出國報告（出國類別：國際研討會）

參加第 39 屆含鹵持久性有機污染物國際研討會（2019 戴奧辛年會）報告

服務機關：行政院環境保護署環境檢驗所
姓名職稱：劉廣尉科長、金孝義助理研究員
派赴國家/地區：日本/京都
出國期間：108 年 8 月 25 至 8 月 30 日
報告日期：108 年 11 月 20 日

摘要

持久性有機污染物 (POPs) 是一種持久存在於環境中的化學物質，可經由食物鏈進行生物累積，並且可能對人類健康和自然環境造成危害，這一類的污染物包括農藥（如滴滴涕）、工業化學品（如多氯聯苯、全氟辛酸）和工業過程的副產品（如戴奧辛和呋喃）等（如圖 1）。

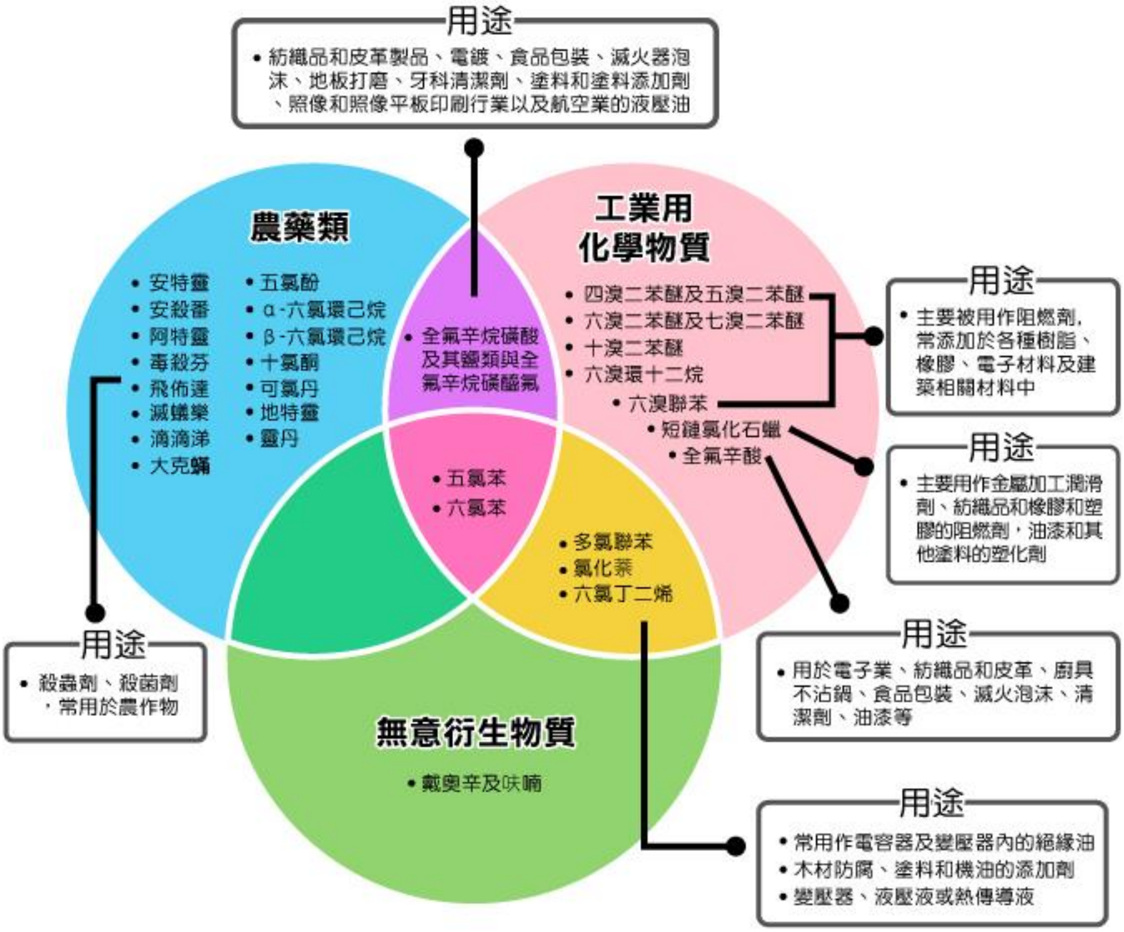


圖 1 POPs 種類及用途

本年度含鹵持久性有機污染物國際研討會，通稱 2019 年戴奧辛年會(The 39th International Symposium on Halogenated Persistent Organic Pollutants Dioxin2019)期程自 108 年 8 月 25 日至 8 月 30 日，共計 6 日，於日本京都國際會議中心舉辦，是一個跨國際之學術交流平台，其內容涵蓋分析和環境化學、生物分析技術、人類與環境毒理學及風險評估與管理。本次會議在日本京都附近的國際會議中心舉辦，有來

自世界各地 700 多位的專家與學者及政府機關的代表，參加了本次戴奧辛年會。在會議期間，總計發表了 569 篇的論文，其中口頭論文 270 篇、壁報論文 299 篇。依據總結會議講者之統計，討論氟化物的論文約占 31%、氯化物約占 27%、溴化物約占 11%、其他類約占 31%。

本所派員參加本次會議，除發表論文分享本所工作成果外，並可提升分析檢測技術，且與國際環境分析之研究人員進行交流。戴奧辛年會於 1980 年在意大利羅馬首次舉辦持久性有機污染物國際研討會，討論戴奧辛的發生和影響。每年皆舉行一次會議，與會的化學、環境工程、農業和生態學等研究人員，在年會中發表和展示戴奧辛、戴奧辛類化合物和持久性有機污染物(POPs)的最新研究成果。會議中會探討如何有效的檢測戴奧辛、戴奧辛類化合物與多氯聯苯等污染物的環境研究論文，並推廣其相關之檢測技術。近年來，國際上關於持久性有機污染物的發展於 2001 年斯德哥爾摩公約通過後，使世界上的專家與學者以此為研究方向，努力的解決由戴奧辛、戴奧辛類化合物與多氯聯苯等，所引起的環境污染問題，並期望藉由舉辦本次研討會能有效的控制全球環境中持久性有機污染物。

參加本次大會之重要心得及建議如下：

一、全氟與多氟烷基化合物等 (Perfluorinated compounds [PFCs]、polyfluorinated alkyl substances [PFAS]) 是指在一個烷類有機物上，以氟取代多數或甚至全部的氫。近年來在美國發生多起 PFAS 等污染事件，例如 2015 年底，美國紐約州境內小鎮 Hoosick Falls 的供水系統被驗出含量超過標準 PFOA (Perfluorooctanoic acid)。本次會中聯合國大學(The United Nations University)發表論文針對於亞洲地區水圈的 PFCs 研究，其利用 LC-MS/MS 系統監測環境水體中 PFCs 含量，該研究進行詳細的監測環境中 PFCs 的含量多寡。經由上述研究，使我們了解到目前國際上非常關切環境中 PFCs 的研究。

二、氯化石蠟(Chlorinated paraffins [CP])常作為塑料（例如 PVC）和橡膠中的添加劑，或是金屬加工應用中的密封劑和粘合劑等。近年來，氯化石蠟產量增加已經非常顯著，其對於人類和環境會造成危害，因此氯化石蠟含量的多寡監測需求也相對增加。根據動物毒性研究，氯化石蠟顯示主要影響肝臟，腎臟和甲狀腺，並導致生殖缺陷和致癌性。氯化石蠟與持久性有機污染物的區別在於氯化石蠟僅具有中度持久性並且更快速的降解或代謝。在部分研究中顯示，短鏈氯化石蠟(Short-chain CPs, SCCPs)與中鏈氯化石蠟(Medium-chain CPs, MCCPs)對於動物體內的生物酶產生活性誘導或抑制，進而造成生物體器官病變。以往，在低解析質譜儀(LRMS)分析氯化石蠟時，因為其他有機氯污染物和氯化石蠟本身會引起 MS 吸收波峰的干擾。為了消除這個問題，一些研究人員依賴高解析質譜儀(HRMS)進行分析。觀察本次年會的論文與近年來的氯化石蠟檢測方法，大多數主要是以飛行時間質譜儀(TOF-MS)或離子阱質譜儀(Orbitrap-MS)技術相結合進行檢測。

三、會議五篇專題演講，如 1.The AhR: A Major Player in Cancer Aggression and Immune Checkpoint Regulation（侵襲性癌症和人體免疫調節的要角：芳香烴受體）；2.Hazardous chemicals in marine plastics and their threat to marine organisms（海洋塑膠中的有害化學物及其對海洋生物的威脅）；3.Modelling persistent organic pollutants: mechanistically linking chemical production to human exposure and health effects（模擬持久性有機污染物：從化學產品到人體暴露和健康影響的機制）；4.Human Biomonitoring and Exposomics of Legacy and Emerging Chemicals（殘留及新興化學物質的人體生物監測與暴露體學）；5.Dioxin and health effects in Vietnamese（越南的戴奧辛及其健康影響）。上述專演有助於本所與會人員了解目前國際上所關切的議題。

四、儀器廠商展示中，有 Waters、MiURA、SHIMADZU、SIBATA、Thermo Fisher 等參加，提供最新的分析儀器與前處理淨化裝置等，使得與會人員了解到目前國外的檢驗分析技術。

五、第 40 屆含鹵持久性有機污染物國際研討會議預定於 2020 年 8 月在法國南特舉行，期望本所內同仁能有機會參與盛會，發表論文及吸取國際同儕先進經驗並交流。

目次

壹、 目的

戴奧辛會議始於 1980 年在義大利羅馬舉行含鹵持久性有機污染物國際專題研討會，其為戴奧辛國際會議的第一屆，會中討論戴奧辛的產生和危害，且經大會委員同意每年舉行一次會議。會議中世界上專業領域的研究人員收集與發表關於戴奧辛、戴奧辛類化合物與持久性有機污染物(POPs)的最新研究成果，同時進行意見交流和技術分享，進而提升 POPs 的研究發展。戴奧辛會議中所討論的議題，包括含鹵持久性有機污染物在環境中的產生和傳輸行為、對於人類和其他生物體的影響及管理含有持久性有機污染物的方法。近 5 年的戴奧辛國際會議於 2014 年在西班牙馬德里，2015 年在巴西聖保羅，2016 年在義大利佛羅倫薩和 2017 年在加拿大溫哥華舉行，2018 年在波蘭克拉科夫舉行。而日本分別於 1986 年在福岡、1994 年在京都及 2007 年在東京舉辦了戴奧辛國際會議，今年再度回到日本京都舉行，其代表的意義是回顧過往的歷史，放眼未來的研究。每年會議中會對於各國的環境研究論文進行討論與發表，並促進國際間檢測技術的開發和交流。

在國際上，斯德哥爾摩公約於 2001 年通過關於持久性有機污染物的約束，使各國的專家與學者，努力朝向控制或降低全球環境中的持久性有機污染物含量。雖然斯德哥爾摩公約最初僅涵蓋 12 種化學物質，但現在已包含了溴化、氯化或氟化等物質，總共 26 種，這些物質已於 2015 年 5 月在斯德哥爾摩公約大會中第七次會議召開時列入公約之下，並在 2017 年 4 月與 2019 年 4 月也陸續將十溴二苯醚、短鏈氯化石蠟等列入公約的附件 A。其中氯化石蠟(CPs)廣泛被用作金屬加工潤滑劑，增塑劑和阻燃劑及工業化學品原料。它們是鏈長範圍為 6 至 38 個碳的多氯化線性烷烴混合物。根據石蠟的鏈長範圍作為分類標準，通常定義短鏈（C10-13，簡稱 SCCP），中鏈（C14-17，簡稱 MCCP）和長鏈（C18-，簡稱 LCCP）。在過去的研究中，受管制的 CP (SCCP)和使用中的 CP（MCCP, LCCP 等）在環境中可持續存在數十年，且

對於人類在內的生物體中也具有生物累積性與危害性。

現今全世界的科學家努力解決由戴奧辛、戴奧辛類化合物和多氯聯苯等所引起的環境問題。在本次會議中，透過國際知名專家分享最新的知識和技術來解決持久性有機污染物的各種問題，今年在日本京都市京都國際會議中心舉辦 2019 年戴奧辛會議，本所參加人員可以藉由本次年會，了解各國對於持久性有機污染物的最新研究技術以及管理持久性有機污染物的措施，並發表論文分享本所為環境保護工作的成果，也可了解國際目前的研究趨勢及分析技術之發展，以提升本所檢測技術能力。

貳、 過程

一、行程紀要

第39屆含鹵持久性有機污染物國際研討會(The 39th International Symposium on Halogenated Persistent Organic Pollutants Dioxin2019)於108年8月25至8月30日在日本京都國際會議中心(Kyoto International Conference Center, ICC Kyoto)（如圖 2）舉行。本屆大會由來自世界各國700多位專業人士參與，會議期間總計發表了569篇的論文（總結會議講者之數據），其中口頭論文270篇、壁報論文299篇。依據總結會議講者之統計，討論氟化物的論文約占31%、氯化物約占27%、溴化物約占11%、其他類約占31%。

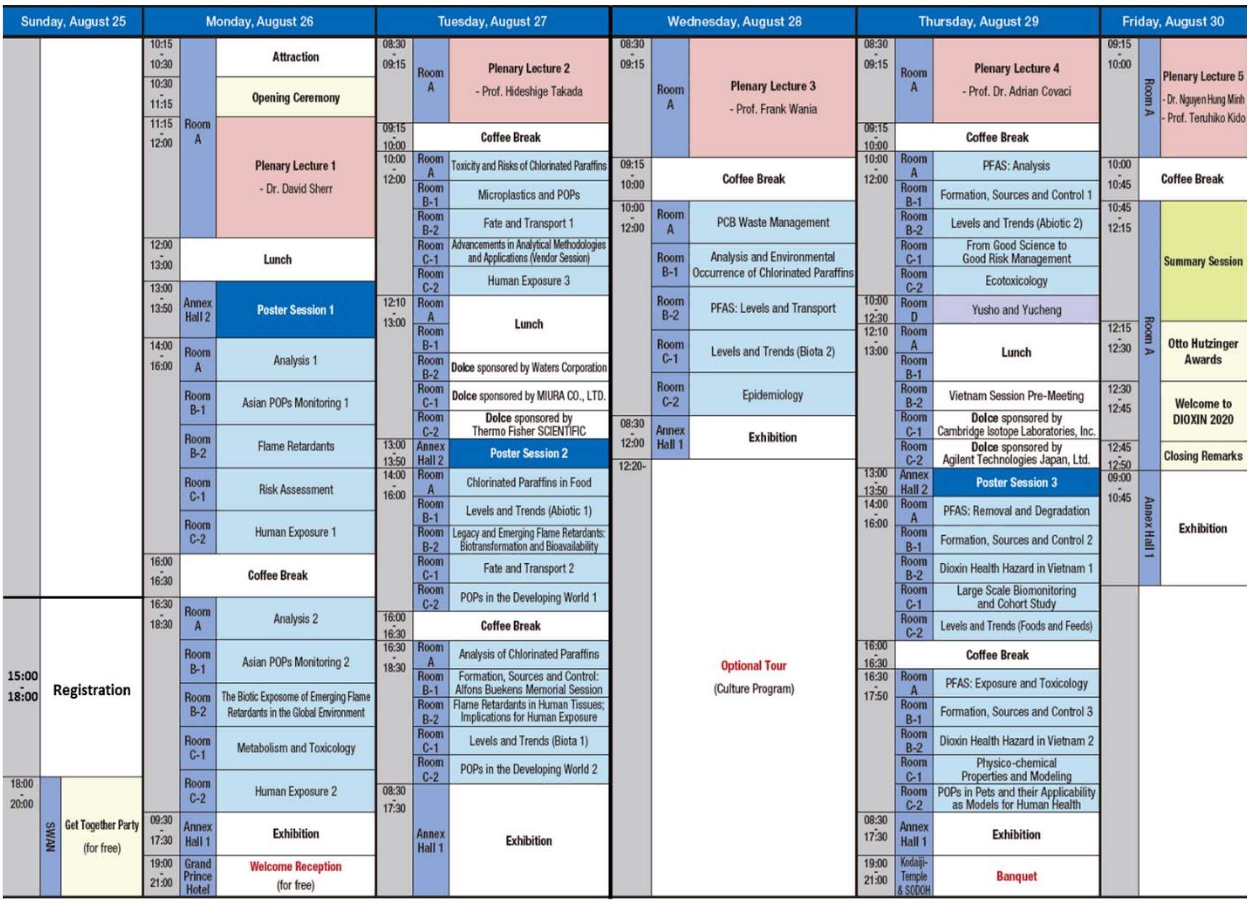
圖 2 日本京都國際會議中心(ICC Kyoto)

