รายงานวิจัยฉบับสมบูรณ์

โครงการการปนเปื้อนและการควบคุม Perfluoroalkyl Substances (PFASs) ในน้ำใต้ดิน

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ธันวาคม 2561

สัญญาเลขที่ RSA5880046

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สังกัด
มหาวิทยาลัยมหิดล

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย
และมหาวิทยาลัยมหิดล

กิตติกรรมประกาศ

รายงานวิจัยฉบับนี้ สำเร็จได้ด้วยดีผู้วิจัยขอขอบคุณการสนับสนุนอย่างต่อเนื่องของ ศ. ดร. จงรักษ์ ผลประเสริฐ และ Prof. Dr. Shigeo Fujii ผู้ผลักดันงานวิจัยด้าน Persistent Organic Pollutants ในประเทศไทยซึ่งทำให้ผู้วิจัยและคณะฯ สามารถพัฒนาห้องปฏิบัติการ สร้างทรัพยากรบุคคลเพื่อการวิจัยในศาสตร์เฉพาะทางนี้ ซึ่งส่งผลให้สามารถดำเนินการวิจัยฉบับนี้ได้สำเร็จด้วยดี ขอขอบคุณ อ. ดร. นรินทร์ บุญตานนท์ ผู้เป็นเบื้องหลังคนสำคัญในการร่วมกันพัฒนาวิธีการตรวจวัด และจัดการแก้ไขปัญหาเครื่องมือตรวจวัดที่จำเป็นต้องใช้ความเชี่ยวชาญเฉพาะทางซึ่งหากต้องพึ่งการซ่อมบำรุงจากทางบริษัทเพียงอย่างเดียวเชื่อมั่นว่างานวิจัยทางด้านนี้คงไม่สามารถดำเนินการได้อย่างต่อเนื่อง ขอขอบคุณนักวิจัยภายในห้องปฏิบัติการซึ่งก็คือนักศึกษาในระดับปริญญาโท และปริญญาเอกทั้ง 7 คน ได้แก่ นางสาวอภิสรา บุญญะอติชาติ นางสาวชนิดาภรณ์ ห้องกระจก นางสาวพุทธิชา บุญชะตา นางสาวสุรัสวดี สุขีสาร นางสาวสนธินี ไวยารัตน์ นายวัชริศ แถบทอง และนายเจษฎา จุ้ยประเสริฐ ขอบคุณที่ทุ่มเทและมีความตั้งใจเสียสละในการทำวิจัยเพื่อให้ได้งานที่มีความถูกต้องเชื่อถือได้

สุดท้ายนี้ขอขอบคุณการสนับสนุนทุนวิจัยจากสำนักงานกองทุนสนับสนุนการวิจัยและมหาวิทยาลัยมหิดล ซึ่งเป็นส่วนที่สำคัญในการพัฒนางานวิจัยของกลุ่มวิจัยนี้ให้มีความต่อเนื่อง ส่งผลให้สามารถผลิตนักวิจัยที่มีความสามารถในการพัฒนาตัวเองเพื่อนำไปสู่การพัฒนางานในอนาคตให้ดียิ่งขึ้น

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รหัสโครงการ: RSA5880046

ชื่อโครงการ: การปนเปื้อนและการควบคุม Perfluoroalkyl Substances (PFASs) ในน้ำใต้ดิน

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หลุมฝังกลบขยะเป็นแหล่งปลดปล่อยมลพิษจำนวนมากสู่สิ่งแวดล้อมและส่งผลต่อปัญหาสุขภาพของทั้งคนและสิ่งมีชีวิตในสิ่งแวดล้อมโดยเฉพาะอย่างยิ่งปัญหาที่สำคัญคือการปนเปื้อนในน้ำใต้ดินจากสารมลพิษที่ตกค้างยาวนานรวมไปถึงสารกลุ่ม PFASs ซึ่งมีการศึกษาเป็นจำนวนมากในประเทศที่พัฒนาแล้วแต่ยังไม่มีการศึกษาในประเทศไทย นอกเหนือจากนั้นเทคโนโลยีในการบำบัดสารกลุ่มนี้ยังไม่มีประสิทธิภาพเพียงพอ เทคโนโลยีเมมเบรนมีศักยภาพในการกำจัดแต่มีข้อเสียในด้านมลพิษหลงเหลือที่แยกออกจากน้ำโดยเมมเบรน ดังนั้นจึงมีความท้าทายในการพัฒนาระบบเมมเบรนแบบผสมผสาน วัตถุประสงค์ของงานวิจัยนี้คือการสำรวจสถานการณ์ปัจจุบันของการปนเปื้อน PFASs ในน้ำใต้ดินและพัฒนากระบวนบำบัดด้วยเทคโนโลยีเมมเมเบรนแบบผสมผสานรวมถึงประเมินประสิทธิภาพโดยได้ทำการเก็บตัวอย่าง บริเวณรอบสถานที่กำจัดขยะมูลฝอย และแหล่งลักลอบทิ้งขยะอุตสาหกรรม โดยสารประกอบ PFASs จะถูกสกัดจากน้ำตัวอย่างด้วยเทคนิค Solid-phase extraction (SPE) และวิเคราะห์โดยวิธี High performance liquid chromatography (HPLC) ร่วมกับ Tandem mass spectrometer (MS/MS)

พบปริมาณการปนเปื้อน PFASs รวมรอบแหล่งลักลอบทิ้งขยะ ต.หนองแหน และ ต.มาบไผ่ ในระดับ 4.43 ถึง 10.80 ng/L และ 2.64 ถึง 42.01 ng/L ตามลำดับ โดยมีปริมาณสาร PFOA และ สาร PFOS มากที่สุด รวมทั้งยังพบว่าสาร PFHxS ถูกตรวจพบมากในน้ำใต้ดิน โดยเฉพาะรอบแหล่งลักลอบทิ้งขยะอุตสาหกรรม ซึ่งอาจเป็นเพราะสาร PFHxS ถูกนำมาใช้ทดแทนสาร PFOS ในกระบวนการอุตสาหกรรม เนื่องจากมีสายคาร์บอนที่สั้นกว่า นอกจากนั้นจากการวิเคราะห์ทางสถิติ ยังพบว่าการปนเปื้อนของสาร PFASs ในน้ำใต้ดินรอบสถานที่กำจัดขยะชุมชนและแหล่งลักลอบทิ้งขยะอุตสาหกรรมมีความแตกต่างกันอย่างมีนัยสำคัญ สำหรับผลการศึกษาไฮบริดเมมเบรนฟิลเตรชั่น (hybrid membrane filtration) ร่วมกับโฟโตแคตาไลสิส (photocatalysis) ผลการทดลองในส่วนของ membrane filtration พบว่าประสิทธิภาพในการกำจัดสารจะเพิ่มขึ้น เมื่อแรงดันและความเข้มข้นของสารเพิ่มขึ้น ในส่วน photocatalysis พบว่าความเข้มข้นของ nZVI และ co-contaminants ในน้ำใต้ดินส่งผลต่อประสิทธิภาพการกำจัดสารเป้าหมาย โดยในส่วนของไฮบริดเมมเบรนฟิลเตรชั่นผลที่ได้พบว่า nanofiltration membrane สามารถบำบัดสาร PFOA ได้ถึง 99.62% หากแต่ส่วนมลพิษที่ถูกแยกออกยังไม่ได้ถูกกำจัดอย่างแท้จริงถ้าถูกปล่อยทิ้งโดยไม่ได้รับการกำจัดที่เหมาะสม การศึกษานี้ออกแบบให้มลพิษถูกส่งต่อไปบำบัดเพื่อการย่อยสลายโดย photocatalysis ซึ่งส่งผลให้สารมลพิษที่เหลือที่ไม่สามารถกำจัดได้จะถูกปล่อยลงสู่สิ่งแวดล้อมเพียง 34.61% ซึ่งเป็นปริมาณที่น้อยมากเมื่อเทียบกับปริมาณที่เหลืออยู่หากกำจัดด้วย nanofiltration membrane เพียงอย่างเดียวถึง 3 เท่า จึงแสดงให้เห็นว่าสาร PFOS และ PFOA เข้มข้นที่ไม่สามารถผ่านเมมเบรนได้ สามารถย่อยสลายได้โดยการใช้ photocatalysis ก่อนที่จะปล่อยออกสู่สิ่งแวดล้อม ซึ่งสามารถกล่าวได้ว่า กระบวนการไฮบริดเมมเบรนฟิลเตรชั่นและโฟโตแคตาไลสิสสามารถเพิ่มประสิทธิภาพการย่อยสลายสาร PFOS และ PFOA และลดข้อเสียของ membrane filtration ถือเป็นระบบที่เป็นมิตรต่อสิ่งแวดล้อมอย่างยิ่งระบบหนึ่ง

คำหลัก : PFOS, PFOA, **น้ำใต้ดิน, เมมเบรน, โฟโตแคตาไลซิส**

Abstract

Project Code: RSA5880046

Project Title: Occurrence and Control of Perfluoroalkyl Substances (PFASs) in Groundwater

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Landfills are sources of a wide range of compounds with environmental, wildlife and human health concerns. Contamination of groundwater with PFASs has been studied in other countries, but not in Thailand. In addition, some technologies do not effectively remove many of these contaminants from water, membrane technologies have been shown to be effective in removing PFASs. However, the significant membrane drawbacks are well-known concentrated pollutants in retentate. It is challenging to develop hybrid membrane that can overcome this major drawback of membrane technology. The overall objectives of this research study are to investigate the current situation of PFASs contamination in groundwater and to develop and evaluate the technical performance of hybrid membrane technology. Groundwater samples were collected around municipal waste disposal sites (MWDS) and industrial waste disposal sites (IWDS). Seven PFCs: PFHpA, PFOA, PFNA, PFDA, PFUnA, PFHxS, and PFOS were extracted by solid-phase extraction (SPE) technique and analyzed by high-performance liquid chromatography-tandem mass spectrometer (HPLC-MS/MS).

The total PFASs in groundwater around Nong Nae industrial waste disposal sites (IWDS) and Map Phai IWDS varied from 4.43 to 10.80 ng/L and 2.64 to 42.01 ng/L, respectively. Similar to those around the municipal waste disposal sites (MWDS) areas, PFOA and PFOS were the most dominant compounds. PFHxS was frequently observed in the groundwater around the IWDSs, suggesting that it has been used as a substitute to PFOS-based compounds in industrial processes. Statistical analysis showed that the levels of PFASs in the groundwater around the IWDSs were significantly higher than those around the MWDSs. For the hybrid membrane system, the spiked water samples were treated by Nanofiltration (NF) and the rejected part was sent to UV contact tank for photocatalysis reaction. For the membrane filtration part, the NF membrane provided higher removal efficiency when applied with higher pressure and concentration. For photocatalysis, the nZVI concentration and co-contaminants in groundwater effected to the removal efficiency. For the hybrid membrane filtration and photocatalysis process, the nanofiltration membrane could remove up to 99.62% of the PFOA. However, for nanofiltration alone, the rejected contaminants might be still released to the environment 100% if the rejected part were not treated properly. In contrast, the nanofiltration membrane coupled with photocatalysis from this study, the contaminants were released to the environment just 34.61%, which was a much better result than treatment by only the nanofiltration membrane alone about 3 times. Thus, the hybrid membrane filtration and photocatalysis method is more effective for removal of the contaminants in groundwater and is also friendlier to the environment and living things.

Keywords: PFOS, PFOA, Groundwater, Membrane, Photocatalysis

Occurrence and Control of Perfluoroalkyl Substances (PFASs) in Groundwater

(1) Introduction

Landfills are sources of a wide range of compounds with environmental, wildlife and human health concerns. As a result of higher demand and better quality of consumer products including paints, oils, electrical products, surfactants, and etc. are potentially deposited at landfills. Over 50 percent of industrial wastes or about 45 million tons were not treated but illegally dumped at legal and illegal landfills in Thailand (ThaiPBSa, 2014). In addition, the situation of groundwater contamination in Thailand is getting much worse as the fire accidents of landfill sites have been often occurred recently (ThaiPBSb, 2014; The Green World Foundation, 2013). The contamination of groundwater resources by emerging pollutants such as persistent organic pollutants (POPs) is a growing concern and relatively poorly understood compared to other freshwater resources. Groundwater in many parts of Thailand is the most important source of drinking water and would have adverse effects on human health caused by POPs contamination. Therefore, it is really needed to understand the occurrence of POPs and its impact as well as to develop of efficient control method to reduce the impacts for Thailand.

POPs especially perfluoroalkyl substances (PFASs) have been widely applied to numerous industrial and commercial products that required surface protection, such as textile coatings, paper treatment, pesticides and fire-fighting foams due to their useful properties, including oil and water repellency and resistance to heat and chemical reactions. However, they have been observed to persist in the environment, bioaccumulate in human and animal tissue, and biomagnify in food chains, and thus may have potentially significant adverse impacts on human health and the environment (Benford *et al*., 2008; Lau *et al*., 2004). Previous studies on landfill leachates and groundwater have evaluated parameters such as organic matter, chemical and biological oxygen demand, nutrients and metal ion (Eggen *et al.*, 2010). Since 2000, new and emerging group of compounds like PFASs are new detectable in most environmental matrix (Boontanon *et al*., 2013; Shivakoti *et al*., 2010; Kunacheva *et al*., 2010; Wang *et al.*, 2013), biota (Zhao *et al*., 2012) and consumer products such as food packaging (Poothong *et al*, 2012), textile (Supreeyasunthorn *et al*., 2016), cosmetic (Keawmanee *et al*., 2015). Among all the PFASs, longer-chain analogues such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been most frequently reported of their contamination in environment. In a former disposal site in Minnesota, PFOA and PFOS have been detected in groundwater at 47,000 µg/L and 3,000 µg/L, respectively. At a site in Cottage Grove, MN, concentration of PFOA and PFOS in groundwater have been as high as 120 and 105 µg/L, respectively (Rumsby *et al*., 2009). The U.S. Environmental Protection Agency published Provisional Health Advisory values of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS in drinking water. Several state regulatory agencies have moved forward to establish action levels and guidelines for PFOA and PFOS. New Jersey established a drinking water guideline

value of 0.04 µg/L for PFOA (State of New Jersey, 2007). These levels are several orders of magnitude lower than concentration of PFOA and PFOS observed in groundwater in US.

However, in Thailand, up to now we do not have any information of PFASs contamination in groundwater at all. Due to their chemical structure, PFASs are very stable. While some technologies do not effectively remove many of these contaminants from water, membrane technologies have been shown to be effective in removing PFASs. However, the significant membrane drawbacks are well-known cost and concentrated pollutants in retentate, which need to be solved properly. It is challenging to develop hybrid membrane that can overcome these major drawbacks of membrane technology. The benefit of this research is considered to derive the existing situation in Thailand for these emerging POPs contamination in groundwater and to develop a new discovery treatment technology with cost effective approach.

Objectives

The overall objectives of this research study are to investigate the current situation of Perfluoroalkyl Substances (PFASs) contamination in groundwater and to develop and evaluate the technical performance of Hybrid Membrane Technology. The specific technical objectives of this project include:

1. To investigate PFASs levels in groundwater around two types of improper waste disposal site: municipal waste disposal sites and industrial waste disposal sites in Thailand; and identify potential sources of PFASs contamination in groundwater
2. To assess human health risks of PFOS, PFOA and PFNA by drinking groundwater
3. To develop a new photocatalyst generated by a simple and effective method to prepare TiO_2/GO/PVA nanofilm for degrading PFOS and PFOA contaminated in water.
4. To investigate the reaction of photocatalysis in terms of nZVI nanoparticles dosage and reaction time, as well as the removal efficiency.
5. To quantify the removal effectiveness and optimize the operation condition of the nanofiltration membrane operation.
6. To evaluate the hybrid membrane filtration and photocatalysis system to reduce the drawbacks of current pollution control techniques especially the aspect of releasing the rejected contaminate part to the environment.

(2) Methodology

To fulfil the objectives, three main tasks for this research include:

Task (1) Investigating of PFASs in groundwater. The behavior and impact from industrial and municipal landfill sites were analysed. Selected water wells were monitored and analyzed. Details of water wells were referred from department of groundwater resource. Solid phase extraction (SPE) coupled with HPLC-ESI-MS/MS were used for the analysis of these compounds. Health risk to people drinking that contaminated groundwater were also assessed.

Task (2) Photocatalysis presents as a great alternative for the oxidation process of organic compounds owning to its excellent characteristics as an effective, economical and environmentally friendly technology. The combination of TiO2 and GO increases photocatalytic activity many times. Polyvinyl Alcohol (PVA) is a synthetic water-soluble hydrophilic polymer having high dielectric strength, good charge storage capacity and dopant dependent electrical and dielectric properties. The addition of TiO_2 and GO nanoparticles into PVA matrix is discovered to achieve conductive polymer nanocomposites with unique properties and the improvement of photocatalytic activity. In this task, a new photocatalyst was generated by a simple and effective method to prepare TiO_2/GO/PVA nanofilm for degrading PFOS and PFOA contaminated in water.

Task (3) Treating of PFASs contaminated groundwater using Hybrid Membrane Filtration. Recently membrane process combined with other advanced technologies like nanoparticles, ultrasonic, electrochemical oxidation was introduced. In this study, membrane hybrid with photocatalytic technology was selected to reduce the drawbacks of current pollution control techniques especially the aspect of releasing the rejected contaminate part to the environment or incinerated as a same old way and will strengthen the productive use of membrane technology. Therefore, this system is not only the separation process but also the degradation process of emerging pollutants to non-harmful end products.

2.1 Standards and reagents

In the first task of this study, seven PFASs standards, including perfluorohaptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) were used in the method. Standard details are given in Table 2.1. Methanol HPLC grade (>99.99%) and ACS grade (>97%) and Acetonitrile HPLC grade (>99.8%) were purchased from EMD Millipore, Germany. Ammonium acetate (99.99%) was purchased from Merck KGaA, Germany. Ultrapure water was produced by a RiOs-DI® Water Purification System (Millipore, Germany).

Table 2.1 List of standards used in this study

Standard	Acronym	Formula	Purity (%)	Supplier
Perfluorohaptanoic acid	PFHpA	$C_7HF_{13}O_2$	96	Wako, Japan
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	>95	Wako, Japan
Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	>95	Wako, Japan
Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	>98	Wako, Japan
Perfluoroundecanoic acid	PFUnA	$C_{11}HF_{21}O_2$	>96	Wako, Japan
Perfluorohexane sulfonate	PFHxS	$C_6HF_{13}O_3S$	>98	Fluka, Italy
Perfluorooctane sulfonate	PFOS	$C_8HF_{17}O_3S$	>98	Wako, Japan

2.2 Sampling sites

Study areas in this work were based on the information from Department of Groundwater Resources (DGR) and Pollution Control Department (PCD) of Thailand which are available on the website. Groundwater samples were collected from groundwater well within 2-3 kilometers from the sources. The sampling locations could be separated into 2 categories, which were around municipal waste disposal sites (MWDS) and industrial waste dumping sites (IWDS). The MWDSs are located in Ayutthaya and IWDS are located in Chachoengsao and Chonburi. The study areas are presented in Figure 2.1. Table 2.2 shows sampling date and sampling information of this study.

Table 2.2 The overall of sample collection information of this study

Sampling Date	Study areas	No. of sample	Approximate volume (mL)	Application	Sampling method
17-Dec-15	Nong Nae IWDSs	4	1000	Consumption	Faucet
16-Feb-16	Bang Chai MWDS	4	1500	Consumption	Faucet
16-Feb-16	Sena MWDS	8	1500	Consumption	Faucet
10-May-16	Map Phai IWDS	15	1500	Consumption	Faucet
24-Sep-16	Map Phai IWDS	12	1500	Consumption	Faucet
11-Feb-17	Nong Nae IWDSs	27	1500	Monitoring	Bailer

2.2.1 Municipal waste disposal sites (MWDS)

In this study, the selected municipal waste disposal sites are located in Bang Chai district and Sena district of Ayutthaya. The map of the study areas in Ayutthaya are presented in Figure 2.2.

The Bang Chai MWDS has been operated since 2007 by a private company. The surrounded areas are used for agriculture. Total amount of waste which dumped in this landfill is around 45 tons per day (Ayutthaya Waste Management Plan for year 2015-2019). Open dumping is which applied for disposal operation. This area comprises of four designed disposal sites with four waste layers for each site. Presently, the second disposal site has been being operated. The Sena MWDS is surrounded by agricultural zone. It has been used as municipal open dumpsite since 1974. The site is operated with open dumping method, which abandoned piles of garbage and debris are left in large quantities on the ground without proper management. Thus, it is necessary to investigate PFASs that might contaminate to groundwater (Office of Natural Resources and Environmental, 2015).

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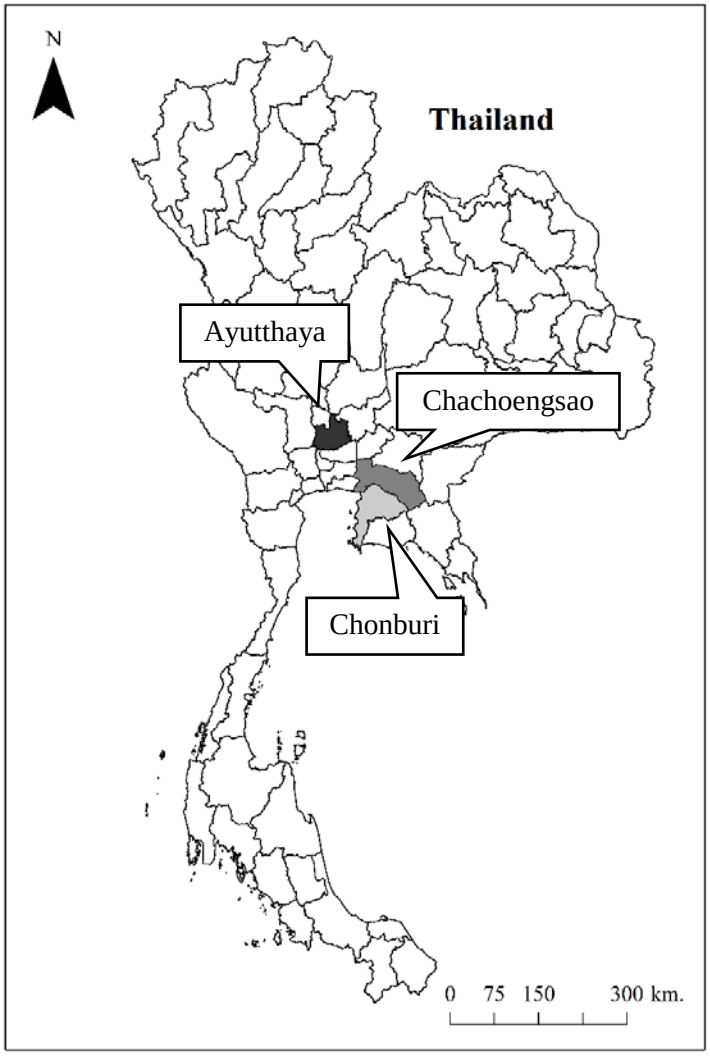

Figure 2.1 The map of the study areas

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The groundwater sampling wells around the source are displayed in Figure 2.3. The groundwater well identifications are listed in Table 2.3.

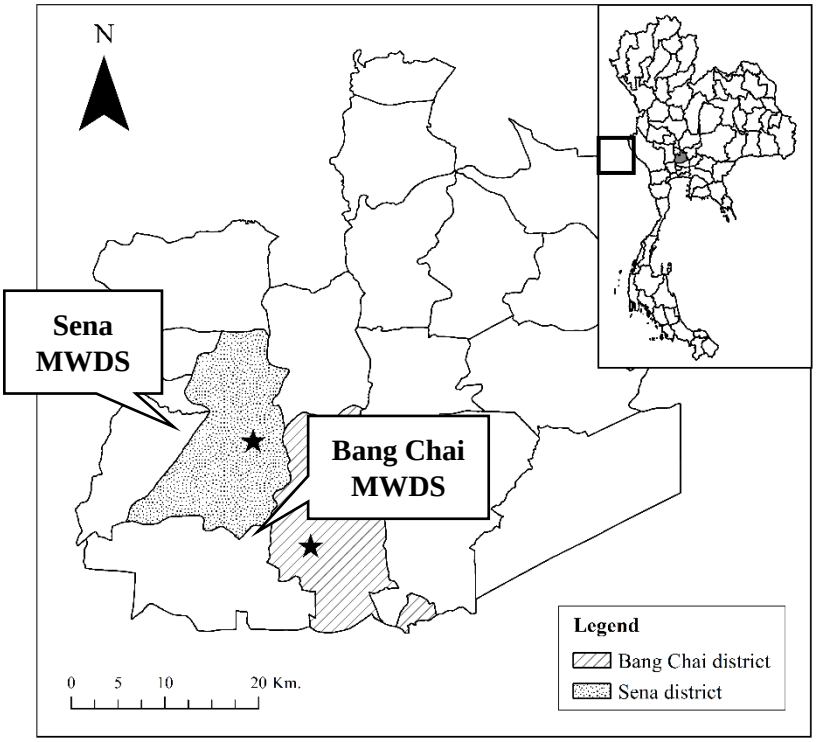


Figure 2.2 The map of Bang Chai district and Sena district in Ayutthaya

Table 2.3 The sampling points around Bang Chai MWDS and Sena MWDS, Ayutthaya

Well	Well size (mm)	Well depth (m)	Water table level (m)	Application	Coordinates	
					X	Y
MW_BC_GW01	-	-	-	Consumption	655256	1570366
MW_BC_GW02	-	-	-	Consumption	655840	1569407
MW_BC_GW03	-	-	-	Consumption	656361	1570341
MW_BC_GW04	150	212	17.0	Consumption	658406	1568328
MW_SN_GW01	-	183	12.2	Consumption	649733	1582016
MW_SN_GW02	-	171	12.2	Consumption	652075	1580995
MW_SN_GW03	150	162	18.0	Consumption	652321	1581849
MW_SN_GW04	150	161	10.0	Consumption	652831	1581755
MW_SN_GW05	-	-	-	Consumption	651126	1581045
MW_SN_GW06	150	162	17.0	Consumption	651217	1579666
MW_SN_GW07	150	174	18.0	Consumption	652645	1579745
MW_SN_GW08	-	-	-	Consumption	652952	1579181

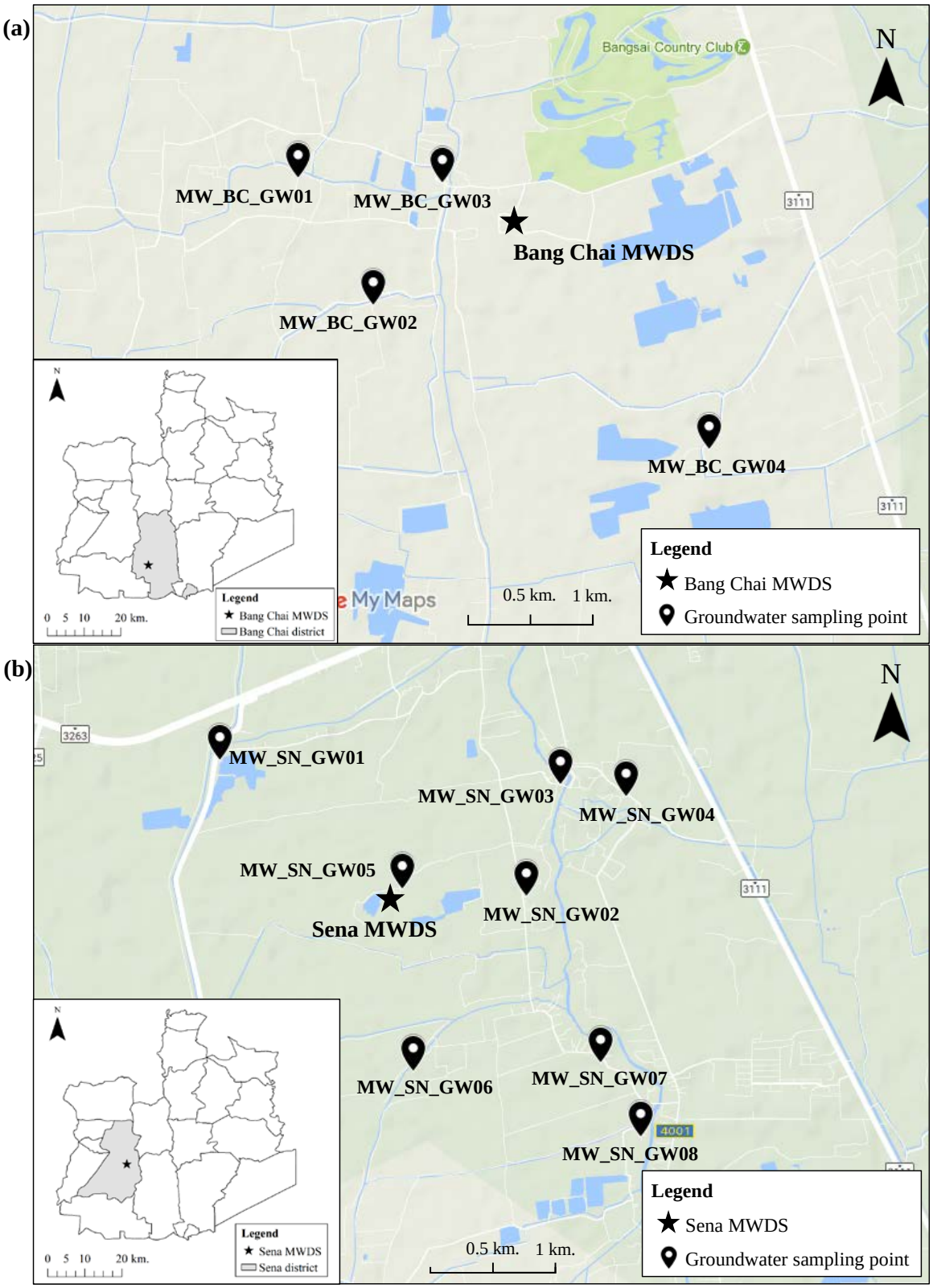


Figure 2.3 The groundwater sampling points around (a) Bang Chai MWDS and (b) Sena MWDS in Ayutthaya

2.2.2 Industrial waste disposal sites (IWDS)

2.2.2.1 Industrial waste disposal sites in Chachoengsao

Chachoengsao is a province in Eastern region of Thailand. It is located on the bank of Bang Pakong River. The west part of the province is the low river plain of the Bang Pa Kong River, which is used extensively for paddy field. Based on the information of Industrial Estate Authority of Thailand, there are 3 main industrial estates in Chachoengsao (Wellgrow Industrial Estate, Gateway City Industrial Estate, and TFD Industrial Estate). Meanwhile, there are several reports related to illegal dumping sites on abandoned lands. Therefore, the results from this study will be a useful data for screening PFASs contamination in groundwater, which used as sources of water consumption. Chachoengsao consists of 11 districts, which further subdivided into 93 sub-districts. The map of Phanom Sarakham district in Chachoengsao and IWDSs are presented in Figure 2.4. The focused study area is in Phanomsarakham district.

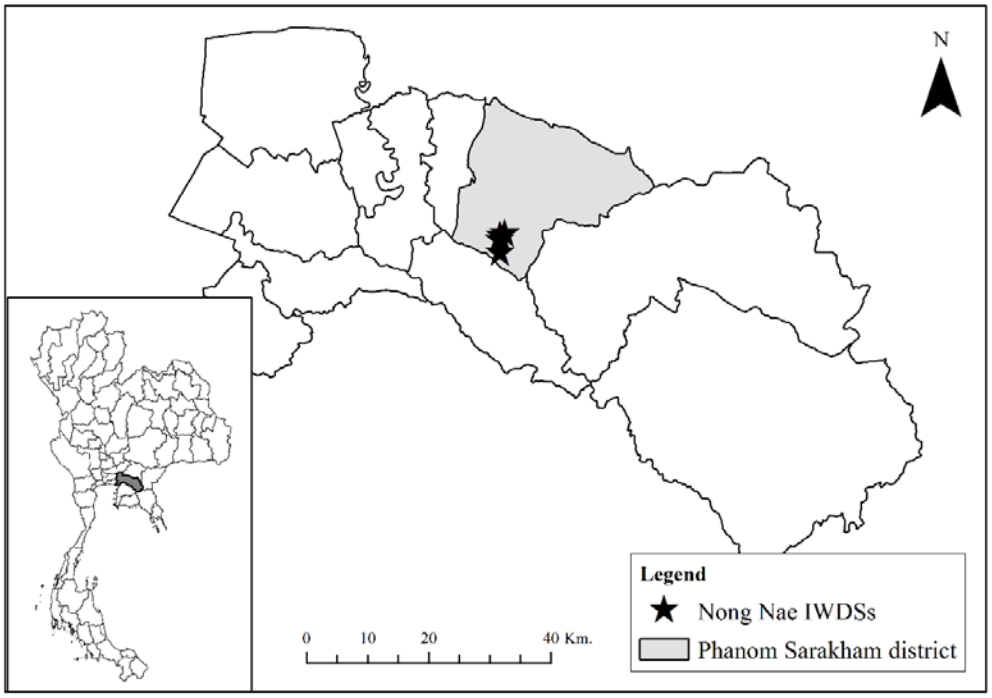


Figure 2.4 The map of Phanom Sarakham district and Nong Nae IWDSs, Chachoengsao

Phanom Sarakham district is subdivided into 8 subdistrict (Tambon), which are further subdivided into 87 villages. The total area is 550 km^2. According to the information from Department of Groundwater Resources (DGR) and Pollution Control Department (PCD) of Thailand, there are several points where used as industrial waste dumping sites in Nong Nae sub-district and Koh Khanun sub-distric. Therefore, this area is selected to be the groundwater sampling location in Chachoengsao. The groundwater sampling wells around the sources are displayed in Figure 2.5.

There are two types of groundwater wells: consumption well and monitoring well. Four samples were collected from consumption well and 26 samples were collected from monitoring well. Groundwater well locations are listed in Table 2.4.

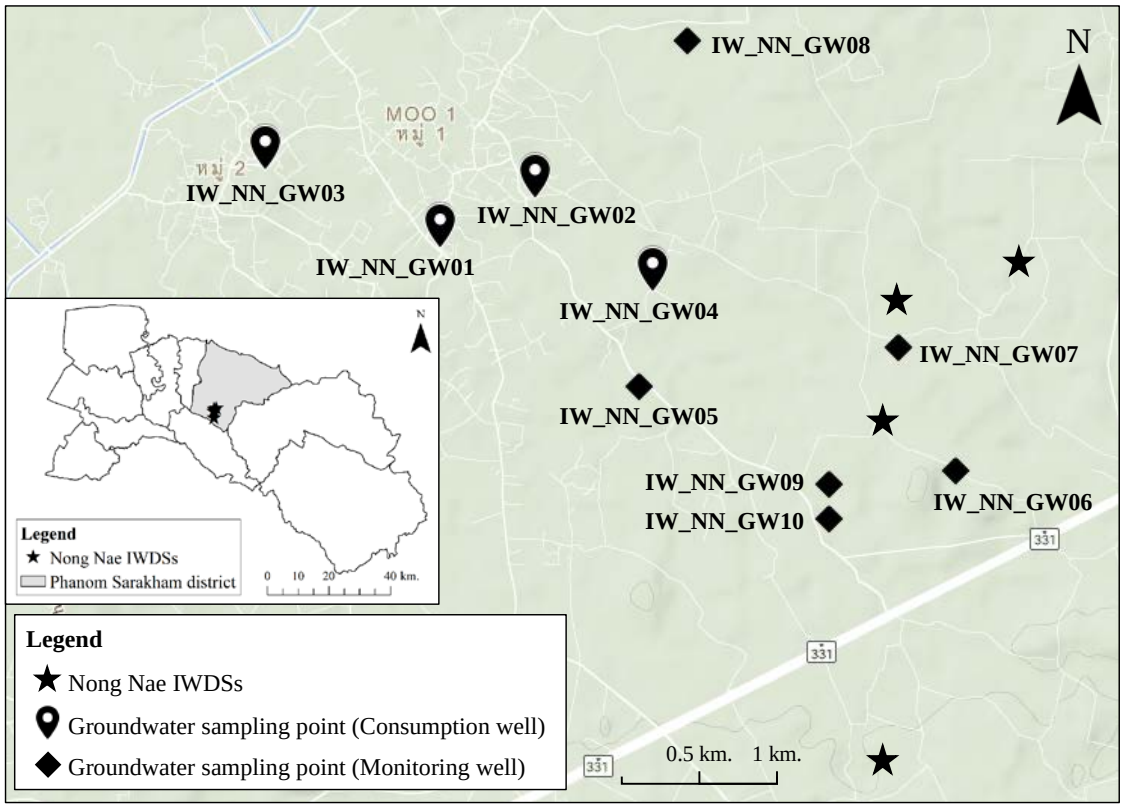


Figure 2.5 The groundwater sampling points around Nong Nae IWDSs, Chachoengsao

Table 2.4 The sampling points around Nong Nae IWDSs, Chachoengsao

Well	Well size (mm)	Well depth (m)	Water table level (m)	Application	Coordinates	
					X	Y
IW_NN_GW01	-	-	-	Consumption	752092	1512593
IW_NN_GW02	-	127	3.0	Consumption	752672	1512897
IW_NN_GW03	150	92	7.0	Consumption	751003	1513061
IW_NN_GW04	-	120	4.0	Consumption	753397	1512337
IW_NN_GW05	150	20	5.4[a]	Monitoring	753331	1511765
IW_NN_GW06	150	21	5.7 [a]	Monitoring	755291	1511268
IW_NN_GW07	150	36	12.0 [a]	Monitoring	754924	1512023
IW_NN_GW08	150	23	4.5 [a]	Monitoring	753607	1513887
IW_NN_GW09	150	35	8.1 [a]	Monitoring	754510	1510966
IW_NN_GW10	150	34	5.3 [a]	Monitoring	754507	1511172

[a] measured at the sampling points on February 11,2017

2.2.2.2 Industrial waste disposal site in Chonburi

Chonburi is a province in the Eastern part of Thailand. Neighboring provinces are Chachoengsao, Chanthaburi, and Rayong (from north clockwise). Chonburi has the high capacity port which called Laem Chabang. It is the main deep sea port for international shipping and becomes one of the highest (trading) growth rates in the world. Moreover, there are several industrial estates in Chonburi as well. From these factors, the population has been rapidly growing. Presently, the registered population as of December 31, 2015 was 1.45 million. Chonburi comprises of 11 districts. These are further divided into 92 sub-districts and 691 villages (Chonburi Governor's Office, 2016; Department of Provincial Affairs, 2015). The map of Chonburi is presented in Figure 2.6. The focused study areas are in Ban Bueng district and Pan Thong district.

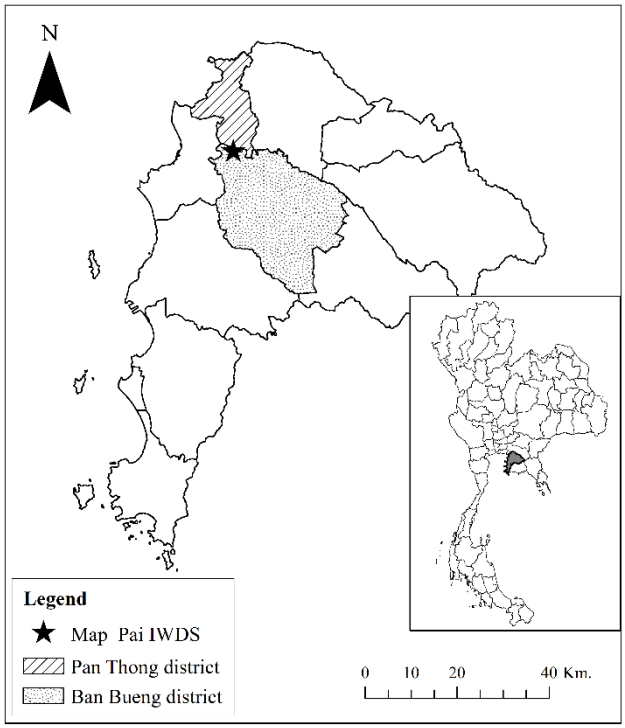


Figure 2.6 The map of Pan Thong and Ban Bueng district in Chonburi

Ban Bueng district consists of eight sub-districts, which are further subdivided into 52 villages. While Pan Thong district consists of 11 sub-districts with 76 villages. Map Phai and Pan Thong sub-district are the study in Chonburi. Map Phai sub-district is located in the Eastern of Chonburi (see Figure 6).

The North of Map Phai sub-district bonded with Phan Thong sub-district, where has been reported as illegal dumping areas particular industrial wastes. Moreover, open burning has been occurred and there were several complaints from villagers. Therefore, this area is selected as the groundwater sampling location. The groundwater sampling wells around the source are displayed in Figure 2.7. The groundwater well locations are listed in Table 2.5.

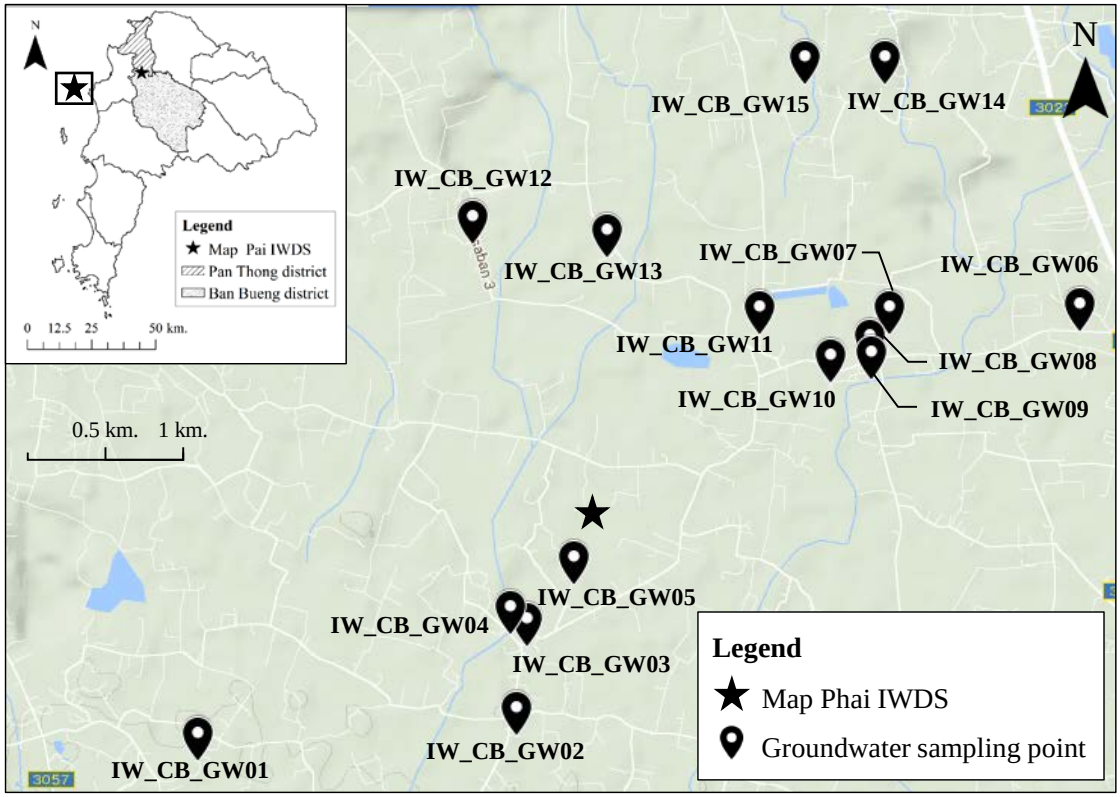


Figure 2.7 The groundwater sampling points around Map Phai IWDS, Chonburi

Table 2.5 The sampling points around Map Phai IWDS, Chonburi

Well	Well size (mm)	Well depth (m)	Water table level (m)	Application	Coordinate	
					X	Y
IW_CB_GW01	-	90	3.0	Consumption	724052	1478059
IW_CB_GW02	-	-	-	Consumption	726009	1478231
IW_CB_GW03	150	54	5.9	Consumption	726067	1478774
IW_CB_GW04	-	86	4.0	Consumption	725966	1478851
IW_CB_GW05	100	32	-	Consumption	726352	1479153
IW_CB_GW06	-	-	-	Consumption	729459	1480736
IW_CB_GW07	-	122	-	Consumption	728284	1480702
IW_CB_GW08	125	51	2.1	Consumption	728165	1480532
IW_CB_GW09	150	122	6.0	Consumption	728174	1480430
IW_CB_GW10	150	120	6.0	Consumption	727924	1480406
IW_CB_GW11	150	69	11.4	Consumption	727485	1480695
IW_CB_GW12	150	90	4.0	Consumption	725712	1481240
IW_CB_GW13	150	72	4.0	Consumption	726545	1481165
IW_CB_GW14	-	73	18.6	Consumption	728248	1482237
IW_CB_GW15	150	74	3.0	Consumption	727750	1482233

2.3 Groundwater sample collection method

2.3.1 Containers preparation

The samples were collected by using new two liters narrow-neck PET bottles with screw caps. The containers were rinsed with methanol, followed by deionized water and dried prior use.

2.3.2 Samples collection

The containers were rinsed by the water samples three times to prepare the same conditions as the samples. There are two types of groundwater well which used different collection methods. The methods are as follows:

- *Monitoring wells*

Groundwater was collected directly from the monitoring wells which installed by DGR by using a bailer sampler. The bailer sampler was purchased from Eijkelkamp Company, the Netherlands (Figure 2.8 and Figure 2.9).

- *Consumption wells*

Groundwater were collected directly from a faucet which connected straight to the plumping system. Before collection, groundwater were flown out for 5-10 minutes to remove remained water in a pipeline system. (Figure 2.10)

Figure 2.8 Bailer sampler for groundwater sampling

Figure 2.9 Monitoring well

Figure 2.10 Consumption well

2.3.3 Samples preservation

After sampling, the samples were kept in cooler box and brought to the laboratory. Then, the samples were filtered within 24 hours after collected. After that, the filtered samples were refrigerated for further analysis.

Glass bottles and glass equipment were avoided during the experiment due to target compounds may bind to the glass in aqueous solutions. Teflon equipment were also avoided because interferences may be introduced to the samples of extracts (Hansen *et al.*, 2002; Yamashita *et al.*, 2004).

2.4 Perfluoroalkyl substances (PFASs) analysis

2.4.1 Sample pre-treatment

In this experiment, solid-phase extraction (SPE) which was explained in previous section would be applied as a sample pre-treatment technique. After the samples were collected, 1500 mL of the samples were filtered by 1 μm GF/B glass fiber filter to separate suspended solids. Before loading, concentrators were washed by methanol at flow rate 10 mL/min for 5 minutes, followed by Milli-Q water at flow rate 10 mL/min for 10 minutes and the cartridges were preconditioned by 10 mL methanol (LC/MS grade), followed by 2×10 mL ultrapure water before use. Then, the filtered

samples were loaded to the PrecepC-Agri (C18) cartridges by using concentrators at a flow rate 10 mL/min which is an appropriate flow rate for all PFASs (Kunacheva, 2009a). Then, bottles were rinsed with *ultrapure* water and loaded into the cartridges at flow rate 10 mL/min for 3 minutes two times. After loading, cartridges were centrifuged to dewater or dried under gently vacuum for 1-2 hour. Then, eluted with 2 mL LC/MS-grade methanol, followed by 2 mL acetonitrile (ACN) into a polypropylene tube. Methanol and ACN percentage affect an elution of PFASs according to hydrophobic and hydrophilic value. In previous experiment, 100% methanol and 100% ACN were suggested as a preferable solvent for elution of PFOS and PFOA by PresepC-Agri (C18) cartridge (Kunacheva, 2009a). Then, eluents were purged with nitrogen gas for dryness. After that the eluents will be reconstituted with 30% acetonitrile. Then, 200 μL of eluents were transferred to LC/MS vials. The liquid phase sample pre-treatment procedures of PFASs are summarized in Figure 2.11.

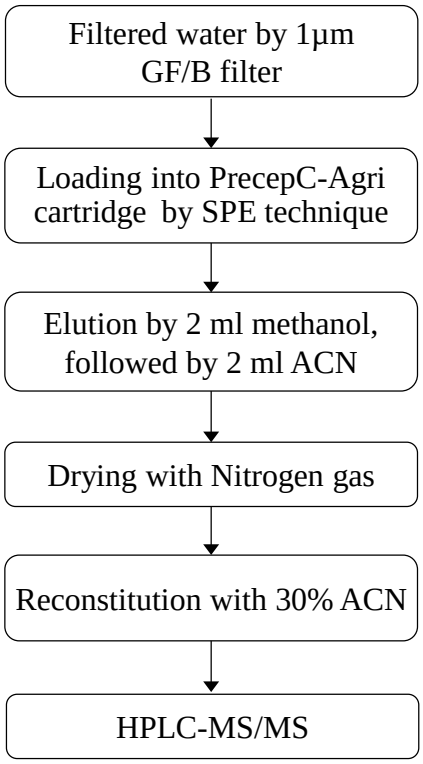


Figure 2.11 A summarization of sample preparation and analysis

2.4.2 Instrumental analysis and Quantification

Analysis of PFASs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, USA). The analytical column used is Agilent Eclipse XDB-C_{18}, 4.6 x 50 mm, 1.8 μm and Plus C_{18}, 2.1 x 100 mm, 1.8 μm. For quantitative determination, HPLC was coupled with Agilent 6400 triple quadrupole mass spectrometer (MS/MS) (Agilent, USA) which shown in Figure 2.12. MS/MS was operated with negative mode of electrospray ionization (ESI). Mobile phase consists of (A) 10mM ammonium acetate in *ultrapure* water (HPLC/MS grade), and (B) 100% acetonitrile (HPLC/MS grade). Specific ions were analyzed by multiple reaction

monitoring (MRM) mode. The column temperature was maintained at 40°C and the injection volume was 10 µl. The operating conditions for ESI were as follows: gas flow was 10 L/min with a capillary voltage of 3500V and gas temperature at 300°C. The operation conditions are shown in Table 2.6. The analytical parameters are listed in Table 2.7 and their chromatograms are presented in Figure 2.13.

Table 2.6 Summary of analytical operation conditions of HPLC-MS/MS

HPLC		MS/MS	
Instrument	Agilent 1200 SL HPLC	Instrument	Agilent 6400 triple Quadrupole mass spectrometer
Column	Agilent Eclipse XDB-C_{18} , 4.6 x 50 mm, 1.8 µm and Plus C_{18}, 2.1 x 100 mm,1.8 µm	MS/MS operation	MRM (multiple reaction mode)
Mobile Phase	A: 10mM CH_3COONH_4/H_2O B: CH_3CN	Source	ESI (electrospray ionization)
Flow	0.25 (mL/min)	Gas flow	10 L/min
Injection volume	10 µL	Capillary voltage	3500V
Column temp.	40°C	Gas temp	300°C

Table 2.7 The analytical parameters by HPLC-MS/MS analysis

Compound	No. of Carbon	Parent ion (m/z)	Daughter ion (m/z)
PFHpA	C7-A	363	319
PFOA	C8-A	413	369
PFNA	C9-A	463	419
PFDA	C10-A	513	469
PFUnA	C11-A	563	519
PFHxS	C6-S	399	80
PFOS	C8-S	499	80

Note: A = Perfluorinated carboxylic acids (PFCAs); S = Perfluorinated sulfonic acids (PFSAs)

Figure 2.12 HPLC coupled with MS/MS

2.4.3 Calibration and validation

Calibration curves were prepared from the PFASs standards. For quantification, calibration curves comprise of five concentration levels covering 0.1-10 μg/L. In case of sample concentrations exceed calibration curve, samples were diluted in order to make the value fall within the range of the calibration curve and reanalyzed. Basically, calibration curve should provide linearity with determination coefficients (R^2) more than 0.999. Practically, limit of detection *(LOD)* and quantification *(LOQ)* of the measurement method were calculated from instrument detection limit (IDL) and instrument quantification limit (IQL). IDL and IQL were defined with signal-to-noise ratios (S/N) equal to 3:1 and 10:1, respectively (Hansen *et al.*, 2002; Yamashita *et al.*, 2004).

2.4.4 Method recovery

The recovery rates were calculated by spiking 10 μg/L of each PFASs standards into one liter of samples before loading to the cartridges. Then, the samples were analyzed by the previous procedure. Blank sample which use Milli-Q water was prepared and done the same procedure as spiked samples.

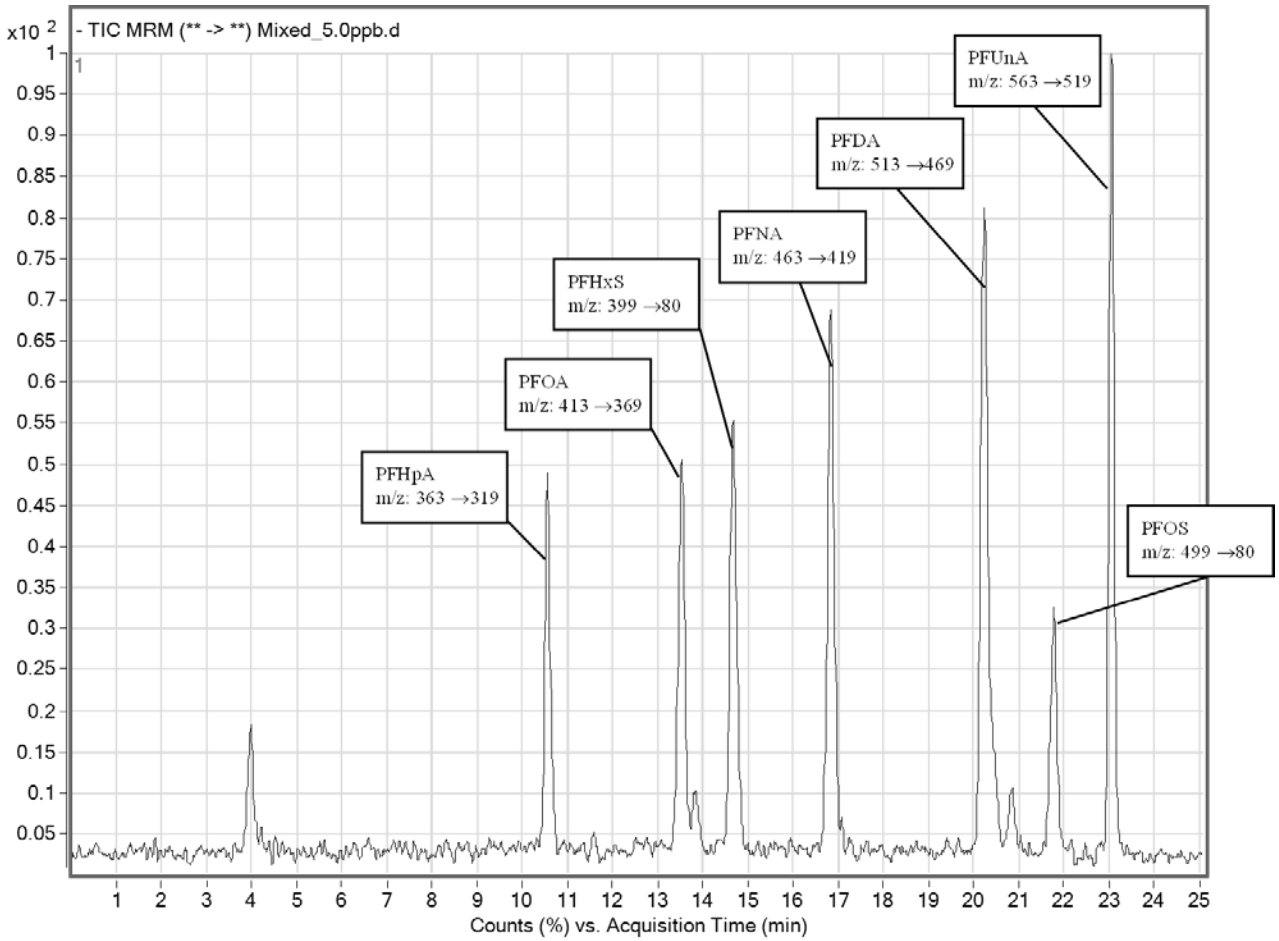


Fig. 2.13 The chromatograms of seven PFASs at 5 µg/L

2.5 Experiments for TiO_2/GO/PVA photocatalysis

2.5.1 Pre-testing for pH value of PFOS and PFOA

The TiO_2/GO/PVA nanofilms were prepared by 20wt% of GO mixed with 80wt% of TiO_2, followed by adding 10 g of PVA and stirring for a while then heated at 120˚C for 3 h to obtain the TiO_2/GO/PVA nanofilms. Water sample was prepared by milli-Q water spiked with PFOS and PFOA for the initial concentration of 100 ppb. Finally, applying the nanofilms in 3 different pH values that divided into pH 3, pH 7, and pH 10.

2.5.2 Preparation of TiO_2/GO/PVA nanofilm

The TiO_2/GO/PVA nanofilm was prepared by the following two steps, which composed of solution casting and heat-treatment process (Lei, 2012).

Solution casting. GO nanoparticles were initially dispersed in 50 mL of milli-Q water under sonication for 2 h while providing TiO_2 solution by the combination of TiO_2 nanoparticles and 50 mL of milli-Q water mixing by hot plate stirrer. Then TiO_2 solution was homogenized with GO solution for 1 h to be TiO_2/GO solution. PVA 10 g was subsequently added into the TiO_2/GO suspension, followed by mechanical stirring at 95˚C for 1 h and turned to 60˚C for 3 h, then followed by sonicated for 30 min to obtain TiO_2/GO/PVA solution. After that, the beaker containing the

solution mixture rested in air to eliminate air bubbles and to cool the solution to room temperature. The resultant viscous bubble-free solution mixture was cast onto a clean aluminum foil cup to give a 1 mm-thick layer. The solvent was allowed to evaporate overnight in the atmosphere at room temperature. Finally, the dried nanofilms were collected from foil cups. The weight ratio of GO to TiO_2 was varied as 0, 10, 15, 20, 25, and 100wt%, and the resulting nanofilms were designated as GO-0, GO-10, GO-15, GO-20, GO-25, and GO-100, respectively. In this experiment, pure PVA was used as a reference under the same conditions.

