出國報告（出國類別：國際會議）

參加第 36 屆國際鹵化持久性有機污染物研討會（2016 戴奧辛年會）報告

服務機關：行政院環境保護署環境檢驗所

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派赴國家：義大利佛羅倫斯

出國期間：105 年 8 月 26 日至 105 年 9 月 03 日

報告日期：105 年 11 月 07 日

摘要

本所派員參加本（105）年於義大利佛羅倫斯舉行第 36 屆國際鹵化持久性有機污染物研討會（通稱 2016 年戴奧辛年會）與會人數約 676 位，其中發表論文含有口頭論文 235 篇及壁報論文 319 篇。此次除發表論文分享本所工作成果外，亦期望藉此機會蒐集大會得到最新的儀器分析技術及新興持久性汙染物的相關議題與關注高風險物質。2016 年戴奧辛年會分為多個議題發表；有分析的新儀器或技術，也有以大面積的領域來監測探討持久性汙染物分布。

參加本次大會之重要心得及建議如下：

一、 大氣壓氣相色譜電離源(APGC)或大氣壓化學離子源(APCI)等大氣進樣技術日漸成熟，雖應用於環境檢測仍是少部分，但其發展的重要性不容忽視。

二、 氣相層析串聯質譜儀(GC-MS/MS)仍是檢測儀器發展的重點，其感度及解析度都已提升到可以分析 ppt 及 ppq 濃度，而且與氣相層析高解析質譜儀(GC/HRMS)有良好的比對性，甚至歐盟已在評估將其列為法規篩選法或確認方法，故本所應持續建置本項技術。

三、 全氟烷化合物(PFASs)對人體或環境的威脅衝擊日趨嚴重，美國多處飲用水水庫被檢測出且超出管制限值，突顯 PFASs 汙染的嚴重性，故本所應強化 PFASs 檢測技術。

四、 第 37 屆國際鹵化持久性有機污染物研討會議預定於 2017 在加拿大溫哥華舉行，期望本署及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。

五、 短鏈氯化石蠟(Short-chained Chlorinated Paraffins, SCCPs)異構物的複雜性造成檢測技術門檻甚高，本次大會有報導建議利用大氣壓化學離子源飛行式質譜儀(APCI/TOF)的方式可以有效降低干擾及分析的成本。然該儀器的建置也需要昂貴的成本，故現階段建議應予持續性關注或以現有的儀器技術來初探國內環境現況。

目次

壹、目的

持久性有機污染物（Persistent Organic Pollutants, POPs）是指人類合成的化學物質，會持久存在於環境中、透過生物食物鏈而累積，進而對環境及人類健康造成危害影響。1997 年聯合國環境規劃署（United Nations Environment Programme, UNEP）決定採取行動，首批將 12 種 POPs 列為管控重點，並推動國際條約「斯德哥爾摩公約」（Stockholm Convention），要求各國必須採取行動，減少環境中該等物質之殘留量，進而確保食品之安全。

首批列管之 12 種 POPs 包括阿特靈（Aldrin）、可氯丹（Chlordane）、滴滴涕（DDT）、地特靈（Dieldrin）、安特靈（Endrin）、飛佈達（Heptachlor）、六氯苯（Hexachlorobenzene）、滅蟻樂（Mirex）、毒殺芬（Toxaphene）等 9 種有機氯農藥，以及戴奧辛（Dioxin）、呋喃（Furans）及多氯聯苯（PCBs）等 3 種有機氯工業品和副產物。

此外，於 2009 年 5 月 4 日第四次締約國大會（COP4）、2011 年 4 月第五次締約國大會（COP5）及 2012 年 5 月第六次締約國大會（COP6）上， 決議納入了第 2 批 9 種、第 3 批 1 種及第 4 批 1 種新的 POPs，包括α-六氯環己烷（Alpha hexachlorocyclohexane）、β-六氯環己烷（Beta hexachlorocyclohexane）、六溴二苯醚及七溴二苯醚（Hexabromodiphenyl ether and heptabromodiphenyl ether）、四溴二苯醚及五溴二苯醚（Tetrabromodiphenyl ether and pentabromodiphenyl ether）、十氯酮（克敵康，Chlordecone）、六溴聯苯（Hexabromobiphenyl）、靈丹（Lindane）、

五氯苯（Pentachlorobenzene）、全氟辛烷磺酸及其鹽類和全氟辛基磺醯氟（Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, PFOSF）、安殺番（Endosulfan）及六溴環十二烷(Hexabromocyclododecane, HBCD)等。

持久性有機污染物具有毒性、難以降解、生物累積性及具有蚱蜢效應（Grasshopper Effect）等特性，能經由不斷蒸發及沈降，在大氣至遠離污染源排放地區間傳遞，藉由空氣、水和遷徙物種作跨越國界的遷移，並沈積在遠離其排放源的地區。隨後在當地的陸域或水域生態系統中蓄積，就連在離污染源數千公里的北極、南極地區純淨的生物棲息地均難倖免。這些物質對野生動物會造成畸胎的發生、腫瘤、免疫力降低、生殖障礙等毒害，且已經有許多證據顯示長期暴露於高濃度的 POPs，對人體會增加畸形兒的比例、不孕、智能減退、致癌等機會，並會降低人體之免疫功能，使其較易受感染。POPs 亦能累積在人體組織內，再經由母體臍帶或受乳時之傳輸進入胎兒，而對發育中的胎兒產生影響。

環境檢驗所（以下簡稱本所）因應斯德哥爾摩公約近程，積極建立 POPs 檢測技術，於民國 84 年 8 月成立戴奧辛小組，先後建立戴奧辛/呋喃、戴奧辛類多氯聯苯、多溴二苯醚(polybrominated diphenyl ethers; PBDEs)及有機氯農藥（organochlorine pesticides, OCPs）等 POPs 之高解析氣相層析質譜儀（gas chromatography/high resolution mass spectrometry, GC/HRMS）分析技術。同時亦持續參與瑞典之國際實驗室比測及通過澳洲 NATA 認證，使本所之 POPs 超微量檢測技術更具公信力。

為持續了解國際 POPs 研究趨勢、分析技術交流及蒐集最新研究成果，本所乃派員參加本（105）年於義大利佛羅倫斯舉行第 36 屆國際鹵化持久性有機污染物研討會（俗稱 2016 戴奧辛年會），除發表論文分享本所工作成果外，亦期望藉此機會吸取先進國家之經驗，提升本所分析技術並與國際潮流接軌。

貳、過程

第 36 屆「國際鹵化持久性有機污染物研討會（The 36rd International Symposium on Halogenated Persistene Organic Pollutants）」於 105 年 8 月 28 至 9 月 2 日於義大利佛羅倫斯國際會議中心(Congress and Exhibition Center)（如圖 1）舉行。本屆大會包含約 52 個國家 676 位專業人士與會；本次比較特別的是特別鼓勵學生及年輕學者能夠參與，故 676 位包括有 159 位年輕學者及 99 位學生，本大會發表之論文涵蓋議題廣泛，其中口頭宣讀 235 篇；壁報展示為 319 篇。

