出國報告（出國類別：國際會議）

參加第 37 屆含鹵持久性有機污染物國際研討會報告

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：加拿大

出國期間：106 年 8 月 18 日至 8 月 26 日

報告日期：106 年 11 月 8 日

摘要

本所自 1995 年建置國內第一個專責戴奧辛實驗室以來，為維繫與國際環境分析之研究趨勢接軌、交流分析技術與成果並廣泛蒐集環境分析相關資訊，即持續每年派員參與戴奧辛年會。該年會自 1980 年起每年於不同國家舉辦，乃國際戴奧辛分析領域各產官學最為重視的國際性研討會議，自 2006 年起該會議將研討議題範圍擴大至環境中各項含鹵有機污染物並更名為含鹵持久性有機污染物國際研討會（The International Symposium on Halogenated Persistent Organic Pollutants）。本所於 2017 年派員出席於加拿大溫哥華舉辦之第 37 屆含鹵持久性有機污染物國際研討會（通稱 2017 戴奧辛年會），除發表論文分享近年本所工作成果外，亦藉此機會吸取先進國家之經驗與技術，以提昇本所含鹵持久性有機環境污染物之檢測技術，躋身國際環境分析舞台。

參加本次大會之重要心得與建議如下：

一、從過去常見的油品污染來源追蹤需求到近年國內外頻頻發生各種環境污染鑑識需求，非目標物檢測技術之發展與鑑識案例探討受到更多重視。本次會議中與非目標物檢測及環境鑑識相關議題包括：環境訴訟 （Environmental litigation）、環境鑑識規劃、樣品採集與管理（Investigation planning, sample collection and management for environmental forensics）、多介質與複雜樣品分析技術（Development of comprehensive analytical techniques for complex mixture analysis）、高階統計分析（Higher level statistics analysis）、污染場址溯源（Contaminated Sites and source tracking）等。但也從發表的論文中看出環境鑑識的領域涵蓋相當複雜的專業學科，每一個鑑識案件都有其獨特的背景歷史與鑑識流程發展，舉凡檢測技術、分析儀器及統計分析等等都只是工具的應用，未來國內在鑑識流程與技術的發展研究尚需針對工業發展現況、地理環境特性、環保法令及社會文化等等在地特性，逐步構築屬於國內的環境鑑識科學。

二、隨著國際間對於持久性有機物染物的管制作為，加上各種化學物質的研發應用推陳出新，每一段時代區間的污染物種類所引發之關注重視往往此消彼長。根據近年全球性的調查研究顯示以往受到極度重視的戴奧辛類及多氯聯苯類化合物環境中流布

的濃度已經有降低的趨勢。但是，過去常用為耐火材料添加劑的多溴二苯醚類化合物雖然已經禁用，但隨著廢棄材料釋出而流布於環境的濃度卻是逐年上升，顯見多溴二苯醚類化合物將是未來國際間環境污染監測管制的重點。另外，多氯化萘（Polychlorinated naphthalenes）、全氟化合物（Per-Fluorinated Compounds）、短鏈石蠟（Short-Chain Chlorinated Paraffins）、有機磷耐燃劑（organophosphorus flame retardants）及揮發性甲基環矽氧烷（volatile methyl siloxanes）等等新興污染物無論是在環境基線調查或檢測技術開發都在研討會中有大量的論文發表，這些污染物的議題也將是未來國內需要重視的方向。

三、檢測儀器發展方向在非目標物檢測的領域，目前主要仰賴的儀器有二維氣相層析飛行式質譜儀（GC×GC/TOFMS）使用二種不同分離效果的層析管柱，以達到快速有效的分離，產生上萬個波峰數，減少波峰共流(coelution)的干擾問題，搭配圖譜解析軟體，可以對波峰共流進行自動重疊解析(deconvolution)，獲得高可靠度的定性判讀，增加可觀測之分析物數量。大氣壓氣相層析質譜（Atmospheric Pressure GC）運用較低能量將樣本離子化，減少離子片段可提高化合物觀測的敏感度與專一性。而且APGC 並非真空技術，因此與各種方式間的平衡時間可縮到最短，迅速簡單的由UPLC 轉換為 GC，針對未知物的質譜解讀判定可提供較佳的檢測資訊。

四、氣相層析離子阱質譜儀（GC-Q-Orbitrap） 是一款結合四極桿、Orbitrap 和離子阱優點之質譜儀，爲此其具有最大的實驗靈活性，特別是針對高度複雜性的生物樣品足以達成極佳的深度檢測。同時在分析濃度極低、複雜性極高的樣品時，亦能以更快的速度識別出更多的化合物與絕佳的定量準確性，且結構分析更是透徹。提供的高分辨率高質量精度(HRAM) 的性能優勢。Orbitrap 系統連接液相層析儀也有助於增強未知化合物的分離並實現高通量工作流程。在會中皆有多篇論文討論，雖然儀器條件的建立較為複雜，然亦不失為所內發展方向之參考。

五、在樣品前處理系統的部分，歐美及日本等國儀器廠商皆有推出新的自動淨化系統如LABO 公司的 Automatische Dioxin-System（DEXTechTM）和日本 MIURA 公司的 Full

Automatic Sample Preparation System for POPs analysis(GO-HT)等都強調在環境基質中持久性有機污染物前處理淨化流程的自動化，在人力成本的考量下不失為實驗室發展的方向。

六、會議六篇專題演講議題包含諸多跨國性議題與合作研究如 Persistent, bioaccumulative and toxic contaminants in marine mammals: a troubling legacy concern for conservationists、Dioxin and The AhR: The Beginnings and No End In Site、Environmental Forensics of Persistent Organics Pollutants、Science and Policy of POPs through Passive Air Sampling、The role of environmental chemicals in obesity、Contamination and human exposure to micropollutants including dioxin-related compounds in informal recycling sites for e-waste and end-of-life vehicles 等，更凸顯出環境議題與持久性有機污染物的跨國界跨世代的特質，國內產官學各部門也應朝此方向，拓展國際學術研究合作，擴大研究領域與視野，不但可與國際接軌更能透合作研究成果的展現更可以爭取國際舞台的地位。

七、為延續得之不易的國際檢測技術交流機會，藉以了解世界環境分析趨勢與最新技術，並把握呈現國內研究成果於國際舞台，建議所內同仁能有機會持續與會。。

目　　次

壹、目的

行政院環保署環境檢驗所（以下簡稱本所）於民國 84 年 8 月成立戴奧辛小組，並於同年 9 月及 85 年 6 月分別於成大及清大成立兩個超微量實驗室，積極進行焚化廠排放相關戴奧辛檢測技術建立；87 年 11 月本所國家環境檢驗大樓正式啟用，戴奧辛超微量實驗室亦正式進駐本所。20 年來在長官的支持與同仁的努力下，對國內環境中戴奧辛之監測、政策擬訂及公害案件等貢獻卓著。為強化本所戴奧辛檢測技術之公信力。本所 1995 年起透過派員參與戴奧辛年會，了解國紀環境分析趨勢與最新技術，並把握呈現國內研究成果於國際舞台。