Heat-treatment process. The regenerated nanofilms which were cut into the squared shape of 30 mm × 30 mm were heat-treated under vacuum at 120˚C in 3 different heat-treatment times that varied to 1 h, 3 h, and 5 h to achieve the TiO_2/GO/PVA nanofilms.

2.5.3 Photocatalytic degradation

The photocatalytic activity of the sample films was evaluated from the degradation rate of PFOS and PFOA in an aqueous solution with an initial concentration of 100 ppb. The photocatalytic reaction was carried out in a UV cabinet. An array of lamps (15 Watt fluorescent source × 4 lamps) locating on a transparent tube acted as the UV B light source with the wavelength of 365 nm. Prior to irradiation, all of the sample films were immersed into 20 ml of milli-Q water spiked with PFOS and PFOA in the plastic beakers, respectively. Subsequently, these beakers were put onto the cabinet in parallel while shaking at 60 rpm throughout the experiment by the shaker. In the first hour of process, all tests were kept in the dark to equilibrium adsorption and desorption of photocatalysis. For 3 h later, the UV light illuminated to the bottom of cabinet. First hour, the samples were taken at 30 and 60 min then changed to collect every 15 min in 3 h later. At given irradiation time intervals, the concentration of PFOS and PFOA was monitored by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) to measure the concentration of PFOA and PFOA.

2.6 *Specification of membrane and its equipment set up*

The major instrument of this study is the nanofiltration membrane (NF) that is used for removing the target contaminants. The membrane model 2540-ACM5-TSF in 2.5” diameter was purchased from Trisep Corporation (USA) and the membrane specification is shown in Table 2.8. According to the specification of the membrane, it has the ability to reject soluble low molecular weight (> 200 Daltons (Da)) neutral and charged organic compounds, so it can remove PFOA, which has a molecular weight of 414 g/mol (USEPA, 2014), or equal to 414 Da. According to a previous study, NF membrane could reject PFOS (one of the most common PFASs) by up to 90-99% (Tang *et al.*, 2007). Depending on respective pore size, the NF membrane should be suitable for removing PFASs from the process (Lutze *et al.*, 2012). Moreover, this membrane can operate at ultra-low pressures at 5-9 bar. Therefore, this membrane was selected to test with both PFOS and PFOA in this study. The type of this membrane is a fully aromatic polyamide

advanced composite membrane, and it is spiral wound and outer wrapped by fiberglass. The active membrane area is 26 ft^2 (2.4 m^2). The average salt rejection and minimum salt rejection of the membrane are 98.5% and 97.5%, respectively. The pump model is A-97516688-P1-1432 (GRUNDFOS, Denmark). Normal volume flow rate and normal pressure are 1.7 m^3/h and 6.5 bar, respectively. The type of motor is a MG80B 1*220-240-2B-C (GRUNDFOS, Denmark) and the power output is 0.9 kilowatts (kW), or 1.21 horse power (HP).

Table 2.8 The nanofiltration membrane specification of model 2540-ACM5-TSF for operational and design data

NF Membrane	Details and operation
Type	Fully aromatic polyamide advanced composite membrane
Configuration	Spiral wound, fiberglass outer wrap
Active membrane area	26 ft^2 (2.4 m^2)
Molecular weight cut-off	200 Da
Recommended applied pressure	100-300 psi (7-21 bar)
Maximum applied pressure	600 psi (41 bar)
Recommended operating temperature	35-113°F (2-45°C)
Feed water pH range	2-11 continuous
Chlorine tolerance	<0.1 ppm
Maximum feed flow	6 gallons/min (1.4 m^3/h)
Minimum brine flow/ permeate flow ratio	5:1
Maximum silt density index (15 minutes)	5:0
Maximum turbidity	1 NTU
Permeate flow	800 gallons/day (3.0 m^3/day)
Average salt rejection	98.5 %
Minimum salt rejection	97.5 %

2.7 Specification of ultrafiltration (UF) membrane and its equipment set up

Another major part of this study is the ultrafiltration membrane (UF) that used for removing the nanoparticles after the photocatalysis process and before releasing the treated water back into the environment. The hollow fiber ultrafiltration membrane model UFH-PST-2021 was purchased from Shanghai Mega Vision Membrane Engineering & Technology (China) and the membrane specification is shown in Table 2.9. The type of this membrane is a hydrophilic

polysulfone modified membrane, and it is a hollow fiber. The active membrane area is 0.25 m^2. The removal of > 200 nm particles of membrane is 100 %. The pump model is a A-97516688-P1-1432 (GRUNDFOS, Denmark).

Table 2.9 The hollow fiber ultrafiltration membrane specification of model UFH-PST-2021 for operational and design data

UF Membrane	Details and operation
Type	Hydrophilic polysulfone modified
Configuration	hollow fiber ultrafiltration module
Nominal membrane area	0.25 m^2
Operating pressure	< 14.50 psi (1 bar)
Maximum applied feed pressure	43.51 psi (3 bar)
Maximum transmembrane pressure	29.01 psi (2 bar)
Maximum backwash transmembrane pressure	20.31 psi (1.4 bar)
Maximum operating temperature	113°F (45°C)
Feed water pH range	2-11 continuous
Instantaneous chlorine tolerance	1000 ppm
Continuous chlorine tolerance	200 ppm
Instantaneous hydrogen peroxide tolerance	200 ppm
Typical design filtrate flux range	70~150 L/m^2/h
Maximum turbidity	200 NTU
Filtrate flow	22~36 L/h
Filtrate turbidity	< 0.1 NTU
Maximum SDI (15 minutes)	< 2
Virus and bacterial removal	≥ 4 log
Colloidal removal	100 %
TOC reduction	0-50 %
Removal > 200 nm particles	100 %

2.8 Phase I: Membrane filtration

For nanofiltration membrane experiments, there are two types of feed water, consisting of synthetic samples and groundwater samples. The synthetic samples were developed in order to find the conditions that were to be used with real groundwater samples. After that, the groundwater samples were run at the selected pressure and concentration. Finally, the PFOS

and PFOA removal efficiency of synthetic and real groundwater samples could be compared under the same conditions. The flowchart of the experimental study of membrane filtration is presented in Figure 2.14. For the schematic diagram of the nanofiltration membrane operation unit, it is shown in Figure 2.15, and the actual nanofiltration (NF) membrane operation unit is shown in Figure 2.16. The PFOS and PFOA removal efficiency was calculated with the equation below.

$$\text{Removal efficiency (\%)} = \frac{\text{(influent conc. - effluent conc.)}\times 100}{\text{influent conc.}}$$

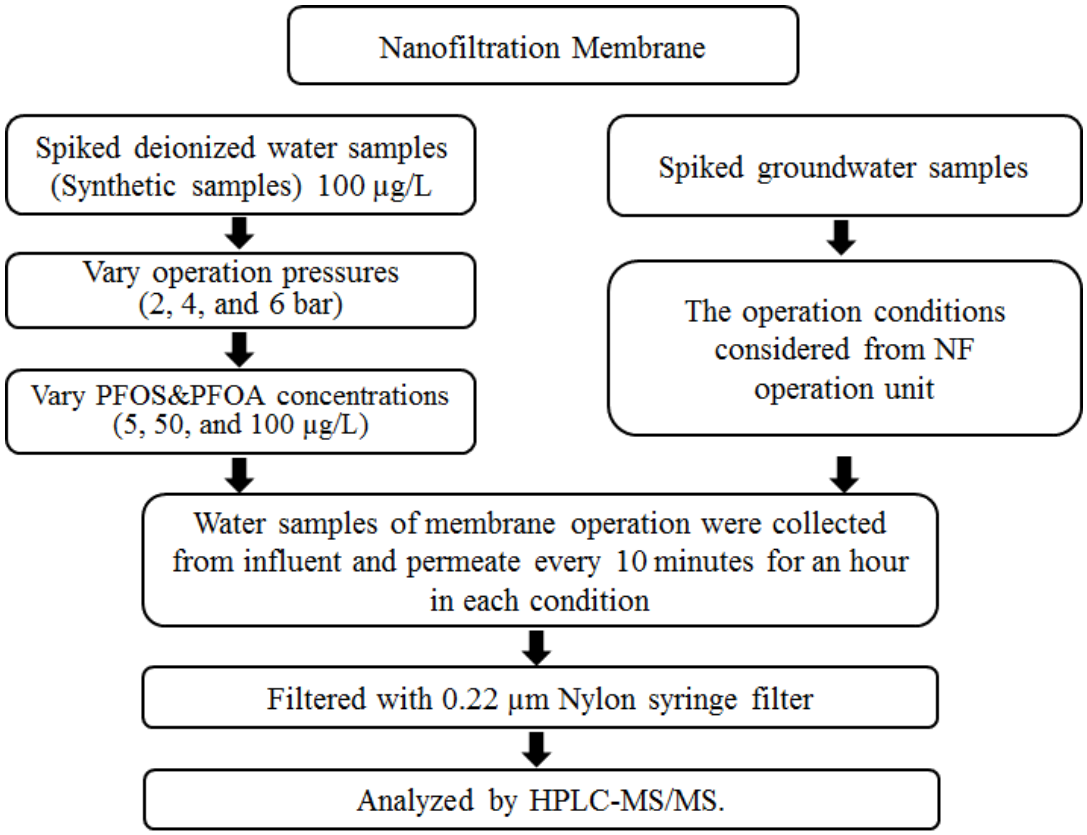


Figure 2.14 Flowchart of membrane filtration experiments

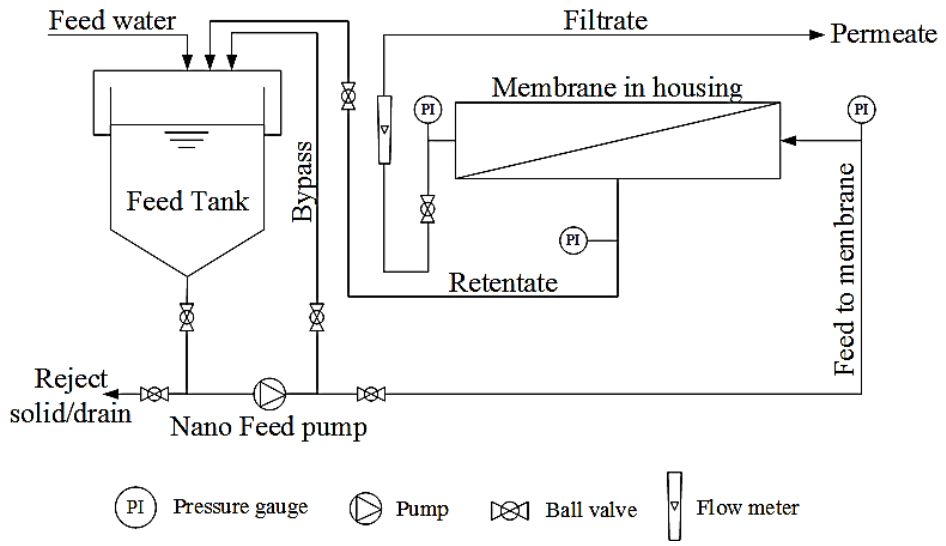


Figure 2.15 Schematic diagram of nanofiltration (NF) membrane operation unit

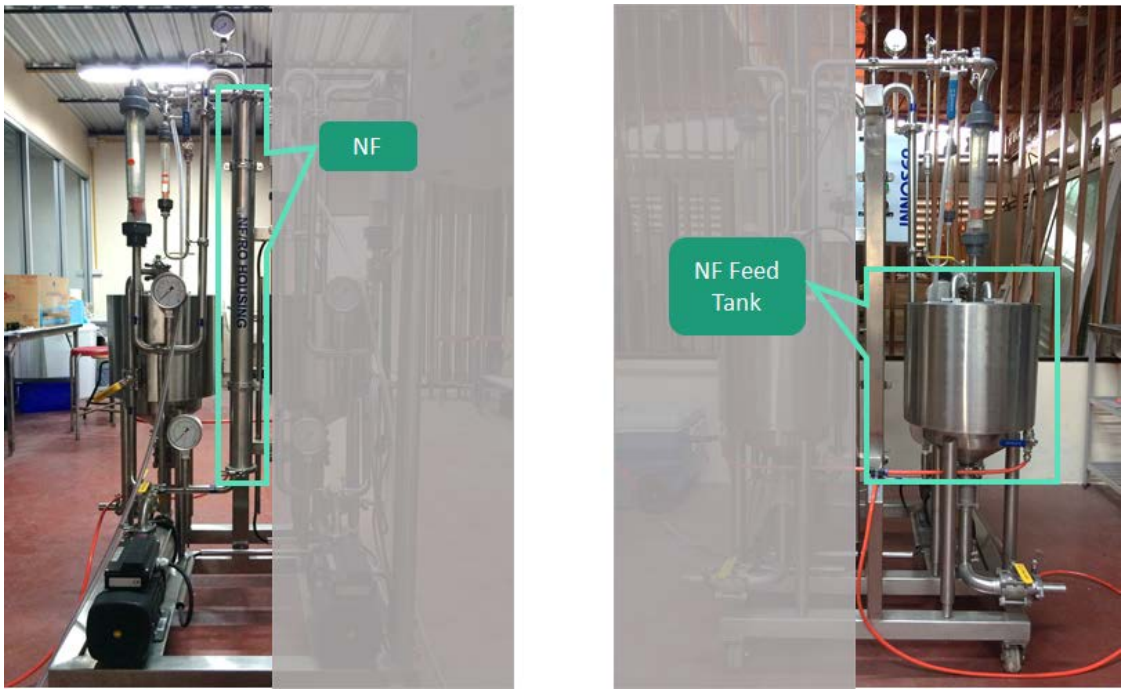


Figure 2.16 The nanofiltration (NF) membrane operation unit

2.8.1 Operation with synthetic samples

Spiked deionized water was used as synthetic samples. Spiked deionized water was controlled at 100 µg/L PFOS and PFOA and focused on the feed (influent) pressure of the membrane. The three operational pressures were 2, 4, and 6 bar, respectively. Furthermore, after determination of appropriate fixed pressure operation, three PFOS and PFOA spiked deionized water concentrations were used at 5, 50, and 100 µg/L. The experimental runs are shown in Table 2.10.

Table 2.10 The experimental runs of spiked deionized water sample and spiked groundwater sample in nanofiltration membrane experiments

Sample	Pressure (bar)	Initial concentration (µg/L)
Spiked deionized water	2	100
	4	100
	6	100
	6	5
	6	50
	6	100
Spiked groundwater	6	50

2.8.2 Operation with groundwater samples

After knowing the PFOS and PFOA concentration in groundwater by solid phase extraction (SPE) coupled with the HPLC-MS/MS technique, a groundwater sample was spiked with 50 µg/L of PFOS and PFOA, which was chosen because it is the lowest PFOS and PFOA concentration with high removal efficiency. The conditions applied for the groundwater batch experiment were based on the synthetic sample operation results. For pressure, the highest PFOS and PFOA removal efficiency was selected.

2.8.3 Samples collection during experiments

Water samples from the membrane operation were collected at 100 mL of each sample from influent and permeate every 10 minutes for an hour in each condition, while conductivity and pH were measured at the same point. The flow rate of permeate was measured every 10 minutes. In addition, the temperature of the influent was controlled and measured under the recommended operating temperature (2-45 $^{\circ}$C) of the membrane as shown in Table 2.8.

2.8.4 Groundwater collection and preparation

The 100 L of groundwater samples were collected from a consumption well near a landfill from Nakhon Pathom province, Thailand. All samples were kept in a plastic storage container and protected from sunlight.

For the groundwater sample, solid phase extraction (SPE) was needed for concentrating PFOS and PFOA in the sample and analyzed by HPLC-MS/MS. The SPE method was explained in the section 2.4.

For the spiked groundwater sample, the 50 µg/L PFOS and PFOA were prepared and spiked into the groundwater sample, which had been collected from Nakhon Pathom province.

Nevertheless, the exact initial concentration of all samples was analyzed by HPLC-MS/MS again including spiked deionized water samples.

2.9 Phase II: Photocatalysis

For the photocatalysis experiments, UV light (254 nm) and nanoparticles are important factors of the process. Zero valent iron nanoparticles (nZVI) were used as the catalyst of the reaction. In this study, there are two types of feed water, consisting of a spiked deionized water sample and a spiked groundwater sample, like in Phase I. The spiked deionized water sample was operated in order to find the optimal conditions to be used with the spiked groundwater sample. After that, the groundwater samples were run at the selected nanoparticles dosage. Finally, the removal efficiency of the spiked deionized water sample and the spiked groundwater sample could be compared under the same conditions, including photolysis (only UV light), only nZVI usage (without UV), and photocatalysis (both UV light and nZVI usage) conditions. The flowchart of the experimental study of photocatalysis is presented in Figure 2.17. The batch experiment of the photocatalysis operation unit is presented in Figure 2.18.

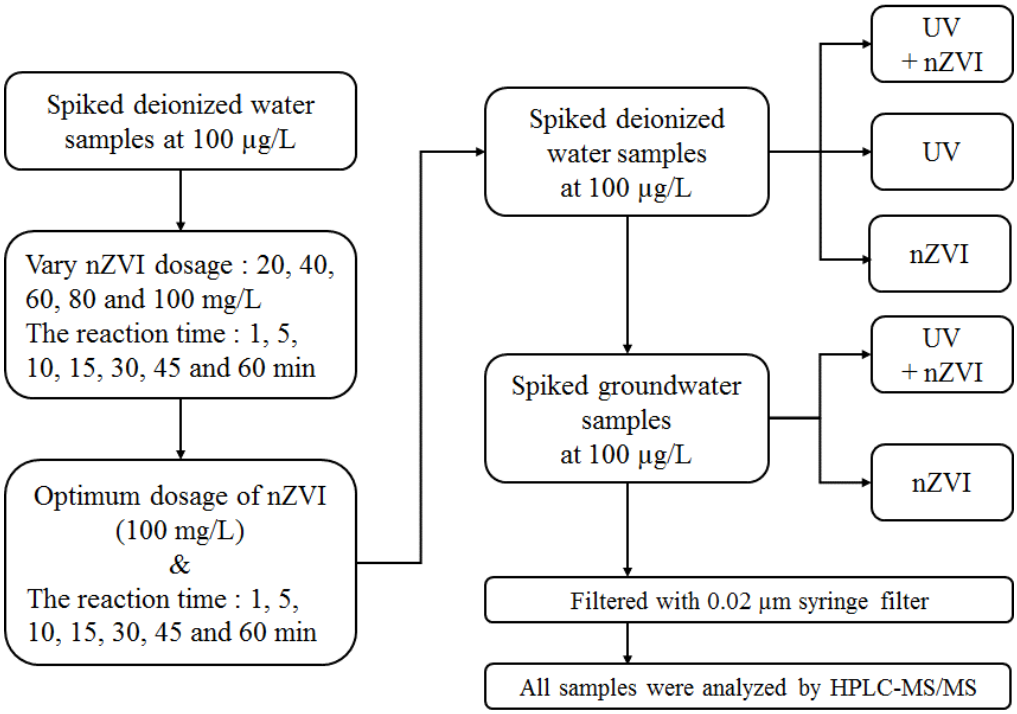


Figure 2.17 Flowchart of photocatalysis experiment

(a)

(b)

(c)

Figure 2.18 Batch experiment of photocatalysis operation unit: (a) the samples on a magnetic stirrer coupled with UV light, (b) the reaction occurred in a closed box for protection from the outer light disturbing the experiment, (c) zero valent iron nanoparticles (nZVI)

2.9.1 Operation with synthetic samples

Spiked deionized water was used as synthetic samples. Spiked deionized water was controlled at 100 µg/L of PFOS and PFOA and the experiment focused on finding the suitable nZVI concentration. Various nZVI concentrations were tried, which were 20, 40, 60, 80 and 100 mg/L, and were conducted by photocatalysis at the same reaction time: 1, 5, 10, 15, 30, 45 and 60 minutes for finding the suitable nZVI dosage. After determination of the appropriate nZVI dosage, the spiked deionized water sample at 100 µg/L PFOS and PFOA was run with different conditions, which are UV light with nZVI (photocatalysis), UV light (photolysis), and only nZVI usage. The experimental runs as shown in Table 2.11.

Table 2.11 The experimental runs of spiked deionized water sample and spiked groundwater sample in photocatalysis experiments

Sample	Initial PFOS and PFOA concentration (µg/L)	nZVI dosage (mg/L)	Reaction time (min)	UV + nZVI	UV	nZVI
Spiked deionized water	100	20	1, 5, 10, 15, 30, 45 and 60	✓		
	100	40		✓		
	100	60		✓		
	100	80		✓		
	100	100		✓		
	100	100	1, 5, 10, 15, 30, 45 and 60	✓		
	100	100			✓	
	100	100				✓
Spiked groundwater	100	100	1, 5, 10, 15, 30, 45 and 60	✓		
	100	100			✓	
	100	100				✓

2.9.2 Operation with groundwater samples

After knowing the PFOS and PFOA concentration in groundwater by SPE coupled with the HPLC-MS/MS technique, the groundwater sample was spiked by 100 µg/L of PFOS and PFOA. The conditions applied in the groundwater batch experiment were considered from the synthetic samples operation results. The experiment was conducted with photocatalysis (UV light coupled with nZVI), photolysis (UV light), and only nZVI usage.

2.9.3 Samples collection during experiments

The experimental run of spiked deionized water samples and spiked groundwater samples are shown in Table 2.11. Water samples from the photocatalysis operation, both synthetic and groundwater samples, were collected with 100 mL of each sample every 1, 5, 10, 15, 30, 45 and 60 minutes.

All samples from this phase were filtered by 0.02 µm syringe filter (Whatman, UK) before being analyzed by HPLC-MS/MS.

2.10 Phase III: Hybrid Process of NF and Photocatalytic

For the hybrid process of nanofiltration membrane and photocatalysis, the conditions were considered from the results of Phase I and Phase II. Synthetic and groundwater samples at 100 µg/L PFOS and PFOA were used as samples for comparing the removal efficiency of membrane filtration and hybrid membrane filtration (using residual PFOS and PFOA concentration

to indicate the removal efficiency of the hybrid process). Furthermore, the mass balance of the hybrid process are presented. The flowchart of the experimental study of the hybrid process is presented in Figure 2.19

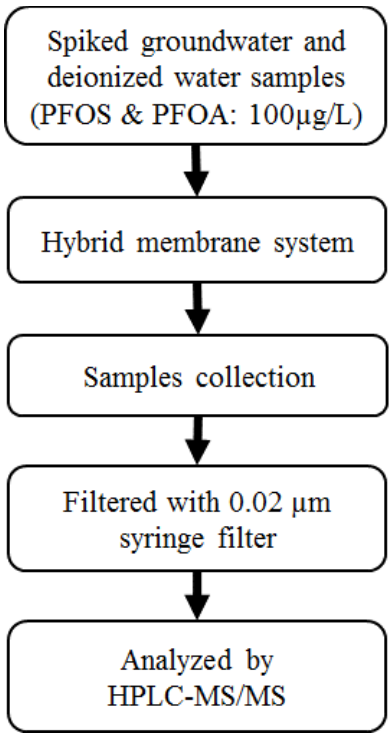


Figure 2.19 Hybrid process of NF membrane and photocatalysis experiment

2.10.1 Operation with synthetic and groundwater samples

In Phase III, spiked deionized water and spiked groundwater were used as samples in this experiment. Both the spiked deionized water sample and the spiked groundwater sample were controlled at 100 µg/L of PFOS and PFOA concentration. For the membrane filtration part, the pressure was chosen from phase I (membrane filtration) which is 6 bar operation pressure. For the photocatalysis part, which occurred in a UV contact tank, the nZVI dosage and reaction time of photocatalysis were selected from the results of phase II (the photocatalysis part), which are 100 mg/L of nZVI and 1, 5, 10, 15, 30, 45 and 60 minutes, respectively. The retentate were sent to the UV contact tank for photocatalysis, which was set up with UV light (254 nm) in the middle of the tank and zero valent iron nanoparticles (nZVI) were used to be the catalyst in this process. Then, nZVI were removed before being released to the environment by using ultrafiltration (UF). The diagram of the hybrid process of the NF membrane and photocatalysis experiment is shown in Figure 2.20. And the operation unit of hybrid NF and photocatalysis in front and back are shown in Figure 2.21

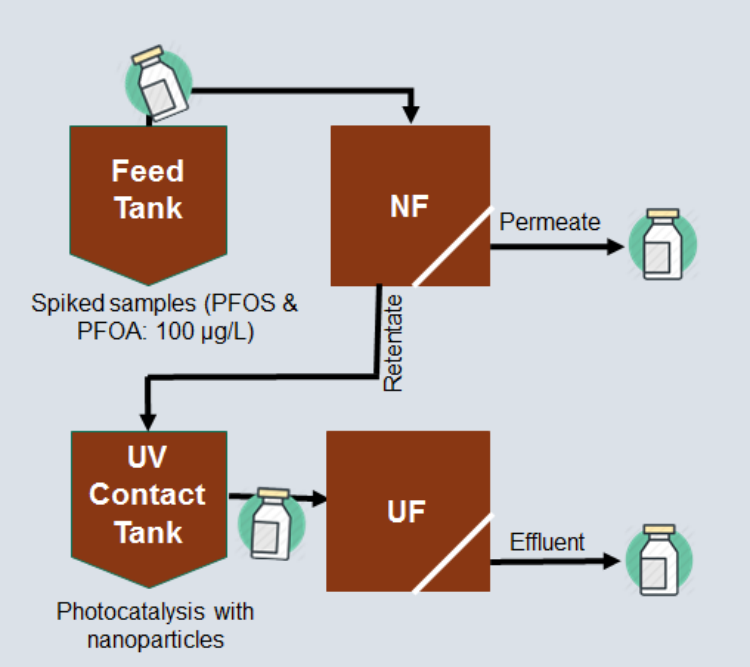


Figure 2.20 Diagram of hybrid process of NF membrane and photocatalysis experiment and sampling points

Figure 2.21 The hybrid NF membrane and photocatalysis operation unit

2.10.2 Samples collection during experiment

The samples of the synthetic and groundwater experiment were collected from NF influent (NF feed tank), NF effluent (every 8 min until the water runs out), the UV contact tank (at 1, 5, 10, 15, 30, 45 and 60 minutes), and UF effluent (at 2, 4, 6, 8 and 10 minutes), which are shown in Figure 2.23. The samples collected from the UV contact tank were filtered by 0.02 µm syringe filter for removal of nanoparticles before being analyzed by HPLC-MS/MS. All samples were analyzed by HPLC-MS/MS directly without the SPE step. The schematic diagram of NF is

shown in Figure 2.22, and the schematic diagram of hybrid membrane filtration and photocatalysis is shown in Figure 2.23.

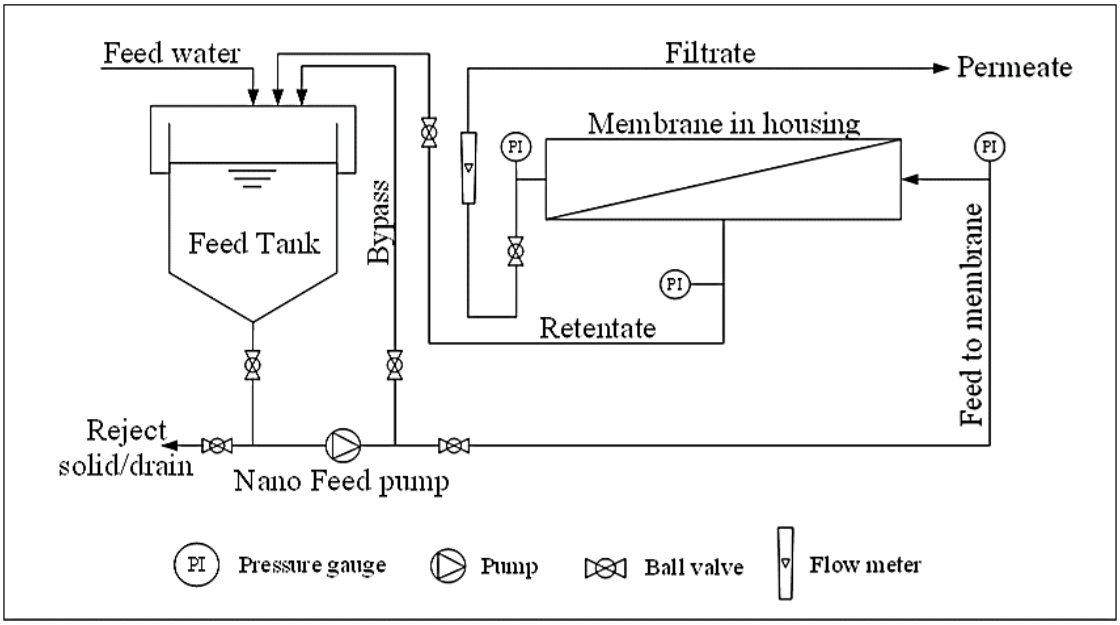


Figure 2.22 Schematic diagram of NF

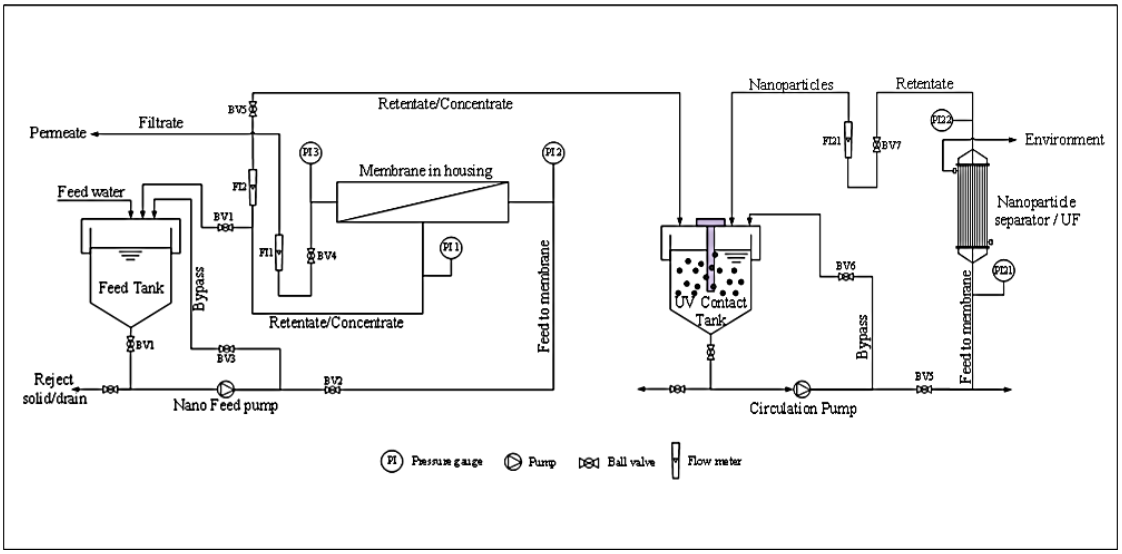


Figure 2.23 Schematic diagram of hybrid membrane filtration and photocatalysis

(3) Results and Discussion

The results and discussion are based on the objectives of this study. The first main part is presented to answer the objective 1-2. The second main part is presented to answer the object 3 and the last part is presented to answer the objective 4-6, accordingly.

Objective 1-2: Occurrence, distribution patterns and health risk assessment of PFASs in groundwater

3.1. Level of PFASs in groundwater and their distributions

3.1.1 PFASs concentration and their distributions in groundwater around the municipal waste disposal sites (MWDS)

The level of PFASs and their distribution profiles in all groundwater samples around two MWDSs are summarized in Table 3.1 and Figure 3.1. The target compounds were detected in all groundwater samples. Six of the seven PFASs were found in all groundwater samples: PFHpA, PFOA, PFNA PFUnA and PFOS from both of the sites in Ayutthaya, while PFHxS was found in only one sample, and PFDA was absent from any of the groundwater samples. The concentrations of total PFASs ranged from 1.68 to 7.75 ng/L. Among them PFOS was outstanding in the samples around Bang Chai MWDS, while PFOA was dominant in the samples around Sena MWDS. Eschauzier *et al.* (2013) also supports the finding that rain input and waste arrangement variations within a waste disposal site may impact the initial leachate components before reaching the groundwater. PFASs in groundwater in this study were found to be slightly higher than the concentrations in tap water in previous studies (Kunacheva, 2009a). It was proved that water treatment can reduce PFASs in tap water. However, groundwater in these study areas is used directly without any treatment. Thus, evaluation of health risk is necessary to ensure whether consumption of this water is safe.

There are some previous studies about PFASs in surface water in Thailand. The discovered PFOS concentrations ranged from 1.7 to 1.9 ng/L and average PFOA was 4.7 ng/L in the Chao Phraya River, while the average PFOS and PFOA concentrations in the Bang Pakong River were both 0.7 ng/L (Boontanon *et al.*, 2012; Kunacheva *et al.*, 2009b). When compared with the previous studies the concentrations from this study show much higher levels. It might be the result of the specific activity associated with the MWDS.

Table 3.1 PFASs concentration in groundwater around Bang Chai MWDS and Sena MWDS, Ayutthaya

Well	Concentration (ng/L)							Total
	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS	PFASs
Bang Chai MSWD								
MW_BC_GW01	<LOQ	0.71	ND	ND	ND	<LOQ	2.54	3.25
MW_BC_GW02	<LOQ	1.33	<LOQ	ND	<LOQ	0.07	3.15	4.56
MW_BC_GW03	0.54	1.23	<LOQ	ND	<LOQ	ND	0.87	2.63
MW_BC_GW04	<LOQ	0.65	0.30	<LOQ	0.29	<LOQ	1.06	2.31
Sena MSWD								
MW_SN_GW01	<LOQ	3.89	0.80	<LOQ	0.40	<LOQ	0.58	5.67
MW_SN_GW02	<LOQ	1.19	0.40	ND	0.29	<LOQ	<LOQ	1.87
MW_SN_GW03	<LOQ	1.55	0.15	ND	<LOQ	<LOQ	1.25	2.95
MW_SN_GW04	0.58	3.76	<LOQ	ND	<LOQ	<LOQ	0.71	5.05
MW_SN_GW05	0.91	2.07	<LOQ	ND	<LOQ	<LOQ	1.27	4.25
MW_SN_GW06	<LOQ	1.09	0.40	ND	0.34	ND	1.18	3.01
MW_SN_GW07	<LOQ	6.22	0.36	<LOQ	0.49	<LOQ	0.68	7.75
MW_SN_GW08	<LOQ	0.97	0.36	ND	0.34	<LOQ	<LOQ	1.68

Note: LOQ=Limit of detection, ND=Not detected

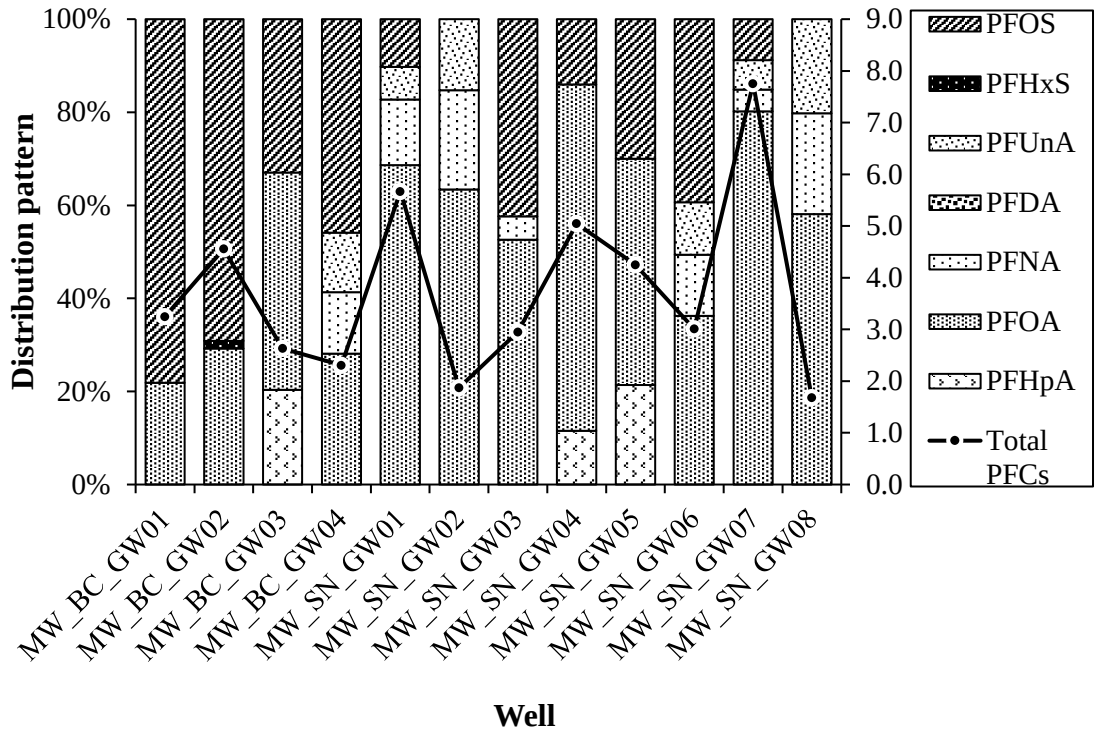


Figure 3.1 The distribution profiles and total PFASs in groundwater around Bang Chai MWDS and Sena MWDS

Because the waste disposal sites were not engineering designed, an open dumping method was applied. Once it has rained PFASs contained in disposed garbage or leachates can

easily be released to surrounding environments including the soils, groundwater, and surface water.

3.1.2 PFASs concentration and their distributions in groundwater around the industrial waste disposal sites (IWDSs)

The levels of PFASs and their distribution profiles in groundwater around IWDS where illegal industrial waste dumping has occurred are presented in Table 3.2 and Figure. 3.2. The concentrations were much higher than those around MWDS. The concentrations in groundwater around Nong Nae IWDS and Chonburi IWDS ranged from 4.43 to 10.80 ng/L and 2.64 to 42.01 ng/L, respectively. All target compounds: PFOA, PFOS, PFHpA, PFNA, PFHxS, PFUnA and PFDA were measured in the samples around Map Phai IWDS, Chonburi; while PFNA, PFDA, PFUnA were absent in those around Nong Nae IWDS, Chachoengsao. Among the target compounds found the dominant ones were PFOA and PFOS. It can be confirmed that PFOS and PFOA are still being used in industrial processes. PFHxS was frequently observed in the groundwater samples around two IWDSs, which might indicate that it has been used as an alternative to PFOS-based compounds due to it having a shorter chain length. This finding is consistent with the report of The Danish Environmental Protection Agency (Poulsen *et al*., 2005). Furthermore, total PFASs concentrations around Map Phai IWDS, Chonburi were noticeably higher than those around Nong Nae IWDS, Chachoengsao, it might be caused by other factors besides direct sources, such as the effect of soil components which are described in section the next section.

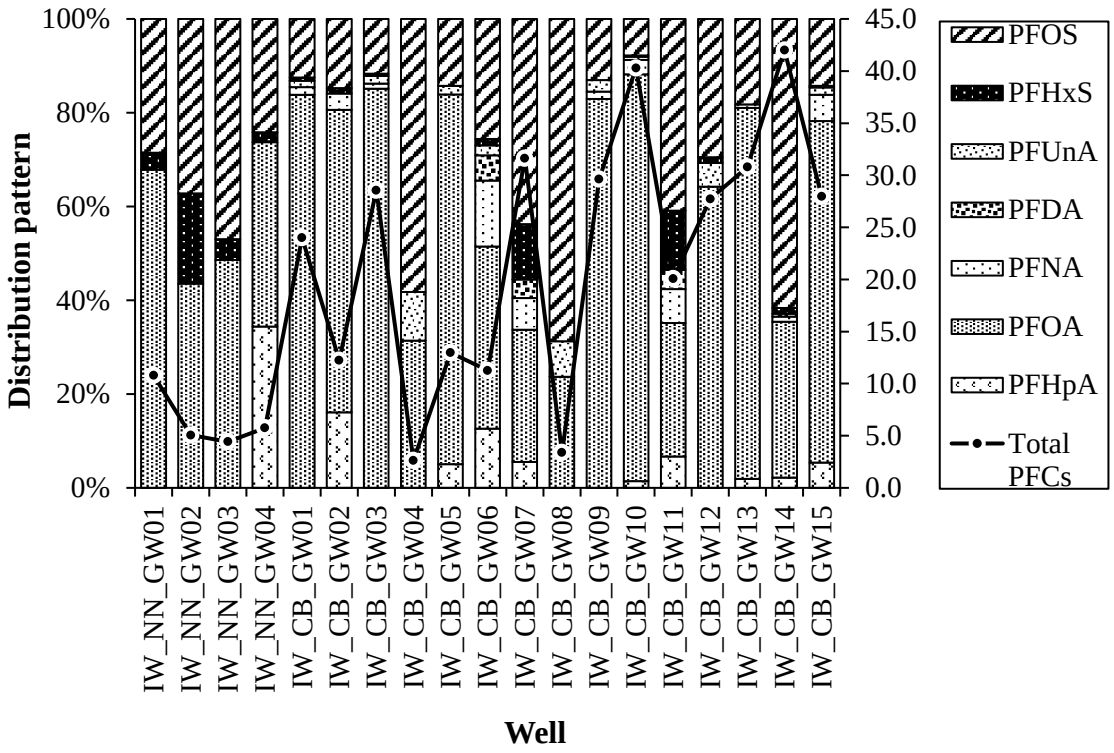


Figure 3.2 The distribution profiles and total PFASs in groundwater around Nong Nae IWDSs, Chachoengsao and Map Phai IWDS, Chonburi

Table 3.2 PFASs concentration in groundwater around Nong Nae IWDSs, Chachoengsao and Map Phai IWDS, Chonburi

Well	Concentration (ng/L)							Total
	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS	PFASs
Chachoengsao								
IW_NN_GW01	<LOQ	7.32	<LOQ	ND	ND	0.39	3.08	10.80
IW_NN_GW02	<LOQ	2.21	<LOQ	ND	ND	0.98	1.89	5.07
IW_NN_GW03	<LOQ	2.16	ND	ND	<LOQ	0.20	2.08	4.43
IW_NN_GW04	1.98	2.26	ND	ND	ND	0.12	1.39	5.75
Chonburi								
IW_CB_GW01	<LOQ	20.11	0.39	ND	0.33	0.17	3.00	24.00
IW_CB_GW02	1.97	7.90	0.43	<LOQ	<LOQ	0.13	1.81	12.24
IW_CB_GW03	ND	24.31	0.31	<LOQ	0.47	0.14	3.33	28.56
IW_CB_GW04	<LOQ	0.83	<LOQ	<LOQ	0.27	<LOQ	1.53	2.64
IW_CB_GW05	0.66	10.22	<LOQ	<LOQ	0.24	ND	1.85	12.96
IW_CB_GW06	1.42	4.38	1.58	0.61	0.24	0.15	2.88	11.27
IW_CB_GW07	1.76	8.91	2.14	1.25	<LOQ	3.73	13.84	31.63
IW_CB_GW08	ND	0.80	<LOQ	<LOQ	0.26	<LOQ	2.33	3.39
IW_CB_GW09	<LOQ	24.57	0.45	<LOQ	0.73	ND	3.87	29.62
IW_CB_GW10	0.59	34.96	1.22	ND	0.28	0.12	3.13	40.30
IW_CB_GW11	1.34	5.71	1.45	0.82	<LOQ	2.54	8.21	20.07
IW_CB_GW12	ND	17.82	<LOQ	<LOQ	1.39	0.35	8.17	27.73
IW_CB_GW13	0.59	24.35	<LOQ	ND	0.24	<LOQ	5.61	30.78
IW_CB_GW14	0.92	13.97	0.46	0.26	<LOQ	0.52	25.88	42.01
IW_CB_GW15	1.51	20.37	1.56	<LOQ	0.45	0.09	3.99	27.96

Note: LOQ=Limit of detection, ND=Not detected

3.1.3 Comparison of PFASs concentrations in groundwater around MWDS and IWDS

In order to compare the level of PFASs in groundwater around MWDS and IWDS, *t*-test analysis was conducted using IBM® SPSS® Statistics 20, which is one of the most widely used statistical tests.

Table 14 shows the results of the statistical analysis. Two groups of data (MWDS and IWDS) were split into an independent (type of waste disposal site) variable and a dependent variable (total PFASs concentration). The model assumes that a difference in the mean score of the dependent variable is found because of the influence of the independent variable. The null hypothesis assumes that mean score of PFASs concentration in groundwater around MWDS or

IWDS is not different, and the alternative hypothesis assumes that the mean score of total PFASs concentration in groundwater around MWDS versus IWDS is different.

Table 3.3 The statistical result (*t*-test) of two types of waste disposal site

	MWDS (*n*=12)		IWDS (*n*=19)		***t*-test**	**P-value**
	$\bar{X}$	SD	$\bar{X}$	SD		
Difference between total PFASs concentration	3.75	1.78	19.54	12.83	-5.28	0.00023*

* P<0.01

According to Table 3.3, the result showed that the P-value (2-tailed) was smaller than 0.01 (99% confidence); thus the major null hypothesis was rejected. It can be said that the difference of total PFASs concentrations in groundwater around MWDS and IWDS was statistically significant at $p<0.01$., so it can be concluded that PFASs contaminations between MWDSs and IWDSs were significantly different. Furthermore, when considering the total PFASs in groundwater and dissolved organic carbon (DOC), which is presented in Figure 3.3, the relationship between total PFASs and DOC showed a direct variation. It should be noticed that high PFASs levels were found in high DOC levels as well. This could be significant evidence to support the hypothesis that the groundwater has been contaminated by the waste disposal sites, particularly the IWDS due to industrial activity and manufacturing processes. Therefore, it can be assumed that the sources of contamination strongly are related to the PFASs levels.

Figure 3.4 presents a bar chart that plots total PFASs and groundwater level between the groundwater wells. Groundwater levels were derived from Department of Groundwater Resources (DGR) and from the survey. Deep groundwater was noticed in the wells around the MWDSs, whereas shallow groundwater was observed in those around the IWDSs. Therefore, groundwater around the IWDSs was easily polluted by many contaminants including PFASs from both point source and non-point source pollution which corresponds to the levels of DOC as presented in the previous figure.

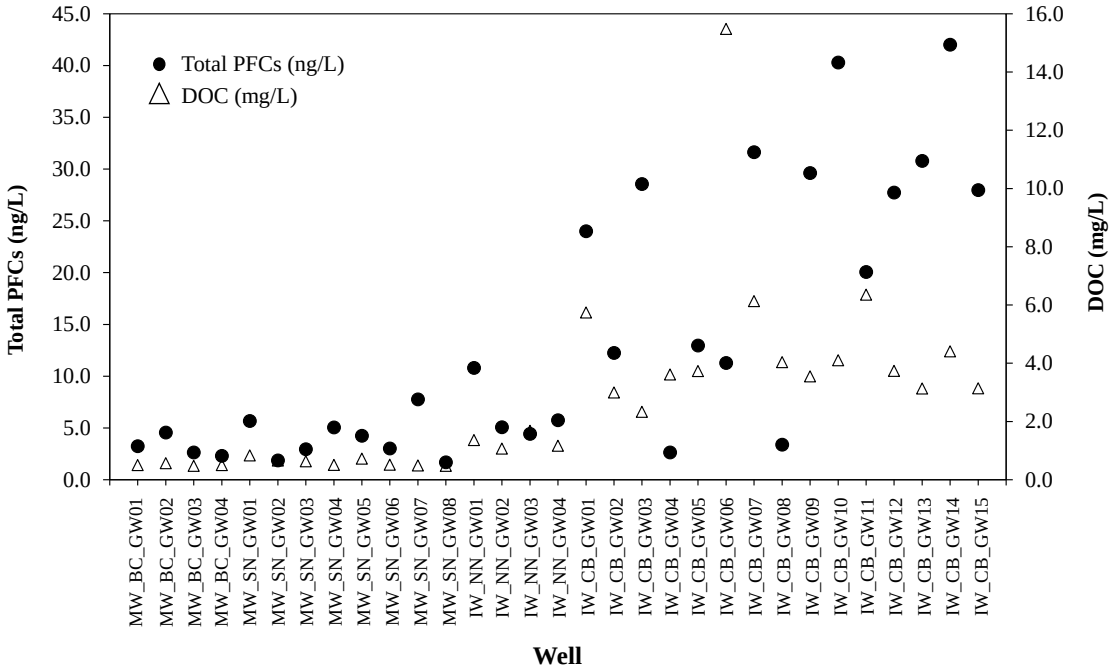


Figure 3.3 Comparison of total PFASs and dissolved organic carbon (DOC)

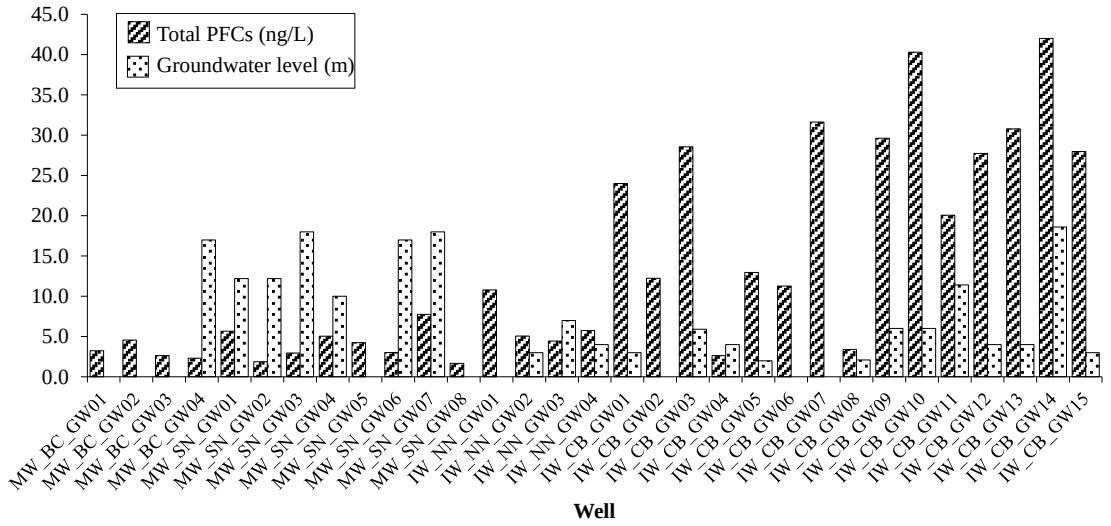


Figure 3.4 Comparison of total PFASs and groundwater levels

However, the concentrations measured in groundwater in this study were smaller than has been reported in previous studies (Moody *et al.*, 2003; Murakami *et al.*, 2009; Reinhardt *et al.*, 2010), this is because in the previous studies, the research areas were focused at specific sites such as fire-training areas.

3.2 Identification of potential sources of PFASs contaminations

The possible sources of PFASs were primarily classified by a hierarchical cluster analysis using IBM® SPSS® Statistics 20, based on analysis of their distribution patterns. The PFASs

distribution patterns could be categorized into 6 clusters. The dendrogram result from the hierarchical cluster analysis of all groundwater samples is presented in Figure 3.5.

Most groundwater samples around Bang Chai and Sena MWDS and Nong Nae IWDS were grouped into cluster 1 and cluster 2, where the areas that are used as rural areas; but the PFASs patterns were slightly different. Total PFASs concentrations in cluster 1 were lower than cluster 2. Moreover, PFOS was the most abundant in cluster 1, while PFOA was the most abundant in cluster 2. This might be due to PFASs substances (e.g. PFASs themselves or degradation of their precursors) used in commercial products.

Clusters 3 and 4 present unique PFASs distribution patterns, PFOS was the most predominant substance found; followed by PFOA, PFHxS, PFNA, PFHpA and PFDA. The well numbers IW_CB_GW07, IW_CB_GW11 and IW_CB_GW14 are far from Map Phai IWDS by 2.15 km., 1.5 km. and 3.4 km., respectively, but IW_CB_GW07 and IW_CB_GW14 are very close to large abandoned ponds, and IW_CB_GW11 is next to a pig farm. A map of these locations is presented in Figure 3.6. It was difficult to pinpoint the pig farm as a potential source of contamination, because the contamination of PFASs in animal feed, and the absorption and elimination of PFASs from animals especially pigs is not commonly reported. Numata *et al.* (2014) reported that PFCAs were removed from pigs at 4.1 days, while PFSAs were removed more slowly. Urinary excretion and fecal excretion were more often reported in other organisms, for example, one previous study reported that PFOA was completely absorbed and excreted in cattle urine (Lupton *et al.*, 2012). Furthermore, a study in rats revealed that excretion of PFOA, PFNA, and PFDA varied 52-80%, 2-51%, and 0.2% of the dose in urine, respectively; while fecal excretion of those was less than 5%. Additionally, it was remarked that fecal matter was a major route of PFDA elimination in rats (Kudo *et al.*, 2001). Fujii *et al.* (2015) also reported that PFOA was rapidly eliminated in mice urine, whereas longer chain lengths (C8-C14) were slowly excreted in the feces. Although there is relatively little research about absorption and elimination of PFASs in pigs, but it could be suspected that the pig farm might be a potential source of PFASs contamination in sampling point IW_CB_GW11, especially if there is no appropriate wastewater or pig manure management. In the case of well number IW_CB_GW07 and IW_CB_GW14, the potential source of PFASs contamination could not be easily identified due to the fact that the use of the large abandoned ponds could not be determined.

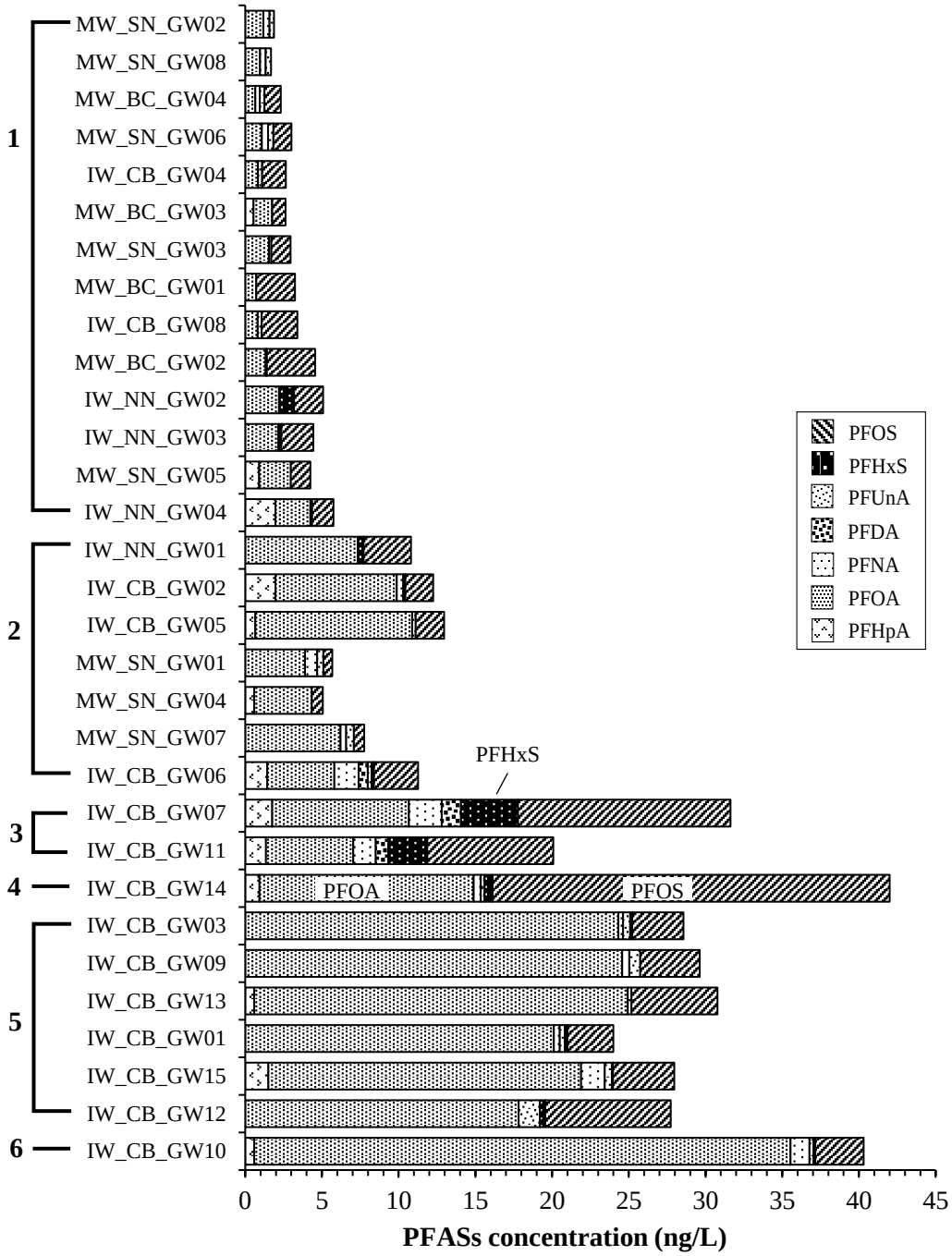


Figure 3.5 The dendrogram result of all groundwater from the hierarchical cluster analysis

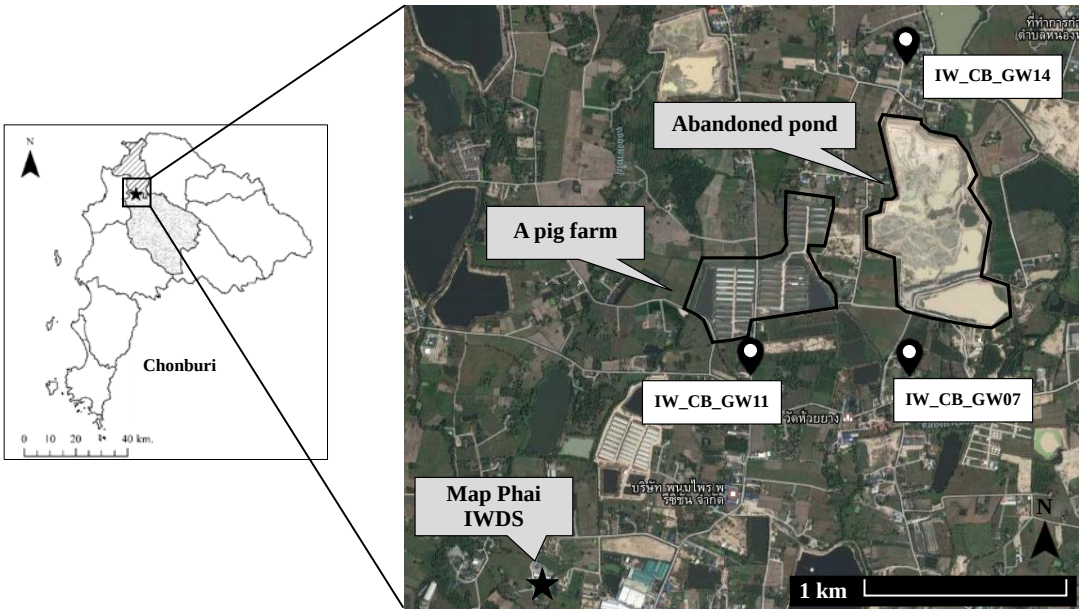


Figure 3.6 Map of Map Phai IWDS, Chonburi, showing a pig farm and abandoned pond nearby well number IW_CB_GW7, IW_CB_GW11, IW_CB_GW14

Clusters 5 and 6 contained most of the groundwater samples collected around Map Phai IWDS. A similar pattern was observed in clusters 5 and cluster 6, in which PFOA was the most abundant, followed by PFOS; the total PFASs concentration in cluster 6 was obviously higher than for those in cluster 5. The greatest concentration was quantified in the groundwater samples around Map Phai IWDS, which is in an industrialized area. Consistent with previous studies, PFASs were detected in industrialized or urbanized area more than rural areas due to the presence of industrial activity (Wang *et al*., 2012; Li *et al*., 2015). It should be remarked that the groundwater samples collected around both Nong Nae IWDSs, Chachoengsao and Map Phai IWDS, Chonburi were classified into different clusters, although they were represented for IWDS. Therefore, their contamination and transportation may involve other factors besides the sources, which will be discussed in the next section.