圖 1、大會主會場

本次研討會仍維持為口頭論文宣讀及壁報論文展示二種。口頭論文宣讀部分共分 2 棟樓共 5 個場地同時進行，早晨九點會安排國際知名教授進行長達約 45 分鐘的專題演講，結束後再由大會安排符合資格的學生進行演講。而後才在各演講廳進行報告，報告方式是使用 Power Point 簡報軟體進行 15 分鐘簡報，然後接受 3

分鐘提問；壁報論文部分因數量較多，分別於 8 月 29 日、8 月 30 日及 9 月 1 日梯次展示（每梯次 1 天）。此次大會將儀器展示與壁報展示分開樓層展示，讓參觀者專心的瀏覽壁報或是聽取儀器介紹，。

大會於 8 月 28 日（星期日）中午就開始受理報到，並開始有儀器廠商辦的周邊會議（Side meeting）介紹最新技術訊息，這樣的周邊會議共有 4 場(如附件 1)，都可以預先透過網路報名；8 月 28 日晚上大會安排一場非正式的雞尾酒晚會，讓與會者在輕鬆的氣氛下進行交誼；而 8 月 29 日至 9 月 1 日是論文及大廳專題演講發表時間；而 9 月 2 日閉幕典禮前，邀請 3 位專家對 5 天來的各主要議題做重點回顧；整個大會於 9 月 2 日中午劃下完美的句點。

參、心得

一、2016 戴奧辛年會主辦單位對外聯絡主要途徑是主要是經由網際網路，網址為 http://dioxin2016firenze.org/ 。由網站中可獲得絕大部分訊息，其中包含主辦單位的邀請函、主辦城市簡介、氣候、論文投稿相關格式、截止日期、如何註冊參加研討會、旅館飯店的預定、研討會期間之社交活動、當地旅遊活動行程簡介及主辦人員電子郵件帳號……等。本次研討會場地分布如圖 2 舉行，

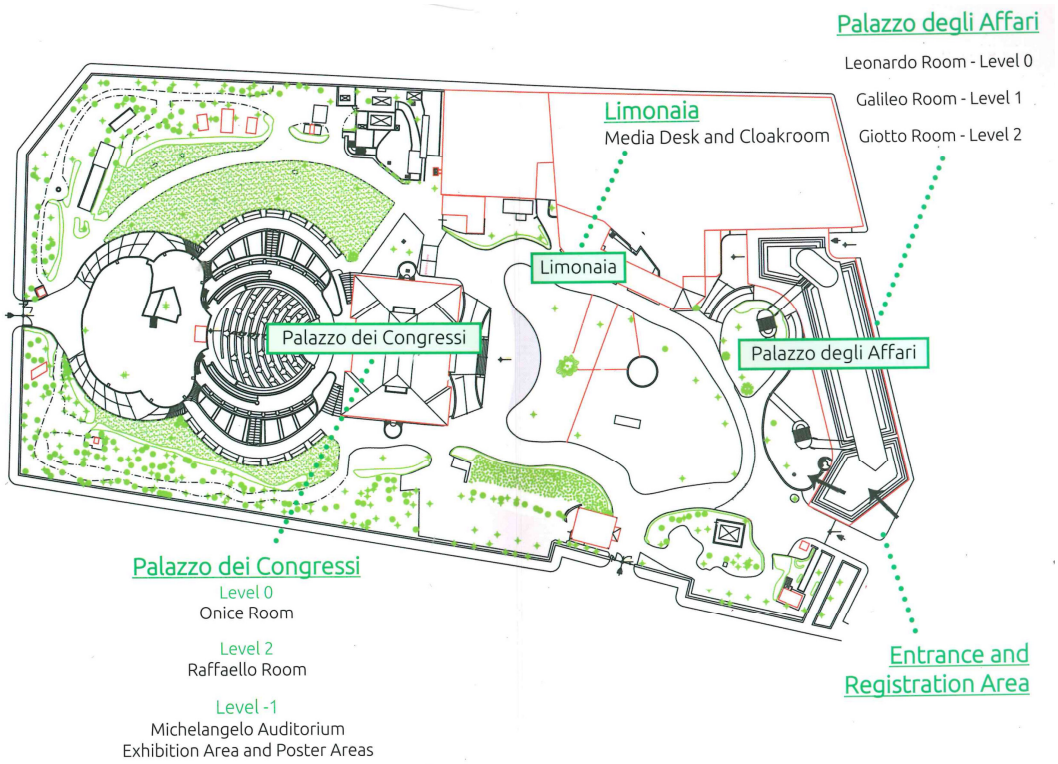
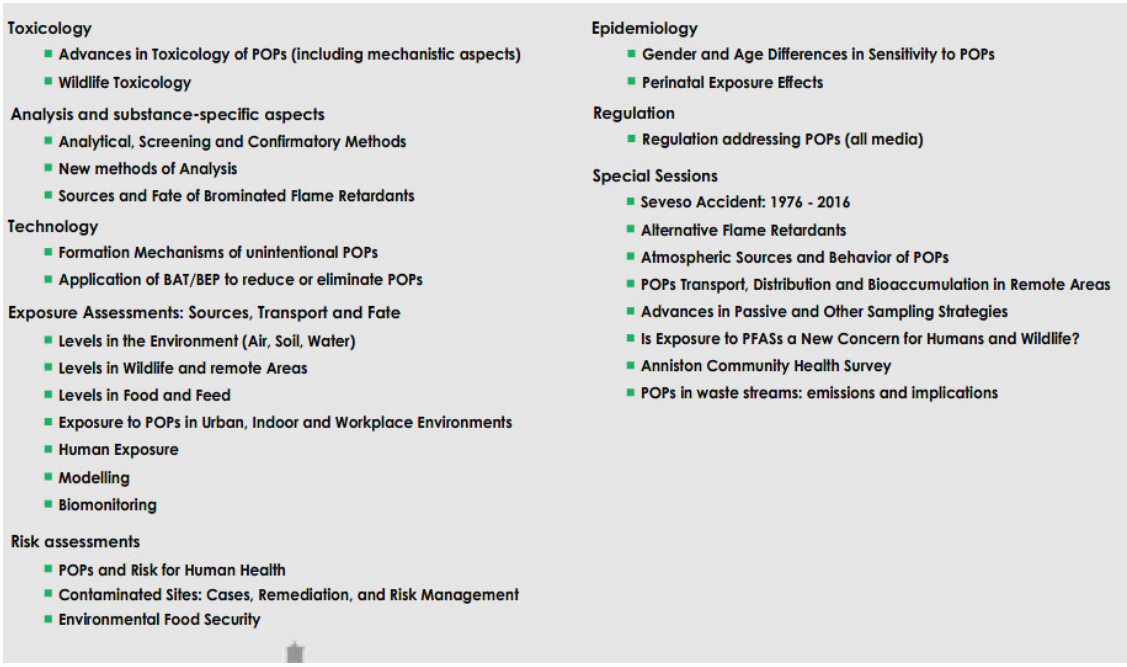