隨著全球工業化的進步各種推陳出新的化學物質不斷被運用來改善人類的物質生活，進而也造成環境的壓力，這些化學物質進入到環境生態中也伴隨著種種未知的危機，尤其是具有難以自然分解、會經由食物鏈在生物體內累積、對於人類的健康與自然生態有毒害的危險性及隨著生物或自然氣候的長距離移動的特性的持久性有機污染物（Persistent organic pollutants，簡稱為 POPs）更受到國際的關注。1995 年，聯合國環境署呼籲全球應針對持久性有機污染物採取一些必要的行動。2004 年 5 月 17 日簽署國批准同意禁用 9 項持久性有機污染物起，截至 2014 年已經有 23 項 POPs 列管，公告禁止或限制使用。我國雖並非公約之締約方，但為表達我國目前政策已符合該公約各類管制時程與作業事項，同時為彰顯我國 POPs 管制方向及積極作為，在 2008 年制定我國「持久性有機污染物斯德哥爾摩公約國家實施計畫」作為推動各項工作之依據，行政院環保署環境檢驗所（以下簡稱本所）也積極致力於持久性有機污染物檢測技術研究及環境基線調查等，目前在戴奧辛及呋喃（Dioxins and Furans）、毒性多氯聯苯（及 Dioxin-like PCBs）、多溴二苯醚（PBDEs）及有機氯農藥（OCPs）等持久性有機污染物均已建置完整之檢測技術。

因應全球環境保護趨勢戴奧辛年會從 2006 年起將研討議題範圍擴大至環境中各項含鹵有機污染物並更名為含鹵持久性有機污染物國際研討會。本所也持續派員與會期與國際趨勢接軌，今 2017 年乃派員參加於加拿大舉辦之第 37 屆含鹵持久性有機污染物國際研討會（通稱 2017 戴奧辛年會），參與人員除代表發表論文分享本所工作成果外，藉此機會將國內研究成果呈現於國際舞台，亦期了解環境檢測最新趨勢，吸取國際間之經驗與技術，作為本所各項檢測技術前瞻發展參考。

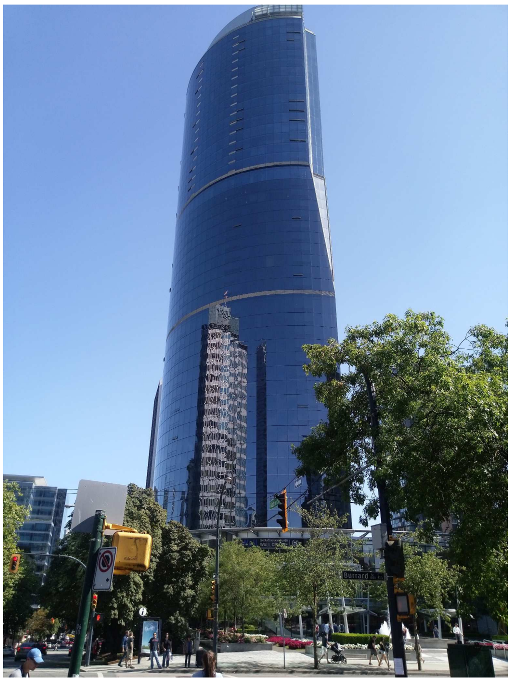
貳、過程

一、行程紀要

2017 年第 37 屆含鹵持久性有機污染物國際研討會（37rd The International Symposium on Halogenated Persistent Organic Pollutants) 於加拿大溫哥華市喜來登華爾中心酒店 (Sheraton Wall Centre Hotel, Vancouver)舉行，會議舉行時間為我國時間 8 月 20 日至 8 月 25 日共計 6 日 (如表一所示) 詳細議程參見附件一。

表一　筆者行程紀要表

日 期	工作內容
8/18（五）～8/19（六）	臺灣→加拿大溫哥華
8/20（日）～8/25（五）	2017 年戴奧辛年會（會議地點：溫哥華）
8/26（六）～8/27（日）	加拿大溫哥華→臺灣（8/27 凌晨 05：00 抵達台灣）



圖一：會議地點 Sheraton Wall Centre Hotel, Vancouver

二、會議紀要

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。大會演講共有 6 場，特定專題以儀器分析技術為主共有 10 個演講議題；分類議題分為 39 類議題包括口頭論文報告 272 篇及壁報論文報告 261 篇。

(一) 大會演講（Plenary）論文摘要詳附件四：

1. Persistent, bioaccumulative and toxic contaminants in marine mammals: a troubling legacy concern for conservationists（環境保護所關注的海洋動物中持久性、生物累積和有毒的污染物）
2. Dioxin and The AhR: The Beginnings and No End In Site（戴奧辛與生物檢測）
3. Environmental Forensics of Persistent Organics Pollutants（環境持久性有機污染物鑑識）
4. Science and Policy of POPs through Passive Air Sampling（空氣中持久性有機污染物被動採樣的學理與政策）
5. The role of environmental chemicals in obesity（環境化學物質在肥胖中作用）
6. Contamination and human exposure to micropollutants including dioxin-related compounds in informal recycling sites for e-waste and end-of-life vehicles（非法電子廢棄物和車輛回收場中戴奧辛類化合物的污染和人體暴露）

(二) 特定專題(Special Events)

特定專題主要為儀器商所提供之儀器發展新知與應用，題目如下：

1. Dioxin, POPs and Emerging Contaminant Workshop: From Sample Prep to Data Analysis（戴奧辛、持久性有機污染物和新興污染物樣品製備到數據分析）
2. DFS Magnetic Sector GC-HRMS（DFS 磁場式高解析氣相層析質譜儀）
3. Dioxins & POPs: Discover the Most Comprehensive GC-MS Portfolio（多選擇性 GC-MS 組合分析戴奧辛和持久性有機污染物）
4. Rapid and reliable determination of PCDD/F and PCB with automatic clean up and GC-MS/MS (7010)（戴奧辛及呋喃與多氯聯苯自動淨化快速測定技術）

5. Cryogenic zone compression to enhance sensitivity in non-targeted mass spectrometry to detect trace levels of POPs in blood plasma（以低溫壓縮提高非目標質譜法靈敏度檢測血漿中微量持久性有機污染物）
6. An Exposomics study of Canadian native populations utilizing Atmospheric GC coupled with HRMS（大氣壓氣相層析質譜技術分析加拿大原住民族群的暴露研究）
7. Challenges of POP analytics in certified routine laboratories and GMP surroundings（認證實驗室和 GMP 環境中持久性有機污染物分析的挑戰）
8. Quicker, greener and cleaner automated clean-up evaluated for any kind of matrix – the responsible approach for current state of the art techniques of POP preparation
9. DEXTech16: automation at its best – A clean up system that automatically runs a sequence of up to 16 samples unattended （持久性有機污染物分析快速自動淨化前處理技術）
10. Science & Policy of Organohalogens Workshop（有機鹵素科學與政策）

(三) 分類議題(Concurent Session)

本次研討會中不提供論文摘要紙本或光碟，所有會議相關資料由與會者依報名時登錄之帳號密碼至會議論文專屬網站下載使用。分類議題分為 39 類議題包括口頭論文報告 272 篇及壁報論文報告共 261 篇。議題整理如下：

1. New methods of Analysis (Analytical)
2. New and alternate instrumental methods of analysis (Analytical)
3. Non-target Screening and Determination (Analytical)
4. Advances in Trace Analysis (Analytical)
5. Environmental Levels of POPs (Levels and trends)
6. POPs in the Arctic (Levels and trends)

7. Persistent Organic Pollutants (POPs) and Emerging Contaminants in Developing Countries (Levels and trends)

8. Emerging Contaminants: Lessons Learned from Past, Current Practices and Future Trends (Levels and trends)

9. Distribution, Transport and Fate of Organohalogens in the Atmosphere (Levels and trends)

10.Gas/Particle Partition of POPs in Air (Levels and trends)

11.PCBs in schools and Other Indoor Sources (Levels and trends)

12.Spatial and Temporal Trends of POPs in Abiotic Compartments (Levels and trends)

13.Spatial and Temporal Trends of POPs in Biota (Levels and trends)

14.Pet Exposure to POPs (Levels and trends)

15.Environmental Transport and Fae, General(Levels tand trends)

16.Agent Orange in Vietnam (Human Exposure)

17.Exposure to POPs in Urban, Indoor and Workplace Environments (Human Exposure)