From the results, it is obvious that hierarchical cluster analysis is a useful analysis tool, which is appropriate for source apportionment of organic pollutants (Xiao *et al.*, 2012), including PFASs. Hierarchical cluster analysis was performed to understand the PFASs composition profiles and to identify potential sources of PFASs contamination since it can reasonably classify the PFASs profiles in groundwater. Thus it is essential for environmental regulation; moreover, additional sources also could be observed.

3.3 Horizontal and vertical distribution of PFASs levels

3.3.1 Horizontal distribution

Regarding the results in the previous section, it is clear that, high concentrations of PFASs were detected in groundwater around IWDSs, indicating that IWDSs play a significant role in the contamination of groundwater. However, difference in PFASs levels in groundwater around

Nong Nae IWDSs and Map Phai IWDSs were remarkable, even though they represent similar sources of contamination. They might very well be affected by other factors. Therefore, study on the horizontal distribution of PFASs could illustrate affecting factors and their possible behaviors. Horizontal distribution was analyzed with geostatistical data (soil map) which was derived from the Land Development Department (LDD) of Thailand. In order to study the horizontal distribution, the data was analyzed using ArcGIS 10.1. Table 3.4 describes characteristics of each established soil series in the study areas.

From Figure 3.7 it can be noticed that most soil series are Ayutthaya (Ay) and Sena (Se). Ay and Se soil series are mostly comprised of clay, so the main physical property is very low water permeability; in addition, major chemical properties are high acidity (pH 5.5 to 6 and 4 to 5.5, respectively), and high cation exchange capacity (CEC) (LDD, 2010). It could be assumed that low concentrations may result from PFASs interaction with cation, which consistent with Xiao *et al.* (2015). Moreover, Wang and Shih (2011) reported that adsorption increases when pH decreases, they also found that Ca^{2+} and Mg^{2+} can form bridges with PFOA anions and PFOS can be bridged by Ca^{2+}. Thus, adsorption seems to be a main mechanism of PFASs contamination in these areas.

Table 3.4 Soil characteristics in study areas

Sampling location	**Established soil series name**	**Characteristics**			
		Soil components	Water permeability	CEC	pH
Bang Chai MWDS Sena MWDS	Ayutthaya (Ay)	clay	very low	high	4.5-6
	Sena (Se)	clay	very low	high	4-5.5
Nong Nae IWDSs	Klaeng (Kl)	clay	very low	moderate	4.5-6
	Don Rai (Dr)	sandy loam, loam	moderate	low	5.0-6.5
	Bangkok (Bk)	clay	very low	high	6.0-8.0
	Chachoengsao (Cc)	clay	very low	high	5.5-8.0
Map Phai IWDS	Ban Bueng (Bbg)	sand, loamy sand	high	low	5.5-8.0
	Chonburi (Cb)	loam, sandy loam	moderate	low	6.5-8.5

Note: CEC = cation exchange capacity

Source: Soil Resources Survey and Research Division

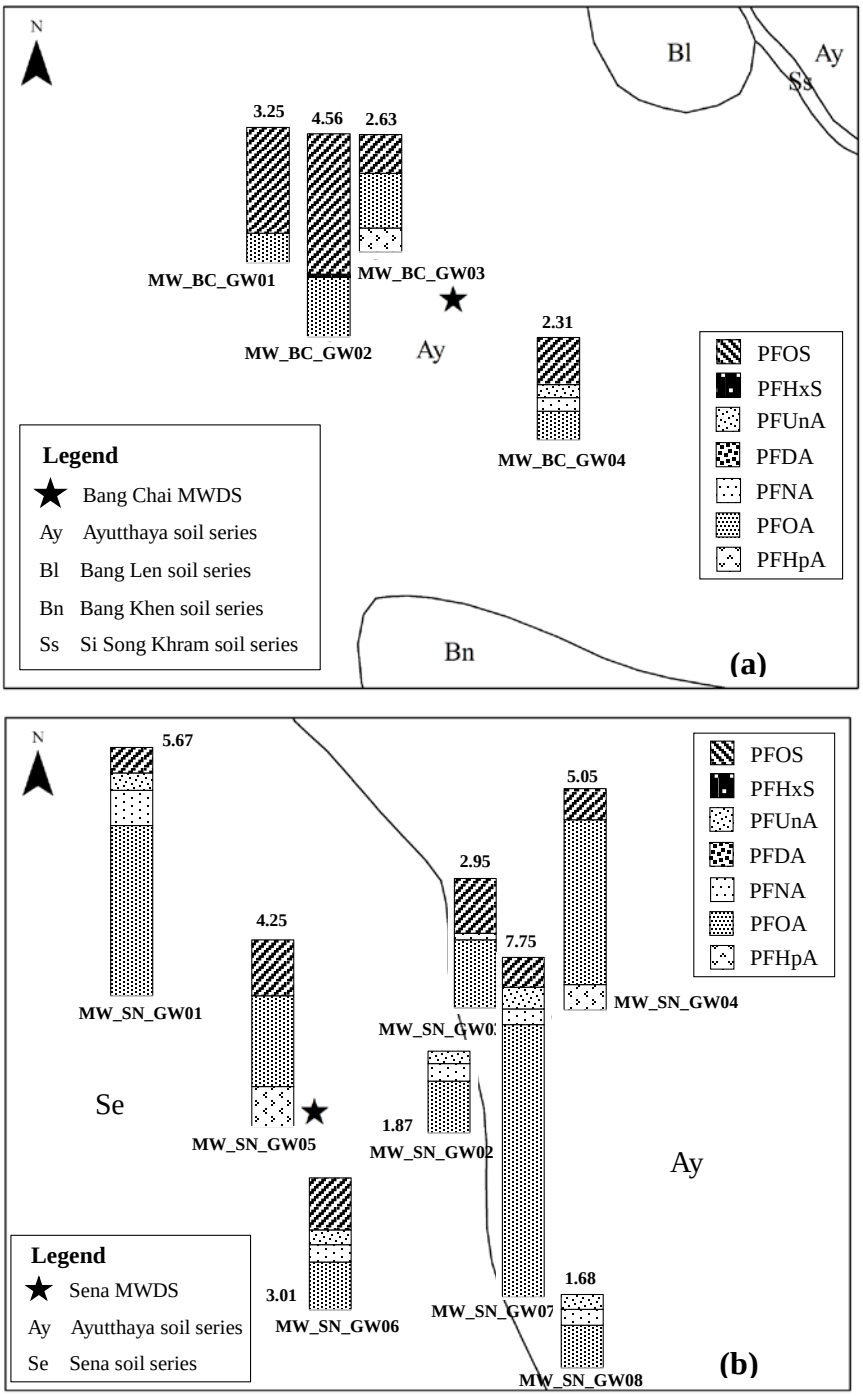


Figure 3.7 Maps of PFASs concentration (ng/L), their distribution patterns and soil series around (a) Bang Chai MWDS and (b) Sena MWDS, Ayutthaya

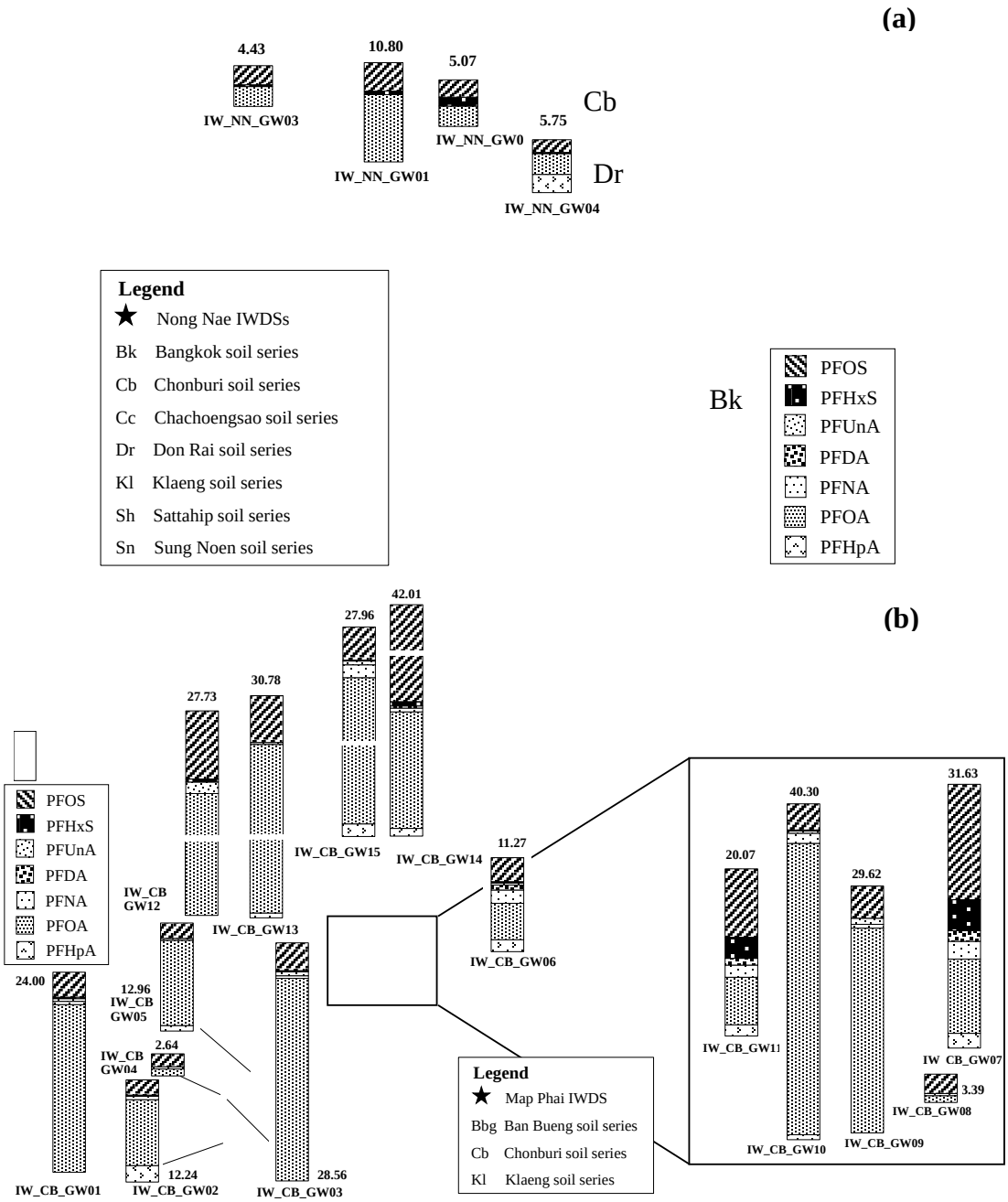


Figure 3.8 Maps of PFASs concentration, their distribution patterns and soil series around (a) Nong Nae IWDSs, Chachoengsao and (b) Map Phai IWDS, Chonburi

Figure 3.8 presents maps of PFASs concentration, their distribution patterns and soil series around Nong Nae and Map Phai IWDS. It can be observed that PFASs concentration in groundwater around Nong Nae IWDSs, Chachoengsao was quite a bit lower than that around Map Phai IWDS, Chonburi. This might be because of different soil properties. Klaeng (Kl) and Don Rai (Dr) are soil series around Nong Nae IWDSs, whereas Ban Bueng (Bbg) and Chonburi (Cb) are soil series around Map Phai IWDS. Kl and Dr soil series contain moderate CEC, low water permeability, and pH of 4.5 -6.4. In contrast, low CEC, high water permeability, and pH of 5.5 – 8.5 were reported for Bbg and Cb soil

series (LDD, 2010). Therefore, water permeability and the interaction of PFASs negative charged form with level of CEC in soil play an important role in the distribution of PFASs contamination.

As noticed in Figure 3.7 and Figure 3.8 contamination of PFASs in the groundwater which collected from the upstream of the waste disposal sites seemed similar as those collected from the downstream, indicating that besides of waste disposal sites, it could have been contaminated by other sources e.g. releasing of PFASs from commercial products used in household. Therefore, study of groundwater flow direction is recommended for further study in order to illustrate their exact contamination pathway.

3.3.2 Vertical distribution

The leaching from PFASs contaminated sites and contaminated soils are known as the major source of vertical transport of PFASs to groundwater. In this study, a depth profile of groundwater was collected at three to five groundwater layers from water table level to well screen level in order to determine the behavior of PFC. PFASs were analyzed with the procedure described in the previous chapter. Table 3.5 shows concentration of seven PFASs in groundwater collected from monitoring wells around Nong Nae IWDSs, Chachoengsao. Total PFASs concentrations and distribution patterns varied among the sampling points. Total PFASs ranged from 2.75 to 12.71 ng/L. PFOA was the most abundant compound, followed by PFOS, PFHpA, PFNA, PFUnA, PFDA, and PFHxS. The levels of total PFASs detected in the monitoring wells were in the same range as those observed in the consumption wells in the same area, presented in Table 3.6, although PFHpA, PFNA, PFDA, and PFUnA were notably observed in the monitoring wells. Moreover, all PFASs compounds were much higher than those in the same sampling points reported by Intaravira *et al.* (2014), indicating that the contaminations have increased compared to the previous study. It is because those areas are still being used as IWDSs. Consistent with the horizontal distribution described in the previous section, lower concentrations were found compared to those around Map Phai IWDS, Chonburi. This has resulted from soil characteristics and interaction between their negative charged ions and cation in soils.

Figure 3.9 presents PFASs distribution patterns in groundwater from the water column. In monitoring well number IW_NN_GW05, all detected PFASs seemed to decrease when depth is increased (although the difference was smaller), except for PFOS at the 6.09 meter level. A similar trend was observed in monitoring well number IW_NN_GW06, but PFOA slightly increased at the 7.3 meter level. In monitoring well number IW_NN_GW07, PFOS and PFOA fluctuated with water depth. PFUnA was observed in the upper layer, while PFHpA was observed in the lower layer, and the rest of the PFASs were not measured. PFHpA, PFDA, PFUnA, PFHxS and PFOS appeared to decrease in monitoring well number IW_NN_GW08, while PFOA and PFNA trends were unnoticeable. PFHpA, PFOA, and PFNA were slightly reduced in monitoring well number IW_NN_GW09, and no trend of any kind could be observed. In case of the monitoring well number IW_NN_GW10 PFASs concentrations were unstable, and there was no observed trend.

Table 3.5 PFASs concentration in groundwater around Nong Nae IWDSs in different depths

Well	Well screen length (m)	Depth (m)	Concentration (ng/L)							
			PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS	Total
IW_NN_GW05	4	-1.5	1.73	10.44	0.86	0.64	0.39	0.30	3.66	18.00
		-3.0	1.41	5.36	0.64	0.45	0.36	0.18	3.06	11.46
		-4.6	1.27	3.61	0.50	0.32	0.27	<LOQ	2.38	8.35
		-6.0	1.12	3.21	0.43	0.32	0.32	<LOQ	11.89	17.28
		-7.6	1.03	3.76	0.41	0.26	0.30	0.08	2.23	8.06
IW_NN_GW06	4	-1.5	<LOQ	3.41	<LOQ	ND	<LOQ	<LOQ	1.35	4.75
		-2.3	<LOQ	0.89	<LOQ	ND	<LOQ	ND	1.16	2.0.6
		-4.4	<LOQ	0.90	<LOQ	ND	0.27	ND	0.94	2.11
		-5.9	<LOQ	0.81	<LOQ	ND	<LOQ	ND	0.86	1.67
		-7.3	<LOQ	1.59	<LOQ	ND	<LOQ	ND	0.83	2.42
IW_NN_GW07		-2.0	<LOQ	2.62	<LOQ	ND	0.31	<LOQ	1.00	3.94
	4	-4.0	<LOQ	1.88	<LOQ	ND	0.26	<LOQ	0.79	2.94
		-6.0	<LOQ	0.70	<LOQ	ND	<LOQ	<LOQ	0.60	1.30
		-8.0	0.49	1.30	ND	ND	<LOQ	ND	0.56	2.35
		-10.0	<LOQ	5.60	ND	ND	<LOQ	ND	0.81	6.42
IW_NN_GW08	4	-2.5	0.56	4.06	0.47	0.37	0.38	0.09	1.37	7.30
		-5.0	0.51	2.04	0.36	<LOQ	ND	0.08	1.17	4.16
		-7.5	0.49	2.53	0.43	<LOQ	ND	<LOQ	1.04	4.49
		-10.0	<LOQ	3.97	0.43	<LOQ	<LOQ	<LOQ	0.91	5.30
IW_NN_GW09	4	-3.8	0.51	1.13	0.42	ND	0.26	<LOQ	0.54	2.86
		-7.6	<LOQ	0.80	<LOQ	ND	<LOQ	<LOQ	<LOQ	0.80
		-11.3	ND	0.72	<LOQ	<LOQ	0.30	0.07	0.64	1.73
IW_NN_GW010	4	-4.1	<LOQ	1.32	<LOQ	ND	<LOQ	<LOQ	0.79	2.11
		-8.3	<LOQ	6.09	<LOQ	ND	0.39	<LOQ	0.74	7.21
		-12.4	<LOQ	4.47	<LOQ	ND	0.27	<LOQ	1.48	6.22
		-16.6	<LOQ	6.77	<LOQ	ND	<LOQ	0.08	0.79	7.64

Note: LOQ=Limit of detection, ND=Not detected

Table 3.6 Comparison on PFASs concentration in groundwater from consumption wells and monitoring wells around Nong Nae IWDSs, Chachoengsao

Well type	Well	Average PFASs (ng/L)						
		PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS
Consumption	IW_NN_GW01	<LOQ	7.32	<LOQ	ND	ND	0.39	3.08
	IW_NN_GW02	<LOQ	2.21	<LOQ	ND	ND	0.98	1.89
	IW_NN_GW03	<LOQ	2.16	ND	ND	<LOQ	0.20	2.08
	IW_NN_GW04	1.98	2.26	ND	ND	ND	0.12	1.39
Monitoring	IW_NN_GW05	1.31	5.27	0.57	0.40	0.33	0.19	4.64
	IW_NN_GW06	<LOQ	1.52	<LOQ	ND	0.27	ND	1.03
	IW_NN_GW07	0.49	2.42	<LOQ	ND	0.29	<LOQ	0.75
	IW_NN_GW08	0.52	3.15	0.42	0.37	0.38	0.08	1.12
	IW_NN_GW09	0.51	0.89	0.42	ND	0.28	0.07	0.59
	IW_NN_GW10	<LOQ	4.66	<LOQ	ND	0.33	0.08	0.95

Note: LOQ=Limit of detection, ND=Not detected

In many studies related to contamination in groundwater, knowledge about vertical distribution of contaminants is valuable, but the investigations are hindered by the lack of data. In this study, the concentrations of PFASs fluctuated at different depths; therefore, the effect of vertical distribution could not be clearly observed. It could be because long well screening obscures the vertical distribution of contaminants (Sukop, 2000). Typically, a standard manufactured length of screen is usually 1.5 m.; but in those wells, 4 m. of well screens were installed. Another reason could be a groundwater inflow direction. Depending upon the well construction, water cannot flow into the well from the well side, therefore it may not much effect to the vertical distribution. By this result, it can be assumed that depth may not be a significant factor in vertical distribution of PFASs in groundwater. In contrast, different water layers could affect a vertical distribution of PFASs particularly PFOS and PFOA in surface water due to fresh water input and incomplete vertical mixing in surface water (Sakurai *et al.*, 2010). Furthermore, vertical distribution of PFASs in soil is suggested for further monitoring study.

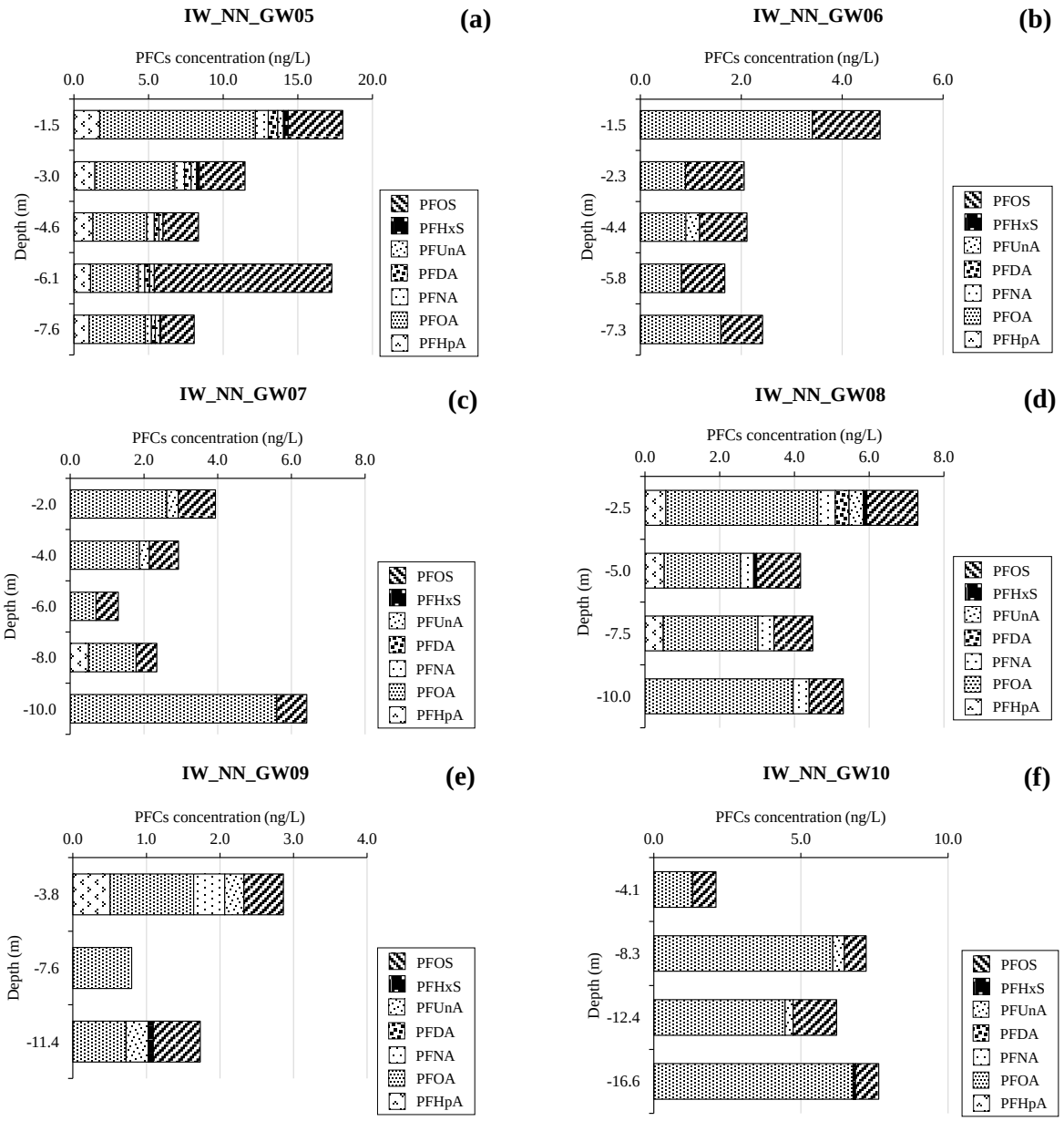


Figure 3.9 PFASs concentration and their distributions in groundwater around Nong Nae IWDSs with different depths: (a) IW_NN_GW05, (b) IW_NN_GW06, (c) IW_NN_GW07, (d) IW_NN_GW08, (e) IW_NN_GW09, and (f) IW_NN_GW10

3.4 Effect of season on occurrence of PFASs in groundwater in Chonburi

Seasonal difference of individual PFASs concentration in groundwater around Map Phai IWDS was considered by independent sample *t*-test using IBM® SPSS® Statistics 20. Mean concentration of each PFASs was separately analyzed, with results presented in Table 3.7. Significant seasonal variations were found for PFOA (p = 0.005) and PFUnA (p = 0.05) between dry season and wet season, while insignificant variation was observed in the rest of the PFASs. Although seasonal variation on PFASs concentration in groundwater is not widely reported, seasonal variation could be reported in surface water which can imply seasonal variation in groundwater PFASs concentration because surface water is directly connected to groundwater. Similar results, i.e. declining of PFOA concentration in the wet season, were noted by Boontanon *et al.* (2012), Zhu *et al.* (2015), and P. Wang *et al.* (2016). Among target compounds, PFOA was the most detected in groundwater both during dry season and wet season, and it might result from its widespread usage and its high water-solubility (US.EPA., 2014).

Table 3.7 Statistical analysis of seasonal variation of individual PFASs concentration in groundwater around Map Phai IWDS, Chonburi

Target PFASs	Dry season (n=12)		Wet season (n=12)		*t*-test	*p*-value
	$\overline{X}$	SD	$\overline{X}$	SD		
PFHpA	0.74	0.63	0.96	0.82	-0.713	0.483
PFOA	16.69	10.14	5.79	6.80	3.092	0.005*
PFNA	0.84	0.70	0.79	0.51	0.188	0.853
PFDA	0.30	0.40	0.29	0.43	0.095	0.925
PFUnA	0.40	0.36	0.16	0.20	2.073	0.050*
PFHxS	0.66	1.20	0.72	0.94	-0.147	0.885
PFOS	6.95	6.86	3.56	4.20	1.462	0.158

* $p \leq 0.05$

Figure 3.10 presents the comparison of PFASs concentrations in groundwater around Map Phai IWDS, Chonburi, in dry season (June 2016) and wet season (September 2016). It can be seen that all PFASs concentrations were plotted lower than the linear line 1:1, indicating that PFASs decreased in the wet season especially for PFOA. Lower PFOA concentrations in the wet season might be because this IWDS had not been used as a disposal site for a few years since it was complained about by villagers. In addition, accumulation of industrial waste was strictly prohibited. Other reasons might be due to adsorption to the aquifer solids and its dilution in the aquifer caused by dissipation over time and a wide area, which is strongly supported by Xiao *et al.* (2015).

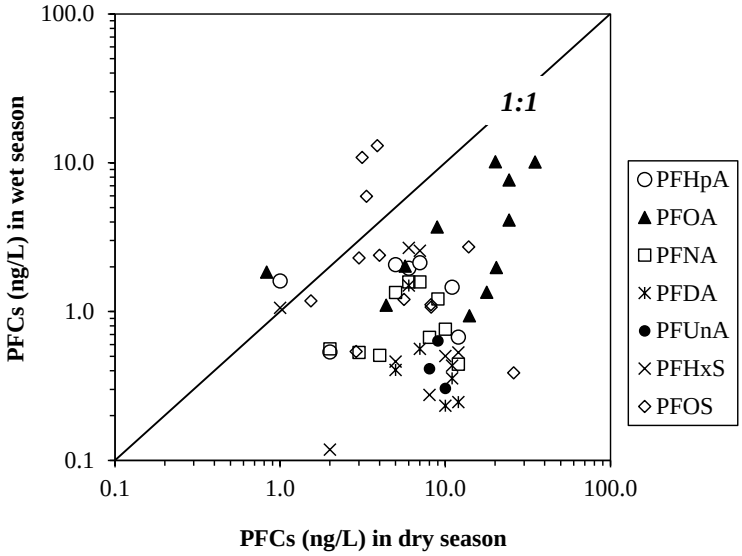


Figure 3.10 Comparison of PFASs concentrations in groundwater around Map Phai IWDS, Chonburi, in dry season and wet season

3.5 Comparison of PFASs contamination in this study to other countries and international guidelines

3.5.1 Comparison of PFASs contaminations in this study and other studies

Among PFASs compounds, PFOA and PFOS were the most abundant in this study and also in other countries. Figure 3.11 shows the average of PFOA and PFOS concentrations in groundwater around MWDSs and IWDSs compared to those that were found in other countries. PFOA and PFOS detected in this study were relatively low compared to those reported in other countries. Extremely high PFOA and PFOS levels in groundwater were detected around a fire-training area in Northern Michigan, USA. The groundwater contained various PFASs concentrations in the μg range, even five years after fire-training had been conducted at that site (Moody *et al.*, 2003). A study in The Netherlands found that PFASs contamination in groundwater had originated from a former landfill, a military camp, and an urban area (Eschauzier *et al.*, 2013). Similar to those findings in The Netherlands, PFOA, PFOS and other PFASs were measured in high concentration at military airports in Stockholm, Sweden (Filipovic *et al.*, 2015). Surprisingly, a study in Tokyo, Japan reported that high PFASs concentration in groundwater was caused by pollution from street runoff and a leaking sewer pipe (Murakami *et al.*, 2009). Those studies indicate that urbanization and industrialization affect the amount of PFASs contamination.

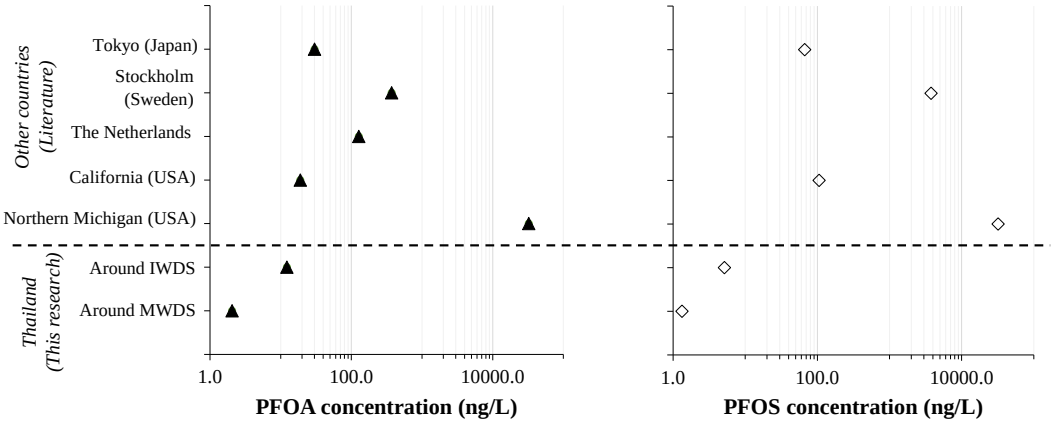


Figure 3.11 Comparison of PFOA and PFOS contaminations in groundwater between this research and previous researches

3.5.2 Comparison of PFASs contamination in this study and PFASs international guidelines

Since 2000, when PFASs environmental impacts were of highest concern, 3M Company and other PFASs related companies had decided to phase out of their production. Later, the US.EPA and eight major fluoropolymer industries (Arkema, Asahi, BASF Corporation, Clariant, Daikin, DuPont, 3M/Dyneon, and Solvay Solexis) collaborated to reduce facility emissions and PFOA product content. PFASs, particularly PFOS, have been of greater concern since they were listed as persistent organic pollutants (POPs) in the Stockholm Convention in 2009. After that, levels of PFASs in drinking water has been recommended by several agencies. Figure 3.12 presents a comparison of PFASs concentrations in groundwater from this study and international guidelines for PFOA, PFNA, PFHXs and PFOS, respectively, in drinking water.

As seen in Figure 3.12, PFASs guidelines were established in developed countries such as the United States, Germany, and Australia due to a great concern that resulted from former production and usage of large amounts of PFASs. In Thailand, there is no specific regulation or guideline for PFASs in drinking water, and it might be because the amount of PFASs production or importation of PFASs has not been evidently clear. Furthermore, PFASs contamination in the environment (e.g. water, groundwater, soil and air) in Thailand has not been widely studied.

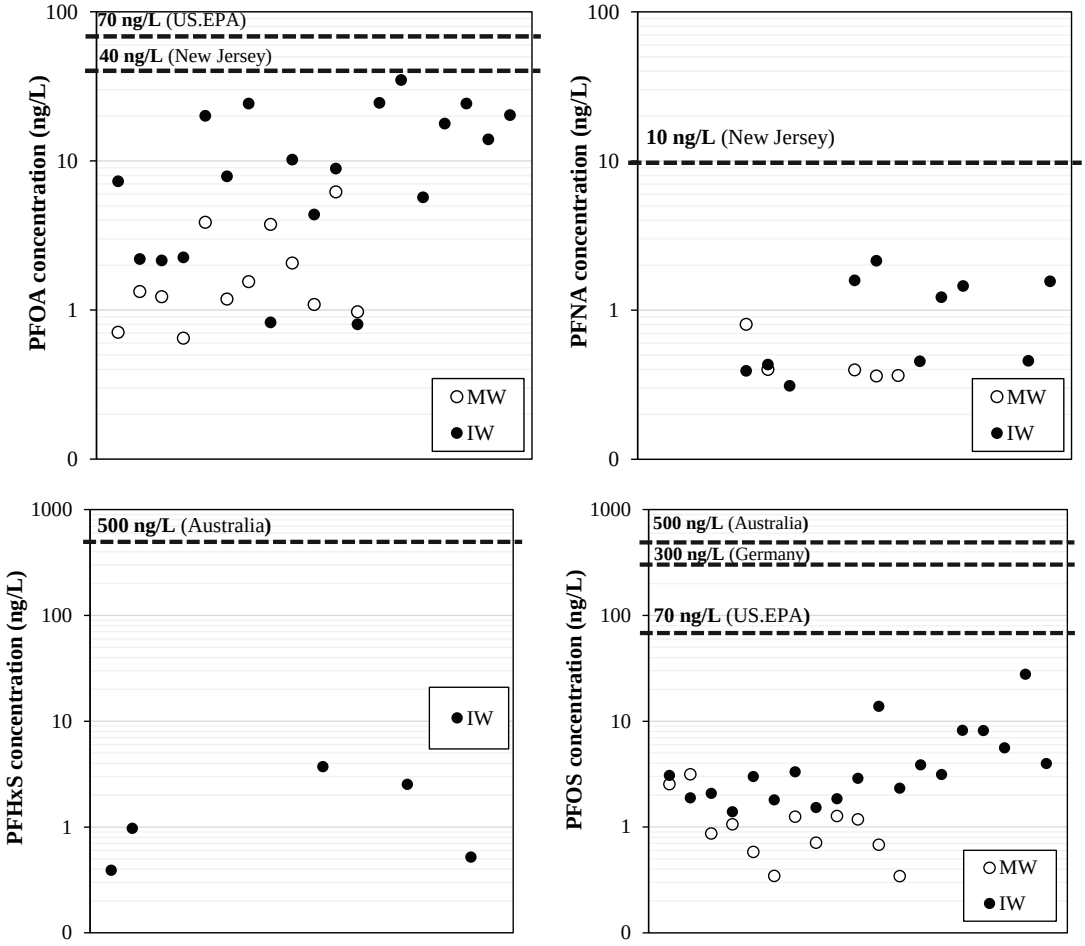


Figure 3.12 Comparison of PFASs concentration in groundwater and international guidelines

3.6 Health risk assessment of drinking groundwater

Ever since PFASs became new emerging chemicals, several countries particularly developed countries have established standard criteria to promote an acceptable level of PFASs that humans can be exposed to without any toxicity effects. Suggested PFASs levels in several countries are presented in Table 3.8.

Generally, humans can be exposed to chemical substances in water via several pathways: oral intake (e.g. drinking water, food, breast milk), dermal intake (e.g. showering, swimming), and inhalation (e.g. dust). Exposure to PFASs induces health effects related to immune modulation, reproductive function in woman and thyroid disease in the general public (Franko *et al*., 2012; Knox *et al*., 2011; Melzer *et al*., 2010), but evidence of PFASs-associated carcinogenesis is still inadequate.

Table 3.8 International guidelines for PFASs

Countries/State/ Agency	Type	Suggested levels (µg/L)				Source
		PFHxS	PFOS	PFOA	PFNA	
United State US.EPA.	Drinking water		0.07 (individual or combined)			(US.EPA., 2016a, 2016b)
New Jersey Department of Environmental	Groundwater			0.04	0.01	(NJDEP, 2015)
Australia Australian Health Protection Principal	Drinking water	0.5	0.5			(enHealth, 2016)
United Kingdom (UK) Drinking Water	Drinking water		1	5		(DWI, 2009)
Germany Ministry of Health			0.3	0.3		(DWC, 2006)

In this study, both non-carcinogen and carcinogen risk were evaluated. Since there are no acceptable limits for non-carcinogen and carcinogen risk levels for target PFASs (PFOS, PFOA, and PFNA) in Thailand, the input parameters for assessment in this study were derived from the US.EPA model and the New Jersey Department of Environmental Protection. The input parameters are presented in Table 3.9.

Table 3.9 The input parameters for health risk assessment

Parameter	Description	Value	Unit	Ref.
RfD for PFOA	Reference dose	0.00002	mg/kg/day	(US.EPA., 2016a)
RfD for PFOS	Reference dose	0.00003	mg/kg/day	(US.EPA., 2016b)
RfD for PFNA	Reference dose	0.00000074	mg/kg/day	(NJDEP, 2015)
IR_{oral}	Intake rate	1.043	L/day	(US.EPA., 2011)
EF	Exposure frequency	365	days/year	
ED	Exposure duration	70	years	(US.EPA., 2011)
BW	Body weight	70	kg	(US.EPA., 2011)
AT	Average time	365×ED	days	
CSF for PFOA	Cancer slope factor	0.07	mg/kg/day	(US.EPA., 2016a)

Table 3.10 Estimation of non-cancer risk and cancer risk of PFOA, PFNA, and PFOS from drinking groundwater

Sample	CDI (mg/kg/day)			Non-carcinogenic risk						Carcinogenic risk		
				HQ			ΣHQ	Concern		Cancer risk[a]	Concern	
	PFOA	PFNA	PFOS	PFOA	PFNA	PFOS		Yes	No		Yes	No
MW_BC01	1.06E-08	-	3.78E-08	0.0005	-	0.0019	0.0024		/	7.40E-10		/
MW_BC02	1.98E-08	-	4.69E-08	0.001	-	0.0023	0.0033		/	1.39E-09		/
MW_BC03	1.83E-08	-	1.29E-08	0.0009	-	0.0006	0.0016		/	1.28E-09		/
MW_BC04	9.68E-09	-	1.58E-08	0.0005	-	0.0008	0.0013		/	6.77E-10		/
MW_SN01	5.80E-08	1.20E-08	8.66E-09	0.0029	0.0162	0.0004	0.0195		/	4.06E-09		/
MW_SN02	1.77E-08	5.95E-09	-	0.0009	0.008	-	0.0089		/	1.24E-09		/
MW_SN03	2.31E-08	-	1.86E-08	0.0012	-	0.0009	0.0021		/	1.62E-09		/
MW_SN04	5.60E-08	-	1.06E-08	0.0028	-	0.0005	0.0033		/	3.92E-09		/
MW_SN05	3.08E-08	-	1.90E-08	0.0015	-	0.0009	0.0025		/	2.16E-09		/
MW_SN06	1.63E-08	5.90E-09	1.76E-08	0.0008	0.008	0.0009	0.0097		/	1.14E-09		/
MW_SN07	9.26E-08	5.38E-09	1.01E-08	0.0046	0.0073	0.0005	0.0124		/	6.48E-09		/
MW_SN08	1.45E-08	5.42E-09	-	0.0007	0.0073	-	0.0081		/	1.02E-09		/
IW_CB01	3.00E-07	5.82E-09	4.47E-08	0.015	0.0079	0.0022	0.0251		/	2.10E-08		/
IW_CB02	1.18E-07	6.42E-09	2.70E-08	0.0059	0.0087	0.0013	0.0159		/	8.24E-09		/
IW_CB03	3.62E-07	4.63E-09	4.96E-08	0.0181	0.0063	0.0025	0.0268		/	2.54E-08		/
IW_CB04	1.23E-08	-	2.29E-08	0.0006	-	0.0011	0.0018		/	8.63E-10		/
IW_CB05	1.52E-07	-	2.76E-08	0.0076	-	0.0014	0.009		/	1.07E-08		/
IW_CB06	6.52E-08	2.36E-08	4.29E-08	0.0033	0.0319	0.0021	0.0373		/	4.57E-09		/
IW_CB07	1.33E-07	3.19E-08	2.06E-07	0.0066	0.0431	0.0103	0.06		/	9.29E-09		/
IW_CB08	1.20E-08	-	3.47E-08	0.0006	-	0.0017	0.0023		/	8.38E-10		/
IW_CB09	3.66E-07	6.75E-09	5.77E-08	0.0183	0.0091	0.0029	0.0303		/	2.56E-08		/
IW_CB10	5.21E-07	1.82E-08	4.67E-08	0.026	0.0245	0.0023	0.0529		/	3.65E-08		/
IW_CB11	8.50E-08	2.16E-08	1.22E-07	0.0043	0.0292	0.0061	0.0396		/	5.95E-09		/
IW_CB12	2.66E-07	-	1.22E-07	0.0133	-	0.0061	0.0194		/	1.86E-08		/
IW_CB13	3.63E-07	-	8.36E-08	0.0181	-	0.0042	0.0223		/	2.54E-08		/
IW_CB14	2.08E-07	6.80E-09	3.86E-07	0.0104	0.0092	0.0193	0.0389		/	1.46E-08		/
IW_CB15	3.04E-07	2.32E-08	5.94E-08	0.0152	0.0313	0.003	0.0495		/	2.12E-08		/

[a] Cancer risk $<10^{-6}$ is acceptable

Although, those PFCs levels did not exceed the health advisory levels for drinking purpose (70 ng/L for individual PFOA and PFOS or combined) (US.EPA., 2016a, 2016b), the long term consumption of the groundwater without any water treatment may cause unexpected

adverse effects. Therefore, evaluation of health risk is necessary to ensure whether consumption of this water is safe.

As mentioned above, health risk assessment was estimated only for exposure by drinking, although the water has been being consumed for showering; but in the general population, dermal absorption of PFCs is extremely slow and not a significant exposure pathway (NCEH, 2017; US.EPA., 2016c). Table 3.10 shows the estimation of non-cancer risk and cancer risk of PFOA, PFNA, and PFOS from drinking groundwater. The non-carcinogenic risk was represented by the HQs which were calculated by the total daily intake and RfDs. There is no instance in which the combined HQ for non-cancer risk of those samples exceeded one, which means the risks were all acceptable. It could be concluded that they were observed as having less potential for non-carcinogenic toxicity.

In terms of the carcinogenic risk, it has only been focused on PFOA because of limited CSF data. The estimated carcinogenic risks of all samples were lower than 10^{-6} (benchmark level), so the risks were all acceptable; suggesting that drinking the groundwater might not induce an unexpected cancer risk, nor would it increase the probability of developing cancer during a person's lifetime.

Objective 3: Control of PFOS and PFOA in groundwater by Immobilization of Titanium Dioxide and Graphene Oxide Nanoparticles in Polyvinyl Alcohol

3.7 The relationship of pH value and PFOS and PFOA removal efficiency

According to the methodology in section 2.5.1, Figure 3.13 displays the relation between PFOS and PFOA removal efficiency (%) and pH value, which portioned to 3, 7, and 10 for 100 ppb of the initial concentration. As seen in the figure, the decrease of PFOS and PFOA degradation efficiency were apparently affected when it became to be an alkalinity. It tended to ionize to form perfluorocarboxylic anion and H^+ in water when the pH of solution was greater than the point of zero charge (pzc) of catalyst (pzc of TiO_2/GO has been reported about 3.2) (Cruz *et al*., 2017). Therefore, pH 3 seemed to be the best enhancement of the PFOS and PFOA removal efficiency at 94.15% and 90.16%, respectively.

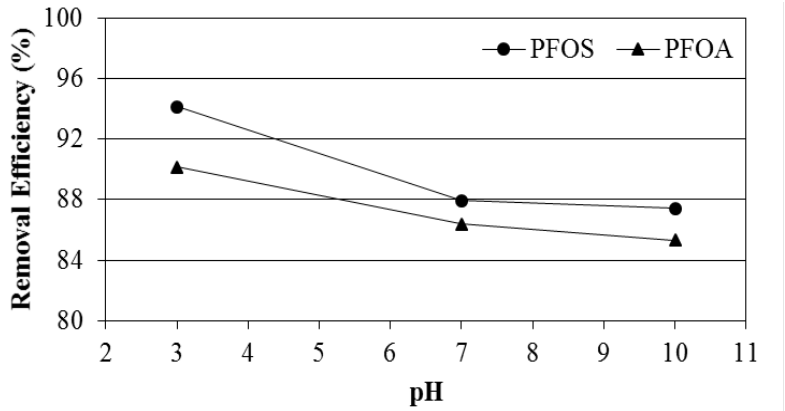


Figure 3.13 The PFOS and PFOA removal efficiency (%) and pH value

3.8 The concentration of graphene oxide (GO)

The influences of different mass ratios of GO, which ranged to 0, 10, 15, 20, 25, and 100 wt% according to GO and TiO_2, including PVA alone, and experimental time on the photocatalytic performances for PFOS and PFOA are shown in Figure 3.14 and Figure 3.15, respectively, which present a plot of C/C_0 versus contact time (min).

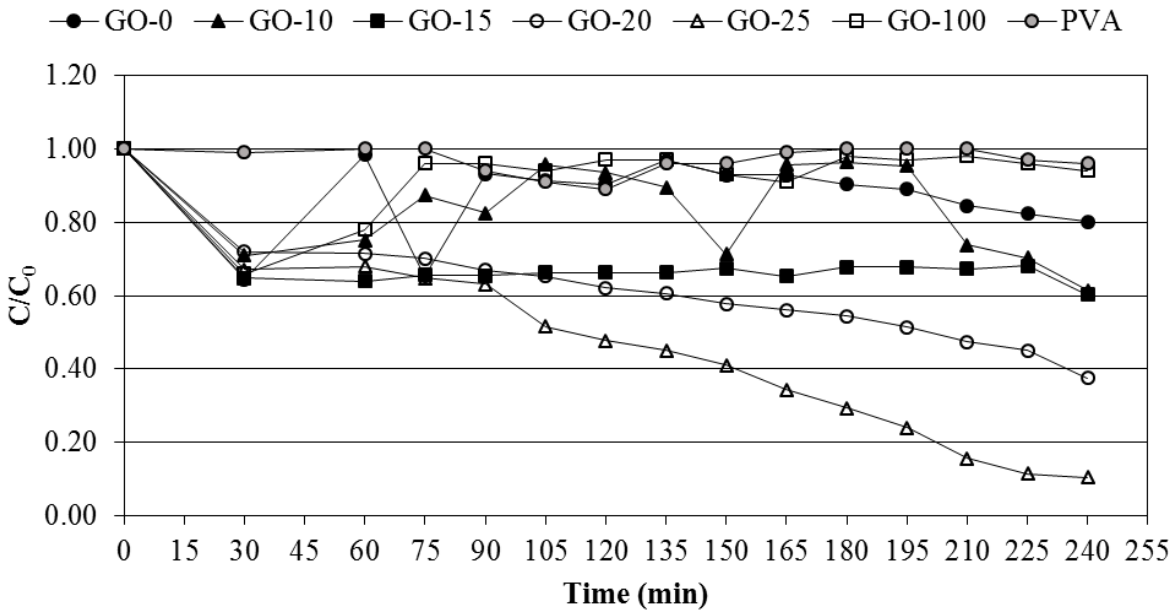


Figure 3.14 The PFOS removal efficiency (%) and time (min) in different GO contents.

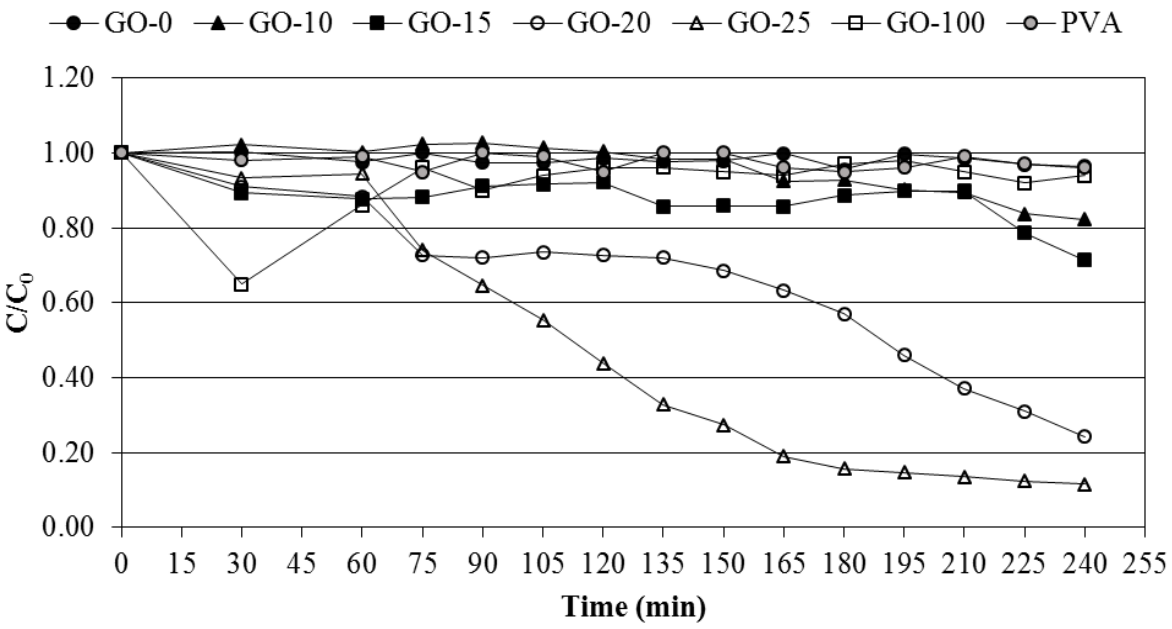


Figure 3.15 The PFOA removal efficiency (%) and time (min) in different GO contents

As can be seen from Figure 3.14 and Figure 3.15, the absorption of TiO_2/GO catalyst continuously decreased between the times at 0 – 30 min and then turned to be increasing until stability when irradiation began after the time at 60 min. The concentration of PFOS and PFOA that was absorbed by GO-0 and GO-10, is existed much more than those that absorbed by GO-15, GO-20, GO-25, and GO-100 due to the density distribution of GO on the surface of PVA was decreasing (Zhang *et al*., 2018). At the time, PVA alone present no photocatalytic activity for PFOS and PFOA degradation. However, a remarkable result was the enhancement of photocatalytic degradation of PFOS and PFOA with the increasing mass ratio of GO and photocatalytic time.

3.8 The dispersion of nanoparticles on PVA matrix

3.8.1 Morphology of TiO_2 and GO nanoparticles.

Figure 3.16 exhibits TEM images from the heated TiO_2/GO/PVA nanofilm that prepared by sonicating method. The low-magnification TEM images of TiO_2 and GO are shown in Figure 3.16(a). and 3.16(b)., respectively. It is evident in Figure 3.16(c). that TiO_2 nanoparticles are interspersed over GO surface, which proves that TiO_2 interact with GO. The fact that the electrons are effectively transferred between TiO_2 and GO, which plays important role in sensing mechanism. As seen in Figure 3.16(d). indicates the lattice fringe of d-spacing around 0.25 nm of TiO_2, referring to the crystallographic planes 101 of rutile (Sun *et al*., 2018).

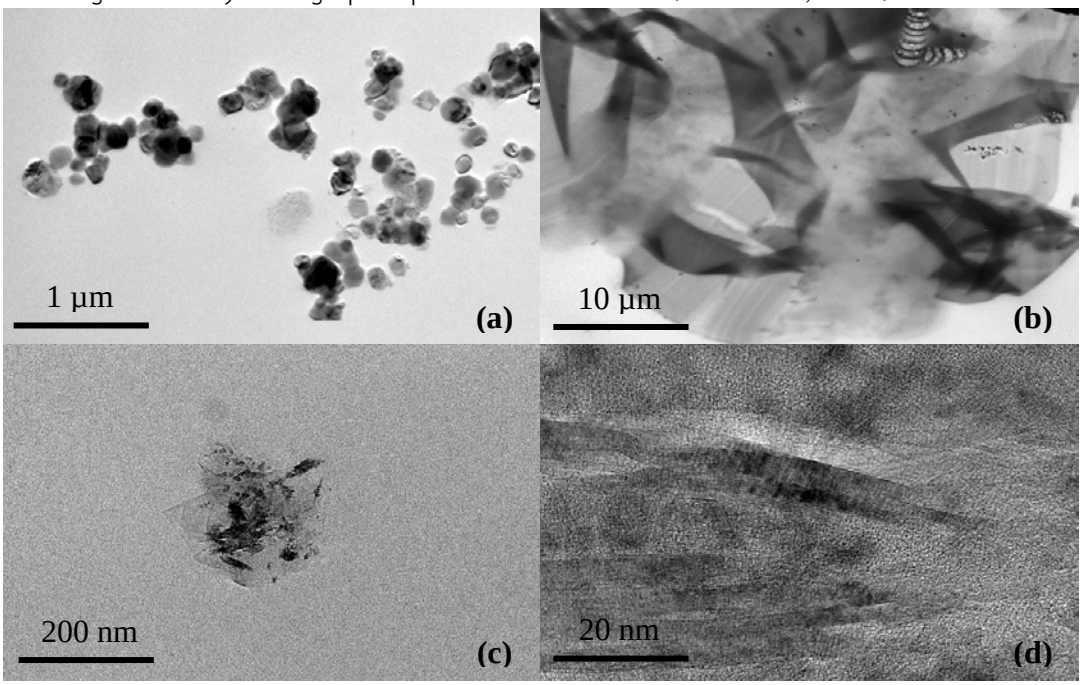


Figure 3.16 The low-magnification TEM images of (a) TiO_2, (b) GO, (c) the high-magnification TEM image of TiO_2/GO, and (d) the high-resolution HRTEM image of TiO_2/GO.

3.8.2 Photocatalytic degradation.

Figure 3.17 presents the influences of different dispersion methods of TiO_2/GO nanoparticles and contact time (min) on the photocatalytic reaction for PFOS and PFOA, which displays as a plot of C/C_0 versus time (min). The concentration of PFOS and PFOA from both magnetic stirring method and ultrasonic sonicating method slightly decreased after 60 min when irradiation. Even though the removal rates of PFOS and PFOA from two dispersion processes were not extremely different, the results of PFOS and PFOA concentration that investigated from sonicated TiO_2/GO/PVA nanofilms after 240 min were less than those results that evaluated from stirred nanofilms approximately 1.09 and 1.08 times comparing with the removal efficiency of PFOS and PFOA.