圖 2、會場分布圖

大會所有活動大致上劃分為二大區塊，壁報論文及儀器展示場地在 Palazo dei Congressi 的地下一樓的位置，而口頭報告分別於 Michelandelo Auditorium、

Raffaello Room、Lennardo Room、Galileo Room 及 Giotto Room。唯一美中不足的是壁報場地過小。每當壁報者跟參加人員於會場討論時，就要左閃右閃的才能通過該會場；口頭報告轉換場次以步行上是需要約 3~5 分鐘才能走到另一個場地，所以若遇到兩個主題在相近的時間在不同場地的時候，就很難聽到完整的演講。

二、本次戴奧辛年會論文內容涵蓋 8 大主題。各主題及所涵蓋之副主題如下：



三、本次儀器的內容介紹係以現場的廠商廣告資料及發表會做為主要參考。周邊會議仍以氣相層析-串聯式質譜儀（GC-MS/MS）為發展的主軸，因感度及解析度都大幅提升，甚至歐盟對戴奧辛類化合物的儀器分析方法部分，都已在評估將 GC-MS/MS 列為篩選方法（Screening Method）。THERMO 公司推出

DualDataXL DFS Magnetic Sector GC-HRMS 及 TSQ 8000 GC/MSMS；Agilent 則發表 7010 GC/QQQ 為這波的儀器推廣重點。GC/HRMS 雖然擁有良好的感度、解析度及公信力，是世界各國當前唯一的法規確認標準方法，但造價昂貴、週邊配備多、操作環境要求嚴苛、電力耗損大、需高度專業人員操作及維護成本驚人等都是其缺點，故現階段未有購入的需求性。

而 7010 GC/QQQ 的感度更是有所提升，其提升感度最主要的原因係改用 $H_{2(gas)}$做為系統的載流氣體。然氫氣使用於實驗室的情形仍佔少數，僅多用於 GC-FID 做為偵測器燃燒用。目前實驗室大宗的使用量為氮氣及氦氣，兩種氣體為惰性氣體，故即使管路有洩漏也無威脅實驗室安全的問題。雖然如此 7010 GC/QQQ 仍是可使用氦氣做為載流氣體，日後仍可繼續關切相關的儀器發展動態。

WATERS 分別發表有關 APGC 和 APCI 等相關應用，而在短鏈氯石蠟(SCCP)也有學者發表利用 APCI 技術來縮短簡化分析過程及避免干擾等優點。大氣壓進樣的技術這幾年也漸漸發展出不同領域的應用，然在環境的使用實際案例應用仍佔少數，若能開發出更多環境端應用或許能發展出新的一片領域。

四、此次壁報的展覽提材也是相當的豐富，不僅能夠學習到實驗的設計及邏輯，也能學習到一些儀器的技術。本次注意了一些相關 TOF-MS 的壁報及演講，其中一篇介紹有關 non-target screening method 技術研究流程探討(圖三)，

圖 3、non-target screening method 建立流程探討

主要的做法是先建立 non-target 的標地物，作者係先配製好特定濃度的已知毒化物(約 200 多項已知毒化物)。在來建立淨化程序的比較，文中用了 3 個 SPE 及 2 個 LLC 方法來評估淨化效果，將配製好的已知毒化物經過不同的淨化程序後上機分析，依不同淨化程序的結果來統計能偵測出毒化物總數及回收率來做比較，結果顯示 SPE 法的 HLB 淨化方式能有最好的回收率，而 SPE 法的 Hypersep 能偵測出最多毒化物的總量。

不同領域的研究環境毒化物總是能吸引目光，此篇作者觀察到日本鵪鶉的鳥蛋內含有兩種阻燃劑 TDCIPP(Tris(1,3-dichloroisopropyl)phosphate) 及 DP(Dechlorane Plus)，所以作者設計了在一控制的環境下施予不同濃度的 TDCIPP 及 DP 來觀察這兩種阻燃劑對於日本鵪鶉的鳥蛋孵化的影響(圖 4)。

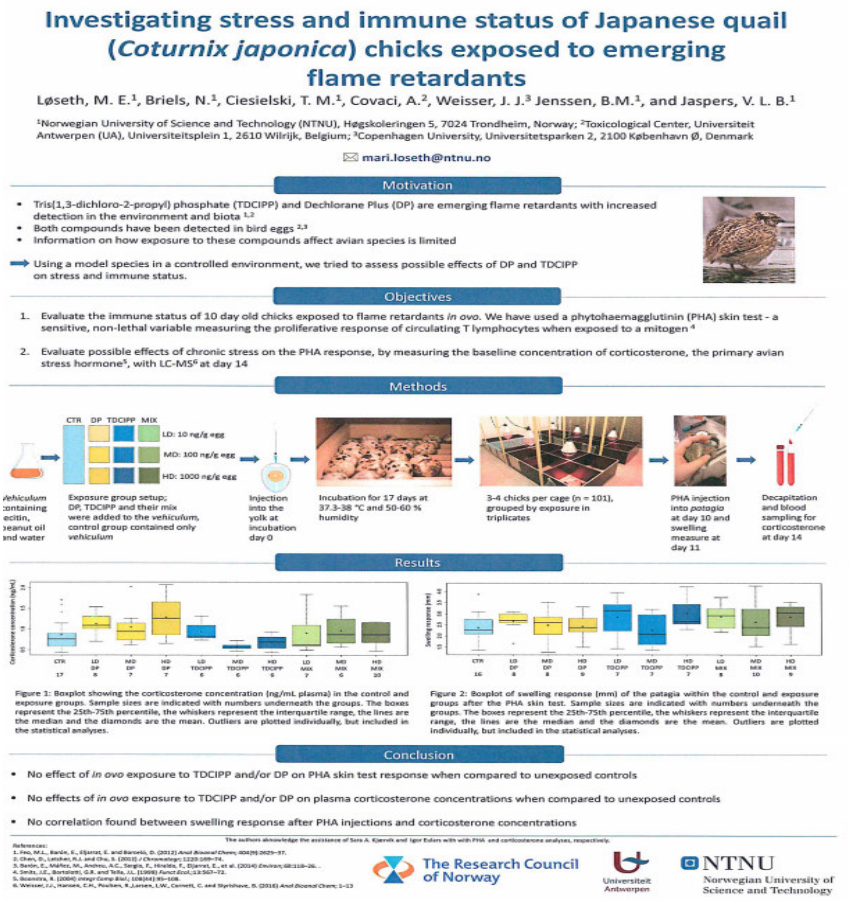


圖 4、TDCIPP 及 DP 阻燃劑對於日本鵪鶉的鳥蛋孵化的影響探討

然而結果顯示在被施予高劑量濃度 1000ng/g TDCIPP 及 DP 的鳥蛋對於孵化是沒有影響的，而同樣在生活在高劑量濃度環境下的母雞仍可正常的下蛋

並孵化成功。結果的顯示 TDCIPP 及 DP 阻燃劑找不出與孵化的相關性，然而對於我們可學習的是環境毒化物的影響評估方法實驗模式，對於日後遇到未知毒性的化學品提供一套評估方式流程實驗設計。