18.Human Exposure to POPs , General (Human Exposure)

19.POPs in Food and Feed (Human Exposure)

20.Ecotoxicology(Human Exposure)

21.Absorption, Distribution, Metabolism and Excretion (ADME) of Legacy and Emerging Persistent Organic Pollutants (POPS) in Animals (Metabolism and Toxicology)

22.Metabolomics and Systems Biology in POPs toxicity studies (Metabolism and Toxicology)

23.Neurotoxicity of Legacy and Emerging Persistent Organic Pollutants (POPs) (Metabolism and Toxicology)

24.Toxicology, General (Metabolism and Toxicology)

25.From Science to Decision Making (Policy)

26.Risk Assessment and Risk Management(Policy)

27.POPs in longitudinal cohorts (Epidemiology)

28.Remediation, Best Available techniques/Best Environmental Practices (Remediation)

29.Formation, Sources and Remediation (Remediation)

30.Are PFASs a New Concern for Wildlife & Humans? (Compound Specific - PFAS)

31.Legacy to emerging fluoroalkyl contaminants in air to biota in the global environment (Compound Specific - PFAS)

32.Total Fluorine Analysis and Total Oxidisable Precursor (TOP) Assay with Special Reference to PFAS and Their Alternatives (Compound Specific - PFAS)

33.Perfluoroalkyl Substances - general (Compound Specific - PFAS)

34.Short and Medium Chain Chlorinated Paraffins (Compound Specific - PCAs)

35.Brominated Flame Retardants (Compound Specific, BFRs)

36.Alternate Flame Retardants: Environmental Presence, Fate and Exposure (Compound Specific - FRs)

37.Polycyclic Compounds (Compound Specific)

38.Environmental litigation (Environmental Forensics)

39.Contaminated Sites and source tracking (Environmental Forensics)

(四) 口頭論文報告(Oral)

在 39 個分類議題中，口頭論文報告共有 272 篇，每天在固定時段分別於 6 間會議室同時進行報告，作者包含國際學者專家、儀器廠商以及在學學生，進行方式以投影片簡報 20 分鐘，隨後進行約 5 分鐘問與答。議程相當緊湊，筆者考量參與研討

會目的與本所現行業務與未來可能發展之相關性，儘可能挑選相關論文報告聽講。參與聽講的報告約 20 篇題目：（論文摘要詳附件五）

1. High resolution oribital trapping mass spectrometry measurement of persistent organic pollutants in cow's milk
2. A GCxGC-HR-TOFMS with Enhanced Sensitivity: Targeted and Non-Targeted Analysis of Highly Complex Environmental Samples
3. Variable energy electron ionization enhances the sensitivity and selectivity of brominated flame retardant analysis by GC/MS and GC x GC TOF/MS
4. National and continuous DIOXIN Air Monitoring networj in Taiwan (2006-2016): Spatial, temporal ariation and Emission sources apportionment via positive Matrix factorization
5. High throughput GC-HRMS acquisition methods for the analysis of PCDD/Fs and PCBs in biological matrices
6. Integration of polybrominated diphenyl ethers (PBDE) and other brominated compounds into the automated sample preparation for dioxines and PCBs
7. Organic and inorganic persistent pollutants monitoring: emission source identification
8. Target, Suspect and Non-Target Screening of Dioxin-Like Compounds in Sediment and Fish Using A Sensitive High-Resolution Time-of-flight Mass Spectrometer
9. Comparison of International Quality Assurance and Quality Control Standards for High Resolution Mass Spectrometry Dioxin Analysis
10. PAHs in Chinese atmosphere: Concentration, source and gas-particle partitioning
11. Occurence and distribution of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in multi-environmental matrices around two fluorochemical manufacturing parks in fuxin, China
12. Environmental impact of biomass and polyethylene waste co-firing: emissions of particulate matter, PCDD/Fs and DL-PCBs

13.Non-target and suspect screening of organic chemicals in indoor dust from five countries

14.Screening halogenated contaminants in the marine environment based on high resolution mass spectrometry profiling

15.Non-Target Analysis of Ambient Air Using Cryogenic Air Sampler

16.PAHs depositions in the environment of a waste incinerator

17.Organohalogen pollutants in surface particulates from workshop floors of four major e-waste recycling sites in China and implications for emission lists

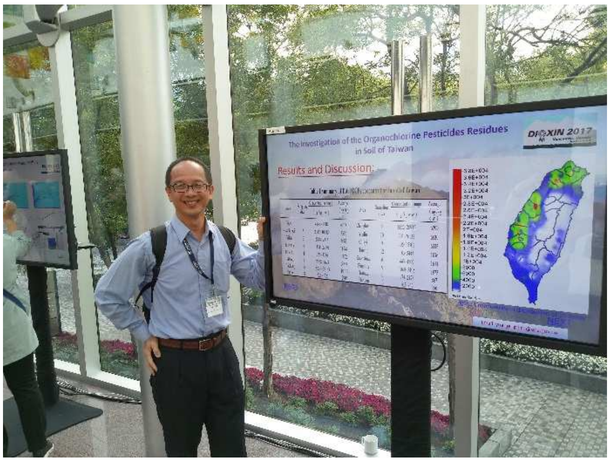
18.Medium-chain and long-chain chlorinated paraffin products predominate in Swedish coastal sediment cores over the past 50 years

19.Short-Chain Chlorinated Paraffins (SCCPs), a Toxic Industrial Chemical Included for Global Prohibition, Contaminate Children’s Toys

20.Characterization of placental transfer of short- and medium-chain chlorinated paraffins in paired maternal and cord serum

(五) 壁報論文報告 (Posters)

此次大會壁報論文的呈現與過去不同，除了基於環境保護、減少資源運用與廢棄物的處理，並且鼓勵論文投稿者能勇於表達介紹自己的研究成果，因此 261 篇壁報論文均是以電視大螢幕定時播放投影片檔(PPT)的方式呈現，並且在每天的固定時段邀請作者在螢幕前介紹自己的論文（mini-orals）。筆者以壁報論文發表方式參與本次研討會，發表論文題目為「The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan」，大會編號 P161-E 被安排在大會議程第二天下午 Poster Session VI 發表。此篇研究係運用高解析氣相層析質譜儀（HRGC/HRMS），以同位素標誌稀釋法分析台灣地區 100 件土壤樣品中 26 種有機氯農藥之調查應用。除了全面性了解台灣地區土壤中有機氯農藥殘留現況外，並驗證 HRGC/HRMS 優異之靈敏度與定性、定量能力，足以提供極低之定量極限與克服基質干擾等問題，特別適合運用於環境背景極低濃度之待測物分析，詳細論文內容及壁報資料參見附件二及三。



圖二：筆者與本所發表之壁報論文

大會期間筆者亦抽空流覽會場多篇壁報論文，藉以吸收新知。簡要列出以下 40 篇可供本所相關業務可參考之論文題目：

1. Tissue-specific bioaccumulation of halogenated methylbipyrroles and long-chain perfluorinated carboxylic acids in marine mammals stranded in northern Japan
2. Organochlorine pesticides in agricultural soils of the main agricultural valleys of Baja California, Mexico
3. Lipid Loading and Elution Profiles for an Automated Cleanup Method for Polychlorinated Biphenyls, Polybrominated Diphenyl Ethers, Dioxins and Furans Analyses
4. GC-MS Identification of Phthalate and Alternative Plasticisers in Medical Devices
5. An Evaluation of Federal and State Perfluorooctanoic acid (PFOA) Drinking Water Standards in the US
6. Organisation of an international interlaboratory study as a first step towards a harmonized approach to Analysis of Chlorinated Paraffins
7. Modified Sample Clean-up for Combined POPs Using Automated Multi-Column Fractionation and Analytical Optimization