本次會議舉行時間為108年8月25日至8月30日共計6日（如表1所示），大會議程如表2。會議內容包含大會演講(Plenary)、特定專題(Special Events)、分類議題口頭論文報告(Oral)及壁報論文報告(Posters)、廠商儀器展示(Exhibits)等項進行。大會專題演講共有5場；分類議題分為45類議題，包括口頭論文報告270篇及壁報論文報告299篇。

表1、參加國際研討會行程表

日　期	地點	工作內容
8/24（六）	臺灣→日本京都	啟程
8/25（日）～8/30（五）	日本京都	2019 年戴奧辛年會
9/1（日）	日本京都→臺灣	返程

表2、大會議程表



Sunday, August 25		
15:00 - 18:00		**Registration**
18:00 - 20:00	SWAN	Get Together Party (for free)

Monday, August 26		
10:15 - 10:30	Room A	**Attraction**
10:30 - 11:15	Room A	**Opening Ceremony**
11:15 - 12:00	Room A	**Plenary Lecture 1** - Dr. David Sherr
12:00 - 13:00		**Lunch**
13:00 - 13:50	Annex Hall 2	**Poster Session 1**
14:00 - 16:00	Room A	Analysis 1
	Room B-1	Asian POPs Monitoring 1
	Room B-2	Flame Retardants
	Room C-1	Risk Assessment
	Room C-2	Human Exposure 1
16:00 - 16:30		**Coffee Break**
16:30 - 18:30	Room A	Analysis 2
	Room B-1	Asian POPs Monitoring 2
	Room B-2	The Biotic Exposome of Emerging Flame Retardants in the Global Environment
	Room C-1	Metabolism and Toxicology
	Room C-2	Human Exposure 2
09:30 - 17:30	Annex Hall 1	**Exhibition**
19:00 - 21:00	Grand Prince Hotel	**Welcome Reception** (for free)

Tuesday, August 27		
08:30 - 09:15	Room A	**Plenary Lecture 2** - Prof. Hideshige Takada
09:15 - 10:00		**Coffee Break**
10:00 - 12:00	Room A	Toxicity and Risks of Chlorinated Paraffins
	Room B-1	Microplastics and POPs
	Room B-2	Fate and Transport 1
	Room C-1	Advancements in Analytical Methodologies and Applications (Vendor Session)
	Room C-2	Human Exposure 3
12:10 - 13:00	Room A	**Lunch**
	Room B-1	**Lunch**
	Room B-2	**Dolce** sponsored by Waters Corporation
	Room C-1	**Dolce** sponsored by MIURA CO., LTD.
	Room C-2	**Dolce** sponsored by Thermo Fisher SCIENTIFIC
13:00 - 13:50	Annex Hall 2	**Poster Session 2**
14:00 - 16:00	Room A	Chlorinated Paraffins in Food
	Room B-1	Levels and Trends (Abiotic 1)
	Room B-2	Legacy and Emerging Flame Retardants: Biotransformation and Bioavailability
	Room C-1	Fate and Transport 2
	Room C-2	POPs in the Developing World 1
16:00 - 16:30		**Coffee Break**
16:30 - 18:30	Room A	Analysis of Chlorinated Paraffins
	Room B-1	Formation, Sources and Control: Alfons Buekens Memorial Session
	Room B-2	Flame Retardants in Human Tissues; Implications for Human Exposure
	Room C-1	Levels and Trends (Biota 1)
	Room C-2	POPs in the Developing World 2
08:30 - 17:30	Annex Hall 1	**Exhibition**

Wednesday, August 28		
08:30 - 09:15	Room A	**Plenary Lecture 3** - Prof. Frank Wania
09:15 - 10:00		**Coffee Break**
10:00 - 12:00	Room A	PCB Waste Management
	Room B-1	Analysis and Environmental Occurrence of Chlorinated Paraffins
	Room B-2	PFAS: Levels and Transport
	Room C-1	Levels and Trends (Biota 2)
	Room C-2	Epidemiology
08:30 - 12:00	Annex Hall 1	**Exhibition**
12:20-		**Optional Tour** (Culture Program)

Thursday, August 29		
08:30 - 09:15	Room A	**Plenary Lecture 4** - Prof. Dr. Adrian Covaci
09:15 - 10:00		**Coffee Break**
10:00 - 12:00	Room A	PFAS: Analysis
	Room B-1	Formation, Sources and Control 1
	Room B-2	Levels and Trends (Abiotic 2)
	Room C-1	From Good Science to Good Risk Management
	Room C-2	Ecotoxicology
10:00 - 12:30	Room D	Yusho and Yucheng
12:10 - 13:00	Room A	**Lunch**
	Room B-1	**Lunch**
	Room B-2	Vietnam Session Pre-Meeting
	Room C-1	**Dolce** sponsored by Cambridge Isotope Laboratories, Inc.
	Room C-2	**Dolce** sponsored by Agilent Technologies Japan, Ltd.
13:00 - 13:50	Annex Hall 2	**Poster Session 3**
14:00 - 16:00	Room A	PFAS: Removal and Degradation
	Room B-1	Formation, Sources and Control 2
	Room B-2	Dioxin Health Hazard in Vietnam 1
	Room C-1	Large Scale Biomonitoring and Cohort Study
	Room C-2	Levels and Trends (Foods and Feeds)
16:00 - 16:30		**Coffee Break**
16:30 - 17:50	Room A	PFAS: Exposure and Toxicology
	Room B-1	Formation, Sources and Control 3
	Room B-2	Dioxin Health Hazard in Vietnam 2
	Room C-1	Physico-chemical Properties and Modeling
	Room C-2	POPs in Pets and their Applicability as Models for Human Health
08:30 - 17:30	Annex Hall 1	**Exhibition**
19:00 - 21:00	Kodaiji-Temple & SODOH	**Banquet**

Friday, August 30		
09:15 - 10:00	Room A	**Plenary Lecture 5** - Dr. Nguyen Hung Minh - Prof. Teruhiko Kido
10:00 - 10:45		**Coffee Break**
10:45 - 12:15	Room A	**Summary Session**
12:15 - 12:30	Room A	**Otto Hutzinger Awards**
12:30 - 12:45	Room A	**Welcome to DIOXIN 2020**
12:45 - 12:50	Room A	**Closing Remarks**
09:00 - 10:45	Annex Hall 1	**Exhibition**

二、會議紀要

(一) 大會專題演講(Plenary)論文

1. The AhR(Aryl Hydrocarbon Receptor): A Major Player in Cancer Aggression and Immune Checkpoint Regulation（侵襲性癌症和人體免疫調節的要角：芳香烴受體）
2. Hazardous chemicals in marine plastics and their threat to marine organisms（海洋塑膠中的有害化學物及其對海洋生物的威脅）
3. Modelling persistent organic pollutants: mechanistically linking chemical production to human exposure and health effects （模擬持久性有機污染物：從化學產品到人體暴露和健康影響的機制）
4. Human Biomonitoring and Exposomics of Legacy and Emerging Chemicals （殘留及新興化學物質的人體生物監測與暴露體學）
5. Dioxin and health effects in Vietnamese （越南的戴奧辛及其健康影響）

(二)特定專題(Special Events)

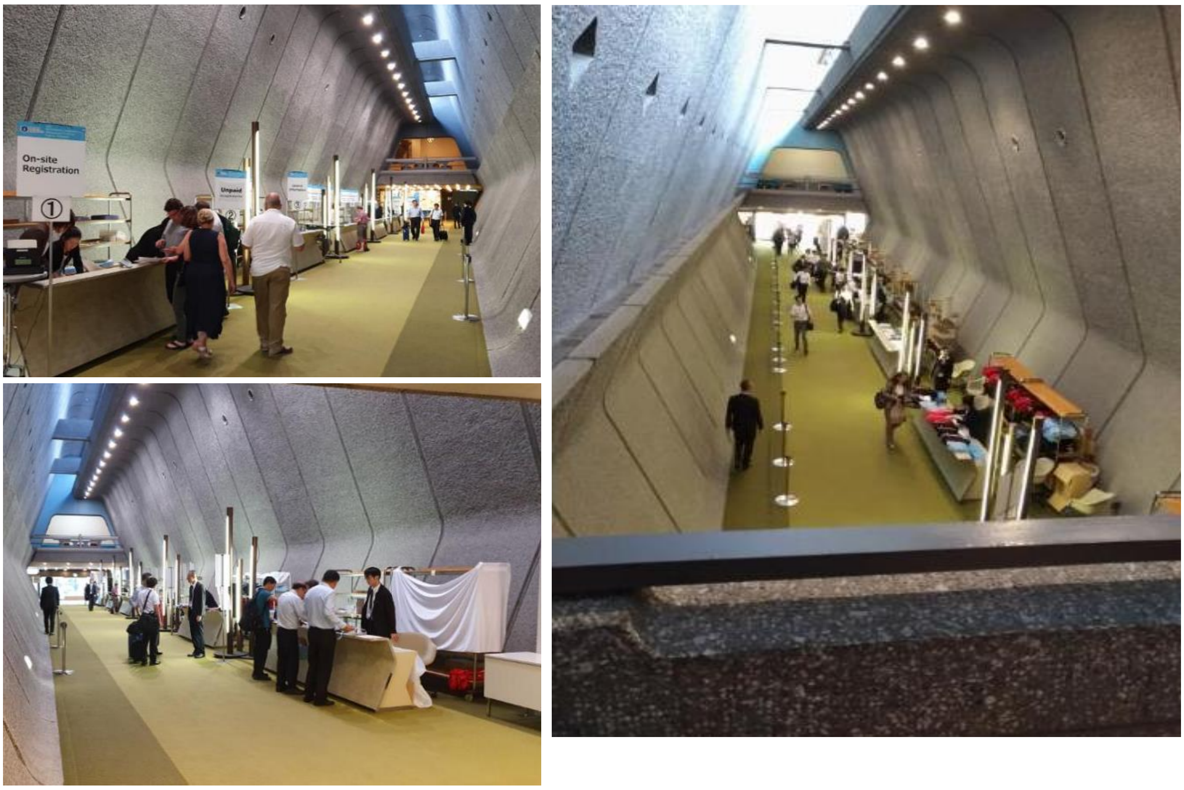
1. Asian POPs Monitoring
2. Status and Perspective on PCB Waste Management
3. Kanemi Yusho, Taiwan Yucheng and PCB/Dioxin Pollution
4. Microplastics as Environmental Vectors for POPs and Additives
5. Chlorinated Paraffins – Pollutants of High Environmental and Health Concern
6. Dioxin Health Hazard in Vietnam
7. POPs in the Developing World
8. POPs in Pets and their Applicability as Models for Human Health
9. From Good Science to Good Risk Management
10. The Biotic Exposome of Emerging Flame Retardants in the Global Environment
11. Legacy and Emerging Flame Retardants: Biotransformation and Bioavailability

12. Flame Retardants in Human Tissues; Implications for Human Exposure

13. Large Scale Biomonitoring

三、會議相關照片

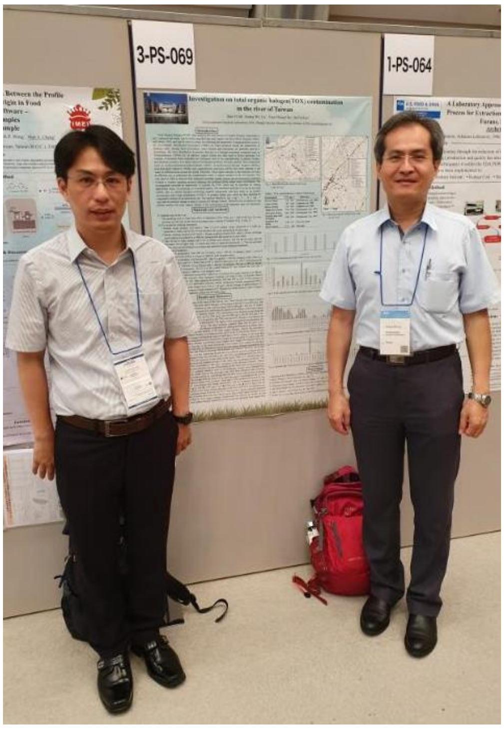
(一)大會報到處照片

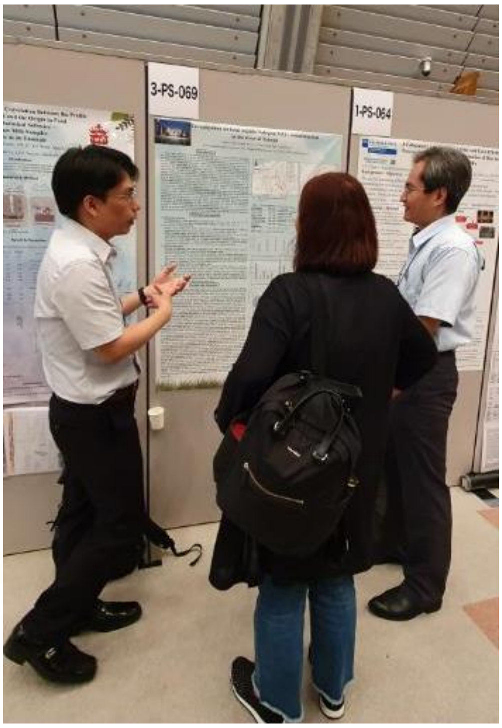


(二)開幕照片

(三)參展廠商照片

(四)海報展場照片





參、 心得

一、2019 戴奧辛年會資訊都可在網際網路(http://www.dioxin2019.org/index.html)上取得相關的資訊，由網站中可獲得絕大部分訊息，其中包含來自主辦單位的公告訊息、註冊資訊、論文投稿的格式、相關議程和主辦城市簡介、氣候、旅館飯店的預定等。本次研討會場地分布如圖 3。

