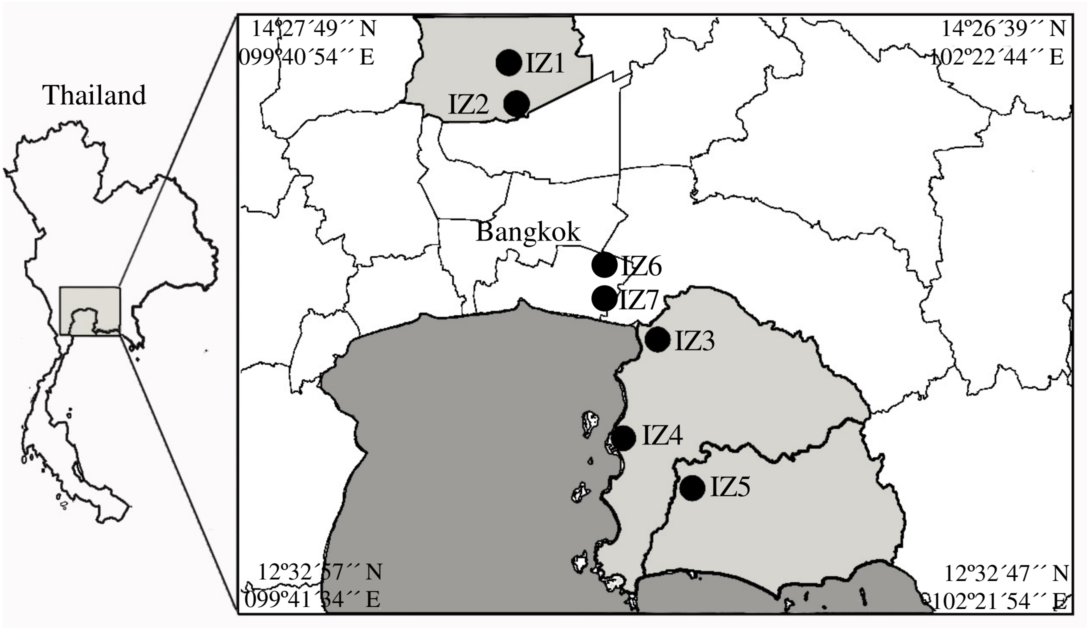


Figure 3.2 Sampling sites of industrial zones

Table 3.3 Details of industrial wastewater sampling

Sampling Date	Industrial Zones	Sample Sources	Number of Sample
24 August 2007	IZ7	Coatings industry	4
		Food industry	
		Plastic industry	
		Textile industry	
18 September 2007	IZ6	Plastic industry	1
8 February 2008	IZ2	Electronic industry	4
		Food industry	
		Plastic industry	
		Textile industry	
8 February 2008	IZ1	Coatings industry	5
		Electronic industry	
		Plastic industry	

Table 3.3 Details of industrial wastewater sampling (Cont.)

Sampling Date	**Industrial zones**	**Sample Sources**	**Number of Sample**
27 July 2008	IZ5	Air-condition industry Electronic industry Glass industry Central wastewater treatment plant	7
22 August 2008	IZ2	Air-condition industry Electronic industry Plastic industry Central wastewater treatment plant	6
22 August 2008	IZ1	Electronic industry Plastic industry Central wastewater treatment plant	6
29 August 2008	IZ3	Central wastewater treatment plant	3
29 August 2008	IZ4	Central wastewater treatment plant	3
29 April 2009	IZ2	Electronic industry Food industry Plastic industry Textile industry	5
30 September 2009	IZ2	Air-condition industry Electronic industry Food industry Plastic industry Central wastewater treatment plant	7
30 September 2009	IZ1	Electronic industry Glass industry Plastic industry Textile industry Central wastewater treatment plant	7
		Total	*58*

3.5 Analytical methods

All of the samples were measured for pH, Temperature, Conductivity, and concentration of PFOS and PFOA. All parameters were analyzed according to the methods as shown in Table 3.4

Table 3.4 Chemical and physical parameters and analytical methods

Parameters	Method of Analysis
pH	pH meter
Temperature	Thermometer
Conductivity	Conductivity meter
Suspended Solid	Dry at 103-105°C
Total Organic Carbon	TOC Analyzer, Model TOC-VCSH
Total Kjeldahl Nitrogen	ASTM D 3590-89 (Kjeldahl method)
Total Dissolved Solid	Dry at 180°C
PFOS and PFOA concentrations	SPE couple with LC-MS/MS

3.5.1 Determination of PFOS and PFOA in water sample

Concentrations of PFOS and PFOA in water samples were measured according to the method outlined in Lien (2007) and Lien *et al.* (2006) which include solid phase extraction (SPE) coupled with LC-MS/MS. The overall framework of the determination of PFOS and PFOA shows in Figure 3.3

3.5.1.1 Standard and chemicals

PFOA acid (98% purity) and potassium salt of PFOS (95% purity) were used for standard solution. Presep-C Agri cartridges (Solid phase: styrene divinylbenzene polymethacrylate) (Presep-C, 220 mg cartridge) and LC/MS-grade methanol were used for sample extraction. All of the above chemicals and cartridges were purchased from Wako Pure Chemicals (GK FINECHEM Co, Ltd, Thailand).

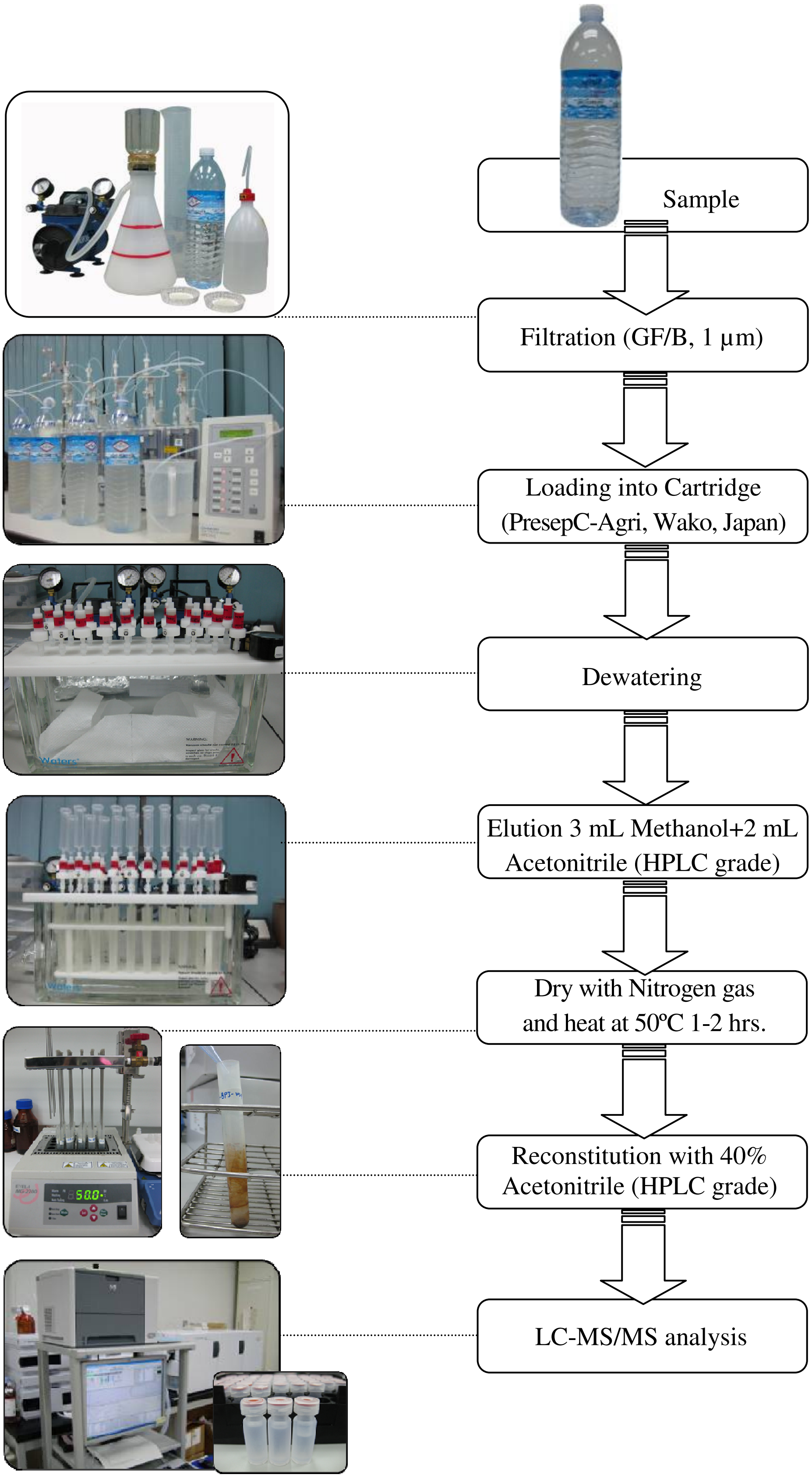


Figure 3.3 PFOS and PFOA analysis procedure

3.5.1.2 Solid phase extraction (SPE)

A sample was firstly filtered through 1 µm glass fiber filter (WHATMAN GF/B) to remove suspended solid. The cartridge was condition by passing 10 mL of LC/MS grade methanol at a flow rate of 10 mL/min and immediately followed by 50 mL Milli-Q water normally (Figure 3.4).

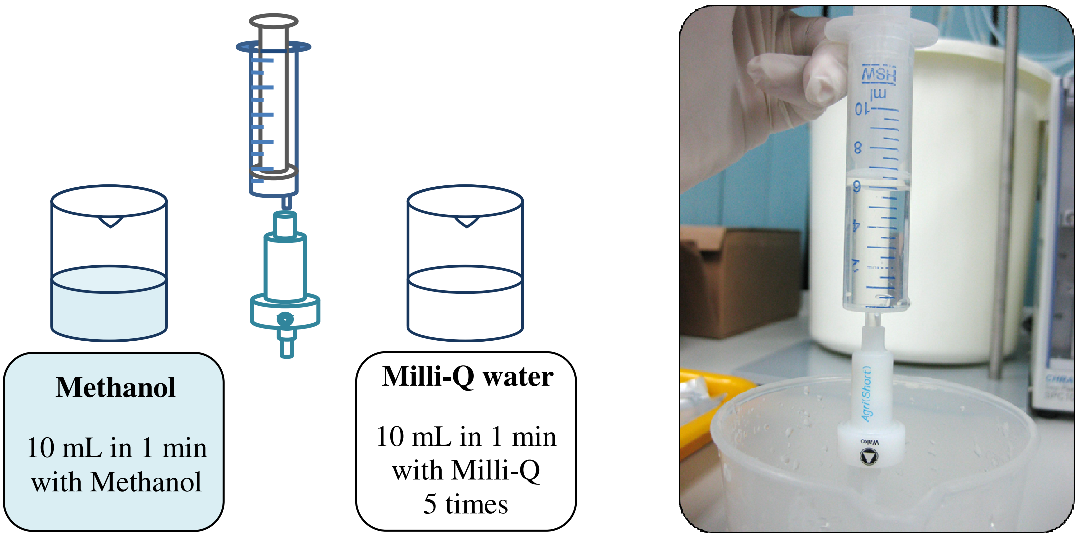
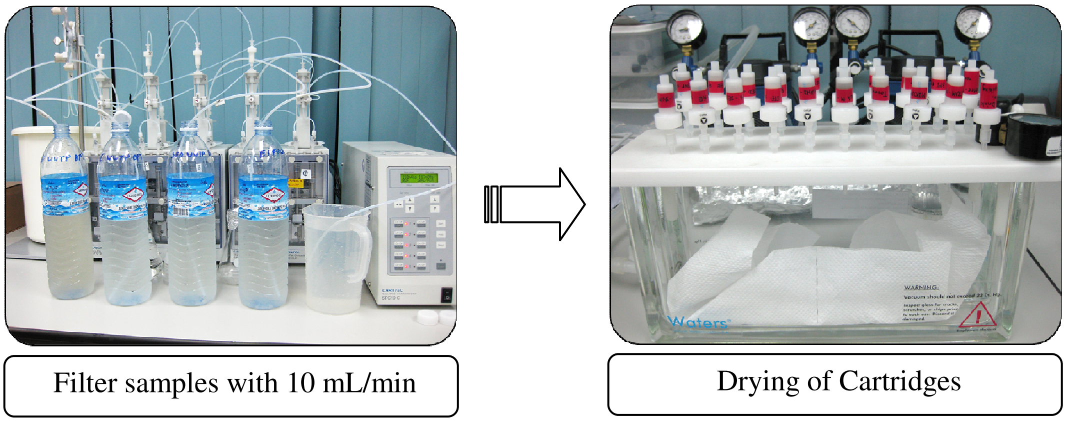


Figure 3.4 Conditioning of cartridge by methanol and milli-Q

An appropriate volume (normally 1L or 0.5L) of the pre-filtered sample was loaded on Presep-C Agri cartridge at a flow rate of 10 mL/min using a concentration system (Concentrator Plus, Waters, Japan or Pump) (Figure 3.5). Concentrator was cleaned by methanol for 3 minutes and followed by Milli-Q water 10 minutes before use.



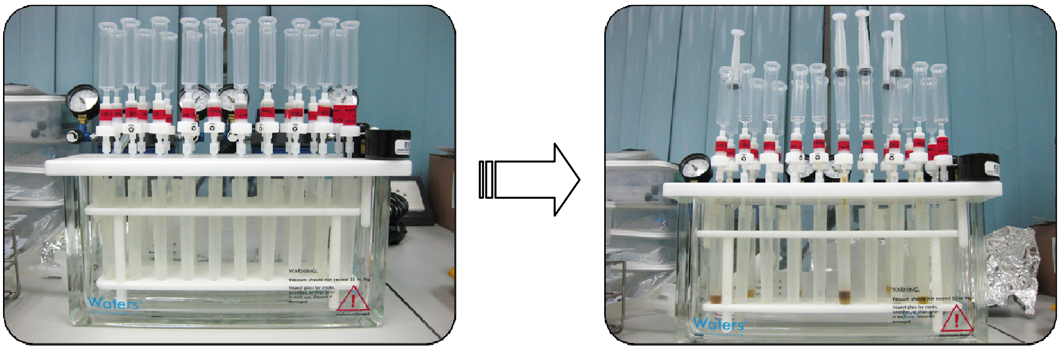
Filter samples with 10 mL/min

Drying of Cartridges

Figure 3.5 Loading samples into Presep-C Agri cartridges by using concentrator

Use vacuum manifold to air dry the cartridge. Fit the cartridge on the manifold, cover it with an aluminum foil layer to avoid contamination then, open the pump and do the vacuum for 1 hr as shown in Figure 3.6.

Keep the cartridge fixed on the vacuum manifold and place a rack inside the vacuum manifold setup and put vials into it. Cover the manifold by the lid containing dried cartridge. Then, put a syringe body (without piston) on the top of the cartridge and add 3 mL methanol (LC/MS grade) and followed by 2 mL acetonitrile. Wait until all acetonitrile pass through the cartridge and then turn on the vacuum pump for 3 min to pumping the residual (Figure 3.6).



Elute by 3 mL methanol and 2 mL Acetonitrile

Apply slight pressure and pumping residual 3 min

Figure 3.6 Eluting of cartridges by LC/MS grade methanol and acetonitrile

Dry methanol inside sample vial (recovered after eluting) by using high purity N_2 gas at the flow rate of 0.5 L/min/vial and set the temperature to 50°C for 1-2 hr. or until the sample in vial completely dried. Clean the nitrogen gas line before using and put the nitrogen line just above the sample level inside the vial (Figure 3.7).