8. External Quality Assessment Schemes (AMAP and Dioxins/Furans) to validate POPs measurement in human serum and a novel approach by APGC-MS/MS to increase the sensitivity of these compounds

9. Characterisation of chlorinated paraffin profiles in sediment and biota by LC-ESI(-)-HRMS and semi-automatic post-acquisition data treatment

10. Atmospheric Concentrations of some Stockholm Convention Persistent Organic Pollutants in West Asia

11. Enhanced Removal of Perfluorinated Alkylated Substances (PFASs) from Aqueous Solution by Mesoporous Graphene Nanosponge

12. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in the South Korean agricultural environment

13. PCNs Congeners in Ambient Air from Technical PCN and Unintentional Formation

14. Atmospheric pressure ionisation for gas chromatography mass spectrometry: New perspectives for the determination of persistent organic pollutants (POPs) in human serum

15. Short-Chain Chlorinated Paraffins (SCCPs), a Toxic Industrial Chemical Included for Global Prohibition, Contaminate Children’s Toys

16. Occurrence and Distribution of Organophosphate Flame Retardants (OPFRs) in Soil and Outdoor Settled Dust from A Multi-waste Recycling Area in China

17. Quantification of total Organohalogens (TOX) in environmental solid samples by using Combustion-ion Chromatography

18. Contamination Status of Dioxin in the sediment of Indus River and Coastal Environment of Pakistan

19. Research, communication, and action: PFAS in food contact materials

20. Development of Canadian Soil Quality Guidelines for PFOS and PFOA

21. Study on Optimum Treatment Conditions for Chlorinated Flame Retardant and Organochlorine Pesticides Using Thermal Method

22. The new method for analysis of selected organophosphorus flame retardants (OPFRs) in indoor dust

23. GC×GC-HR-TOFMS for screening of organohalogenated compounds in cat hair

24. Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Naphthalenes (PCNs) in Sediment of Hyogo Prefecture, Japan

25. Occurrence of persistent organic compounds in the surface water from the lower stretch of the River Ganga in India

26. Persistent Organic Pollutants in Groundwater: Exposure profiles of PAHs and OCPs at an agricultural site of a north Indian terai region

27. Characteristics of contamination for DDT in the Air and Soil in Republic of Korea

28. Assessment of the automated clean-up system DEXTech + for determination of PBDEs along with PCDD/Fs and PCBs in environmental samples

29. Screening for Dioxin-Like Compounds in Sediment Using Modified QuEChERS and a GC-TOF Mass Spectrometer with Atmospheric Pressure Chemical Ionization

30. Determination of short chain chlorinated paraffins (SCCPs) in commercial chlorinated paraffins (CPs) products using comprehensive two-dimensional gas chromatography coupled with tandem mass spectrometry

31. Passive sampling of POPs in the Black Sea

32. Levels of PFOS and the other perfluorinated organic compounds in Polish inland waters and Baltic Sea coastal waters

33. Analysis of BFRs and dioxins and dioxin-like PCBs on a dual column GC-MS/MS system

34. Application of LC-Orbitrap HRMS with positive/negative ion-switching for analysis of Pharmaceutical and Personal Care Products (PPCPs)

35. Examination of Commercial Samples of Perfluoroethylcyclohexane Sulfonate: Another Source of PFOS Isomers

36. Use of Passive Samplers to Monitor PCBs in the Effluent Water from a Waste Water Treatment Plant

37. The occurrence of OCPs, PCBs, and PAHs in the soil, air, and particle deposition of provincial and metropolitan Naples areas, Italy: Implications for potential risk and environmental cycling

38. Thermal desorption GC/MS analysis method for analysis of POPs in solid sample

39. Review of the worldwide concentrations of medium-chain chlorinated paraffins (MCCP) in environmental samples and biota

40. New methodologies for the analysis of halogenated persistent organic pollutants using GC-Q-Orbitrap

(六) 廠商儀器展示 (Exhibits)

本次大會邀請了多家廠商參展，展出內容包括標準品、自動前處理系統、空氣採樣器材及最新款之高階分析儀器，據觀察本所未來業務發展應用相關的儀器有 LECO 公司和 Thermofisher 公司的 GC×GC/TOFMS，Agilent 公司、Thermofisher 公司、Shimadzu 公司的 GC-MS/MS，Waters 公司的 APGC/HRMS，Thermofisher 公司的 GC-Q-Orbitrap 等等，都是目前在持久性污染物或非目標物篩檢的主要工具，可作為本所未來儀器設備添購的參考方向。另外，訴求快速方便前處理系統也是這次廠商展示的重點，特別是開發廠商較以往多元化，不再集中於少數廠牌。空氣採樣器材與監測器材近年來變化不大，不過，符合歐規的 $PM_{2.5}$ 高流量採樣氣倒是在會場吸引不少注意，基於待測物的微量檢測需要更大量更迅速的採樣工具而言，或許可作為國內的參考方向。

參、心得

本次筆者參加於加拿大舉辦之第 37 屆含鹵持久性有機污染物國際研討會，在一週的會期當中，超過500篇的口頭及壁報發表論文，相當緊湊且內容豐富，實際上並無法全部涉獵了解，所以此行主要設定與本所業務相關的三大方向做為學習的主軸，並依序簡述心得如下，相關之論文題目及摘要詳見附錄：

一、 非目標物檢測技術

近年國內屢屢發生重大公害案件，政府公權力對污染來源追查、公害責任求償與危害影響程度等均面臨重大挑戰，凸顯法規目標物檢測已不敷需求。然而目前所使用的化學物質超過百萬種，想要用一種檢測儀器或一種檢測方法找出一個或數個未知的污染物種幾乎是緣木求魚。因此，透過各種高階篩檢儀器如 GC×GC/TOFMS 運用二維氣相層析技術使得待測物在層析管柱中的分離更加完整清楚，再結合飛行式質譜的全質譜蒐集技術使得待測物的質譜資訊可以完整地偵測獲得，最後再運用日益進步的質譜比對資料庫和質譜解構重組軟體獲得非目標物的資訊。HPLC/Q-Orbitrap 則可以針對偏極性的化學物質進行篩檢，其具有質量準確度，解讀能力，動態範圍和高靈敏度的特性，適用於高級蛋白質組學分析和小分子研究，對未知物的檢測提供精準的質量數資訊。APGC 可將樣本離子化後，搭配各種形式質譜儀使用，因為離子化的過程採用較低的能量，能使得許多化合物觀測到的片段少於 EI 等其他方式。因此可提高敏感度與專一性，因此可簡化 MS/MS 分析的前驅離子挑選，使得未知物的篩檢較為簡便可行。

在非目標物的檢測技術領域，各種檢測儀器均可能須依每個鑑識案件的檢測需求進行各種搭配組合。另外，質譜比對資料庫和質譜解構重組軟體更是決定非目標物檢測成功與否的關鍵因素，尤其是質譜資料庫有可能因所採用的儀器種類和條件而有所差異，所以雖然許多廠商都發展出屬於自家的商用資料庫，但使用者運用過往經驗自建資料庫仍是不可或缺的一部分。最後，除了儀器與軟體，人員的鑑識經驗是最重要的一部分，雖說工欲善必先利其器，但如果只有優良的工具卻沒有豐富鑑識經驗的人來運用，恐怕也只是落