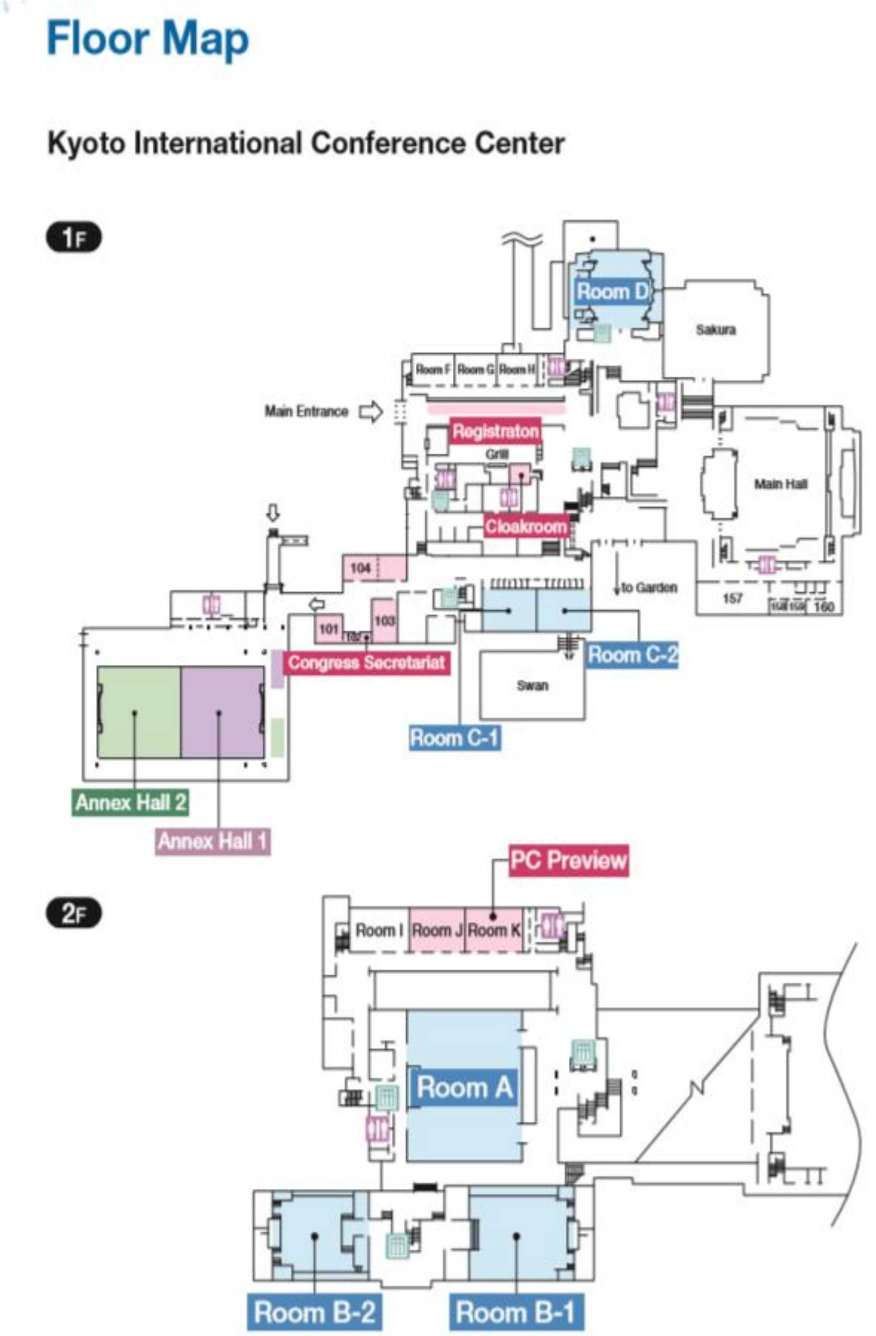
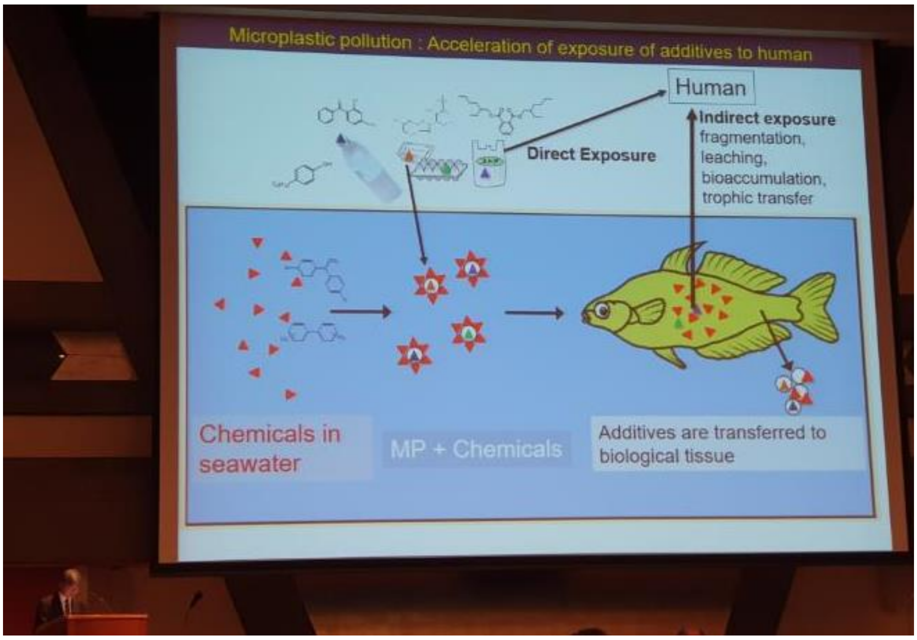


圖 3 大會會場平面圖

二、本次與會人員參加日本京都第 39 屆含鹵持久性有機污染物國際研討會 2019 戴奧辛年會(The 39th International Symposium on Halogenated Persistent Organic Pollutants Dioxin2019)，於 8 月 25 日為年會報到日，需要在大會入口處進行簽到與領取大會手冊等資料。研討會期間除了專題演講、口頭發表與論文發表及廠商展示外，其開幕儀式於當地時間 8 月 26 日早上 10 點半舉行，並於早上 9 點半開始有廠商展示會；每天早上都有約 45 分鐘的專題演講作為開頭，第二天與第三天皆從早上開始至下午 6 點半，第四天只有早上的時間有專題演講與口頭發表，同日下午則進行工廠參觀或是京都文化導覽，第五天從早上 8 點半開始至下午 5 點 50 分，有專題演講與口頭發表，第六天早上 9 點 15 分開始專題演講，於 10 點 45 分進行大會總結議題討論。今年度海報展覽講解分成三組，總計有 299 篇壁報論文，分別於第 2 天、第 3 天與第 5 天下午 1 點至 1 點 50 時進行展示，本所本次發表的壁報論文標題為：Investigation on total organic halogen(TOX) contamination in the river of Taiwan（臺灣河川水體總有機鹵含量調查），壁報編號為 3-PS-069，被安排於第 5 天下午展示。今年度整個大會行程緊湊且所發表之口頭報告等皆是目前世界上所關注的議題。

三、專題演講題目 2. Hazardous chemicals in marine plastics and their threat to marine organisms 中，提到各種尺寸的海洋塑膠和塑膠微粒會被海洋生物攝取。自 20 世紀 70 年代以來，新聞經常報導大型海洋生物如鯨魚、海龜和海鳥攝取較大的塑膠物品（例如厘米大小），而貝類和小型魚類攝取較小的塑膠，即塑膠微粒(小於 5mm)，這些生物經由食物鏈的轉移加速了整個海洋生態系統中塑膠的分散與累積，其中以大型塑膠物品對生物群造成的物理損害較為嚴重，而塑膠微粒則是對海洋生物造成毒性累積，其最終也會對人類造成危害（如圖 4）。一般的添加劑與聚合物分子之間沒有發生化學結合，因此隨著時間增加，添加劑分子

會慢慢洩逸而出，塑膠製的器材都可能因添加劑洩逸而污染所接觸的物質，接觸時間愈長或溫度愈高，則遭污染之機率愈大。



Microplastic pollution : Acceleration of exposure of additives to human

Human

Direct Exposure

Indirect exposure
fragmentation,
leaching,
bioaccumulation,
trophic transfer

Chemicals in seawater

MP + Chemicals

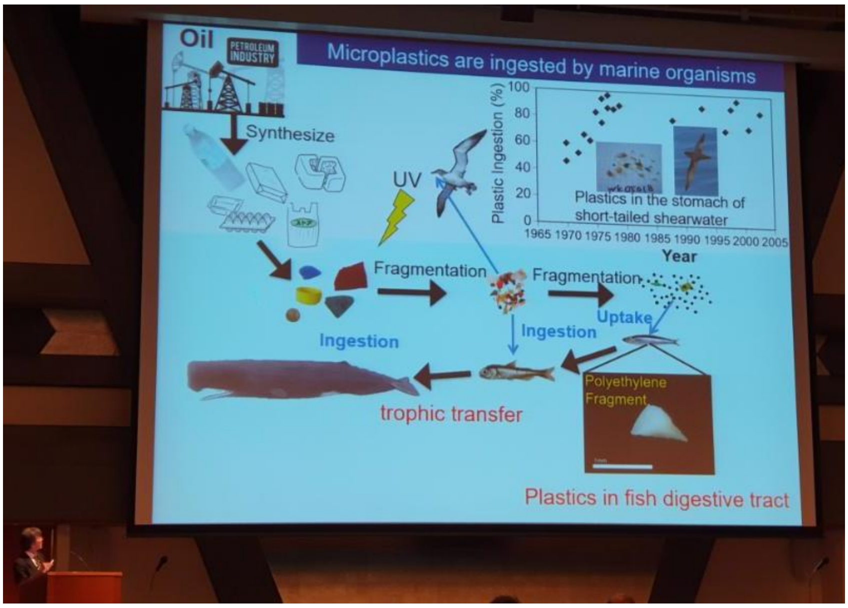
Additives are transferred to biological tissue

圖 4 塑膠微粒增加了添加劑在環境與人類的危害

海洋中的塑膠除了造成生物體的物理損害外，也還會產生化學毒性，因為它們本身含有多種危險化學物質，且大多數塑膠產品含有添加劑，例如塑化劑，UV 穩定劑，抗氧化劑，阻燃劑等，在這其中以含有疏水性添加劑的海洋塑膠和海洋塑膠微粒最為明顯，主要是其能吸附和積累來自周圍海水中的持久性有機污染物(POPs)。

國際顆粒監測組織(International Pellet Watch [IPW])已經證明了世界各地海灘上的微塑料中含有持久性有機污染物的積累。IPW 發現在偏遠地區檢測到具有高濃度持久性有機污染物的塑膠微粒，這意味著塑膠微粒將持久性有機污染物帶到污染較少的偏遠地區（背景地區），即「蚱蜢效應」(grasshopper effect)，其凸顯出持久性有機污染物對塑料的吸附與排出緩慢及不可降解的本質。當塑膠在海洋環境中碎裂成較小的碎片並被海洋生物攝取時，它們可能與消化道中

油溶性組織接觸，並且轉移與累積在生物組織中，這是目前塑膠添加劑等對於海洋生物傳輸與累積的途徑（如圖 5）。



Microplastics are ingested by marine organisms

圖 5　塑膠添加劑在海洋生物體中傳輸與累積的途徑

因此當評估生物體攝入塑膠中的化學品風險時，也要考慮其與環境背景的關聯性，如果在背景污染程度較高的地區時，例如具有殘留多氯聯苯污染的工業區，塑膠所造成的化學物質暴露可能是微不足道的。然而，在污染較低的背景區，因大量塑膠滯留的偏遠海灘中，塑膠所造成的危害是顯著的，過去在相關研究中已顯示攝取塑膠的海鳥體內含有高濃度的溴化二苯醚。未來在研究海洋環境中的塑膠時需要考慮其化學物質的危害性，因為塑膠對疏水性化合物具有高親和力，其可將海底沉積物中遺留的 POPs 重新活化，且可能擴散。本篇提供了目前日本對於海洋塑膠的研究與污染行為，並深入探討其化學物質對於海洋的污染。本所於 2018 年時也針對臺灣沿岸與離島等地區進行微塑膠含量檢測，與世界各國的研究趨勢一致，且收集世界各國相關檢測資料等做為未來評估環境檢測與污染的參考依據。

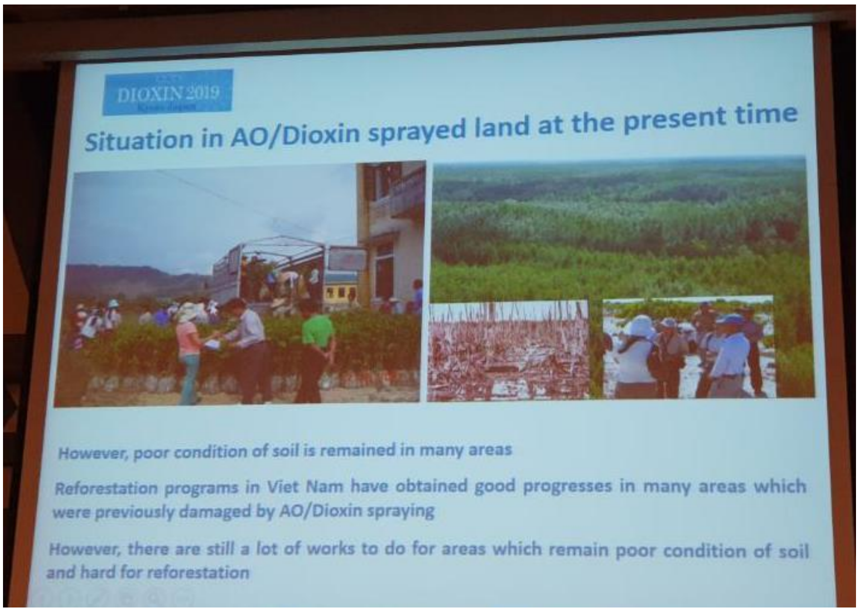
四、海報論文(3-PS-225)（如附件 1）：全氟有機化合物(PFCs)，其代表了這一類被受關注的新興污染物。它的特性為具有全球分佈性，環境持久性，生物累積性等危害。在環境中最常發現的兩種 PFC 化合物，其是指全氟辛烷磺酸(PFOS)和全氟辛酸(PFOA)。這些化合物已經商業化生產數十年，並且廣泛用於工業和消費產品應用上，例如烹飪鍋上的表面塗層，製造防水和防油產品，消防泡沫和食品包裝等。這些污染物的主要暴露於環境中通過飲食進入生物體內。由於它們具有持久性與生物累積性，對於存在環境介質中之生物群和人類體內有危害性等，因此歐盟限制了它們的生產並將全氟辛烷磺酸被列入“關於持久性有機污染物的斯德哥爾摩公約”附件 B，使得各國對全氟辛烷磺酸和全氟辛酸等化合物質的關注增加。本篇論文提供了如何利用自動清洗之固相萃取(SPE)儀器淨化污染水體中之 PFCs，但論文中所使用的設備對於 PFCs 淨化的數量約只有 10 多種，因全氟有機化合物有數百種的結構異構式與官能基變化，往往在進行前處理中就會逸散或消失，所以如果能直接進行水樣分析而不經過前處理淨化，則可避免在前處理過程中所造成的干擾，目前本所是以直接進樣的分析方式(LC-MS/MS)來提升對 PFCs 的檢測能力。