另外也在會場有看到一則與本所目前研究相關的議題(土壤中有機污染物濃度與實際污染強度關聯性調查計畫)有相關性。該作者評估是否有可能在已受到戴奧辛及多氯聯苯汙染的土壤進行玉米的栽種(圖 5)。

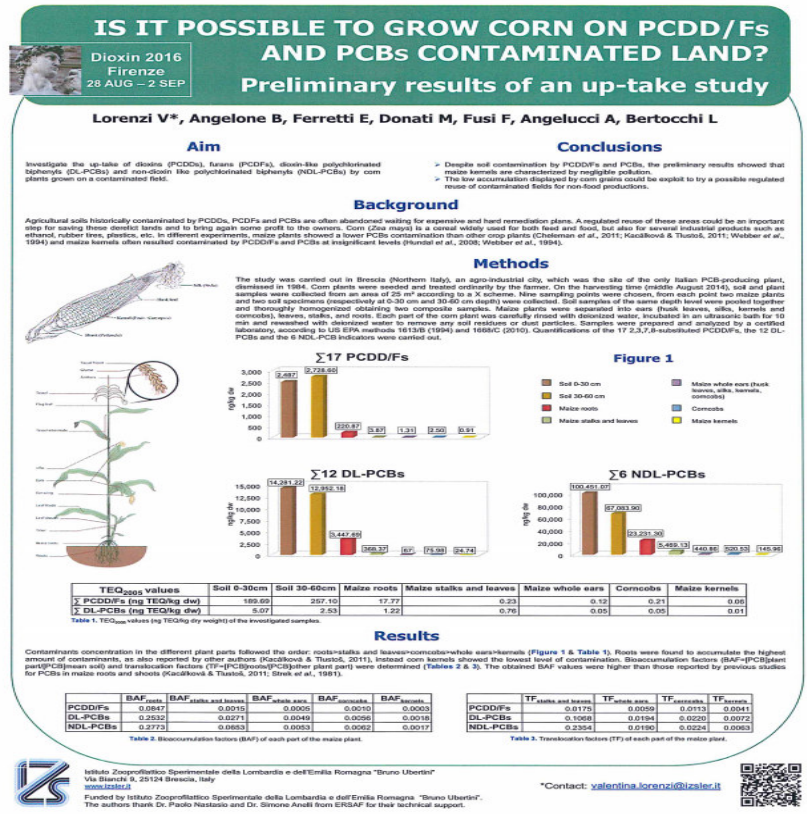
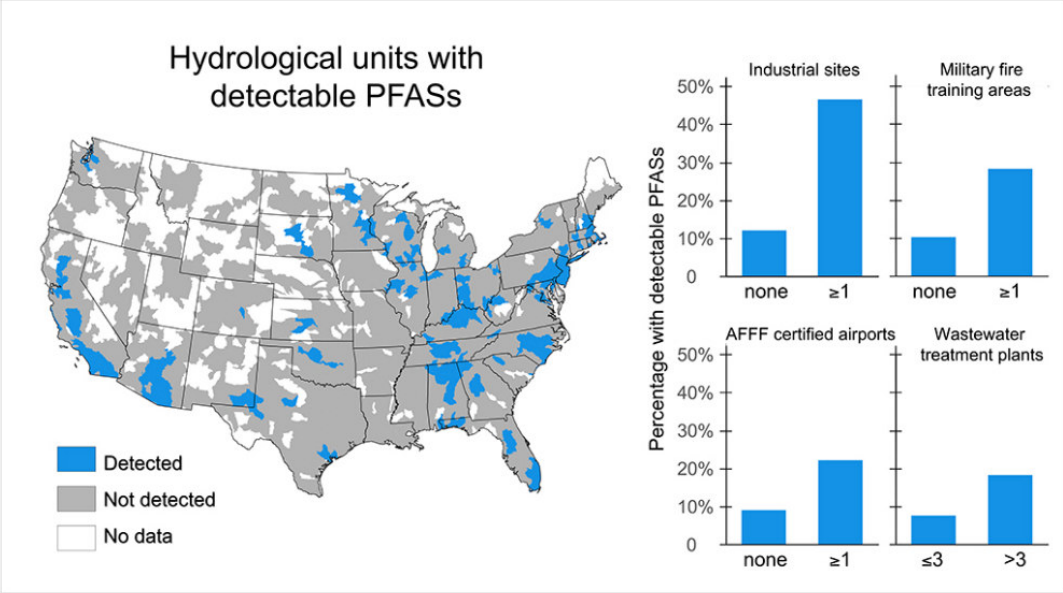


圖 5、玉米栽種於含戴奧辛及多氯聯苯土壤之探討

作者分別將栽種的土壤與玉米的根、莖葉、玉米鬚根、玉米粒…等分別檢測戴奧辛及多氯聯苯的總毒性當量，結果顯示隨著離土壤越遠其總毒性當量越

低，也就是傳輸力也隨之降低。可惜的是土壤未做有機質的探討，未能提供有土壤汙染強度的關聯性，但仍是一篇值得參考的文獻。

2016 戴奧辛年會特別探討了 PFASs 對於環境或人衝擊的憂慮，本次大會最具衝擊性的報導不外乎就是美國多個提供飲用水的水庫被檢測 PFASs 的存在並且超出美國 EPA 的管制值(70ng/L)(圖 6)，部份樣本檢出濃度高達 349 ng/L PFOA 及 1800 ng/L PFOS。



This map is based on publicly available data provided by the U.S. EPA (https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule). Areas highlighted in blue indicate zip codes where PFASs were detected in one or more water samples from 2013-15 that were at or above the minimum reporting levels required by the U.S. EPA. Zip codes that are elevated in PFASs do not represent all drinking water sources in that region. Individuals concerned about their drinking water should consult with their local water suppliers. More detailed maps based on the U.S. EPA data are available from the Environmental Working Group (http://www.ewg.org/enviroblog/2015/08/your-drinking-water-contaminated-toxic-non-stick-chemicals).
Credit: Hu et al, Environmental Science & Technology Letters
http://pubs.acs.org/doi/pdf/10.1021/acs.estlett.6b00260

圖 6、美國水庫 PFASs 調查結果報導

結果顯示鄰近工廠、軍事練習場、含有水成膜泡沫(AFFF)的飛機及廢水植種植物等是主要被檢出超標的地區。在大會最後一天總結時也特別提出本事件(圖7)，再一次顯出 PFASs 對於環境或人衝擊憂慮的嚴重程度。