入看著數據編故事的陷阱。因此，人員的鑑識技術與經驗培養，是未來本所發展非目標物檢測最迫切需要克服的問題。

二、新興污染物檢測技術

“新興污染物（Emerging Contaminants）”主要為「新認定或之前未確認」、「未受法規規範」、「且對人體健康及生態環境具有風險性」的化學污染物，此類污染物通常經由人類活動（包括：工商業、農業、醫療場所、製藥廠，甚至一般家庭生活等）所產生且不容易於環境中分解。新興污染物所涵蓋的範圍非常廣泛，舉凡新興的環境污染物、食品添加物及污染物、濫用藥物及毒品，以及存在各式物品內之化學物種等。環境中之新興污染物包括存在於各種環境介質（水體、土壤及空氣）中之各式環境荷爾蒙（屬內分泌干擾物質 EDCs，例如：戴奧辛、有機氯殺蟲劑、鄰苯二甲酸酯、壬基酚等）、藥物及個人保健用品 PPCPs（例如：抗生素、類固醇、抗菌消毒劑、清潔劑等）以及釋放於環境中之各式奈米物質（例如：奈米銀、奈米碳管、二氧化鈦奈米顆粒等）等；新興食品污染物則包括：三聚氰胺、孔雀綠、防腐劑、色素、微生物、人工甘味，以及農藥等；至於存在一般物件內之新興化學污染物質則包括有衣服內之螢光劑、家俱/地毯/電子元件內之阻燃劑、保麗龍之高分子單體等。由於這些化學物質的種類繁多，加上其所存在的基質環境複雜的關係，導致要偵測到這些物質必須依賴具高效率的層析分離及質譜偵測器，但是因為有明確的檢測對象，相對上只要在檢測的技術上克服微量檢測的瓶頸即可。

從目前的趨勢看來亦即所謂之氣相層析串聯式質譜儀（GC-MS/MS）及液相層析串聯式質譜儀（LC-MS/MS）都是發展的主流儀器。另外，從此次年會發表論論文可以發現近年來國際間對於環境中持久性有機污染物的關切主要有溴化阻燃劑（brominated flame retardants, BFRs）包括多溴二苯醚（polybrominated diphenyl ethers, PBDEs）和六溴環十二烷（hexabromocyclododecane, HBCD），全氟化合物（perfluoroalkyl substances, PFAS），斯德哥爾摩公約管制的五氯苯和六氯苯（penta- and hexachlorobenzene , PeCB and HCB），多氯化萘（Polychlorinated naphthalenes, PCNs），短鏈石蠟（Short-Chain Chlorinated Paraffins, SCCPs），有機磷阻燃劑（organophosphorus flame retardants, OPFRs ）和揮發性甲基環矽氧烷（volatile methyl siloxanes, VMS），目前本所除了短鏈石蠟、有機磷阻燃劑、六溴

環十二烷和揮發性甲基環矽氧烷外，均已建立檢測技術，未來或可在此四類化合物的檢測技術上加以嘗試開發。

三、檢測儀器發展方向

本所在 2007 年即已購入二維氣相層析飛行式質譜儀，然而該層析技術受限於電腦擷取數據之速度、質譜資料庫比對困難及質譜處理軟體未臻成熟的限制，並未能在非目標物檢測的領域上有所進展。然而時隔 10 年之後，包括 LECO 公司和 Thermofisher 公司均推出更新型的 GC×GC/TOFMS，尤其 Thermofisher 公司宣稱其最新款之儀器檢測所獲得之質譜可直接與國際間常用之 NIST 質譜資料庫進行比對，更是大大強化其實用性，可作為環境鑑識業務儀器設備添購的參考方向。在已知物的定量分析部分，Agilent 公司、Thermofisher 公司、Shimadzu 公司的 GC-MS/MS，其靈敏度和解析度都有大幅度的改進，尤其強調節能、操作方便及易於維護的特性，對於國內減碳節能的訴求越來越高的情形下，應可作為老舊檢測儀器逐步汰換的參考對象。

Waters 公司的 APGC/HRMS，Thermofisher 公司的 GC-Q-Orbitrap 則是具有鮮明的特色，因為 APGC/HRMS 屬於一種大氣壓下的離子化系統，該廠商宣稱其離子化的技術較 EI「柔軟」，所以許多化合物觀測到的片段較少，可提高敏感度與專一性，因此可簡化 MS/MS 分析的前驅離子挑選，更可以搭配各種形式的質譜儀使用，使其應用面更為廣泛。GC-Q-Orbitrap 則是具有質量準確度，解讀能力，動態範圍和高靈敏度的特性，對未知物的檢測提供精準的質量數資訊，這樣的特性如果再結合其他儀器所提供之質譜片段資訊，對於未知物的結構重組判讀上會有相當的助益。本所於 2013 年購入 UPLC－Orbitrap-MS 並在環境基質中全氟化合物及個人保健用品 PPCPs（例如：抗生素、類固醇、抗菌消毒劑、清潔劑等）建立相當成熟之檢測技術，而這些化合物也都是目前國際間所關切的議題。唯 APGC 大氣壓下的離子化系統，本所仍尚未有使用經驗與技術，日後可考慮進一步評估其實用性。空氣採樣器材與監測器材近年來變化不大，不過，瑞士廠商主推符合歐規的 $PM_{2.5}$ 高流量採樣器（Digitel DHA-80）倒是在會場吸引不少注意，基於待測物的微量檢測需要更大量更迅速的採樣工具而言，此採樣器具備自動化與程式化，濾紙自動更換功能以及電子控制器，可滿足各種採樣條件以及長時間連續採樣的需求，彈性佳且大幅節省採樣人力。或許可作為國內的參考方向。

誠如所知，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），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際邊界的遷移，並沈積在遠離其排放地點的地區。因此在會議中可以發現在環境監測部分，多數的研究報告探討的範圍並不侷限於單一個城市、地區甚至國家，而是擴及到更大範圍的區域調查與污染物長程傳輸之影響等相關議題（如「New and emerging POPs in the Group of Latin America and Caribbean (GRULAC) Region」、「Science and Policy of POPs through Passive Air Sampling」）。或者是屬於長期性的追蹤研究（如「Per- and polyfluoroalkyl substances in human milk from Swedish mothers: individual and geographical differences and temporal trends, 1972-2015」、「Levels, Temporal trends of PCDDs/PCDFs at IPTD area using passive air sampler and correlation with active air sampling between 2012-2017」）如此規模的研究議題和論文在國內似乎較少，以國內的檢測技術水平，如能再結合更多的產學各界合作將研究觸角延伸至更大區域，相信應該會有更高更好的學術成就與貢獻。

肆、建議

本次筆者參加第 37 屆含鹵持久性有機污染物國際研討會，對於國際間目前在持久性有機污染物檢測及環境鑑識技術的發展，有更深一層的瞭解與值得學習的地方，希望這次蒐集的國際資訊在未來能與國內專家交流，並實際應用到國內的環境鑑識上。關於這次研討會後，最後歸納有幾點建議如下：

1. 環境鑑識技術是一門跨領域的複雜學門，無論是地質學、海洋學、大氣學、環境工程學、化學分析、統計學、資訊科學等，都是鑑識技術發展的基礎科學，國內在這部分的整合平台似乎尚嫌不足，如果只想憑藉尖端高階的檢測儀器和技術來解決複雜的環境鑑識問題，仍然稍嫌力有未逮。因此，未來本所在環境鑑識的推動上，需要擴大學術研究機構結合，培養合約實驗室與學術研究應用團隊，互補產官學鑑識量能之不足。方能在緊急公害事件發生時，得以明確鑑識污染物種、迅速追蹤污染源、掌控並排除危害、執行公害責任追償，保障民眾生命財產安全。