五、海報論文(2-PS-227)（如附件 2）：因 PFCs 的具有強疏水性，導致它們能在海洋生物體中進行生物累積，並於頂端食物鏈時危害人類健康。因此，世界各國皆在監測環境中 PFC 等的存在量。本研究是從新加坡各地收集水體和沈積物樣品後，進行淨化與測定 9 種特定之 PFC 化合物。相關地點經過精心挑選後進行採樣，其地點以涵蓋新加玻全國、選擇具有代表性的環境生態點、覆蓋各種類型的地表（如河流，沿海和水庫）水域，同時能包含乾旱季節等。這些樣品經過前處裡後，在利用液相層析-串聯質譜分析。結果顯示，特別較短的烷基鏈 PFCs，易存在於所有水樣中，另一方面，較長的烷基鏈 PFCs，則在沉積物樣品中常被

檢測出。在乾旱季節時，工業區旁邊的河水中被檢測到最高量的全氟辛酸(PFOA)(6.5 ng/L)和全氟辛烷磺酸(PFOS)(24.2 ng/L)。由其研究結果顯示，PFCs 污染物在新加坡的地表水中主要貢獻來自都市污水和工業廢水，因此新加坡的相關機構或學校對 PFCs 等化合物會持續地進行檢測與研究。本篇提供了亞州其他國家對於環境中 PFCs 含量檢測結果，在論文中作者從西元 2016 年至西元 2018 年，開始監測新加坡水體中 PFOA、PFOS 及 PFCs（以短鏈化合物為觀測物）的存在量，其皆有逐年增加的趨勢，並且也收集了其它國家對於 PFOA 與 PFOS 的檢測數據進行比對，這些研究資料可做為未來本所對於 PFCs 檢測技術的參考。

六、專題演講題目 5. Dioxin and health effects in Vietnamese 中，美國陸軍在 1961 年至 1972 年，執行除草作戰方案(Herbicidal warfare)與牧場手行動(Operation Ranch Hand)，噴灑了約 7,400 萬升的除草劑，以摧毀越南的作物及森林，避免越共使用叢林游擊戰。美軍使用的除草劑中，約有 5,000 萬公升的橙劑含有劇毒的副產物戴奧辛和呋喃(PCDD/Fs)。因橙劑主要就是由除草劑 2,4,5-三氯苯氧乙酸(2,4,5-T)與 2,4-二氯苯氧乙酸(2,4-D)混合而成，兩種物質平均含有 2～3 ppm 的戴奧辛。當時越戰期間並沒有人質疑其使用方式等，直到戴奧辛的毒性近年來逐漸被研究出來，且同時遭到橙劑噴灑的地區，在戰爭結束之後，有許多畸形嬰兒以及出現的許多怪病，例如唇腭裂、智力不足、疝氣和多指症等。本研究對棲息在受污染區域的動物進行體內 PCDD/Fs 的生物蓄積性調查，顯示其因棲息地積累過多的橙劑，使得動物體內有較高的 PCDD/Fs 濃度，其中以魚類體內中之 PCDD/Fs 的濃度為 75 至 288 pg-TEQ/g 濕重為最高。因為儲存桶槽的洩漏和溢出，使得橙劑污染熱點皆在美軍駐紮地區，導致該土壤中 PCDD/Fs 的濃度增加。橙劑已知會影響免疫系統，生殖，神經系統和類固醇激素的變化。過去

研究主要是以橙劑對於美國退伍軍人的健康進行調查，而越南人的健康與戴奧辛毒性的研究很少。有研究表明，美國在越南服役的退伍軍人增加患癌症的比率。在越南的退伍軍人有咽喉癌，急、慢性白血病、肺癌、結腸癌、肝癌等的比率較高。因此，越南官方目前非常關注戴奧辛的污染影響與其管理監測。該專題研究的目的是評估越南橙劑污染熱點地區 1 至 7 歲兒童中戴奧辛對腎上腺類固醇激素的干擾作用。研究人員取當地自 2008 年至 2011 年，年齡約 20 至 30 歲的哺乳期母乳樣本，利用氣相層析-高解析質譜法(GC-HRMS)進行測量，發現類固醇激素等可作為戴奧辛影響健康的早期指標。



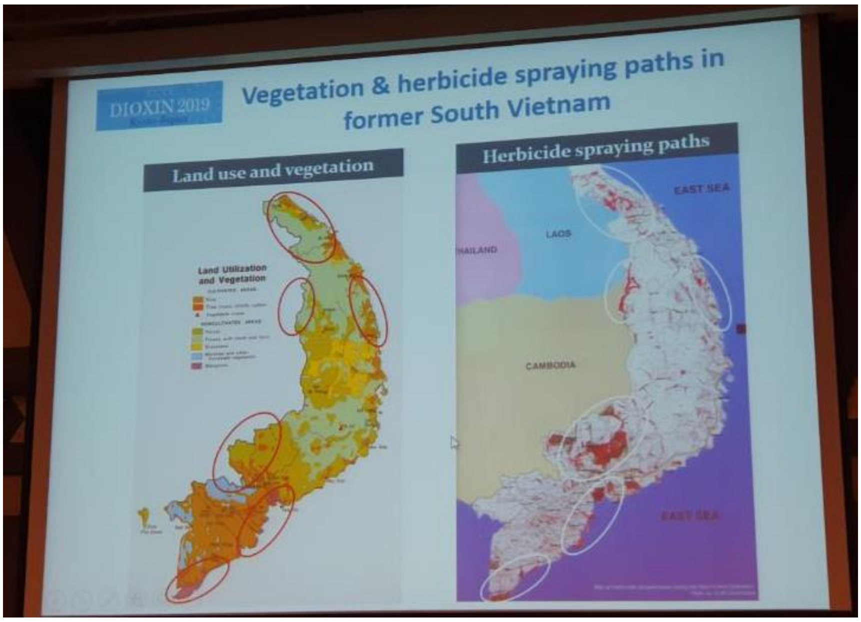
Situation in AO/Dioxin sprayed land at the present time

However, poor condition of soil is remained in many areas

Reforestation programs in Viet Nam have obtained good progresses in many areas which were previously damaged by AO/Dioxin spraying

However, there are still a lot of works to do for areas which remain poor condition of soil and hard for reforestation

圖 6 越戰期間被噴灑橙劑的土地目前現況



DIOXIN 2019

Vegetation & herbicide spraying paths in former South Vietnam

Land use and vegetation

Herbicide spraying paths

圖 7 越戰期間越南被噴灑除草劑區域及其植被

肆、 建議

1. 大會議論文中提到，美國環保署(USEPA)提出全氟辛酸(PFOA)等可在人體內存留長達 4 年，且動物實驗證實此類化合物會造成腫瘤等研究，引起世界各國的專家學者注意。今年度會議中有很多的論文皆在探討 PFOA、PFOS、PFCs 與環境的關聯性。建議本所能與世界各國一樣持續地對全氟辛酸等污染物進行檢測與分析。

2. 在今年度的大會專題演講與口頭發表中，塑膠微粒與戴奧辛等被與會的人員廣泛的討論,建議本所對於塑膠微粒及戴奧辛檢測能持續的進行研究與技術發展，其有助於未來與國外專家學者進行檢測技術之交流。

3. 新興污染物如短鏈氯化石蠟(Short-chain chlorinated paraffins, SCCP)，近年來被列入持久性有機污染物斯德哥爾摩公約附件的名單中，今年度大會中也有相關的論文發表，其介紹如何提升 SCCP 檢測技術與儀器間檢測的差異性，建議本所可持續發展短鏈氯化石蠟之檢測技術，以符合國際趨勢。

4. 第 40 屆含鹵持久性有機污染物國際研討會議（2020 年戴奧辛年會）預定於 2020 年 8 月在法國南特舉行，期望本所同仁能有機會參與盛會，發表論文及吸取國際間先進的研究經驗。

伍、 參考資料

1. 第 39 屆含鹵素持久性有機污染物國際研討會論文集。

2. 第 39 屆含鹵素持久性有機污染物國際研討會網站，http://dioxin2019.org/。

3. 吳仲平，參加第 38 屆國際有機鹵化環境污染物及持久性有機污染物研討會(2018 戴奧辛年會)報告，行政院環境保護署環境檢驗所，中華民國 107 年。

4. Dung Quang Le, Hideshige Takada, et al. Temporal and spatial changes in persistent organic pollutants in Vietnamese coastal waters detected from plastic resin pellets, Marine Pollution Bulletin. 109, 320-324.

6. 表 2 來源 http://www.dioxin2019.org/index.html。

5. 圖 1 照片來源 https://topic.epa.gov.tw/pop。

7. 圖 3 照片來源 http://www.dioxin2019.org/index.html。

附件 1

AUTOMATED CLEAN-UP METHOD FOR THE PFAS DETERMINATION IN HEAVY POLLUTED WATERS

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Introduction

Perfluorinated organic compounds (PFCs) represents an emerging class of contaminants of great concern. They are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful. The two most commonly used and PFCs found in the environment are Perfluoro-1-octanesulfonic acid (PFOS) and Perfluoro-n-octanoic acid (PFOA). These compounds have been commercially produced for decades and were employed in a wide range of industrial and consumer applications such as surface coatings on cooking pans, in making water and oil repellent products, in firefighting foams, and in food packaging[1,2].

The main exposure to these pollutants is through diet[3]. As a consequence of their persistence, bioaccumulation potential, toxicity, and widespread presence in environmental media, biota, and humans, the EU restricted their production[4] and PFOS was included in Annex B of the Stockholm Convention on Persistent Organic Pollutants[5].

The concerns about PFOS and PFOA increase the need to develop innovative and automated analytical methods for the determination of these pollutants. The most commonly applied method for PFCs purification is Solid Phase Extraction (SPE). This study points to the development of a simple method for the determination of PFOS, PFOA and PFDA (Perfluoro-n-decanoic acid) performed by an automated clean-up system.

Materials and methods

An autosampler loaded each sample to cartridges placed on one of three SPE purification modules (J2 Scientific, Missouri, USA).

Sample clean-up procedures were performed using two different cartridges to assess the recovery of PCFs on each:

- 500 mg of Styrene/Divinyl Benzene Copolymer Resin base material (Super-Clean ENVI-Chrom, Supelco, USA) according to the EPA method 537[6]
- 60 mg of polymeric reversed-phase adsorbent (Oasis HLB, Waters)

PFOS, PFDA and PFOA analytical determinations were performed by an isotopic dilution technique (LC/HRMS). Table 1 shows the list of native PFC standards (Wellington Laboratories, Canada), at a working concentration of 1 ng/ul, used in this study. The native PCFs were spiked at a rate of 10 ng/ml in 10mL of water. The water was further fortified with the 13C-labeled surrogate standards used for 'isotopic dilution' quantification, listed in Table 2 (Wellington Laboratories, Canada).

Super-Clean ENVI-Chrom cartridges were conditioned with 15 mL of methanol and 15 mL of Milli-Q water. The 10mL water samples were loaded on the cartridges at a flow rate of 5 mL/min and eluted with 20 mL of methanol at 5 mL/min.

Oasis HLB cartridges were conditioned with 10 mL of ethyl acetate, 10 mL of methanol and 10 mL of Milli-Q water. The 10mL water samples were loaded on the cartridges at a flow rate of 5 mL/min and eluted with 10 mL of ethyl acetate and 10 mL methanol containing 2 % ammonia

The eluate from each cartridge was manually concentrated to 100 µl and spiked with 13C-labelled standards (Wellington Laboratories, Canada), reported in table 3, and finally submitted to instrumental analysis.

Table 1: List of the Native PFCs standards

Compound	Abbreviation	CAS
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-1-octanesulfonic acid	PFOS	207596-29-0

Table 2: List of the labelled PFCs in extraction standards

Compound	Abbreviation
Perfluoro-n-[$^{13}C_8$] octanoic acid	$^{13}C_8$-PFOA
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$] decanoic acid	$^{13}C_6$-PFDA
Perfluoro-1-[$^{13}C_8$] octanesulfonic acid	$^{13}C_8$-PFOS

Table 3: List of the labelled PFCs in recovery standards

Compound	**Abbreviation**
Perfluoro-n-[1,2-$^{13}C_2$] octanoic acid	$^{13}C_2$-PFOA
Perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	$^{13}C_2$-PFDA
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate	$^{13}C_4$-PFOS

Instrumental analysis:
Samples were analyzed using liquid chromatography-high resolution mass spectrometry (LC/HRMS). Detailed instrumental conditions are reported in table 4.

TABLE 4: Detailed instrumental conditions:

HPLC instrument:	Agilent 1200 series pumps and? autosampler
Column:	XBridge MS C18, 100x2.1 mm, 3.5 µm
Solvent A:	Ammonium acetate 10 mM in water
Solvent B:	Acetonitrile
Gradient:	From 1 to 99% B in 18 min; 99% B for 5 min
Flow:	200 µL/min
Injection volume	8 µL
HRMS instrument	Thermo Q Exactive
Ionization source	ESI, negative ions
Acquisition method:	Full scan MS (R=35000) and dd2-MS/MS (R=17500)

Isotopic dilution method was used for quantitative analyses using external calibration standard solutions for each substance. PFCs masses are listed in Table 5

Table 5: List of PFCs masses

Compound	**Mass 1**	**Mass 2**
PFOA	412.9664	368.9766
PFDA	512.9600	468.9702
PFOS	498.9302	
$^{13}C_8$-PFOA	420.9933	376.0001
$^{13}C_2$-PFOA	414.9731	369.9800
$^{13}C_6$-PFDA	518.9802	473.9870
$^{13}C_2$-PFDA	514.9667	469.9736
$^{13}C_8$-PFOS	506.9571	
$^{13}C_4$-PFOS	502.9436	

Results and discussion:
In order to evaluate the quantitative performance of the semi-automatic clean-up system, the 13C-labeled PFC's (which reflect the actual analyte recovery when using isotopic dilution techniques) mean recoveries and standard

Table 6: Mean recoveries and standard deviation of labeled PFCs

Sample	**$^{13}C_8$-PFOA**		**^{13}C $_6$-PFDA**		**^{13}C $_8$-PFOS**	
	Super-Clean ENVI-Chrom	**Oasis HLB**	**Super-Clean ENVI-Chrom**	**Oasis HLB**	**Super-Clean ENVI-Chrom**	**Oasis HLB**
1	82%	39%	51%	12%	66%	10%
2	89%	72%	81%	11%	88%	17%
3	86%	47%	89%	12%	82%	13%
4	92%	18%	99%	28%	98%	26%
5	97%	32%	69%	13%	72%	12%
6	100%	31%	65%	30%	80%	32%
7	92%	10%	68%	49%	71%	35%
Ave.	91%	36%	75%	22%	80%	21%
St.Dev.	6%	20%	16%	14%	11%	10%

deviations (%) obtained using the automated system and the two different SPE cartridges are shown in Table 6. Analyses were performed on 7 replicates.