Finally, the dried samples were reconstituted by adding a volume of 1 or 2 mL of 40% acetonitrile. Use the vibration to mix the samples properly at least 1 min. Then put the samples inside the auto sampler vials for LC-MS/MS quantification (Figure 3.7).

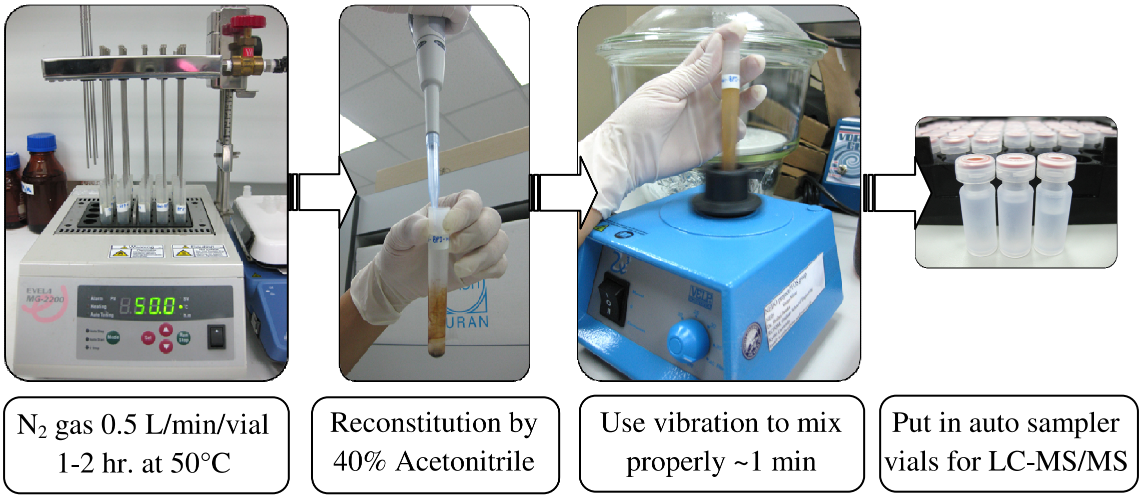


Figure 3.7 Drying the eluted samples with N_2 gas and reconstitution

3.5.1.3 LC-MS/MS Quantification

Prior to detection, the extract was separated by the HPLC system with a 4.6x50 mm (1.8 µm) and 2.1x100 mm (1.8 µm) Agilent Eclipe XDB-C18 column. The mobile phase consisted of (A) 5 mM ammonium acetate in ultrapure water and (B) 100% Acetonitrile. At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B) as shown in Table 3.5. The total running time was 34 min for each sample. For quantitative determination, Agilent 6410 Triple Quad mass spectrometer was used with electrospray ionization (ESI) negative mode.

Table 3.5 Running time of mobile phase

	Time (min)	**Mobile phase**		**Flow rate (mL/min)**
		5 mM ammonium acetate (A) (%)	**Acetonitrile (B) (%)**	
1	0	70	30	0.25
2	16.5	50	50	0.25
3	16.6	30	70	0.25
4	21	10	90	0.25
5	22	70	30	0.25

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Phase I synthetic wastewater

This phase was studied about the relation of organic components (C, N, and TDS) to the measurement technique of PFOS and PFOA by using synthetic wastewater. The characteristic of synthetic wastewater for each experimental run was shown in Table 3.1, Chapter III.

The chemicals used for synthetic wastewater were glucose, ammonium sulphate, and sodium chloride. These chemicals were calculated the molecular weight to make the varied concentration and diluted in Milli-Q water. The exact concentrations of synthetic wastewater were also measured as shown in Table 4.1. After that, PFOS and PFOA standard solution were added in synthetic wastewater at the concentration of 5 μg/L for each sample. Samples were analyzed by LC-MS/MS for quantitative determination. High performance liquid chromatography (HPLC) was interfaced with an Agilent 6410 Triple Quadrupole mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reaction monitoring (MRM) mode.

The calibration curves for quantification, consisting of five points covering 2 ng/mL – 10 ng/mL, generally provided linearity with determination coefficients (R^2) more than 0.999 as shown in Figure 4.1 for PFOS and Figure 4.2 for PFOA. The retention time (RT) of PFOS and PFOA were 10.9 minutes and 4.8 minutes, respectively, as shown in Figure 4.3. Limit of detection (LOD) for LC-MS/MS was defined as concentration with signal to noise ratio (*S/N*) equal to 3:1. Practically, Limit of Quantification (LOQ) was used for quantifying analytes, which was defined by S/N 10:1 (Saito *et al*., 2003; Hansen *et al*., 2001). The identified LOQ was shown in Table 4.2.

The experimental study of phase I was divided into three sections. First section, the sample was directly injected to LC-MS/MS analysis (without solid phase extraction or SPE processes). Second section, the samples were pretreated by solid phase extraction (SPE) processes which were concentrated by C18 cartridge before analyze by LC-MS/MS. This second section was focused on the SPE process which the treated sample by SPE process was cleaner than the sample without SPE process. And also in the second section, the drainage synthetic wastewater after passed C18 cartridge was measured for TOC, TKN, and TDS to find out the adsorption ability of C18 cartridge on C, N, and TDS source. The last study section of phase I was compared the relation between the first and the second sections or SPE and non-SPE process. Our understanding of the sample with SPE process is cleaner than the sample without SPE process. Hence, this section was illustrated how different of SPE and non-SPE process which presented by a concentration of PFOS and PFOA.

Table 4.1 The calculated and measured concentration of synthetic wastewater

	Calculated concentration (mg/L)	**Measurement concentration (mg/L)**
C source ($C_6H_{12}O_6$)	0.0	5.6
	50.0	51.4
	100.0	99.1
	500.0	468.2
	1000.0	958.7
N source ($(NH_4)_2SO_4$)	0.0	1.4
	10.0	11.2
	50.0	56.1
	100.0	112.1
	500.0	576.2
TDS source (NaCl)	0.0	5.0
	100.0	98.0
	500.0	475.0
	1000.0	988.0
	3000.0	2999.0

Table 4.2 Analytical parameters of each PFOS and PFOA by LC-MS/MS analysis

Compound	**No. of Carbon**	**Parent ion (*m/z*)**	**Daughter ion (*m/z*)**	**Retention Time (min.)**	**LOD (ng/L)**	**LOQ (ng/L)**
PFOS	C-8S	499	80	10.9	0.07	0.24
PFOA	C-8A	413	369	4.7	0.08	0.27

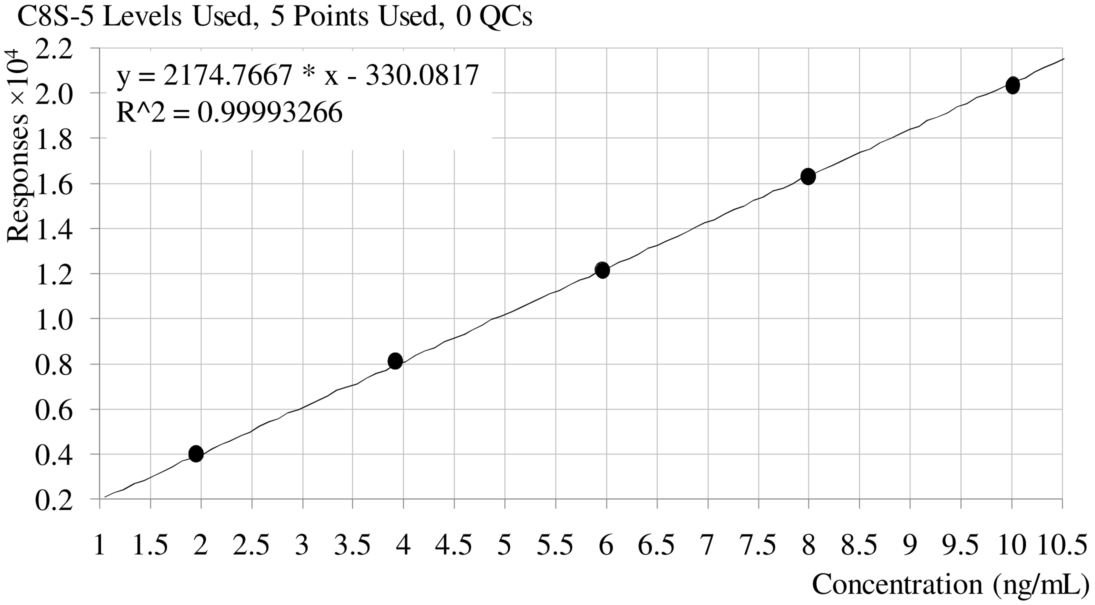


Figure 4.1 The calibration curves for quantification of PFOS consisting of five points covering 2 ng/mL – 10 ng/mL

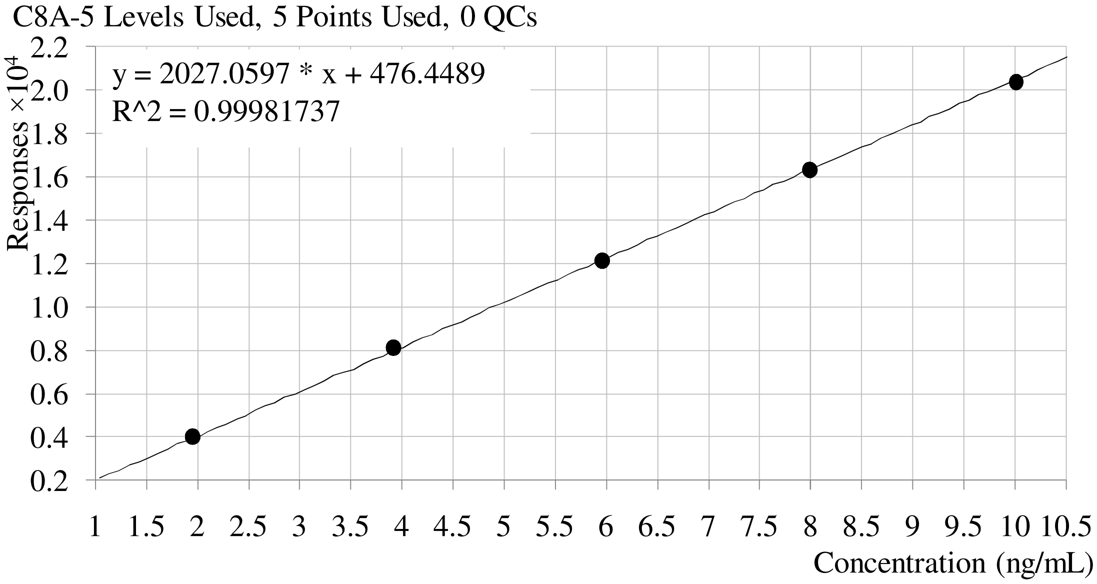


Figure 4.2 The calibration curves for quantification of PFOA consisting of five points covering 2 ng/mL – 10 ng/mL

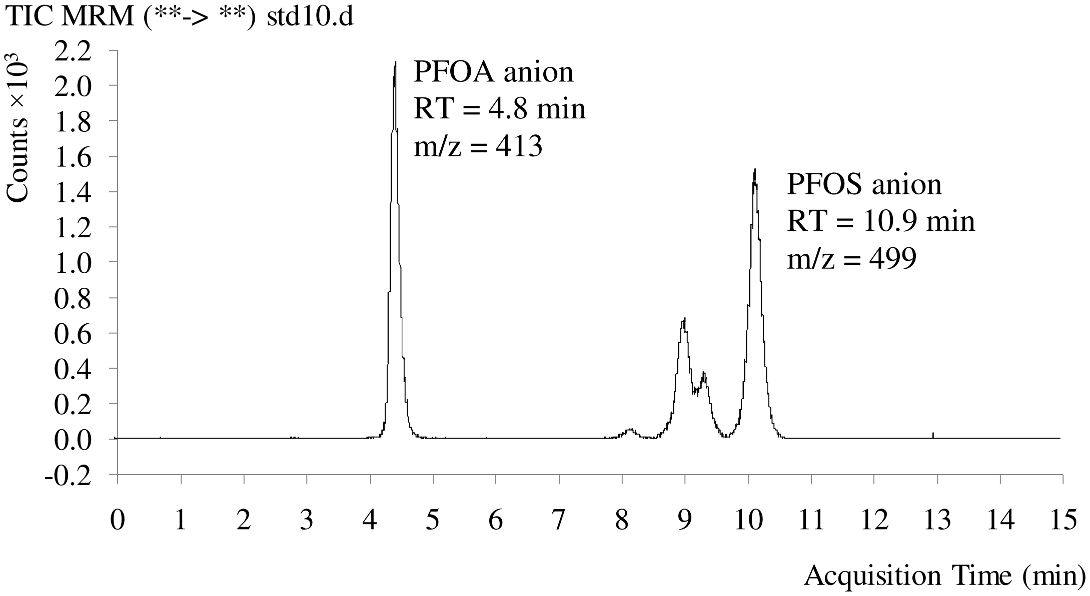


Figure 4.3 Mass Chromatographs of PFOS and PFOA at 10 µg/L

4.1.1 The effect of wastewater components to the measurement of PFOS and PFOA with direct analysis by LC-MS/MS

The first section was studied the effect of wastewater component (C, N, and TDS) to the measurement technique. The experiment of this section was used only LC-MS/MS which the samples were not passed solid phase extraction processes but were directly analyzed by LC-MS/MS. Results of the first section (Figure 4.4) identify by the word of LC and markers illustrate by the grey color (● PFOS, ▲ PFOA). The X-axis represents the concentration of wastewater components (C, N, and TDS) in the unit of mg/L and the Y-axis represents the concentration of PFOS and PFOA in the unit of µg/L. The three figures upper show the variation of each wastewater component with the zero concentration of others components. The three figures below show the variation of each wastewater components with the constant concentration of others components.