2. GCxGC/TOFMS 運用二維氣相層析技術使得待測物在層析管柱中的分離更加完整清楚，再結合飛行式質譜的全質譜蒐集技術使得待測物的質譜資訊可以完整地偵測獲得，最後再運用日益進步的質譜比對資料庫和質譜解構重組軟體獲得非目標物的資訊。此等功能對於非目標物篩檢技術有相當的助益，建議持續追蹤了解其發展現況並評估在國內應用的可行性。
3. APGC/HRMS 屬於一種大氣壓下的離子化系統，離子化的技術較 EI「柔軟」，所以許多化合物觀測到的片段較少，可提高敏感度與專一性，因此可簡化 MS/MS 分析的前驅離子挑選，更可以搭配各種形式的質譜儀使用，使其應用面更為廣泛，建議持續追蹤了解其發展現況並評估在國內應用的可行性。
4. 基於待測物的微量檢測需要更大量更迅速的採樣工具而言， PM2.5 高流量採樣器具備自動化與程式化，濾紙自動更換功能以及電子控制器，可滿足各種採樣條件以及長時間連續採樣的需求，彈性佳且大幅節省採樣人力，或許可作為國內的參考方向。
5. 新興污染物檢測技術發展的部分，在本所二十多年來建立的超微量分析基礎上，可考慮先針對斯德哥爾摩公約公告管制之短鏈石蠟（Short-Chain Chlorinated Paraffins, SCCPs）和六溴環十二烷（hexabromocyclododecane, HBCD)先行研發檢測技術，後續再規劃有機磷阻燃劑（organophosphorus flame retardants, OPFRs ）和揮發性甲基環矽氧烷（volatile methyl siloxanes, VMS）的檢測技術開發。以期與國際環保關注議題接軌。
6. 環境基質中全氟化合物及個人保健用品 PPCPs（例如：抗生素、類固醇、抗菌消毒劑、清潔劑等）都是目前國際間所關切的議題，本所在這部分檢測技術已有相當的成熟技術，未來可考慮投入更實質面的研究，落實於國民健康與環境保護之效能。
7. 結合更多的產學各界合作將研究觸角延伸至更大區域，擴及到更大範圍的區域調查與污染物長程傳輸之影響等相關議題，或者是屬於長期性的追蹤研究進而結合毒理及風險評估等專家，使未來國內在環境持久性有機污染物的研究更加全面性立體性。
8. 為延續得之不易的國際檢測技術交流機會，藉以了解世界環境分析趨勢與最新技術，並把握呈現國內研究成果於國際舞台，建議所內同仁能有機會持續與會。

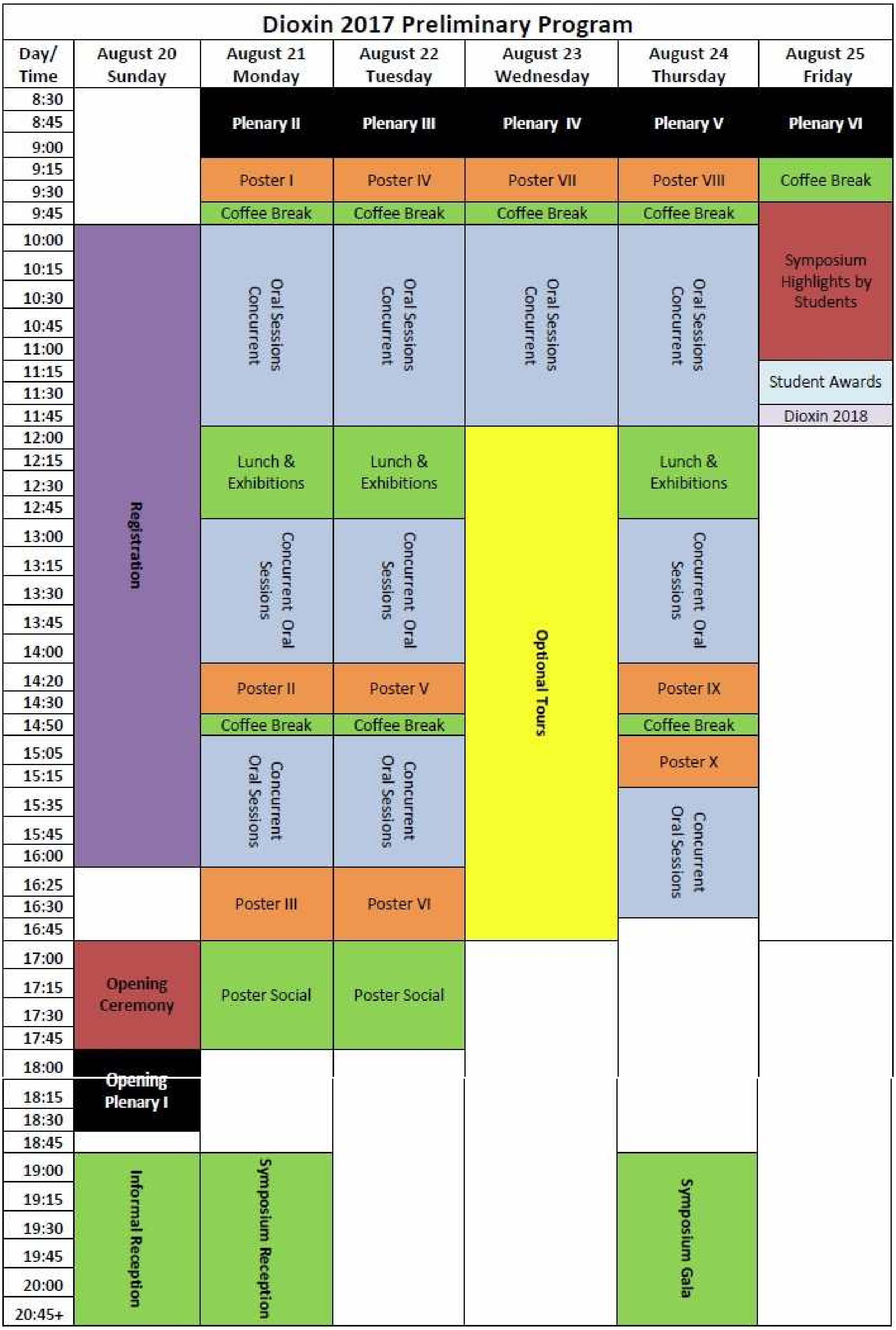
伍、參考文獻

(1) 第 37 屆「含鹵持久性有機污染物國際研討會」大會網站 http://www.dioxin2017.org。

(2) 第 37 屆「含鹵持久性有機污染物國際研討會」論文網站 https://venuewest.quickmobile.center。

(3) 參加第 36 屆「含鹵持久性有機污染物國際研討會」出國報告。

附件一 大會議程



Dioxin 2017 Preliminary Program

Day/ Time	August 20 Sunday	August 21 Monday	August 22 Tuesday	August 23 Wednesday	August 24 Thursday	August 25 Friday
8:30		Plenary II	Plenary III	Plenary IV	Plenary V	Plenary VI
8:45						
9:00						
9:15		Poster I	Poster IV	Poster VII	Poster VIII	Coffee Break
9:30						
9:45		Coffee Break	Coffee Break	Coffee Break	Coffee Break	Symposium Highlights by Students
10:00	Registration	Oral Sessions Concurrent	Oral Sessions Concurrent	Oral Sessions Concurrent	Oral Sessions Concurrent	
10:15						
10:30						
10:45						
11:00						
11:15						Student Awards
11:30						
11:45						Dioxin 2018
12:00		Lunch & Exhibitions	Lunch & Exhibitions	Optional Tours	Lunch & Exhibitions	
12:15						
12:30						
12:45						
13:00		Concurrent Oral Sessions	Concurrent Oral Sessions		Concurrent Oral Sessions	
13:15						
13:30						
13:45						
14:00						
14:20		Poster II	Poster V		Poster IX	
14:30						
14:50		Coffee Break	Coffee Break		Coffee Break	
15:05		Concurrent Oral Sessions	Concurrent Oral Sessions		Poster X	
15:15						
15:35					Concurrent Oral Sessions	
15:45						
16:00						
16:25		Poster III	Poster VI			
16:30						
16:45						
17:00	Opening Ceremony	Poster Social	Poster Social			
17:15						
17:30						
17:45						
18:00	Opening Plenary I					
18:15						
18:30						
18:45						
19:00	Informal Reception	Symposium Reception			Symposium Gala	
19:15						
19:30						
19:45						
20:00						
20:45+						