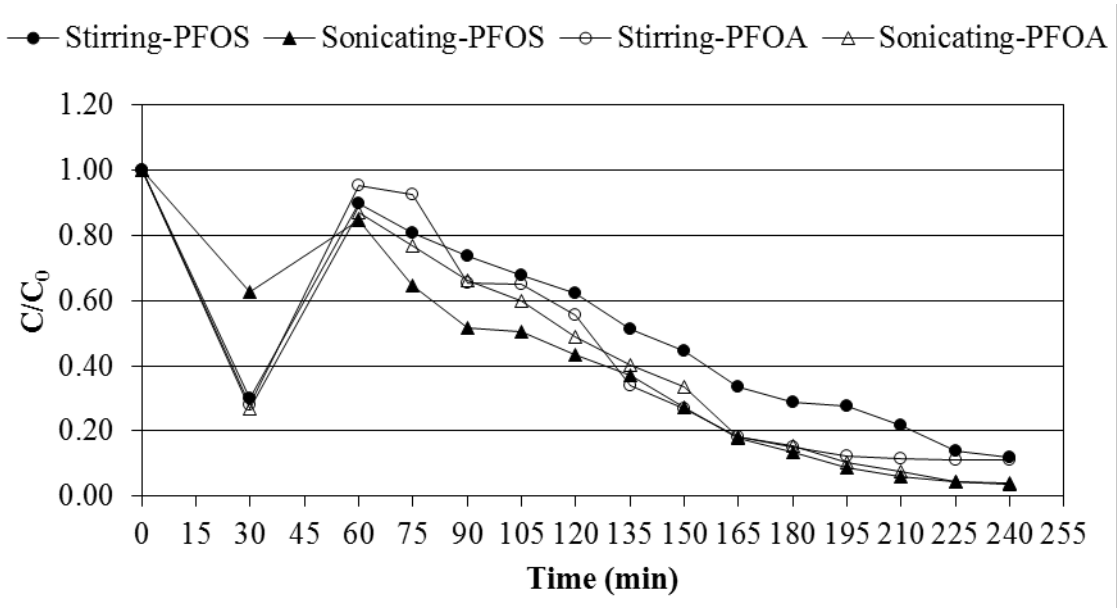


Figure 3.17 PFOS and PFOA removal efficiency and time (min) for different dispersion methods

3.9 The heat-treatment times

3.9.1 Chemical bonding immobilized TiO_2 and GO in PVA matrix

The structure characterization of TiO_2/GO/PVA nanocomposites was performed as FT-IR spectra by using Fourier Transform-Infrared (FT-IR) Spectrometer. The wavenumbers were determined in the spectral range of 600 – 4000 cm^{-1}. Figure 3.18. shows FT-IR spectra of unheated-nanofilm and heated-nanofilm at 120°C for various times of 1 h, 3 h, and 5 h, respectively. It displays as a plot of percent transmittance (%) versus wavenumber (cm^{-1}). As seen in Figure 3.18, the most characteristic of FT-IR spectra of GO correspond to the vibration of hydroxyl groups (C-OH) positioned around 3000 – 3600 cm^{-1}, a broad peak at 1725 cm^{-1} owning to the stretching vibration of carbonyl groups (C=O), the bonding of C-OH groups placed around 1331 – 1379 cm^{-1}, including two peaks of C-H stretching at 2924 and 2852 cm^{-1} (Cruz *et al*., 2017). In addition, the breathing vibrations at 1058, 1227, 1401, and 1630 cm^{-1} related to C-O bonding, epoxy groups (C-O-C), O-H bonding, and C=C bonding, respectively (Sun *et al*., 2018). The absorption band of bare

TiO_2 indicates a common characteristic band, typical of the TiO_2 substance corresponding to Ti-O-Ti bonds around 800 - 950 cm^{-1}. Moreover, the FT-IR spectra of PVA associated to C-C stretching at 1143 cm^{-1}. For heated TiO_2/GO/PVA nanofilm, a new peak was discovered at 1237 cm^{-1}, which is defined as the vibration of Ti-O-C bonds. Meanwhile, the other new peaks at 797 and 843 cm^{-1} is assigned to hypsochromic shift of C-C and O-C-C, respectively, owning to the change in the chemical bonding caused by the formation of Ti-O-C bonds (Lei *et al*., 2012).

Figure 3.18 FT-IR spectra of nanofilms that heated in different times (h) of H-0 (unheated nanofilm), H-1 (1 h), H-3 (3 h), and H-5 (5 h)

3.9.2 Photocatalytic degradation

Figure 3.19 indicates the influences of different times for heat-treatment process of TiO_2/GO/PVA nanofilms and contact time (min) on the photocatalytic reaction for PFOS and PFOA, respectively. For both figures display as a plot of C/C_0 versus time (min). The removal efficiency of PFOS and PFOA from 1 h heat-nanofilms were discovered around 85 – 87%, which could imply that really high, not the optimal time for heated-treat TiO_2/GO/PVA nanofilm. It implicated to the loss of

TiO_2/GO catalysts due to the absence of interaction between TiO_2 and GO nanoparticles and PVA (Lei *et al*., 2012). In the same way, 5 h heat-nanofilms displayed the result of PFOS and PFOA degradation efficiency, which is significantly reduced to 85 – 86%, still not the suitable time for heated-treat TiO_2/GO/PVA nanofilm because the absorption capacity of TiO_2/GO/PVA photocatalyst would diminish at long-heated-treat time and the photocatalytic reaction of PFOS and PFOA on nanofilm surface gradually decreased then removal efficiency weakened correspondingly (Wu *et al*., 2017). gradually decreased then removal efficiency weakened correspondingly (Wu *et al*., 2017). Nanofilms that heated for 3 h evidenced to be the best result for the heat-treatment time showed PFOS and PFOA removal efficiency about 95.99 and 96.86%, respectively.

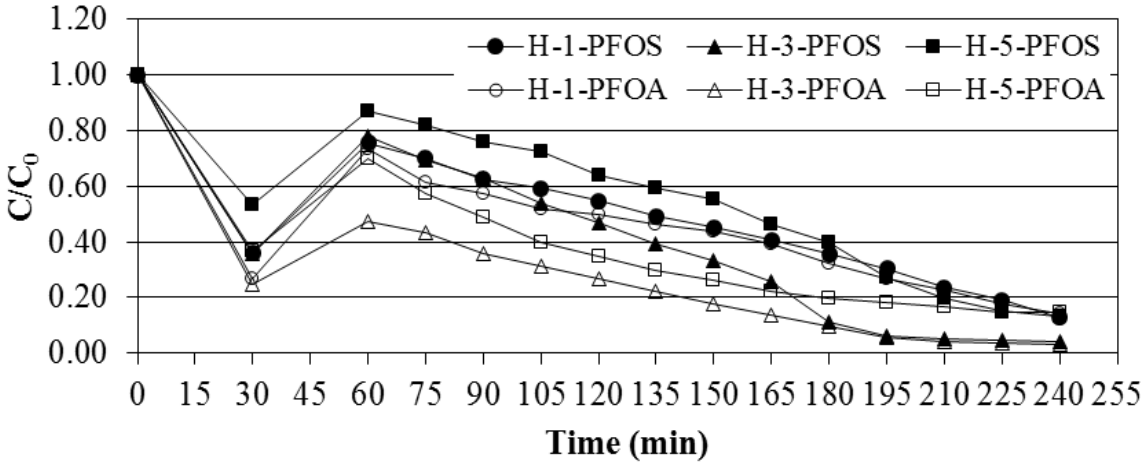
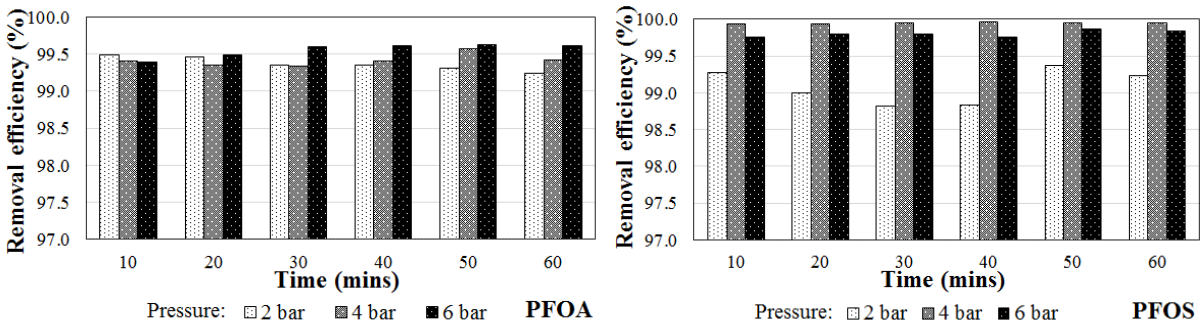


Figure 3.19 PFOS and PFOA removal efficiency and time (min) for different heat-treatment times

Objective 4-6: Control of PFOS and PFOA in groundwater by Nanofiltration and Photocatalysis

3.10 Membrane operation with nanofiltration membrane

3.10.1 PFOS and PFOA removal efficiencies by pressures variation



(a) (b)

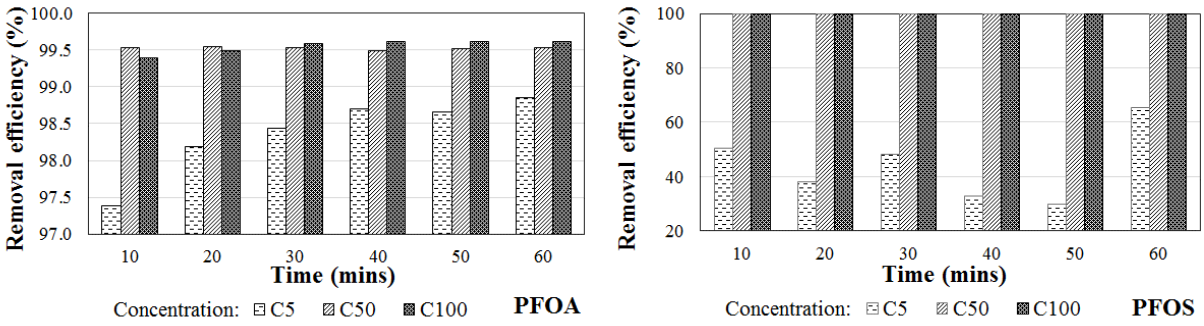
Figure 3.20 The removal efficiencies of (a) PFOA and (b) PFOS in different pressures

For membrane operation condition of the varied pressure experiment, PFOA concentration was controlled at 100 µg/L and pressures were controlled at 2, 4, and 6 bar,

respectively. Figure 3.20 (a) presents that PFOA removal efficiencies of pressure 2, 4, and 6 bar were slightly different. PFOA removal efficiencies were 99.49 - 99.24 %, 99.40 - 99.42 %, and 99.39 - 99.62 %, respectively, at 10 to 60 minutes of experiment. Figure 3.20 (b) shows that the PFOS removal efficiencies of pressures 2, 4, and 6 bar were 98.82 – 99.37 %, 99.94 - 99.96 %, and 99.75 – 99.87 %, respectively. In the previous study, the higher applied pressure affected the removal efficiency of PFOS in wastewater, which was highly improved at 13.79 bar (200 psi) applied pressure (Tang *et al.*, 2007). The results from this study also found that at higher applied pressure, the removal efficiency got higher than at lower applied pressure. However, it was seen that the removal efficiency of every varied pressure condition was over 98 % during the experiment. Thus, this NF membrane could see the trend of higher pressure providing better removal efficiency but was not so significantly different.

3.10.2 PFOS and PFOA removal efficiencies by concentrations variation

The pressure that was applied in these different concentrations conditions was obtained from the pressure variation experiments, in which the highest permeate flow rate with the lowest concentration was selected. The condition of this experiment, pressure at 6 bar, was fixed for 5, 50, and 100 µg/L concentration operation as shown in Figure 3.21 (a) shows that the PFOA removal efficiencies of 5, 50, and 100 µg/L were 97.39 – 98.85 %, 99.51 - 99.54% and 99.39 – 99.62 % respectively.



(a) (b)

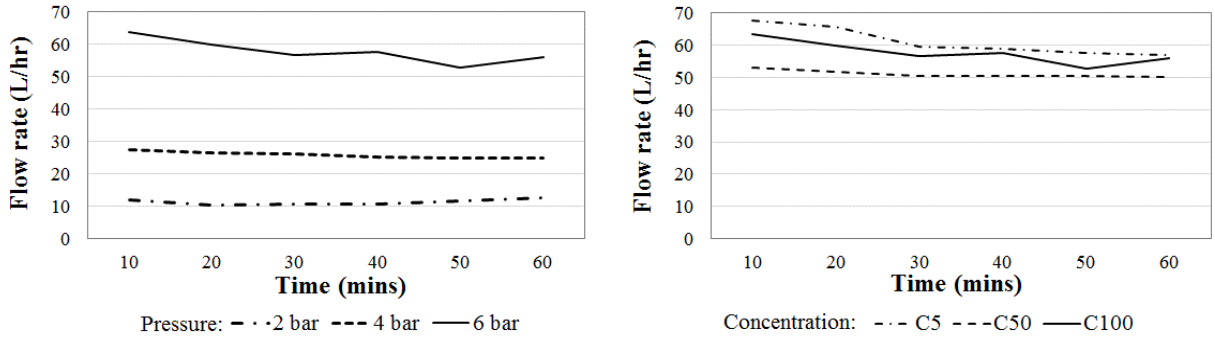
Figure 3.21 The removal efficiencies of (a) PFOA and (b) PFOS in different concentrations

For the PFOS removal efficiencies are shown in Figure 3.21 (b); the removal efficiency of 5, 50, and 100 µg/L were 29.92 – 65.22 %, 99.66 – 99.94 %, and 99.75 – 99.87 %, respectively. For PFOA, at low concentration of 5 µg/L, the removal efficiency was lower than those of 50 and 100 µg/L, but the removal efficiency of PFOS at 50 µg/L was slightly higher than 100 µg/L of PFOS. Nevertheless, from the results, the NF membrane could provide higher removal efficiency when applied with higher concentration. To support the result, a prior study reported that the rejection increased at higher concentration (Tang *et al.*, 2006). When comparing the removal efficiency with the influent concentrations, it was found that at high concentration, the decreasing rate of the influent concentration was much higher than at low concentration. Furthermore, when the initial

concentration increased, the removal efficiency was not significantly different because the maximum removal efficiency of the membrane was reached.

3.10.3 The flow rate of permeate in different pressures and concentrations

As shown in Figure 3.22 (b), the flow rate of permeate from 10 minutes to 60 minutes of the spiked deionized samples with concentration of 5, 50, and 100 µg/L decreased at 15.80 %, 5.31 %, and 12.11 %, respectively, indicating that the flow rates decreased when the time of experiments were increased. For the flow rate of the different pressure experiment, shown in Figure 3.22 (a), lower pressure provided lower flow rate. During the time of operation, the flow rate was lower due to clogging that occurred. Similar to the previous study, the flux decline is probably associated with PFOS accumulation on the membrane surface (Tang et al., 2006). At low pressure, the flow rate decreased slightly, unlike in the high-pressure operation where the flow rate was obviously decreased because substances flowing through the membrane in big volume made the performance of the membrane decline faster.



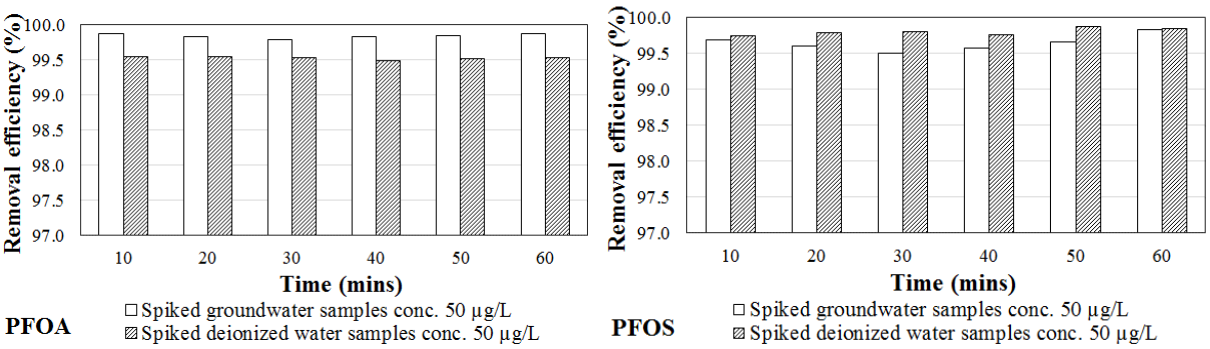
(a) (b)

Figure 3.22. (a) The flow rate of permeate in different pressures, (b) The flow rate of permeate in different concentrations

3.10.4 Comparison of removal efficiency and flow rate between spiked groundwater and spiked deionized water samples

The groundwater sample was collected from a groundwater well in Kampaeng Saen district in Nakhon Pathom Province; this well is in an inhabited zone near a landfill and plantation. The average PFOA and PFOS concentrations in the groundwater were 1.20 and 2.46 ng/L, respectively.

To compare the removal efficiency between spiked deionized water samples and spiked groundwater samples by NF membrane, the operation conditions were controlled similarly. The highest removal efficiency at the lowest concentration of PFOA and PFOS from the synthetic sample was chosen because the removal efficiency of PFOA and PFOS at 50 µg/L was not much different from 100 µg/L at 6 bar pressure. Next, the synthetic and groundwater samples were spiked with 50 µg/L of PFOA and PFOS.



(a) (b)

Figure 3.23 The PFOA (a) and PFOS (b) removal efficiency by comparing between spiked groundwater samples at concentration of 50 µg/L and spiked deionized water samples at concentration 50 µg/L

The spiked groundwater removal efficiency was not much different from the spiked deionized water under the same condition, by 99.78 - 99.87% compared to 99.49 - 99.54%, respectively for PFOA, as shown in Figure 3.23 (a). For PFOS, under the same condition the spiked groundwater removal efficiency was not much different from the spiked deionized water, by 99.50 - 99.82% compared to 99.66 - 99.94%, respectively, as shown in Figure 3.23 (b). According to the results of the spiked groundwater and deionized water samples at concentration 50 µg/L, the removal efficiency of both PFOS and PFOA were above 99% due to the average salt rejection of the nanofiltration membrane being high, up to 98.5%.

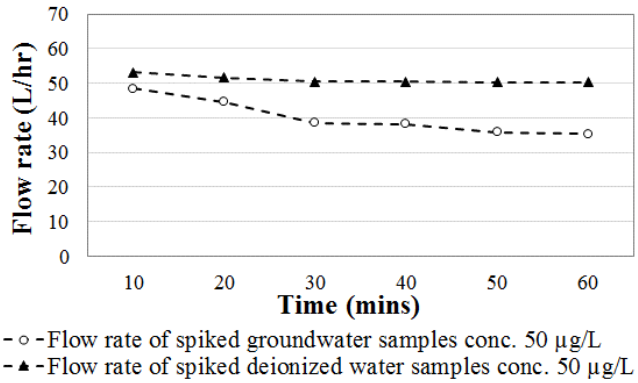


Figure 3.24 The flow rate of permeate by comparing between spiked groundwater samples at a concentration of 50 µg/L and spiked deionized water samples at a concentration of 50 µg/L

As shown in Figure 3.24, it was found that the flow rate decreased 32.80 % for PFOA 50 µg/L spiked groundwater, while the flow rate of PFOA 50 µg/L spiked deionized water only decreased 5.31%, indicating that the membrane performance most likely decreased due to the total dissolved solids (TDS) in the groundwater (1,400 µS/cm as shown in Table 2) being more than in the spiked deionized water (55 µS/cm). Normally, groundwater has a combination of dissolved minerals and solvent from the rocks which it is in contact with (USGS, 2013). Thus, TDS is also an important factor because the mineral content in groundwater is typically high. In the

previous study at a longer duration, the PFOS rejection improvement might be due to PFOS molecules entrapped in the polyamide layer. While the further passage of both water and PFOS molecules will be hindered by some entrapment to cause a flux decline (Tang *et al.*, 2007), the mineral content in groundwater could be accumulated and hinder the water causing the membrane performance to decrease. Hence, it could be said that the different matrix of water samples affected the performance of the NF membrane for PFOA removal.

3.10.5 The effect of temperature and pH

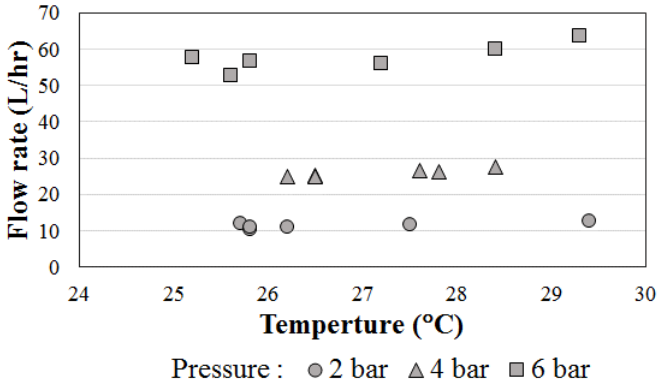


Figure 3.25 The relation of permeate flow rate and temperature at different pressures

In the varied pressure membrane experiments, the flow rate of permeate was measured every 10 minutes and temperature was measured and controlled under 45°C as the recommended operating temperature of the membrane. In Figure 3.25, the results show that the temperature is involved with the change of permeate flow rate in all different pressure conditions (2, 4, and 6 bar). When the temperature increased, the flow rate also slightly increased. Similar to the case of the NF membrane, when the temperature increases, the permeate flux will increase (The Dow Chemical Company, 2016). However, the change of temperature in this experiment was varied in the range between 25 and 30 °C, which did not significantly affect the analysis of the other results.

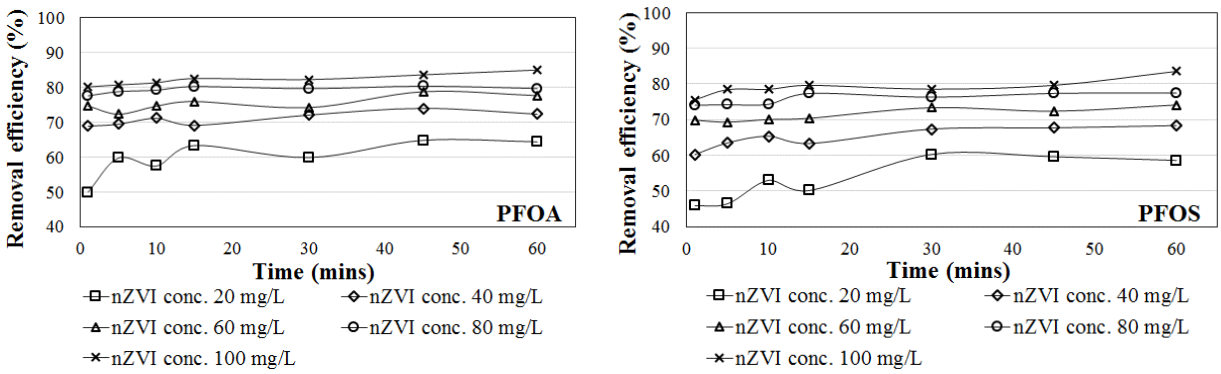
In the experiment, pH was measured from influent and effluent of all spiked deionized water and spiked groundwater samples every 10 minutes for an hour. The results show that the ranges of pH for the synthetic samples were 6.49 - 10.02 and 8.5 - 9.1 and for the real groundwater samples were 7.72 - 8.0 and 5.5 - 6.0 for influent and permeate, respectively. As a result, PFOA removal efficiencies in all synthetic samples and real groundwater samples were in the range of 97.39 – 99.62 % and 99.78 - 99.87% respectively; compared with the slight variation of pH, it was found that the influence of pH was not so significant when applied with groundwater. Nonetheless, a previous study with deionized water to understand the use of NF membranes for water recycling and the results showed that the rejection of Perfluorooctane Sulfonamide (FOSA, one of the PFASs) increased from 70% at pH = 2.8 to >99% at pH = 10. Decreasing the pH to less than 3 decreases rejection significantly (Steinle-Darling and Reinhard, 2008). Furthermore, the

results of a recent study revealed that the influence of hydrophobic acid organic matter (HpoA) on estrone rejection by the NF membrane would be affected by water chemistry, such as pH and ionic strength (IS), on rejection performance of the membrane process (Jin and Hu, 2015).

3.11 Photocatalysis

For the photocatalysis experiment, a spiked deionized water sample was used to find the conditions for use with the spiked groundwater sample, which are nZVI dosage and reaction time. After that, the removal efficiency of the spiked deionized water sample and the spiked groundwater sample were compared under the same conditions including photolysis (only UV light), only nZVI usage (without UV), and photocatalysis (both UV light and nZVI usage). All of these experiments were run in the batch test. The samples were collected at 0, 1, 5, 10, 15, 30, 45, and 60 minutes, respectively.

3.11.1 PFOS and PFOA removal efficiencies by nZVI concentration variation



(a) (b)

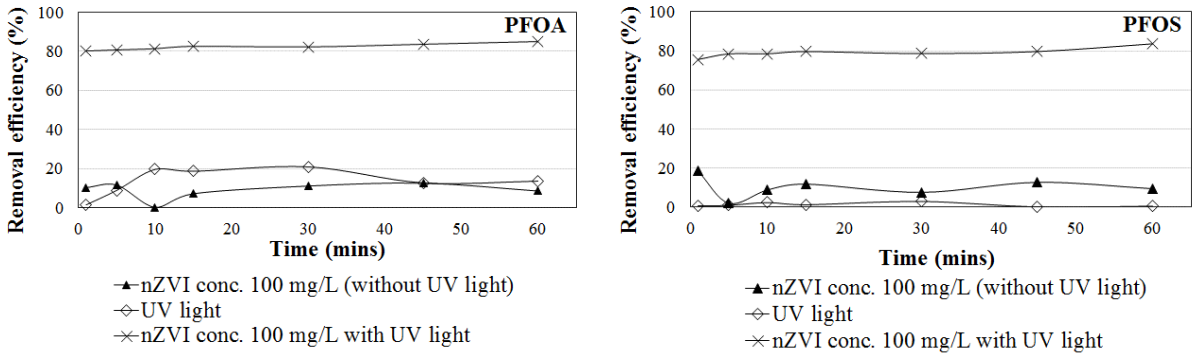
Figure 3.26 The PFOA (a) and PFOS (b) removal efficiencies in different nZVI concentrations

The spiked deionized water was used as samples for finding the nZVI dosage. The nZVI concentrations were varied at 20, 40, 60, 80, and 100 mg/L. The PFOA removal efficiencies of nZVI concentrations at 20, 40, 60, 80, and 100 mg/L are shown in Figure 3.26 (a), and were: 49.95 – 64.81%, 68.85 – 73.99%, 72.29 – 78.75%, 77.58 – 80.34%, and 80.14 – 84.98%, respectively. For the PFOS removal efficiencies of nZVI concentrations at 20, 40, 60, 80, and 100 mg/L as shown in Figure 3.26 (b), they were: 45.85 – 60.26%, 60.24 – 68.36%, 69.33 – 74.13%, 74.05 – 77.45%, and 75.57 – 83.56%, respectively. From these results, nZVI concentration at 100 mg/L was the highest removal efficiency when compared with 80, 60, 40, and 20 mg/L of nZVI. It could be said that when nZVI was used in high concentration, the removal efficiency was higher than when in low nZVI concentration for both PFOA and PFOS. According to a previous study it was revealed that when nZVI concentration modified with Mg-aminoclay (MgAc) is increased, the PFASs removal efficiencies will increase (Arvaniti *et al.*, 2014). In this study, though nZVI was not modified with other materials, increasing the concentration still affected the removal efficiency. For the effect

of reaction times of 1, 5, 10, 15, 30, 45, and 60 minutes on PFOA and PFOS removal efficiencies, Figure 4.9 exhibits a similar trend: that the nZVI reactions with the PFOA and PFOS were rapid at the 1-minute reaction time and higher but not that much higher until reaching the 60-minutes reaction time. Similar to a previous study, the PFOA removal efficiency by using nZVI was 92.77 ± 1.26% at 1 minute of reaction time, while the removal efficiency at the reaction time of 60 minutes was 96.24 ± 0.94%, which was almost identical (Khatikarn, 2009).

3.11.2 PFOS and PFOA removal efficiencies by nZVI with UV light

In this part, the spiked deionized water was used as samples for comparing the removal efficiency of PFOS and PFOA in conditions of photolysis which used only UV light, nanoparticles usage which used 100 mg/L of nZVI, and photocatalysis which used nZVI coupled with UV light.



(a) (b)

Figure 3.27 The PFOA (a) and PFOS (b) removal efficiencies in different conditions

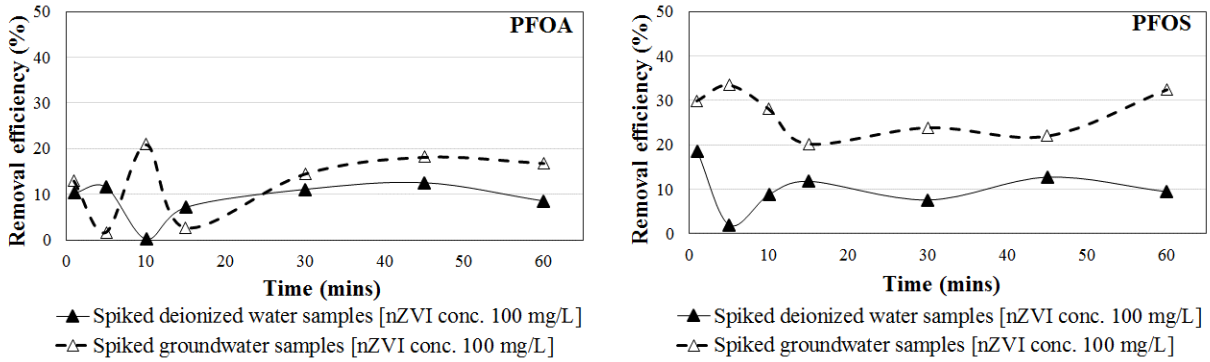
The PFOA removal efficiencies in nZVI usage, photolysis, and photocatalysis were 0.17 – 12.53%, 1.45 - 20.87% and 80.14 – 84.98%, respectively, as shown in Figure 3.27 (a). For PFOS, the removal efficiency in nZVI usage, photolysis, and photocatalysis were 1.98 – 18.57%, 0.09 – 2.30% and 75.57 – 83.56%, respectively (Figure 3.27 (b)). As the results illustrate, the removal efficiency of only nZVI and UV light usage could treat both PFOS and PFOA in quite low percentage. In contrast, with photocatalysis, which used both nZVI and UV light, the removal efficiency was high when compared with other methods. According to a previous study, ZnO nanoparticles at every concentration with exposure to sunlight had higher PFOA removal efficiency due to the photocatalysis activity of ZnO (Khatikarn, 2009). Thus, UV light enhances the nanoparticles to decompose PFOS and PFOA. The reaction times of all these three conditions including photolysis, nanoparticles usage, and photocatalysis were 1, 5, 10, 15, 30, 45, and 60 minutes; the removal efficiencies of PFOA and PFOS were slightly higher when the reaction times were increased.

3.11.3 Comparison of spiked groundwater and spiked deionized water samples

After the nZVI concentrations and the conditions for the experiment were selected by using spiked deionized water samples, the same conditions were used with the spiked groundwater samples for comparing the PFOS and PFOA removal efficiencies with spiked deionized water samples in different conditions as follows:

3.11.3.1 Nanoparticles usage (nZVI)

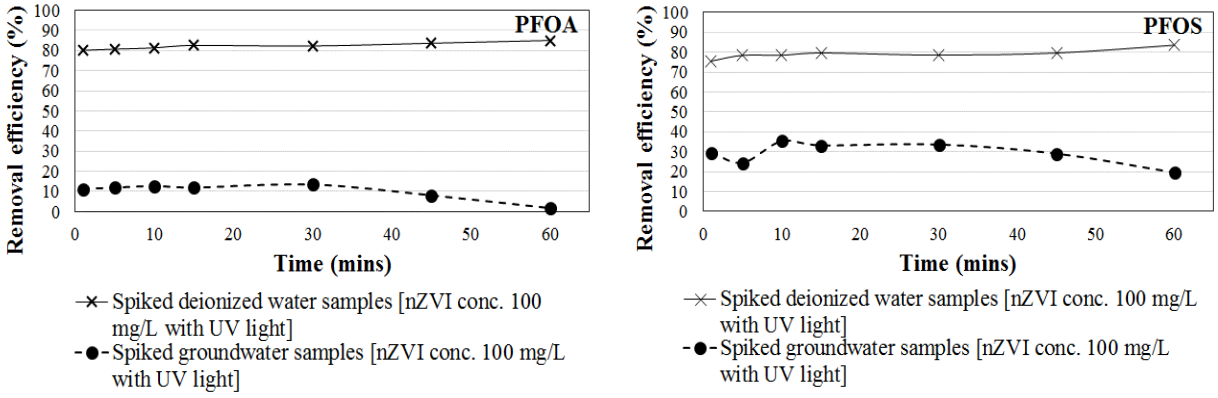
The spiked deionized water and groundwater samples were compared in the only nZVI usage condition at a concentration of 100 mg/L. Figure 3.28 (a) shows the PFOA removal efficiency of spiked deionized water and groundwater samples, which were 0.17 – 12.53% and 1.61 – 18.18%, respectively. For Figure 3.28 (b) the PFOS removal efficiency of spiked deionized water and groundwater samples were 1.98 – 18.57% and 20.24 – 33.50%, respectively. For both PFOS and PFOA, the removal efficiency of spiked groundwater sample was higher than for the spiked deionized water sample. The PFOS and PFOA removal efficiencies of this experiment were quite low in both the spiked deionized water and groundwater samples based on the section 3.11.2; the results in Figure 3.27 shows that the removal efficiency of nZVI usage (without UV light) was lower than the photocatalysis (nZVI usage with UV light) condition, due to the fact that UV light could affect the PFOA and PFOS removal efficiency. Besides, nZVI were effective for detoxification and transformation of chlorinated organic solvents, polychlorinated biphenyls (PCBs), and organochlorine pesticides in the groundwater due to nZVI having a large surface area (Rajan, 2011).



(a) (b)

Figure 3.28 The PFOA (a) and PFOS (b) removal efficiencies by comparing between spiked deionized water samples and spiked groundwater samples in only nZVI usage (without UV light) at a concentration of 100 mg/L.

3.11.3.2 Photocatalysis (UV light with nanoparticles)



(a) (b)

Figure 3.29 The PFOA (a) and PFOS (b) removal efficiencies by comparing between spiked deionized water samples and spiked groundwater samples in photocatalysis condition

The PFOS and PFOA removal efficiencies of the spiked deionized water and groundwater samples were compared in photocatalysis, which was composed of 100 mg/L of nZVI and UV light. Figure 3.29 (a) and (b) show the removal efficiencies by comparing between spiked deionized water samples and spiked groundwater samples in the photocatalysis condition for PFOA and PFOS, respectively. The PFOA removal efficiencies of spiked deionized water and groundwater samples were 88.14 – 84.98% and 1.52 – 12.62%, respectively. The PFOS removal efficiencies of spiked deionized water and groundwater samples were 75.57 – 83.50% and 19.37 – 35.40%, respectively. As the results illustrate, the removal efficiency of the spiked deionized water sample was better than the spiked groundwater sample because in the photocatalysis reaction, the co-contaminants in groundwater could affect the removal efficiency due to the reaction that will occur with organic compounds that are easy to degrade before.

3.12 Hybrid nanofiltration and photocatalysis with groundwater

3.12.1 Nanofiltration

For the nanofiltration part of the experiment, the pressure was operated at 6 bar and the samples were collected every 8 minutes. The PFOA removal efficiency of the spiked groundwater and deionized water samples were 98.81 - 99.22% and 99.15 – 99.94%, respectively, as shown in Figure 3.30. The other study found that nanofiltration could reject the Perfluorooctane Sulfonate (PFOS), which is one of the PFCs, up to 90-99% (Tang *et al.*, 2007). As the results illustrated, the spiked groundwater removal efficiency was not much different from the spiked deionized water at the same condition, even though the removal efficiency of the spiked deionized water sample was slightly higher than the spiked groundwater sample. This is because the co-contaminants in groundwater were not majorly affecting the PFOA removal efficiency by membrane filtration, while the removal efficiency of membrane filtration depends on the size of pollutants and membrane pore size.

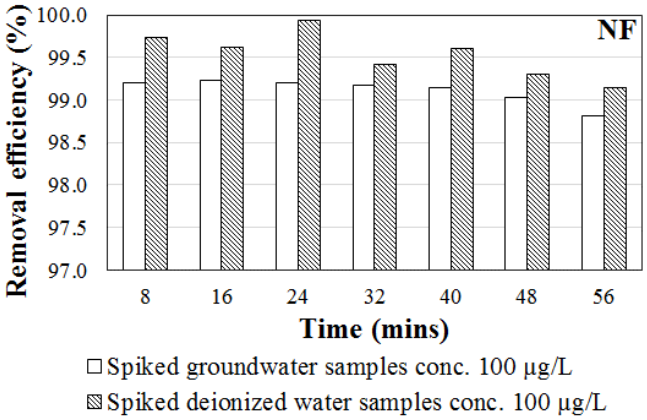


Figure 3.30. The PFOA removal efficiency by comparing between spiked deionized water samples and spiked groundwater samples of nanofiltration in hybrid membrane system

3.12.2 Photocatalysis

For the photocatalysis part of the experiment, the feedwater samples were sent from the rejected part of nanofiltration to the UV contact tank. In Figure 3.31, the results show the PFOA removal efficiencies of the spiked groundwater and deionized water samples were 58.72-62.09% and 72.07-75.83%, respectively. The PFOA removal efficiency of the spiked deionized water sample was higher than for the spiked groundwater samples. This is owing to the co-contaminants in groundwater having an effect on the removal efficiency because of the reaction that will occur with easily degradable organic compounds beforehand.

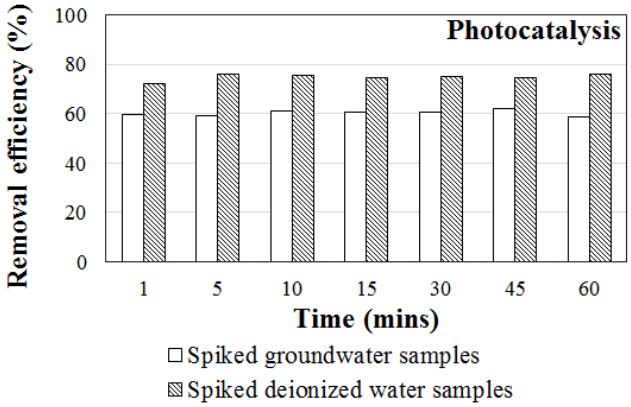


Figure 3.31. The PFOA removal efficiency by comparing between spiked deionized water samples and spiked groundwater samples of photocatalysis in hybrid membrane system

Even though the removal efficiencies of the spiked deionized water sample were higher than those of the spiked groundwater sample, nevertheless the efficiency still was low, due to the UV contact tank not having a mixer for mixing nanoparticles, and also setting the UV light bulb only in the middle of the tank might not be good enough, so it could be the cause of the low efficiency in photocatalysis. These points should be considered in further study. The

previous study which investigated the combined process of photocatalysis and ozonation ($UV/TiO_2/O_3$) found the PFOA degradation efficiency was 99.1% after 4 hours reaction time (Huang *et al.*, 2016). Besides, the size of this experiment was quite a pilot scale project and scaling up the experiment to batch from pilot scale might decrease the removal efficiency even if the operating conditions are controlled. According to our previous study in batch scale, the PFOA removal efficiency of spiked deionized water by zero valent iron photocatalysis was up to 80.14 – 84.98% (Boonya-atichart, 2017).

3.12.3 Mass Balance in hybrid nanofiltration membrane and photocatalysis

The mass balance of the hybrid nanofiltration and photocatalysis process was determined to discover the fate of mass when the contaminants were treated by the hybrid nanofiltration and photocatalysis operation unit, to show the outcome of the improved system. The average PFOA concentration was multiplied by the water sample volume for determining the mass of PFOA. The water sample volume was calculated from the flow rate in each part of the operation unit. The actual flow rates were measured on the experimental run day. The PFOA mass was calculated from the following equation:

$$\text{Mass (µg)} = \text{volume of water sample (L)} \times \text{average concentration (µg/L)}$$

The volume and concentration of the test system are presented in Figure 8. The volume of the water samples in the NF feed tank, permeate, retentate, and UF effluent were 34 L, 14.47 L, 19.53 L, and 19.53 L, respectively. The PFOA average concentration in the NF feed tank, permeate, retentate, and UF effluent were 98 µg/L, 0.87 µg/L, 169.96 µg/L, and 58.40 µg/L, respectively, as shown in Figure 3.32. For the retentate, the water sample volume and PFOA concentration of all rejected parts were 19.53 L and 169.96 µg/L, respectively, for which the concentration of the PFOA concentration after photocatalysis (after UV contact tank) was 68.60 µg/L. After calculating the mass in each part, the mass balance of the system was calculated and shown in the percentages based on the calculation by the following equation:

$$\text{The percentage of each part} = \left(\frac{\text{mass in each part}}{\text{mass of NF feed tank}} \right) \times 100$$

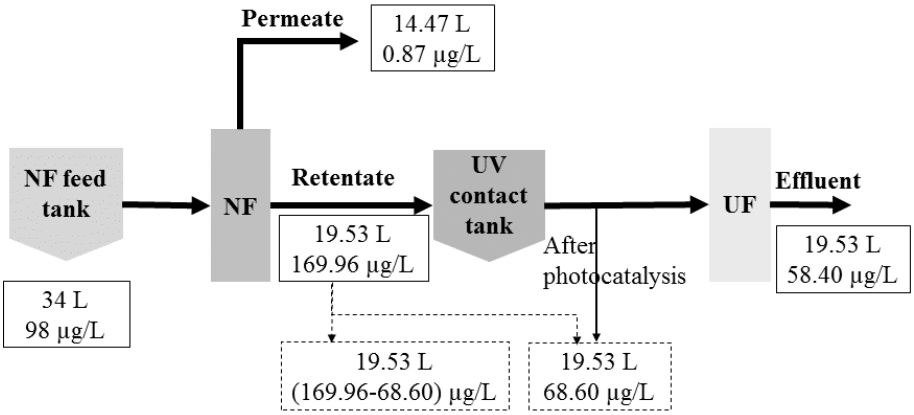


Figure 3.32. Volume and concentration of water samples of hybrid membrane system

As shown in Figure 3.33 (b), at the NF feed tank before treating by nanofiltration membrane, the mass of PFOA was 100% and after treating by nanofiltration membrane, the residual of PFOA in permeate was 0.38% and the rejected part sent to the UV contact tank was 99.62%. In the photocatalysis part, the mass of PFOA after treatment by photocatalysis was 40.21%, so the PFOA that was degraded by photocatalysis was 59.41% and the average removal efficiency of photocatalysis was up to 59.64%. Then the sample was sent to the ultrafiltration membrane for removing the nanoparticles before releasing the treated water to the environment. The mass of PFOA released to the environment was 34.23%; thus, 5.98% of PFOA was trapped by the ultrafiltration membrane.

(a)

(b)

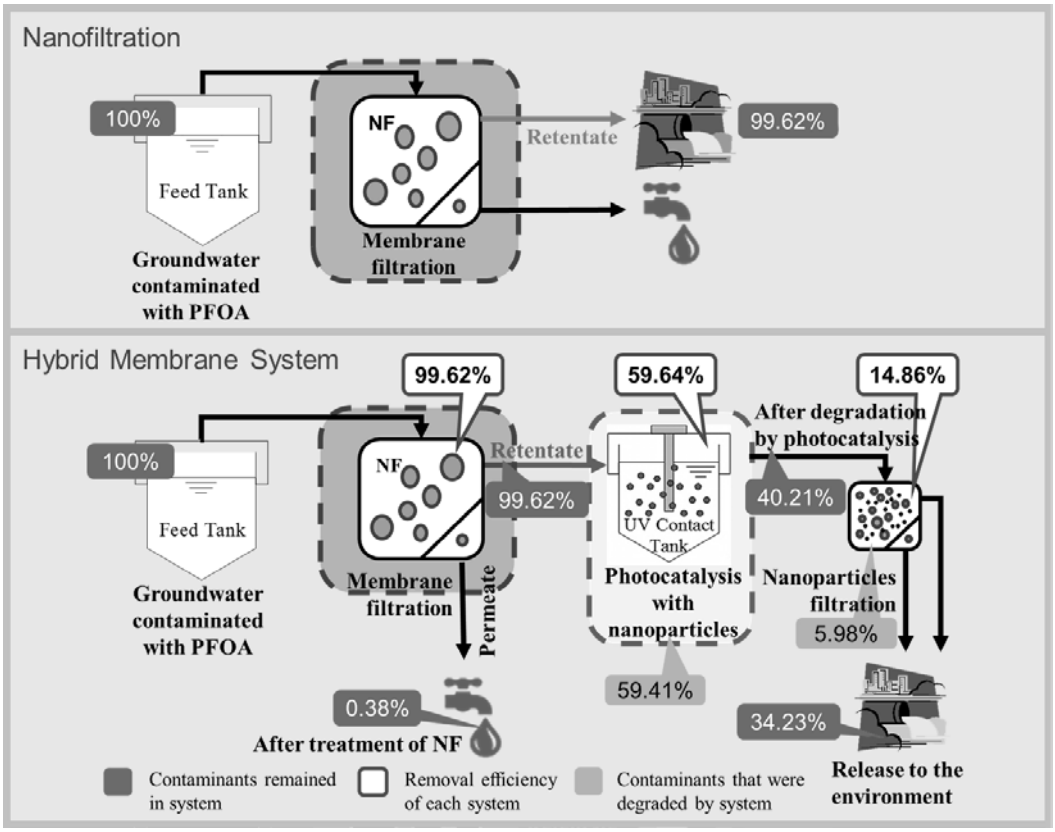


Figure 9. Comparison of mass balance and removal efficiency between (a) conventional membrane filtration and (b) hybrid membrane system

The comparison between the nanofiltration system (Figure 3.33 (a)) and the hybrid membrane system (Figure 3.33 (b)) shows the difference in the amounts of contaminants that were released to environment from each system. For the nanofiltration system, the contaminants after being treated by nanofiltration were released to the environment up to 99.62%.

In contrast, the nanofiltration membrane coupled with photocatalysis, the contaminants were released to the environment just 34.61%, which was a much better result than treatment by only the nanofiltration membrane about 3 times. Thus, the hybrid membrane filtration and photocatalysis method is more effective for removal of the contaminants in groundwater and is also friendlier to the environment and living things.

(4) Conclusions

The overall objective of this research project is to investigate the current situation of Perfluoroalkyl Substances (PFASs) contamination in groundwater; develop and evaluate the technical performance of Hybrid Membrane Technology for controlling of Perfluoroalkyl Substances (PFASs) in groundwater.

Seven PFCs: PFHpA, PFOA, PFNA, PFDA, PFUnA, PFHxS, and PFOS were extracted by solid-phase extraction (SPE) technique and analyzed by high-performance liquid chromatography-tandem mass spectrometer (HPLC-MS/MS). Total PFCs in groundwater around the MWDSs varied from 1.68 to 7.75 ng/L, where PFOA and PFOS were the most abundant ones, while PFDA was not observed. The total PFCs in groundwater around Nong Nae IWDS and Map Phai IWDS varied from 4.43 to 10.80 ng/L and 2.64 to 42.01 ng/L, respectively. Similar to those around the MWDS areas, PFOA and PFOS were the most dominant compounds. PFHxS was frequently observed in the groundwater around the IWDSs, suggesting that it has been used as a substitute to PFOS-based compounds in industrial processes. Statistical analysis showed that the levels of PFCs in the groundwater around the IWDSs were significantly higher than those around the MWDSs. Furthermore, the results of hierarchical cluster analysis revealed that other than the types of waste source, other factors could have been involved. Besides the impact of waste sources, soil characteristics and interaction between PFCs negative charged and cation in soil played an important role in the PFCs contamination in groundwater. The effect of seasonal variation showed that PFCs decreased in the wet season especially for PFOA and PFUnA, probably resulting from dilution and dissipation over time and a wide area. For health risk assessment, the results of both non-cancer and cancer risks in all samples were acceptable.

For the membrane filtration part, the NF membrane provided higher removal efficiency when applied with higher pressure and concentration, for photocatalysis, the nZVI concentration and co-contaminants in groundwater effected to the removal efficiency. The results of hybrid membrane system in spiked groundwater sample showed that the PFOA removal efficiency of nanofiltration was 99.62% and the rejected part that was degraded by photocatalysis

at the efficiency of 59.64%. So, the contaminants were released to the environment were 34.61%, which was much lower than the residual that remained in the rejected water from only nanofiltration membrane. Therefore, some concentrated PFOS and PFOA after filtration by nanofitration could be degraded using photocatalysis before being release to the environment. Accordingly, hybrid membrane filtration and photocatalysis could enhance the degradation of PFOS and PFOA and overcome the membrane filtration drawback and as a result the system was environmentally friendly to the water environment.

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1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

(1) Boonya-atichart A, Boontanon S.K, Boontanon N. Removal of perfluorooctanoic acid (PFOA) in groundwater by nanofiltration membrane. Water Science and Technology. 2016;74(11):2627-33. (Corresponding author, published)

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2. การนำผลงานวิจัยไปใช้ประโยชน์

2.1 เชิงนโยบาย

1. ได้มีการนำข้อมูลไปใช้ประกอบเพื่อการจัดทำแผนแม่บทและแผนปฏิบัติการระดับชาติในการตรวจวิเคราะห์และการติดตามตรวจสอบสารมลพิษที่ตกค้างยาวนาน

2. ได้มีการนำข้อมูลไปใช้ประกอบเพื่อทบทวนและปรับปรุงแผนจัดการระดับชาติและทำเนียบข้อมูลสารมลพิษที่ตกค้างยาวนานประเภทสารเคมีอุตสาหกรรม

2.2 เชิงวิชาการ

1. พัฒนานักวิจัยรุ่นใหม่ (ปริญญาโท 4 คน ปริญญาเอก 3 คน) ทางด้านการตรวจวัดสารมลพิษที่ตกค้างยาวนานและออกแบบพัฒนาวิธีการควบคุมบำบัดจัดการสารมลพิษที่ตกค้างยาวนานโดยใช้องค์ความรู้ที่ได้จากงานวิจัยนี้เพื่อให้นักศึกษามีทักษะที่สำคัญในการพัฒนาตัวเองเพื่อต่อยอดต่อไปอย่างต่อเนื่อง

2. สร้างความร่วมมืออย่างต่อเนื่องกับหน่วยงานภายในประเทศยกตัวอย่างเช่น การประปานครหลวง สำนักงานพัฒนาวิทยาศาสตร์และเทคโนโลยีแห่งชาติ (สวทช.) และหน่วยงานต่างประเทศ Environmentally-friendly Industries for Sustainable Development Laboratory, Graduate School of Global Environmental Studies, Kyoto University, Prof. Shigeo Fujii and Dr. Shuhei Tanaka โดยมีการส่งนักศึกษาระดับปริญญาโทและเอกเพื่อร่วมทำวิจัย ได้แก่

1. Ms. Chanidaporn Hongkachok เพื่อเป็นนักศึกษาแลกเปลี่ยนในการทำวิจัยเกี่ยวกับ การตรวจวัด วิเคราะห์และสำรวจการปนเปื้อน Perfluoroalkyl Substances (PFASs) ระหว่างเดือน มีนาคม ถึง กันยายน พ.ศ. 2559
2. Ms. Suratsawadee Sukeesan เพื่อเป็นนักศึกษาแลกเปลี่ยนในการทำวิจัยเกี่ยวกับ Adsorption of Perfluoroalkyl Substances (PFASs) ระหว่างเดือน มีนาคม ถึง กันยายน พ.ศ. 2560

นอกเหนือจากนั้นหัวหน้าโครงการ (ดร.สุวรรณา) ได้ไปสอนนักศึกษาระดับบัณฑิตศึกษาที่ประเทศญี่ปุ่น และร่วมประชุมงานวิจัยเกี่ยวกับ Perfluoroalkyl Substances (PFASs) ที่ Kyoto University ในช่วงวันที่ 25-29 เมษยาน พ.ศ. 2559 และ 22-26 พฤษภาคม 2560

3. อื่นๆ

3.1 ผลงานตีพิมพ์ (Conference Proceeding) ในที่ประชุมวิชาการระดับนานาชาติ

(1) Hongkachok C, Boontanon SK, Boontanon N, Surinkul N, Boonya-atichat A, Tanjai R. Occurrence of perfluorinated compounds (PFCs) in surface water and groundwater near unsuitable disposal sites in Thailand. The 12th International Symposium on Southeast Asian Water Environment (SEAWE2016), Hanoi, Vietnam, November 28-30, 2016.

(2) Boonya-atichart, A., Boontanon, S. K., & Boontanon, N. (2017). Study of Hybrid Membrane Filtration and Photocatalysis for Removal of Perfluorooctanoic Acid (PFOA) in Groundwater. 10th Micropol & Ecohazard Conference, 17 – 20 September 2017, Vienna, Austria. (Corresponding author)

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(6) Waiyarat, S., Boontanon, S.K., Boontanon, N., Sukeesarn, S., Chuiprasert, J., & Fujii, S. (2018). Perfluoroalkane sulfonates (PFSAs) and heavy metals in surface water around an informal e-waste recycling site at Kalasin Province, Thailand. 3rd Regional IWA Diffuse Pollution Conference, 19-22 November 2018, Chiang Mai, Thailand. (Corresponding author)

3.2 การเสนอผลงานในที่ประชุมวิชาการระดับนานาชาติ (Poster Presentation)

(1) Hongkachok C, Boontanon SK, Boontanon N. Investigation of perfluorinated compounds (PFCs) in groundwater near unsuitable disposal sites in Thailand. International Symposium on Global Environmental Studies Education and Research in Asia, Nakhon Pathom, Thailand, November 13-15, 2016.

(2) Boonya-atichat A, Boontanon SK, Boontanon N. Study of hybrid membrane filtration and photocatalysis for removal of PFOA in groundwater. International Symposium on Global Environmental Studies Education and Research in Asia, Nakhon Pathom, Thailand, November 13-15, 2016.

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ภาคผนวก

ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

และ

Conference Proceeding ในที่ประชุมวิชาการระดับนานาชาติ

Removal of perfluorooctanoic acid (PFOA) in groundwater by nanofiltration membrane

Apisara Boonya-atichart, Suwanna Kitpati Boontanon and Narin Boontanon

ABSTRACT

Perfluorooctanoic acid (PFOA) is very persistent in the environment and resistant to typical degradation processes. PFOA has been widely used in surface-active agents and as an emulsifier in several products and can contaminate groundwater. Groundwater is considered as an important source of water; hence removal of PFOA contamination in groundwater is needed. This study aimed to examine the removal of PFOA in spiked deionized water and spiked groundwater samples by nanofiltration (NF) membrane. PFOA removal efficiency was performed by using NF membrane and all samples were analysed by high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). For groundwater concentration, solid phase extraction is needed before being analysed by HPLC-MS/MS. The results showed that at higher pressures and higher PFOA concentrations, the PFOA removal efficiencies were slightly higher. The PFOA removal efficiency of spiked deionized water and spiked groundwater sample were 99.78–99.87% and 99.49–99.54%, respectively, which were not significantly different.

Key words | groundwater, LC-MS/MS, nanofiltration, perfluorooctanoic acid

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INTRODUCTION

Perfluorooctanoic acid (PFOA) is one of the perfluorinated compounds (PFCs), which are persistent organic pollutants (USEPA 2014). PFOA was widely used in surface-active agents and as an emulsifier for many industries such as paints, fire-fighting foam, paper coating, cleaning products and a variety of food packages (State Water Resources Control Board 2010). However, they are extremely persistent in the environment and cannot be photolyzed, hydrolyzed, or degraded under normal environmental conditions; so they can also bioaccumulate in animal tissues and the environment (USEPA 2014). Moreover, PFOA has been recommended by the United States Environmental Protection Agency (USEPA) to be considered as a 'probable human carcinogen' based on animal studies (State Water Resources Control Board 2010).

Groundwater is an important water resource that serves as a source of drinking water and water supply (Alley *et al.* 2013). PFOA is easily dissolved in water due to the fact that PFOA is a surfactant that can be in both hydrophilic and hydrophobic groups (State Water Resources Control Board 2010). These characteristics cause PFOA contamination in groundwater from wastewater leaching from sewer pipes, surface runoff, infiltration of river water, and leaking of leachate from landfills (Eschauzier *et al.* 2012). Some previous studies have indicated PFOA is present in soils and groundwater in some areas such as US metropolitan areas (Xiao *et al.* 2015), mostly located where PFOA and related compounds were manufactured and disposed of (State Water Resources Control Board 2010). The concentration of PFOA near the disposal site was around 20,000 ng/L and further away from the site at 1.4 km was <100 ng/L in wells (Xiao *et al.* 2015). In the city of Tokyo, the PFOA concentration in groundwater was 0.47–60 ng/L (Murakami *et al.* 2009). In Thailand, the occurrence of PFOA in groundwater from the central region of Thailand was between 0.02 and 38.72 ng/L; the most PFOA found in a sample site was near the municipal landfill in Nakhon Pathom province (Intraravirat *et al.* 2014).

Currently, membrane technology is being used as a filtration method for PFOA removal in water (USEPA 2014), especially in wastewater (Hang *et al.* 2015). Nanofiltration (NF) and reverse osmosis are effective technologies for

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removing PFOA from water (State Water Resources Control Board 2010). Nevertheless, the characteristics of each water type are different; likewise, the treatment methods are different. The typical characteristics of groundwater generally are high mineral content and low turbidity (Ojo *et al.* 2012), which are different from wastewater, surface water, and also deionized water. Therefore, the objectives of this research were to examine the removal efficiency of PFOA, in different conditions of pressure and concentration, and to compare the efficiency between spiked deionized water samples and spiked groundwater samples by NF membrane.

MATERIALS AND METHODS

Chemicals and standards

PFOA (>95%) was purchased from the Wako Company (Japan). For solvents, methanol HPLC (high-performance liquid chromatography) grade (99.9%) and acetonitrile HPLC grade (99.8%) were ordered from Merck (Germany). In addition, pure ammonium acetate that was used for preparing HPLC-MS/MS (HPLC coupled with tandem mass spectrometry) mobile phase was supplied from Merck (Germany).