From the results in Figure 4.4, focusing on the upper three figures were found significantly decreasing of the concentration of PFOS and PFOA in the variation of N-source (Figure 4.4(b)) and TDS-source (Figure 4.4(c)). However, the concentration of PFOS and PFOA were almost constant when C-source was increased to higher concentration (Figure 4.4(a)). Focusing on the lower three figures (Figure 4.4(d)-(f)) were found similar results as the upper three figures (Figure 4.4(a)-(c)) but the concentration of PFOS and PFOA, which were varied on C, N, and TDS–source with the mix constant concentration of others source, were lower than the upper one. Although, the concentration of PFOS and PFOA were almost constant at the lower concentration when the concentration of C-source was increased. These might be caused of the N and TDS-sources which were effected to the reduction of the concentration of PFOS and PFOA. Previous study by Lien (2008) reported that there could be little relation between contamination of PFOS-PFOA and dissolved organic carbon (DOC). However, Lin *et al.* (2009) reported that the Perfluorinated acids (PFAs) were not associated with the TOC content which was similar to this study. These might be supported to the results which C-source was not associated to the measurement of PFOS and PFOA by LC-MS/MS. From the Figure 4.4(a)-(f), the concentrations of PFOS were found lower than the concentrations of PFOA in all of samples. These might be related to the measurement efficiency which were defined by the recovery ratio of analysis as shown in Figure 4.5(a) – (f). The results of recovery ratio in this study were represented as a percentage (%) value. The blank of wastewater components added with 5 µg/L of PFOS and PFOA standard was found the recovery ratio of PFOS and PFOA were 71% and 93%, respectively. Focusing on the upper three figures, when the concentration of C-source (Figure 4.5(a)) was increased, recovery ratio of PFOS and PFOA were slightly decreasing from 71% to 68% and 93% to 89%, respectively. In case of N-source as shown in Figure 4.5(b), when the concentration of N-source was increased, recovery ratio of PFOS and PFOA were decreasing from 71% to 25% and 93% to 76%, respectively. In case of TDS-source as shown in Figure 4.5(c), when the concentration of TDS-source was increased, the recovery ratio of PFOS and PFOA were decreasing from 71% to 22% and 93% to 70%, respectively. Focusing on the lower three figures, when the concentration of C-source (Figure 4.5(d)) was increased, recovery ratio of PFOS and PFOA were decreasing from 71% to 19% and 93% to 71%, respectively. In case of N-source as shown in Figure 4.5(e), when the concentration of N-source was increased, recovery ratio of PFOS and PFOA were decreasing from 71% to 15% and 93% to 65%, respectively. In case of TDS-source as shown in Figure 4.5(f), when the concentration of TDS-source was increased, the recovery ratio of PFOS and PFOA were decreasing from 71% to 20% and 93% to 73%, respectively. Focusing on the variation of C-source (Figure 4.5(a) and (d)), the recovery ratio of PFOS and PFOA were very slightly decreased. Although, the concentration of PFOS and PFOA in the Figure 4.5(d) was much lower than Figure 4.5(a), which were explained by the other wastewater components (TDS-source or N-source) might be effected to PFOS and PFOA analysis. Focusing on the variation of N and TDS sources, the recovery of PFOA were decreased when concentration of N and TDS sources were increasing especially, for the recovery ratio of PFOS was significantly decreasing. Study on the correlation coefficient (*R*) between C, N, and TDS sources and the concentration of PFOS and PFOA, the less correlation coefficient was found between C-source and PFOS/PFOA which were -0.20 and -0.22, respectively. The greater correlation coefficient was found between N-source and PFOS/PFOA which were -0.44 and -0.50, respectively. Similar to TDS-source was also found the greater correlation coefficient between TDS-source and PFOS/PFOA which were -0.56 and -0.68, respectively. Some research found the recoveries of PFOS in tap water and environmental water samples which were assumed as less contamination of interfere, were lower than PFOA (Sinclair *et al.*, 2006 and Skutlarek, 2006). Fujii *et al.* (2007), reported the recoveries in environmental water samples were 87% for PFOS and 95% for PFOA (in average). These might be explained by the water solubility of PFOS and PFOA, which the water solubility is 680 mg/L for PFOS (OECD, 2002) and 9,500 mg/L for PFOA (US EPA, 2005). Previous studies were reported the higher concentration of PFOA was depended on the higher water solubility (Lien, 2008, Yamashita, 2005, and Berger, 2004). The effect of N and TDS-sources were showed the decreasing of the concentration of PFOS and PFOA, when the concentration of N and TDS-sources were increasing. It might be explained by the interference of N and TDS-source in samples to the measurement technique of LC-MS/MS. The reason of these phenomena still was not clear, but some studies reported the decreased biological matrices such as plasma, whole blood, serum and milk which are compound with C, H, O, N, and etc., were effected to the measurement and accuracy of analysis (Ehresman *et al.*, 2007, Kannan *et al.*, 2004, and Karrman *et al.,* 2005). Recently, there has no experimental research about the relation between N or TDS-source and PFOS or PFOA. This is the first study shown the effect of N to the measurement of PFOS and PFOA by conducting the experiments in laboratory. However, more study of these phenomena is required to approve this hypothesis and then the next section experiment in 4.1.2 was conducted.

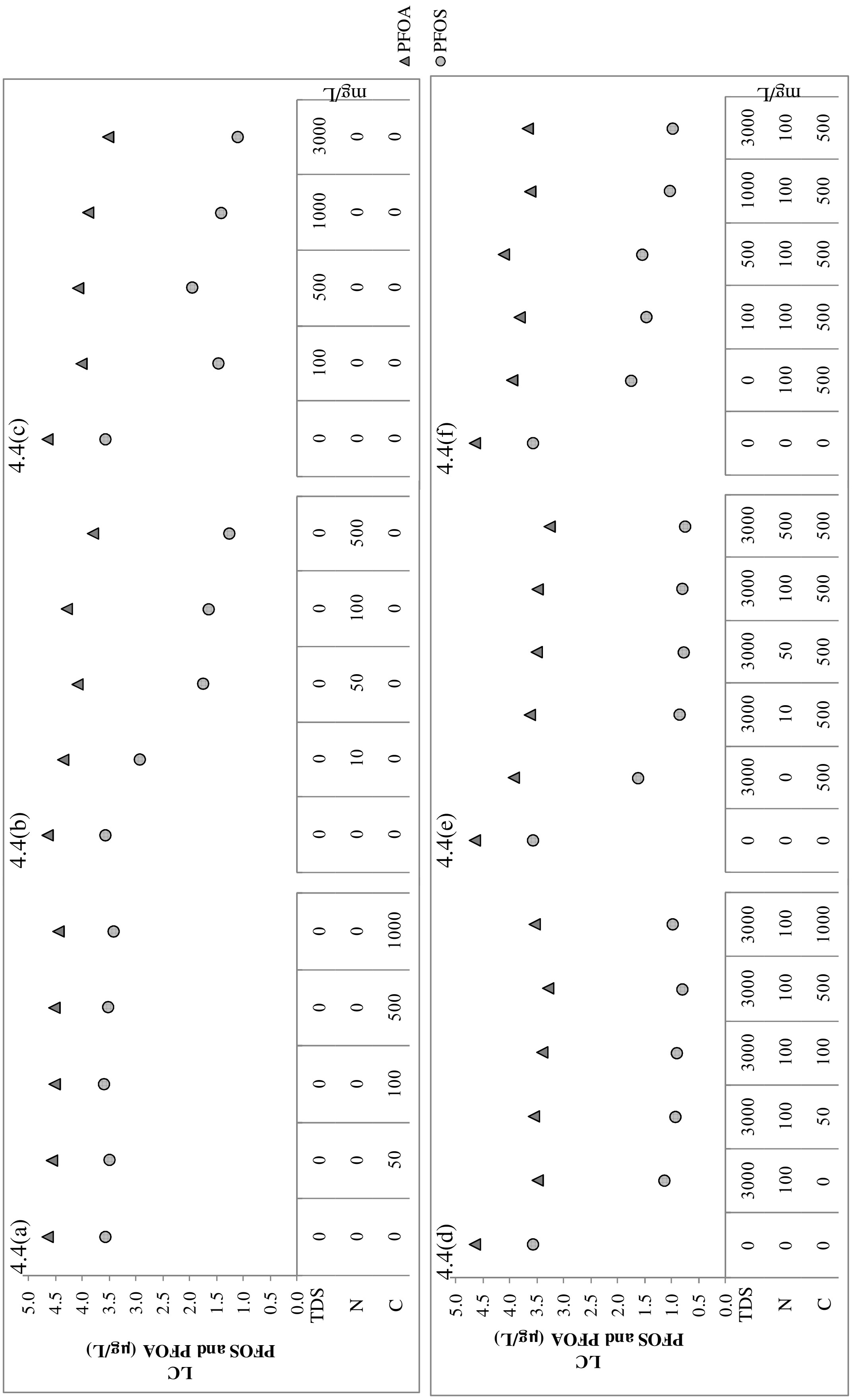


Figure 4.4 The relation of wastewater components to the concentration of PFOS and PFOA by directly analyze with LC-MS/MS

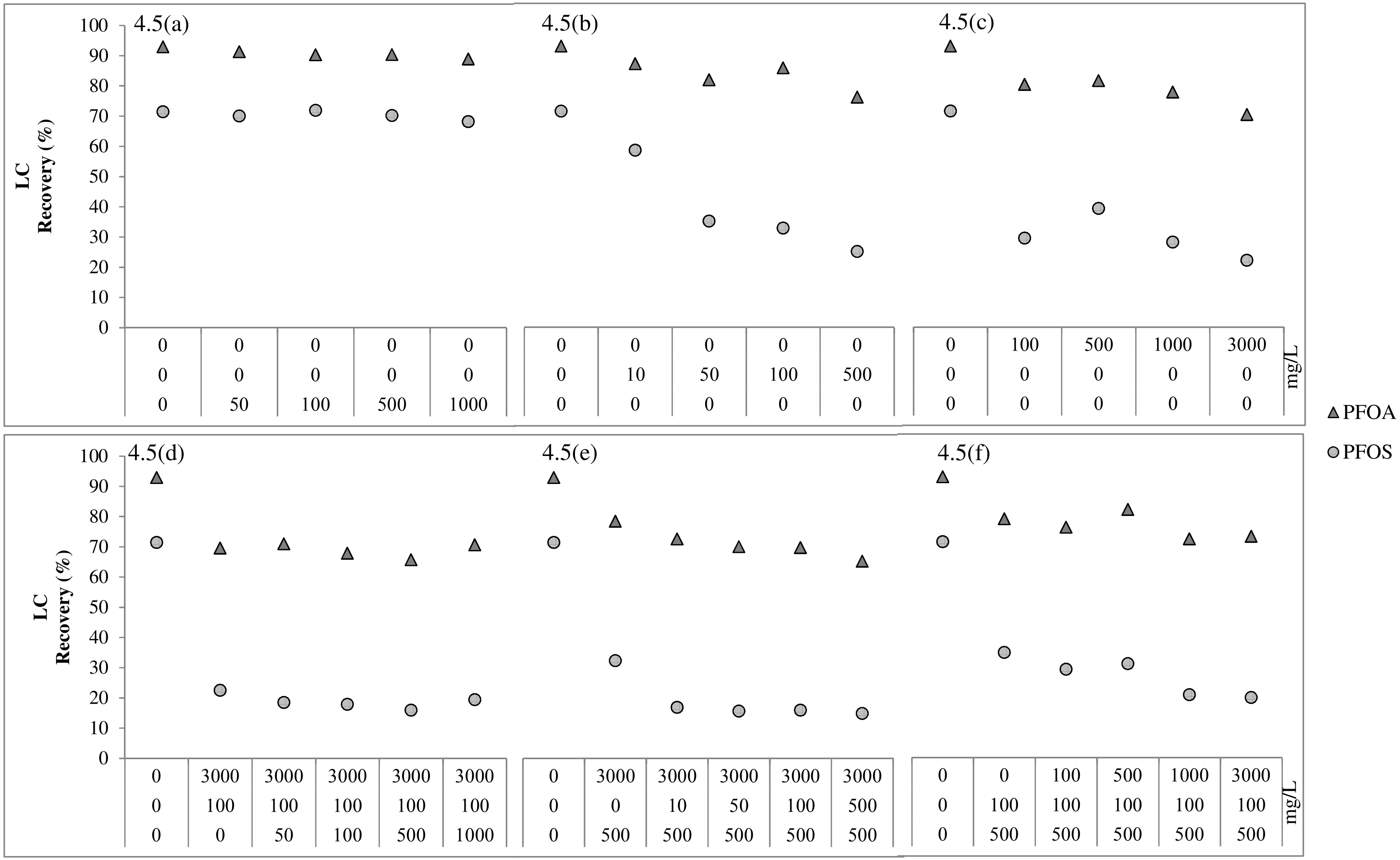


Figure 4.5 Recovery ratio of PFOS and PFOA with the variation of wastewater components by directly analyze with LC-MS/MS

4.1.2 The effect of wastewater components to the measurement of PFOS and PFOA with SPE process coupled with LC-MS/MS

The second section was studied the effect of wastewater component (C, N, and TDS) to the measurement technique which was focused on the measurement process. The method of solid phase extraction (SPE) process coupled with LC-MS/MS was applied to this section. The experiment process of this section was identical done as the real industrial wastewater. The purposed of this section study was to investigate the concentration of PFOS and PFOA by using of SPE process and studied the effect of C, N, and TDS sources to the measurement of PFOS and PFOA. Figure 4.5 shows the results of the second section which was identified by the word of LC+SPE and markers illustrate by the white color (○ PFOS, △ PFOA). The X-axis represents the concentration of wastewater components (C, N, and TDS) in the unit of mg/L and the Y-axis represents the concentration of PFOS and PFOA in the unit of µg/L. The three figures upper show the variation of each wastewater component with the zero concentration of others components. The three figures below show the variation of each wastewater components with the constant concentration of others components.

From the results in Figure 4.6, focusing on the upper three figures were found significantly decreasing of the concentration of PFOS and PFOA in the variation of N-source (Figure 4.6(b)) and TDS-source (Figure 4.6(c)) which were similar to the result in section 4.1.1. Similarly with the C-source variation result, the concentration of PFOS and PFOA were almost constant when C-source was increased to higher concentration (Figure 4.6(a)). The lower three figures (Figure 4.6(d)-(f)), also show the similar trend of PFOS and PFOA when the concentration of wastewater components were changed, as in the upper three figures (Figure 4.6(a)-(c)). Study on the recovery ratio of analysis as shown in Figure 4.7(a) – (f). The results of recovery ratio were represented as a percentage (%) value. The blank of wastewater components was found the recovery ratio of PFOS and PFOA were 85% and 71%, respectively. Focusing on C-source (Figure 4.7(a) and (d)), the recovery ratio of PFOS and PFOA were almost constant when the concentration of C-source was increased which were similar to the result in section 4.1.1. In case of N-source at the upper figure (Figure 4.7(b)), recovery ratio of PFOS and PFOA were decreasing from

85% to 68% and 71% to 2%, respectively. In case of N-source at the lower figure (Figure 4.7(e)), recovery ratio of PFOS and PFOA were decreasing from 85% to 70% and 71% to 34%, respectively. In case of TDS-source at the upper figure (Figure 4.7(c)), when the concentration of TDS-source was increased, the recovery ratio of PFOS was decreasing from 85% to 69%. However, PFOA was increasing from 71% to 83%. In case of TDS-source as shown in lower figure (Figure 4.5(f)), when the concentration of TDS-source was increased, the recovery ratio of both PFOS and PFOA were decreasing from 85% to 65% and 71% to 16%, respectively. Study on the correlation coefficient (*R*) between C, N, and TDS sources and the concentration of PFOS and PFOA, the less correlation coefficient was found between C-source and PFOS/PFOA which were -0.30 and -0.33, respectively. The greater correlation coefficient was found between N-source and PFOS/PFOA which were -0.66 and -0.86, respectively. Similar to TDS-source was also found the greater correlation coefficient between TDS-source and PFOS which were -0.83. The correlation coefficient between TDS-source and PFOA was lower than previous result (4.1.1) which was -0.35. Comparing of recovery ratio between section 4.1.1 and this section was found the similar results which the variation of C-source was not effected to measurement of PFOS and PFOA. Meanwhile, an increasing of N and TDS source showed the decreasing trend of both PFOS and PFOA.

To support this hypothesis, the backup experiment was set up by analyzing the concentration of C, N, and TDS in the drainage of synthetic wastewater which was passed the C18 cartridge. Figure 4.6 shows the relationship of concentration in the drainage wastewater which was measured for the concentration of C, N, and TDS. The X and Y axis represent the concentration of synthetic wastewater components in the unit of mg/L. Plots fluctuated around the linear line 1:1 and the black line with black square (—■—) represents the influent of synthetic wastewater to C18 cartridge (before passing C18 cartridge), the dot line with white square (-□-) represents the drainage of synthetic wastewater from C18 cartridge (after passed the C18 cartridge).