附件二　投稿論文摘要

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

Hsu YC[1], Wu CP[1], Sung YY[1], Huang YJ[1], Weng YM[1]
[1]Environmental Analysis Laboratory, Taiwan EPA, Chungli, Taiwan 320

Introduction

Organochlorine Pesticides (OCPs) are hydrocarbon compounds containing multiple chlorine substitutions. They were introduced since 1940s and have been widely used in agriculture as pest control. There are four main types of OCPs: dichlorodiphenylethanes, chlorinated cyclodienes, chlorinated benzenes and chlorinated cyclohexanes. Nine of the 12 most hazardous persistent organic pollutants (POPs) targeted by the Stockholm Convention in 2001 are OCPs. Consequently, residual POPs might cause significant impacts on human health and the environment. The health risk of POPs has been widely debated globally in recent years and came to a consensus agreement of the Stockholm Convention on Persistent Organic Pollutants in 2001 that prohibit the production and use of these chemicals. Most of them have been banned or restricted in the industrialized world. However, some non-targeted OCPs such as Endosulfan, Lindane and DDT are still employed in developing countries for mosquito and malaria control. Organochlorine pesticides such as DDT, BHC, Lindane have been banned in Taiwan since 1977. In the same time, EPA Taiwan has been carrying out a systematic tracking on the residual concentration of organochlorine pesticides in environment with analytical tools such as GC/ECD for the past thirty years. Recently, we initiated the use of the isotope dilution method with HRGC/HRMS to analyze 26 organochlorines and their metabolites in environmental samples so as to determine the residual OCPs in a more accurate way. We have collected 100 soil samples from selected 16 counties of Taiwan. The average total concentration of 26 OCPs in soil samples is 4296 ng/kg d.w. and the concentrations ranged 164.8~39,183 ng/kg d.w.. The highest OCPs level found in the soil sample of Taiwan is still well below the official regulated risk threshold limit. The highest total concentration of samples 39,183 ng/kg is found in a site located at Taichung.-The highest average total concentration is found in Taoyuan area. Those areas located in the east of Taiwan such as Taitung and Hualien exhibited lowest total average concentration. The ratio of DDT and its metabolites can be served as indicators for possible liable pollution sources as well as the degree of degradation. The ratio of Σ（DDD+DDE）/Σ(DDT+DDD+DDE) in the 95 out of 100 collected samples were found to be higher than 0.52 implicating that these DDT contamination in soil of Taiwan might be accumulated from the aged pollutants in the long past.

Material and methods

(1) Sample collection, extraction and clean-up

Samples were collected from 16 selected counties of Taiwan. 100 sampling sites were chosen based on the scale of agriculture in each county. Sampling time were scheduled from March to August during the busy agriculture season. The analyzed level of organochlorine in the soil samples can therefore reflect the use of pesticides in the land field. All samples were dried, ground and homogenized before being spiked with 13C-isotopes of the target compounds and extracted by Soxtherm with (1+1)Acetone/n-Hexane solvent mixture. Target compound standards and isotope labeled spiking solution were purchased from Chembridge Corporation. The extracts were concentrated to about 1 mL by turbo evaporation. Then we substitute the residual solvent with 1 mL hexane for subsequent pretreatment process. The extracts were cleaned up with Florisil SPE column. Gel permeation chromatography were used to remove the high molecular weight interference such as polymeric materials, humic acids, lipids and so on.

(2) HRGC/HRMS analysis

26 organochlorine pesticides were analyzed by isotope dilution in according to the official standard method NIEA M905.00B of Taiwan EPA with high resolution mass spectrometer (HRMS) (AutoSpec Premier^{TM}) coupled with gas chromatograph equipped with cold injection system. Pesticides were chromatically separated with J&W (Agilent Technologies) DB-1701 column (30m×0.25mm×0.25μm).

Results and discussion

The concentrations of 26 organochlorine pesticides in soil samples ranged within 164.8~39,183 ng/kg d.w. The average concentration is 4296 ng/kg d.w.. All OCPs level found in the soil samples of Taiwan were well below the official risk threshold limit. The highest level were found in those sampling sites of Taoyuan and Taichung, of which the total average concentration fell between 10,000~15,000 ng/kg d.w.. The lower level range between 5,000~10,000 ng/kg d.w. were found in those sampling sites of New Taipei, Miaoli, Changhua, Yunlin and Chiayi. others The analyzed OCPs levels of other areas are under 5,000 ng/kg d.w. as shown in Tab.1. and Fig.1.

Higher detection ratio are found than most previous reports. Up to 81% Organochlorine pesticides are detected in all samples possibly due to that HRGC/HRMS has lower detection limit compared with traditional GC/ECD and GC/MS. Pentachlorobenzene, Hexachlorobenzene, BHC, Chlordane, DDT and their metabolites are found in most samples of this study as shown in Fig.2. As we compare the analyzed data between OCPs and their metabolites, the detection ratio of OCPs metabolites are very close to the ratio of their OCPs originates. The only exception is Oxychlordane of which its detection ratio is 18% that is much lower as compared with the number of 90% for both Chlordane and Nonachlor. Residual Chlordane and Nonachlor in soil metabolized to Oxychlordane generally took a long time, but the half-life of Oxychlordane is much shorter than those of Chlordane and Nonachlor. Oxychlordane in soil tends to metabolize into other compounds in a short time. We observed that the average level of chlordane in soil (144 ng/kg d.w.) was higher than that of nonachlor(75 ng/kg d.w.). One possible explanation can be attributed to the slower rate of metabolism of chlordane in soil.

As regard to the acute toxicity, carcinogenic and residual level of OCPs are shown in Fig.3. It is obvious that DDTs and their metabolites have biggest triangle area, therefore their residual level in soil should be of more concern in Taiwan. The second OCPs group that are worthwhile to be noticed include Aldrin and Endosulfan~~s~~. Although the residual level (182 ng/kg d.w.) of Aldrin is relatively lower than other OCPs and its detection ratio is only 67%, it is advised to keep alert due to its potential high toxicity and carcinogenic. Endosulfans has the second highest residual level (364 ng/kg d.w.) and also has high toxicity. Though Endosulfans have been banned by the Stockholm Convention since 2011, there is still possibility to observe occasional discharge of this chemical to the environment and impacts on bio system and human health need to be continuously monitored.

Some of previous research works revealed that the half-lives of DDTs in soil are about two years or longer. It is reported in some previous research papers that DDTs will last longer than eight years in tissue before being metabolized to DDDs and DDEs. In this study we found that p,p’-DDE and p,p’-DDD were detected in all samples (100%) while p,p’-DDT was found in only less than 30% of collected soil samples. Similar phenomenon are observed in the case of o,p’ -DDE, o,p’ -DDD and o,p’ -DDT family group. Residual data of these congeners reflects the widely usage of DDTs in the past. Nevertheless, the average concentrations of DDTs (3,047 ng/kg d.w.) found in all soil samples of this investigation are far below the regulated level for soil (3 mg/kg d.w.).

F_{DDTs} is a frequently used indicator for the degree of DDT degradation as show below:

$$\mathbf{F_{DDTs} = \Sigma\,(DDD+DDE)\,/\,\Sigma\,(DDT+DDD+DDE)}$$

For the fresh DDT, the F_{DDTs} will generally fall within the lower range of 0.52. On the other hand, aged DDT contaminations usually exhibit higher values. As illustrated in Fig.4, F_{DDTs} of all 95 samples are higher than 0.52. It implied that little fresh DDT has been found in these samples as shown in Fig.3. The only two site that have lower F_{DDTs} than 0.52 are both found in samples collected from sites in Kaohsiung. Further investigation is needed to confirm whether it is due to illegal use of the banned pesticides or it is coming from other sources into this area via some transmission path.