圖 7、閉幕式總結演講

五、2017 年戴奧辛年會

第 37 屆國際鹵化持久性有機污染物研討會議預定於 2017 年 8 月 20 日~8 月 25 日在加拿大溫哥華（Vancouver）舉行，相關網址資料為 www.dioxin2017.org。期望本署及所內同仁有機會參與盛會，發表論文及吸收先進經驗。2017 年會主辦單位網站主網頁上的邀請函如下（如圖 8）。

圖 8、2017 年戴奧辛年會邀請函

肆、建議

一、 大氣壓氣相色譜電離源(APGC)或大氣壓化學離子源(APCI)等大氣進樣技術日漸成熟，應用於環境檢測仍是少部分，但其發展的重要性不容忽視。

二、 氣相層析串聯質譜儀(GC-MS/MS)仍是檢測儀器發展的重點，其感度及解析度都已提升到可以分析 ppt 及 ppq 濃度，而且與 GC/HRMS 有良好的比對性，甚至歐盟已在評估將其列為法規篩選法或確認方法，故本所應持續建置本項技術。

三、 全氟烷化合物(PFASs)對人體或環境的威脅衝擊日趨嚴重，美國多處飲用水水庫被檢測出超出其限值，突顯 PFASs 汙染的嚴重性，故本所應持續強化 PFASs 檢測技術。

四、 第 37 屆國際鹵化持久性有機污染物研討會議預定於 2017 在加拿大溫哥華舉行，期望本署及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。

五、 短鏈氯化石蠟(Short-chained Chlorinated Paraffins, SCCPs)異構物的複雜性造成檢測技術門檻甚高，本次大會有多篇的報導建議利用 APCI 的方式可以有效降低干擾及分析的成本。然該儀器的建置也需要昂貴的成本，故現階段建議應予持續性關注或以現有的儀器技術來初步調查環境現況。

伍、參考資料

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2. 第 36 屆「國際鹵化持久性有機污染物研討會」論文集。
3. 第 36 屆「國際鹵化持久性有機污染物研討會」網站，http://www.dioxin2016firenze.org/
4. 陳元武，參加第 33 屆國際有機鹵化環境污染物及持久性有機污染物研討會（2013 戴奧辛年會）報告，行政院環境保護署環境檢驗所，中華民國 102 年。
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6. DEVELOPMENT OF A COMPREHENSIVE NON-TARGETED SCREENING METHOD FOR ORGANIC CONTAMINANTS IN HUMAN PLASMA, G. Codling, Research Centre for Toxic Compounds in the Environment Kamenice 753/5, pavilon A29 625 00 Brno Czech Republic.
7. INVESTIGATING STRESS AND IMMUNE ST ATUS OF JAP ANESE QUAIL (COTURNIX JAPONICA)CHICKS EXPOSED TO EMERGING FLAME RET ARDANTS, M.E. Løseth, Department of Biology, Norwegian University of Science and Technology (NTNU).
8. IS IT POSSIBLE TO GROW CORN ON PCDD/FS AND PCBS CONT AMINATED LAND? PRELIMINARY RESUL TS OF AN UP-T AKE STUDY, V . Lorenzi, Istituto Zooprofilattico Sperimentale della Lombardia e dell'Emilia Romagna.
9. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. Environ. Sci. Technol. Lett. 2016, 3, 344−350.

附件 1 大會 4 場周邊會議（Side meeting）

Waters

Title：Waters User Meeting in POPs Analysis and Research
Date：August 28 (Sun.), 2016
Time：12:00 – 17:30
Venue：The Westin Excelsior, Piazza Ognissanti 3

Thermo

Title：Thermo Scientific Lunch & Learn
Date ：August 29 , 2016
Time：13:00 – 13:45
Venue：LEONARDO ROOM

Agilent

Title：Agilent Lunch Seminar
Date ：August 30 , 2016
Time：13:00 – 13:45
Venue：LEONARDO ROOM

MIURA

Title：MIURA Lunch Seminar
Date：SEPTEMBER 1st, 2016
Time：13:00 – 13:45
Venue：LEONARDO ROOM

附件 2 本次大會本所共同發表論文

Cod: 5.1006

EVALUATION OF THE RELATIVE HEALTH RISK IMPACT OF ATMOSPHERIC PCDD/FS IN PM2.5 IN TAIWAN

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Introduction

$PM_{2.5}$ (particle matter with an aerodynamic of less than or equal to 2.5 μm) is a crucial air pollutant on the basis of its adverse human health effects and degradation of visibility[1]. The standard has been strengthened in 2012 and currently set at 35 μg/m^3 for 24 hours and 15 μg/m^3 for annual average in the U.S. Epidemiological and toxicological studies have demonstrated that increased particulate matter cause increased cardiovascular mortality and morbidity, and this PM toxicity may increase as the particle size decreases. $PM_{2.5}$ is a complex mixture from both natural and anthropogenic sourced, including primary and secondary particle species, and consists mainly of water soluble ions, carbonaceous species (OC and EC) and elements (Al, Si, Mg, Fe, Pb, Zn, etc)[2,3]. Exposure to fine particulate matter ($PM_{2.5}$) was associated with increased risk of active tuberculosis, in addition, traffic-related air pollution including nitrogen dioxide, nitrogen oxides and carbon monoxide was associated with tuberculosis risk[4]. Particularly, the contents of dioxin-like compounds and other pollutants exist in suspended particles. One of the dioxin-like compounds, the 2,3,7,8-TeCDD was classified by International Agency for Research on Cancer (IARC) as a "known human carcinogen"[5]. The objective of this study is to survey the information regarding the environmental burdens of PCDD/Fs in the vicinity of the stationary pollution sources in air were established, while human relative health risks for the population living in the vicinity of the stationary pollution sources and other regions (urban area and suburban area) were also assessed.

Materials and method

In this study, we collected ambient air samples at different regions (urban, suburban, industrial area) around Taiwan during winter and summer season in 2014 and 2015 (Figure 1). The atmospheric concentrations of seventeen 2, 3, 7, 8-substituted PCDD/Fs in suspended particles were monitored. The sampling procedures were performed following the main guideline of European Union EN-14907 $PM_{2.5}$ for ambient air collection. Ambient air samples for both vapor phase and solid phase of dioxin-liked compounds were collected. The ambient sampling instruments consisted of HVS $PM_{2.5}$ sampler (Analitica), the samplers were equipped with Whatman quartz fiber filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs were used for retaining PCDD/F compounds in the vapor phase. HVS $PM_{2.5}$ sampler (Analitica) was connected to a vacuum pump and 700 m^3 of air mass was collected in 24 h at a sampling flow rate of 500 L/m^3. The PUF and filter samples were than Soxhlet extracted with toluene for 24 hours, treated with concentrated sulfuric acid, and then passed through a series of clean-up columns containing sulfuric acid-silica gel, acidic aluminum oxide and celite/carbon. In this study, the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W). In addition, the concentration of PCDD/Fs are used to calculate Relative Ratio (RR) with Taiwan Cancer Registry database, and then investigated the relationships of PCDD/Fs concentrations and disease deaths rate at different regions.