Three upper figures showed the variation of C (Figure 4.8(a)), N (Figure 4.8(b)) and TDS (Figure 4.8(c)) with the zero concentration of the others components. Three lower figures showed the variation of C (Figure 4.8(d)), N (Figure 4.8(e)) and TDS (Figure 4.8(f)) with the constant concentration of the others components. Figure

4.8(a) and 4.8(b) illustrate the linear line 1:1 of C-source, plot fluctuation of the drainage concentration of C-source was found higher than the influent concentration. It meant the C-source was not adsorbed by C18 cartridge. In additional higher C-source concentration might be cause from methanol which was used to clean up for the loading processes. N-source results were shown in Figure 4.8(b) and 4.8(e), the drainage concentration of N-source was found lower than the influent concentration, suggesting that N-source were adsorbed by C18 cartridge. Also with the backup experiment of TDS-source as shown in Figure 4.8(c) and 4.8(f), were found the lower drainage concentration of TDS-source than the influent concentration. This might explain by the adsorbed ability of C18 cartridge and elution process, N and TDS source might be remained in the treated sample and effected to the measurement technique of LC-MS/MS analysis. When the water or wastewater was contaminated by several components such as organic, inorganic compound, metal, solid particles, and etc., these might be interfered to the measurement process. Especially, if the target pollutant is in the small unit such as μg/L, ng/L, or pg/L which are easy to get an incorrect data, these should be concern about an interference of measurement process. Some studies found the strength of concentration of matrices were affected to the measurement of LC-MS/MS. Especially, studies of the effect of matrices on the serum, plasma, milk, blood, or protein in human sample to the measurement technique of PFOS and PFOA which were represented the lower recoveries of both PFOS and PFOA concentration in aqueous samples (Ehresman *et al.* 2007, Karrman *et al.* 2006). From the result in previous section and this section, found the different concentration of PFOS and PFOA which were caused from the different of measurement process. Hence, the next section in 4.1.3 was compared the concentration of PFOS and PFOA between the use of SPE and non-SPE process.

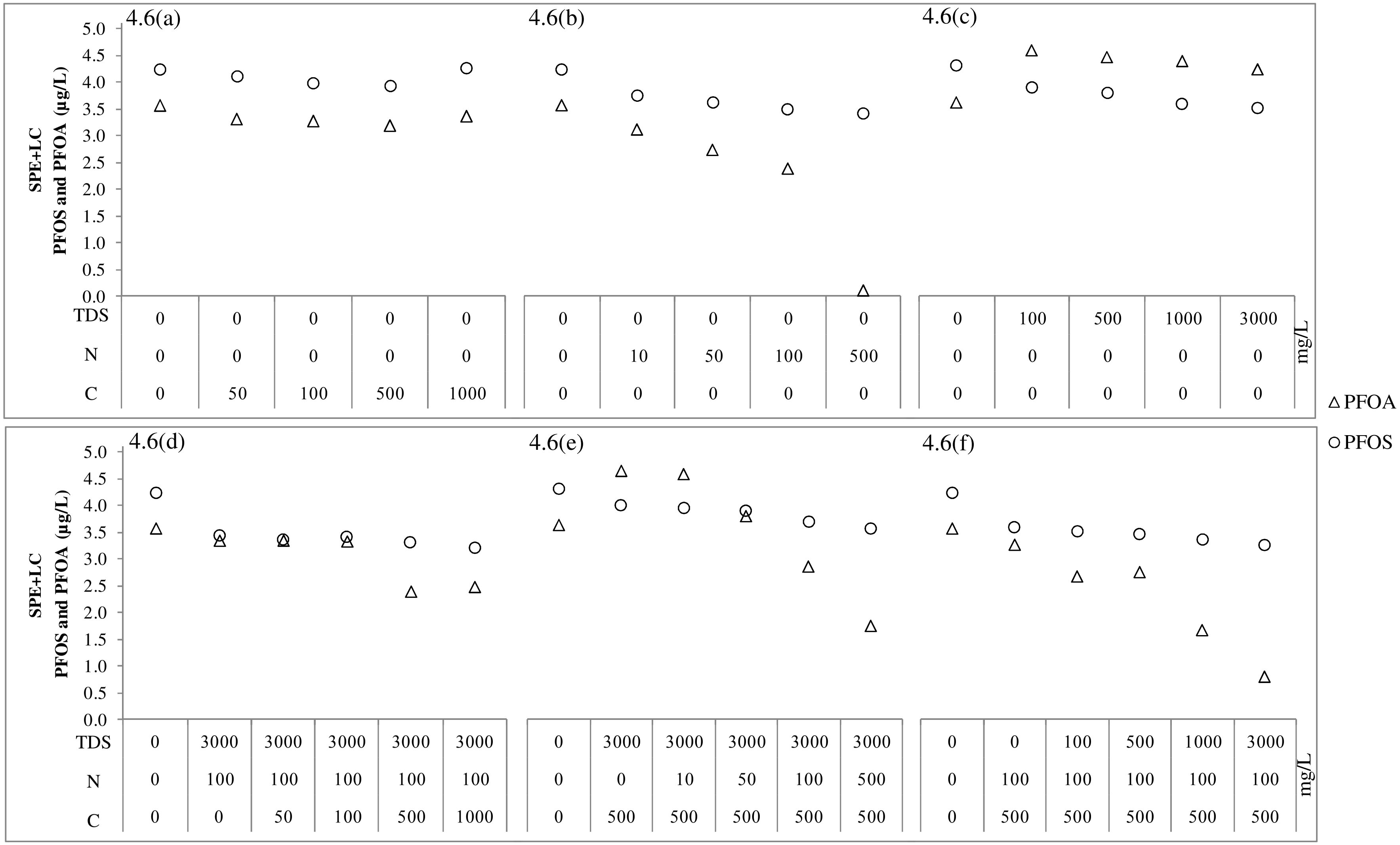


Figure 4.6 The relation of wastewater components to the concentration of PFOS and PFOA by the method of SPE couple with LC-MS/MS

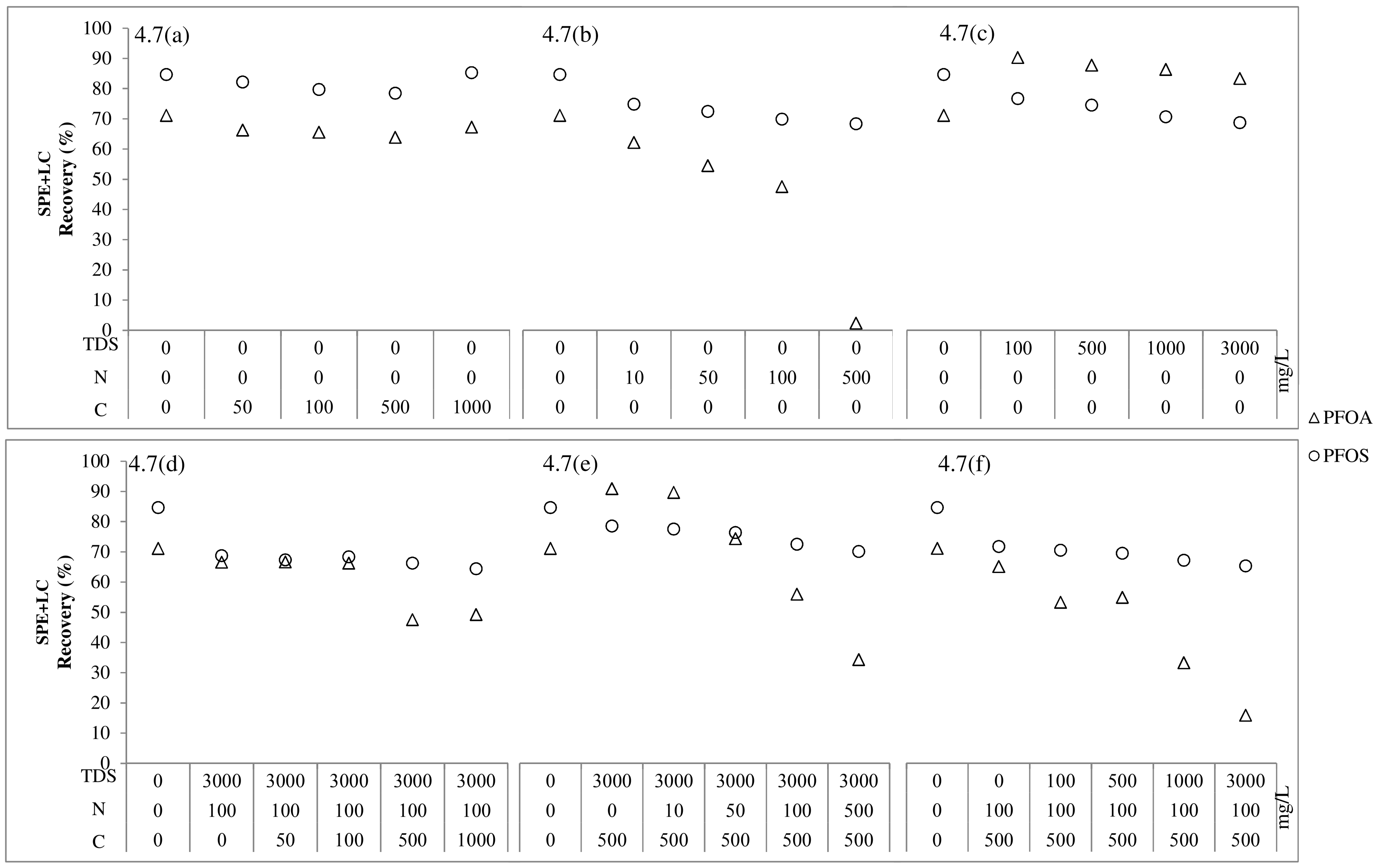


Figure 4.7 Recovery ratio of PFOS and PFOA with the variation of wastewater components by the method of SPE couple with LC-MS/MS

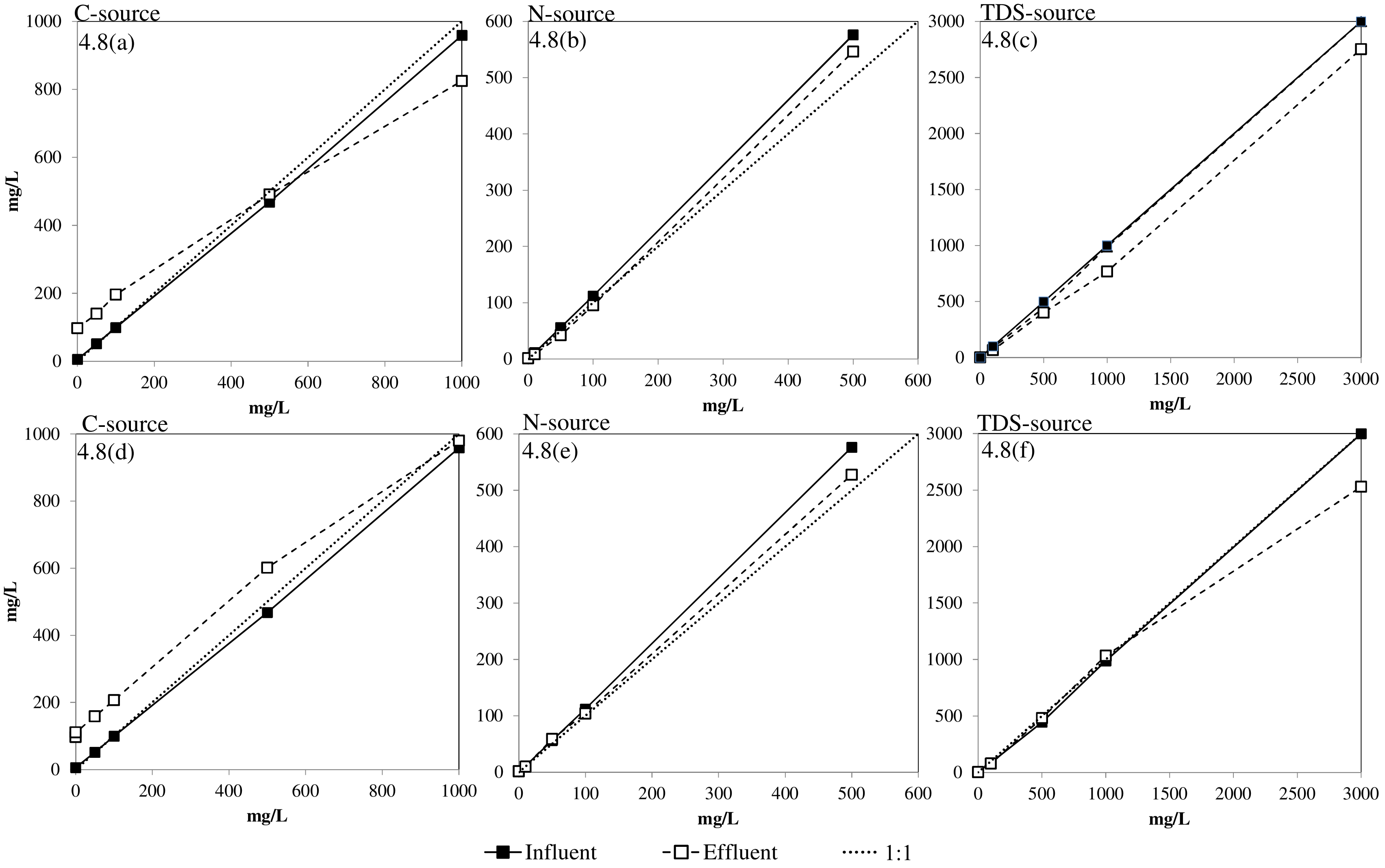


Figure 4.8 The characteristic of synthetic wastewater at the influent and the effluent of C18 cartridge

4.1.3 Comparison of the analysis procedure between SPE and non-SPE process to the concentration of PFOS and PFOA

From the result in section 4.1.1 and 4.1.2 (Figure 4.4 and 4.6), which were used different analysis procedure of PFOS and PFOA. In the section of 4.1.1 was directly injected the synthetic wastewater sample to LC-MS/MS but in the section 4.1.2 was applied the solid phase extraction (SPE) before analyzed by LC-MS/MS. That meant to the sample in section 4.1.2 was cleaner than the sample in 4.1.1. Then, this section was proposed to compare the concentration of PFOS and PFOA between using of SPE and non-SPE process as shown in Figure 4.9 for PFOS and Figure 4.10 for PFOA. The grey circle (●) and grey triangle (▲) represent the non-treated sample (without SPE process) of PFOS and PFOA, respectively. The white circle (○) and white triangle (△) represent the treated sample (with SPE process) of PFOS and PFOA, respectively. In case of PFOS (Figure 4.9) was found the significantly different between SPE and non-SPE processes. The white circle or the method of SPE couple with LC-MS/MS was shown the higher concentration of PFOS than non-SPE process (grey circle) in all of the samples. Comparing between SPE and non-SPE process of PFOS (Figure 4.11), the recovery ratio of PFOS by the method of non-SPE process was found lower than the method of SPE process. Focusing on the recovery ratio of PFOS by using the method of SPE couple with LC-MS/MS (Figure 4.11), found that the recovery ratio of PFOS was almost constant which was in the range of 65% - 85% although, there was varied with the concentration of wastewater components. Different from the method of non-SPE process, the recovery ratio was varied in the lower range of 15% - 71%. However, the concentration of PFOA as shown in Figure 4.10 was found no significant different between the method of SPE and non-SPE process. Moreover, the concentration of PFOA by using the method of SPE process was found lower than using the method of non-SPE process. The recovery ratio of PFOA (Figure 4.12) by using the method of non-SPE process was in the range of 65% - 93% while, the recovery ratio of PFOA by using the method of SPE process was found in the lower range of 2% - 71%. That might be explained the SPE process was advantaged to the measurement of PFOS more than PFOA. Loading volume or the capacity of C18 cartridge might be limited to the quantity or concentration of absorbed chemical.