Recoveries obtained from Super-Clean ENVI-Chrom are higher than those obtained from OASIS HLB, in particular using Super-Clean ENVI-Chrom $^{13}C_8$-PFOA recoveries range from 82 to 100%, $^{13}C_6$-PFDA range from 51 to 99%, $^{13}C_6$-PFOS range from 66 to 98%, while using OASIS HLB recoveries range from 10 to 72%, from 11 to 49% and from 10 to 35% respectively. Moreover the relative standard deviations of recoveries obtained from Super-Clean ENVI-Chrom are less than 30%, in agreement with the requirements of the reference method to evaluate the accuracy of the procedure[6]. In more detail recovery standard deviation is 6%, 16% and 11% for $^{13}C_8$-PFOA, $^{13}C_6$-PFDA and $^{13}C_6$-PFOS respectively.

In order to evaluate the precision of the method, the results of the replicate analysis from Super-Clean ENVI-Chrom, their average and standard deviation are reported in Table 7.

Table 7: results of replicate analysis from Super-Clean ENVI-Chrom

Sample	PFOA	PFDA	PFOS
1	11.1 ng/ml	9.1 ng/ml	9.4 ng/ml
2	12.0 ng/ml	8.1 ng/ml	9.7 ng/ml
3	11.1 ng/ml	8.9 ng/ml	8.8 ng/ml
4	12.1 ng/ml	9.9 ng/ml	10.0 ng/ml
5	11.0 ng/ml	9.8 ng/ml	8.1 ng/ml
6	11.6 ng/ml	8.5 ng/ml	9.6 ng/ml
7	11.3 ng/ml	8.8 ng/ml	9.4 ng/ml
Ave.	11.5 ng/ml	9.0 ng/ml	9.3 ng/ml
St. Dev	0.4 ng/ml	0.7 ng/ml	0.6 ng/ml
St.Dev/True Value	4%	7%	6%

The analytical results obtained are in agreement with the precision requirements of the reference method, showing a standard deviation less than 20% of the true value. In particular the standard deviation obtained in 4%,7% and 6% of the true value for PFOA, PFDA and PFOS

Examples of chromatograms of PFOA and PFOS obtained using Super-Clean ENVI-Chrom HLB are reported in Fig.1, Fig.2 respectively.

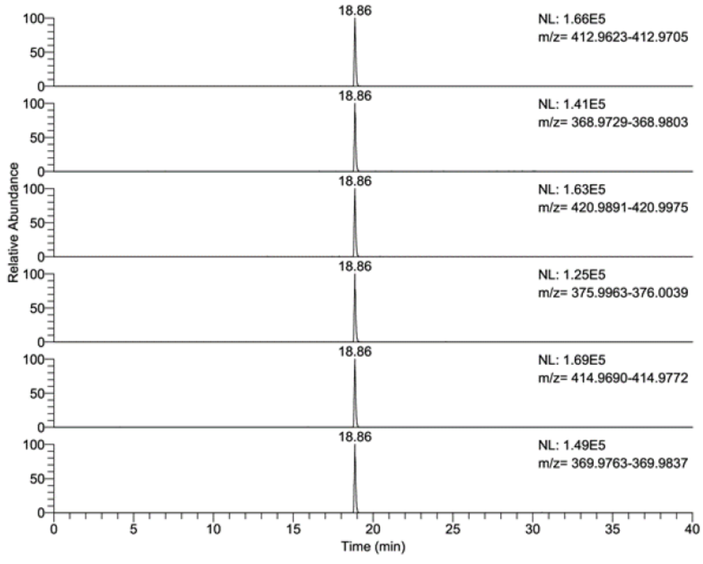

Figure 1: Example of chromatogram of PFOA obtained from Super-Clean ENVI-Chrom.

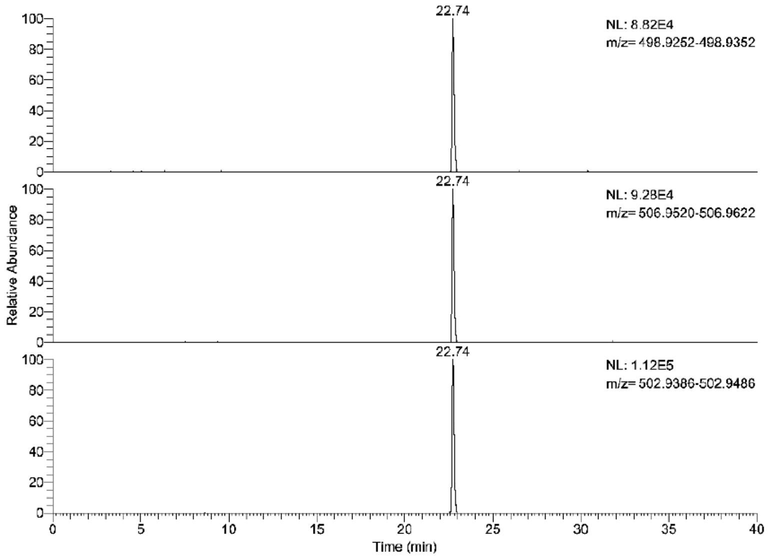

Figure 2: Example of chromatogram of PFOS obtained from Super-Clean ENVI-Chrom.

Our next goal is complete automation of the cleanup procedure. The current automated system is able to send each fraction eluted from the SPE to an in-line evaporation system where they are concentrated then directly injected into vials, prior to the instrumental analysis. Particular attention will be paid to the PFCs behavior during the evaporation step.

Acknowledgemets:
We want to thanks J. Salmons and M. Tanner, from J2 Scientific Llc, for their revision of the paper.

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附件 2

Solid-phase extraction and LC-MS/MS for the quantitative analysis of nine perfluorinated compounds across Singapore

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Introduction

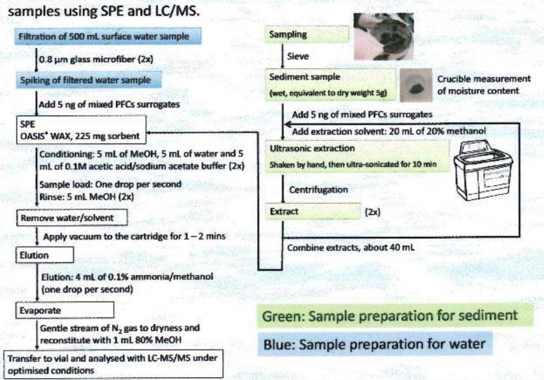
- Perfluorinated compounds (PFCs), in particular perfluorooctanoic acid and perfluorooctane sulfonic acid, are persistent environmental contaminants.
- The prevalent use of PFCs in grease-proof and water-proof coatings and sprays, such as Teflon, paints, coating for food packaging etc., has resulted in their significant release into the environment (at concentrations ranging from pg/kg to µg/kg).
- Recent studies have demonstrated their propensity to bioaccumulate and biomagnify, and their potential to induce harmful effects on human health and the environment. Hence, there is a need for constant monitoring of their concentrations in the environment.
- Waters and sediments across Singapore were sampled and subjected to solid-phase extraction (SPE) for clean-up and pre-concentration.
- Determination of PFCs in the extract was carried out by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

PFCs monitored in this project

Standard Compounds	Abbreviation	Formula	Internal Standards
Perfluoro-n-butanoic acid	PFBA	$C_4HF_7O_2$	$^{13}C_4$PFBA
Perfluoro-n-hexanoic acid	PFHxA	$C_6HF_{11}O_2$	$^{13}C_2$PFHxA
Perfluoro-n-octanoic acid	PFOA	$C_8HF_{15}O_2$	$^{13}C_4$PFOA
Perfluoro-n-nonanoic acid	PFNA	$C_9HF_{17}O_2$	$^{13}C_5$PFNA
Perfluoro-n-decanoic acid	PFDA	$C_{10}HF_{19}O_2$	$^{13}C_2$PFDA
Perfluoro-n-undecanoic acid	PFUnA	$C_{11}HF_{21}O_2$	$^{13}C_2$PFUnA
Perfluoro-n-dodecanoic acid	PFDoA	$C_{12}HF_{23}O_2$	$^{13}C_2$PFDoA
Perfluoro-1-hexanesulfonate	PFHxS	$C_6F_{13}SO_3H$	$^{13}O_2$PFHxS
Perfluoro-1-octanesulfonate	PFOS	$C_8F_{17}SO_3H$	$^{13}C_4$PFOS

Methodology

Method ISO 25101: 2009: Determination of PFOS and PFOA - Method for unfiltered samples using SPE and LC/MS.



Filtration of 500 mL surface water sample
0.8 µm glass microfiber (2x)
Spiking of filtered water sample
Add 5 ng of mixed PFCs surrogates
SPE
OASIS® WAX, 225 mg sorbent
Conditioning: 5 mL of MeOH, 5 mL of water and 5 mL of 0.1M acetic acid/sodium acetate buffer (2x)
Sample load: One drop per second
Rinse: 5 mL MeOH (2x)
Remove water/solvent
Apply vacuum to the cartridge for 1 – 2 mins
Elution
Elution: 4 mL of 0.1% ammonia/methanol (one drop per second)
Evaporate
Gentle stream of N_2 gas to dryness and reconstitute with 1 mL 80% MeOH
Transfer to vial and analysed with LC-MS/MS under optimised conditions

Sampling
Sieve
Sediment sample
(wet, equivalent to dry weight 5g)
Crucible measurement of moisture content
Add 5 ng of mixed PFCs surrogates
Add extraction solvent: 20 mL of 20% methanol
Ultrasonic extraction
Shaken by hand, then ultra-sonicated for 10 min
Centrifugation
Extract
(2x)
Combine extracts, about 40 mL

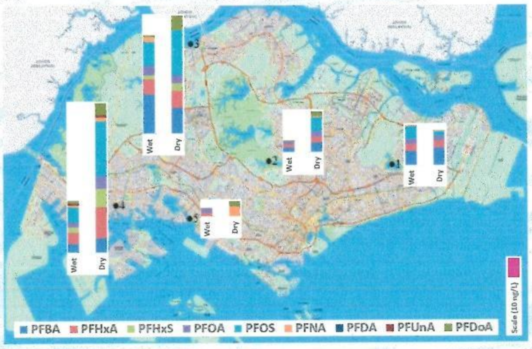
Green: Sample preparation for sediment

Blue: Sample preparation for water

LC conditions	
Mobile phase A	2 mM ammonium acetate water solution
Mobile phase B	Methanol
Trapping Column	ChromaNik Technologies Inc. Sunrise C28 (30 mm × 3 mm, 3 µm)
Main Column	Shim-Pack XR-ODS II (100 mm × 2 mm, 2.2 µm)

Results and Discussion

(1) Distribution of PFCs in Singapore's environment (2018)



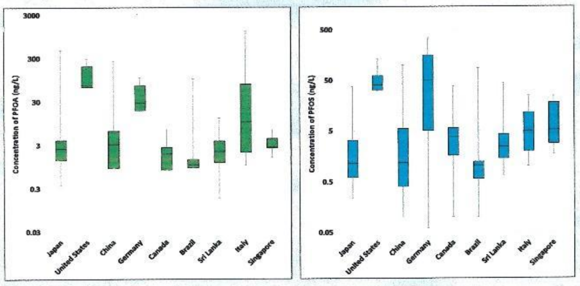
Sampling locations in January (wet season) and March (dry season) in 2018:
[1] Bedok Reservoir (BR, floating deck, water catchment and recreational area),
[2] MacRitchie Reservoir (MR, floating deck, water catchment and recreational area),
[3] Kranji (KR, coastal area near wood industries),
[4] Jurong Industrial Canal (JIC, outside National Oxygen Pte Ltd, industrial area),
[5] West Coast Park (WCP, near Promenade Lookout Jetty, recreational and maritime area)

Analyte	Canal water (JIC) [a]	Reservoir water (BR, MR) [a]	Coastal water (KR, WCP) [a]	Sediment (JIC) [b]	Sediment (KR, BR, MR, WCP) [b]
PFOS	5.2 – 24.2	N.D.[c] – 3.3	N.D. – 23.6	2.7 – 4.3	N.D. – 5.6
PFOA	2.5 – 6.5	1.4 – 2.7	N.D. – 5.0	N.D.	N.D.
Other PFCs	N.D. – 16.0	N.D. – 9.1	N.D. – 20.7	N.D. – 5.7	N.D. – 5.0

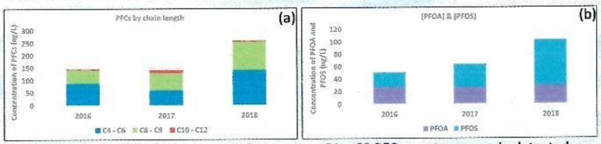
[a] In ng/L; [b] In ng/g (dry weight); [c] Not detected

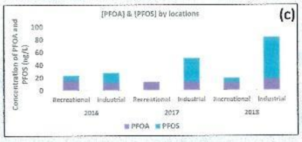
Analyte	PFBA	PFHxA	PFHxS	PFOA	PFOS	PFNA	PFDA	PFUnA	PFDoA
Practical quantitation limit (ng/L)	2.4	0.4	1.9	0.6	1.6	0.4	1.6	0.9	0.3

(2) Distribution of PFOA and PFOS in surface waters across countries, in comparison to Singapore's (2018)



(3) Comparison of (a) PFCs by chain length (b) PFOA & PFOS and (c) PFOA & PFOS in recreational and industrial areas, in water (2016 – 2018)





- C4 – C9 PFCs most commonly detected
- Gradual increase of PFOS and PFOA detected
- [PFOA] is comparable between recreational and industrial areas (~14 ng/L).
- [PFOS] remains at ~5ng/L for recreational areas but steadily increase in industrial areas (16 ng/L → 37 ng/L → 66 ng/L).

Conclusions

- PFCs were detected in all five locations from river, reservoir and coastal waters around Singapore.
- Shorter alkyl-chains-PFCs were mainly detected in water samples, while longer alkyl chains-PFCs were mainly detected in sediments.
- Highest total PFC concentrations were detected at KR and JIC - within the industrial estate; the major contributions of PFCs in Singapore surface water came from municipal and industrial wastewater disposal.
- Dry season data indicated higher concentrations of PFCs detected compared to the wet season for the same location – higher volume of rainfall diluted the source of water samples during the wet season.
- The median concentrations of PFOS and PFOA in environmental waters in Singapore were lower than those in the USA and Germany.
- Increased concentrations of PFOS found in the industrial areas over the past 3 years, but further monitoring is needed to study trends.

Acknowledgements

This work is in collaboration with, and supported by, the United Nations University and Shimadzu Corporation. The authors are appreciative of these two organisations.