Results and discussion

The results shown in Tables 1 to 3 indicated the $PM_{2.5}$ concentrations in daily average measured at different area in Taiwan, the higher $PM_{2.5}$ (60.4±7.39 μg/m^3, 35.1±4.75 μg/m^3) concentrations were measured at industrial station (Site I4) and urban station (Site U6), respectively. For the PCDD/F analysis, Fig. 2 demonstrated that the PCDD/Fs concentrations of $PM_{2.5}$ samples in winter and summer season, the highest concentration of PCDD/Fs was 122±51.1 fg I-TEQ/m^3 measured at Site I4. In addition, the results indicated that the atmospheric PCDD/Fs mostly distributed in solid phase ($PM_{2.5}$) especially during the winter season. Moreover, the higher concentration of PCDD/Fs was 31.1±16.3 fg

I-TEQ/m^3 at Site I1 and higher percentage concentration of PCDD/Fs in vapor phase. Especially for the northern urban area (Site U4), the total quantity of PCDD/Fs in $PM_{2.5}$ (1,182±294 pg I-TEQ/g) were higher than other station (Figure 3). The northern urban area (Site U4) was set up at the city with higher densely populated and also was affected by traffic and monsoon. In summer, the higher total quantity of PCDD/Fs in $PM_{2.5}$ was 698±159 pg I-TEQ/g at Site I6. All the measurements indicated that the atmospheric PCDD/Fs measured in this study were all lower than the air quality standards for dioxins in Japan (0.6 pg-TEQ/m^3). Table 4 indicated that the health relative risk of all causes and cancers of liver and intrahepatic bile ducts in high $PM_{2.5}$ concentration exposure all group were significant higher than low $PM_{2.5}$ concentration exposure all group. In addition, the health relative risk of malignant neoplasms (Relative risk= 1.4145, CI= 1.083-1.847, P= 0.011) in high $PM_{2.5}$ concentration exposure female group were significant higher than low $PM_{2.5}$ concentration exposure female group. However, Table 5 indicated that the health relative risk of the cancers of trachea, bronchus and lung (Relative risk= 1.898, CI= 1.039-3.468, P= 0.037) and female breast cancer (Relative risk= 2.321, CI= 1.027-5.245, P= 0.043) in high PCDD/Fs exposure female group were significant higher than low PCDD/Fs exposure female group. The results demonstrated that the chemical content and levels in $PM_{2.5}$ will be much important than the mass concentration.

Acknowledgements
The authors gratefully acknowledge the financial support provided by Taiwan Environmental Protection Administration (EPA-103-1604-02-05 and EPA-104-1604-02-01) and the Ministry of Science and Technology (MOST 104-2628-M-010-001-MY3) of Taiwan. Assistance provided by Prof. M. B. Chang, Mr. S. H. Chang and Dr. P. C. Hung of National Central University in analyzing the data is also acknowledged.

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Cod: 8.10015

THE CHARACTERISTIC OF PCDD/F IN FINE PARTICLE FROM FLUE GAS AND SOURCE APPORTIONMENT VIA POSITIVE MATRIX FACTORIZATION IN TAIWAN

Y.N. Li[1], Y.T. Liou[1], M.B. Chang[2], C.C.K. Chou[3], Y.W. Chen[4], Y.Y. Sung[4], K.H. Chi[1]

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Introduction

Dioxins (polychlorinated dibenzo-p-dioxin, PCDDs) and furans (polychlorinated dibenzofurans, PCDFs) and other pollutants as persistent organic pollutants which listed "hazardous air pollutants (Hazardous Air Pollutants, HAPs) substances. PCDD/Fs are formed and released unintentionally from anthropogenic sources. PCDD/Fs are ubiquitous in air, water, soil, sediment, plants, and are released as byproducts during various thermal processes of combustion, incineration, and metal smelting[1,2,3]. Municipal solid waste incinerators (MSWIs) have been historically associated with emissions of toxic chemicals, such as PCDD/Fs and heavy metals, among other pollutants[4]. Particularly, the contents of dioxin-like compounds and other pollutants exist in suspended particles. $PM_{2.5}$ (particle matter with an aerodynamic of less than or equal to 2.5 μm) is a crucial air pollutant on the basis of its adverse human health effects and degradation of visibility and the chemical composition of $PM_{2.5}$ is a key to fully understanding and assessing its impacts on climate, air quality[5]. Positive matrix factorization (PMF) has become a factor analytic (FA) model of choice for quantitative source apportionment of contaminants in many air quality monitoring studies[6,7]. In this study, the PCDD/Fs major emission sources such as industrial boiler, municipal waste incinerators (MWI), electric arc furnace (EAF), and the vicinity of stationary pollution sources have been investigated regarding the distribution of PCDD/Fs, trace metals, carbon, water-soluble ions in $PM_{2.5}$. The PMF model has been used in this study to analyze the source apportionment of PCDD/Fs. The objective of this study is to figure out the chemical profiles of stack gas and the vicinity atmosphere, moreover, estimate the relative contribution of various sources around the stationary pollution source regions.

Materials and methods

In this study, the flue gas samples were collected for analysis of PCDD/Fs from three stationary pollution sources and ambient air samples in the vicinity of the three investigated industries simultaneously duration of 24 hours during summer season 2015. We chose industrial boiler, MWI, and EAF is located in the industrial region of Taoyuan county, Taipei city, and Miaoli county, respectively. According to the direction of the monsoon, we set up the sampler at upwind and downwind site in the vicinity of stationary pollution sources (Figure 1). In addition, the atmospheric concentrations of seventeen 2, 3, 7, 8-substituted PCDD/Fs, trace metal content and water soluble ions in suspended particles were monitored in central Taiwan (Mountain Lulin) as the background site. The sampling procedures were performed following the main guideline of the Taiwan EPA NIEA A101.75C for flue gas collection, European Union EN-14907 $PM_{2.5}$ for ambient air collection. Both of stack gas and ambient air samples for both vapor phase and solid phase of dioxin-liked compounds were collected. The ambient sampling instruments consisted of HVS $PM_{2.5}$ sampler (Analitica), the samplers were equipped with Whatman quartz fiber filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs were used for retaining PCDD/F compounds in the vapor phase. HVS $PM_{2.5}$ sampler (Analitica) was connected to a vacuum pump and 700 m^3 of air mass was collected in 24 h at a sampling flow rate of 500 L/m^3. In this study, the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed by high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (JEOL JMS-700). The quartz fiber filter was used to determine a range of elements (Al, Fe, Na, Mg, K, Ca, Sr, Ba, Ti, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sn, Sb, Tl, Pb, V, Cr, As, Y, Se, Zr, Ge, Rb, Cs, Ga, La, Ce, Nd) by inductively coupled plasma-mass spectrometry (ICP-MS)(NexIon 300X, Perkin-Elmer). The quartz fiber filter was used to analyze the water-soluble ions (Na^+, NH_4^+,K^+, Mg^{2+},Ca^{2+}, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) by ion chromatography (IC). Organic carbon (OC) and elemental carbon (EC) were measured with IMPROVE_A thermal/optical reflectance (TOR) protocol. Besides, the software Positive Matrix Factorization (PMF, version 5.0),