In this section was studied on synthetic wastewater which purposed to identify the cause of decreasing of PFOS and PFOA by focused on the major wastewater constituent such as carbon, nitrogen, and total dissolved solid source. From the result found that nitrogen and total dissolved solid source were seemed to affect to the measurement of PFOS and PFOA, whereas carbon source has no affect to PFOS and PFOA. Therefore, the next section was purposed to study on the real industrial wastewater.

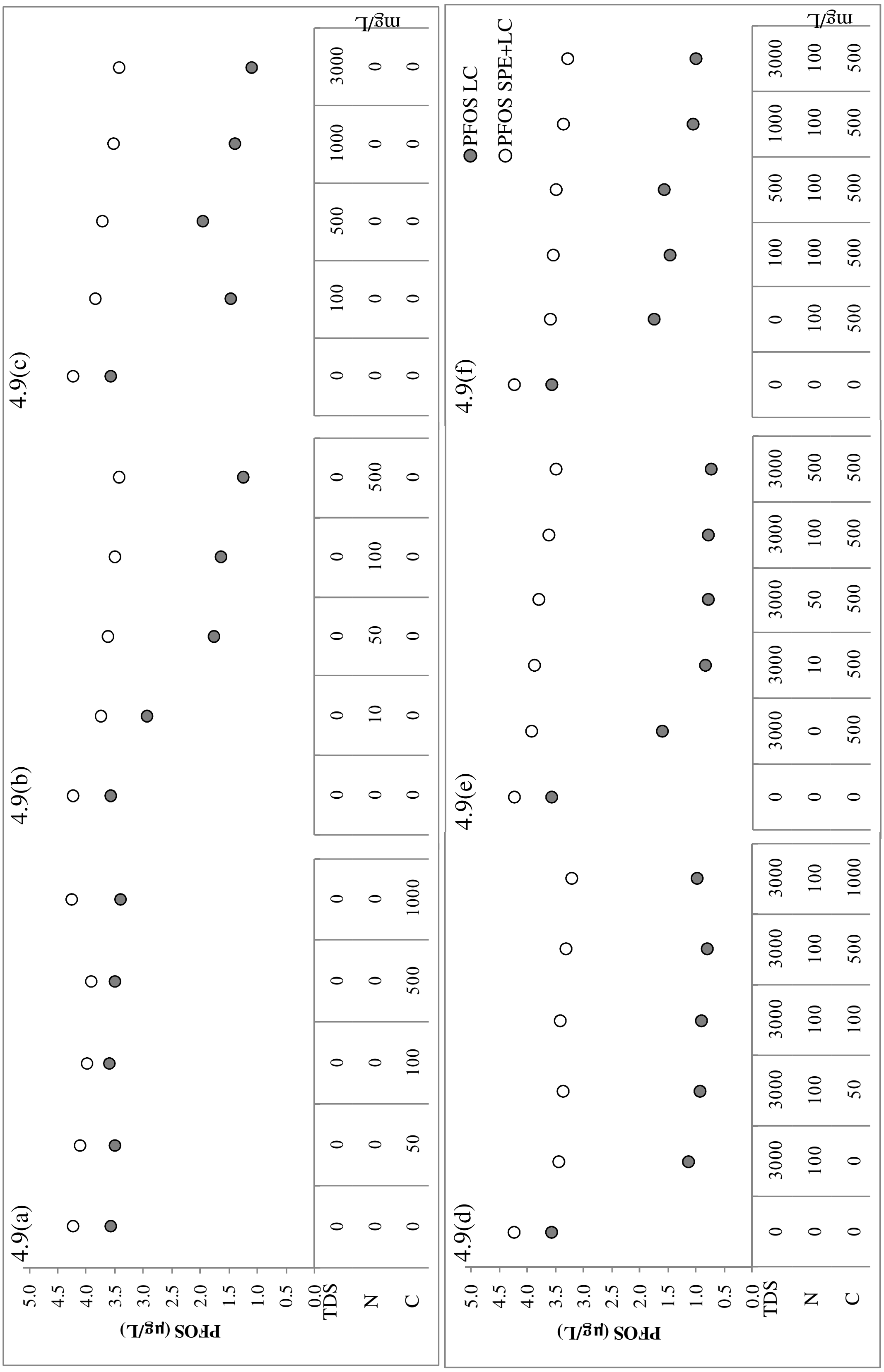


Figure 4.9 The comparison of PFOS concentration between using SPE and non-SPE processes.

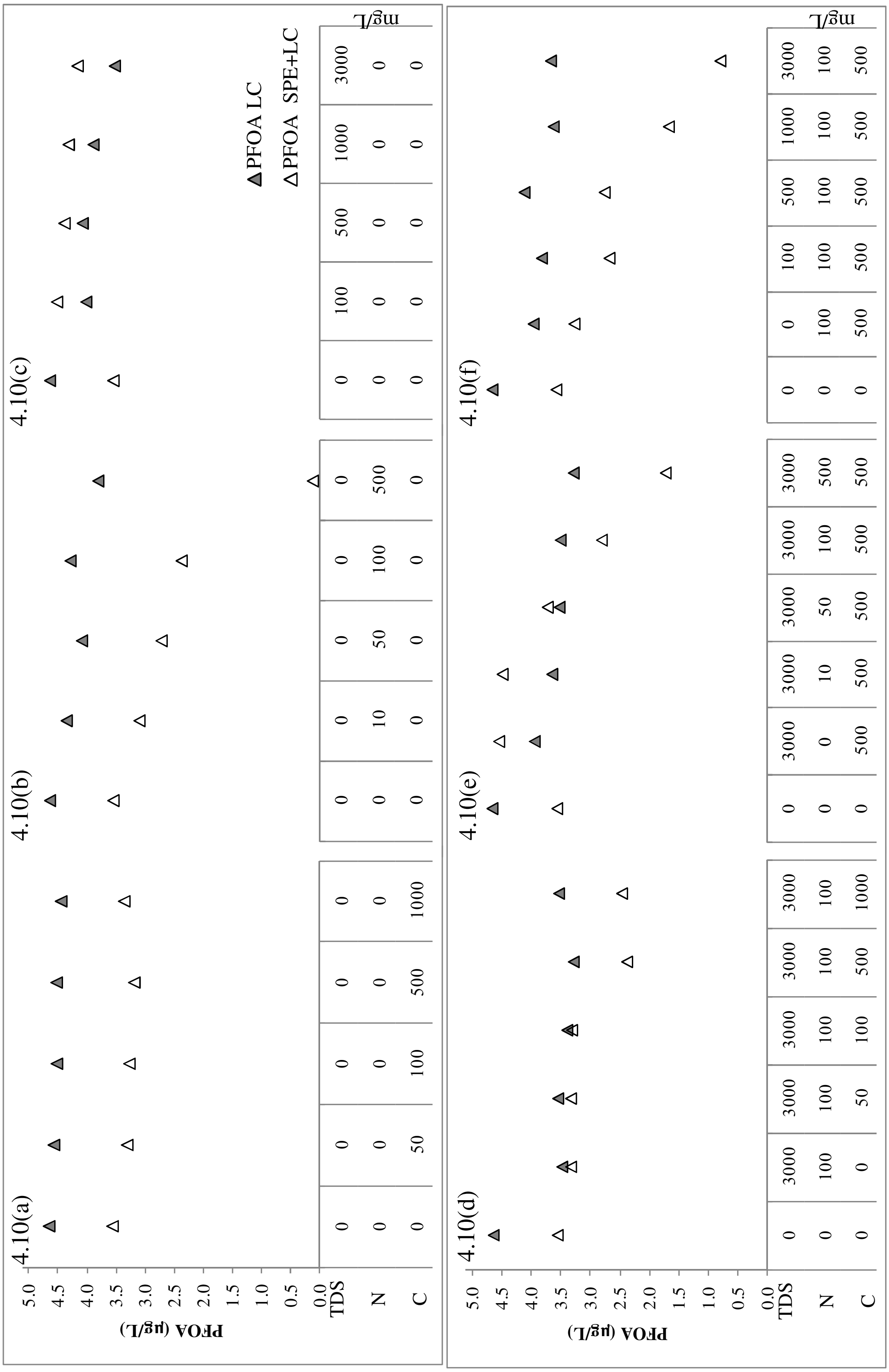


Figure 4.10 The comparison of PFOA concentration between using SPE and non-SPE processes.

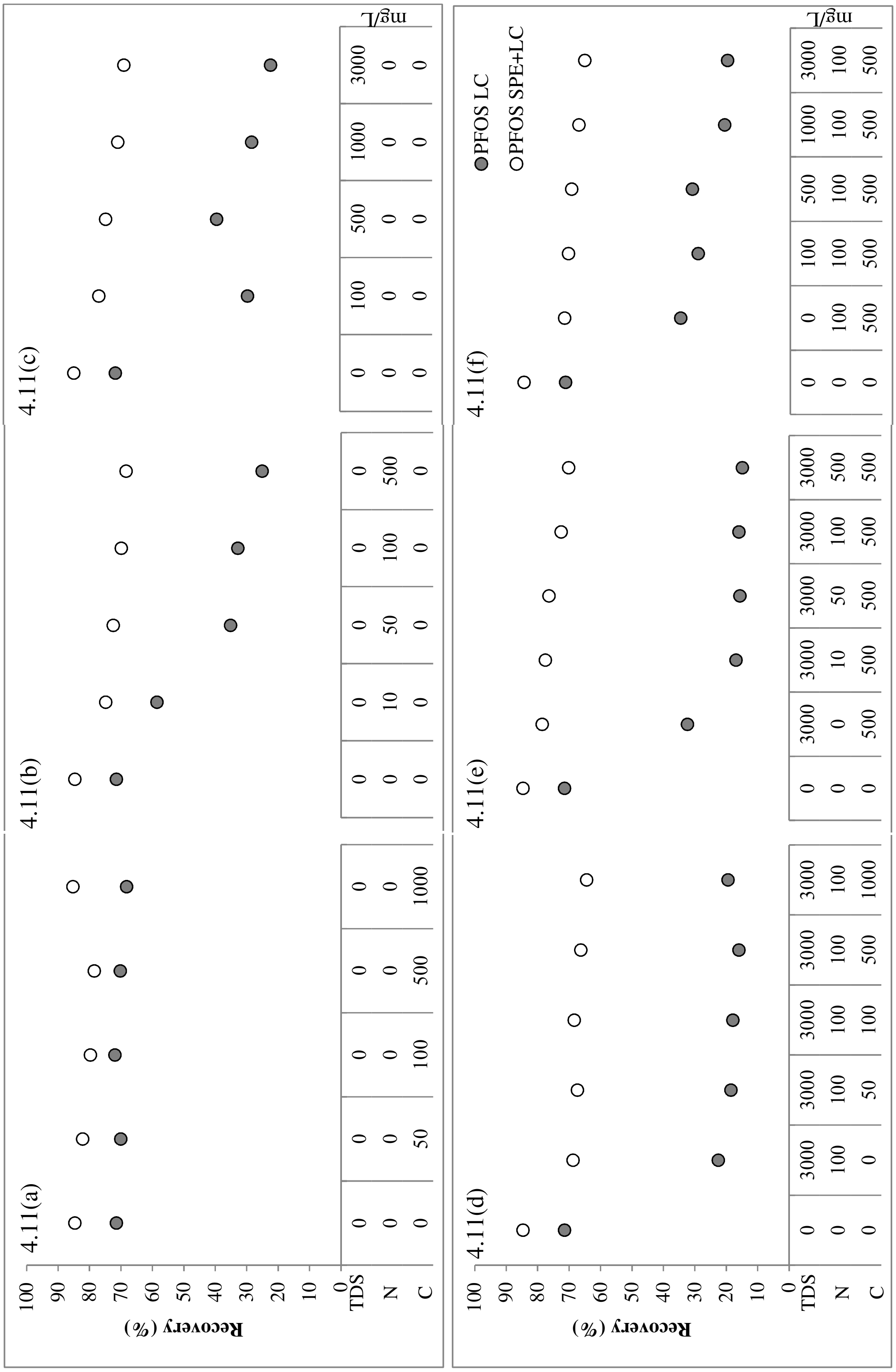


Figure 4.11 The comparison of PFOS recoveries between using SPE and non-SPE processes.

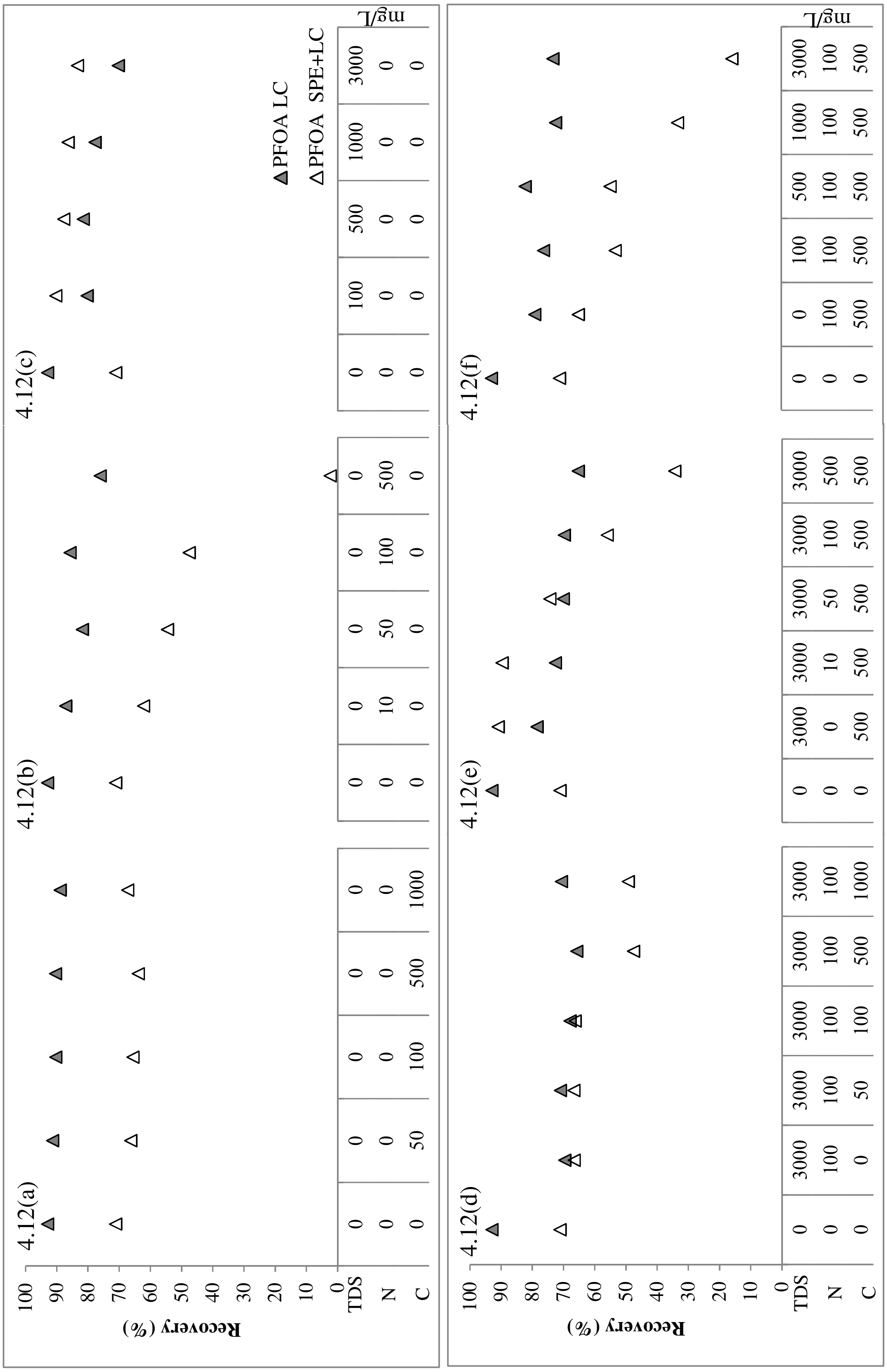


Figure 4.12 The comparison of PFOA recoveries between using SPE and non-SPE processes.