附錄 I　本次研討會投稿論文摘要

Investigation on total organic halogen(TOX) contamination in the river of Taiwan

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Introduction

Total Organic Halogen (TOX) often analyzes the total amount of organic halogen compounds in soil , sediment and water, can be further specified into total organic chlorine (TOCl), bromine (TOBr), and iodine (TOI), and can be used as a basis for reflecting the parameters of organochlorine levels in the environment. Disinfection by-products (DBPs) are often produced during the disinfection of drinking water. Among these by-products, since chlorine and chloramine are generally used as a disinfectant, the main disinfection by-product detected is a halogen-containing compound such as Trihalomethanes (THMs) etc. In addition, organic halides are often used in factory processes. For example, brominated flame retardants are commonly used in the manufacturing of plastics, textiles, and electronic products. It is likely cause environmental pollution. Recently, specific TOX compounds, such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane isomers (HCHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been detected in the water of different areas around the world. Therefore, Total organic halogen, a sum indicator, provides an efficient way to understand the contamination status of organic halogens in the environment. This was done in order to discover how industrial activities, human factors and environmental conditions (related to weather sampling seasons) influence the pollution of the inland water environment. The investigations provided an opportunity to examine the TOX, which may be important for finding appropriate means of evaluating environmental quality. USEPA 9020B provides a standard method for detecting total organic halides in water. The method mainly uses an activated carbon to adsorb an organic compound containing chlorine, bromine and iodine, washes off the inorganic halide remaining on the activated carbon with a nitric acid solution, and generates a halogen ion (X^-) by high-temperature combustion. This method uses a microcoulometric-titration detection to detect the total halogen content, but cannot measure fluorine-containing organic compounds, nor can it measure the total organic halide adsorbed on the insoluble solids, and is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times. ISO/FDIS 9562 also provides a similar test method: acidification of water samples with nitric acid, adsorption of organic compounds with activated carbon, followed by aqueous of sodium nitrate acidified to remove inorganic halides. After the activated carbon tube is burned, the halide ion is measured by titration. In this study, referring to the above two methods, the water sample was pretreated and analyzed using a total organic halogen analyzer. The instrument principle is to use an activated carbon tube to adsorb halogen-containing organic compounds and burn them in an aerobic environment and a high temperature of 950 ˚C to produce halide ions, which are then analyzed by coulometric titration in an electrolytic cell. The reaction formula is: $Ag \rightarrow Ag^+ + e^-$; $X^- + Ag^+ \rightarrow AgX$ and its potential change is used to estimate the halogen content. So far, reports from studies on TOX contamination in environments are limited. Therefore, how to effectively and quickly monitor the total organic halides in the environment is an important topic for discussion.

Materials and methods

(1) Sample sites in the river:
The sampling time is from June 2018 to September 2018. There are 7 sites in the Lao Jie river, and there are 21 sites in the factory discharge water, totaling 93 samples. (Fig. 1) (Fig. 2)

(2) Pre-treatment cleaning instrument:

1. Nitrate, stock solution (0.2 mol/L): Take 17 g of sodium nitrate dissolved in a 1000 mL quantitative bottle, add 25 mL of concentrated nitric acid, and quantify in pure water.
2. Nitrate washing solution (0.01 mol/L): Nitrate washing solution (0.01 mol/L): 50 mL of Nitrate stock solution was placed in a 1000 mL dosing bottle and quantified in pure water.
3. Take 50 mL of water sample, add 5 mL of nitrate stock solution, and test the pH value with PH test paper. If it is higher than > 2, please add HNO_3 to adjust the sample pH < 2. The two activated carbon tubes are then placed in a column and attached to a pre-treatment instrument.

(3) Electrolyte preparation :

1. Solution A preparation: Take 200 mL of Acetic Acid + 500 mL of ultrapure water + 4 mL of concentrated nitric acid to a volume of 1000 mL with ultrapure water.
2. Solution B preparation: (A) Solution B1: Take 4 g gelatin + 400 mL ultrapure water. Place in a 500 mL beaker, soak for 3 hours, heat to 40 ˚C, dissolve and cool to 18 ~ 22 ˚C. (B) Solution B2: Take 1.0 g of Thymol + 0.3 g Thymol Blue + 500 mL of methanol. Put into a 1000 mL beaker. (C) Solution B

preparation: Slowly pour the cooled Solution B1 into Solution B2, and filter it thoroughly and dilute to 1000 mL with ultrapure water.

(4) Chlorine analysis electrolyte preparation: Take 8 mL of solution B to make solution A to 100 mL.

(5) TOX(MultiX 2500, Analytik Jena, Germany) Analysis: (A) Add 15 mL of chlorine analysis electrolyte to the cell. (B) After opening the software, first add 100 μL 0.01 N HCl solution to perform titration test. (C) Instrument condition setting: combustion chamber temperature 950 ˚C.

(6) The blank analysis values ranged from 0.42 to 1.60 μg/L with an average of approximately 0.77 μg/L and a standard deviation of approximately 0.32. Because the sample analysis value is obtained by the instrument automatically subtracting the blank value.

Results and discussion:

TOX contamination status in the water of the Lao Jie river. Observing the total organic halogen data (Fig. 3), it was found that the total organic halogen concentration at the site O1 was 223 μg/L, and the total organic halogen concentration at other site was about 335 to 404 μg/L. The site O1 organic halogen measurement value is obviously low, which may be caused by the dilution of the water volume of the tributary Tian Xin Zi river. Spatially, higher TOX concentrations are detected at sites along the metropolitan area and near the plant: site O2 (350 μg/L), site O3 (404 μg/L), site O4 (342 μg/L), site O5(335 μg/L) and site O6 (379 μg/L). However, a low TOX concentration (184 μg/L) was found at the site O7 away from metropolitan area and factories. The highest AOX concentration was detected at site O3 which was located near the factory. The plant produces synthetic fibers that are used in the production process to contain organic halogen compounds for cleaning and bleaching synthetic fibers. On the continuous monitoring and analysis of the total organic halogen, observe the distribution histogram of the total organic halogen concentration at the site O1 (Fig. 5). Due to the influence of the rainfall, the total organic halogen measurement value of some days is low in August. It was found that the total organic halogen concentration from August 26 to August 30 increased by 75.2 μg/L from 16.0, and the total organic halogen concentration from August 28 to August 30 remained above 60 μg/L, which was higher than that of the usual monitoring. From August 26 to August 30, the daily rainfall was 18 to 67 mm (Fig. 6). During this period, the total organic halogen concentration was not affected by the rainfall, and it did not fall. The inference was related to the heavy rain at that time. Except for the heavy rain that washed and hoisted the river sediment and soil, it did not rule out the possibility of discharging sewage from the heavy rain. The TOX concentration in the Lao Jie river is compared with the TOX concentration in other parts of the world(Table 1). It indicates that river areas are polluted by industrial and domestic sewage. In this study, the concentration of site O2 ~ O6 was higher than the TOX concentration (240 μg/L) measured in the previous reference. Human activities, especially industrial activities, are one of the reasons for this observation, as the Lao Jie river is surrounded by heavily polluted industries such as electroplating, printed circuit boards, chemicals and paper. Our studies showed that discharge water from these industries often contained relatively high TOX concentrations(Fig. 4), even though they had been strictly treated before discharge into the Lao Jie river. The sewage from the factory is an important source of pollutants in the Lao Jie river. The TOX concentration results from 21 plants, which show TOX contributions around the Lao Jie river and the TOX concentration will change significantly with the production process of the factory: site ★1 (815 μg/L), site ★7 (932 μg/L), site ★8 (686 μg/L), site ★12 (531 μg/L) and site ★16 (516 μg/L). The results of this study indicate that most of the river water TOX concentrations are lower than the factory discharge water. However, the high TOX concentration is mainly caused by industrial activities and secondary to human daily activities. Observing the data of total organic halogen in river samples, it was found that the total organic halogen measurement was affected by rainfall, but the relationship between total organic halogen measurement and rainfall was abnormal from August 28 to August 30.

Acknowledgements:

We would like to express our deep gratitude to the support from the Taiwan EPA. This work was supported by the National Science Development Fund of Taiwan.

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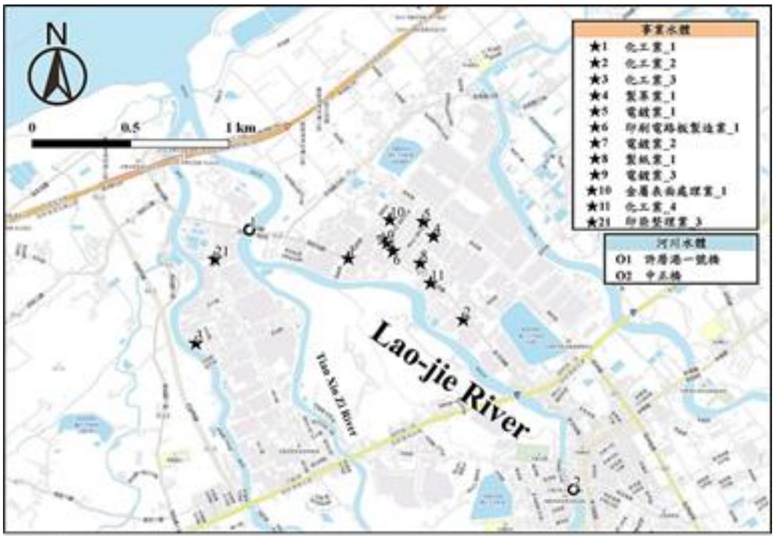

Fig. 1. Map showing the sample sites in the Lao Jie river.

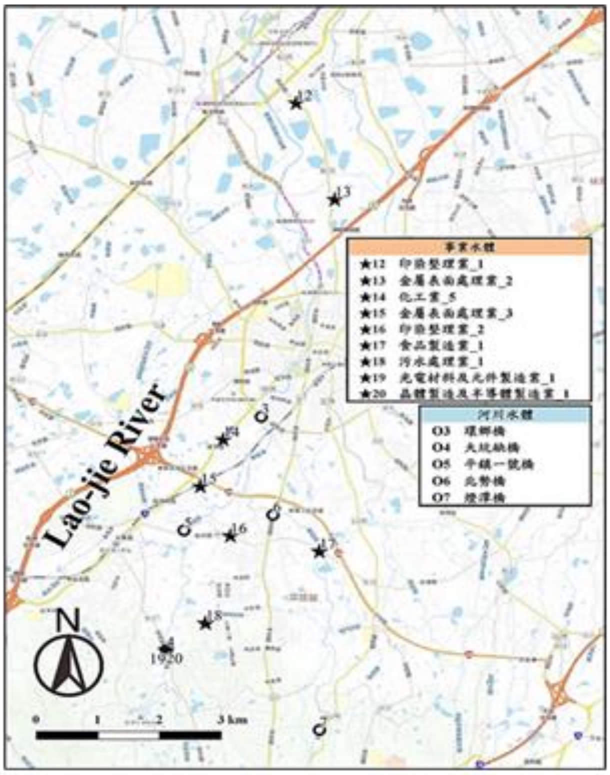

Fig. 2. Map showing the sample sites in the Lao Jie river.

Table 1. TOX concentrations in water of other areas.

Environments	TOX (μg/L)	References
Rivers, Poland	5.0 ~ 215	(Kaczmarczyk et al., 2005)
Lakes, Sweden	12.0 ~ 160	(Asplund et al., 1989)
Rivers, Sweden	6.0 ~ 120	(Asplund et al., 1989)
Tallinn bay, Estonia	27.0 ~ 74.0	(Kankaanpaa et al., 1997)
Vyborg bay, Russia	26.0 ~ 55.0	(Kankaanpaa et al., 1997)
Sovetskiy near Gulf of Finland	180 ~ 240	(Kankaanpaa et al., 1997)
Hangzhou Bay, China	140 ~ 716	(Xie et al., 2018)
Rivers, Taiwan	N.D. ~ 404	This study

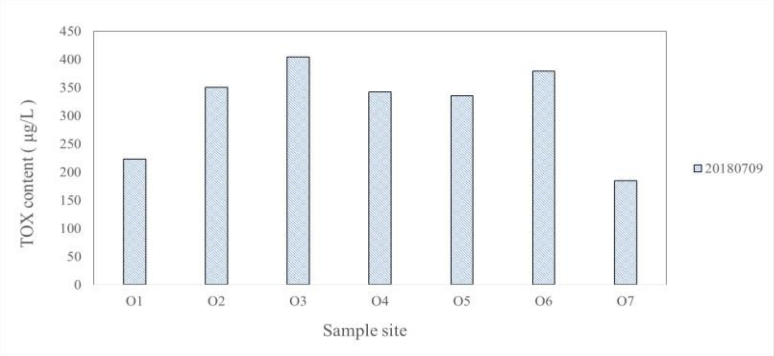

Fig. 3. TOX concentrations in the water of the Lao Jie river.

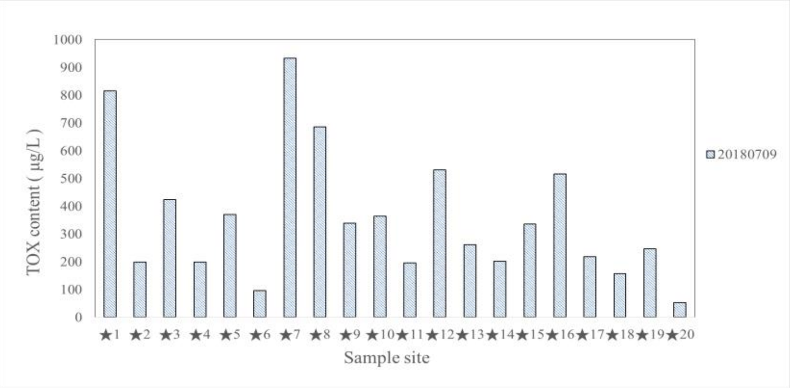

Fig. 4. TOX concentrations in the discharge water of the factory.

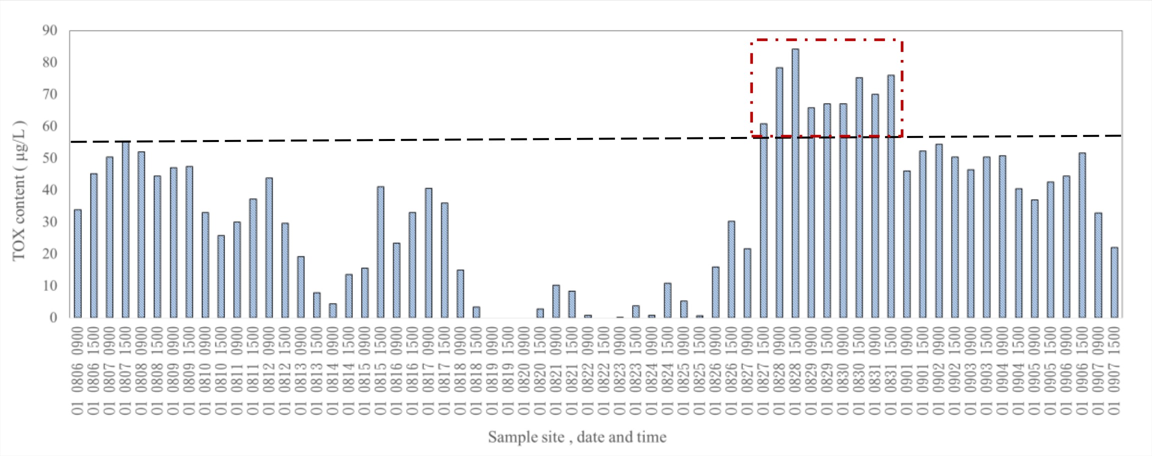

Fig. 5. TOX concentrations in the water of the Lao Jie river is continuously monitored.