Specification of membrane and its equipment set-up

The major instrument of this study is the NF membrane that is used for removing the target contaminants. The membrane model 2540-ACM5-TSF, 2.5″ diameter, was purchased from Trisep Corporation (USA) and membrane specifications are shown in Table 1. According to the specification of the membrane, it has the ability to reject soluble low molecular weight (>200 Daltons (Da)) neutral and charged organic compounds; so it can remove PFOA, which has a molecular weight of 414 g/mol (USEPA 2014), which is equal to 414 Da. According to a previous study, NF membrane could reject the perfluorooctane sulfonate (PFOS) (one of the PFCs) up to 90–99% (Tang *et al.* 2007). Depending on respective pore size, the NF membrane should be suitable for removing PFCs from the process (Lutze *et al.* 2012). Moreover, this membrane can operate at ultra-low pressures at 5–9 bar. Therefore, this membrane was selected to test with PFOA in this study. A schematic diagram of the membrane operation unit is shown in Figure 1. The type of this membrane is a fully aromatic polyamide advanced composite membrane and it is spiral wound and outer wrapped by fiberglass. The active membrane area is 26 ft^2 (2.4 m^2). The average salt rejection and minimum salt rejection of the membrane are 98.5% and 97.5%, respectively. The pump model was A-97516688-P1-1432 (Grundfos, Denmark). Normal volume flow rate and normal pressure were 1.7 m^3/h and 6.5 bar, respectively. The type of motor was MG80B 1*220-240-2 B-C (Grundfos, Denmark) and the power output was 0.9 kW or 1.21 HP.

Table 1 | The membrane specification of model 2540-ACM5-TSF for operational and design data

Membrane	Details and operation
Type	Fully aromatic polyamide advanced composite membrane
Configuration	Spiral wound, fiberglass outer wrap
Active membrane area	26 ft^2 (2.4 m^2)
Molecular weight cut-off	200 Da
Recommended applied pressure	100–300 psi (7–21 bar)
Maximum applied pressure	600 psi (41 bar)
Recommended operating temperature	35–113 °F (2–45 °C)
Feed water pH range	2–11 continuous
Chlorine tolerance	<0.1 ppm
Maximum feed flow	6 gallons/min (1.4 m^3/h)
Minimum brine flow/ permeate flow ratio	5:1
Maximum silt density index (15 minutes)	5:0
Maximum turbidity	1 NTU
Permeate flow	800 gallons/day (3.0 m^3/day)
Average salt rejection	98.5%
Minimum salt rejection	97.5%

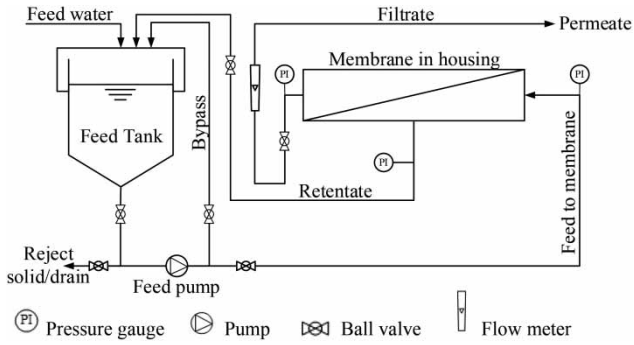

Figure 1 | Schematic diagram of membrane operation unit.

NF membrane experiments

In this study, there are two types of feed water, consisting of synthetic samples and groundwater samples. Synthetic samples were developed in order to find the conditions used with real groundwater samples. After that, the groundwater samples were run at the selected pressure and PFOA concentration. Finally, the PFOA removal efficiency for synthetic and real groundwater samples could be compared at the same conditions. The PFOA removal efficiency was calculated as the equation below.

$$\text{Removal efficiency (\%)} = \frac{(\text{influent conc.} - \text{effluent conc.}) \times 100}{\text{influent conc.}}$$

Operation with synthetic samples

Spiked deionized water was used as synthetic samples. Spiked deionized water was controlled at 100 μg/L PFOA and focused on the feed (influent) pressure of membrane. Three operational pressures were 2, 4 and 6 bar, respectively. Furthermore, after determination of appropriate fixed pressure operation, three PFOA-spiked deionized water concentrations were used: 5, 50 and 100 μg/L (Table 2).

Operation with groundwater samples

After knowing the PFOA concentration in groundwater by solid phase extraction (SPE) coupled with HPLC-MS/MS technique, the groundwater sample was spiked by a selected PFOA concentration. The conditions applied for the groundwater batch experiment were based on the synthetic sample operation results. The lowest PFOA concentration with high removal efficiency was chosen (50 μg/L). For pressure, the selected pressure operation was set at 6 bar.

Table 2 | The experimental runs of spiked deionized water sample and spiked groundwater sample

Sample	Conductivity (μS/cm)	Pressure (bar)	Initial PFOA concentration (μg/L)
Spiked deionized water	50	2	100
	47	4	100
	69	6	100
	76	6	5
	55	6	50
	69	6	100
Spiked groundwater	1,400	6	50

Sample collection during experiments

The experimental runs of spiked deionized water sample and spiked groundwater sample are shown in Table 2. Water samples from membrane operation were collected: 100 mL of each sample from influent and permeate every 10 minutes for an hour in each condition, while conductivity and pH were measured at the same points. For the permeate point, flow rate was measured every 10 minutes. In addition, the temperature of influent was controlled and measured under recommended operating temperature (2–45 °C) of the membrane as shown in Table 1.

Groundwater collection and preparation

A hundred liters of groundwater samples were collected near the landfill from Nakhon Pathom province, Thailand, in April 2015. All samples were kept in plastic storage and protected from sunlight.

For the groundwater sample, SPE is needed for concentrating PFOA in the sample. Collected groundwater sample was filtrated by GF/B glass microfiber filter (Whatman, UK) for removing suspended solids. The filtrated samples were percolated into a cartridge (Precep C-Agri, C_{18}, Wako, Japan) with a flow rate of 10 mL/min. After concentration, all cartridges were vacuum dried for 2 hours by using a vacuum manifold. All dried samples were eluted by 4 mL of methanol (HPLC grade) and 2 mL of acetonitrile (HPLC grade). After elution, the eluents were dried by high-purity nitrogen gas at 60 °C. and reconstituted by 1 mL of 40% acetonitrile (volume/volume) (HPLC grade). Finally, final extracts were transferred to HPLC vials and analyzed by HPLC-MS/MS

For the spiked groundwater sample, PFOA was prepared and spiked into the groundwater sample that had been collected from Nakhon Pathom province until the 50 μg/L PFOA concentration was reached. Nevertheless, the exact initial concentration of all samples was analyzed by HPLC-MS/MS again including spiked deionized water samples.

Instrumental analysis

Quantification of PFOA was performed by using an Agilent 1200SL high-performance liquid chromatograph (Agilent Technologies, USA) which interfaced with an Agilent 6400 triple quadrupole mass spectrometer (Agilent Technologies,

Table 3 | HPLC-MS/MS conditions for analysis of PFOA by MRM in negative ion mode

Compound	Precursor ion (m/z)	Product ion (m/z)	Dwell time (ms)	Collision energy (eV)	Retention time (min)	Polarity
PFOA	413	369	50	5	4.0	Negative

USA). The protective guard column was an Agilent ZORBAX Eclipse XDB-C_{18} (4.6 × 50 mm, 1.8 μm particle size) and was series connected with analytical column Agilent ZORBAX Eclipse Plus C_{18} (2.1 × 100 mm, 1.8 μm particle size). The column was maintained at 40 °C. For optimum separation, a binary gradient consisting of 10 mM ammonium acetate (solvent A) and acetonitrile (solvent B) at a flow rate of 0.25 mL/min was used. The elution gradient setting was: 45% (B), 0–5 min: 50%; 5–5.5 min: 60%; 5.5–10 min: 60%; 10–15 min: 90%; back to initial condition for 10 min. The total running time was 25 minutes for each sample. The injection volume was 10 μL. For quantitative analysis, the mass spectrometer was operated with the electrospray ionization negative mode. Multiple reaction monitoring (MRM) mode was used to monitor analyte ions. Capillary voltage was 3,500 V. Gas temperature and gas flow were 300 °C and 10 L/min, respectively. HPLC-MS/MS conditions are shown in Table 3.

RESULTS AND DISCUSSION

Results of membrane operation with synthetic samples

PFOA removal efficiency by varied pressures

For membrane operation condition of varied pressure experiments, PFOA concentration was controlled at 100 μg/L and pressures were controlled at 2, 4 and 6 bar, respectively, as shown in Table 2. Figure 2(a) shows that PFOA removal efficiencies of pressures 2, 4 and 6 bar were slightly different. PFOA removal efficiencies were 99.49–99.24%, 99.40–99.42%, and 99.39–99.62%, respectively, at 10 to 60 minutes of experiment. In a previous study, the higher applied pressure affected the removal efficiency of PFOS in wastewater, which was highly improved at 13.79 bar (200 psi) applied pressure (Tang *et al.* 2007). The results from this study also found that at higher applied pressure, the removal efficiency got higher than at lower applied pressure. However, it was seen that the removal efficiency of every varied pressure condition was over 99% during the experiment. Thus, this NF membrane showed the trend of higher pressure providing better removal efficiency, but not so significantly different.

PFOA removal efficiency by concentration variation

The pressure that was applied in these different PFOA concentrations conditions was obtained from the pressure variation experiments, in which the highest permeate flow rate with the lowest concentration was selected. The condition of this experiment, pressure at 6 bar, was fixed for 5, 50 and 100 μg/L PFOA concentration operation as shown in Table 2. Figure 2(b) shows that the removal efficiency of 5, 50 and 100 μg/L were 97.39–98.85%, 99.51–99.54% and 99.39–99.62%, respectively. At low concentration of 5 μg/L, the removal efficiency was lower than those of 50 and 100 μg/L. From the result, the NF membrane could provide

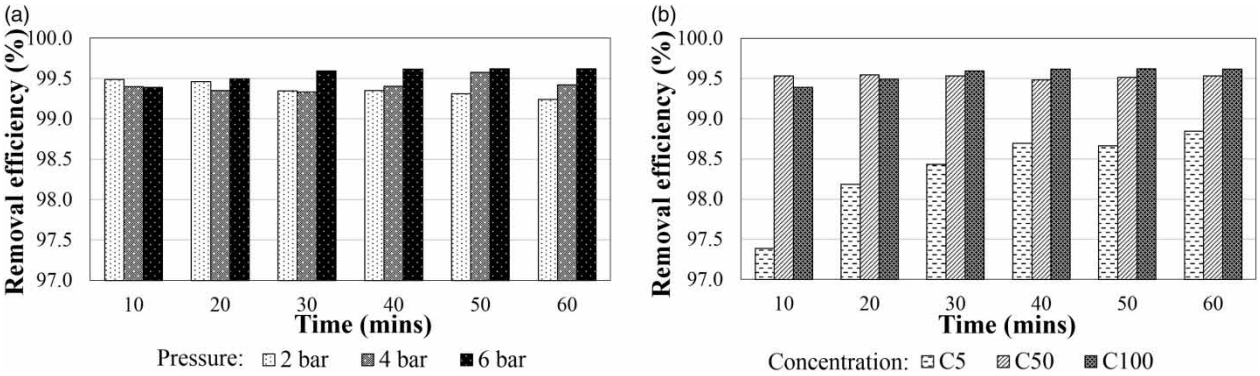

Figure 2 | (a) The PFOA removal efficiency in different pressures. (b) The PFOA removal efficiency in different PFOA concentrations.

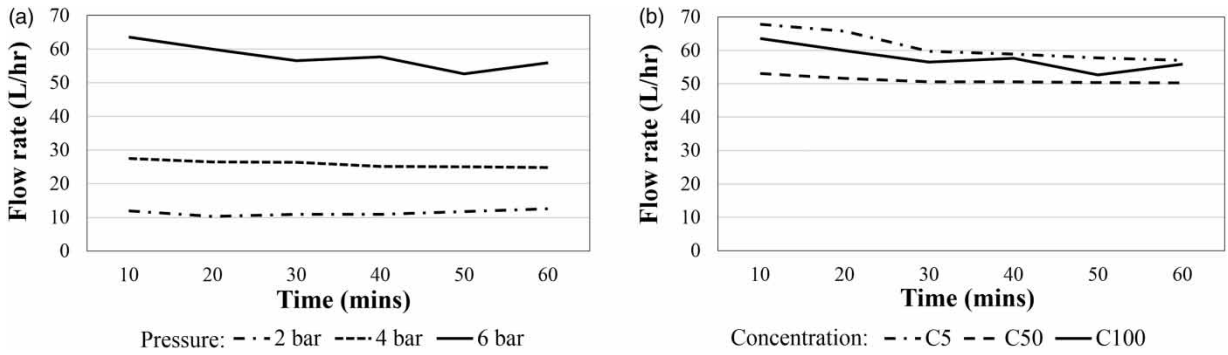

Figure 3 | (a) The flow rate of permeate in different pressures. (b) The flow rate of permeate in different PFOA concentrations.

higher removal efficiency when applied with higher concentration. To support the result, a prior study reported that the rejection increased at higher concentration (Tang *et al.* 2006). When comparing the removal efficiency with the influent concentrations, it was found that at high concentration, the decreasing rate of the influent concentration was much higher than at low concentration. Furthermore, when the initial concentration increased, the removal efficiency was not significantly different because the maximum removal efficiency of the membrane was reached.

The flow rate of permeate in different pressures and concentrations

As represented in Figure 3(b), the flow rate of permeate, from 10 minutes to 60 minutes, of the spiked deionized samples with concentration of 5, 50, and 100 μg/L decreased by 15.80%, 5.31%, and 12.11%, respectively, indicating that the flow rates decreased when the time of experiments was increased. For the flow rate of different pressure experiment as shown in Figure 3(a), lower pressure provided lower flow rate. During the time of operation, the flow rate was lower due to clogging that occurred. Similarly to the previous study, the flux decline is probably associated with the PFOS accumulation on the membrane surface (Tang *et al.* 2006). At low pressure, the flow rate was slightly decreased, unlike in the high pressure operation where the flow rate was obviously decreased because substances flowed through the membrane in big volume, making the performance of the membrane drop down faster.

The effect of temperature and pH

In varied pressure membrane experiments, the flow rate of permeate was measured every 10 minutes and temperature

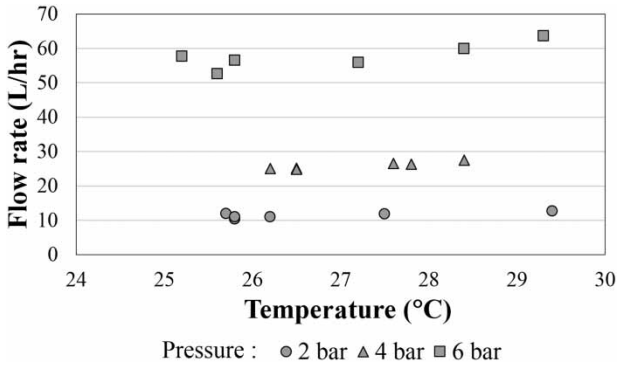

Figure 4 | The relation of permeate flow rate and temperature at different pressures.

was measured and controlled under 45 °C as the recommended operating temperature of the membrane. In Figure 4, the results show that the temperature involved a change of permeate flow rate in all different pressure conditions (2, 4 and 6 bar). When the temperature increased, the flow rate also slightly increased. Similarly to the principle of NF membrane when the temperature increases, the permeate flux will increase (The Dow Chemical Company 2016). However, the temperature in this experiment was varied in the range between 25 and 30 °C, which did not significantly affect analysis of the other results.

In the experiment, pH was measured from influent and effluent of all spiked deionized water and spiked groundwater samples every 10 minutes for an hour. The results show the range of pH for synthetic samples was 6.49–10.02 and 8.5–9.1, and for real groundwater samples was 7.72–8.0 and 5.5–6.0, for influent and permeate respectively. PFOA removal efficiencies in all synthetic samples and real groundwater samples were in the range of 97.39–99.62% and 99.78–99.87%, respectively, and comparing with the slight variation of pH, it was found that the influence of pH was not so significant for groundwater. Nonetheless, a previous study with deionized water in order to understand

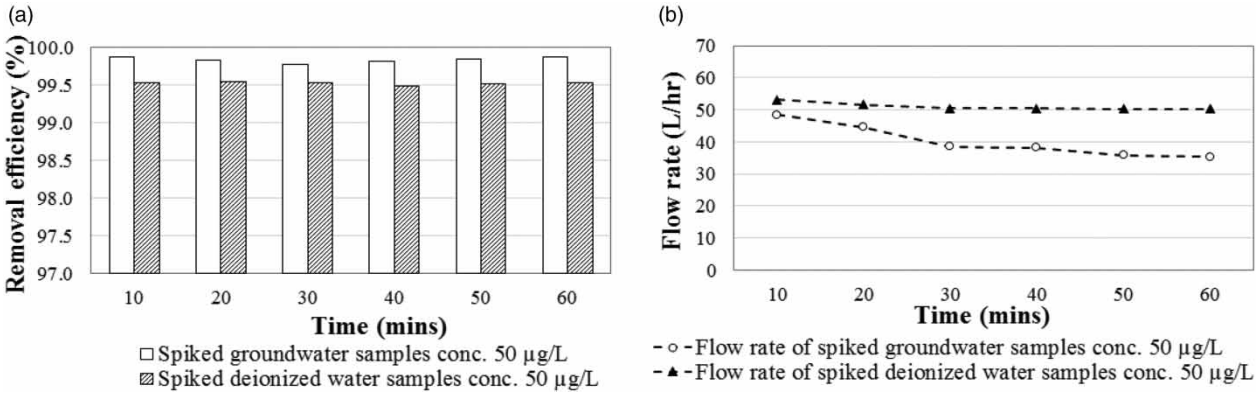

Figure 5 | (a) The PFOA removal efficiency comparing spiked groundwater samples and spiked deionized water samples, at concentration 50 µg/L. (b) The flow rate of permeate comparing spiked groundwater samples and spiked deionized water samples, at concentration of 50 µg/L.

the use of NF membranes for water recycling showed that the rejection of perfluorooctane sulfonamide (one of the PFCs) increased from 70% at pH = 2.8 to >99% at pH = 10. Decreasing the pH to less than 3 decreases rejection significantly (Steinle-Darling & Reinhard 2008). Furthermore, the results of a recent study revealed that the influence of hydrophobic acid organic matter on estrone rejection by NF membrane would be affected by water chemistry such as pH and ionic strength (Jin & Hu 2015).

Comparison of spiked groundwater and spiked deionized water samples

Groundwater sample was collected from a groundwater well at Kampaeng Saen district in Nakhon Pathom province; this well is in the residential zone near landfill and plantation. The average PFOA concentration in groundwater was 0.31 ng/L.

To compare the removal efficiency between spiked deionized water samples and spiked groundwater samples by NF membrane, the operation conditions were controlled similarly. The highest removal efficiency at the lowest PFOA concentration with high removal efficiency found for the synthetic sample was chosen because the removal efficiency of 50 µg/L PFOA was not much different from that of 100 µg/L at 6 bar pressure. Thus, the synthetic and groundwater samples were spiked with 50 µg/L of PFOA.

The spiked groundwater removal efficiency was not different from the spiked deionized water at the same condition, being 99.78–99.87% and 99.49–99.54%, respectively, as shown in Figure 5(a). In Figure 5(b), it was found that the flow rate decreased 32.80% for PFOA-spiked groundwater while the flow rate of PFOA-spiked deionized water decreased 5.31%. Results indicated the membrane performance decreased due to the total dissolved solids (TDS) in groundwater (1,400 µS/cm as shown in Table 2), which was higher than in the spiked deionized water (55 µS/cm). Normally, groundwater contains dissolved minerals and solvent from the rocks which it is in contact with (USGS 2013). Thus, TDS is also an important factor because of the mineral content in groundwater being typically high. In a previous study at longer duration, increasing of the PFOS rejection might be due to PFOS molecules being entrapped in the polyamide layer; therefore, the further passage of water and entrapment of PFOS molecules will be hindered, to cause a flux decline (Tang *et al.* 2007). The mineral content in groundwater could accumulate and hinder the water, causing the membrane performance decrease. Hence, it could be said that the different matrix of water samples affected the performance of NF membrane for PFOA removal.

CONCLUSIONS

According to the results of this study, higher pressure increased the PFOA removal efficiency. Furthermore, when the NF membrane was applied to higher PFOA concentration, it could provide higher removal efficiency. Although the PFOA removal efficiency of spiked deionized water sample was not significantly different to that of spiked groundwater sample, the TDS in groundwater affected the operation performance of the NF membrane for PFOA removal. The performance of operation could be disturbed by other characteristics of groundwater. Thus, the factors that influence performance in a long-term test for PFOA and other emerging contaminants removal should be further studied.

ACKNOWLEDGEMENTS

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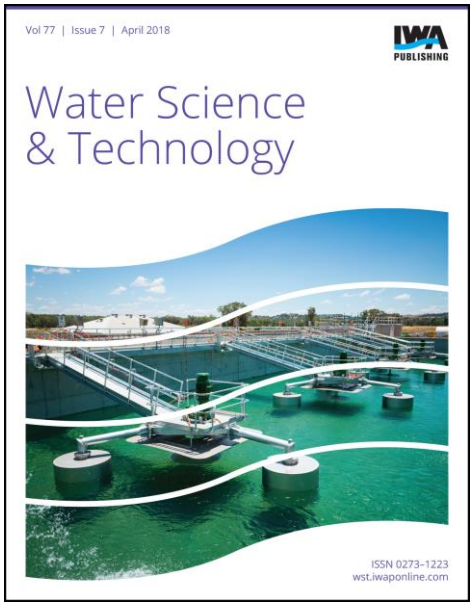

Study of hybrid membrane filtration and photocatalysis for removal of perfluorooctanoic acid (PFOA) in groundwater

Apisara Boonya-atichart, Suwanna Kitpati Boontanon and Narin Boontanon

ABSTRACT

Groundwater contamination in Thailand from leaking of leachate due to improper solid waste disposal can cause contamination by PFOA (one of the perfluorinated compounds). This study proposed a new idea for the removal of PFOA from groundwater using a combination of membrane filtration and photocatalysis. Spiked groundwater samples were treated by nanofiltration and the rejected part was sent to a UV contact tank for photocatalysis. All samples were analyzed by high-performance liquid chromatography-tandem mass spectrometer (HPLC-MS/MS). The results showed that the removal efficiency of nanofiltration was 99.62%, and the rejected part was degraded by photocatalysis at an efficiency of 59.64%. Thus, the contaminants released to the environment were only 34.23%, which is around three times lower than nanofiltration alone. The results of this technical feasibility study proved that hybrid membrane filtration and photocatalysis are able to remove and degrade the contaminants in the rejected part significantly before being released to the environment, which has been the biggest gap in the processing of membrane filtration, and should be studied further in other aspects, such as fouling effects, energy consumption, and operating costs in a long-term pilot run.

Key words | groundwater, hybrid membrane filtration and photocatalysis, perfluorooctanoic acid (PFOA)

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INTRODUCTION

Nowadays, improper disposal of solid waste is a significant problem in Thailand; only 7.2 million tons of municipal solid waste (MSW) received appropriate sanitary management, out of 26.77 million tons of MSW in 2013 (Department of Environmental Quality Promotion 2016). Leaking of leachate can be a cause of perfluorooctanoic acid (PFOA) contamination in groundwater (Stuart & Lapworth 2013). PFOA is one of the predominant perfluorinated compounds (PFCs). PFOA has been used in a variety of products, such as a surfactant in many manufactured products in coating additives, cleaning products, and fire-fighting foam. The characteristics of PFOA are persistence, biological accumulation, toxicity, and long-range transportation (USEPA 2014). USEPA also has recommended that PFOA be labelled as a probable human carcinogen. In addition, PFOA is long-lived and not degradable in the natural environment (State Water Resources Control Board 2010). PFCs are still found in drinking water that comes from drinking water and wastewater treatment in the conventional processing techniques in several countries including the USA, Germany, Switzerland, and other countries.

Conventional oxidative techniques such as UV/H_2O_2, Fenton process, ozonation, and biological degradation for pollutant control seem not to be suitable for PFC degradation (Lutze *et al.* 2012). The effective technologies for removal of PFOA from water are nanofiltration (NF) and reverse osmosis. Nanofiltration is one alternative for removing PFOA from groundwater (Federal Provincial Territorial Committee on Drinking Water 2016); the PFOA removal efficiency of spiked groundwater samples by using nanofiltration have been up to 99.49–99.54% (Boonya-atichart *et al.* 2016). However, a disadvantage of the application of

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membrane filtration still remains the concentration of contaminants such as PFOA in the reject. For complete destruction of contaminants this flow needs to be incinerated (USEPA 2014).

More recently, advanced oxidation has been used for PFOA degradation, including photocatalysis (USEPA 2016). For the catalyst, nanoscale zero-valent iron (nZVI) is used in *in situ* applications for soil and groundwater remediation, because nZVI can transform or degrade many environmental contaminants effectively, especially in groundwater (Christensen *et al.* 2015). After filtration, the concentrated contaminants are degraded by photocatalysis, then the toxic chemicals can be removed before releasing the groundwater to the environment. In other words, eliminating the concentrated pollutants is necessary before releasing water to the environment. Hence, this study proposed the new idea of combining membrane filtration with photocatalysis for the removal of PFOA from groundwater.

MATERIALS AND METHODS

Chemicals and standards

PFOA (>95%) was purchased from the Wako Company (Japan). For solvents, methanol high-performance liquid chromatography (HPLC) grade (99.9%) and acetonitrile HPLC grade (99.8%) were ordered from Merck (Germany). In addition, pure ammonium acetate (≥98%) used for preparing the high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) mobile phase was supplied from Merck (Germany). nZVI (≥65–80%) from Nano Iron (Czech Republic) was used as the catalyst in the photocatalysis. The average particle size and average surface area of the nZVI were 50 nm and 20–25 m^2/g, respectively.

Specification of membranes and their equipment set up

Nanofiltration

The main instrument used for removing the target contaminant was the NF membrane. Membrane model 2540-ACM5-TSF 2.5 inches (6.4 cm) in diameter was purchased from Trisep Corporation (USA); the membrane specifications are shown in Table 1.

Ultrafiltration

Another major part of this study was the ultrafiltration (UF) that was used for removing the nanoparticles after the photocatalysis process and before releasing the treated water back into the environment. The hollow-fiber ultrafiltration membrane model UFH-PST-2021 was purchased from Shanghai Mega Vision Membrane Engineering &

Table 1 | The membrane specification of model 2540-ACM5-TSF for operational and design data (Boonya-atichart *et al.* 2016)

Membrane	Details and operation
Type	ACM fully aromatic polyamide advanced composite membrane
Configuration	spiral wound, fiberglass outer wrap
Active membrane area	26 ft^2 (2.4 m^2)
Molecular weight cut-off (MWCO)	200 Da
Recommended applied pressure	100–300 psi (7–21 bar)
Maximum applied pressure	600 psi (41 bar)
Recommended operating temperature	35–113°F (2–45 °C)
Feed water pH range	2–11 continuous
Chlorine tolerance	<0.1 ppm
Maximum feed flow	6 GMP (1.4 m^3/h)
Minimum brine flow/permeate flow ratio	5:1
Maximum SDI (15 min)	5:0
Maximum turbidity	1 NTU
Permeate flow	800 GPD (3.0 m^3/d)
Average salt rejection	98.5%
Minimum salt rejection	97.5%

Technology (China) and the membrane specifications are shown in Table 2. This type of membrane is a hydrophilic polysulfone-modified membrane. The active membrane area was 0.25 m^2. The removal of >200 nm particles of membrane was 100%. The pump model was a A-97516688-P1-1432 (Grundfos, Denmark).

Table 2 | The hollow-fiber ultrafiltration membrane specification of model UFH-PST-2021 for operational and design data

UF membrane	Details and operation
Type	Hydrophilic polysulfone modified
Configuration	Hollow-fiber ultrafiltration module
Nominal membrane area	0.25 m^2
Operating pressure	<14.50 psi (1 bar)
Maximum applied feed pressure	43.51 psi (3 bar)
Maximum transmembrane pressure	29.01 psi (2 bar)
Maximum backwash transmembrane pressure	20.31 psi (1.4 bar)
Maximum operating temperature	113°F (45 °C)
Feed water pH range	2–11 continuous
Instantaneous chlorine tolerance	1,000 ppm
Continuous chlorine tolerance	200 ppm
Instantaneous hydrogen peroxide tolerance	200 ppm
Typical design filtrate flux range	70–150 L/m^2/h
Maximum turbidity	200 NTU
Filtrate flow	22–36 L/h
Filtrate turbidity	<0.1 NTU
Maximum SDI (15 min)	<2
Virus and bacterial removal	≥4 log
Colloidal removal	100%
TOC reduction	0–50%
Removal >200 nm particles	100%

Photocatalysis

For the photocatalysis experiments, UV light (254 nm) and nanoparticles are the important factors of the process. The catalyst used for the reaction was nZVI. The UV contact tank, which contained a UV lamp hung in the middle of the tank, and nanoparticles are the main elements of photocatalysis. The diameter and height of the tank were 25 cm and 45 cm, respectively. The length of the UV lamp was 26 cm. The schematic diagram of the UV contact tank is shown in Figure 1 and photographs of the hybrid nanofiltration photocatalysis unit are shown in Figure 2.

Operation with synthetic samples

Nanofiltration

Spiked deionized water containing 100 μg/L PFOA was used as the synthetic feed. The three operation pressures were controlled at 2, 4, and 6 bar, respectively. After that, the experiments of varied PFOA concentration at 5 and 100 μg/L were carried out with the fixed pressure operation at 6 bar.

Photocatalysis

Spiked deionized water was used as the synthetic feed. It was controlled at 100 μg/L of PFOA and the experiment focused on finding the suitable nZVI concentration. Various

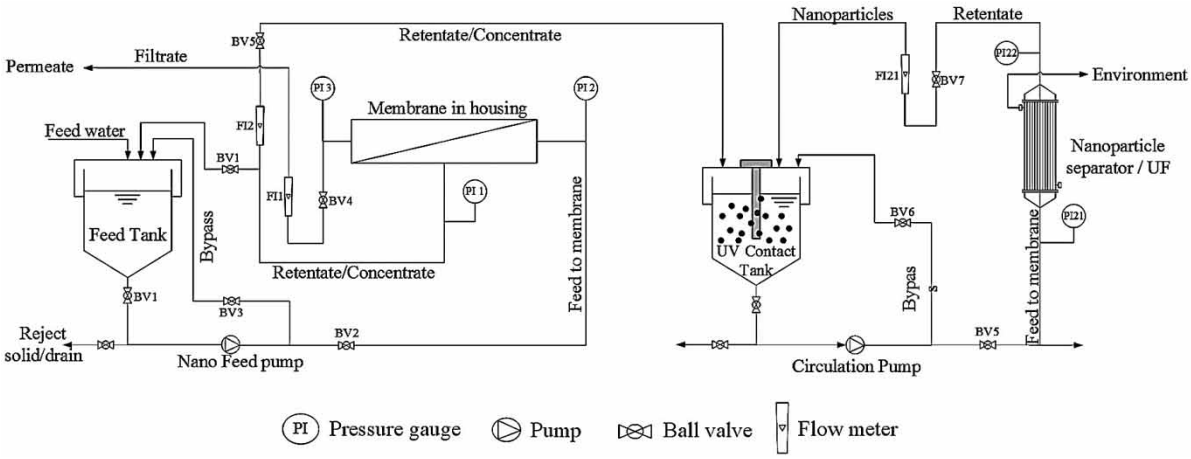

Figure 1 | Schematic diagram of hybrid membrane filtration and photocatalysis.

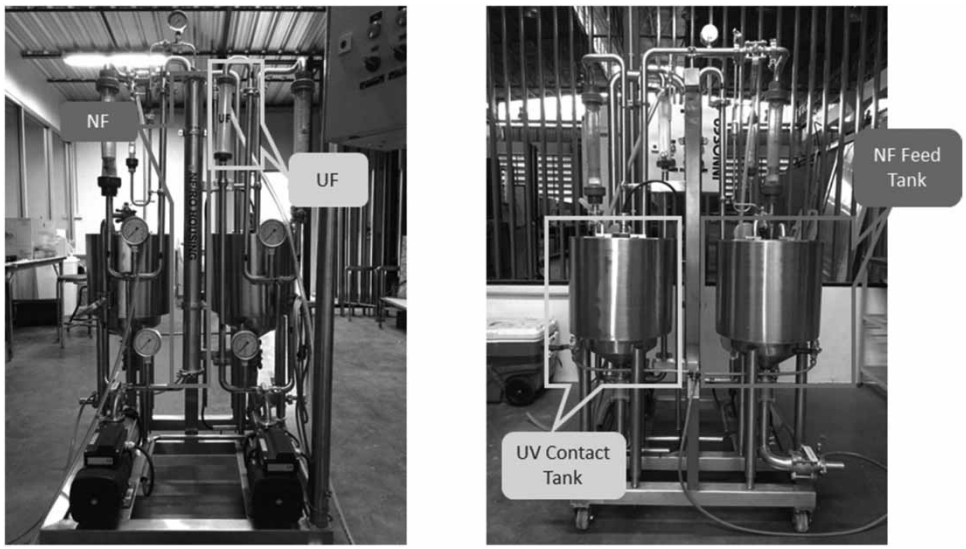

Figure 2 | The hybrid NF membrane and photocatalysis operation unit, showing the front of the unit (left) and the back of the unit (right).

nZVI concentrations were tried, i.e. 20, 40, 60, 80 and 100 mg/L, and were used in the photocatalysis for the same reaction times: 1, 5, 10, 15, 30, 45 and 60 min.

Hybrid process of nanofiltration and photocatalysis experiments

For the hybrid process of nanofiltration and photocatalysis, synthetic and groundwater samples with 100 μg/L of PFOA were used as samples for comparing the removal efficiency of nanofiltration and hybrid membrane filtration (using residual PFOA concentration to indicate the removal efficiency of nanofiltration and the hybrid process). The groundwater samples were collected near a landfill in Nakhon Pathom province, Thailand. Furthermore, the mass balance of the hybrid process is presented. The removal efficiency was calculated from the equation below.

$$\text{Removal efficiency (\%)} = \frac{(\text{influent conc.} - \text{effluent conc.}) \times 100}{\text{influent conc.}}$$

Sample collection during experiment

The samples of the synthetic and groundwater experiment were collected from NF influent (NF feed tank), NF retentate (every 8 min until the water ran out), the UV contact tank (at 1, 5, 10, 15, 30, 45, and 60 minutes), and UF retentate (at 2, 4, 6, 8, and 10 minutes). The samples collected from the UV contact tank were filtered through a 0.02 μm syringe filter for the removal of nanoparticles before being analyzed by high-HPLC-MS/MS. All samples were injected and analyzed by HPLC-MS/MS. The samples collection points of the hybrid process between the NF membrane and photocatalysis are shown in Figure 3.

Instrumental analysis

Quantification of PFOA was performed by using Agilent 1200SL HPLC (Agilent Technologies, USA) which

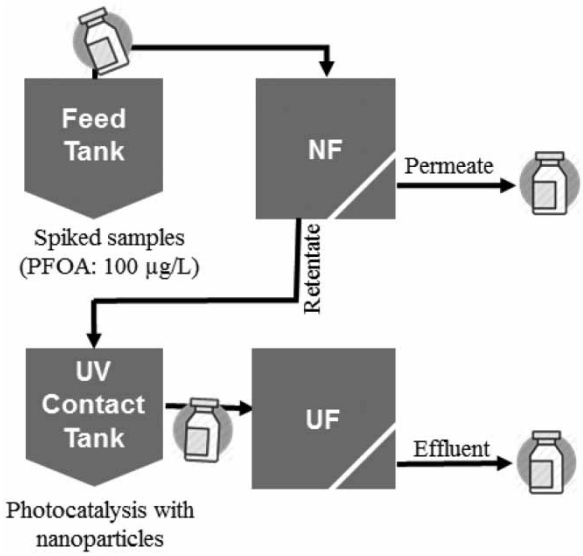

Figure 3 | The sample collection points of the hybrid process between the NF membrane and photocatalysis.

Table 3 | HPLC-MS/MS conditions for analysis of PFOA by MRM in negative ion mode (Boonya-atichart *et al.* 2016)

Compound	Precursor ion (m/z)	Product ion (m/z)	Dwell time (ms)	Collision energy (eV)	Retention time (min)	Polarity
PFOA	413	369	50	5	4.0	Negative

interfaced with an Agilent 6400 Triple Quadrupole mass spectrometer (MS/MS, Agilent Technologies, USA). The protective guard column was Agilent ZORBAX Eclipse XDB-C_{18} (4.6 × 50 mm, 1.8 μm particle size) and the series connect was with analytical column Agilent ZORBAX Eclipse Plus C_{18} (2.1 × 100 mm, 1.8 μm particle size). The column was maintained at 40 °C. For optimum separation, a binary gradient consisting of 10 mM ammonium acetate (solvent A) and acetonitrile (solvent B) was used at a flow rate of 0.25 mL/min. The elution gradient setting was: 45% (B); 0–5 min: 50%; 5–5.5 min: 60%; 5.5–10 min: 60%; 10–15 min: 90%; back to initial conditions for 10 min. The total running time was 25 min for each sample. The injection volume was 10 μL. For quantitative analysis, the mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Multiple reaction monitoring (MRM) mode was used to monitor analyte ions. Capillary voltage was 3500 V. Gas temperature and gas flow were 300 °C and 10 L/min, respectively (Boonya-atichart *et al.* 2016). HPLC-MS/MS conditions are shown in Table 3.

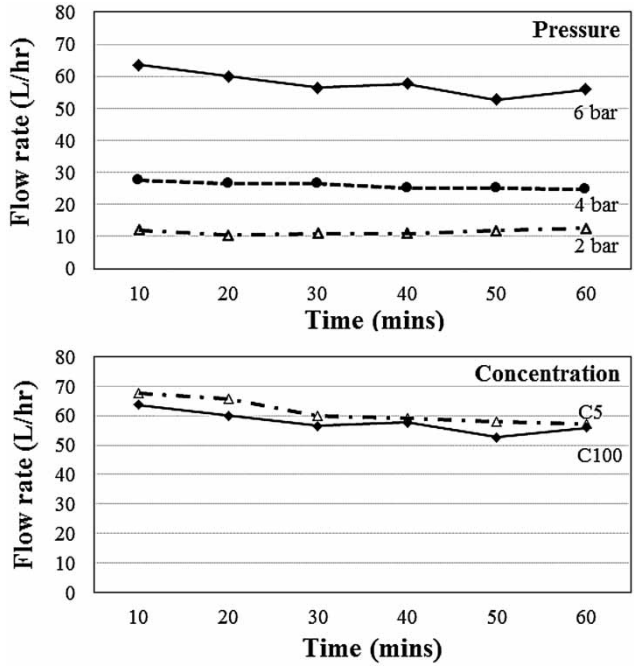

Figure 4 | The flow rate of permeate at different pressures and concentrations.

RESULTS AND DISCUSSION

Results of nanofiltration and photocatalysis tests with synthetic water

The effect of different pressures and concentrations

The effect of different pressures and concentrations of spiked deionized water samples on flow rate of the permeate in nanofiltration are shown in Figure 4. For the flow rate of the different concentrations experiment, for both the concentrations of 5 and 100 μg/L PFOA, the change was the same direction, which is that the flow rates decreased when the experiment times were increased, but not significantly. For the different pressures experiment, the results show that the pressures did affect the permeate flow rates, because higher pressures provided higher flow rates and were significant to the experimental run. So, PFOA accumulation on the membrane surface probably caused the flux decline (Tang *et al.* 2006).

PFOA removal efficiencies by nZVI concentration variation

The spiked deionized water was used as samples for finding the nZVI dosage. The PFOA removal efficiencies of nZVI concentrations at 20, 40, 60, 80, and 100 mg/L are shown in Figure 5, and were: 49.95–64.81%, 68.85–73.99%, 72.29–78.75%, 77.58–80.34%, and 80.14–84.98%, respectively. From these results, the nZVI concentration of 100 mg/L had the highest removal efficiency, in other words, when nZVI was used at the high concentration, the removal efficiency was higher than at the low nZVI concentration. According to a previous study, when the nZVI concentration modified with Mg-aminoclay (MgAc) is increased, the PFC removal efficiencies increase (Arvaniti *et al.* 2014). In this study, though nZVI was not modified with other materials, increasing the concentration still affected the removal efficiency. For the effect of reaction times of 1, 5, 10, 15, 30, 45, and 60 min on PFOA removal efficiency, Figure 5 exhibits a trend: that the nZVI reactions with the PFOA were rapid at

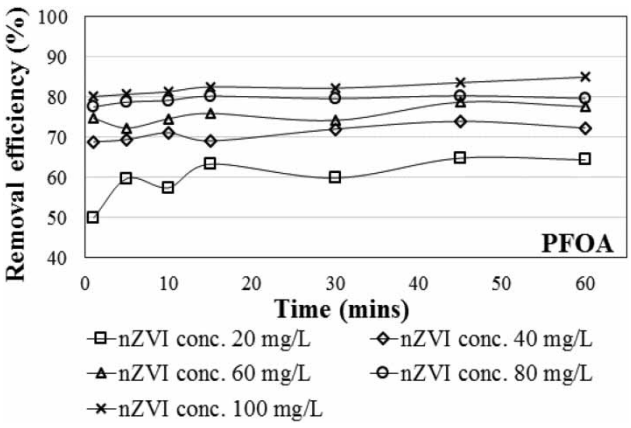

Figure 5 | The PFOA removal efficiency at different nZVI concentrations.

the 1-min reaction time, and higher but not that much higher at the 60-min reaction time. Similar to a previous study, the PFOA removal efficiency using nZVI was 92.77 ± 1.26% at 1 min of reaction time, while the removal efficiency at the reaction time of 60 min was 96.24 ± 0.94%, which was almost identical (Khatikarn 2009).

Results of hybrid nanofiltration and photocatalysis with groundwater

Nanofiltration

For the nanofiltration part of the experiment, the pressure was operated at 6 bar and the samples were collected every 8 minutes. The PFOA removal efficiencies of the spiked groundwater and deionized water samples were 98.81–99.22% and 99.15–99.94%, respectively, as shown in Figure 6. Another study found that nanofiltration could reject up to 90–99% of perfluorooctane sulfonate (PFOS), which is one of the PFCs (Tang *et al.* 2007). As the results illustrate, the spiked groundwater removal efficiency was not much different from the spiked deionized water under the same conditions, even though the removal efficiency of the spiked deionized water sample was slightly higher. This is because the co-contaminants in groundwater did not majorly affecting the PFOA removal efficiency by membrane filtration, while the removal efficiency of membrane filtration depends on the size of pollutants and membrane pore size.

Photocatalysis

For the photocatalysis part of the experiment, the feedwater samples were sent from the rejected part of nanofiltration to the UV contact tank. In Figure 7, the results show the PFOA removal efficiencies of the spiked groundwater and deionized water samples were 58.72–62.09% and 72.07–75.83%, respectively, making PFOA removal efficiency for the spiked deionized water samples higher than for the spiked groundwater samples. This is because the co-contaminants in groundwater reacting with easily degradable organic compounds beforehand.

Even though the removal efficiencies of the spiked deionized water sample were higher than those of the spiked groundwater sample, nevertheless the removal efficiency still was low, due to the UV contact tank not having a mixer for mixing nanoparticles. The fact that the UV light bulb was only in the middle of the tank might not have been good enough, so it could be another cause of the low efficiency of the photocatalysis. These points should be considered in a further study. The previous study which

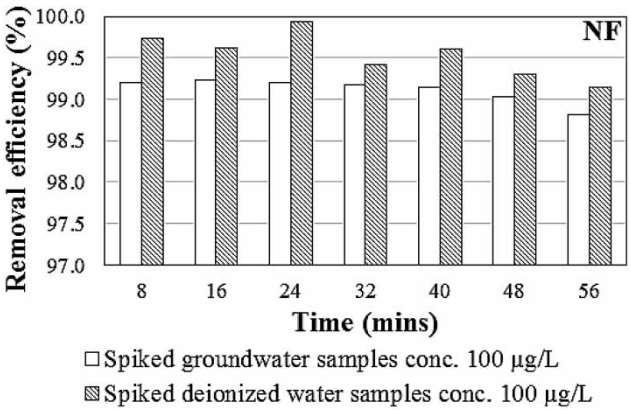

Figure 6 | The PFOA removal efficiencies of spiked deionized water samples and spiked groundwater samples by nanofiltration in the hybrid membrane system.

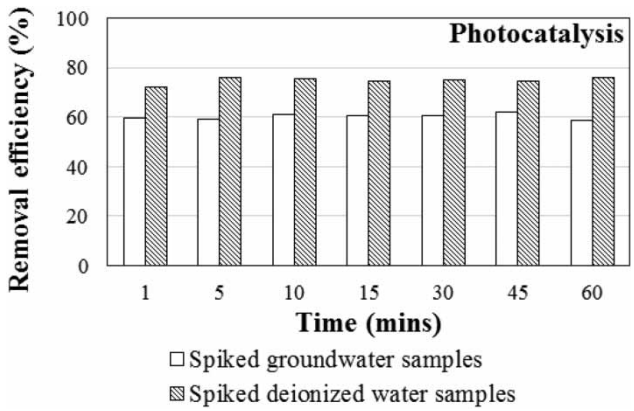

Figure 7 | The PFOA removal efficiencies of spiked deionized water samples and spiked groundwater samples by photocatalysis in the hybrid membrane system.

investigated the combined process of photocatalysis and ozonation ($UV/TiO_2/O_3$) found the PFOA degradation efficiency was 99.1% after 4 hours' reaction time (Huang *et al.* 2016). Besides, the size of this experiment was a pilot-scale project, and scaling up the experiment to batch from pilot scale might decrease the removal efficiency even if the operating conditions are controlled. According to our previous study in batch scale, the PFOA removal efficiency of spiked deionized water by nZVI photocatalysis reached 80.14–84.98% (Boonya-atichart 2017).

Mass balance in hybrid nanofiltration membrane and photocatalysis

The mass balance of the hybrid nanofiltration and photocatalysis process was determined to discover the fate of mass when the contaminants were treated by the hybrid nanofiltration and photocatalysis operation unit, to show the outcome of the improved system. The average PFOA concentration was multiplied by the water sample volume for determining the mass of PFOA. The water sample volume was calculated from the flow rate in each part of the operation unit. The actual flow rates were measured on the experimental run day. The PFOA mass was calculated from the following equation:

$$\text{Mass } (\mu g) = \text{volume of water sample } (L) \times \text{average concentration } (\mu g/L)$$

The volume and concentration of the test system are presented in Figure 8. The volume of the water samples in the NF feed tank, permeate, retentate, and UF effluent were 34 L, 14.47 L, 19.53 L, and 19.53 L, respectively. The PFOA average concentration in the NF feed tank, permeate, retentate, and UF effluent were 98 μg/L, 0.87 μg/L, 169.96 μg/L, and 58.40 μg/L, respectively, as shown in Figure 8. For the retentate, the water sample volume and PFOA concentration of all rejected parts were 19.53 L and 169.96 μg/L, respectively, for which the PFOA concentration after photocatalysis (in the UV contact tank) was 68.60 μg/L. After calculating the mass in each part, the mass balance of the system was calculated and shown as percentages in Figure 9 based on the calculation by the following equation:

$$\text{Percentage of each part} = \left(\frac{\text{mass in each part}}{\text{mass of NF feed tank}}\right) \times 100$$

As shown in Figure 9(b), at the NF feed tank before treatment by the nanofiltration membrane, the mass of PFOA was 100% and after treatment by the nanofiltration membrane, the residual of PFOA in permeate was 0.38% and the rejected part sent to the UV contact tank was 99.62%. In the photocatalysis part, the mass of PFOA after treatment by photocatalysis was 40.21%, so the PFOA that was degraded by photocatalysis was 59.41% and the average removal efficiency of photocatalysis was up to 59.64%. Then the sample was sent to the ultrafiltration membrane for removing the nanoparticles before releasing the treated water to the environment. The mass of PFOA released to the environment was 34.23%; thus, 5.98% of PFOA was trapped by the ultrafiltration membrane.

The comparison between the nanofiltration system (Figure 9(a)) and the hybrid membrane system (Figure 9(b)) shows the difference in the amounts of contaminants that were released to environment from each system. For the nanofiltration system, up to 99.62% of the contaminants

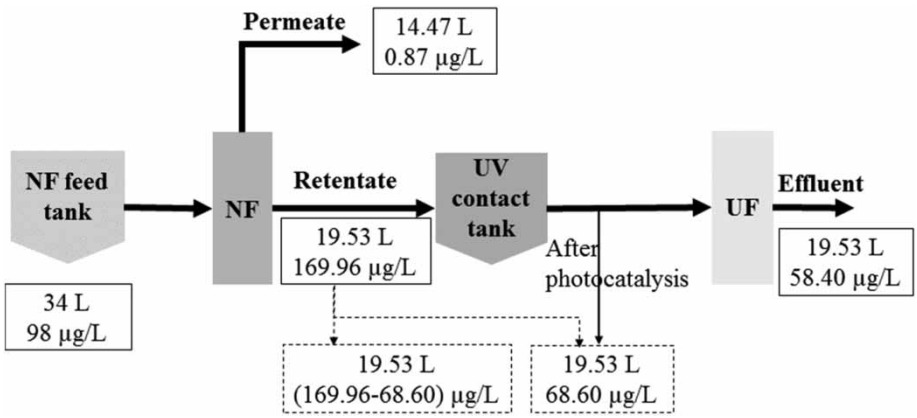

Figure 8 | Volume and concentration of water samples of the hybrid membrane system.

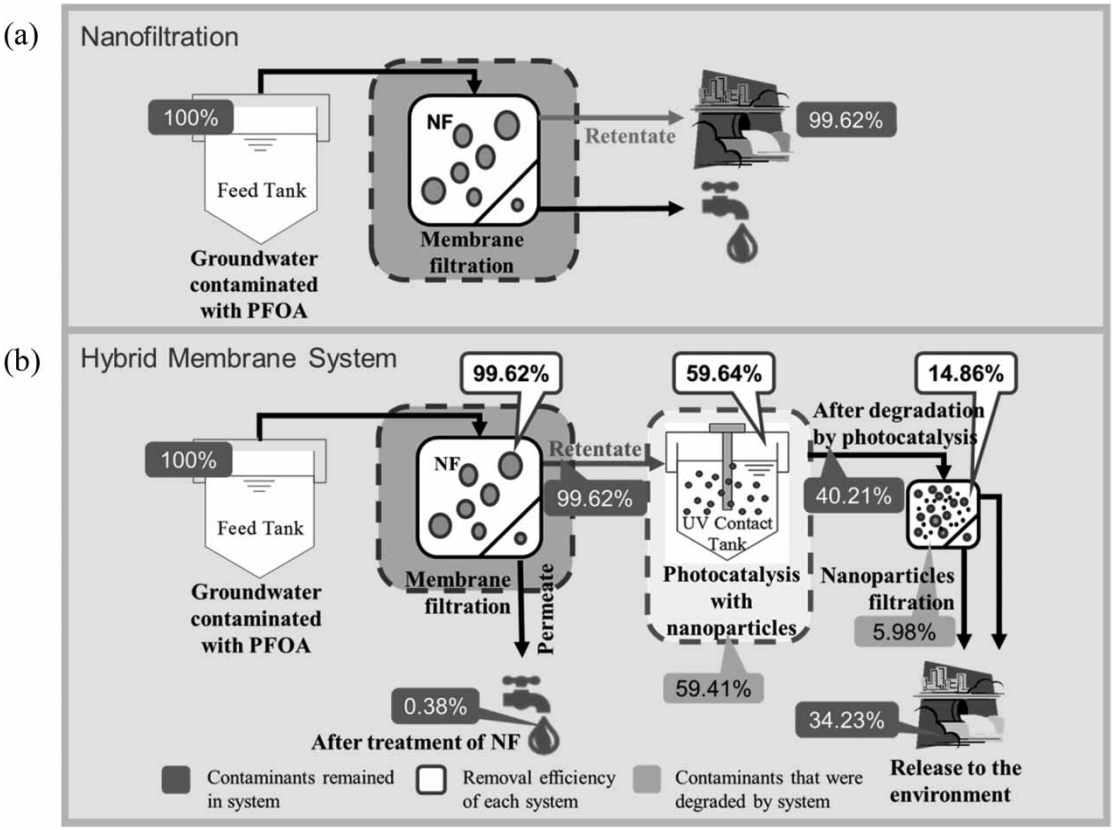

Figure 9 | Comparison of mass balance and removal efficiencies: (a) conventional membrane filtration and (b) hybrid membrane system.

were released to the environment after being treated by nanofiltration. In contrast, the results of the hybrid membrane system show that some concentrated PFOA after filtration was degraded by using photocatalysis, so that the toxic chemical that was removed before being released to the environment was just 34.23%, which is significantly lower than nanofiltration only.

CONCLUSIONS

The hybrid membrane filtration and photocatalysis system was tested with PFOA. The transmembrane pressures and PFOA accumulation on the membrane surface probably caused the flux decline. Moreover, the nZVI reactions with the PFOA were rapid at the 1-minute reaction time. The combination of membrane filtration and photocatalysis not only removed the PFOA from the water, but also degraded the contaminant released to the environment to a level at least three times lower, based on this study. Therefore, this new hybrid membrane system will be beneficial for reducing the release of rejected contaminants to the environment, and will strengthen the productive use of membrane technology. The concept of hybrid membrane filtration and photocatalysis has been shown to be an environmentally friendly system, and should be studied further for exploring aspects such as fouling effects, energy consumption, and operating costs in a long-term pilot run.

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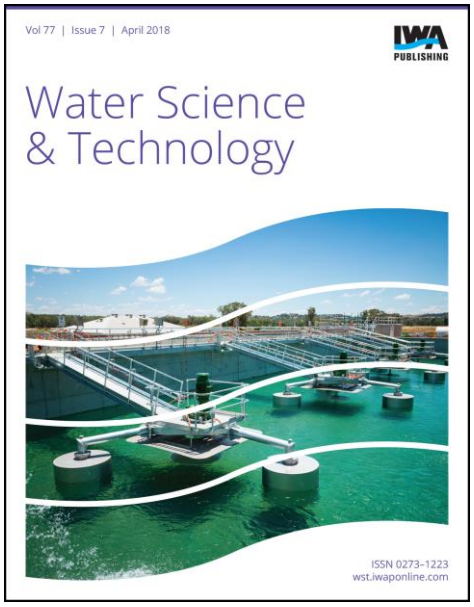

Levels of perfluorinated compounds (PFCs) in groundwater around improper municipal and industrial waste disposal sites in Thailand and health risk assessment

Chanidaporn Hongkachok, Suwanna Kitpati Boontanon, Narin Boontanon, Shigeo Fujii, Shuhei Tanaka and Yuji Suzuki

ABSTRACT

The aims of this study were to examine the levels of perfluorinated compounds (PFCs) in groundwater around improperly developed municipal and industrial waste disposal sites, including estimating non-cancer risk and cancer risk from ingestion of the groundwater. A total of 27 groundwater samples were collected from two cities in Thailand, Ayutthaya and Chonburi. Seven target compounds were extracted by solid phase extraction (SPE) and analyzed by high-performance liquid chromatography–tandem mass spectrometer (HPLC–MS/MS). The results showed that the total PFCs in groundwater around municipal waste disposal sites (MWDSs) varied from 1.68 to 7.75 ng/L. In groundwater around the industrial waste disposal site (IWDS), total PFCs varied from 2.64 to 42.01 ng/L, which were significantly different from those found in groundwater around the MWDSs at $p < 0.01$. PFOS and PFOA were ubiquitous in both areas, while perfluorohexane sulfonate (PFHxS) was frequently found in the samples around IWDS. The findings possibly suggest that PFHxS has been introduced for use as an alternative substance for most current C8 and higher due to it having shorter chain length and shorter half-lives. The results for both non-cancer risk and cancer risk in all samples were acceptable.

Key words | groundwater, health risk assessment, perfluorinated compounds, Thailand, waste disposal sites

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INTRODUCTION

Perfluorinated compounds (PFCs) are anthropogenic chemicals which were first synthesized in the early 1940s and nowadays are being massively reported in all environments in term of concentrations, sources of contamination, and implications. The most prevalent ones are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Due to their unique characteristics: stability, surfactivity, hydrophobicity, and lipophobicity; they have been commonly used in a variety of consumer products, e.g. textiles and leather, metal plating, paper and packaging, coating additives, cleaning products, and pesticides (Prevedouros *et al.* 2006). Besides their useful properties, their persistency, toxicity and bioaccumulative nature have caused many environmental and human health problems (Jahnke & Berger 2009). Some researchers have revealed that exposure to PFCs may affect the reproductive function in women and cause thyroid disease in the general public (Knox *et al.* 2011; Melzer *et al.* 2010). Aquatic environments are potentially expected to be their sink disposal in the environment because of their high water solubility and low volatility. Therefore, they are frequently detected in wastewater, drinking water, tap water, surface water, and groundwater.

Groundwater is an important freshwater resource in rural areas in Thailand because it is fresh and clean water that is easily extracted. However, groundwater pollution may not be avoidable owing to there being many potential sources, especially improperly developed waste disposal sites. Furthermore, in Thailand, landfill burning has been occurring often in dumps set up for illegal disposal of garbage, especially involving toxic waste. In addition, over 50% of industrial waste is not being properly treated, but is illegally dumped at legal and illegal landfills. These sites

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are suspected to be important sources of PFCs contamination. Other suspected sources of contamination could be leachate from landfills near groundwater wells. The study of trace elements such as PFCs in Thailand's groundwater has been limited. Therefore, it was necessary to undertake such a study in order to provide information for further study and for developing environmental standards and regulation. This study aimed to analyze and compare the existence of PFCs in groundwater around municipal waste disposal sites (MWDSs) and an industrial waste disposal site (IWDS), as well as estimate health risks of non-carcinogenic and carcinogenic effects from drinking groundwater.