4.2 Phase II real industrial wastewater

This phase was studied the relation of wastewater components and measurement efficiency by method of solid phase extraction and LC-MS/MS in the real industrial wastewater. The sampling of industrial wastewater was conducted in 2 industrial estate (defined as IZ1 and IZ2), which located in Ayutthaya province, Thailand. The details of sampling see Table 3.2, Chapter III. The recovery ratio of PFOS and PFOA were in the range of 70% - 100% and 66% - 97%, respectively (Figure 4.13).

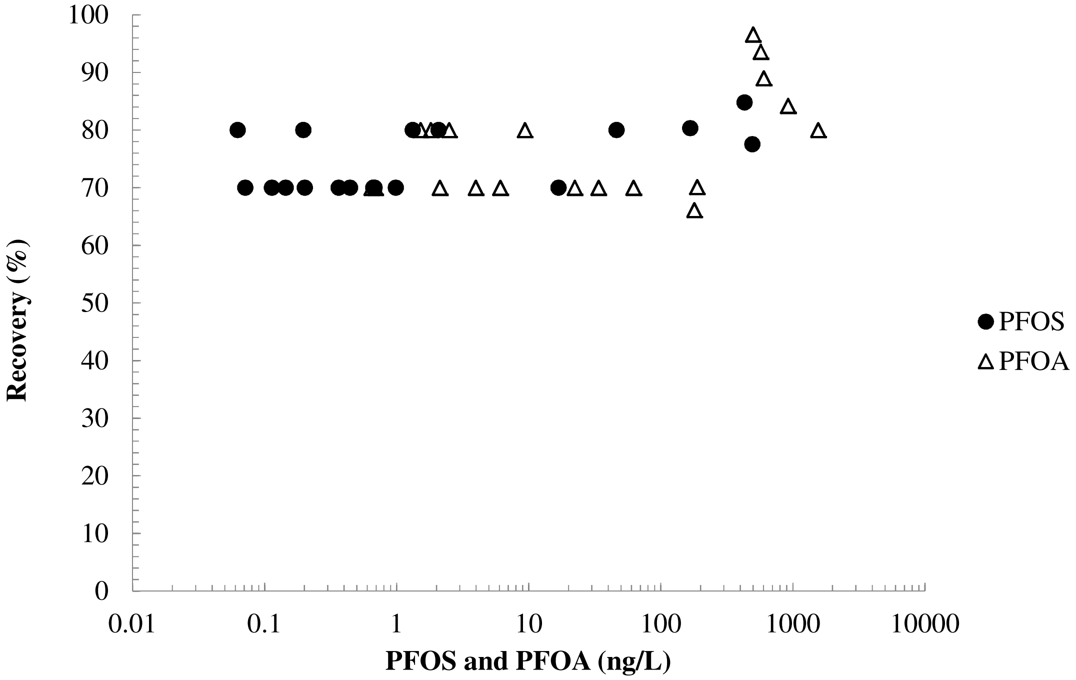


Figure 4.13 Recoveries ratio of PFOS and PFOA in real wastewater samples

Figure 4.14 showed the correlation coefficient between PFOS, PFOA and TOC. The X-axis shows the concentration of PFOS and PFOA in the unit of ng/L and the Y-axis shows the concentration of TOC in the unit of mg/L. The black circle (●) illustrates the concentration of PFOS and the white triangle (Δ) illustrates the concentration of PFOA. The black line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 10 ng/L and rather than 10 ng/L, the dot line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 50 ng/L and rather than 50 ng/L. Focus on PFOS, the correlation coefficient between PFOS and TOC which in the range of 0.01 ng/L - 10 ng/L was 0.65 and the correlation coefficient between PFOS and TOC when PFOS was greater than 10 ng/L was -0.47. Focus on the correlation coefficient between PFOS and TOC which in the range of 0.01 ng/L - 50 ng/L was 0.32 and the correlation coefficient when PFOS was greater than 50 ng/L was 0.76. From that results seemed the negative correlation between PFOS and TOC was occurred in the range of 10 ng/L -50 ng/L. Focus on PFOA, the correlation coefficient between PFOA and TOC which in the range of 0.01 ng/L - 10 ng/L was 0.72 and the correlation coefficient between PFOA and TOC when PFOA was greater than 10 ng/L was 0.33. Focus on the correlation coefficient between PFOA and TOC which in the range of 0.01 ng/L - 50 ng/L was 0.14 and the correlation coefficient when PFOA was greater than 50 ng/L was 0.82. The strong positive correlation was found in the relationship between PFOA and TOC.

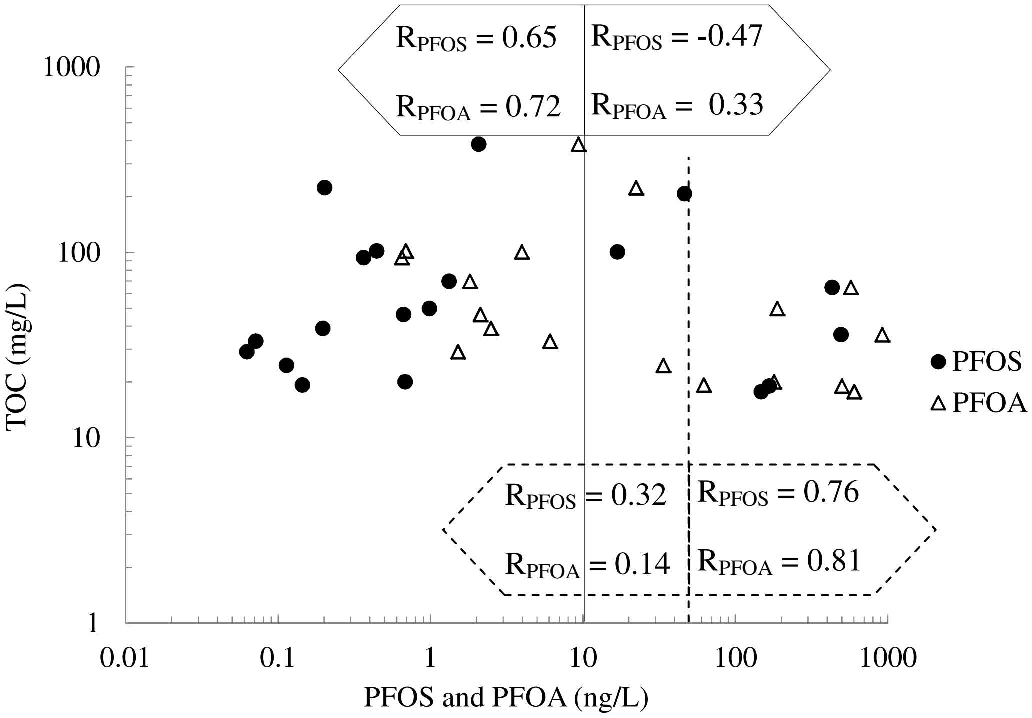


Figure 4.14 Correlation coefficient between PFOS, PFOA and TOC

Figure 4.15 shows the correlation coefficient between PFOS, PFOA and TKN. The X-axis shows the concentration of PFOS and PFOA in the unit of ng/L and the Y-axis shows the concentration of TKN in the unit of mg/L. The black circle (●)

illustrates the concentration of PFOS and the white triangle (Δ) illustrates the concentration of PFOA. The black line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 10 ng/L and rather than 10 ng/L, the dot line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 50 ng/L and rather than 50 ng/L. Focus on PFOS, the correlation coefficient between PFOS and TKN which in the range of 0.01 ng/L - 10 ng/L was 0.50 and the correlation coefficient between PFOS and TKN when PFOS was greater than 10 ng/L was -0.04. Focus on the correlation coefficient between PFOS and TKN which in the range of 0.01 ng/L - 50 ng/L was 0.20 and the correlation coefficient when PFOS was greater than 50 ng/L was -0.48.

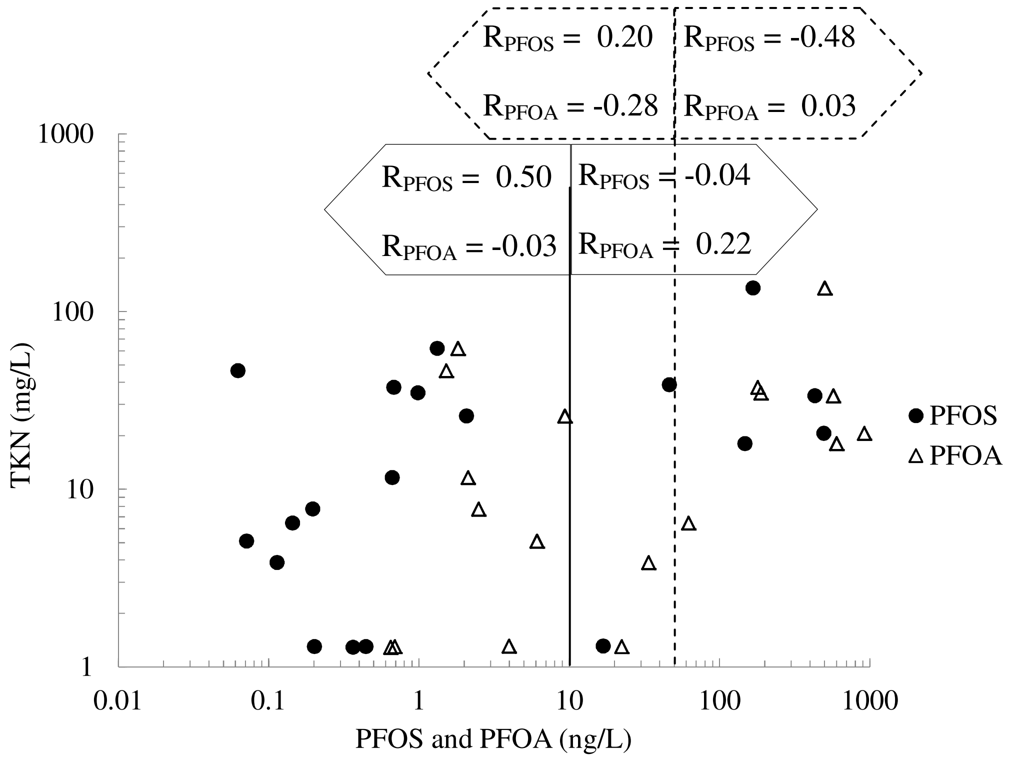


Figure 4.15 Correlation coefficient between PFOS, PFOA and TKN

From that results seemed the slightly negative correlation between PFOS and TKN was occurred when the concentration of PFOS was rather than 10 ng/L and was found significantly positive correlation when the concentration of PFOS was rather than 50 ng/L. Focus on PFOA, the correlation coefficient between PFOA and

TKN which in the range of 0.01 ng/L - 10 ng/L was -0.03 and the correlation coefficient between PFOA and TKN when PFOA was greater than 10 ng/L was 0.22. Focus on the correlation coefficient between PFOA and TKN which in the range of 0.01 ng/L - 50 ng/L was -0.28 and the correlation coefficient when PFOA was greater than 50 ng/L was 0.82. The slightly negative correlation between PFOA and TKN was found at the low concentration which in this study was in the range of 0.01 ng/L – 50 ng/L.

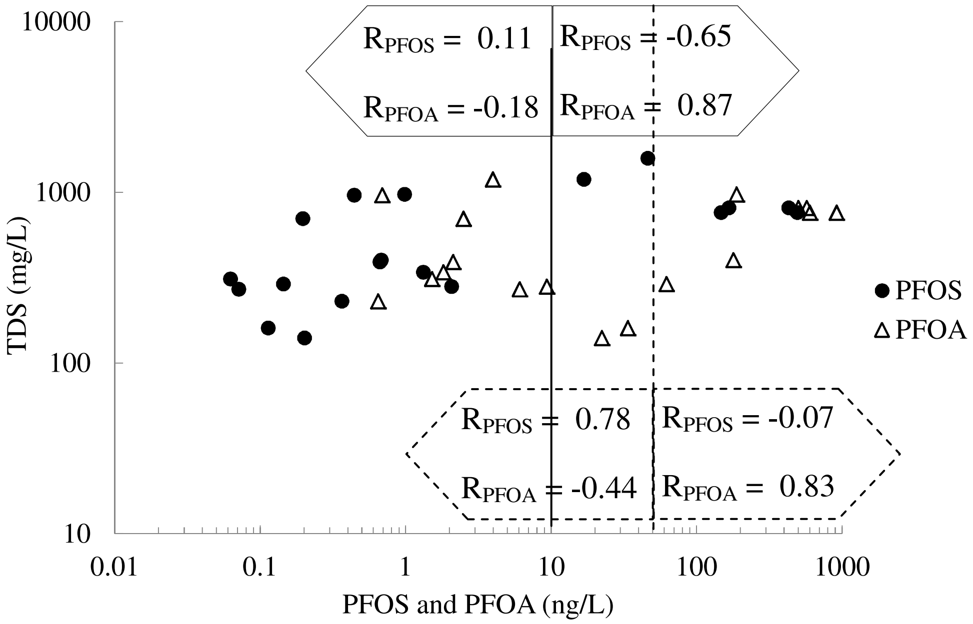


Figure 4.16 Correlation coefficient between PFOS, PFOA and TDS

Figure 4.16 shows the correlation coefficient between PFOS, PFOA and TDS. The X-axis shows the concentration of PFOS and PFOA in the unit of ng/L and the Y-axis shows the concentration of TDS in the unit of mg/L. The black circle (●) illustrates the concentration of PFOS and the white triangle (Δ) illustrates the concentration of PFOA. The black line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 10 ng/L and rather than 10 ng/L, the dot line was divided the concentration of PFOS and PFOA between the range of 0.01 ng/L – 50 ng/L and rather than 50 ng/L. Focus on PFOS, the correlation coefficient between PFOS and TDS which in the range of 0.01 ng/L - 10 ng/L was 0.11 and the correlation coefficient between PFOS and TDS when PFOS was greater than 10 ng/L was -0.65. Focus on the correlation coefficient between PFOS and TDS which in the range of 0.01 ng/L - 50 ng/L was 0.78 and the correlation coefficient when PFOS was greater than 50 ng/L was -0.07. From that results seemed the negative correlation between PFOS and TDS was occurred when the concentration of PFOS was rather than 10 ng/L. Focus on PFOA, the correlation coefficient between PFOA and TDS which in the range of 0.01 ng/L - 10 ng/L was -0.18 and the correlation coefficient between PFOA and TDS when PFOA was greater than 10 ng/L was 0.87. Focus on the correlation coefficient between PFOA and TKN which in the range of 0.01 ng/L - 50 ng/L was -0.44 and the correlation coefficient when PFOA was greater than 50 ng/L was 0.83. The significantly negative correlation between PFOA and TDS was found at the low concentration which in this study was in the range of 0.01 ng/L – 50 ng/L.