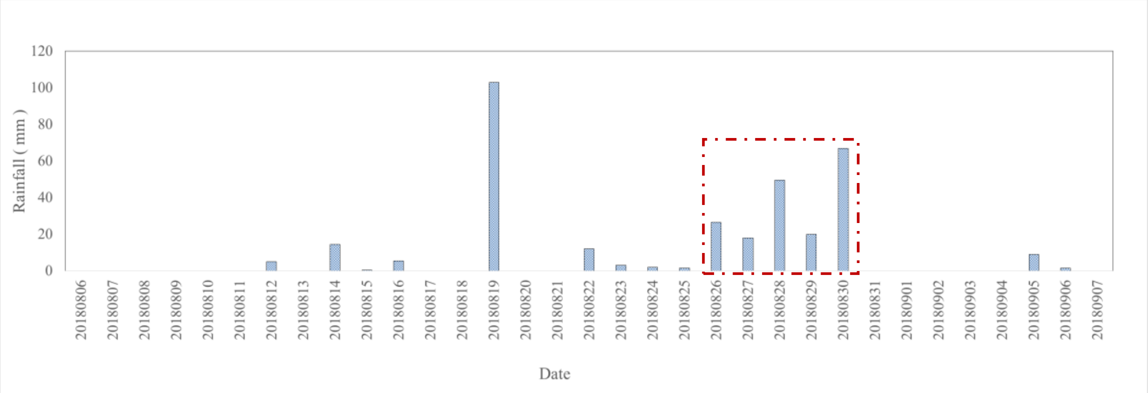

Fig. 6. Rainfall data of Taoyuan City from August to September 2018.

附錄Ⅱ 本次研討會本所發表之壁報

Investigation on total organic halogen(TOX) contamination in the river of Taiwan

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Introduction

Total Organic Halogen (TOX) often analyzes the total amount of organic halogen compounds in soil , sediment and water, can be further specified into total organic chlorine (TOCl), bromine (TOBr), and iodine (TOI), and can be used as a basis for reflecting the parameters of organochlorine levels in the environment. Disinfection by-products (DBPs) are often produced during the disinfection of drinking water. Among these by-products, since chlorine and chloramine are generally used as a disinfectant, the main disinfection by-product detected is a halogen-containing compound such as Trihalomethanes (THMs) etc. In addition, organic halides are often used in factory processes. For example, brominated flame retardants are commonly used in the manufacturing of plastics, textiles, and electronic products. It is likely cause environmental pollution. Recently, specific TOX compounds, such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane isomers (HCHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been detected in the water of different areas around the world. Therefore, Total organic halogen, a sum indicator, provides an efficient way to understand the contamination status of organic halogens in the environment. This was done in order to discover how industrial activities, human factors and environmental conditions (related to weather sampling seasons) influence the pollution of the inland water environment. The investigations provided an opportunity to examine the TOX, which may be important for finding appropriate means of evaluating environmental quality. The instrument principle is to use an activated carbon tube to adsorb halogen-containing organic compounds and burn them in an aerobic environment and a high temperature of 950˚C to produce halide ions, which are then analyzed by coulometric titration in an electrolytic cell. The reaction formula is: $Ag \rightarrow Ag^+ + e^-$; $X^- + Ag^+ \rightarrow AgX$ and its potential change is used to estimate the halogen content. Therefore, how to effectively and quickly monitor the total organic halides in the environment is an important topic for discussion.

Materials and methods

(1) Sample sites in the river:

The sampling time is from June 2018 to September 2018. There are 7 sites in the Lao Jie river, and there are 20 sites in the factory discharge water, totaling 93 samples. (Fig. 1) (Fig. 2)

(2) Pre-treatment cleaning instrument:

1. Nitrate, stock solution (0.2 mol/L): Take 17 g of sodium nitrate dissolved in a 1000 mL quantitative bottle, add 25 mL of concentrated nitric acid, and quantify in pure water.
2. Nitrate washing solution (0.01 mol/L): Nitrate washing solution (0.01 mol/L): 50 mL of Nitrate stock solution was placed in a 1000 mL dosing bottle and quantified in pure water.
3. Take 50 mL of water sample, add 5 mL of nitrate stock solution, and test the pH value with PH test paper. If it is higher than > 2, please add HNO_3 to adjust the sample pH < 2. The two activated carbon tubes are then placed in a column and attached to a pre-treatment instrument.

(3) Electrolyte preparation :

1. Solution A preparation: Take 200 mL of Acetic Acid + 500 mL of ultrapure water + 4 mL of concentrated nitric acid to a volume of 1000 mL with ultrapure water.
2. Solution B preparation: (A) Solution B1: Take 4 g gelatin + 400 mL ultrapure water. Place in a 500 mL beaker, soak for 3 hours, heat to 40˚C, dissolve and cool to 18 ~ 22˚C. (B) Solution B2: Take 1.0 g of Thymol + 0.3 g Thymol Blue + 500 mL of methanol. Put into a 1000 mL beaker. (C) Solution B preparation: Slowly pour the cooled Solution B1 into Solution B2, and filter it thoroughly and dilute to 1000 mL with ultrapure water.

(4) Chlorine analysis electrolyte preparation: Take 8 mL of solution B to make solution A to 100 mL.

(5) TOX(Multi X 2500, Analytik Jena, Germany) Analysis: (A) Add 15 mL of chlorine analysis electrolyte to the cell. (B) After opening the software, first add 100 μL 0.01 N HCl solution to perform titration test. (C) Instrument condition setting: combustion chamber temperature 950˚C.

(6) The blank analysis values ranged from 0.42 to 1.60 μg/L with an average of approximately 0.77 μg/L and a standard deviation of approximately 0.32. Because the sample analysis value is obtained by the instrument automatically subtracting the blank value.

Results and discussion

TOX contamination status in the water of the Lao Jie river. Observing the total organic halogen data (Fig. 3), it was found that the total organic halogen concentration at the site O1 was 223 μg/L, and the total organic halogen concentration at other site was about 335 to 404 μg/L. The site O1 organic halogen measurement value is obviously low, which may be caused by the dilution of the water volume of the tributary Tian Xin Zi river. Spatially, higher TOX concentrations are detected at sites along the metropolitan area and near the plant: site O2 (350 μg/L), site O3 (404 μg/L), site O4 (342 μg/L), site O5(335 μg/L) and site O6 (379 μg/L). However, a low TOX concentration (184 μg/L) was found at the site O7 away from metropolitan area and factories. The highest AOX concentration was detected at site O3 which was located near the factory. The plant produces synthetic fibers that are used in the production process to contain organic halogen compounds for cleaning and bleaching synthetic fibers. On the continuous monitoring and analysis of the total organic halogen, observe the distribution histogram of the total organic halogen concentration at the site O1 (Fig. 5). Due to the influence of the rainfall, the total organic halogen measurement value of some days is low in August. It was found that the total organic halogen concentration from August 26 to August 30 increased by 75.2 μg/L from 16.0 μg/L, and the total organic halogen concentration from August 28 to August 30 remained above 60 μg/L, which was higher than that of the usual monitoring. From August 26 to August 30, the daily rainfall was 18 mm to 67 mm (Fig. 6). During this period, the total organic halogen concentration was not affected by the rainfall, and it did not decrease. The inference was related to the heavy rain at that time. Except for the heavy rain that washed and hoisted the river sediment and soil, it did not rule out the possibility of discharging sewage from the heavy rain. The TOX concentration in the Lao Jie river is compared with the TOX concentration in other parts of the world (Table 1). It indicates that river areas are polluted by industrial and domestic sewage. In this study, the concentration of site O2 ~ O6 was higher than the TOX concentration (240 μg/L) measured in the previous reference. Human activities, especially industrial activities, are one of the reasons for this observation, as the Lao Jie river is surrounded by heavily polluted industries such as electroplating, printed circuit boards(PCB), chemicals and paper. Our studies showed that discharge water from these industries often contained relatively high TOX concentrations(Fig. 4), even though they had been strictly treated before discharge into the Lao Jie river. The sewage from the factory is an important source of pollutants in the Lao Jie river. The TOX concentration results from 20 plants, which show TOX contributions around the Lao Jie river and the TOX concentration will change significantly with the production process of the factory: site ★1 (815 μg/L), site ★7 (932 μg/L), site ★8 (686 μg/L), site ★12 (531 μg/L) and site ★16 (516 μg/L). The results of this study indicate that most of the river water TOX concentrations are lower than the factory discharge water. However, the TOX concentration is mainly caused by industrial activities and secondary to human daily activities. Observing the data of total organic halogen in river samples, it was found that the total organic halogen measurement was affected by rainfall, but the relationship between total organic halogen measurement and rainfall was abnormal from August 28 to August 30.

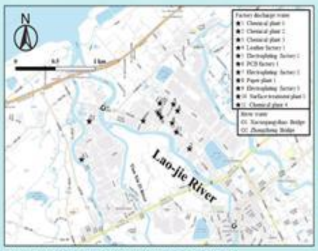

Fig. 1. Map showing the sample sites in the Lao Jie river.

Fig. 2. Map showing the sample sites in the Lao Jie river.

Table 1. TOX concentrations in water of other areas.

Environments	TOX (μg/L)	References
Rivers, Poland	**5.0 ~ 215**	**(Kaczmarczyk et al., 2005)**
Lakes, Sweden	**12.0 ~ 160**	**(Asplund et al., 1989)**
Rivers, Sweden	**6.0 ~ 120**	**(Asplund et al., 1989)**
Tallinn bay, Estonia	**27.0 ~ 74.0**	**(Kankaanpaa et al., 1997)**
Vyborg bay, Russia	**26.0 ~ 55.0**	**(Kankaanpaa et al., 1997)**
Sovetskiy near Gulf of Finland	**180 ~ 240**	**(Kankaanpaa et al., 1997)**
Hangzhou Bay, China	**140 ~ 716**	**(Xie et al., 2018)**
Rivers, Taiwan	**N.D. ~ 404**	**This study**

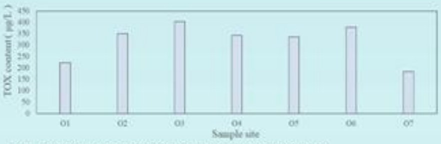

Fig. 3. TOX concentrations in the water of the Lao Jie river.

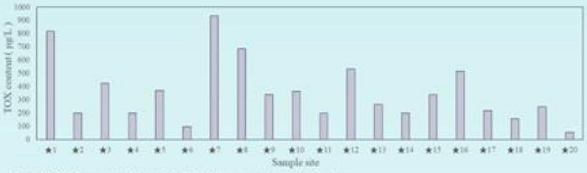

Fig. 4. TOX concentrations in the discharge water of the factory.

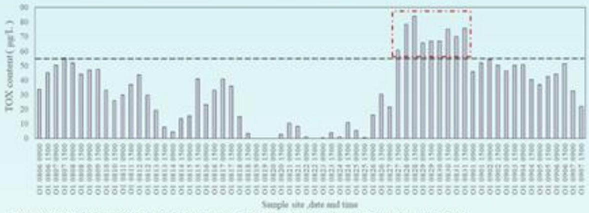

Fig. 5. TOX concentrations in the water of the Lao Jie river is continuously monitored.

Fig. 6. Rainfall data of Taoyuan City from August to September 2018.

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附錄Ⅲ　5 篇專題演講論文摘要

The AhR: A Major Player in Cancer Aggression and Immune Checkpoint Regulation

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Dr. Sherr received his B.A. from Brandeis University in 1973 and his PhD from Cornell University in 1978. He was a postdoctoral fellow at Harvard Medical School in the laboratories of Drs. Baruj Benacerraf (Nobel Laureate, 1980) and Martin Dorf from 1978 to 1981, after which he was appointed to the position of Assistant Professor (1982) and then Associate Professor (1987) of Pathology at Harvard Medical School. In 1993 Dr. Sherr was recruited to Boston University as Professor of Environmental Health and Professor of Pathology and Laboratory Medicine and is the Director of the Boston University Superfund Research Program and Director of the Find The Cause Breast Cancer Foundation Research Consortium. Since that time he has studied the role of the AHR in immune cell development and in tumorigenesis, specifically with regard to its role in production and function of immunosuppressive immune cells. He has published 127 peer-reviewed manuscripts. His lab has been continually funded by the NIH since 1986. He has trained 26 postdoctoral and 13 predoctoral fellows and 8 undergraduates, has served on 67 doctoral committees, and has won The Boston University School of Public Health Excellence in Teaching Award 3 times.

Hazardous chemicals in marine plastics and their threat to marine organisms

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Marine plastic and microplastics are ingested by various sizes of marine organisms depending on the sizes of plastic fragments. Ingestion of larger items (e.g., ~ cm) by large marine organisms such as whales, sea turtles, and seabirds has been often reported since 1970s. Recently, ingestion of smaller plastics, i.e., microplastics (< 5mm), by shellfish and fish has been reported. Trophic transfer accelerates dispersion of plastic throughout marine ecosystem. Large plastic items give physical damages on the biota. Microplastics may pose particle toxicity to marine organisms and ultimately to human.

In addition to the physical damages, marine plastics pose chemical threat to marine organisms because they contain variety of hazardous chemicals (Yamashita et al., 2018). Most of plastic products (i.e., user plastics) contain additives such as plasticizers, UV stabilizers, antioxidants, flame retardants to maintain their properties. Hydrophobic additives are retained in plastics and microplastics (Yeo et al., in this conference) in marine environment. Furthermore, plastics and microplastics sorb and accumulate persistent organic pollutants (POPs) from surrounding seawater due to their hydrophobic nature. International Pellet Watch (IPW;http://www.pelletwatch.org/) has been demonstrating the accumulation of POPs in microplastics on beaches across the world. Important finding of IPW is that microplastics with high concentrations of POPs aresporadically detected in remote areas, implying that microplastics carry POPs to remote areas with low background pollution. This is due to slow sorption/desportion of POPs to/from plastics and non-degradable nature of plastics.

Transfer of the hazardous chemicals from ingested plastics and their accumulation into the tissue of marine organisms has been demonstrated by leaching experiment (Tanaka et al., 2015), feeding experiment (Tanaka et al., in this conference; Teuten et al., 2009), exposure experiment (Wardrop et al., 2016), and field observations (Yamashita et al., 2011; Tanaka et al., 2013). Though hydrophobic additives are compounded into consumer plastics, their leaching from the products to food and drinks and exposure to human are basically unlikely due to their hydrophobic nature. However, when plastics are fragmented into smaller pieces in marine environment, and ingested by marine organisms, they may contact with oily components of digestive tract and additives can be leached to digestive fluid, transferred and accumulated in biological tissues. This is a new route of exposure of plastic additives to marine organisms and ultimately to human who consume seafood.

When risk associated with chemical exposure from ingested plastics is evaluated, it should be compared with that through natural prey. In case where background pollution level is higher such as industrial areas with legacy PCBs pollution, plastic-mediated exposure could be insignificant. However, in remote beaches where background pollution is low but huge amounts of plastics are stranded, plastic-mediated exposure is significant (e.g., Mizukawa et al., in this conference). Also, plastics could be a significant pathway of such additive that is not biomagnified to higher-trophic-level organisms. Accumulation of higher brominated diphenylethers in seabirds ingesting plastics is a typical example (Tanaka et al., 2013).

Microplastics are originally floating on sea surface but some of them sink to the bottom following the attachment of biofilm on microplastics (Zettler et al., 2013) which gives settling force to the microplastics. Microplastics were detected in bottom sediments (e.g., Matsuguma et al., 2017). Because of their low density, microplastics can be easily resuspended and laterally transported. Plastics have high affinity of hydrophobic compounds including legacy POPs in bottom sediments. Therefore, microplastics may remobilize the legacy POPs and may prolong the legacy pollution for longer time. Dynamic transport of microplastics in marine environments as well as their role as vector of POPs should be studied in future efforts.