MATERIALS AND METHODS

Standards and reagents

In this study, there are seven PFCs standards: perfluorohaptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS) were selected. Methanol HPLC grade (>99.99%) and methanol ACS grade, acetonitrile HPLC grade (>99.8%), and ammonium acetate (98%) were purchased from Merck KGaA (Millipore, Germany). Ultrapure water was produced by a RiOs-DI® Water Purification System (Millipore, Germany). Potassium Hydrogen Phthalate (KHP) was used to prepare a standard curve for dissolved organic carbon (DOC) analysis.

Sampling sites and sample collection

Study areas in this work were based on information obtained from the Department of Groundwater Resources (DGR 2015) and Pollution Control Department (PCD) of Thailand. The sampling points were chosen in two cities in Thailand, which were reported to have a large amount of accumulated waste; the maps are shown in Figure 1. The groundwater samples were collected from domestic groundwater wells around Bang Chai MWDS (Figure 1, 1(a)) and Sena MWDS (Figure 1, 2(a)), Ayutthaya province ($n = 12$) and Map Phai IWDS (Figure 1(b)), Chonburi province ($n = 15$). The samples were directly collected from faucets connected to the groundwater well and pumping system by using PET

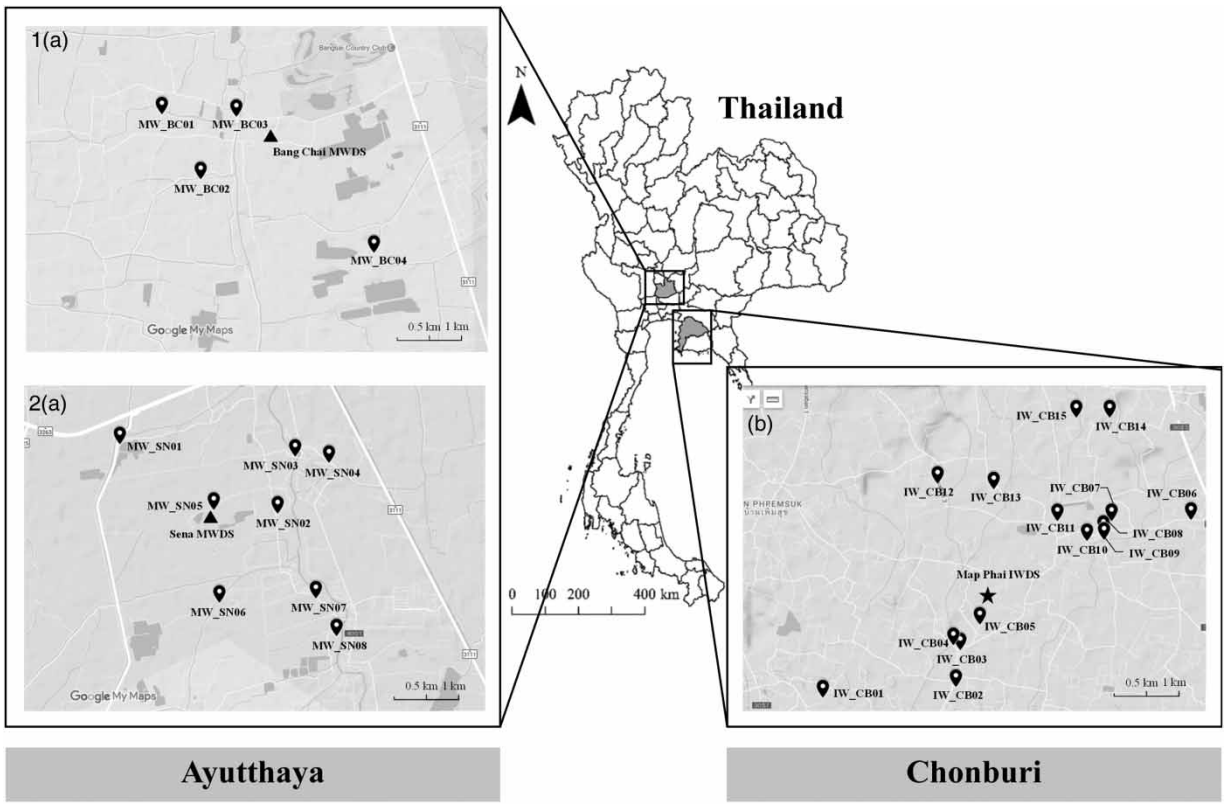

Figure 1 | Illustration of study areas: municipal waste disposal sites (1a and 2a) and industrial waste disposal site (b) and groundwater sampling points.

bottles with screw caps, which were rinsed with methanol and dried prior to use. The containers were rinsed by the water samples three times to prepare the same conditions as the samples before collection. After sampling, the samples were stored in a cooler box and brought back to the Water Quality Analysis Laboratory, Mahidol University. The samples were filtered by GF/B glass filter. Glass bottles and glass equipment were avoided during the experiment because target compounds may bind to the glass in aqueous solutions. Teflon equipment was also avoided because interferences may be introduced to the samples of extracts (Hansen *et al.* 2002; Yamashita *et al.* 2004).

Sample extraction and PFC analysis

PFCs were extracted by solid phase extraction (SPE) technique. SPE has become a more popular sample preparation compared to liquid–liquid extraction (LLE) and has been applied in many studies. The reasons that it has surpassed LLE is low consumption of organic solvents and ease of operation (Zhao *et al.* 2007). A 1,500 mL water sample was filtered into PrecepC-Agri (C18) cartridges using concentrators at a flow rate of 10 mL/min. Before loading, the concentrators were washed by methanol at a flow rate of 10 mL/min for 5 min, followed by milli-Q water at a flow rate of 10 mL/min for 10 min and the cartridges were preconditioned by 10 mL of methanol, followed by two times of 10 mL milli-Q water. After that, target analytes were eluted by 4 mL of methanol, followed by 2 mL of acetonitrile. Eluents were gently purged by nitrogen gas and reconstituted with 0.5 mL of 30% acetonitrile. Analysis of target PFCs was performed by using Agilent 1200SL HPLC. The target compounds were quantified using Agilent 6400 MS/MS, in negative mode of electrospray ionization. The analytical parameters are listed in Table 1. Mobile phases consisted of (A) 10 mM ammonium acetate in ultrapure water and (B) 100% acetonitrile (HPLC/MS grade). The initial mobile phase was 30% acetonitrile, and then ramped up to 60% acetonitrile at 16.5 min, and kept for 3.5 min. At 23 min, acetonitrile went up to 70%, and then linearly ramped up from 70% to 90% at 26 min. After that, the mobile phase gradient ramped down again to 30% acetonitrile for 4 min. The total running time was 30 min.

Quality assurance

Five points of a calibration curve covering 0.1 to 10 μg/L were prepared with the regression coefficient (R^2) > 0.999.

Table 1 | The analytical parameters by HPLC-MS/MS analysis

Compound	No. of Carbon	Parent ion (m/z)	Daughter ion (m/z)	Retention time (min)
PFHpA	C7-A	363	319	10.6
PFOA	C8-A	413	369	13.9
PFNA	C9-A	463	419	16.4
PFDA	C10-A	513	469	20.7
PFUnA	C11-A	563	519	22.8
PFHxS	C6-S	399	80	15.0
PFOS	C8-S	499	80	22.2

Note: A, perfluorinated carboxylic acids (PFCAs); S, perfluorinated sulfonic acids (PFSAs).

Limit of detection (LOD) and limit of quantification (LOQ) of the measurement method were defined as the concentration with signal-to-noise ratios (S/N) equal to 3:1 and 10:1, respectively. Recovery experiments were done by spiking 10 μg/L of each PFC standards into the samples before the extraction process. A blank sample using Milli-Q water was prepared and analyzed with the same procedure as the spiked samples. The recoveries of the seven PFCs in groundwater matrix were 95.9 ± 2.86% for PFHpA, 106.94 ± 7.14% for PFOA, 99.02 ± 1.81% for PFNA, 91.36 ± 3.39% for PFDA, 83.82 ± 7.06% for PFUnA, 100.87 ± 1.69% for PFHxS, and 93.16 ± 4.74% for PFOS, which are displayed in Table 2.

Dissolved organic carbon analysis

Five points of a standard curve were prepared by potassium hydrogen phthalate (KHP). A 25 mL of water sample was filtered by 1 μm GF/B glass fiber filter coupled with vacuum filtration apparatus. Then, the DOC was automatically analyzed by a total organic carbon analyzer (TOC-VCSH/ASI-V/SSM-5000A, Shimadzu, Japan) using the non-purgeable organic carbon (NPOC) method.

Statistical analysis

A difference of mean PFC levels in the groundwater around the MWDSs and the IWDS was analyzed by the independent sample *t*-test using IBM® SPSS® Statistics 20 to illustrate whether there was significance. Correlations between DOC and individual PFCs concentrations were performed by Pearson Product Moment.

Table 2 | Recovery rates of PFCs in groundwater samples

	Recovery rates (%)						
Quintuplicate	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnA**	**PFHxS**	**PFOS**
1	92.19	102.74	98.52	94.20	88.14	103.80	99.72
2	97.88	106.75	97.18	87.65	73.26	99.73	89.95
3	95.88	118.56	98.12	87.66	83.02	100.11	88.04
4	94.16	106.90	99.37	93.50	82.65	99.86	91.99
5	99.38	99.77	101.94	93.80	92.02	100.87	96.12
Average	95.90	106.94	99.02	91.36	83.82	100.87	93.16
Minimum	92.19	99.77	97.18	87.65	73.26	99.73	88.04
Maximum	99.38	118.56	101.94	94.20	92.02	103.80	99.72
SD	2.86	7.14	1.81	3.39	7.06	1.69	4.74

SD, standard deviation.

Health risk assessment

Health risk assessment has been considered as the probability of harmful effects to human health resulting from exposure to chemical contaminants. Ever since PFCs have become new emerging contaminants, several countries have developed standard criteria to promote an acceptable level of PFCs that humans can be exposed to without any adverse effects. However, no PFC levels were ever recommended in Thailand, therefore, the thresholds and input parameters for assessment in this study were derived from the United States Environmental Protection Agency (US EPA) model and information provided by the New Jersey Department of Environmental Protection (US EPA 2011, 2016a, 2016b; NJDEP 2015). The baseline information for the parameters are provided in Table 3.

Table 3 | The input parameters for health risk assessment

Parameter	**Description**	**Value**	**Unit**
RfD for PFOA	Reference dose	0.00002	mg/kg/day
RfD for PFNA	Reference dose	0.00000074	mg/kg/day
RfD for PFOS	Reference dose	0.00003	mg/kg/day
IR_{oral}	Intake rate	1.043	L/day
EF	Exposure frequency	365	days/year
ED	Exposure duration	70	years
BW	Body weight	70	kg
AT	Average time	$365 \times ED$	day
CSF for PFOA	Cancer slope factor	0.07	mg/kg/day

Calculation of PFCs daily intake

The magnitude of the chemical exposures, typically represented as the contaminant daily intake (CDI), was estimated from frequency and duration of human exposure over a lifetime, as shown in Equation (1) for the parameters in the risk assessment.

$$CDI_{oral} = \frac{(C_{water} \times IR_{oral} \times EF \times ED)}{BW \times AT} \quad (1)$$

where CDI_{oral}, C_{water}, IR_{oral}, BW, and AT represent chronic daily intake (mg/kg/day), concentration of PFCs in groundwater (ng/L), intake rate (L/day), body weight (kg), and averaging time (day), respectively.

Risk characterization

Typically, the health risk can be expressed in terms of a non-carcinogenic risk and a carcinogenic risk.

The non-carcinogenic risk

The non-carcinogenic risk was determined from CDI and reference dose (RfD) to produce a hazard quotient (HQ). The HQ is the ratio of exposure of hazardous chemicals and their reference dose (RfDs) (Equation (2)), if the HQ value is equal to or less than one, the risk is not considered significant to human health.

$$HQ = \frac{CDI}{RfD} \quad (2)$$

where HQ is the hazard quotient (unit-less), CDI is the chronic daily intake (mg/kg/day), and RfD is a reference dose.

The carcinogenic risk

The carcinogenic risk was estimated through multiplying the CDI by cancer slope factor (CSF), given in Equation (3). CSF represents a probability of developing cancer during an individual lifetime. The carcinogenic risk which does not exceed 10^{-6} has been accepted. This benchmark was adopted by the US EPA (US EPA 2000) and is commonly used worldwide.

$$\text{Carcinogenic risk} = \text{CDI} \times \text{CSF} \quad (3)$$

where CDI is the chronic daily intake (mg/kg/day) and CSF is cancer slope factor (mg/kg/day).

RESULTS AND DISCUSSION

PFCs concentrations and their distributions in groundwater around the municipal waste disposal sites (MWDSs) and industrial waste disposal site (IWDS)

As can be seen in Figures 2, 1(a) and 2(a), six of the seven PFCs were detected in groundwater around the MSWDs, which were PFHpA, PFOA, PFNA, PFUnA, PFHxS, and PFOS; however, PFHxS was found in only one sample at a very low level. PFDA was absent from any of the groundwater around the MWDSs. The total PFC levels in the samples around the MWDSs varied from 1.68 ng/L to 7.75 ng/L. Among them PFOA and PFOS were outstanding. PFOA made major contributions that ranged from 21.84% up to 80.20%, followed by PFOS (8.78% to 78.16%), PFHpA (11.52% to 21.36%), PFUnA (6.37% to 20.21%), PFNA (4.65% to 21.68%), and the remainder was PFHxS (1.64%). Figure 2, 1(b) and 2(b) show the PFCs concentrations and their distribution profiles in groundwater around the IWDS, in which all the PFCs compounds were measured. The total PFCs around the IWDS was quantified at concentrations of 2.64 ng/L to 42.01 ng/L, which were much higher than those around the MWDSs. Similar to those found in the groundwater around MWDSs the prevalent ones were PFOA and PFOS. PFOA showed the highest distribution in groundwater around IWDS with a frequency that ranged from 23.71% to 86.75%, followed by PFOS (7.77% to 68.75%), PFHpA (1.46% to 16.10%), PFNA (1.09% to 14.04%), PFHxS (0.31% to 12.64%), PFUnA (0.68% to 10.42%), and PFDA (0.62% to 5.41%), respectively. In addition to PFC variations in the groundwater, this could be mainly influenced by leachate components and properties which resulted from many factors such as rain input, waste arrangement, waste filling procedure, age and waste composition, etc. (Eschauzier *et al.* 2013; Yan *et al.* 2015).

Besides the concentration, PFHxS was frequently observed in the samples around IWDS, which might indicate that it has been used as an alternative substance to long-chain perfluorinated compounds in industrial processes due to it having a shorter chain length, or it might be from the degradation product of other alternative compounds such perfluorohexane sulfonyl fluoride (PHxSF, $C_6F_{13}SO_2F$)-based and their derivatives (Wang *et al.* 2013). The statistical analysis result indicates that the difference between the total PFCs concentrations in groundwater around the MWDSs and the IWDS was statistically significant at $P < 0.01$. However, this was not a big surprise. It is similar to the previous research, which reported that high PFCs concentrations were found in the industrial wastewater treatment plant effluent compared to the municipal wastewater treatment plant effluent in Taiwan (Lin *et al.* 2010). Additionally, the contamination of PFCs in groundwater in this study were found to be higher than the concentrations in tap water as well as river water in Thailand reported in previous studies (Kunacheva 2009; Kunacheva *et al.* 2009; Boontanon *et al.* 2012).

Comparison of PFCs contaminations in groundwater in this study and those from other countries

Table 4 shows the concentration ranges of PFCs in groundwater around the MWDSs and IWDS compared to those found in other countries. When compared to the levels found in other studies, PFHpA and PFHxS detected in this study were comparable to, while PFOA, PFNA and PFOS were quite higher compared to those previously reported in Vietnam. The PFCs concentrations in Japan and China groundwater were reported in greater quantity than this study. Surprisingly, the study in Tokyo, Japan reported that high PFCs concentration in groundwater was caused by pollution from street runoff and a leaking sewer pipe (Murakami *et al.* 2009). Extremely high PFC levels in groundwater were detected around a fire-training area in Northern Michigan, USA. The groundwater contained various PFCs concentrations in the μg/L level, even 5 years after fire-training had last been conducted at that site

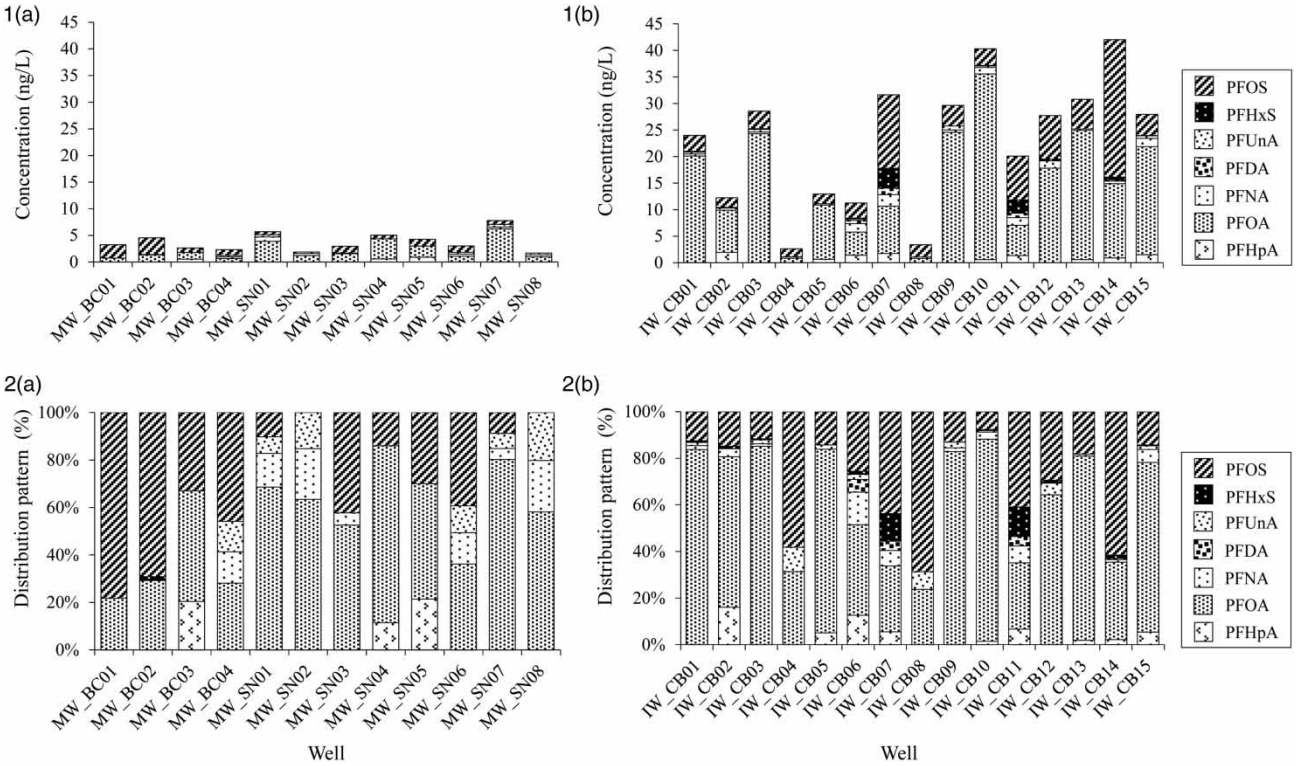

Figure 2 | Total PFCs concentrations (1a and 1b) and their distribution profiles (2a and 2b) in groundwater around the MWDSs and the IWDS, respectively.

Table 4 | Comparison of PFCs contaminations (ng/L) in groundwater in this study and those from other countries

Study location	PFHpA	PFOA	PFNA	PFHxS	PFOS	Reference
Thailand						
Around MWDSs, Ayutthaya	<LOQ-0.91	0.65–6.22	N.D.-0.80	N.D.-0.07	<LOQ-3.15	This study
Around IWDS, Chonburi	N.D.-1.98	0.80–34.96	N.D.-2.14	N.D.-3.73	1.39–25.88	This study
Vietnam						
Hanoi	N.D.-1.3	N.D-2.5	N.D-0.45	N.D.	N.D.-0.64	Duong *et al.* (2015)
Ho Chi Minh	N.D.-0.58	N.D.-4.5	N.D.-0.36	N.D.-6.0	N.D.-8.2	Duong *et al.* (2015)
Japan						
Tokyo	0.47–60	<0.1–20	0.1–94	N.A.	0.28–133	Murakami *et al.* (2009)
China						
Eastern China	<0.5–99.7	<0.1–475	<0.1–22	<0.5–1.9	<0.5–94.9	Chen *et al.* (2016)
USA						
San Jose, California	N.D.-8.1	N.D.-28	N.A.	N.D.-17	19–192	Plumlee *et al.* (2008)
Michigan	N.A.	N.D.-105,000	N.A.	9,000–120,000	4,000–110,000	Moody *et al.* (2003)
The Netherlands						
The central part	<LOQ-320	0.5–1,800	<LOQ-0.1	<LOQ-99	N.A.	Eschauzier *et al.* (2013)

MWDS, represents municipal waste disposal site; IWDS, represents industrial waste disposal site; N.A., represents not analyzed; N.D., represents not detected; <LOQ, represents less than limit of quantification.

(Moody *et al.* 2003). A study in the Netherlands showed the PFCs concentration was much higher than detected in this study. They found that PFCs contamination in groundwater had originated from a former landfill, a military camp, and an urban area (Eschauzier *et al.* 2013) similar to those findings in the USA and Sweden. Those studies indicated that high PFC levels were observed in urbanized and industrialized areas which strongly support the results of this study.

Relationship between PFCs concentrations and DOC concentrations

When considering the total PFCs in groundwater and DOC, which is presented in Figure 3, the relationship between total PFCs and DOC showed a direct variation. It should be noticed that in the sampling points where higher PFC levels were observed, DOC levels were also found to be higher in those samples. This could be significant evidence to support the hypothesis that the groundwater has been contaminated by the waste disposal sites, particularly the IWDS due to industrial activity and manufacturing processes, suggesting that industrial waste disposal plays an important role in PFCs contamination in groundwater.

Due to a long-term leaching behavior as well as the complexity of PFCs movement, the mobility and contamination of PFCs is not only dependent on their physical–chemical properties, but also their associations with solution-specific properties such as organic carbon content. Statistically positive correlations between DOC and concentration of some PFCs compounds were observed, high correlations ($P < 0.01$) were found for PFNA ($r = 0.610$) and PFDA ($r = 0.606$). A moderate correlation ($P < 0.05$) was found for PFHpA ($r = 0.478$), while a non-statistically significant and small correlations were found for PFOA ($r = 0.241$), PFUnA ($r = 0.034$), PFHxS ($r = 0.087$), and PFOS ($r = 0.107$). Similar findings have been previously reported by Gallen *et al.* (2017), where significant correlations between PFCs and organic carbon were also found. This is consistent with the association between hydrophobicity properties and the potential of hydrophobic partitioning with organic carbon. The sorption of PFCs to natural sediments is highly influenced by sediment-specific parameters, in which the organic carbon content resulted from the importance of hydrophobic interactions (Higgins & Luthy 2006). Since PFCs are hydrophobic and lipophobic, they could interact with the hydrophilic surface of minerals and be absorbed. Therefore, this could be one factor contributing to the PFCs concentrations in a water environment.

Human health risk assessment

Although, those PFC levels did not exceed the health advisory levels for drinking purpose (70 ng/L for individual PFOA and PFOS or combined) (US EPA 2016a, 2016b), the long term consumption of the groundwater without any water treatment may cause unexpected adverse effects. Therefore, evaluation of health risk is necessary to ensure whether consumption of this water is safe.

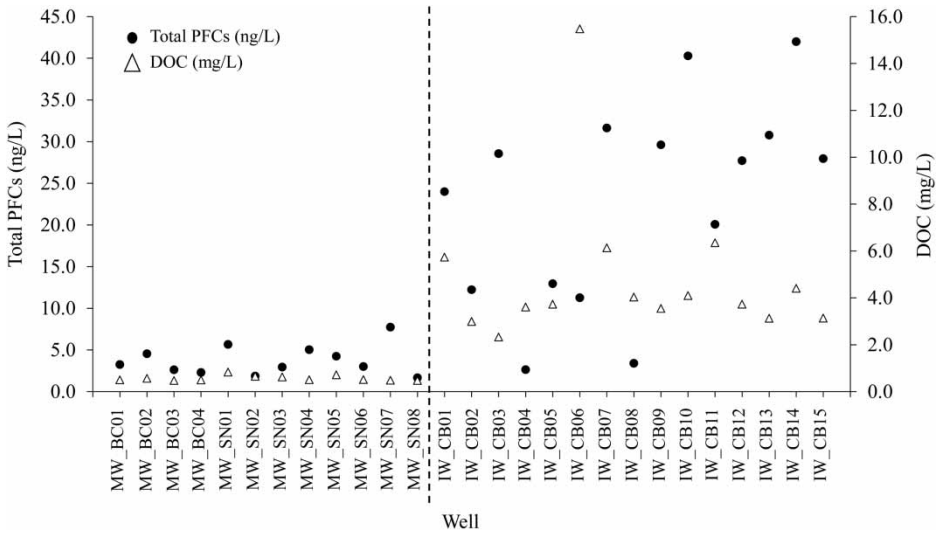

Figure 3 | Comparison of total PFCs around the MWDSs and IWDS relative to DOC.

As mentioned above, health risk assessment was estimated only for exposure by drinking, although the water has been being consumed for showering; but in the general population, dermal absorption of PFCs is extremely slow and not a significant exposure pathway (US EPA 2016c; NCEH 2017). Table 5 shows the estimation of non-cancer risk and cancer risk of PFOA, PFNA, and PFOS from drinking groundwater. The non-carcinogenic risk was represented by the HQs which were calculated by the total daily intake and RfDs. There is no instance in which the combined HQ for non-cancer risk of those samples exceeded one, which means the risks were all acceptable. It could be concluded that they were observed as having less potential for non-carcinogenic toxicity.

In terms of the carcinogenic risk, it has only been focused on PFOA because of limited CSF data. The estimated carcinogenic risks of all samples were lower than 10^{-6} (benchmark level), so the risks were all acceptable; suggesting that drinking the groundwater might not induce an unexpected cancer risk, nor would it increase the probability of developing cancer during a person's lifetime.

Table 5 | Estimation of non-cancer risk and cancer risk of PFOA, PFNA, and PFOS from drinking groundwater

				Non-carcinogenic risk						Carcinogenic risk		
	CDI (mg/kg/day)			HQ				Concern			Concern	
Sample	PFOA	PFNA	PFOS	PFOA	PFNA	PFOS	ΣHQ	Yes	No	Cancer risk[a]	Yes	No
MW_BC01	1.06E-08	–	3.78E-08	0.0005	–	0.0019	0.0024		\	7.40E-10		\
MW_BC02	1.98E-08	–	4.69E-08	0.001	–	0.0023	0.0033		\	1.39E-09		\
MW_BC03	1.83E-08	–	1.29E-08	0.0009	–	0.0006	0.0016		\	1.28E-09		\
MW_BC04	9.68E-09	–	1.58E-08	0.0005	–	0.0008	0.0013		\	6.77E-10		\
MW_SN01	5.80E-08	1.20E-08	8.66E-09	0.0029	0.0162	0.0004	0.0195		\	4.06E-09		\
MW_SN02	1.77E-08	5.95E-09	–	0.0009	0.008	–	0.0089		\	1.24E-09		\
MW_SN03	2.31E-08	–	1.86E-08	0.0012	–	0.0009	0.0021		\	1.62E-09		\
MW_SN04	5.60E-08	–	1.06E-08	0.0028	–	0.0005	0.0033		\	3.92E-09		\
MW_SN05	3.08E-08	–	1.90E-08	0.0015	–	0.0009	0.0025		\	2.16E-09		\
MW_SN06	1.63E-08	5.90E-09	1.76E-08	0.0008	0.008	0.0009	0.0097		\	1.14E-09		\
MW_SN07	9.26E-08	5.38E-09	1.01E-08	0.0046	0.0073	0.0005	0.0124		\	6.48E-09		\
MW_SN08	1.45E-08	5.42E-09	–	0.0007	0.0073	–	0.0081		\	1.02E-09		\
IW_CB01	3.00E-07	5.82E-09	4.47E-08	0.015	0.0079	0.0022	0.0251		\	2.10E-08		\
IW_CB02	1.18E-07	6.42E-09	2.70E-08	0.0059	0.0087	0.0013	0.0159		\	8.24E-09		\
IW_CB03	3.62E-07	4.63E-09	4.96E-08	0.0181	0.0063	0.0025	0.0268		\	2.54E-08		\
IW_CB04	1.23E-08	–	2.29E-08	0.0006	–	0.0011	0.0018		\	8.63E-10		\
IW_CB05	1.52E-07	–	2.76E-08	0.0076	–	0.0014	0.009		\	1.07E-08		\
IW_CB06	6.52E-08	2.36E-08	4.29E-08	0.0033	0.0319	0.0021	0.0373		\	4.57E-09		\
IW_CB07	1.33E-07	3.19E-08	2.06E-07	0.0066	0.0431	0.0103	0.06		\	9.29E-09		\
IW_CB08	1.20E-08	–	3.47E-08	0.0006	–	0.0017	0.0023		\	8.38E-10		\
IW_CB09	3.66E-07	6.75E-09	5.77E-08	0.0183	0.0091	0.0029	0.0303		\	2.56E-08		\
IW_CB10	5.21E-07	1.82E-08	4.67E-08	0.026	0.0245	0.0023	0.0529		\	3.65E-08		\
IW_CB11	8.50E-08	2.16E-08	1.22E-07	0.0043	0.0292	0.0061	0.0396		\	5.95E-09		\
IW_CB12	2.66E-07	–	1.22E-07	0.0133	–	0.0061	0.0194		\	1.86E-08		\
IW_CB13	3.63E-07	–	8.36E-08	0.0181	–	0.0042	0.0223		\	2.54E-08		\
IW_CB14	2.08E-07	6.80E-09	3.86E-07	0.0104	0.0092	0.0193	0.0389		\	1.46E-08		\
IW_CB15	3.04E-07	2.32E-08	5.94E-08	0.0152	0.0313	0.003	0.0495		\	2.12E-08		\

[a]Cancer risk $<10^{-6}$ is acceptable.

CONCLUSIONS

In this study, the contamination of PFCs in groundwater was investigated in order to understand their contamination and their potential harmfulness to the consumers. All target PFCs were detected in most samples particularly in the groundwater around the IWDS. Among them, PFOS and PFOA were predominant in the samples both around MWDSs and IWDSs, which could confirm that PFOS and PFOA are still being used. Moreover, this study also found that total target PFCs have highly contaminated the groundwater around the industrial waste disposal site (IWDS) compared to those quantified in the groundwater around the municipal waste disposal sites (MWDSs) with statistical significance, which could be remarked that the IWDS might be a potentially serious source of contamination. In comparison to the recommendation levels, the concentrations did not exceed the health advisory levels for drinking purposes suggested by the US EPA; however, regular measurements by government agencies for the reduction of PFCs in groundwater in sensitive areas around waste disposal sites are necessary. Furthermore, strict law enforcement should be used to control and eliminate illegal waste disposal. In terms of the relationship of total PFCs and DOC, they showed a direct correspondence. This could be noteworthy evidence to support the idea that groundwater has been contaminated by the waste disposal sites, particular the IWDS. In addition, positive correlations between some PFCs and DOC were observed, indicating the associations of hydrophobicity of PFCs chain and organic matter. By health risk assessment, the estimated risk for the non-carcinogenic effects as well as the carcinogenic risk were not observed in any groundwater samples. However, continuous monitoring should be important to follow up their contaminations since they are persistent and bioaccumulative. Further investigation on PFCs sorption potential on soil particles would be beneficial for waste management in order to understand their movement mechanism and to evaluate their potential release to the surrounding environment, especially groundwater.

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Occurrence of perfluorinated compounds (PFCs) in surface water and groundwater near unsuitable disposal sites in Thailand

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Abstract

Contaminations of perfluorinated compounds (PFCs) in the environment have been intensely reported. The most prevalent were perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). The purpose of this study was to investigate the PFCs contamination in groundwater and surface water around unsanitary waste disposal sites in Ayutthaya, representing municipal solid waste disposal sites and Chachoengsao, representing industrial waste dumping sites. 16 groundwater and two surface water were collected. PFCs were analyzed by high-performance liquid chromatography with tandem mass spectrometer (HPLC-MS/MS). The results showed that the total PFCs concentration in Ayutthaya's samples ranged from 2.22 to 8.15 ng/L in which PFOS and PFOA were dominant. Similar to those from Ayutthaya, PFOA and PFOS were predominant in Chachoengsao's samples, total PFCs varied from 4.82 to 11.16 ng/L. Perfluorohexane sulfonate (PFHxS) was only found in Chachoengsao's samples possibly indicating that PFHxS has been used as a replacement product for PFOS. For surface water from Ayutthaya, total PFCs ranged from 25.41 to 259.95 ng/L, which is several times higher than those in groundwater. Although the total PFCs seemed small, the statistical results showed that the concentrations from industrial disposal areas are significantly different from those found in municipal disposal areas at $p=0.05$.

Keywords: disposal site, groundwater, perfluorinated compounds, solid waste, surface water

1. Introduction

Perfluorinated compounds are extremely persistent, have excellent thermal and chemical stability, and have long atmospheric half-lives. Among the differentiation of PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are predominant. Owing to their structures, those have been very popular for use in industrial and commercial products such as textiles and leather products, metal plating, photographic industry, photolithography, semi-conductors, paper and packaging, coating additives, cleaning products, and pesticides (Prevedouros *et al*., 2006). For decades their contamination in all environmental elements have been reported, including in sediment (Zushi *et al*., 2010), sludge (Higgins *et al*., 2005), municipal wastewater (Yu *et al*., 2009), drinking water (Kunacheva *et*

al., 2010), tap water (Mak *et al*., 2009), groundwater (Enevoldsen and Juhler, 2010), dust (Moriwaki *et al*., 2003) throughout the world.

PFCs contamination in groundwater was first reported by Moody and Field (1999), who collected samples from fire-training facilities in the United States. Furthermore, in 2003, groundwater wells around the fire-training area at Wurtsmith Air Force Base (WAFB) in northern Michigan, USA were found to have four PFCs contaminants: PFOS, PFHxS, PFOA, and PFHxA ranging from 3 to 120 µg/L. The conclusion of these studies indicated that perfluorinated surfactants are potential sources of contamination in groundwater (Moody *et al*., 2003). Whereas, some literature has revealed that PFCs are also found from landfill effluents in Denmark and Nordic countries (Bossi *et al*., 2008).

According to Thailand State of Pollution Report 2014, the data from the Pollution Control Department (PCD) showed that the amount of municipal waste from the whole country has been increasing by year and some parts of the country has been improperly disposing of them due to lack of effective management, and limitations of sanitary landfills and budgets, as shown in **Fig 1(a)**. Generated volume of industrial hazardous waste is also given in **Fig. 1(b)**.

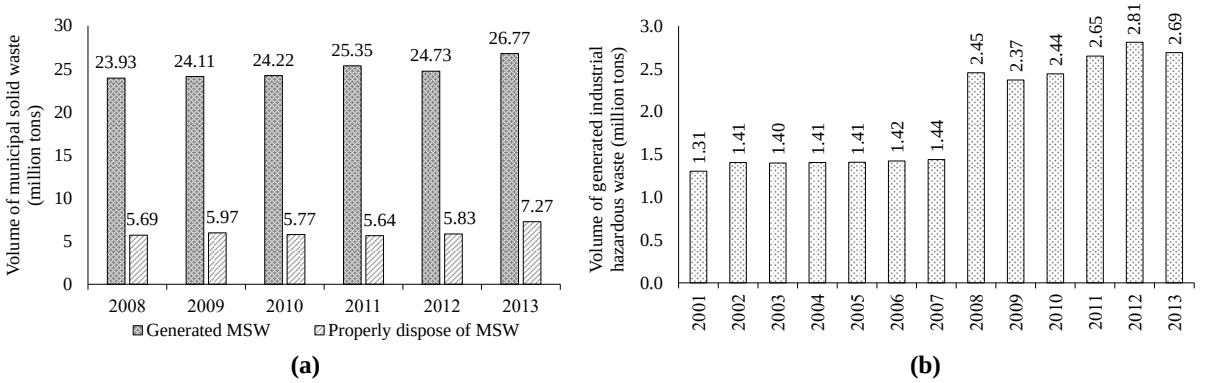

Fig. 1. (a) proportions of total volume of generated municipal solid waste (MSW) and properly disposed, (b) total volume of generated industrial waste in Thailand (PCD, 2014)

Mostly, municipal solid waste in the country ends up at a disposal site. Whereas, the rest of it is dumped on abandoned land without any treatment (PCD, 2014). Due to the waste situation, groundwater, which is an important water resource, is potentially vulnerable to PFCs contamination. Sena and Bang Sai municipal waste disposal sites located in Ayutthaya, and an illegal industrial waste dumping site in Nong Nae sub-district, Chachoengsao were selected for this study. Sena and Bang Sai disposal sites have been operating since 1974 and 2007, respectively. They have been receiving waste of around 53 and 45 tons per day. Open dumping on the land without liner sheet has been used as the disposal method there. Meanwhile, abandoned areas and ponds in Nong Nae sub-district have been used as illegal dumping sites for industrial waste, and have been complained about by neighboring villagers. The aim of this research was to investigate the occurrence of seven PFCs in groundwater near unsanitary disposal sites in Ayutthaya, representing municipal waste disposal sites, and Chachoengsao, representing industrial waste dumping sites. Differentiation between unsuitable municipal and industrial sites was also analyzed.

2. Materials and methods

2.1 Standards and reagents

In this study, seven PFCs standards, including perfluorohaptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) were selected. Methanol HPLC grade (>99.99%) and ACS grade and Acetonitrile HPLC grade (>99.8%) were purchased from Merck KGaA (Millipore, Germany). Ammonium acetate (98%) was purchased from Merck KGaA, Germany. Ultrapure water was produced by a RiOs-DI® Water Purification System (Millipore, Germany).

2.2 Sampling sites

The groundwater well locations were obtained from the Department of Groundwater Resources, Thailand. Groundwater samples were collected around Bang Sai and Sena municipal solid waste disposal sites, Ayutthaya province, and the illegal industrial waste dumping site in Nong Nae sub-district, Phanomsarakham district, Chachoengsao province within two kilometers. Surface water samples were collected from ponds near Bang Sai and Sena municipal solid waste disposal sites. Coordinates of sampling locations are given in the Universal Transverse Mercator (UTM) system which expressed in two-dimensional (X and Y) projection of the earth surface. A description of sampling locations is provided in **Table 1**.

Table 1 A description of sampling locations

Type of waste	Sampling location	Sample type	District	Sampling code	Coordinates	
					X	Y
Municipal solid waste	Ayutthaya	Groundwater	Bang Sai	1	655256	1570366
				2	655840	1569407
				3	656361	1570341
				4	658406	1568328
			Sena	5	649733	1582016
				6	652075	1580995
				7	652321	1581849
				8	652831	1581755
				9	651126	1581045
				10	651217	1579666
				11	652645	1579745
				12	652952	1579181
		Surface water	Bang Sai	13	658285	1570521
			Sena	14	651142	1581080
Industrial waste	Chachoengsao	Groundwater	Phanom-sarakham	15	752092	1512593
				16	752672	1512897
				17	751003	1513061
				18	753397	1512337

2.3 Sample collection

For groundwater, the samples were directly collected from faucets which connected straight to the groundwater plumping system by using new two liters narrow-neck PET

bottles with screw caps. For surface samples and leachate samples, the samples were collected by grab-sampling using a bucket and kept in the PET bottle. The containers were washed with methanol and dried prior to use. The containers were rinsed by the samples three times to prepare the same conditions for all samples. After sampling, the samples were kept in a cooler box and brought back to the Water Quality Analysis Laboratory, Mahidol University. Then the samples were filtered by GF/C glass filter within 24 hours after being collected. After that, the filtered samples were refrigerated for further analysis.

2.4 Extraction and instrumental analysis

Solid Phase Extraction (SPE) was applied as a sample pre-treatment technique. 1500 mL of groundwater and surface water samples was filtered by 1 μm GF/B glass fiber. PrecepC-Agri (C18) cartridges were used for extraction of samples. Preconditioning of the cartridges with 10 mL of methanol, 10 mL of ultrapure water twice in a sequence was conducted prior to use. Before loading, the concentrator was washed by methanol at a flow rate of 10 mL/min for 5 minutes, followed by ultrapure water at a flow rate of 10 mL/min for 10 minutes, and the filtered samples were loaded with a flow rate of 10 mL/min to the C18 cartridges by using concentrators. Elution was done by 4 mL of methanol, followed by 2 mL of acetonitrile. All elutes were softly dried by nitrogen stream and reconstituted with 0.5 mL 30% acetonitrile. Analysis of seven PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC) coupled with Agilent 6400 triple quadrupole mass spectrometry (MS/MS), (Agilent, USA) in negative mode of electrospray ionization (ESI).

2.5 Calibration and validation

Calibration curves were prepared from PFCs standards comprised of five concentration levels covering 0.1-10 μg/L. Limit of detection *(LOD)* and quantification *(LOQ)* of the measurement method were defined as the concentration with signal-to-noise ratios (S/N) equal to 3:1 and 10:1, respectively. Recoveries of the seven PFCs in groundwater matrix were 95.9 ± 2.86% (PFHpA), 106.94 ± 7.14% (PFOA), 99.02 ± 1.81% (PFNA), 91.36 ± 3.39% (PFDA), 83.82 ± 7.06% (PFUnA), 100.87 ± 1.69% (PFHxS), and 93.16 ± 4.74% (PFOS).

2.6 Statistical analysis

The independent sample *t-test* was performed by using IBM® SPSS® Statistics 20. Two groups of data (municipal disposal site and industrial disposal site) were split into independent (type of disposal site) and dependent (total PFCs concentration) variables. The model assumes that a difference in the mean score of the dependent variable is found because of the influence of the independent variable. It is one of the most widely used statistical tests.

3. Results and discussion

3.1 PFCs concentration and distribution patterns in groundwater and surface water

The target compounds were detected in all groundwater and surface water samples. Five of the seven PFCs species, which were PFHpA, PFOA, PFNA PFUnA and PFOS, were found in all groundwater samples from both of the sites of Ayutthaya, while PFDA and PFHxS were

not observed in any samples. The concentrations of total PFCs ranged from 2.22 to 8.15 ng/L (see **Fig. 2(a), 2(b**)). Among them PFOA and PFOS were the most outstanding.

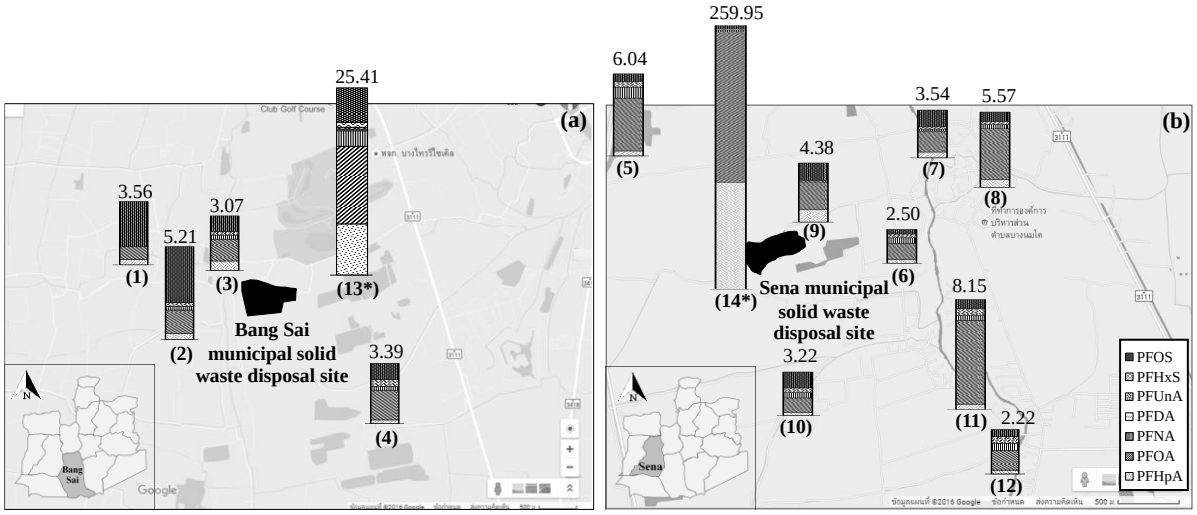

Fig 2. Maps of total PFCs concentrations (ng/L) in groundwater and surface water around municipal solid waste disposal sites in Ayutthaya, (a) Bang Sai district (b) Sena district. Surface water samples are presented with asterisks.

In groundwater from Chachoengsao where illegal industrial waste dumping is located, the concentrations ranged from 4.82 to 11.16 ng/L, slightly higher than those from municipal disposal sites (**Fig. 3**). Five PFCs: PFOA, PFOS, PFHpA, PFHxS and PFUnA were detected, respectively. Among the target compounds the dominant ones were PFOA and PFOS. Occurrence of PFHxS was in only the groundwater samples from illegal industrial waste dumping in Chachoengsao, which might indicate that it has been used as an alternative to PFOS-based compounds due to it having a shorter chain length that is consistent with the report of The Danish Environmental Protection Agency (Poulsen *et al*., 2005). Despite the concentrations from both municipal disposal sites and the illegal industrial waste dumping, they seemed lower than those in other countries (Filipovic *et al*., 2015). However, the statistical output from IBM® SPSS® Statistics 20 showed a significant difference in the mean concentration score at $p=0.05$. The average concentration from industrial disposal sites was significantly higher than those from municipal disposal sites.

An explanation of the discoveries probably illustrates that PFCs were released in greater concentration from industrial waste more than from domestic waste, which is similar to the case of China (Li *et al*., 2015). Even though the amount of PFCs used in industrial sectors in Thailand is not known yet and there is no published data about PFCs in Thailand groundwater, it can nevertheless be expected that industrial plants are major sources of PFCs emission. Moreover, a previous report also concluded that industrial wastewater was one of the major sources of PFOS emission in the environmental waters of Bangkok, Thailand (Boontanon *et al*., 2012).

For surface water collected from ponds near municipal disposal sites in Ayutthaya, the total PFCs were 25-fold higher than those in groundwater from all areas, indicating that surface water was firstly affected from the disposal sites. The concentrations ranged from 25.41 to 259.95 ng/L in which PFOA and PFHpA were mostly detectable, followed by PFOS, PFNA, PFHxS, PFUnA and PFDA, in a sequence. There are some previous studies about PFCs in surface water in

Thailand. The discovered PFOS concentrations ranged from 1.7 to 1.9 ng/L and average PFOA was 4.7 ng/L in the Chao Phraya River, whereas the average PFOS and PFOA concentrations in the Bang Pakong River were both 0.7 ng/L (Boontanon *et al*., 2012; Kunacheva *et al*., 2009).

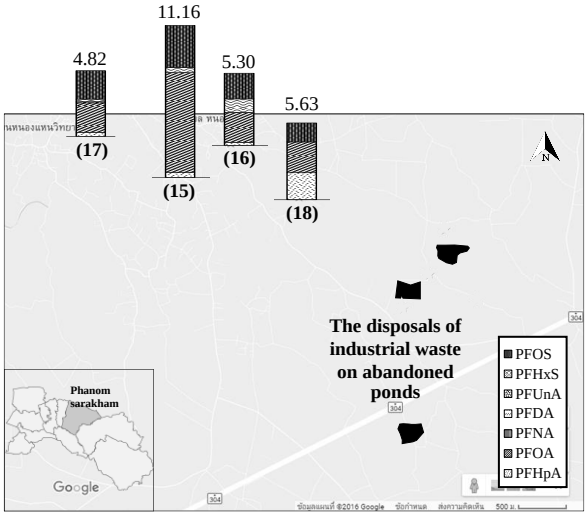

Fig 3. The map presents PFCs concentration (ng/L) in groundwater around the illegal industrial waste dumping site in Nong Nae sub-district, Phanomsarakham district, Chachoengsao.

When compared with the previous studies, the concentrations from this study showed much higher levels. This might result from land use activities. The surface water samples in this study were collected from the areas which were used as municipal disposal sites. The sites were not well engineered by design; rather, an open dumping method was applied. Once it rained, PFCs contained in disposed garbage or leachates could easily be released to surface water more than groundwater. It can be supposed that the disposal site has potentially risked PFCs contamination in surrounding surface water.

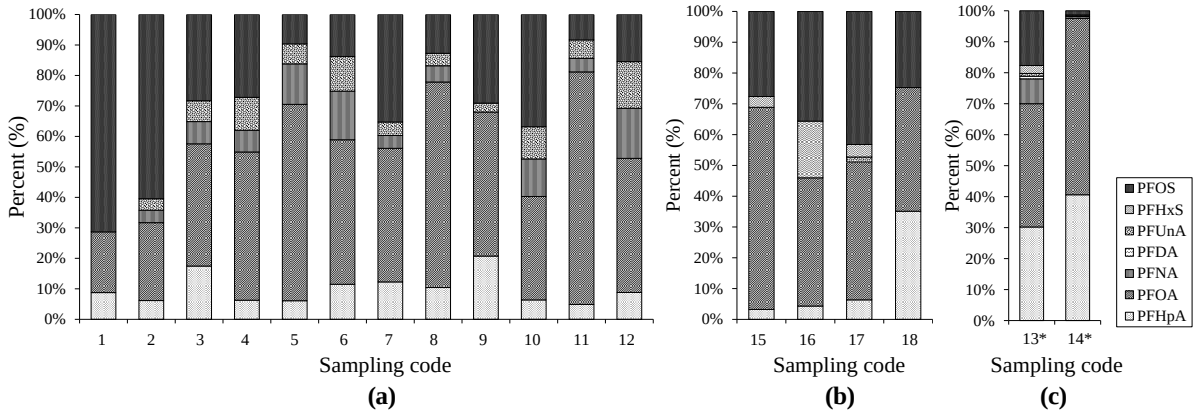

Fig 4. The distribution profiles of PFCs in all samples, (a) groundwater around Bang Sai municipal solid waste disposal site (sampling code 1-4) and Sena municipal solid waste disposal site (sampling code 5-12), (b) groundwater around the illegal industrial waste dumping site in Chachoengsao (sampling code 15-18), and (c) surface water near Bang Sai and Sena municipal solid waste disposal site (sampling code 13-14, presented with asterisks).

The distribution profiles are given in **Fig. 4**. In groundwater samples around Bang Sai municipal disposal sites, Ayutthaya, PFOS made major contributions that ranged from 27.18 %

up to 71.31 %, followed by PFOA from 19.93% to 48.63% and the rest were PFHpA (6.15%-17.47%), PFUnA (3.8%-10.81%), PFNA (4.07%-7.31%), respectively while PFDA and PFHxS were not observed. On the other hand, PFOA showed the highest distribution with a frequency ranged from 33.94% up to 76.29%, followed by PFOS (8.35%-36.83%), PFHpA (4.88%-20.74%), PFNA (4.43%-16.42%), and PFUnA (2.91%-15.30%) in groundwater around Sena municipal disposal sites, Ayutthaya, while PFDA and PFHxS were not quantified similarly to those from Bang Sai (**Fig. 4(a)**). Five of the target substances were observed in groundwater samples around the illegal industrial waste dumping site in Chachoengsao (**Fig. 4(b)**). Overall, PFOA provided the main contribution that ranged from 40.16%-65.63%, followed by PFOS (24.71%-43.21%), PFHpA (3.23%-35.13%), PFHxS (3.50%-18.42%) and PFUnA (1.67%), in a sequence, while PFNA and PFDA were not found.

For the surface water samples (**Fig. 4(c)**), seven PFCs were detectable. PFOA was accounted for the majority of total PFCs (39.81%-56.96%), followed by PFHpA (30.20%-40.61%), PFOS (1.32%-17.65%), PFNA (0.7%-8.01%), PFHxS (0.37%-2.58%), PFUnA (0.04%-0.91%), and PFDA (0.84%). The difference in PFCs distributions might be caused by different PFCs used in products. In addition, the results confirmed that PFOS and PFOA were still in popular use. However, the studies on PFCs contamination in the country are still limited.

4. Conclusions

This study was an initial stage to understand the PFCs situation in groundwater and additionally provide PFCs concentrations in surface water in Thailand. The sampling sites were selected based on areas used for waste disposal. PFOA and PFOS were abundant in groundwater samples from both municipal and industrial disposal areas, which support the contention that both of them are still popularly used. Furthermore, the results from statistical analysis showed that the total PFCs in groundwater from industrial disposal areas were significantly different from the municipal disposal sites at $p=0.05$. Whereas, PFHxS was frequently quantified in groundwater from the illegal industrial waste dumping site, possibly suggesting that PFHxS, which has a shorter chain, might have been introduced for replacement of PFOS in the industrial sector. Total PFCs concentrations in surface water presented several times much higher than those found in groundwater from all areas; surface water might be first contaminated from some factors such as runoff or leachate before the PFCs reach to the groundwater. However, the studies on new emerging contaminants such as PFCs in the country are still limited.

5. Acknowledgement

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Perfluoroalkane sulfonates (PFSAs) and heavy metals in surface water around an informal e-waste recycling site at Kalasin Province, Thailand

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Abstract
This study characterizes concentrations of perfluoroalkane sulfonates (PFSAs) which includes perfluorooctane sulfonate acid (PFOS) and perfluorohexane sulfonic acid (PFHxS), and seven heavy metals (Cd, Cr, Cu, Fe, Mn, Ni and Zn) in surface water collected from an informal e-waste recycling site in Kalasin Province, Thailand. The results showed that the levels of PFOS and PFHxS in surface water ranged from 3.29-168.93 ng/L and <LOQ-25.75 ng/L, respectively. In particular, the average concentrations of Cd, Cr, Cu, Fe, Mn, Ni and Zn were 0.11, 0.03, 0.22, 2.16, 0.77, 0.41 and 1.00, respectively. When compared with Thailand surface water standards, Cd and Ni were considered the most harmful element as all samples exceed standard levels. It was clearly seen that, the average concentrations of PFOS, Cr, Cu, Cd, Zn and Mn in surface water in e-waste landfill site were higher than paddy fields and residential areas. Moreover, PFOS concentrations were found to increase with direction of wind flow from the e-waste landfill site. The results suggested that e-waste landfill site could represent the emission source of PFOS, Cr, Cu, Cd, Zn and Mn contaminations on surrounding surface waters. Therefore, these harmful chemicals should be appropriately managed as they could also be the sources of contamination in other environmental matrices such as air and soils in this area.

Keywords
E-waste, Heavy Metals, PFOS, PFHxS, Thailand

INTRODUCTION

Increasing electronic waste (e-waste) generation under inefficient management systems has become a serious social problem and an environmental concern in recent years (Feldt et al., 2014; Pharino, 2017). Most e-waste from developed countries are exported to developing Asian countries including China, Vietnam and Thailand for recycling due to their inexpensive labour costs and weak enforcement of environmental laws in these countries (Tue et al., 2013; Wu et al., 2015). In recent times, Thailand has become one of the largest dumpsites for e-waste from developed countries since China banned the import of plastic waste. In 2017, approximately 64,437 tonnes of e-waste were imported into Thailand (Thai Customs Department, 2018). In addition, according to a study conducted by PCD (2017a), which calculated the total amount of e-waste from the number of electronic products that people use in the country, results showed that e-waste generation rose every year from 359,070 tonnes in 2012 to 393,070 tonnes in 2016. It is a large quantity of e-waste in Thailand. The hazard of e-waste lies in the high content of several harmful substances. However, its appropriate management, recycling and disposal does not exist. This leads to the release of toxic substances to several environmental media (air, soil, water and others), which causes various environmental problems gets accumulated in biota and causes serious health problems (Olafisoye et al., 2013; Zheng et al., 2013).

Among various substances in the e-waste, perfluoroalkane sulfonates (PFSAs) and heavy metals (cadmium, chromium, copper etc.) are of significant concern as these chemicals are widely used in electrical and electronic products such as cell phones, televisions, computers and refrigerators (Tue et al., 2013). Both chemical groups have the characteristic of high toxicity, long-range atmospheric transportability, environmental persistence and non-biodegradability (Ning et al., 2011; Wu et al., 2015). Therefore, they are released into environment media and are accumulated in biota including humans and are thus affecting human health (Zheng et al., 2013). For example, these chemicals from e-waste leach into the soil and pollute the surface water by rain or flood. Moreover, water is a polar

molecule, and hydrogen bonding enables water to dissolve, and absorb different compounds. Thus, water can easily acquire contaminants from its surrounding (Michael et al., 2013; Olafisoye et al., 2013). Subsequently, these toxic substances can be accumulated by plants and aquatic organisms, and ultimately transferred to the food chain into vital organs in the human body. Exposure to these substances may cause adverse health effects such as cardiovascular, blood and bone diseases, kidney damage, decreased mental capacity, and neurological damage (Olafisoye et al., 2013; Zheng et al., 2013).

Kalasin Province is one of the largest and highly risky informal e-waste recycling sites in Thailand. Most businesses in this province are family based and e-waste is recycled in their houses. The recycling methods include uncontrolled dismantling in common facility households, open burning and dumping at unsafe e-waste landfill site (Khok Sa-ad Subdistrict Administrative Organization, 2017). The lack of proper e-waste management has resulted in the abundance of dangerous substances in high concentrations which are contaminating environment matrices and biota in this area. To date, little information in this area is available on the concentration of heavy metals in surface water, soils and plants (Jamsai et al., 2016; Thanomsangad et al., 2016) and there has been no study on the PFSAs including perfluorooctane sulfonate (PFOS) and perfluorohexane sulfonate (PFHxS) concentration in surface water in this area. Therefore, this study aims to investigate PFSAs and seven heavy metals in surface water from the informal e-waste recycling site of Kalasin Province, and to evaluate the status of these emerging contaminants in this area. This information will help support protection of the environment through environmentally sound e-waste management in this area.