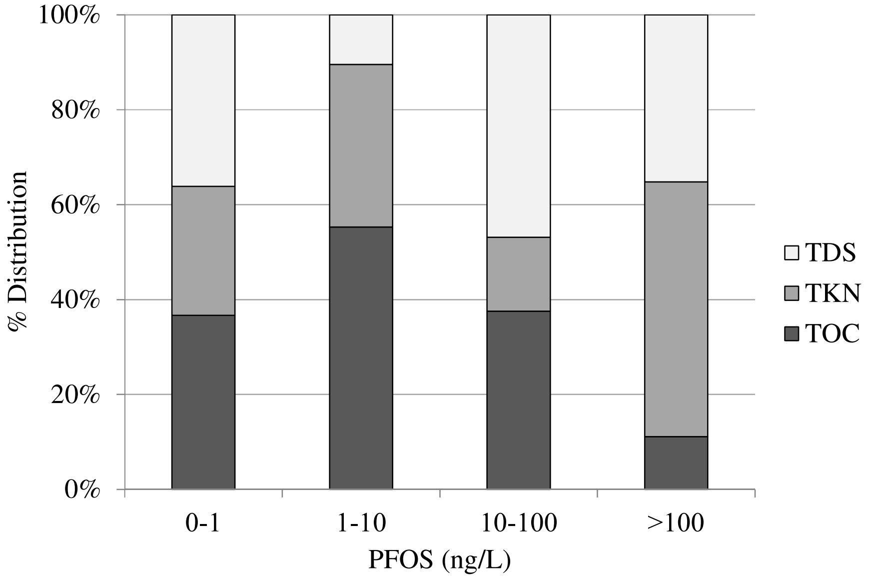


Figure 4.17 Relative abundances of TOC, TKN, and TDS with PFOS

The negative correlation between PFOS and TOC, TKN, and TDS were found at the high concentration of PFOS (Figure 4.14 – 4.16) which was meant the concentration of TOC, TKN, and TDS were increased while, the concentration of PFOS was decreasing. At the high concentration of PFOS might be given the effects to the measurement technique more than the low concentration. From Figure 4.17, shows the relative abundances of TOC, TKN, and TDS with PFOS. The X-axis shows the distribution (%) of TOC, TKN, and TDS and the Y-axis shows the range of concentration of PFOS. At the higher concentration of PFOS was found and increasing of TKN and TDS. When the concentration of PFOS was higher with an increasing of TKN and TDS, the effects of measurement technique might be occurred.

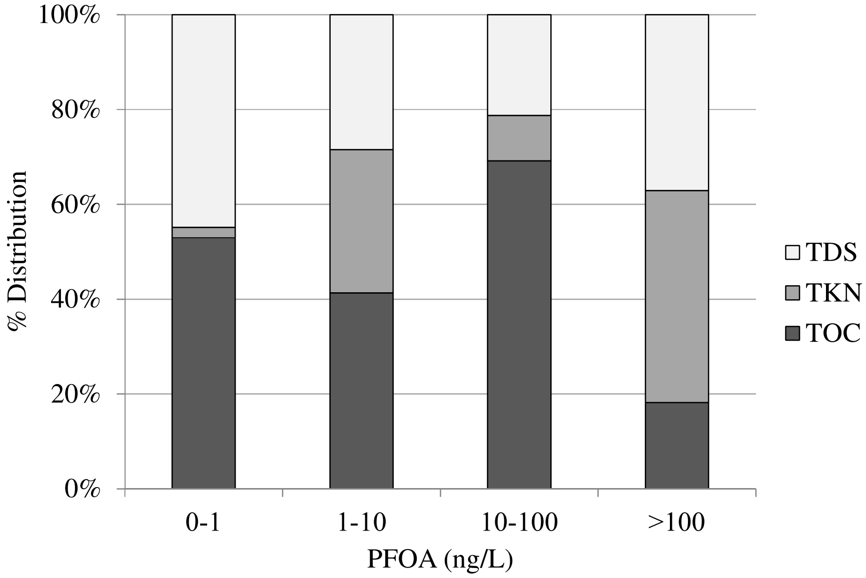


Figure 4.18 Relative abundances of TOC, TKN, and TDS with PFOA

The negative correlation between PFOA and TOC, TKN, and TDS were found at the low concentration of PFOA (Figure 4.14 – 4.16). That was meant at the low concentration of PFOA might be given the effects to the measurement technique more than the high concentration. Figure 4.18, shows the relative abundances of TOC, TKN, and TDS with PFOA. The X-axis shows the distribution (%) of TOC, TKN, and TDS and the Y-axis shows the range of concentration of PFOA. From Figure 4.13, at the low concentration of PFOA (0 - 10 ng/L) seemed the concentration of TKN and TDS were higher than the high concentration of PFOA (10 – 100 ng/L). Hence, the concentration of TKN and TDS were effected to the measurement of PFOS and PFOA which was related to the results in the first objective. Except the effect of TOC to PFOS which was shown at the high concentration of PFOS in real wastewater. However, the effects to the measurement of PFOS and PFOA were shown in the different level which PFOS was found the effect at the higher concentration of PFOS but PFOA was found the effect at the lower concentration of PFOA. TKN and TDS were the major parameter to control the wastewater characteristic and they should be concerned as an effect to the measurement of PFOS and PFOA. However, not only TKN and TDS that could effect to the measurement of PFOS and PFOA, but the others compound should be studied.

4.3 Contamination of PFOS and PFOA in selected industrial wastewater and central wastewater treatment plant of industrial zones

In this section was studied on the contamination of PFOS and PFOA in the real industrial wastewater. The recoveries of the measurement process must be required to represent as an efficiency analysis which the recoveries for this study were in the range of 40% – 194% for PFOS and 10% - 162% for PFOA. The sampling of industrial wastewater was conducted in 7 industrial zones, Thailand were shown in 3.4.2 in Chapter III. The existing data of previous sampling were included in this study. The samplings were conducted in 7 industrial zones (IZ) for 12 times from August 2007 to September 2009. Totally 58 samples were collected from air-conditioning, coating, electronic, food, glass, plastic, textile industries and central wastewater treatment plant (WWTP). In the central wastewater treatment plant (WWTP), the samples were collected from influent, aeration tank, and effluent.

Those industries are possible to use PFOS or PFOA in their manufacture process. Kunacheva (2009) found the contamination of PFOS and PFOA in the discharge from those industries, even on food industries. This study was collected the wastewater from various kind of industry and food industry was supposed to the non-contaminate of PFOS and PFOA or used for a blank sample in this study.

All of industrial wastewater samples were concentrated by solid phase extraction (SPE) processes before LC-MS/MS analysis. For quantitative determination, the HPLC was interfaced with an Agilent 6410 Triple Quadrupole mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reaction monitoring (MRM) mode.

4.3.1 Contamination of PFOS and PFOA in industrial wastewater

Totally 58 samples of industrial wastewater were collected from wastewater discharges of air conditioning, coating, electronic, glass, food, plastic, textile industries and central wastewater treatment plants. Figure 4.19 shows the median and range concentration of PFOS and PFOA in aqueous phase. In case of the discharges from industry, the highest level of PFOS median concentration was found in coating industry at 62.58 ng/L with the maximum concentration at 125.11 ng/L. Other industries were found the concentration of PFOS in the range of <LOD – 46.35 ng/L. The highest level of PFOA median concentration was found in electronic industry at 91.30 ng/L and the highest concentration of PFOA was also found in electronic industry at 6,355.66 ng/L. Other industries were found the concentration of PFOA in the range of 1.82 – 45.64 ng/L. These results show that PFOS and PFOA were still applied in various kinds of industry. In the case of central wastewater treatment plants (WWTPs), the highest median concentration of PFOS and PFOA were found in aeration tank at 98.39 ng/L and 141.72 ng/L, respectively. However, the highest concentration of PFOS and PFOA were found in the effluent of wastewater treatment plant at 997.56 ng/L and 601.96 ng/L, respectively. The effluent of WWTPs were discharged to river or canal, hence PFOS and PFOA were directly contaminated to nearby natural water resources.

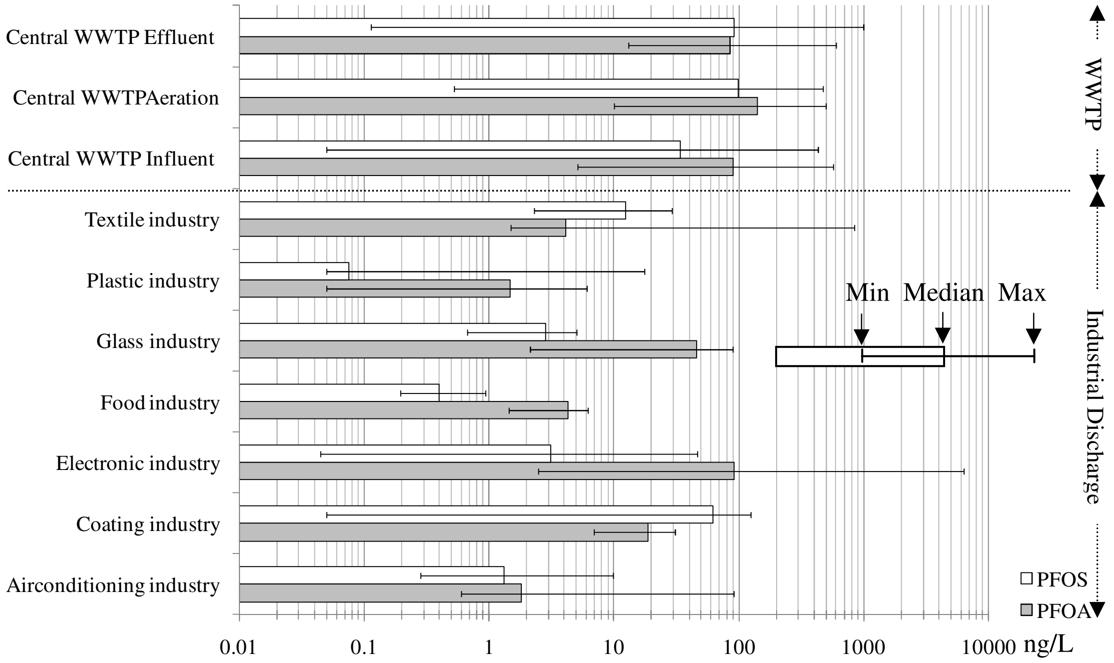


Figure 4.19 Median Concentration of PFOS and PFOA in Industrial Wastewater.

From Figure 4.19, the concentration of PFOA was found higher than concentration of PFOS in 7 out of the 10 samples which were similar to the study by

Lin *et al.* (2009), reported that high concentration of PFOA were found in electronic industry wastewater and higher than PFOS in 16 out of 18 samples with the range of 1.6 – 46.2 μg/L. An important source of both PFOS and PFOA that were contaminated in water resources come from the discharge of treated wastewater from WWTPs. Also with the study by Hu (2007) were reported the discharges of treated wastewater from central wastewater treatment plant of industrial estate were the major source of PFOS and PFOA in environment.

For production process, water is the one important source for water-based industrial processes, such as: heating, cooling, processing, cleaning, and rinsing. The resources of raw water supplied from the natural water which located nearby that industry. Two assumptions to identify the source of PFOS and PFOA are (1) PFOS and PFOA were contaminated in the raw water and (2) PFOS and PFOA were produced from the industrial process. Tap water from each industry was present as raw water which was collected from IZ1, IZ2, and IZ5. This section were compared the contamination of PFOS and PFOA between the raw water and the wastewater. The study of contamination of PFOS and PFOA in tap water from each industrial estates found the concentration of both PFOS and PFOA in the range of <LOQ – 7.59 ng/L. The maximum concentration of PFOS and PFOA in tap water were found in industrial zone 5 (IZ5) at 5.94 ng/L and 7.59 ,g/L, respectively as shown in table 4.3.

Comparing of the contamination of PFOS and PFOA between tap water and wastewater, the highest concentration of PFOS and PFOA in wastewater were found in IZ2 which in the range of <LOQ – 180.87 ng/L for PFOS and 0.60 – 242.83 ng/L for PFOA. Lower concentrations of PFOS and PFOA in industrial wastewater were found in IZ5 and IZ1. The raw water resource used for IZ2 is the same resource as consumption water in household. So, the concentration of PFOS and PFOA in IZ2 were lower than IZ1 and IZ5. Comparing of PFOS and PFOA contamination in tap water and wastewater in IZ1, IZ2, and IZ5, were found the concentration in wastewater was 2, 1507, and 9 times higher than tap water for PFOS and 46, 936, and 12 times for PFOA. The result indicated that the major part of PFOS and PFOA contamination was not derived from their source water (or tap water), but from the industrial production processes releasing these compounds (Kunacheva *et al.*, 2008). However, an occurrence of PFOS and PFOA in raw water resource might be contaminated from the

discharge of industrial zone or the distribution system such as pipe leakage (Kunacheva, 2009).

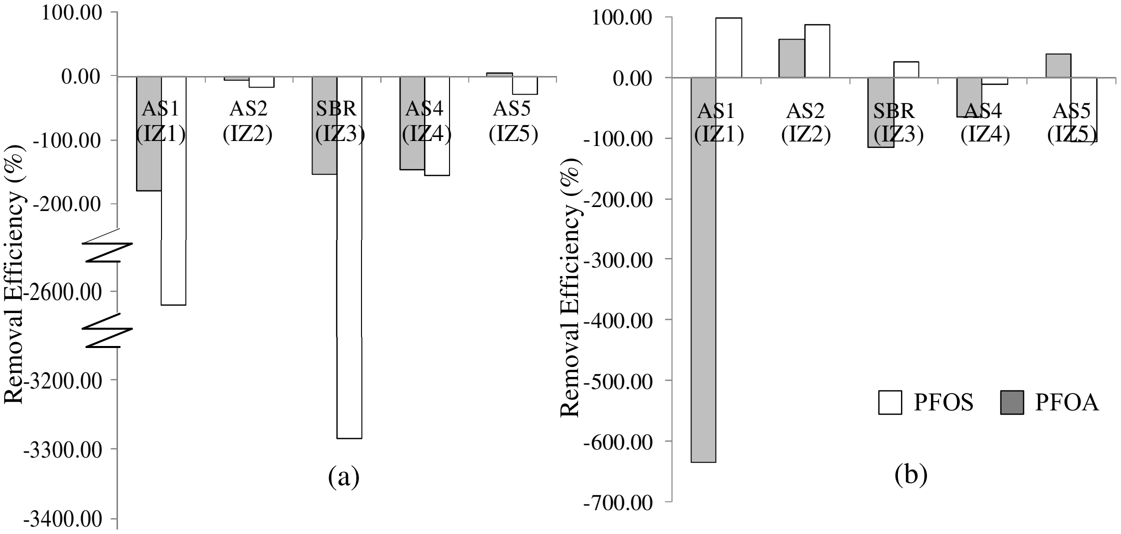
Table 4.3 Contamination of PFOS and PFOA in tap water and wastewater from industries

	Industrial zone	**PFOS (ng/L)**	**PFOA (ng/L)**
Wastewater in industries	IZ1	<LOQ – 1.36	3.15 – 45.97
	IZ2	<LOQ – 180.87	0.60 – 242.83
	IZ5	5.07 – 98.39	85.22 – 91.30
	Average	41.98	73.64
	Industrial zone	**PFOS (ng/L)**	**PFOA (ng/L)**
Tap water in industries	IZ1	0.31	0.53
	IZ2	0.06	0.13
	IZ5	5.94	7.59
	Average	2.10	2.69

4.3.2 Removal efficiency of PFOS and PFOA in central wastewater treatment plants

This section was studied on the concentration of PFOS and PFOA in central wastewater treatment plant. The wastewater samples were collected from five central wastewater treatment plants (WWTP) at the influent, aeration tank, and effluent. Some studies reported that the current wastewater treatment plant processes were ineffective to remove PFOS and PFOA, even the mass fluxes of them increased from influent to effluent (Lien *et al.*, 2008 and Qiu, 2007). So, this study was investigated PFOS and PFOA in WWTP and also the removal efficiency of PFOS and PFOA in five wastewater treatment plants (WWPTs) as shown in Figure 4.20.