MODELLING PERSISTENT ORGANIC POLLUTANTS: MECHANISTICALLY LINKING CHEMICAL PRODUCTION TO HUMAN EXPOSURE AND HEALTH EFFECTS

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This presentation will seek to briefly retrace the history of mechanistic environmental fate modeling of persistent organic pollutants, with a particular focus on how the scope of such modeling has gradually expanded from initial efforts to quantify individual chemical fate processes to integrated modeling systems that can link the production volume of an organic chemical with the biological effects that may be expected to occur in humans and wildlife. The motivations for mechanistic modeling of exposure to persistent organic pollutants are manifold, and include risk assessment and management, support of biomonitoring and epidemiological investigations, and the identification of chemicals and human populations with high exposure potential. A particular focus will be on highlighting the benefits of adopting an integrated modelling strategy for persistent organic pollutants, specifically with respect to the ability to account for lag periods between emissions and exposure as well as for shifts in the main exposure route over time. If there had been a change in chemical use and emission scenario, exposure factors, or the environment over time, a mechanistic representation of the relevant processes allows for the quantification of the implications of such changes for the time-variant contaminant exposure of organisms at the top of the food chain. Examples include bans on production and use of a substance, intergenerational changes in the dietary habits of an exposed population, or climate change. We will also address the key challenge of integrated modelling approaches, which is to preserve the simplicity and parsimony of successful modeling practice while acknowledging the inherent complexity of the processes and relationships to be described.

HUMAN BIOMONITORING AND EXPOSOMICS OF LEGACY AND EMERGING CHEMICALS

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Human biomonitoring methods are well established for the exposure assessment of many chemicals, including persistent organic pollutants (POPs). Such methods have resulted in establishing measures for regulations, following time trends of concentrations in human populations and in establishing reference values and ranges for a selected group of 250–300 known persistent and non-persistent chemicals.

Yet, as more and more chemicals are added to the market, there is an increasing need to estimate the human exposure to these emerging contaminants. Recent efforts and advances in mass spectrometry have seen the unprecedent rise of screening techiques with the aim to identify emerging contaminants and/or their metabolites present in humans. Such analytical approaches are 1) target screening; 2) suspect screening and 3) non-target (or untargeted) screening by high-resolution mass spectrometry (HRMS). Using such advanced tools, we can capitalize even more on the identification of life style-specific exposure profiles, i.e. compounds that may differ in relation to specific behavioural patterns.

Furthermore, the use of HRMS screening techniques allows the coupling of human biomonitoring with the exposome approach. An exposomic approach (exposomics) theoretically includes all exposures of potential health significance, whether they are derived from exogenous sources (e.g., pollutants, diet, drugs) or endogenous sources (e.g., hormones, human and microbial metabolites). Since levels of chemicals in biological samples reflect a wide range of exposures (biomarkers of exposure), but also consequences of exposures (biomarkers of effect), exposomic biomonitoring offers an efficient means for characterizing the overall individual exposure profiles. Incorporating the exposome paradigm into traditional biomonitoring approaches offers a means to improve exposure assessment in many ways.

With only a few hundred chemicals routinely measurable through targeted methods and with limitations for short-lived compounds, exposomic approaches are critical to understanding the daily exposure to thousands of chemicals and the consequences of exposure in exposome-wide association studies (EWAS).

The processing of rich sets of data from untargeted analyses offers a path for discovering health-impairing exposures that have thus far escaped scrutiny, a largely unrecognized benefit of exposomics. This should give guidance towards more accurate prevention measures that protect against exposure to (emerging) environmental contaminants and their substitutes in new materials and products.

DIOXIN AND HEALTH EFFECTS IN VIETNAMESE
PART 1. ENVIRONMENTAL DIOXIN IN VIETNAM

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Introduction

From 1961 to 1972, under the Operation Ranch Hand carried out by the US Army, about 74 million liter of defoliants were sprayed to destroy forest canopies and crops belonging to the North Liberty Army[1].The defoliants contained the chlorinated phenoxy herbicides as active ingredients in the formulations labelled as Agent Orange, Agent Purple and Agent White with Agent Orange nearly contributing half of total defoliant volume[2].

More importantly, most of the defoliants contained the extremely toxic by-products dibenzo-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The total amount of PCDD/F sprayed during Vietnam war was between 366 and 1223 kg toxicity equivalency quotient (TEQ)[2] which can be compared to today's global dioxin inventory of approximately 140 kg/year[3].

Agent Orange/Dioxin hot spots that exist today are USA military areas where Agent Orange was stored, leaked and spilled thereby causing elevated contamination of PCDD/Fs in soils[4]. It should be noted that so far, the contaminated soil in two major Agent Orange hot spots in Da Nang and Phu Cat have been remediated using "in-pile thermal desorption" and "secure landfill", respectively.

Besides, about 1.125 million ha of land was sprayed once by the defoliants while 0.382, 0.136, 0.048, and 0.019 million ha were documented as being sprayed 2, 3, 4, and ≥5 times, respectively[5]. The results of this spraying were that large areas of land were denuded of broad leaf vegetation as well as grasses.

PCDD/Fs are also known to be formed and emitted from different thermal processes such as waste incineration, metallurgical production, cement production, coal-fired power plants and industrial boilers. Besides, concerns on emission of dioxin and dioxin related chemicals with regards to uncontrolled burning of wastes in Vietnam have also been increasing. In this context, open burning of municipal wastes and thermal processing of e-waste for metal recovery are of concerns.

In this study, results from recent studies in Vietnam on contamination and emission of dioxin from such above important source categories are compiled to provide an assessment on current status of the environment contamination and sources of PCDD/Fs in Vietnam.

Material and method

Soil and sediment were collected from various sites in Vietnam for determination of the 17 most toxic PCDD/Fs congeners. Sampling sites included Agent Orange hotspots and their vicinities, lands sprayed by Agent Orange in the past, open dumping sites and e-waste recycling villages.

Stack gas samples were collected by isokinetic method (US EPA method 23) from industrial facilities for waste incineration, metallurgical production, cement production, coal-fired power plants. Bottom ash samples were also collected accordingly.

All samples were determined for 17 PCDD/Fs congeners by isotope dilution method using high resolution gas chromatography coupled with high resolution mass spectrometer (HRGC/HRMS, R>10,000).

Results and discussion

Contamination of PCDD/Fs in AO hot spots and their vicinities

The Da Nang airbase was a major Ranch Hand facility during the American War in Vietnam. Levels of dioxin have been found to be as much as 365,000 pg TEQ/g, more than 365 times the Vietnamese standard for industrial soil. In a joint US-Vietnam project, about 94,000 m3 of the contaminated soil/sediment plus an additional 68,000 m^3 of "lower risk material" were decontaminated using in-pile thermal desorption and landfill technologies, respectively[6].

In Phu Cat airbase, several sites were found to have levels of PCDD/Fs higher than the remediation standard (1000 pg TEQ/g for in soil or 150 pg TEQ/g for sediment). The Government of Vietnam implemented a cooperation project with UNDP for containment of 7,000 cubic meters of dioxin contaminated soil on the base using secure landfill technology.

The Bien Hoa airbase (south of Vietnam) is now the most severe AO hot spot in Vietnam. PCDD/Fs concentration was 7.6-960,000 and 17-4,860 pg TEQ/g in soil and sediment, respectively, implying very high contamination in this airbase. A study funded by USAID has estimated 408,500 to 495,300 m^3 of contaminated soils and sediments are located on or nearby the airbase. On May 11, 2018, USAID and the Vietnam Ministry of National Defense signed a non-refundable aid agreement for the decontamination of Bien Hoa airport. The cooperation was projected to take 10 years at an estimated cost of \$390 million and approximately 500,000 m^3 of soil and sediment are to be decontaminated[7].

Surveys on bioaccumulation of PCDD/Fs in animals living in the above airbases demonstrated that local animals such as fish, chicken, duck can accumulate elevated PCDD/Fs levels depending on their habitats. For example, in Bien Hoa airbase, PCDD/F concentration in fish collected within the airbases are from 75 to 288 pg TEQ /g wet wt. Biota samples outside of the hot spots have lower PCDD/F concentrations. In Bien Hoa airbase, TEQ in lipid basis were 26 pg/g for fish, 13 pg/g for eggs, 20 pg/g for chicken, 4.5 pg/g for meat. The mean TEQ in Da Nang airbase was slightly lower, 12.9 pg/g for fish, 8.7 pg/g for eggs, 5.9 pg/g for chicken, 6.7 pg/g for meat and 0.17 pg/g for vegetables[8-9].

Elavated concentrations of PCDD/Fs in mother breast milk are observed in corhots living near the Bien Hoa, Da Nang and Phu Cat hot spots, ranging from 9.3 - 23 pg TEQ/g lipid which is significantly higher compared to those in the scraft communes and agriculture villaages (1.4 – 4.3 pg TEQ/g lipid)[10-12].

Contamination of PCDD/Fs from industrial and municipal sources

In open dumping sites, toxic chemicals such as PCDD/Fs, PCBs, etc can be formed and released to the environment due to uncontrolled burning of municipal solid wastes by waste pickers and natural methane gas generation. PCDD/F levels in soil from dumping areas in Hanoi and Hochiminh city ranged from 0.4 to 850 TEQ pg/g compared to 1 to 1.15 pg/g in control sites[13]. Suzuki et al also reported elevated PCDD/Fs levels in soil at open-burning sites (3.8-143 TEQ pg/g) compared to those in e-waste processing workshops (0.28-17.6 pg TEQ/g)[14].

Studies for PCDD/F releases from industrial thermal processes in Vietnam showed that stack gas PCDD/F concentrations were 0.048 - 0.166 ng TEQ/Nm_3 in steel plants, 0.033 - 0.837 ng TEQ/N m^3 in cement kilns[15], 0.07 – 44 ng TEQ/Nm_3 in industrial waste incinerators, 0.012 – 0.44 TEQ ng/Nm^3 in medical waste incinerators, 0.016 – 0.31 ng TEQ/Nm^3 in coal-fired power plants, 0.016 – 1.66 ng TEQ /Nm^3 in coal-fired industrial and craft boilers[16]. PCDD/Fs in ambient air in three different regions in Vietnam (Hochiminh, Da Nang and Lao Cai cities) were studied, showing concentration of 139 fg I-TEQ/ Nm_3, 65.2 fg I-TEQ/ Nm_3 and 21.3 fg I-TEQ/ Nm_3, respectively[17]. Interestingly, while congener profile of PCDD/Fs in Hochiming city is mostly related to industrial sources, those in Da Nang city demonstrated an important source of 2,3,7,8-TCDD which is suspected to be from the nearby Agent Orange hot spot.

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PART 2. DIOXIN AND HEALTH IN VIETNAM

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Introduction

Between 1962 and 1971, the United States Air Force sprayed approximately 107 million pounds of herbicides in South Vietnam for the purpose of defoliation and crop destruction. During the course of this operation, hundreds of thousands of U.S. service personnel and millions of Vietnamese were exposed to the chemicals in the air, water, and soil and through food raised on contaminated farms. Agent Orange is known to affect immune system, reproduction, nervous system, and changing steroid hormone levels. Most studies on the adverse health effects induced by herbicide/dioxin have been focused on American veterans, whereas there are few studies concerning the relationship between dioxin and health effects in Vietnamese. Since 2002, we have been continuously researching the dioxin and health in Vietnam. Recently, we have focused the steroid hormone as an early indicator of dioxin-induced health effects[1-3]. The aim of this study is to evaluate the endocrine-disrupting effect of dioxin levels on adrenal steroid hormones in children from 1 to 7-year-old children in a previous herbicide-exposed regions in Vietnam.

Materials and methods

Three regions, namely Phu Cat, Binh Dinh Province and Bien Hoa, Dong Nai Province (hot-spots) and Kim Bang, Ha Nam Province (non-exposed region), were selected for study. Breast milk samples were obtained from lactating mothers aged 20 to 30 years from both regions between 2008 and 2011, who had given birth to their children aged from 4 to 16 weeks. In the first cohort study, in 2011 saliva samples from 3-year-old children and in 2013 and 2015, blood samples from grown-up 5 and 7-year-old children were collected in the morning each time in Phu Cat and Kim Bang. Finally, 78 children (34 from Phu Cat region and 44 from Kim Bang region) participated in this cohort study. In the second cohort study, since 2011 saliva samples from 1-year-old children and in 2013 and 2015, saliva and blood samples from grown-up 3 and 5-year-old children were collected in the morning each time in Bien Hoa and Kim Bang. Finally, 52 children (26 from Bien Hoa region and 26 from Kim Bang region) participated in this cohort study.

Three salivary hormones (cortisol, cortisone, dehydroepiandrosterone (DHEA)) and 6 serum hormones (cortisol, cortisone, 17-OH- progesterone (p4), progesterone, androstenedione (A-dione), testosterone) were determined by liquid-chromatography/tandem mass spectrometry (LC-MS/MS); dioxin levels in breast milk were measured by gas-chromatography-high resolution mass spectrometry (GC-HRMS).

Results and discussion

Dioxin levels in breast milk were significantly higher in hot-spot than non-sprayed region. In the first cohort study, on comparison of steroid hormones in saliva of 3-year-old children between two regions, DHEA was significantly lower in female of hot-spot than those in non-exposed region, while other steroid hormones showed no significant difference. On comparison of steroid hormones in serum of 5-year-old children between two regions, testosterone showed significantly lower concentrations in both sexes of hot-spot rather than those in non-exposed region. On comparison of steroid hormones in serum of 7-year-old children between two regions, progesterone and A-dione showed significantly higher concentrations in both sexes of hot-spot rather than those in non-exposed region, while testosterone showed significantly lower concentrations in both sexes of hot-spot rather than those in non-exposed region . On the relationship between dioxin levels in breast milk and steroid hormones in serum of 5-year-old children, testosterrone showed significantly negative relationships of both sex. On relationship between dioxin levels in breast milk and steroid hormones in serum of 7-year-old children, progesterone and A-dione showed significantly positive relationships of both sex and testosterrone showed significantly negative relationships only in male.

In the second study, age-related change in DHEA, cortisol and testosterone levels are given. Levels of DHEA increased from 1 year of age to 3 years of age, and decreased from 3 years of age to 5 years of age in Bien Hoa. Levels of testosterone decreased from 3 years of age to 5 years of age in the hotspot district, but increased from 3 years of age to 5 years of age in the non-sprayed district.

Our recent study showed dioxins effected the synthesis of dehydroepiandrosterone in three-year-old Vietnamese children[2]. From this study, we could confirm dioxin affected some steroid hormones till seven-year-old children. Dioxin exposure through breast milk might reflect the body burden of fetus and suppose a critical period of 35 dioxin exposure to disrupt endocrine at least in the childhood. Levels of testosterone decreased from 3 years of age to 5 years of age in the hotspot district, but increased from 3 years of age to 5 years of age in the non-sprayed district.

Acknowledgements

We would like to thank all the participants in Phu Cat, Bien Hoa and Kim Bang. This study was supported by the grants from the Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research, (B) No.15H05285.

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