flue gas (Table 1). The distribution of dioxin species, industrial boiler flue gas and MWI flue gas had higher proportion of PCDDs than PCDFs, but EAF flue gas had higher proportion of PCDFs than PCDDs in $PM_{2.5}$ and vapor phase. In industrial boiler flue gas of $PM_{2.5}$, the main metal were Ca, Al, Fe, the highest water-soluble ions was SO_4^{2-} ,and OC/EC ratio was 0.78. In MWI and EAF flue gas of $PM_{2.5}$, the main metal were Ca and Zn respectively, the highest water-soluble ions were Cl^- and OC/EC ratios were greater than 2.0 (Figure 2). An OC/EC ratio greater than 2.0-2.2 has been used for identification and evaluation of secondary organic aerosols[8,9]. In the vicinity of stationary sources, the highest concentration of $PM_{2.5}$ was 35.1±4.75 μg/m^3 at site E (investigated EAF downwind site), the highest dioxin concentration was 31.1±16.3 fg I-TEQ/m^3 at site B (investigated industrial boiler downwind site) (Table 2). All the measurements indicated that the atmospheric PCDD/Fs measured in this study were all lower than the air quality standards for dioxins in Japan (0.6 pg-TEQ/m^3). The distribution of atmospheric PCDD/Fs species around the stationary sources were PCDFs in vapor phase, the main metal were Na, K and Ca, the highest concentrations of water-soluble ions were SO_4^{2-},and OC/EC ratios were greater than 2.0 that indicated the species generated from secondary aerosol (Figure 3). The result (Table 3) of PMF also showed that analysis of atmospheric dioxins in the vicinity of industrial boiler, around 23.7% dioxins were provided from industrial boiler investigated. In the vicinity of the MWI, around 8.3% from the incinerator investigated. In the vicinity of the EAF, around 52.2% from the EAF investigated. The results of this study has been initially completed the fingerprint characteristics of industrial boiler, MWI, EAF in Taiwan.

Acknowledgements
The authors gratefully acknowledge the financial support provided by Taiwan Environmental Protection Administration (EPA-104-1604-02-01) and Environmental Analysis Laboratory of Taiwan.

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Table 1. PCDD/Fs concentration in vapor and solid (PM and $PM_{2.5}$) phases measured at different stationary plant.

ΣPCDD/Fs (ng I-TEQ/Nm^3)	Vapor	PM	Vapor	$PM_{2.5}$
Industrial boiler	**0.006**	**0.002**	**0.003±0.003**	**0.0005±0.0003**
MWI	**0.017±0.005**	**0.005±0.001**	**0.026±0.013**	**0.004±0.002**
EAF	**0.202±0.030**	**0.004±0.002**	**0.205±0.106**	**0.001±0.0003**

Investigation of persistent organic pollutant concentration and species distribution in water

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Introduction

Persistent organic pollutants (POPs) are featured by numerous processes, including refractory biological decomposition and accumulation. The long-term accumulation of POPs in the environment may adversely affect the human body through food chain. The United Nations Environment Programme (UNEP) has listed 12 species of POPs as the key control objects in the first batch (2005) to promote the international agreement of the *Stockholm Convention*. UNEP asked each contracting party to contribute in reducing the accumulation of such pollutants in the environment to lessen the human body's exposure hazard. In the following several contracting party conferences, many POPs species were successively included. Japan has established a complete Dioxins emission inventory of environmental media, including air, soil, waste, and water, for a long time as well as an integrated background investigation data aiming at brominated flame retardants (BFRs). Taiwan has also completed its investigation and control measures of Dioxins in the air, soil, waste, and food, which still lack relevant investigation report on water samples. Therefore, this research aims to establish the concentration and distribution investigation of POPs in water.

Materials and methods

A water sampling equipment was designed to adopt a microcomputer automatic control device to filtrate and concentrate water samples, with the help of a fiber glass filter and foam to absorb the POPs of the suspended and dissolved states in the water. Analyses on follow-up extraction and purification were then completed. This research accomplished water sampling and analysis of 21 underground water samples in 19 science parks, industrial parks, steel plants, vinyl chloride plants, incinerators, and contaminated sites, as well as the raw water samples of two water treatment plants in Taiwan, to investigate Dioxin compounds and polybrominated diphenyl ethers (PBDE) concentration and distribution condition in environmental water. Each sample collected was approximately 150~250 L, which first passed a double-layer stainless steel filter disk device (PALL Type A/D Glass Fiber Filter, 3.1 μm hole diameter and Advantec GC-50, 0.5 μm hole diameter) to filtrate out the pollutants of the suspended state in the water and passed the foam (3-inch-thick cylinder polyurethane foam, with density greater than 0.022 g/cm^3) to filtrate out the pollutants of the dissolved state. After finishing the aforementioned filtrations, we performed Soxhlet extraction of the standard substance in the filter and foam by methylbenzene and then purified using acidic silica gel and activated carbon tubular column (CAPE Technologies, Carbon Mini-Columns, 4%). Finally, 17, 12, and 24 species of Dioxins, PCBs, and PBDEs, respectively, were separated by adding the recovery standard substance through a high-resolution mass spectrometer (Thermo Finnigan MAT95XL and Thermo DFS) with 60 m × 0.25 mm i.d. × 0.25 μm and 15 m × 0.25 mm i.d. × 0.10 μm tubular columns.

Results and discussion

The research was conducted between 2014 and 2015 to investigate 21 underground water samples of 19 science parks, industrial parks, steel plants, vinyl chloride plants, incinerators, and contaminated sites, together with the raw water samples of two water treatment plants in Taiwan. In addition, this research intended to analyze 17, 12, and 24 species of Dioxins, Dioxin-like PCBs, and PBDEs, respectively. Table 1 presents the analysis results in detail. The results showed that Dioxin concentration varies between 0.004 and 0.642 pg WHO-TEQ/L, in which the concentrations of underground water near the industrial park

(SI05) and incinerator (I03a) are the highest. The concentration of Dioxin-like PCBs in both underground and raw water is generally low (DN–0.461 pg WHO-TEQ/L) but that of the incinerator (I03a) is high. The measured value in I03a is high probably because the sampling site is located close to the incinerator and landfill site. This research also analyzed the tri- to deca-BDE. The results also showed that PBDE concentration ranges from 10.2 to 64710 pg/L, in which the concentration of underground water near the incinerator (I02) is the highest followed by that of the industrial park (SI05). Although the use of BFRs has been limited, they also have traces of PBDEs in minor water areas.