In case of aqueous phase as shown in Figure 4.20 (a), both of PFOS and PFOA could not be removed from WWTPs, except 6% removal efficiency of PFOA in activated sludge (AS) 5. In case of particulate phase (Figure 4.20(b)), AS1 and AS2 could remove PFOS with removal efficiency more than 85 %. As the characteristics of PFOS and PFOA were strong hydrophobic properties, they were accumulated in activated sludge (Qiu *et al.* 2007) and existed in the circulation of activated sludge process.



AS = Activated Sludge SBR = Sequencing Batch Reactor

Figure 4. 20 Removal efficiency of PFOS and PFOA in central wastewater treatment plants (a) aqueous phase (b) particulate phase

Figure 4.21 shows the concentration of PFOS and PFOA in influent, aeration tank, and effluent of wastewater treatment plants. In aqueous phase, PFOS (Figure 4.21(a)) and PFOA (Figure 4.21(c)) were found accumulated in aeration tank and increased in the range of 0.9 – 52.0 times from raw influent. Some studies reported the accumulation of PFOS and PFOA in aeration tank, which were significantly increased during aeration (Nozoe *et al.*, 2008 and Becker *et al.,* 2008). Moreover, PFOS and PFOA were increased in final effluent in the range of 0.9 – 2.8 times higher than that in raw influent. Previous research also reported the concentration of PFOS in final effluent was 1.5 – 3.8 times higher than that in raw influent, and PFOA was 1.2 – 2.0 times higher than that raw influent (Nozoe *et al.,* 2008). In particulate phase, the concentration of PFOS (Figure 4.21(b)) and PFOA (Figure 4.21(d)) were significantly increased in aeration tank for 0.1 – 7.9 times higher than other locations. Concentration of PFOS in particulate phase was higher than concentration of PFOA, which indicated that PFOS could be adsorbed on activated sludge more strongly than PFOA (Nozoe *et al.,* 2008). And also, using of PFOS in the production process might be more than PFOA which was applied in many kinds of production.

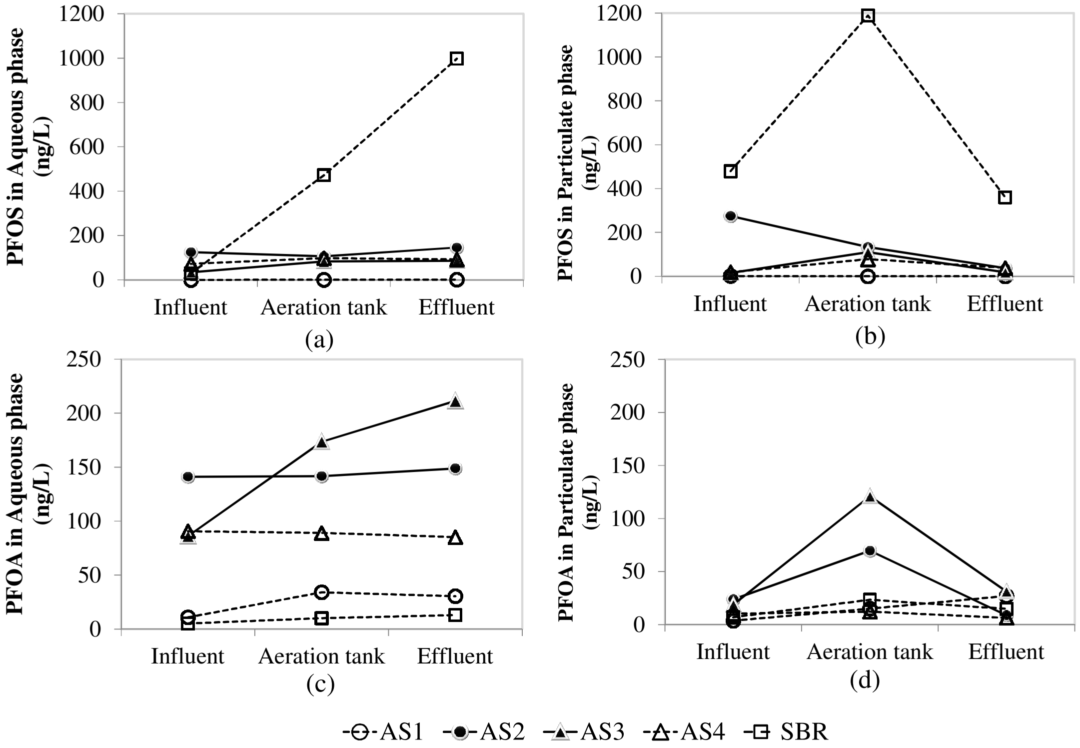


Figure 4.21 Concentration of PFOS and PFOA in wastewater treatment plants (a) PFOS in aqueous phase (b) PFOS in particulate phase (c) PFOA in aqueous phase (d) PFOA in particulate phase

An increasing of PFOS and PFOA might be explained by the biodegradation of some precursors, which were contributed to increase the concentration of PFOS and PFOA in wastewater (Murakami *et al.*,2009, Yu, *et al.* 2009, Nozoe *et al.* 2008, Suwanna, *et al.* 2008, Loganathan, *et al.* 2008, Schultz, *et al.* 2008, and Sinclair, 2006).

Concentration of PFOS which collected from industrial zone (IZ) 3, was higher than other activated sludge (AS) systems, collected from IZ1, IZ2, IZ4, and IZ5. These might be related to the number of the possible sources such as air conditioning, chemical, coating, electronic, electric, foam, glass, and surfactant industries (Table 4.4), discharged wastewater contaminated PFOS to WWTP of each industrial zone. From the data of each industrial zone, it was found that IZ3 has numbers of these types of industries around 4 times higher than other industrial zones (IZ1, IZ2, IZ4, and IZ5). In addition, the results of our study in the previous section found that wastewater from electronic industries presented highest concentration of PFOS and PFOA. IZ3 was found numbers of electronic industry 3.3 times higher than other industrial zones. This result suggests that numbers and types of industry were effected to the concentration of PFOS and PFOA in central wastewater treatment plants and in the water environment as well.

Table 4.4 Number of the types of industry in each industrial zones

	Number of industries	Types of industry						
		Electronic and Electric	Mechanical device and Metal	Chemical	Air-conditioner	Foam	Glass	Painting
IZ1/AS1	86	25	18	1	1	0	0	0
IZ2/AS2	121	45	19	1	1	3	3	0
IZ3/SBR	457	90	107	12	14	5	11	17
IZ4/AS3	65	17	6	2	2	0	0	2
IZ5/AS4	94	24	23	3	4	6	1	2

4.3.3 PFOS and PFOA mass loading from industrial estates to the water resources

From the result in 4.3.1 and 4.3.2, industrial production process was the major source of PFOS and PFOA in water environment. Industrial zone was included with various kinds of industry such as; air-conditioning, coating, electronic, electric, food, glass, plastic, textile, and etc. which were found the different level of both concentration of PFOS and PFOA. Although, every industrial zones have a central wastewater treatment plant (WWTP) but, from the result in 4.3.2 was found that current WWTPs was ineffective to remove both of PFOS and PFOA. That means the discharges of PFOS and PFOA from industrial estate was greater than or equal to the quantity of initial substance of PFOS and PFOA in production process.

Table 4.5 PFOS and PFOA loading

IZ	Treatment Processes*	Flow rate (m^3/day)	PFOS Effluent Conc. (ng/L)	PFOS Loading (g/d)	PFOA Effluent Conc. (ng/L)	PFOA Loading (g/d)
IZ1	AS	16,800	1.46	0.02	57.42	0.96
IZ2	AS	12,000	183.33	2.20	157.70	1.89
IZ3	SBR	20,000	1,357.30	27.15	27.90	0.56
IZ4	AS	6,000	104.11	0.62	242.56	1.46
IZ5	AS	14,000	131.50	1.84	91.56	1.28
		Total		31.83		6.15

Note: * AS = Activated Sludge, SBR = Sequencing Batch Reactor
**Source : Industrial Estate Authority of Thailand (http://www.ieat.go.th)

Table 4.5 shows the loading of PFOS and PFOA discharged from industrial estates. The highest discharge concentration of PFOS was found in IZ3 at 27.15 g/d and the highest discharge of PFOA was found in IZ2 at 1.89 g/day. In addition, the discharge points of the treated wastewater were the natural water resource which use for consumption as well.

4.4 Comparison of recovery ratio of PFOS and PFOA between synthetic wastewater and real wastewater

Table 4.6 shows the recovery ratio of PFOS and PFOA which were studied in Phase I, Phase II, and real wastewater samples. Study on Phase I was divided into 2 sections, the first one was used the method of directly analysis by LC-MS/MS or non-SPE process (in Table 4.6 defined as LC). The second one was used the method of SPE couple with LC-MS/MS (in Table 4.6 defined as SPE+LC). Phase II was studied on the real industrial wastewater which was included the existing data from previous research. An average recovery of PFOS and PFOA in Phase I which used the method of directly analysis by LC-MS/MS (LC) were 39.53% and 80.07%, respectively. When the method of SPE was applied (SPE+LC), an average recovery of PFOS was improved to 75.00%. However, an average recovery of PFOA was decayed to 63.00%. This study showed that SPE process was effective to improve the recovery ratio of PFOS. In case of PFOA, this study did not mean that SPE process was ineffective to improve the recovery ratio of PFOA but, the decreasing recovery might be caused of the wastewater components or an interference of other components. An average recovery of PFOS and PFOA in the real wastewater were 80.28% and 86.56%, respectively. There showed the similar recovery ratio between PFOS and PFOA which might be explained that the component of real industrial wastewater was more complex and many of interference. Hence, it could not be defined the cause of the phenomena of this problem which were from the SPE process or the C, N, or TDS sources. However, the future study should be concern to the other components of wastewater or development of method to improve the recovery ratio of PFOS and PFOA analysis.

Table 4.6 Recovery ratio of PFOS and PFOA in synthetic wastewater and real wastewater

Recovery (%)	**Synthetic wastewater**				**Real Industrial wastewater**	
	Phase I (LC)		**Phase I (SPE+LC)**		**Phase II Real industrial wastewater**	
	PFOS	**PFOA**	**PFOS**	**PFOA**	**PFOS**	**PFOA**
Minimum	15.00	65.27	64.00	2.00	10.00	40.00
Maximum	71.85	92.88	85.00	91.00	161.60	193.55
Average	39.53	80.07	75.00	63.00	80.28	86.56

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The measurement technique of PFOS and PFOA in wastewater were applied for many years. Since, PFOS and PFOA were identified as a toxic chemical as in a low concentration. Hence, the measurement technique was very important to reach the high efficiency or high recovery of analyze. At present, the problem of the matrix in wastewater was not solved. This study was focused on the major component such as C-source, N-source, and TDS-source.

In the case of synthetic wastewater for 1st objective which was done in the lab scale, found that C-source has non-relation between total organic carbon (TOC) and the concentration of PFOS and PFOA in wastewater sample. There might be suggesting that the changing of TOC or C-source in wastewater has no effect to PFOS and PFOA. In the lab scale was represented the decreasing of PFOS and PFOA concentration when the TKN and TDS sources were increasing. The backup experiment was also represented the remaining of TKN and TDS sources in C18 cartridge which might be given an effect to the measurement process. N-source and TDS might be one of caused that were decreased the recovery of PFOS and PFOA analysis in the lab scale.

In case of real wastewater for 2nd objective, the negative correlation coefficient was found both of PFOS and PFOA. At the high concentration of PFOS, TKN and TDS were effected to the measurement of PFOS. At the low concentration of PFOA, TKN and TDS were effected to the measurement of PFOA. This result was supported by the results in 1st objective which used the high concentration of standard PFOS and PFOA solution at 5 µg/L as represented in 4.1.1 (Phase I), found the decreasing of the concentration of PFOS while the concentration of TKN and TDS were increased. The results in 4.1.2 (Phase I) was used the low concentration of standard PFOS and PFOA solution at 5 ng/L, found the decreasing of the concentration of PFOA while the concentration of TKN and TDS were increasing. Thus, the effects of TKN and TDS were shown in the different range of concentration between PFOS and PFOA.

The recovery ratio of PFOS and PFOA was found significantly different between synthetic wastewater and real wastewater. An average recovery of PFOS and PFOA in real wastewater was found higher than the synthetic wastewater which might be explained that in the lab scale was controlled the concentration of wastewater components. Hence, it was easy to see the significant decreasing trend of the recovery ratio. But, in the real wastewater was more complex of wastewater components than the lab scale and could not measure or categorize the whole types of wastewater components. So, it was difficult to define the cause of low or high of the recovery of PFOS and PFOA in the real wastewater come from C, N, or TDS sources.

Due to the matrix interference was effected on the measurement technique of PFOS and PFOA. The recovery of the measurement process was in the range of 40% – 194% for PFOS and 10% - 162% for PFOA. The sampling of industrial wastewater was conducted in 7 industrial zones. Samples were collected from air-conditioning, coating, electronic, food, glass, plastic, textile industries and central wastewater treatment plant (WWTP). Both of PFOS and PFOA were detected in all types of industrial wastewater, even on the discharge from food industries. The concentration of PFOA was almost found higher than the concentration of PFOS. Air conditioning, coating, electronic, glass, and textile industry were found a high level of PFOS and PFOA. However, the highest concentration of PFOS and PFOA were found in central wastewater treatment plants. Especially, the treated effluent wastewater was detected a high level of PFOS and PFOA. In aqueous phase, concentration of PFOS and PFOA were increased from influent to effluent, which was indicated ineffective removal of PFOS and PFOA in conventional treatment processes. In particulate phase, concentration of PFOS and PFOA were increased in aeration tank and accumulated in activated sludge process. Currently, the contamination of PFOS and PFOA are widely detected in the environment such as air, water, animals, even in humans. Thus, the proper measurement technique and treatment technique, in addition the developing substitute materials to replace PFOS and PFOA must be concerned.

5.2 Recommendations

1) Small fraction or the functional group of nitrogen compounds in real wastewater should be studied to solve to the different effect on PFOS and PFOA between synthetic wastewater and real wastewater.

2) More sample of real wastewater which varied on the concentration of PFOS and PFOA should be required to study on the correlation coefficient between PFOS, PFOA and TKN and TDS.

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