MATERIALS AND METHODS

Study area

Sample collection was conducted in an informal e-waste recycling site located in Khok Sa-ad Subdistrict, Kong Chai District, Kalasin Province, Thailand (Figure 1). In these areas, informal e-waste recycling activities take place in homes and their recycling through primitive methods include 1) manual classification and dismantling, 2) manual separation, 3) shredding, 4) open burning and 5) residue dumping into open fields. Simultaneously, the villages still maintain traditional production and livestock. Fourteen surface water sampling sites were sampled which included the e-waste landfill site (W1-W4), paddy fields near the e-waste landfill site (W5-W9) and residential areas where e-waste recycling activities are taking place (W10-W14). The details of the sampling sites from these locations are shown in Table 1.

Table 1. Description of sampling locations

Area zone	Sample station	Sample location
E-waste landfill site	W1 – W4	Surface water pond in the e-waste landfill site (open-burning and dumping site)
Paddy fields	W5 – W9	Surface water pond in paddy field, an area around the e-waste landfill site
Residential areas	W10	Surface water pond, an area near Nong Bua Sub-district Health Promoting Hospital
	W11	Surface water pond, an area near Nong Bua Sub-district Health Promoting Hospital and near the e-waste recycling workshop
	W12	Surface water pond, an area near Sai Tong Nong Mou Temple and e-waste recycling workshop
	W13	Surface water pond, an area near Kok sa-ad Subdistrict Administrative Organization
	W14	Surface water pond, an area in Sa-ad Village where e-waste recycling workshop is located

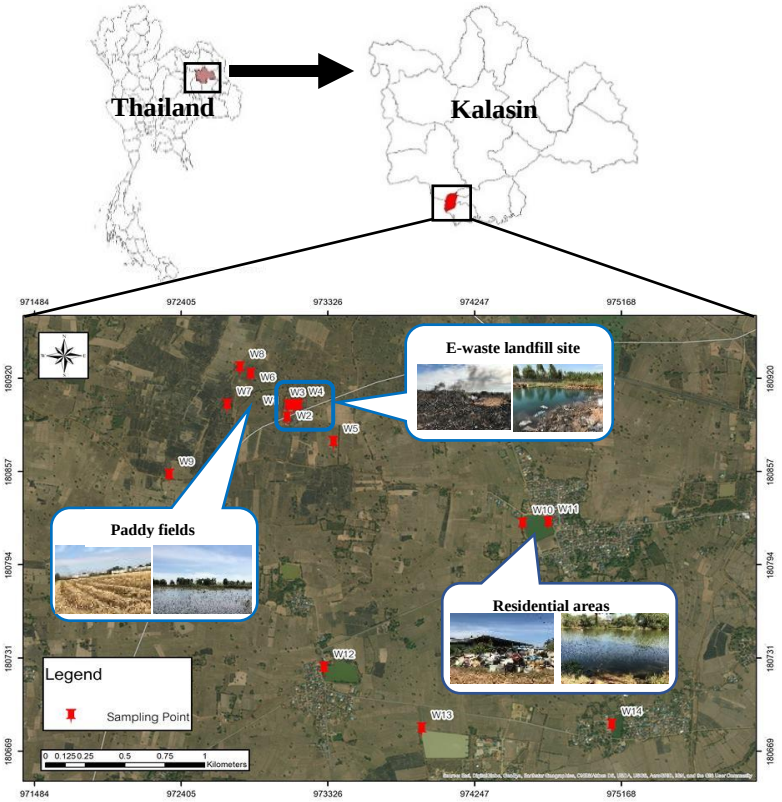

Figure 1. The area of study and sampling locations

Sample collection

The surface water samples were collected from the informal e-waste recycling site in November 2017. The map of the area and the position of the sampling sites are presented in Figure 1. At each sampling site, the surface water samples were collected from a depth of 30 cm below the surface water using grab sampling technique. For heavy metals, the surface water samples were collected in 250 mL of acid-washed polypropylene (PP) bottles and were acidified with 1 mL of HNO_3 in order to achieve a pH <2, to preserve the metals and also to reduce precipitation. For PFSAs, 1,500 mL water samples were collected from each site in separate polyethylene terephthalate (PET) bottles. Before sample collection of PFSAs, all sample bottles were thoroughly pre-cleaned with milli-Q water, followed by methanol at laboratory, and then rinsed with water sample prior to sample collection. After sample collection of both heavy metals and PFSAs, all surface water samples were stored in ice-packed coolers and then delivered to the laboratory.

Sample preparation and extraction

After all water samples returned to the laboratory, for heavy metals, the water samples were vacuum filtered through Whatman GF/F glass fiber filters (pore size 0.45 µm) prior to analysis. For PFSAs, the 1,500 mL water samples were vacuum filtered through GF/F (Whatman, 0.7 µm, 47 mm) glass fibre filter to remove the particles. Then, the filtrates were concentrated by solid phase extraction (SPE) process using PrecepC-Agri (C18) cartridges. The SPE procedure was referenced from previous studies methods (Filipovic et al., 2015; Braunig et al., 2017; Hongkachok et al., 2017). Before loading, the cartridges were pre-conditioned by passing them with 10 mL of methanol, followed by 2 ×10 mL of ultrapure water. Then, the filtered samples were loaded into the pre-conditioned cartridges. After loading, the analytes were eluted with 4 mL of methanol, followed by 2 mL of acetonitrile. The elute was concentrated and evaporated by gentle stream of nitrogen gas. Finally, the solution was reconstituted with 0.5 mL of 30% acetonitrile and transferred to LC-MS vial prior to LC-MS/MS analysis.

Instrument Analysis

PFSAs (PFOS and PFHxS) were analyzed using Agilent 1200SL HPLC coupled with Agilent 6400 tandem mass spectrometry (MS/MS). The mass spectrometry was operated by electrospray ionization (ESI) negative mode. The five points calibration curve was proven to be linear ($R^2 > 0.99$) for both PFOS and PFHxS. Limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio of 3:1 and 10:1 respectively. For seven heavy metals (Cd, Cr, Cu, Fe, Mn, Ni and Zn), the filtrates were measured by atomic absorption spectrophotometer (AAS).

RESULTS AND DISCUSSION

Heavy Metals

The content of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni and Zn) in the surface water samples collected in November 2017 are presented in Figure 2. Six metals including Cd, Cu, Fe, Mn, Ni and Zn were detected in all samples, whereas Cr were detected in only nine out of fourteen samples. The concentrations of Cd, Cr, Cu, Ni, Zn, Fe and Mn were observed in the range of 0.14-0.20 mg/L, 0.02-0.06 mg/L, 0.46-1.25 mg/L, 0.19-0.71 mg/L, 1.09-5.33 mg/L, 0.39-15.76 mg/L and 0.05–4.61 mg/L, respectively. When compared to Thailand surface water standards (PCD (2017b), the concentrations of Cd and Ni in all sampling sites exceeded the threshold value (0.005 and 0.1 mg/L, respectively). Similarly, Cu and Zn in four stations (W1-W4) exceed 0.1 and 1.0 mg/L. Cr in station W1 and W4 exceed 0.05 mg/L. Mn in station W3-W5 exceed the standard concentration level (1.0 mg/L). It could be seen that the levels of Cu, Cd, Ni, Zn and Mn of the surface water in e-waste landfill site (W1-W4) were significantly higher than other sampling sites. Two possible reasons could be attributed to this. The first reason could be because the e-waste landfill site had various e-waste types that contained heavy metals. The second reason could be because the e-waste landfill site received the remains of burned and buried valueless items that attributed to the contamination. The heavy metals could then enter the surface water pond that is located in the e-waste landfill site. In terms of individual metals, it is interesting to note that, the concentrations of Cu and Zn of the surface water in the e-waste landfill site exceeded 10 times the concentration in paddy fields and residential areas. This may be due to the presence of Zn in e-waste used in monitor glass including computer and television (Olafisoye et al., 2013), and the presence of Cu in printed circuit boards including wires and cables (Wu et al., 2015). After the e-waste were separated in the workshop, they were burned and dumped to the ground in the e-waste landfill site. Due to this, the Zn and Cu could get released to the soils thereby polluting the surface water in high levels at the e-waste landfill site.

Although the concentrations of Cd were found to exceed the standard in all stations, these concentrations were lower than other metals. This may be because of the presence of Cd in chip resistors, infrared detectors, semiconductors and photocopying-machines (printer drums) (Li et al., 2011; Olafisoye et al., 2013), which can be reused in the market, limiting the amount of Cd being burned or discarded in the recycling site. Ni also occured at high concentrations in the e-waste landfill site. This may be due to the presence of Ni in batteries and cathode ray tubes (Li et al., 2011). Especially in stations W3 and W4, valueless cathode ray tubes were found to be burned and dumped in the e-waste landfill site. Therefore, high concentrations of Ni in surface water in e-waste landfill site were found. Similarly, the concentration of Ni was found to be high in the surface waters of stations W12 – W14 because of dismantling activities of cathode ray tubes being carried out in that area. The valueless cathode ray tubes were laid near the pondside before transferring it to disposal site, which might explain the high concentration of Ni in the surface waters close to this area. From previous studies in the same area, results obtained from Thanomsangad et al. (2017) and Jamsai et al. (2016) showed higher levels of heavy metals than this study in the same e-waste landfill site. Although in this study, sampling was done during the dry season, it had rained before sampling. Therefore, lower concentrations could probably be due to the effect of rain water, i.e., the heavy metals could have been transported or diluted by rain water and thus the levels of heavy metals were

found to be comparatively less. However, the result was in agreement with observations from previous studies (Guo et al., 2009; Olafisoye et al., 2013; Akesh, 2017) that found decreased heavy metals concentrations from the rainy season to dry season. Compared with finding of other studies around the world, Cd, Cu, Zn and Mn in the surface water samples of this study were two to five times lower than those reported for e-waste recycling area in South China (Zheng et al., 2013) and ten times lower than Wu et al. (2015) who observed the concentrations in e-waste recycling area in Longtang and Guandong, China. In the other hand, Cd concentration in surface water was comparable to e-waste dumpsite in Southwestern Nigeria (Olafisoye et al.,2013). The result found that Cd concentrations were five to ten times lower than this study.

PFSAs

PFOS were detected in all samples, whereas PFHxS were detected in 92.85% (13 out of 14) of all surface water samples. The concentration of PFOS and PFHxS ranged from 3.29-168.93 ng/L and <LOQ -25.75 ng/L, respectively (Table 2). The concentrations of PFOS and PFHxS in various stations are shown in Figure 3. The highest PFOS concentration was found in e-waste landfill site. Especially, the highest PFOS concentration measured at e-waste landfill site was in station W3, and its value was 168.93 ng/L. In Thailand, there is no standard for the concentration of PFOS of surface waters, and there also is no any standard for this around the world. However, the EPA, in its drinking water guideline, recommends that the concentration of PFOS in drinking water should not exceed 70 ng/L (US EPA, 2016). It was estimated that the high level of PFOS in the surface water of the e-waste landfill site in this study was partly because the landfill site had several e-waste types that contained PFOS. In addition, it could be seen that PFOS concentrations increased with dominant direction of wind flow (Figure 4). Groffen et al. (2018) explains that PFOS has long-range emission and persistence in the atmosphere for a long time. Therefore, they get deposited in the surface water via wind and consequently polluted them. During the sampling time, wind direction was from southeast to northwest. Therefore, PFOS concentrations in surface water at downstream were higher than upstream, following the wind direction. For example, PFOS concentrations in surface water in station W8 were higher than concentrations in stations W6 and W7, because station W8 was located downstream from the e-waste landfill site and was affected from the direction of wind. Moreover, although stations W10 and W11 were located in the same surface water pond, there were differences in PFOS concentrations. This may be because the PFOS were transported from stations W11 to W10 due to the wind. In Station W3, concentrations of PFOS and PFHxS were found to be the highest. This implies that this station had very large amounts of discarded e-wastes. These e-wastes were dumped in the surface water pond side. Morover, station W3 is located in the downstream of wind direction from station W1, W2 and W4. Therefore, the e-waste that contained PFOS and PFHxS were released to these surface waters and they got trasported via wind from upstram to the downstream station. Both chemical levels were higher in comparison to other sites. In addition, the maximum PFOS and PFHxS levels detected in surface water were ten-fold lower as compared to the highest levels measured in fire-fighting training area in the surface waters of Australia (Braunig et al., 2017). On the other hand, PFOS concentrations in this study were two times higher than that examined in surface water from military airport in Stockholm, Sweden (0 - 45.1 ng/L) (Filipovic et al., 2015). Similarly, the PFOS concentrations in surface water in this study were eight times higher than concentrations measured in surface water in Huangpu River in Shanghai, China (2.89 -13.17 ng/L). However, PFHxS concentrations in surface water in this study were two times lower than concentrations reported by Sun et al. (2018). This might be because PFHxS has been widely used as replacement alternatives to PFOS in China. In Thailand, the process of regulating the replacement of these substances were slower than in other countries. Therefore, the study found the concentrations of PFHxS in surface water lower than the concentrations in other countries.

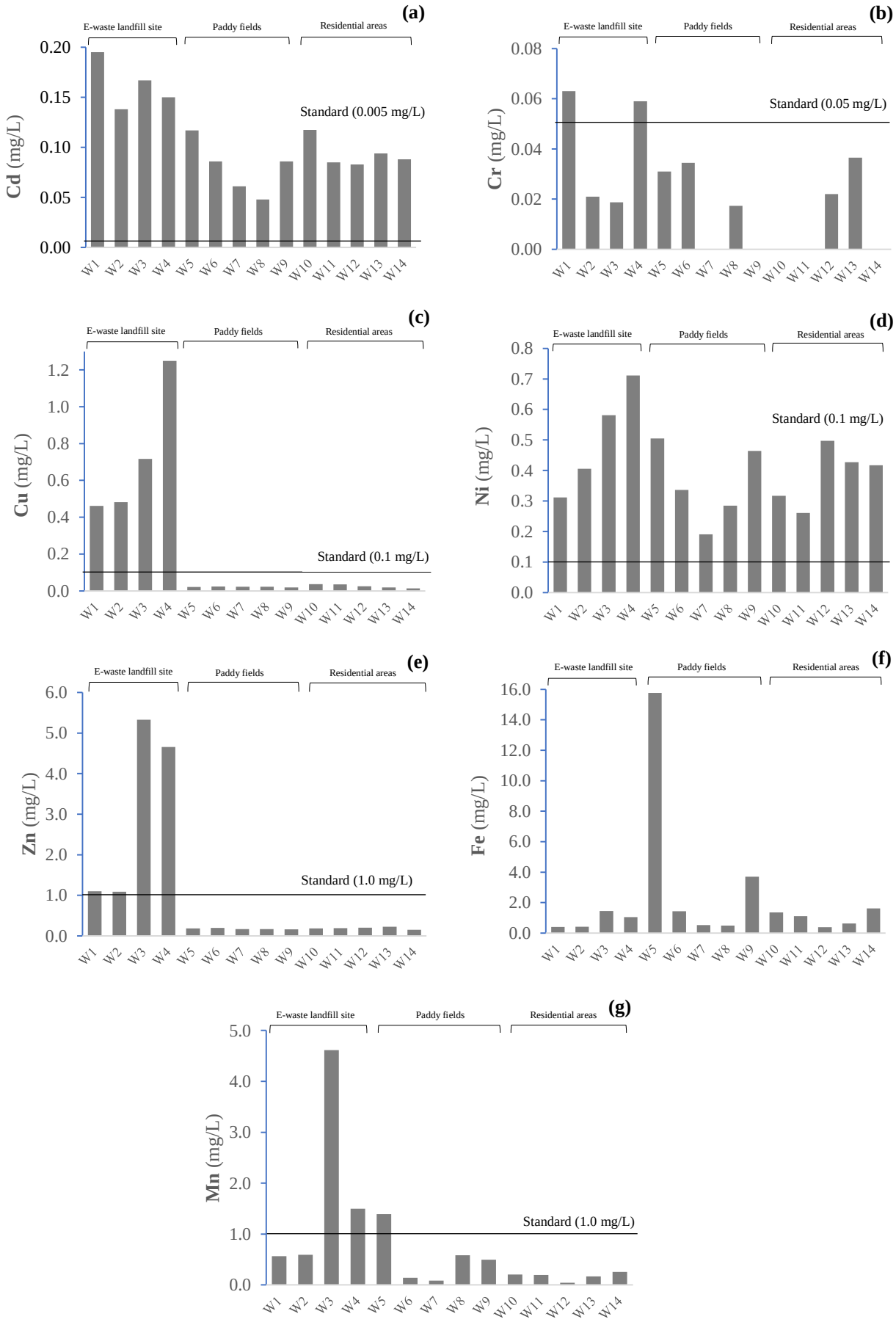

Figure 2. Concentration of heavy metals in surface water

Table 2 Range of concentrations and standard deviation (SD) of PFSAs in surface water

Location	Statistics	Compounds (ng/L)	
		PFHxS	PFOS
E-waste landfill site (n=4)	Mean±SD	8.67±17.79	102.27±46.03
	Range	(<LOQ-25.75)	(78.42-95.47)
Paddy fields (n=5)	Mean±SD	0.15±0.08	49.61±33.70
	Range	(0.03-0.24)	(14.16 - 95.35)
Residential area (n=5)	Mean±SD	0.76±0.74	24.75±37.23
	Range	(0.03-1.58)	(3.29-89.87)

<LOQ, represents less than limit of quantification.

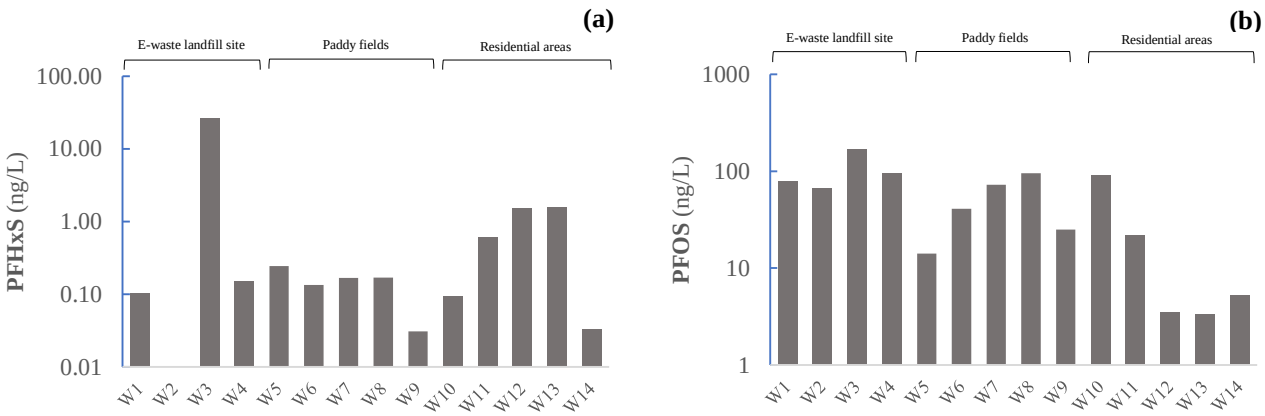

Figure 3. Concentration of PFHxS (a) and PFOS (b) in surface water

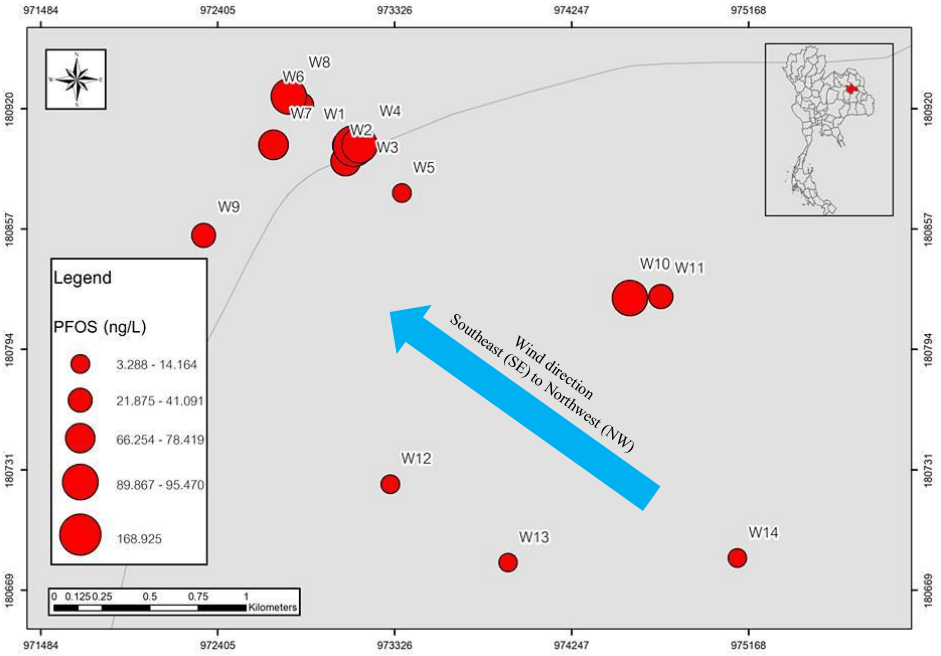

Figure 4. PFOS concentrations with dominant direction of wind flow

CONCLUSIONS

This is the first study to report PFSAs concentrations in surface water in an informal e-waste recycling site. The study found that the informal e-waste recycling site had led to widespread PFSAs and heavy metal contamination in surface water in this area. This suggests that e-waste landfill site has several e-waste types that contain many toxic substances. Moreover, e-wastes were burned and dumped in this area. Therefore, the concentrations of PFOS and seven metals in surface water at e-waste landfill site (W1-W4) were significantly higher than the concentrations in paddy fields (W5-W9) and residential areas (W10-W14). The results suggested that e-waste landfill site could represent the emission source of PFOS and the contamination of seven metals on the surrounding surface waters. Furthermore, the evaluation of these chemicals and other persistent organic pollutants (POPs) in the water environrment (surface water and groundwater) from the informal e-waste recycling site should be a matter of concern because these chemicals could also contaminate other environmental matrices such as air and soils in this area.

ACKNOWLEDGMENTS

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Contamination of PFOA, PFOS and other perfluoroalkyl substances in water treatment plants of Bangkok, Thailand

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Abstract: Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are highly-persistent and non-degradable contaminants. They are found in the environment, especially in water sources which are used to produce tap water for people in Bangkok, Thailand. This study aimed to investigate the levels of contamination as well as the capability to remove PFOA, PFOS, and other substances in the PFASs group from Bangkok's tap water production processes at present, in comparison with another advanced technology used in tap water production which is practiced in an industrial estate. According to the results of the study, Bangkok's tap water production process consists of coagulation, sedimentation, filtration, and chlorination, which together are unable to reduce the contamination levels of PFOA and PFOS. In contrast, advanced technology treatment, especially reverse osmosis, could reduce the contamination of PFOA and PFOS by over 90%. Nevertheless, the concentration levels of PFOA and PFOS in treated water from Bangkok's tap water production process are at 0.96 ng L^{-1} and 0.31 ng L^{-1}, respectively, which are not high when compared to the recommended levels of the U.S. Environmental Protection Agency.

Keywords: Coagulation, Perfluorooctanoic acid, Perfluorooctane sulfonate, Reverse osmosis, Water treatment plants

Introduction

Perfluoroalkyl substances (PFASs), especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), are substances that are highly persistent and have been found to accumulate in the environment (EFSA, 2008; US EPA 2013). Moreover, such compounds are also found in living organisms and the human body. In many countries, PFOA and PFOS contaminants have been found in tap water and drinking water (Boontanon et al., 2013; Flores et al., 2013; Hu et al., 2011; Kunacheva et al., 2010; Rahman et al., 2014; Takagi et al., 2011; Thompson et al., 2011a), which is one of the factors causing the accumulation of PFOA and PFOS in the human body. Due to the widespread use of such substances in the environment, and because their side effects in toxicology and human epidemiology studies remain unclear, many countries have attempted to limit the production and release of such substances including PFOA and PFOS into the environment in drinking water. The US EPA has established the health advisory levels at 70 ng L^{-1} for the combined concentrations of PFOA and PFOS (US EPA, 2016), and the State of New Jersey Department of Environmental Protection has set the guideline value of PFOA in drinking water to not exceed 40 ng L^{-1} (NJDEP, 2007). For the water supply in Thailand, particularly in Bangkok, there has been no control of PFOA and PFOS contamination because water quality in Bangkok is being regulated by recommendations from WHO guidelines (MWA, 2014), which still do not control for these substances. In addition, a previous study found contamination of PFOS in industrial wastewater with an average concentration of 264.3 ng L^{-1} (up to 6,000 ng L^{-1}) around the Chao Phraya River, which is the main river through Bangkok and is used as the

raw water source for the production of water supply and drinking water for the people in Bangkok.

Therefore, the purpose of this study was to assess the ability to remove PFOA and PFOS, including other PFASs, from the water treatment process in the production of treated water supplies in Bangkok, and then to compare this to a water treatment plant using advanced technology.

Materials and Methods

Reagents and Chemicals

Seven PFASs were selected for analysis: Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluoroundecanoic acid (PFDA), Perfluorododecanoic acid (PFUnA), Perfluorohexane sulfonate (PFHxS), and Perfluorooctane sulfonate (PFOS). All standard chemicals as aforementioned were purchased from the Wako Company of Japan, with purity levels > 95%, except for that of PFHxS, which was purchased from the Fluka Company, Italy. All PFASs standard solutions were mixed together in a solution of 30% acetonitrile (HPLC grade) at a concentration of 100 μg L^{-1}, and stored in a bottle of polypropylene (PP) at 4°C. Furthermore, Ammonium Acetate, methanol (HPLC grade), and acetonitrile (HPLC grade) were purchased from Merck KGaA, Germany.

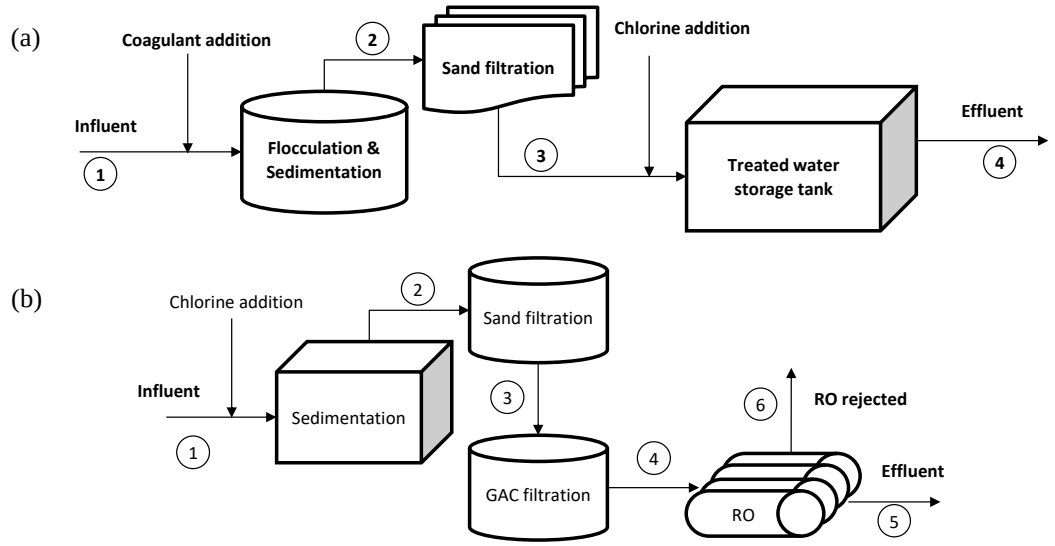

Figure 1. Schematic diagram of water treatment processes: (a) Water treatment plants for Bangkok residential area (W1 and W2), and (b) A recyclable water treatment plant for an industial estate (W3)

Sampling Location

Three water treatment plants (W1-W3) were selected to collect water samples. Figure 1(a) presents the water treatment processes of W1 and W2 which produce water supplied from rivers and distributed to residences and the public for more than 10 million people in Bangkok. W1 plant is located on the eastern side of the Chao Phraya River and uses untreated water from the Chao Phraya River in its treatment process. W2 plant is located on the western side of the Chao Phraya River and uses untreated water from the Mae Klong River. Both

plants are treating water by the conventional treatment processes, for which sampling points consist of influent, clarified water, filtered water, and effluent. In addition, the treatment process of WTP (W3) is shown in Figure 1(b), which is a recyclable water treatment process to produce reusable water from treated industrial wastewater. The water treatment process for W3 consists of chlorination, sedimentation, sand filtering, granular activated carbon, and reverse osmosis. Water samples are collected at each stage of the treatment processes. The sampling of all WTPs was conducted twice between April and October 2014.

Sample Collection and Preparation

All samples were collected and stored in PET bottles. Glass bottles and any suspected fluoropolymer materials were avoided throughout the analysis. 1.5L samples were firstly filtered using a glass fiber filter (GF/B, Whatman) and then solid phase extraction (SPE) was carried out. The filtrate was loaded onto a Presep-C Agri (C18) cartridge (Wako Pure Chemical Industries, Japan), which was conditioned by 10 mL methanol (HPLC grade), followed by 20 mL milli-Q water. The cartridge was then dried, eluted using HPLC-grade methanol, evaporated to dryness with nitrogen gas, and finally reconstituted with 0.5 mL of 30% HPLC-grade acetonitrile.

Instrumental Analysis, Quantification and Validation

An Agilent 1200SL HPLC interfaced with a triple quadrupole Agilent 6400 LC/MS system was applied to detect PFASs in the water samples in the electrospray negative ionization mode. The HPLC columns used were an Agilent Eclipse XDB-C18 (4.6 x 50 mm, 1.8-mm particle size) and an Agilent Eclipse Plus C18 (2.1 x 100 mm, 1.8 mm particle size), maintained at a temperature of 40°C. The mobile phase consisted of a mobile phase (A) with 10mM ammonium acetate in Milli-Q water, and (B) 100% acetonitrile (HPLC grade) at a flow rate of 0.25 mL min $^{-1}$, wherein the separation process began with a ratio of 30% (B) in the first minute which increased to 35% (B) and flowed constantly until 16 minutes had elapsed. After that, the flow rate at 16.5 minutes increased to 50% (B) and 60% (B), respectively, and after 23 minutes increased to 70% (B); at 26 minutes, it increased to 90% (B), and then decreased back to 30% (B) at the end of the measurement process.

Table 1: Analytical parameters of each PFOA, PFOS and other perfluoroalkyl substances using HPLC/MS/MS analysis

Compound	No. of Carbon	Cas No.	Retention time (min)	Parent ion (m/z)	Daughter ion (m/z)	Recovery (%)	LOQ (ng L^{-1})
PFHpA	C7-A	375-85-9	10.5	363	319	108.72	0.10
PFOA	C8-A	335-67-1	14	413	369	119.84	0.10
PFNA	C9-A	375-95-1	17	463	419	119.01	0.17
PFDA	C10-A	335-76-2	21	513	469	97.69	0.13
PFUnA	C11-A	2058-94-8	23.5	563	519	74.18	0.07
PFHxS	C6-S	355-46-4	15.1	399	80	115.92	0.17
PFOS	C8-S	1763-23-1	22	499	80	111.09	0.17

The calibration curves of mixed PFASs solution, consisting of 5 concentration levels in the range 0.1-10 µg L^{-1} were prepared in 30:70 (v/v) acetonitrile and ultrapure water, which had a linear response of $R^2 \geq 0.99$. Limit of Quantitation (LOQ), calculated with Instrument Quantitation Limit (IQL) was defined by S/N equal to 10:1 and the concentration factor proportionally through the SPE process, which was used for quantification analysis. The analytical parameters of each PFAS by HPLC-MS/MS analysis is shown in Table 1.

Results and Discussion

Occurrences of PFASs in water treatment processes

The PFASs contamination in the water treatment processes of plants W1 and W2, consisting of coagulation, flocculation, and sedimentation processes, are presented in Table 2. PFOA (C-8A) and PFOS (C-8S) were detected in all processes of water treatment at 0.62-0.96 ng L^{-1} and 0.22-0.31 ng L^{-1}, respectively. For other PFASs contamination was also detected in some treatment processes in the range of <LOQ-0.27 ng L^{-1} as follows: PFHpA concentration in the range of <LOQ-0.19 ng L^{-1}, PFNA concentration in the range of <LOQ-0.20 ng L^{-1}, PFUnA concentration in the range of <LOQ-0.11 ng L^{-1}, while PFDA and PFHxS were detected in very low levels (<LOQ) in all types of water samples. Clarifier process could reduce PFASs contamination in the influent water. PFOA in clarifier water was found at 0.62 ng L^{-1} or a decrease of about 28% of PFOA in influent with initial concentration at 0.86 ng L^{-1}. PFOS contamination was also found to be decreased when passed through the clarifier process whereas average concentration of PFOS in clarified water was at 0.25 ng L^{-1}, decreasing from influent with average initial concentration of PFOS at 0.29 ng L^{-1} or decreasing for about 14%. This was consistent with the work of Xiao et al. (2013), who found that coagulation process and flocculation process could remove PFOA and PFOS for about 10-30% depending on alum dosage.

Table 2 PFASs concentration in water treatment plants (WTP) W1 and W2 in Bangkok, Thailand.

Type of samples	Concentration ± SD (ng L^{-1})								
	n	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS	ΣPFASs
WTPs									
Inf.	4	0.13±0.05	0.86±0.27	<LOQ	<LOQ	<LOQ	<LOQ	0.29±0.24	1.28±0.57
Cw.	4	0.14±0.04	0.62±0.24	<LOQ	<LOQ	<LOQ	<LOQ	0.25±0.16	1.01±0.52
Fw.	4	0.15±0.06	0.71±0.34	<LOQ	<LOQ	0.07±0.05	<LOQ	0.22±0.12	1.15±0.48
Eff.	4	0.19±0.06	0.96±0.30	0.20±0.09	<LOQ	0.11±0.10	<LOQ	0.31±0.17	1.77±0.55

***Note**: PFDA and PFHxS in all samples <LOQ; Inf. = Influent, Cw. = Clarified water, Fw. = Filtered water, Eff. = Effluent*

Water treatment plant W1 is located at the eastern side of Bangkok. The Chao Phraya River is the raw water source for this plant. The average concentration of each PFAS for W1 is shown in Figure 2(a). Each substance was at the range of <LOQ - 1.32 ng L^{-1}, in which PFOA was the maximally detected substance and had an average concentration at 1.25 ng L^{-1} and PFOS had an average concentration at 0.40 ng L^{-1}. When looking at the concentrations of PFOA and PFOS in the influent of W1, the average concentrations were 1.09 ng L^{-1} and 0.44

ng L^{-1}, respectively, which was quite less than in the previous study, which found PFOA and PFOS concentrations in the influent at 9.57 ng L^{-1}, and 5.02 ng L^{-1}, respectively (Kunacheva et al., 2010). In addition, when compared to PFOA and PFOS contamination in the Chao Phraya River (Boontanon et al., 2013), which is the primary raw water source of W1, it was found that PFOA and PFOS concentration in the influent of W1 was less than in the Chao Phraya River in a previous study as well, where the location of the sampling point in that study was lower downriver than the sampling point of the W1 influent. When the water in the Chao Phraya River flows downstream, it is likely to accumulate PFOA and PFOS from wastewater discharging from households, industries, and several subsidiary canals.

Water treatment plant W2, which is located on the western side of Bangkok, has the Mae Klong River as its raw water source. The average concentration of each PFAS for W2 is shown in Figure 2(b). The average PFASs concentration in influent was 1.14 ng L^{-1}. Each substance was in the range of <LOQ - 0.63 ng L^{-1}, for which PFOA was the maximally detected substance, the same as for W1. The average concentration of PFOS was lower than LOQ, and the concentration of other PFASs were in the range of <LOQ - 0.12 ng L^{-1}. It was found that the contamination of PFHpA (C-7A) in influent of W2 was similar to that of PFOS, with an average concentration at 0.12 ng L^{-1}. For PFASs contamination in effluent of W2, the average concentration of all 7 PFASs was detected at 1.15 ng L^{-1} with concentration of each substance in the range of <LOQ - 0.66 ng L^{-1}, and PFOA was the maximally detected substance as well. The average concentration of PFOS in effluent was 0.21 ng L^{-1}, and for other PFASs low concentrations were found, the same as in influent with concentration in the range of <LOQ - 0.29 ng L^{-1}.

From the detection result finding contamination of all seven PFASs in both water treatment plants as shown in Figure 3, it indicates that W1 contamination content was more than W2 for almost the entire time. It is possible that W1 influent has been using raw water from a lower part of the Chao Phraya River, where the river has taken up quite a bit more wastewater from households and industries, resulting in quite higher PFASs contamination than those samples from W2. It was different from W2 because the influent is being taken from the Mae Klong River, which is the river coming from the Mae Klong dam and near to the upstream area, which does not have much wastewater contamination being discharged from households or industries. As a result, the PFASs contamination in the influent of W1 were detected to be higher than that of W2, indicating that the quality of water sources for the water treatment plants is a significant factor for PFASs contamination in the treated water.

The results of influent and effluent water samples for both W1 and W2 found that PFOA concentration was higher than PFOS. Several studies (Prevedouros et al., 2006; Scott et al., 2006) have investigated PFOA and PFOS concentrations in rainwater and found that PFOA concentration in rainwater is higher than that of PFOS. In Thailand, several previous studies (Boontanon et al., 2013; Kunacheva et al., 2010; Kunacheva et al., 2011) have investigated PFOA and PFOS concentrations in surface water and tap water, and have found that PFOA concentration in surface water has been higher than that of PFOS as well. It is quite possible that PFOA is more widely used than PFOS and other substances in the group of PFASs for these areas.

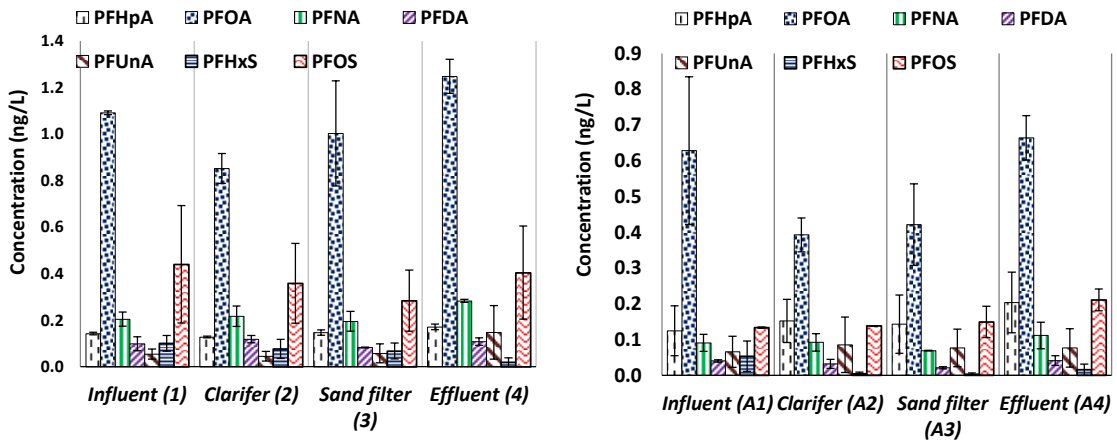

Figure 2 PFASs concentration in the water treatment process of W1 and W2

Behaviour of PFASs in water treatment processes

The average PFASs concentrations in the influent for W1 and W2 were 2.13 ng L^{-1} and 1.14 ng L^{-1}, respectively. The influent of the water treatment process was a principal factor, which caused the difference in effluent concentrations of W1 and W2. The average PFASs concentrations in the effluent for W1 and W2 were 2.25 ng L^{-1} and 1.15 ng L^{-1}, respectively. Although PFOA and PFOS concentration were reduced by 16% - 22% when passing through a clarifier, its efficiency was not good enough to significantly reduce PFOA and PFOS contamination because PFOA and PFOS levels in the WTP effluent were still higher than PFOA and PFOS concentrations in the influent (Figure 3 (a) and (b)). The results are consistent with several studies reporting that the sand filter treatment process could not remove PFOA and PFOS (Eschauzier et al., 2012; Takagi et al., 2008; Takagi et al., 2011). It has been unclear which factors have affected PFASs to be higher in the effluent. It is possible that PFASs contamination might be from some equipment inside the water storage tank. Another possible explanation for why PFASs concentration increased might be due to the degradation of precursors that could be dissolved in the water and are able to transform to the stable perfluorinated carboxylates and sulfonates under a variety of environmental conditions. Mechanisms of the transformation processes remain unknown, and many of the precursor compounds exhibit properties that are very different than the carboxylate or sulfonate end products (Conder et al., 2010). The final stage of the water treatment process for W1 and W2 is comprised of chlorination, which is one of the oxidation processes used for the disinfection of the water supply. Earlier work done by Schröder and Meesters (2005) found some oxidizing reagents were ineffective in degrading PFOA and PFOS, but could break down some precursors of PFOA, PFOS and partly fluorinated molecules. PFASs, especially PFOA and PFOS, adsorbed into the organic matter, which becomes degraded by chlorine in the process of chlorination, are likely to release in the water. However, the relationship between chlorination and the increase of PFASs, especially PFOA and PFOS, is not clearly understood and requires further study. In addition, the finding that different variables could be affecting the increase of PFASs in the final effluent should be further studied.

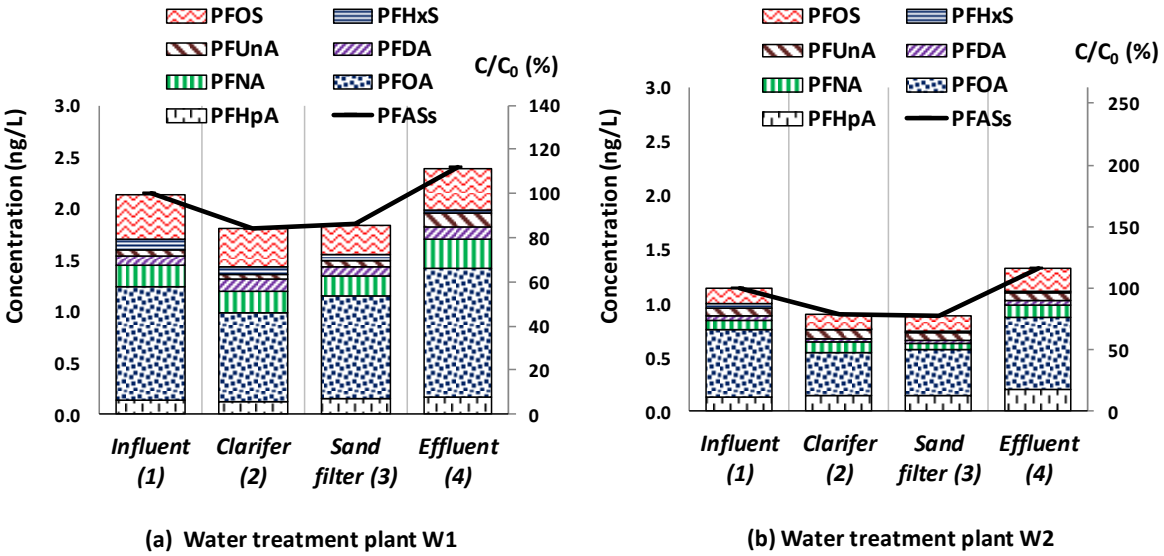

Figure 3. The average concentration of seven PFASs in water samples of each process of W1 and W2 water treatment plants

When comparing with the advanced treatment process (W3) by reverse osmosis for treating industrial wastewater to use as tap water for distribution to factories inside an industrial estate, there was more effective reduction of PFOA contamination, with the efficiency of more than 90%. The removal percentage of PFHpA, PFNA, PFDA, PFUnA, PFHxS, and PFOS were different, as shown in Figure 4, at 96.79%, 91.00%, 91.68%, 77.40%, 82.80%, and 61.73%, respectively. The average PFASs concentration in the influent and effluent for W3 was 183.91 ng L^{-1} and 12.0 ng L^{-1}, respectively. The Reverse Osmosis (RO) process has been the key process enabling the removal of PFASs. This finding is consistent with several studies (Flores et al., 2013; Quiñones & Snyder, 2009; Rahman et al., 2014; Thompson et al., 2011b) showing that high pressure membrane or reverse osmosis was found to be able to effectively remove PFOA and PFOS, as well as other perfluoroalkyl substances.

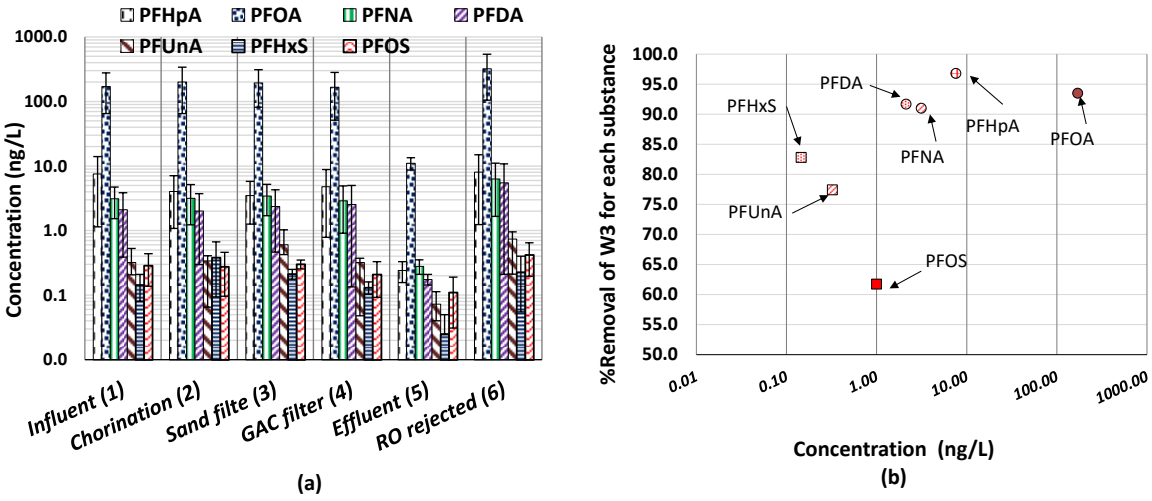

Figure 4. PFASs concentration in the W3 water treatment plant

Conclusions

The water treatment processes, consisting of clarifier, sand filter and chlorination, were in existing water treatment plants in Bangkok used for the production and distribution of tap water to residences in the city. PFOA and PFOS were abundantly discovered in all water samples of water treatment processes in this study at 0.62-0.96 ng L^{-1} and 0.22-0.31 ng L^{-1}, respectively. For PFHpA, PFNA, and PFUnA, they were all detected particularly in some sample groups. PFDA and PFHxS were <LOQ in all water samples. The average concentration of each PFASs was found in the range of 1.05-1.77 ng L^{-1} (for all 7 PFASs) whereas it was maximally detected in effluent.

The raw water quality of the water treatment process was found to be a major factor, which caused the concentration of PFASs in the two water treatment plants to be different. The average PFASs concentrations in the influent for W1 and W2 were 2.13 ng L^{-1} and 1.14 ng L^{-1}, respectively, and in the effluent for W1 and W2 they were 2.25 ng L^{-1} and 1.15 ng L^{-1}, respectively. Although during the processes, the concentration of PFOA, PFOS and other PFASs were partly reduced, it was also found that the contamination of PFOA, PFOS and other PFASs in water samples of WTP effluent had actually increased in the final stage and was higher than in WTP influent. When comparing the water treatment process of Bangkok city with another advanced treatment process, which has been using reverse osmosis for the production of tap water in an industrial estate, there was more effective reduction of PFOA and PFOS contamination by more than 90%. In the future, Bangkok water treatment plants will need to develop the advanced treatment system to deal with such emerging contaminants like PFASs.

Acknowledgement

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Perfluorinated compounds in groundwater of Thailand: Occurrence, source identification and spatial distribution

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Abstract

Contamination of groundwater with PFCs has been studied in other countries, but not in Thailand, where groundwater is a precious fresh water resource and is being increasingly drawn for consumption. However, large amounts of municipal and industrial refuse has been improperly disposed of and as a result, landfill leachate derived from waste disposal sites can be one of the potential sources of groundwater contamination. The composition patterns of PFCs, distribution and soil characteristics significantly contribute to their source analysis. The objectives of this study were: (1) to examine the levels of PFCs in Thailand groundwater, (2) to identify potential sources, and (3) to study the spatial distribution of PFCs. Groundwater samples were collected around municipal waste disposal sites (MWDS) and industrial waste disposal sites (IWDS). Seven PFCs: PFHpA, PFOA, PFNA, PFDA, PFUnA, PFHxS, and PFOS were extracted by solid-phase extraction (SPE) technique and analyzed by high-performance liquid chromatography-tandem mass spectrometer (HPLC-MS/MS). Total

PFCs in groundwater around the MWDSs varied from 1.68 to 7.75 ng L^{-1}, where PFOA and PFOS were the most abundant ones, while PFDA was not observed. The total PFCs in groundwater around Nong Nae IWDS and Map Phai IWDS varied from 4.43 to 10.80 ng L^{-1} and 2.64 to 42.01 ng L^{-1}, respectively. Similar to those around the MWDS areas, PFOA and PFOS were the most dominant compounds. PFHxS was frequently observed in the groundwater around the IWDSs, suggesting that it has been used as a substitution of PFOS-based compounds due to it having a shorter chain length or resulting from degradation of fluorotelomers. In addition to source identification, the hierarchical cluster analysis showed that other than the waste disposal site, other factors or activities could have been involved. It was found that livestock farming and an abandoned pond very close to the groundwater well could have affected the levels of PFCs in the groundwater. Moreover, spatial distribution showed that besides the impact of waste sources, soil characteristics and interaction between negative charged PFCs and cation in the soil played an important role in the PFCs contamination in groundwater.

Key words: Groundwater; perfluorinated compounds; municipal waste disposal site; industrial waste disposal site; soil properties; sources identification

1. Introduction

Perfluorinated compounds (PFCs) are emerging contaminants which have been used in a wide range of manufacturing including semiconductors, coatings for paper food packaging and textiles, and aqueous fire-fighting foams (AFFF) (Prevedouros *et al.*, 2006; Renner, 2001). Because of their strong carbon and fluorine bonds and hydrophilic and lipophilic characteristics, they are extremely persistent, thermal and chemical durable as well as bioaccumulative (Buck *et al.*, 2011). In a differentiation of PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been under continual investigation globally

in the environment, animal tissues, and human blood (Giesy & Kannan, 2001; Kannan *et al.*, 2004).

Ever since then global public health and environmental concern involving PFCs have been increasing considerably, and their large-scale production and uses have been restricted. In Thailand, although the usage and imported amounts of PFCs are currently unknown, their occurrence has been investigated since 2007, and this investigation is being continuously carried out. The presence of PFCs in Thailand has been reported in numerous environments, consumer products, and other materials: river water, wastewater, raw water, tap water, bottled water, air, cosmetics, food packaging, and textiles (Boontanon *et al.*, 2012; Keawmanee *et al.*, 2015; Kunacheva, 2009a; Kunacheva *et al.*, 2009b; Kunacheva *et al.*, 2010; Pattanasuttichonlakul *et al.*, 2014; Poothong *et al.*, 2012; Shivakoti *et al.*, 2010; Supreeyasunthorn *et al.*, 2016).

Groundwater is known as a precious fresh water resource and is being increasingly drawn upon in Thailand, particularly in rural areas where surface water is insufficient and polluted. Although groundwater is naturally purified by soil and deep-rock layers, nevertheless, groundwater pollution could be seriously affected by numerous sources of pollution. Furthermore, in Thailand large amounts of municipal and industrial refuse has been improperly disposed of due to lack of effective management and monitoring budgets. Several research studies have documented that one of potential sources of groundwater contamination could be landfill leachate derived from waste disposal sites. Landfill leachate can contain a wide range of compounds with environmental and human health concerns (Eggen *et al.*, 2010). Levels of PFCs reported in landfill leachate were from the ng range up to several μg range in other countries (Benskin *et al.*, 2012; Busch *et al.*, 2010; Eggen *et al.*, 2010), while there is no data on the occurrence of PFCs in groundwater in Thailand. Therefore, this study aimed to determine PFCs levels in groundwater, identify expected potential sources of the contamination, and study their spatial distribution. This study would be beneficial for

76 understanding their contamination in groundwater, for providing information for further
77 study, and for implementation of environmental standards and regulations.
78
79 **2. Materials and Methods**
80 *2.1 Standards and reagents*
81 Seven PFCs standards: perfluorohaptanoic acid (PFHpA), perfluorooctanoic acid
82 (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA),
83 perfluoroundecanoic acid (PFUnA), perfluorohexane sulfonate (PFHxS), and perfluorooctane
84 sulfonate (PFOS) were selected. High purity solvents: methanol HPLC grade (>99.99%),
85 methanol ACS grade, and acetonitrile HPLC grade (>99.8%); and ammonium acetate (98%)
86 were purchased from Merck KGaA (Millipore, Germany). All the standard solutions were
87 prepared in methanol HPLC grade. Ultrapure water used in chemical analysis was produced
88 by a RiOs-DI® Water Purification System (Millipore, Germany).
89 *2.2 Sampling sites and sample collection*
90 The groundwater sampling points were chosen in three cities in Thailand, which are given
91 in **Figure 1**. The groundwater was collected from domestic groundwater wells nearby waste
92 disposal sites in Bang Sai and Sena MWDS, Ayutthaya (*n*=12), Nong Nae IWDS, and
93 Chachoengsao (*n*=4), which have been in continual operation, and Map Pai IWDS, Chonburi
94 (*n*=15), which has been completely closed. The samples were directly collected from faucets
95 connected to the groundwater wells and pumping systems by using 1.5-L PET bottles, which
96 were rinsed with methanol and dried prior to use. The containers were rinsed by the water
97 samples three times to prepare the same conditions as the samples before collection. After
98 sampling, the samples were stored in a cooler box and brought back to the Water Quality
99 Analysis Laboratory, Mahidol University. The samples were filtered by GF/B glass filter.
100 Glass bottles and glass equipment were avoided during the experiment due to the fact that
101 target compounds may adhere to the glass in aqueous solutions. Teflon equipment was also

avoided because interferences may be introduced to the samples of extracts (Hansen *et al.*, 2002; Yamashita *et al.*, 2004).

2.3 Sample extraction and instrumental analysis

PFCs were extracted by Solid Phase Extraction (SPE) technique. A 1500 mL of water sample was filtered by 1 μm GF/B glass fiber filter and then loaded into PrecepC-Agri (C18) cartridges using concentrators at a flow rate of 10 mL/min. Before loading, the concentrators were washed by methanol at a flow rate of 10 mL/min for 5 min, followed by milli-Q water at a flow rate of 10 mL/min for 10 min and then the cartridges were preconditioned by 10 mL of methanol, followed by 2 times of 10 mL milli-Q water. After that, target analytes were eluted by 4 mL of methanol, followed by 2 mL of acetonitrile. Eluents were gently purged by nitrogen gas and reconstituted with 0.5 mL of 30% acetonitrile. Analysis of target PFCs was performed by using Agilent 1200SL HPLC coupled with Agilent 6400 MS/MS, in negative mode of electrospray ionization (ESI). Mobile phases consisted of (A) 10 mM ammonium acetate in ultrapure water and (B) 100% acetonitrile (HPLC/MS grade). The initial mobile phase was 30% acetonitrile, and then ramped up to 60% acetonitrile at 16.5 minutes, and kept for 3.5 minutes. At 23 minutes, acetonitrile went up to 70%, and then linearly ramped up from 70% to 90% at 26 minutes. After that, the mobile phase gradient ramped down again to 30% acetonitrile for 4 minutes. The total running time was 30 minutes. The analytical parameters by HPLC-MS/MS analysis are given in **Table 1**.

2.4 Quality control

Five points of a calibration curve comprising 0.1 to 10 μg L^- were prepared with the determination coefficients (R^2) more than 0.999. Limit of detection (LOD) and limit of quantification (LOQ) of the measurement method were defined as the concentration with signal-to-noise ratios (S/N) equal to 3:1 and 10:1, respectively (Yamashita *et al.*, 2004). The recoveries of the seven PFCs in groundwater matrix were evaluated by spiking 10 μg L^- of

each of the PFCs standards into one liter of the sample. A blank sample which used ultrapure water was prepared and the same procedure as the spike samples was followed. The recovery rates of target compounds are shown in **Table 1**.

2.5 Statistical analysis

Source identification was evaluated by hierarchical cluster analysis using IBM® SPSS® Statistics for Windows 20. The Ward's method (squared Euclidean distance) was used as an agglomeration technique. Cluster analysis is considered as the multivariate statistical method for source apportionment of organic pollutants (Xiao *et al.*, 2012) and normally is used to identify groups of individuals or objects that are similar to each other. Similarity patterns of PFCs were agglomerated in the same cluster. Before the analysis, concentrations higher than or equal to limit of detection (LOD) but less than limit of quantification were assigned with a concentration twice that of the LOD, and those at or below the LOD were assigned as zero (Yao *et al.*, 2014).