Figure. 1 to 3 show Dioxin, Dioxin PCB, and PBDE species along with their concentration characters. The figures indicate that the Dioxin in water is mainly the high-chloride PCDD/Fs, in which PCDFs is 29.8% and PCDDs is 43.3%. PCBs are mainly composed of PCB-81 and PCB-118, and some are mainly composed of PCB-126 with high toxicity (appearing in steel plants). The PBDE species distribution is dominated by BDE-209 deca-BDE, averagely occupying 79.3% of the total PBDEs. Although the solubility of POPs in water is extremely low, the investigation results showed that a huge amount of underground water also contains high Dioxin concentration and PBDE. The pollution sources are supposed to come from the incinerators, landfill sites, or industrial parks nearby. In our future works, we intend to investigate POPs concentration and distribution in water for some high-pollution potential areas.

Acknowledgements

The authors acknowledge gratefully the support of the following: the Soil and Groundwater Pollution Remediation Fund Management, and Environmental Analysis Laboratory, EPA, Executive Yuan, R.O.C.

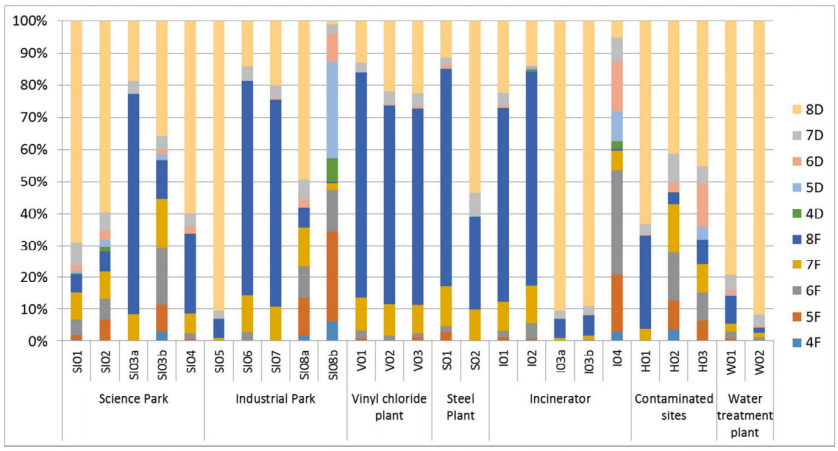

Fig. 1. PCDD/F congener distribution in groundwater and raw water

Table 1. Concentrations of PCDD/Fs, DLPCBs, and PBDEs in water

		PCDD/Fs (pg WHO-TEQ/L)	PCBs (pg WHO-TEQ/L)	PBDEs (pg/L)
Science Park	SI01	0.007	0.0005	68.2
	SI02	0.010	ND(0.0001)	65.8
	SI03[a]	0.011	0.001	47.6
	SI03[b]	0.007	0.0006	35.2
	SI04	0.010	0.0009	18.5
Industrial Park	SI05	0.642	0.001	12108
	SI06	0.009	0.0004	33.1
	SI07	0.008	0.001	10.2
	SI08[a]	0.006	0.002	--
	SI08[b]	0.004	0.0006	19.5
Steel Plant	S01	0.010	0.001	34.4
	S02	0.013	0.001	184
Vinyl Chloride Plant	V01	0.016	0.001	10.4
	V02	0.012	0.0003	--
	V03	0.010	0.001	156
Incinerator	I01	0.010	0.001	4230
	I02	0.009	0.0004	64710
	I03[a]	0.642	0.461	--
	I03[b]	0.059	0.045	164
	I04	0.156	0.007	--
Contaminated Sites	H01	0.150	0.006	15.2
	H02	0.004	ND(0.00001)	121
	H03	0.011	0.0005	226
Water Treatment Plant	W01	0.045	0.0002	1002
	W02	0.035	0.003	281

--: refers to the undetected values
[a,b]: refers to the measuring values in the same sampling site of different sampling times

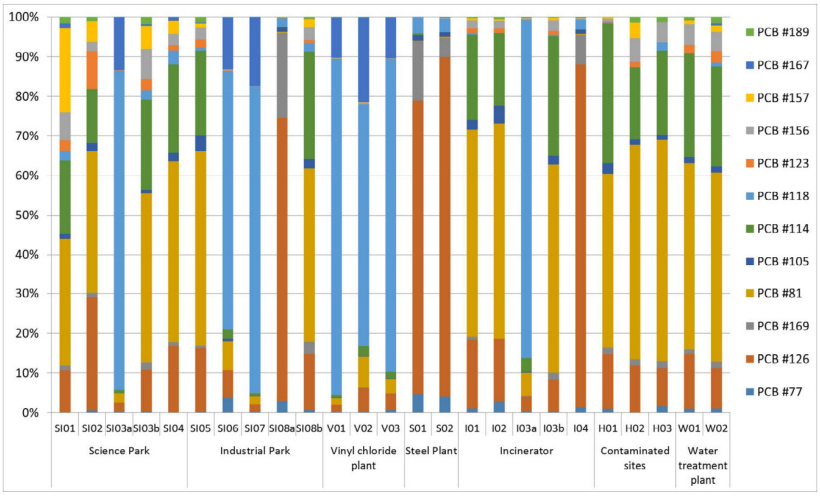

Fig. 2. PCB congener distribution in groundwater and raw water

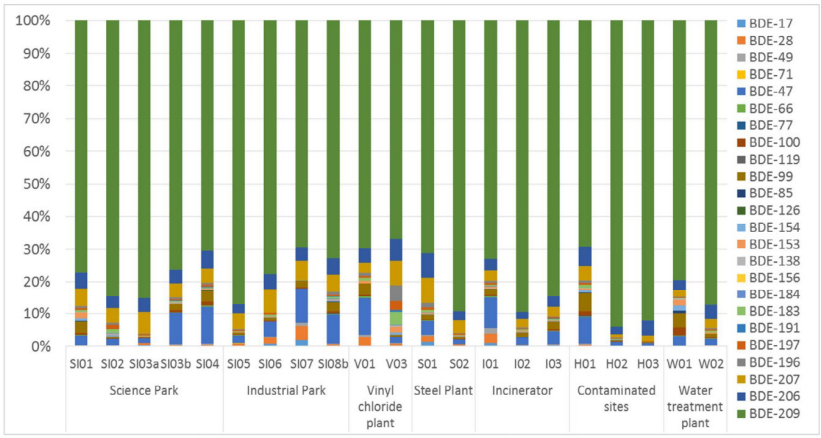

Fig. 3. PBDE congener distribution in groundwater and raw water