3. Results and Discussion

3.1 Concentrations of PFCs in groundwater around the municipal waste disposal sites (MWDSs) and the industrial waste disposal sites (IWDSs) and their distribution patterns

The concentrations of PFCs in all groundwater samples around the MWDSs and the IWDSs are summarized in **Table 2**. Six target compounds: PFOS, PFOA, PFHpA, PFNA, PFUnA, and PFHxS were detected in all groundwater samples collected around Bang Sai MWDS, while PFDA was undetectable from any of the groundwater samples around Bang Sai MWDS. Five of seven PFCs: PFOA, PFOS, PFNA, PFUnA, PFHpA were observed in the groundwater around Sena MWDS, whereas PFDA and PFHxS were absent. The concentrations of total PFCs in groundwater around both MWDSs ranged from 1.68 to 7.75 ng L^{-1}. Among them, PFOS was the most abundant one in the groundwater around Bang Chai MWDS, followed by PFOA, PFHpA, PFNA, PFUnA, and PFHxS, respectively, while PFOA was

dominant in the samples around Sena MWDS. It could be noticed that the PFCs distribution pattern varied among the areas although they were surrounded by the MWDS. This could be affected by rain input and waste arrangement variations within a waste disposal site, which may impact the initial leachate components before reaching the groundwater (Eschauzier *et al.*, 2013). The levels of total PFCs in the groundwater around Nong Nae IWDSs and Map Pai IWDS, where illegal industrial waste dumping has occurred, varied from 4.43 to 10.80 ng L^{-1} and 2.64 to 42.01 ng L^{-1}, respectively. It could be seen that the concentrations were much higher than those around MWDS. Four target compounds: PFOA, PFOS, PFHxS, and PFHpA were measured in the samples around Nong Nae IWDSs, while all PFCs were detected in those around Map Pai IWDS. Among the target compounds found the dominant ones were PFOA and PFOS, which is similar to those found in other countries. It could be confirmed that PFOS and PFOA are still being used in industrial processes or are a part of chemicals used in consumer products. Importantly, PFHxS was frequently observed in the groundwater samples around two IWDSs, which might indicate that it has been used as a substitution of PFOS-based compounds due to it having a shorter chain length, or having resulted from degradation of fluorotelomers. However, PFHxS may not be a good alternative because it has been determined that it has much more liver toxicity than PFOS (Lloyd-Smith & Senjen, 2015). Therefore, this could be a greater human health concern if the water is used as a drinking water resource. In addition to total PFCs concentrations around the IWDSs, it could be seen that total PFCs around Map Pai IWDS were noticeably higher than those around Nong Nae IWDS; it might be caused by other factors besides sources, such as the effect of soil components which are described further.

3.2 Potential source identification

The possible sources of PFCs were primarily classified by a hierarchical cluster analysis using IBM® SPSS® Statistics for Windows 20, based on analysis of their distribution patterns. The PFCs distribution patterns could be categorized into 3 clusters. The dendrogram

result from the hierarchical cluster analysis of all groundwater samples is presented in **Figure 2**.

Most groundwater samples around Bang Chai MWDS, Sena MWDS and Nong Nae IWDS were classified into cluster 1, which are surrounded by villages in rural areas. Although Nong Nae IWDS was represented as an industrial waste site category, the concentrations found in this area were classified into the same group with those around the municipal waste disposal sites. It should be remarked that other than types of waste source, other factors may be involved.

In clusters 2, three wells: IW_CB07, IW_CB11 and IW_CB14 were classified in the same group. This cluster presented unique PFCs distribution patterns, with PFOS being the most predominant substance found, followed by PFOA, PFHxS, PFNA, PFHpA, and PFDA. Surprisingly, these wells are quite far from Map Pai IWDS by 2.15 km, 1.5 km, and 3.4 km, respectively, but the concentrations were high. This might be caused by other potential sources, because IW_CB07 and IW_CB14 are very close to large abandoned ponds, and IW_CB11 is next to a pig farm. A map of these locations is presented in **Figure 2**. It was difficult to pinpoint the pig farm as a potential source of contamination, because the contamination of PFCs is in animal feed, and the absorption and elimination of PFCs from animals especially pigs is not commonly reported, but wastewater from the livestock also could not be ignored. Lai *et al.* (2016) reported that wastewater from livestock industries are consider to be potential contamination sources of PFCs in Kinmen Lake, Taiwan. Therefore, it is suspected that the pig farm might be a potential source of PFCs contamination in sampling point IW_CB11, especially if there has been no appropriate wastewater or pig manure management. In the case of well number IW_CB07 and IW_CB14, the potential source of PFCs contamination could not be easily identified because the use of the large abandoned ponds could not be determined.

Clusters 5 and 6 contained most of the groundwater samples collected around Map Phai IWDS. A similar pattern was observed in clusters 5 and cluster 6, in which PFOA was the most abundant followed by PFOS; the total PFCs concentrations in cluster 6 were obviously higher than for those in cluster 5. The greatest concentration was quantified in the groundwater samples around Map Phai IWDS, which is in an industrialized area. Consistent with previous studies, PFCs were detected in industrialized or urbanized areas more than rural areas due to the presence of industrial activity (Wang et al., 2012). It should be remarked that the groundwater samples collected around both Nong Nae IWDSs, Chachoengsao and Map Phai IWDS, Chonburi were classified into different clusters, although they were representing IWDS. Therefore, their contamination and transportation might involve other factors besides the sources, which is discussed in the next section.

3.3 Spatial distribution of PFCs in groundwater around the MWDSs and the IWDSs

Regarding the results that have been discussed previously, it is clear that high concentrations of PFCs were detected in groundwater around the IWDSs, indicating that IWDSs play a significant role in the contamination of groundwater. However, the difference in PFCs levels in groundwater around Nong Nae IWDSs and Map Pai IWDSs were remarkable, even though they both represent similar sources of contamination. As mentioned previously, they might very well be affected by other factors. Therefore, study on the horizontal distribution of PFCs could illustrate effecting factors and their possible behaviors. Horizontal distribution was analyzed with geostatistical data (soil map) which was derived from the Land Development Department (LDD) of Thailand. In order to study the horizontal distribution, the data were analyzed using ArcGIS 10.1.

From **Figure 3 (a, b)**, it can be noticed that the soil series in the Ayutthaya area where the sampling points are located is comprised of soil series named Ayutthaya (Ay) and Sena (Se). The Ay and Se soil series mostly consist of clay, so the main physical property is very low water permeability; in addition, major chemical properties are high acidity (pH 5.5 to 6 and 4

to 5.5, respectively), and high cation exchange capacity (CEC) (LDD, 2010). It could be assumed that low PFCs concentrations in groundwater around the MWDSs might result from PFCs interaction with cation, which is consistent with the study reported by Xiao *et al.* (2015). In addition, Wang and Shih (2011) also reported that adsorption increases when pH decreases, they also found that Ca^{2+} and Mg^{2+} can form bridges with PFOA anions and PFOS can be bridged by Ca^{2+}. Therefore, adsorption seems to be the main mechanism of PFCs contamination in these areas.

In the case of the PFCs concentration around the IWDSs, the concentration and their distribution patterns plotted with soil series in the areas are presented in **Figure 4 (a, b)**. It can be observed that PFCs concentration in groundwater around Nong Nae IWDSs was quite lower than those around Map Pai IWDS. This might be because these two areas consist of different soil series and soil properties. The soil series, named Klaeng (Kl) and Don Rai (Dr), are soil series around Nong Nae IWDSs where the sampling points are located, whereas the soil series named Ban Bueng (Bbg) and Chonburi (Cb) are soil series around Map Pai IWDS where the sampling points are located. The Kl and Dr soil series contain moderate CEC, low water permeability, and pH of 4.5 - 6.4 which is similar to the soil properties in the Ayutthaya areas. In contrast, low CEC, high water permeability, and pH of 5.5 – 8.5 were reported for Bbg and Cb soil series (LDD, 2010). Therefore, water permeability and the interaction of a negative charged form of PFCs with level of CEC in the soil most likely play an important role in the distribution of PFCs contamination.

4. Conclusions

There was variability in the distribution of PFCs in groundwater around the MWDSs and the IWDSs. PFCs were quantified in all groundwater samples. Total PFCs varied from 1.68 to 7.75 ng L^{-1} and 2.64 to 42.01 ng L^{-1} around MWDSs and IWDSs, respectively. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were the most dominant ones found in all

samples. The occurrences of PFCs in groundwater around IWDSs were significantly higher than those around MWDSs, indicating more PFCs are intensively released from IWDSs. In terms of potential sources identification, it was performed by hierarchical cluster analysis. Classification of groundwater samples was based not only on total concentrations, but also on similar PFCs composition patterns. It should be remarked that not only direct sources of contamination influence the PFCs contamination, but other factors could have been involved. Besides the impact of sources, interaction between soil characteristics and PFCs properties plays an important role in PFCs contamination in groundwater. Additionally, a deep clay layer which is a major soil characteristic around the two MWDSs in Ayutthaya and Nong Nae IWDSs in Chachoengsao, can protect the aquifer, reduce movement, and adsorb the contaminants better than the sandy soil found around Map Pai IWDS, Chonburi. Moreover, further study related to movement of PFCs in the soil column is recommended in order to illustrate and confirm their transportation mechanism. In conclusion, we firmly conclude that waste disposal site leachate could be a significant source of PFCs in Thailand groundwater.

5. Acknowledgements

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List of Figures

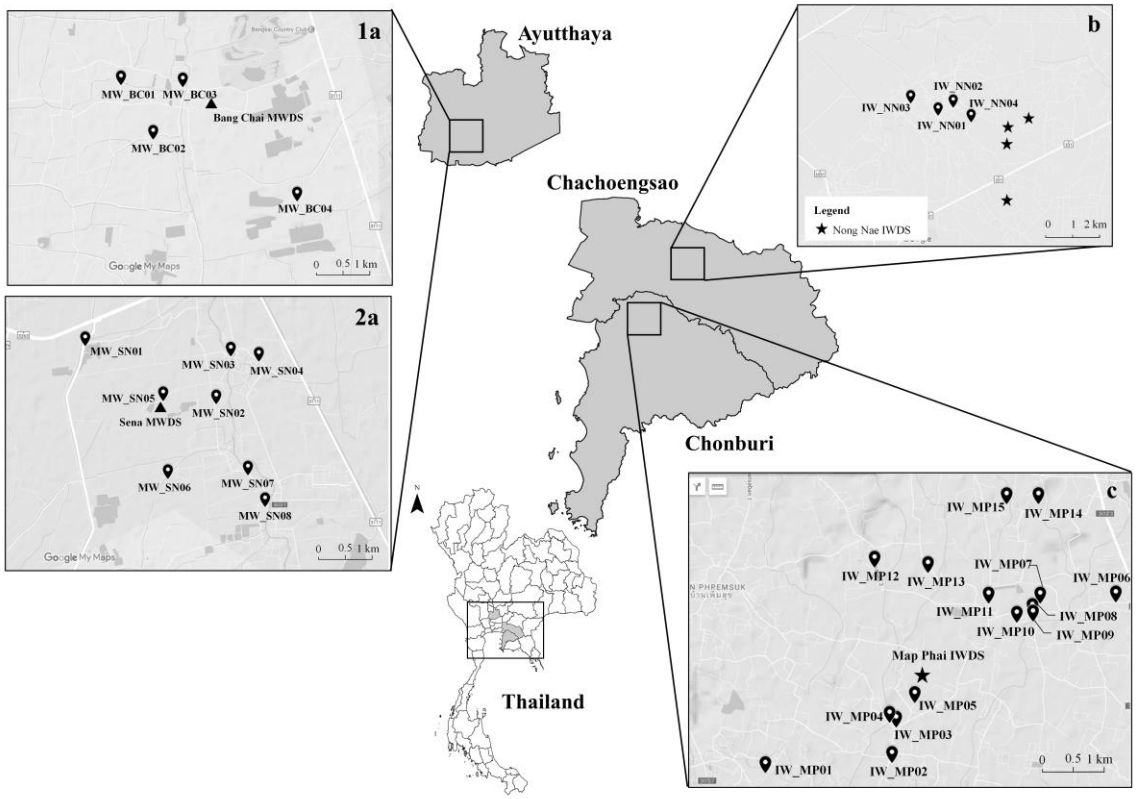

Figure 1 Groundwater sampling points in the selected study areas (1a) around Bang Sai MWDS, (2a) around Sena MWDS, (b) around Nong Nae IWDSs, and (c) Map Pai IWDS

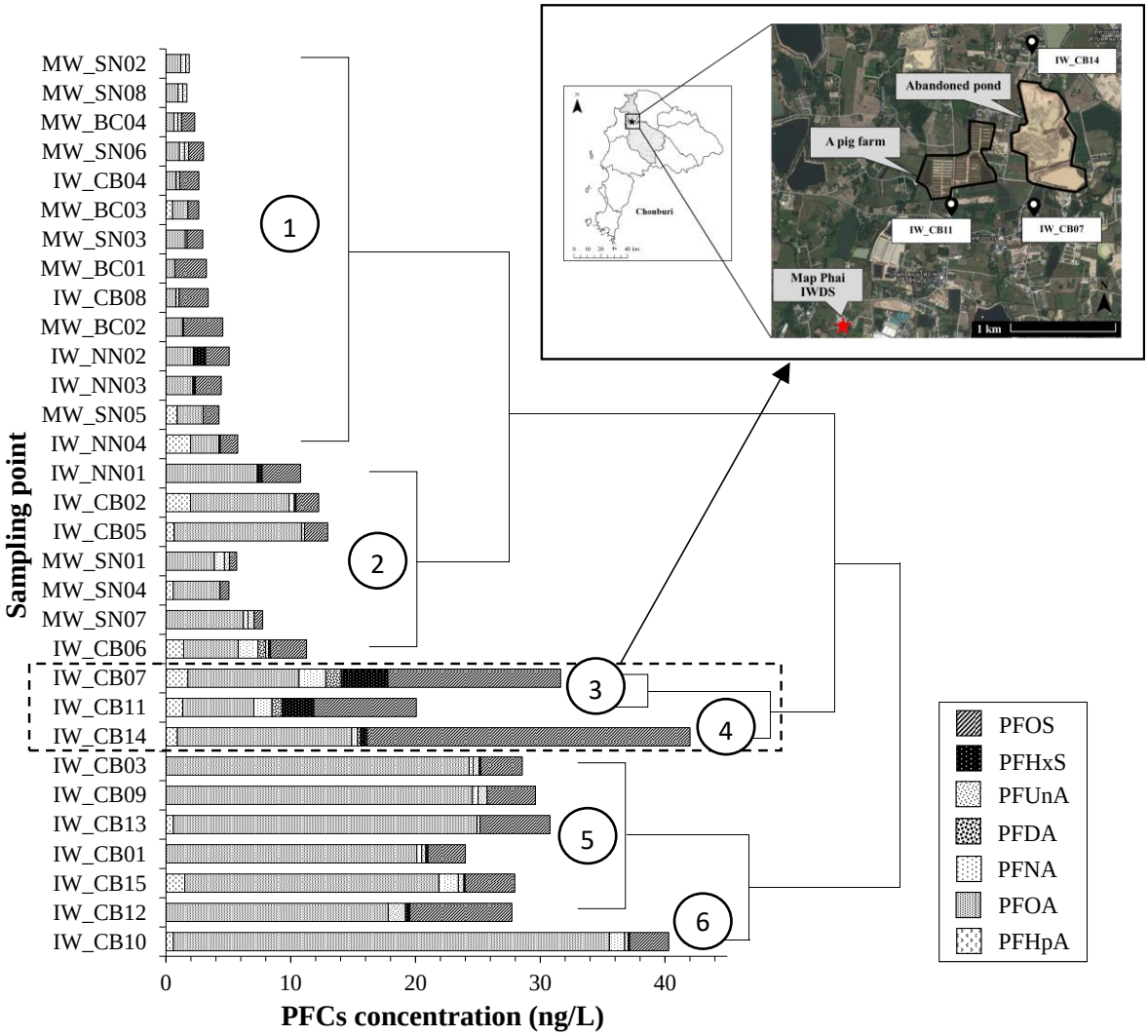

Figure 2. The dendrogram results from hierarchical cluster analysis

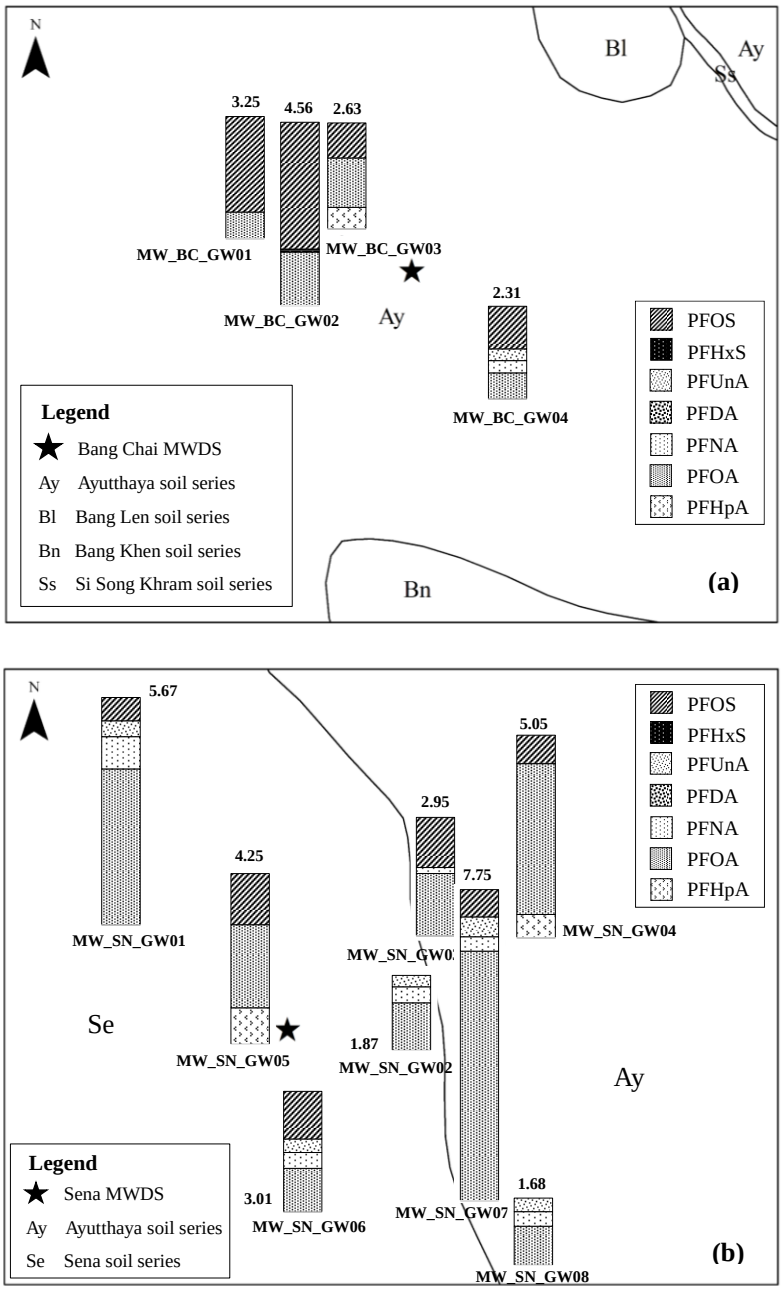

Figure 3 Map of PFCs concentration (ng L^{-1}) around MWDSs, their distribution patterns and soil series around (a) Bang Sai MWDS, (b) Sena MWDS

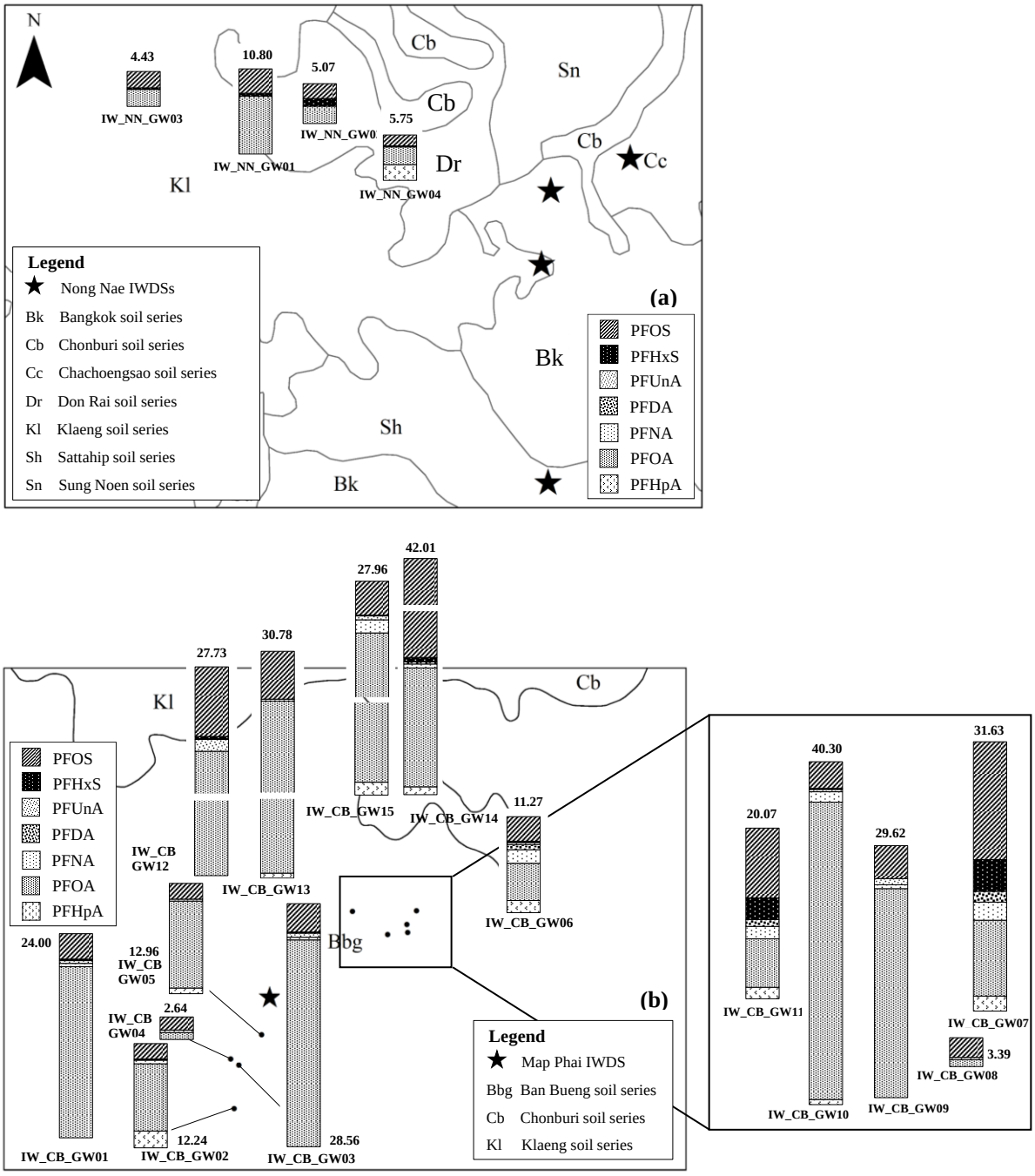

Figure 4 Map of PFCs concentration (ng L^{-1}) around IWDSs, their distribution patterns and soil series around (a) Nong Nae IWDS, and (b) Map Pai IWDS

List of Tables

Table 1. Analytical parameters by HPLC-MS/MS analysis and recovery rates (%) of PFCs in spiked water samples

Compound	Parent ion (m/z)	Daughter ion (m/z)	Retention time (min)	LOD[a] (ng L^{-1})	LOQ[b] (ng L^{-1})	Recovery (n = 5)	
						Range[c]	Mean[c]
PFHpA	363	319	10.6	0.13	0.45	92.19-99.38	95.90
PFOA	413	369	13.9	0.11	0.37	99.77-118.56	106.94
PFNA	463	419	16.4	0.09	0.30	97.18-101.94	99.02
PFDA	513	469	20.7	0.07	0.23	87.65-94.20	91.36
PFUnA	563	519	22.8	0.07	0.23	73.26-92.02	83.82
PFHxS	399	80	15.0	0.02	0.07	99.73-103.80	100.87
PFOS	499	80	22.2	0.11	0.37	88.04-99.72	93.16

[a] Limit of detection
[b] Limit of quantification
[c] Ten nano gram per liter of each PFCs standards were spiked into the samples

680 **Table 2** PFCs concentration (ng L^{-1}) in groundwater around the municipal waste disposal
681 sites and the industrial waste disposal sites
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Sampling location	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFHxS	PFOS
Bang Sai MWDS							
MW_BS01	<LOQ[a]	0.71	N.D.[b]	N.D.[b]	N.D.[b]	<LOQ[a]	2.54
MW_BS02	<LOQ[a]	1.33	<LOQ[a]	N.D.[b]	<LOQ[a]	0.07	3.15
MW_BS03	0.54	1.23	<LOQ[a]	N.D.[b]	<LOQ[a]	N.D.[b]	0.87
MW_BS04	<LOQ[a]	0.65	0.30	<LOQ[a]	0.29	<LOQ[a]	1.06
Sena MWDS							
MW_SN01	<LOQ[a]	3.89	0.80	<LOQ[a]	0.40	<LOQ[a]	0.58
MW_SN02	<LOQ[a]	1.19	0.40	N.D.[b]	0.29	<LOQ[a]	<LOQ[a]
MW_SN03	<LOQ[a]	1.55	0.15	N.D.[b]	<LOQ[a]	<LOQ[a]	1.25
MW_SN04	0.58	3.76	<LOQ[a]	N.D.[b]	<LOQ[a]	<LOQ[a]	0.71
MW_SN05	0.91	2.07	<LOQ[a]	N.D.[b]	<LOQ[a]	<LOQ[a]	1.27
MW_SN06	<LOQ[a]	1.09	0.40	N.D.[b]	0.34	N.D.[b]	1.18
MW_SN07	<LOQ[a]	6.22	0.36	<LOQ[a]	0.49	<LOQ[a]	0.68
MW_SN08	<LOQ[a]	0.97	0.36	N.D.[b]	0.34	<LOQ[a]	<LOQ[a]
Nong Nae IWDS							
IW_NN01	<LOQ[a]	7.32	<LOQ[a]	N.D.[b]	N.D.[b]	0.39	3.08
IW_NN02	<LOQ[a]	2.21	<LOQ[a]	N.D.[b]	N.D.[b]	0.98	1.89
IW_NN03	<LOQ[a]	2.16	N.D.[b]	N.D.[b]	<LOQ[a]	0.20	2.08
IW_NN04	1.98	2.26	N.D.[b]	N.D.[b]	N.D.[b]	0.12	1.39
Map Pai IWDS							
IW_MP01	<LOQ[a]	20.11	0.39	N.D.[b]	0.33	0.17	3.00
IW_MP02	1.97	7.90	0.43	<LOQ[a]	<LOQ[a]	0.13	1.81
IW_ MP03	N.D.	24.31	0.31	<LOQ[a]	0.47	0.14	3.33
IW_ MP04	<LOQ[a]	0.83	<LOQ[a]	<LOQ[a]	0.27	<LOQ[a]	1.53
IW_ MP05	0.66	10.22	<LOQ[a]	<LOQ[a]	0.24	N.D.[b]	1.85
IW_ MP06	1.42	4.38	1.58	0.61	0.24	0.15	2.88
IW_ MP07	1.76	8.91	2.14	1.25	<LOQ[a]	3.73	13.84
IW_ MP08	N.D.	0.80	<LOQ[a]	<LOQ[a]	0.26	<LOQ[a]	2.33
IW_ MP09	<LOQ[a]	24.57	0.45	<LOQ[a]	0.73	N.D.[b]	3.87
IW_ MP10	0.59	34.96	1.22	N.D.[b]	0.28	0.12	3.13
IW_ MP11	1.34	5.71	1.45	0.82	<LOQ[a]	2.54	8.21
IW_ MP12	N.D.[b]	17.82	<LOQ[a]	<LOQ[a]	1.39	0.35	8.17
IW_ MP13	0.59	24.35	<LOQ[a]	N.D.[b]	0.24	<LOQ[a]	5.61
IW_ MP14	0.92	13.97	0.46	0.26	<LOQ[a]	0.52	25.88
IW_ MP15	1.51	20.37	1.56	<LOQ[a]	0.45	0.09	3.99

683 [a] <LOQ refers to values less than limit of quantification
684 [b] N.D. refers to not detected
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Water Science and Technology

Immobilization of Titanium Dioxide and Graphene Oxide Nanoparticles in Polyvinyl Alcohol for PFOS and PFOA Photocatalytic Degradation

--Manuscript Draft--

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Immobilization of Titanium Dioxide and Graphene Oxide Nanoparticles in Polyvinyl Alcohol for PFOS and PFOA Photocatalytic Degradation

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Abstract
Nanocrystalline titanium dioxide (TiO_2) is often used as a photocatalyst in environmental remediation to remove PFOS and PFOA from wastewater. Here, TiO_2 nanoparticles were combined with nano graphene oxide (GO) and then immobilized in a polyvinyl alcohol (PVA) sheet as a TiO_2/GO/PVA nanofilm. PFOS and PFOA were diversified into pH 3, pH 7, and pH 10 pre-testing solutions to mimic samples of aquatic pollution. GO dosages, nanoparticle dispersion methods, and heat treatment were studied to investigate transportation of nanoparticle electron-hole pairs and photocatalytic removal degradation. Results suggested that GO 25 wt% and TiO_2 75 wt% blended by sonication and heated at 120 °C for 3 h represented optimal conditions for PFOS and PFOA removal at 95.99% and 96.86%, respectively.

Keywords
graphene oxide, PFOA, PFOS, photocatalysis, polyvinyl alcohol, titanium dioxide

INTRODUCTION

Water pollution by perfluorinated compounds (PFCs) has become a severe environmental problem. Two perfluorinated compounds commonly used in various applications are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). They have unique properties including strong C-F bonds and are applied in many consumer products and industrial processes as paper and cloth coatings, protective coatings for carpets and furniture, fire-fighting foams, textiles products, and semiconductors (Xu *et al.* 2015). PFOS and PFOA are highly toxic and non-biodegradable; contamination by these products causes problems for both the environment and living organisms. They have been widely detected in drinking water, groundwater, air, and human blood. Detailed research has suggested that they may be associated with human ailments such as thyroid disease, liver tumors, chronic kidney disease, high uric acid, and immune toxicity (Jian *et al.* 2017). Tap water in the Chinese cities of Guangzhou and Shenzhen was contaminated with PFOS and PFOA concentrations exceeding 10 ng/L (Jin *et al.* 2009) with elevated levels in surface soils at 12.2 and 8 ng/g, respectively (Xiao *et al.* 2015). In addition, PFOS and PFOA concentrations in Italian women of reproductive age were 2.43 and 1.55 ng/g, respectively (Felip *et al.* 2015).

Many methods have been used to remove PFOS and PFOA from aqueous effluents including adsorption, ozonation, electrochemical process, reverse osmosis, and membrane filtration (Trojanowicz *et al.* 2018). Photocatalysis offers a promising alternative for oxidation of organic compounds with excellent characteristics as an effective, economical and environmentally friendly technology (Fontana *et al.* 2018). Research at Hunan University, China validated effective degradation of PFOS and PFOA by photochemical technology (Wang *et al.* 2017), while heterogeneous photocatalytic treatment achieved more than 99% decomposition and 38% complete mineralization of PFOA in 7 h (Panchangam *et al.* 2009).

Titanium dioxide (TiO_2) is the most widely used semiconductor in photocatalysis due to its high photocatalytic activity, non-toxicity, low cost, high stability to light illumination, and ability to regenerate several times without significantly reducing effectiveness (Gomez-Ruiz *et al.* 2018). TiO_2 exists in three polymorphic forms as anatase, rutile and brookite. Both anatase and rutile forms have demonstrated efficiency in the degradation of organic and inorganic compounds with anatase showing higher photocatalytic activity (Fontana *et al.* 2018). Although TiO_2 is an efficient photocatalyst, its band gap of 3.2 eV restricts use to the ultraviolet region but this can be overcome by doping with other electron acceptor materials. Graphene oxide (GO) is a new type of carbon nanomaterial that has attracted extensive attention due to its large surface area, fast electron mobility, and high Young's modulus and thermal conductivity (Xu, 2018). With these exceptional properties, graphene has proved to be an outstanding electron photocatalyst which enhances photocatalytic properties of catalysts including TiO_2 (White *et al.* 2018). TiO_2/GO nanocomposites have been extensively studied for photocatalysis among carbon materials or metal oxide nanocomposites. Combining TiO_2 and GO greatly increases photocatalytic activity (Kumar *et al.* 2015) but small-sized nanoparticles are very difficult to remove after usage.

TiO_2 and GO can be immobilized onto a variety of supports without significant reduction in photocatalytic efficiency for more convenient nanoparticle removal from liquid substances. Polyvinyl alcohol (PVA) is a synthetic water-soluble hydrophilic polymer with high dielectric strength, good charge storage capacity and dopant dependent electrical and dielectric properties (Abd El-aziz *et al.* 2017). Addition of TiO_2 and GO nanoparticles into a PVA matrix resulted in a conductive polymer nanocomposite with unique properties and improved photocatalytic activity (Ningaraju *et al.* 2018).

Here, a new photocatalyst was generated by a simple and effective preparation method using TiO_2/GO/PVA nanofilm for degrading PFOS and PFOA water contamination. A TiO_2/GO/PVA catalyst was used to optimize the efficiency of photocatalytic activity through the related factors of GO concentration, dispersion method, and heat treatment time. Concentrations of PFOS and PFOA were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) to obtain photocatalytic efficiency and optimal indices to generate TiO_2/GO/PVA nanofilm.

MATERIALS AND METHODS

Pre-testing pH values of PFOS and PFOA

TiO_2/GO/PVA nanofilms were produced by mixing 20 wt% GO with 80 wt% TiO_2 and then adding 10 g of PVA. The mixture was briefly stirred and then heated to 120 °C for 3 h to obtain TiO_2/GO/PVA nanofilm. A water sample was formulated by spiking Milli-Q water with PFOS and PFOA at an initial concentration of 100 ppb. Nanofilms were prepared at 3 different pH values as pH 3, pH 7, and pH 10.

Preparation of TiO_2/GO/PVA nanofilm

Preparation of TiO_2/GO/PVA nanofilm following two steps as solution casting and heat treatment (Lei *et al.* 2012).

Solution casting. GO nanoparticles were dispersed in 50 mL of Milli-Q water under sonication for 2 h, while TiO_2 solution was prepared by combining TiO_2 nanoparticles and 50 mL of Milli-Q water and mixing using a hotplate stirrer. The two solutions were homogenized for 1 h. Ten grams of PVA were then added into the TiO_2/GO suspension, followed by mechanical stirring at 95 °C for 1 h and

at 60 °C for 3 h before sonication for 30 min to obtain TiO_2/GO/PVA solution. The solution mixture was rested in a beaker to eliminate air bubbles and cool to room temperature. The resultant viscous bubble-free solution mixture was then cast onto clean aluminum foil cups to give a 1 mm-thick layer and the solvent was allowed to evaporate overnight at room temperature. Finally, dried nanofilms were collected from the foil cups. Weight ratio of GO to TiO_2 was varied as 0, 10, 15, 20, 25, and 100 wt%, and the resulting nanofilms were designated as GO-0, GO-10, GO-15, GO-20, GO-25, and GO-100, respectively. Pure PVA was used as a reference under the same conditions.

Heat treatment process. Regenerated nanofilms were cut into square shapes of 30 mm × 30 mm and heat treated under vacuum at 120 °C for 1 h, 3 h, and 5 h to achieve TiO_2/GO/PVA nanofilms.

Photocatalytic degradation

Photocatalytic activity of the sample films was evaluated from the degradation rate of PFOS and PFOA in an aqueous solution with an initial concentration of 100 ppb. The photocatalytic reaction was carried out in a UV cabinet. Four 15-Watt fluorescent lamps were located on a transparent tube as the UV B light source with wavelength of 365 nm. Prior to irradiation, all sample films were immersed into 20 mL of Milli-Q water in plastic beakers spiked with PFOS and PFOA. The beakers were then placed in the cabinet in parallel with shaking at 60 rpm throughout the experiment. During the first hour, all test solutions were kept in the dark to achieve adsorption-desorption photocatalysis equilibrium. Three hours later, the UV light was illuminated at the bottom of the cabinet. Samples were taken at 30 and 60 min and then collected every 15 min for a further 3 h. At given irradiation time intervals, concentrations of PFOS and PFOA were monitored by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS).

RESULTS AND DISCUSSION

pH values of PFOS and PFOA

Figure 1 displays the relation between PFOS and PFOA removal efficiency (%) and pH values at 3, 7, and 10 for 100 ppb initial concentration. Decrease in PFOS and PFOA degradation efficiency was apparent when the solution became alkaline and ionized to form perfluorocarboxylic anion and hydrogen ions at pH value greater than point of zero charge (pzc) of the catalyst (pzc of TiO_2/GO was reported at about 3.2) (Cruz *et al*. 2017). Results showed that pH 3 represented optimal PFOS and PFOA removal efficiency at 94.15% and 90.16%, respectively.

Concentration of graphene oxide (GO)

Influence of different mass ratios of GO and TiO_2 at 0, 10, 15, 20, 25, and 100 wt% including only PVA, and experimental photocatalytic performance times for PFOS and PFOA are shown in Figures 2 and 3, respectively, as a plot of C/C_0 versus contact time (min).

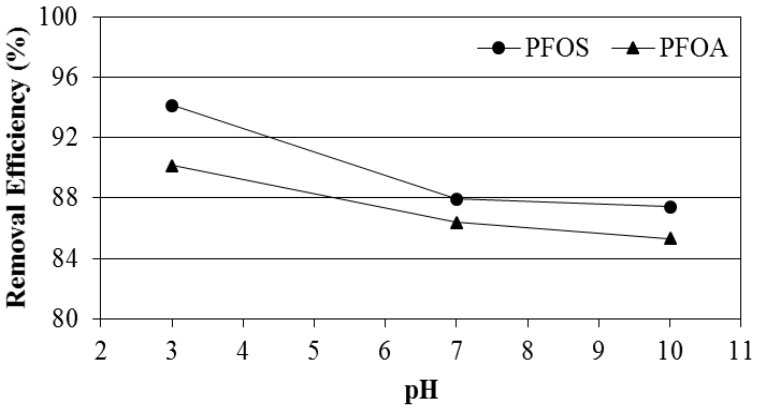

Figure 1. PFOS and PFOA removal efficiency (%) and pH values.

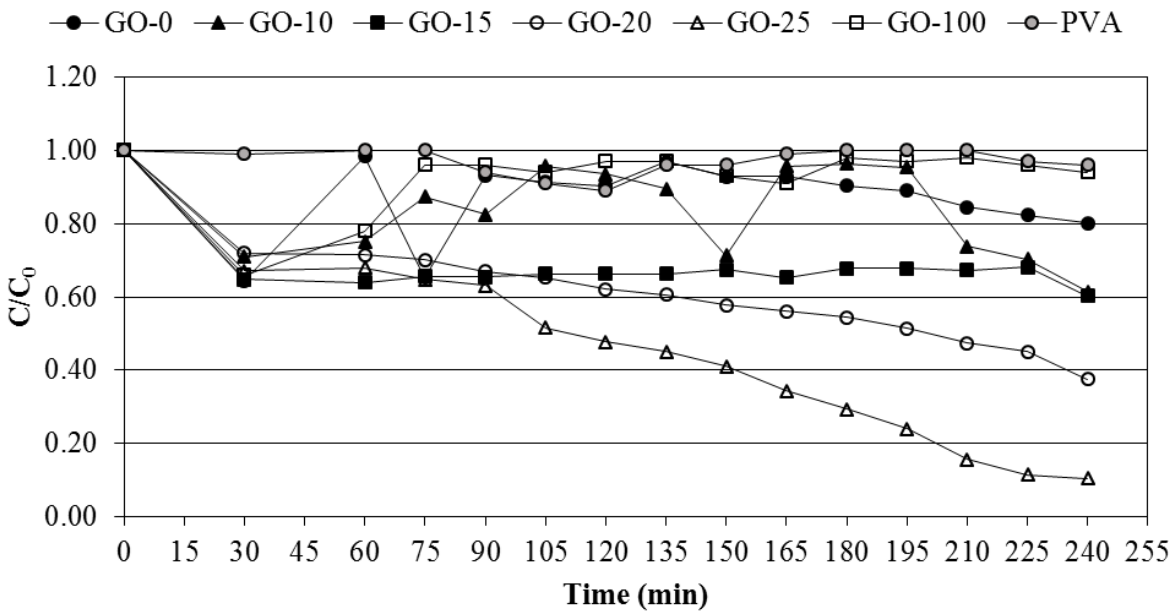

Figure 2. PFOS removal efficiency (%) and time (min) for different GO contents.

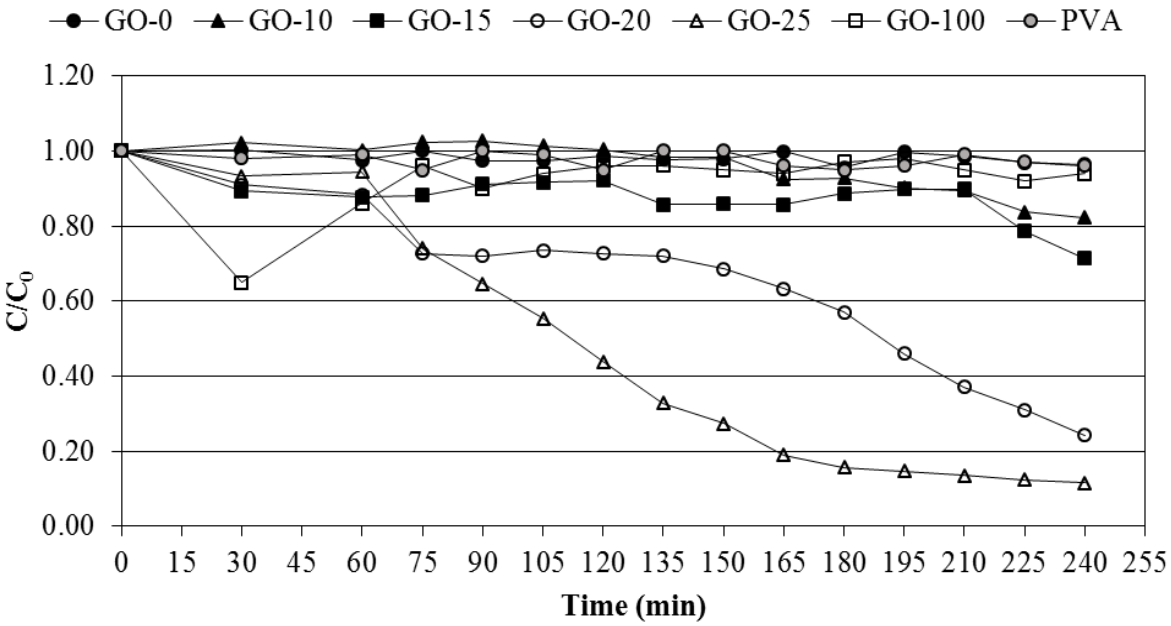

Figure 3. PFOA removal efficiency (%) and time (min) in different GO contents.

Figures 2 and 3 show that absorption of TiO_2/GO catalyst continuously decreased between 0 and 30 min and then increased to achieve stability after 60 min of light irradiation. Higher concentrations of PFOS and PFOA were absorbed by GO-0 and GO-10 than by GO-15, GO-20, GO-25, and GO-100 due to decreasing density distribution of GO on the surface of PVA (Zhang *et al*. 2014). PVA alone presented no photocatalytic activity for PFOS and PFOA degradation. However, remarkably, photocatalytic degradation of PFOS and PFOA was enhanced with increasing mass ratio of GO and photocatalytic time.

Dispersion of nanoparticles on PVA matrix

Morphology of TiO_2 and GO nanoparticles. Figure 4 exhibits transmission electron microscopy (TEM) images from heated TiO_2/GO/PVA nanofilms prepared by sonication. Low-magnification TEM images of TiO_2 and GO are shown in Figures 4(a) and 4(b), respectively. In Figure 4(c), high-magnification TiO_2 nanoparticles are interspersed over the GO surface, proving that TiO_2 interacted with GO. Electrons are effectively transferred between TiO_2 and GO, and play an important role in the sensing mechanism. Figure 4(d) shows the lattice fringe of d-spacing around 0.25 nm of TiO_2, referring to the 101crystallographic plane of rutile (Sun *et al*. 2018).

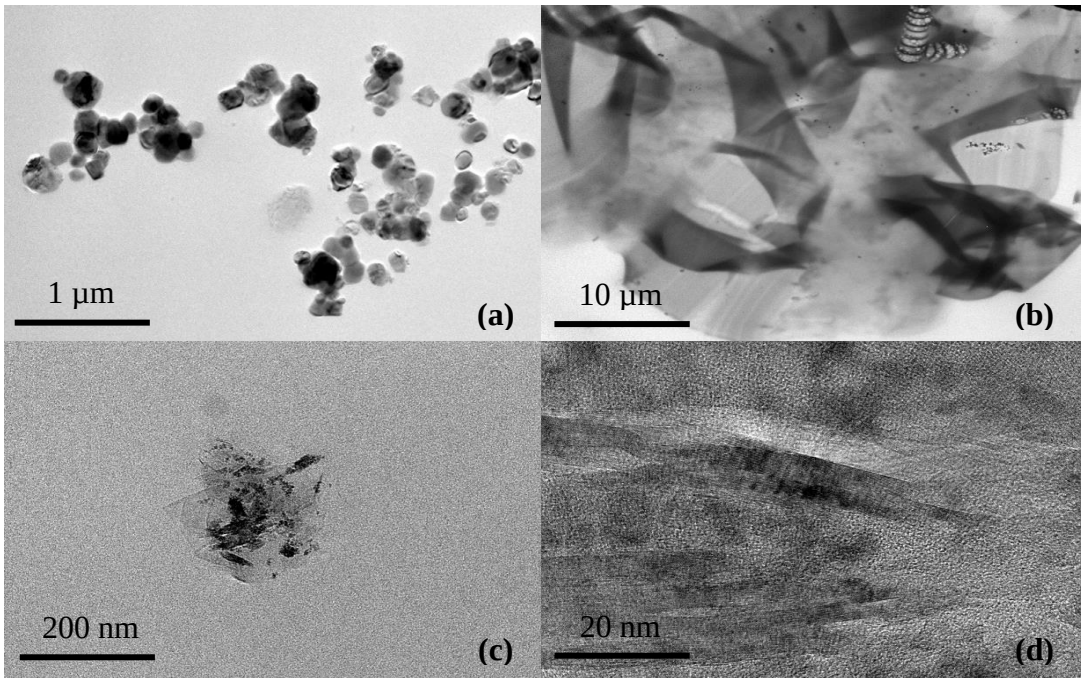

Figure 4. Low-magnification TEM images of (a) TiO_2, (b) GO, (c) high-magnification TEM image of TiO_2/GO, and (d) high-resolution TEM image of TiO_2/GO.

Photocatalytic degradation. Figure 5 presents the influence of different dispersion methods of TiO_2/GO nanoparticles and contact time (min) on PFOS and PFOA photocatalytic reaction displayed as a plot of C/C_0 versus time (min). Concentrations of PFOS and PFOA from both magnetic stirring and ultrasonic sonication methods decreased after 60 min of light irradiation. Removal rates of PFOS and PFOA by the two dispersion processes were not significantly different. PFOS and PFOA removal efficiencies, investigated by sonicated TiO_2/GO/PVA nanofilms after 240 min, were less than results evaluated from stirred nanofilms by factors of 1.09 and 1.08, respectively.

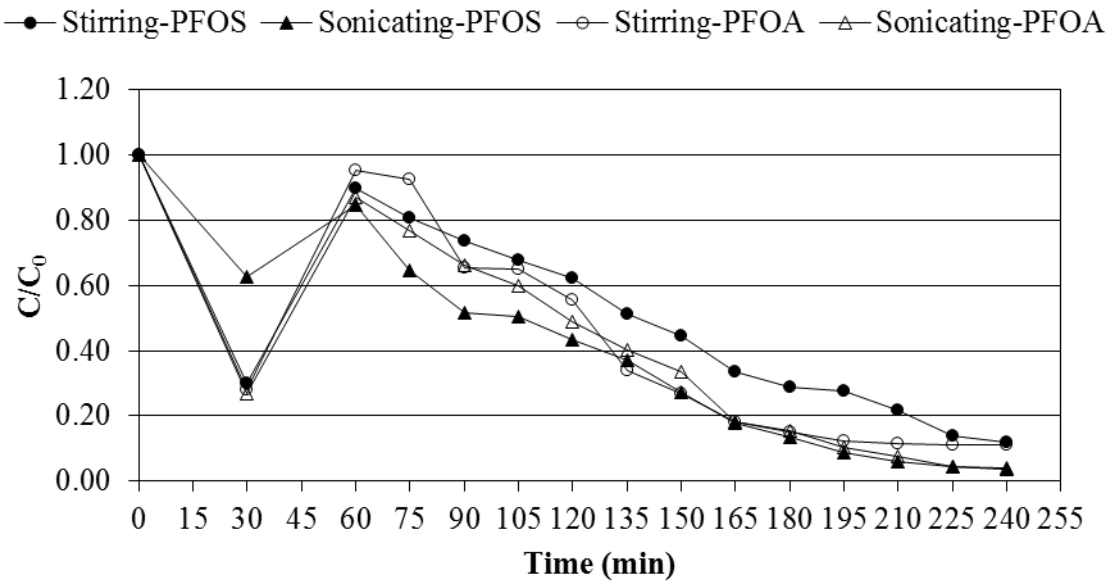

Figure 5. PFOS and PFOA removal efficiency and time (min) for different dispersion methods.

Heat treatment

Chemical bonding immobilized TiO_2 and GO in PVA matrix. TiO_2/GO/PVA nanocomposites were characterized by a Fourier Transform-Infrared (FT-IR) Spectrometer. Wavenumbers were determined within spectral range 600–4000 cm^{-1}. Figure 6 shows FT-IR spectra of unheated nanofilm and heated nanofilm at 120 °C for 1 h, 3 h, and 5 h as a plot of transmittance (%) versus wavenumber (cm^{-1}). The most characteristic FT-IR spectra of GO correspond to vibration of hydroxyl groups (C-OH) at around 3000–3600 cm^{-1}, with a broad peak at 1725 cm^{-1} owing to stretching vibration of carbonyl groups (C=O), bonding of C-OH groups at around 1331–1379 cm^{-1}, and two peaks of C-H stretching at 2924 and 2852 cm^{-1} (Cruz *et al*. 2017). In addition, breathing vibrations at 1058, 1227, 1401, and 1630 cm^{-1} relate to C-O bonding, epoxy groups (C-O-C), O-H bonding, and C=C bonding, respectively (Sun *et al*. 2018). The absorption band of bare TiO_2 indicates a common characteristic typical of TiO_2 corresponding to Ti-O-Ti bonds at around 800–950 cm^{-1}. Moreover, FT-IR spectra of PVA are associated with C-C stretching at 1143 cm^{-1}. For heated TiO_2/GO/PVA nanofilm, a new peak was discovered at 1237 cm^{-1}, defined as the vibration of Ti-O-C bonds. Other new peaks at 797 and 843 cm^{-1} were assigned to hypsochromic shifts of C-C and O-C-C, respectively, owing to change in chemical bonding caused by the formation of Ti-O-C bonds (Lei *et al*. 2012).

Photocatalytic degradation. Figure 7 shows the influence of different heat treatment times for TiO_2/GO/PVA nanofilms (min) on PFOS and PFOA photocatalytic reactions, respectively displayed as a plot of C/C_0 versus time (min). Removal efficiencies of PFOS and PFOA at 1 h were around 85–87%, implying high but not optimal time for TiO_2/GO/PVA nanofilm heat treatment, and reduction in TiO_2/GO catalyst efficiency due to lack of interaction between TiO_2 and GO nanoparticles and PVA (Lei *et al*. 2012). Similarly, nanofilms heated for 5 h displayed significantly reduced PFOS and PFOA degradation efficiency at 85–86%. Five hours was not a suitable time for TiO_2/GO/PVA nanofilm heat treatment because absorption capacity of TiO_2/GO/PVA photocatalyst diminished over time, and photocatalytic reaction of PFOS and PFOA on the nanofilm surface gradually decreased as removal efficiency weakened (Wu *et al*. 2015). Nanofilms heated for 3 h gave optimal heat treatment results with PFOS and PFOA removal efficiency at 95.99 and 96.86%, respectively.

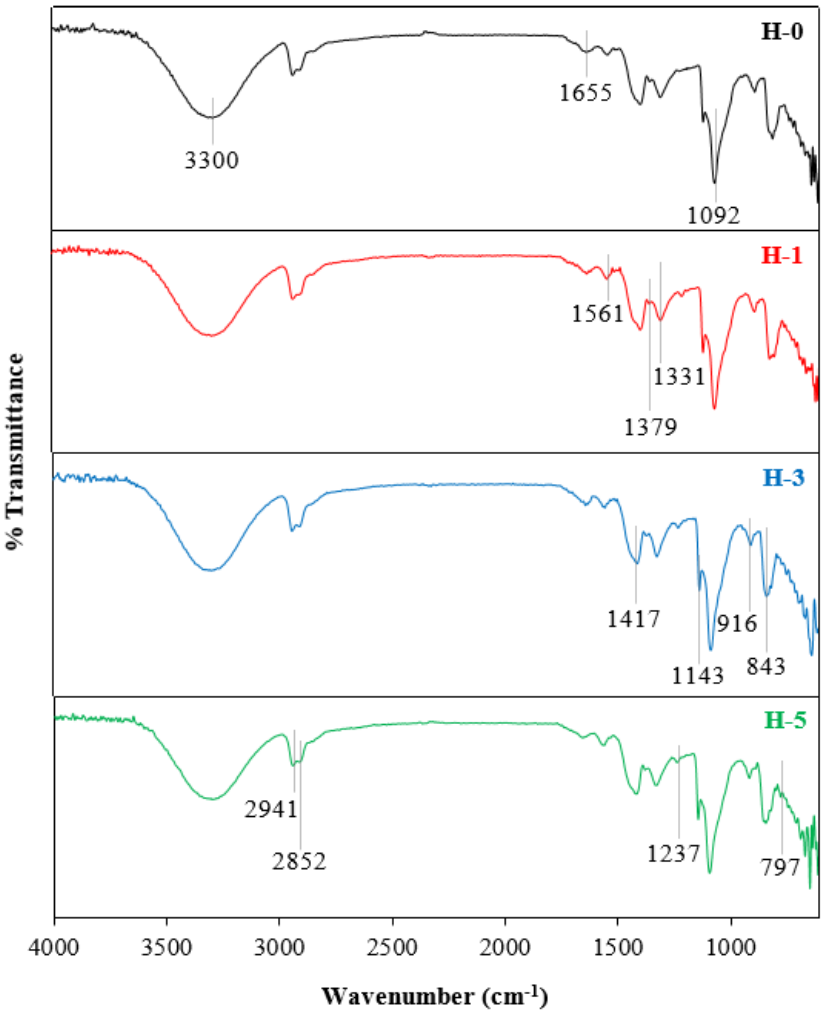

Figure 6. FT-IR spectra of nanofilms heated for different times (h); H-0 (unheated nanofilm), H-1 (1 h), H-3 (3 h), and H-5 (5 h).

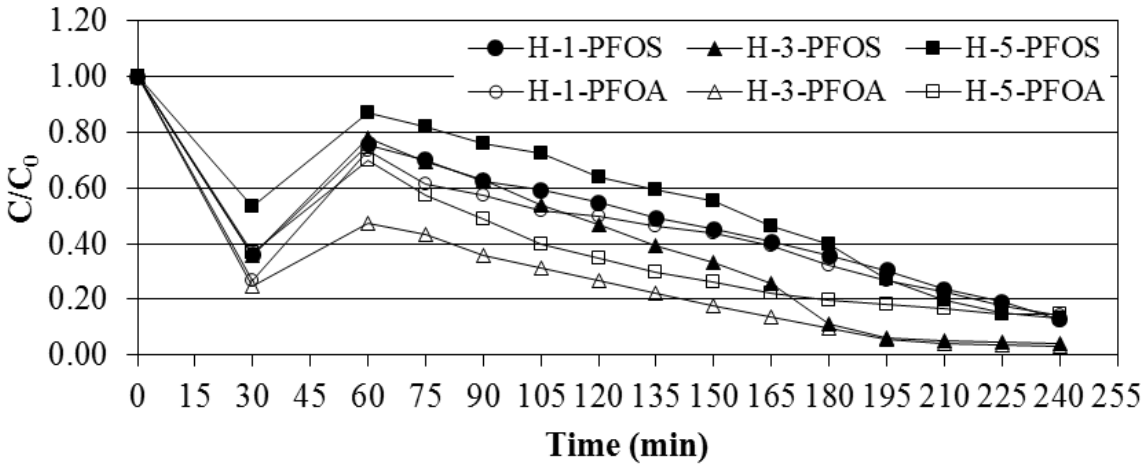

Figure 7. PFOS and PFOA removal efficiency and time (min) for different heat treatment periods.

CONCLUSIONS

An optimal series of TiO_2/GO/PVA photocatalysts was prepared from TiO_2 with GO content of 25% embedded on polyvinyl alcohol by the sonication method with heat treatment for 3 h. The obtained photocatalysts were investigated for their photocatalytic degradation efficiency. Influences on photocatalytic performance as oxidation time and GO content were examined by measuring degradation of PFOS and PFOA under visible light irradiation. Optimal degradation efficiencies of PFOS and PFOA were 95.99% and 96.86%, respectively. In addition, the morphology of TiO_2 and GO nanoparticles on PVA was investigated by TEM and chemical structure characterization of TiO_2/GO/PVA nanocomposites was performed by FT-IR. Research results suggested GO concentration, dispersion method, and heat treatment time as essential indicators for photocatalytic degradation. Our prepared TiO_2/GO/PVA photocatalyst has potential application for water or wastewater treatment to effectively and efficiently reduce PFOS and PFOA concentrations.

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