The concentration distribution of the 26 targeted OCPs in Tainan, Yunlin and Chiayi counties are very similar-possibly due to that the topographic features and their agriculture activities~~e~~ are quite similar in these three areas. However, the average total concentration of Tainan (1,035 ng/kg d.w.) is five times lower than the other two areas (6,539 and 6,333 ng/kg d.w.). One possible explanation is that due to Tainan is located in more south part of Taiwan. Average temperature in the year is higher and has generally more sunny days. It is possible that more and faster OCPs in soil will be metabolized. The average total concentration of Tainan is therefore lower and close to Kaohsiung (1,611 ng/kg d.w.) that are both located in the south ends of Taiwan. The concentration distribution of the 26 OCPs in those samples collected from sites of Changhua, Miaoli and Nantou varied from each other significantly. We attribute these differences to the complex agricultural product and pesticides applcation patterns in the past years.

Acknowledgments

We would like to express our deep gratitude to the support from the Soil and Groundwater Fund Management Board of Taiwan

EPA.

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2.Hong, H. S., Chen, W. Q., Xu, L., Wang, X. H., Zhang, L. P.: Distribution and fate of organochlorine pollutants in the pearl river estuary. Marine Pollution Bulletin 39, 376-382 (1999)

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Table 1 Summary of Total OCPs concentration in soil of Taiwan

Area	Sampling sites	Concentration range （ng /kg d.w.）	Average （ng /kg d.w.）	Area	Sampling sites	Concentration range （ng /kg w.w.）	Average （ng /kg d.w.）
Taipei	1	4148~4148	4148	Changhua	8	1152~20932	6299
New Taipei	3	2312~10045	5396	Yunlin	10	601~26133	6539
Yilan	3	2848~7873	4683	Chiayi	9	705~15302	6333
Taoyuan	5	2431~27197	11544	Tainan	12	183~5443	1036
Hsinchu	4	525~3336	2122	Kaohsiung	6	443~4709	1611
Miaoli	4	2308~9693	5958	Pingtung	9	1060~3405	1973
Taichung	6	3226~39183	10129	Taitung	6	174~2178	867
Nantou	8	225~4221	2906	Hualien	6	165~946	556

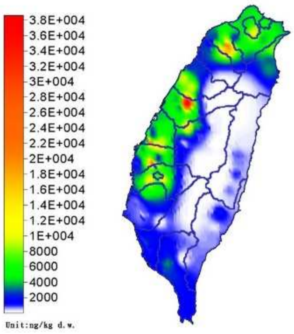

Figure 1 concentration distribution of 16 Areas.

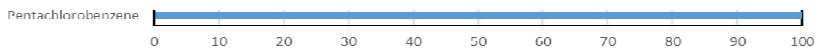

Figure 2 Detected percentage of 26 OCPs.

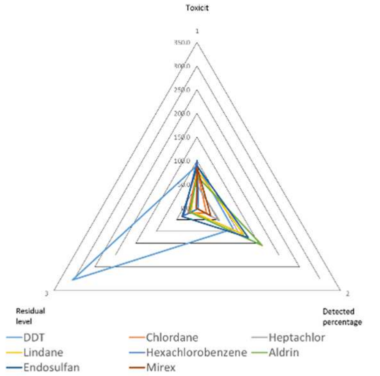

Figure 3 Impact estimate of 26 OCPs in soil.

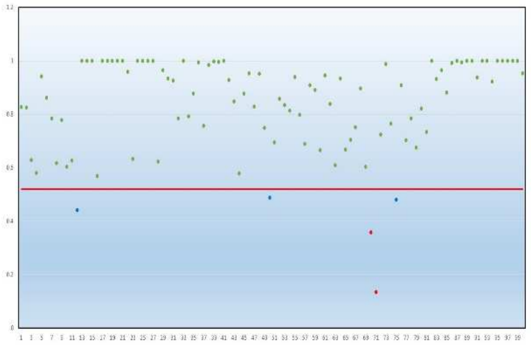

Figure 4 Index for evaluating the degradation of DDT in soil.

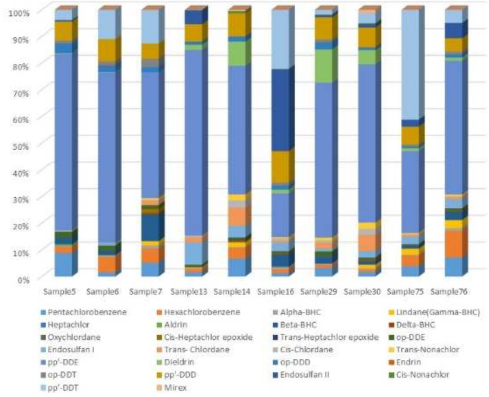

Figure 5 concentration distribution of 26 OCPs in Yunlin

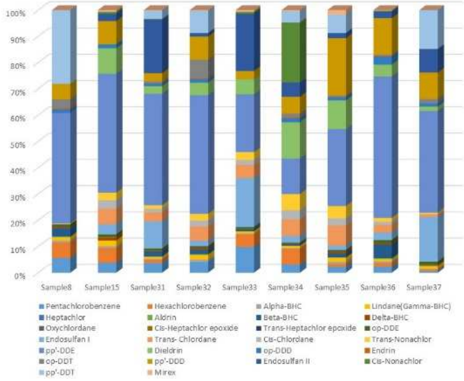

Figure 6 concentration distribution of 26 OCPs in Chiayi

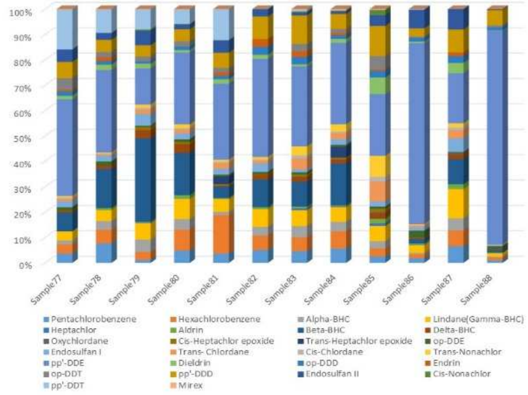

Figure 6 concentration distribution of 26 OCPs in Tainan

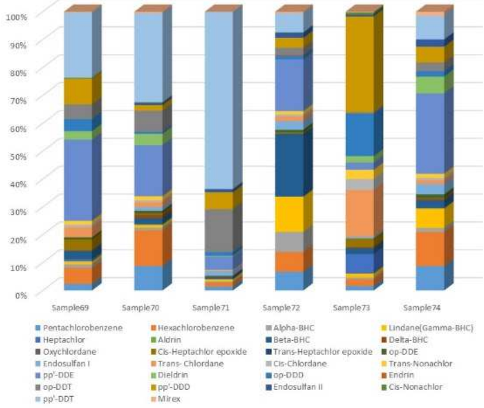

Figure 7 concentration distribution of 26 OCPs in Kaohsiung

附件三　投稿論文壁報

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

DIOXIN 2017
Vancouver, Canada

Hsu YC, Wu CP, Sung YY, Huang YJ, Weng YM
Environmental Analysis Laboratory, Taiwan EPA, Chungli, Taiwan 320

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We initiated the use of the isotope dilution method with HRGC/HRMS to analyze 26 organochlorines and their metabolites in environmental samples so as to determine the residual OCPs in a more accurate way.

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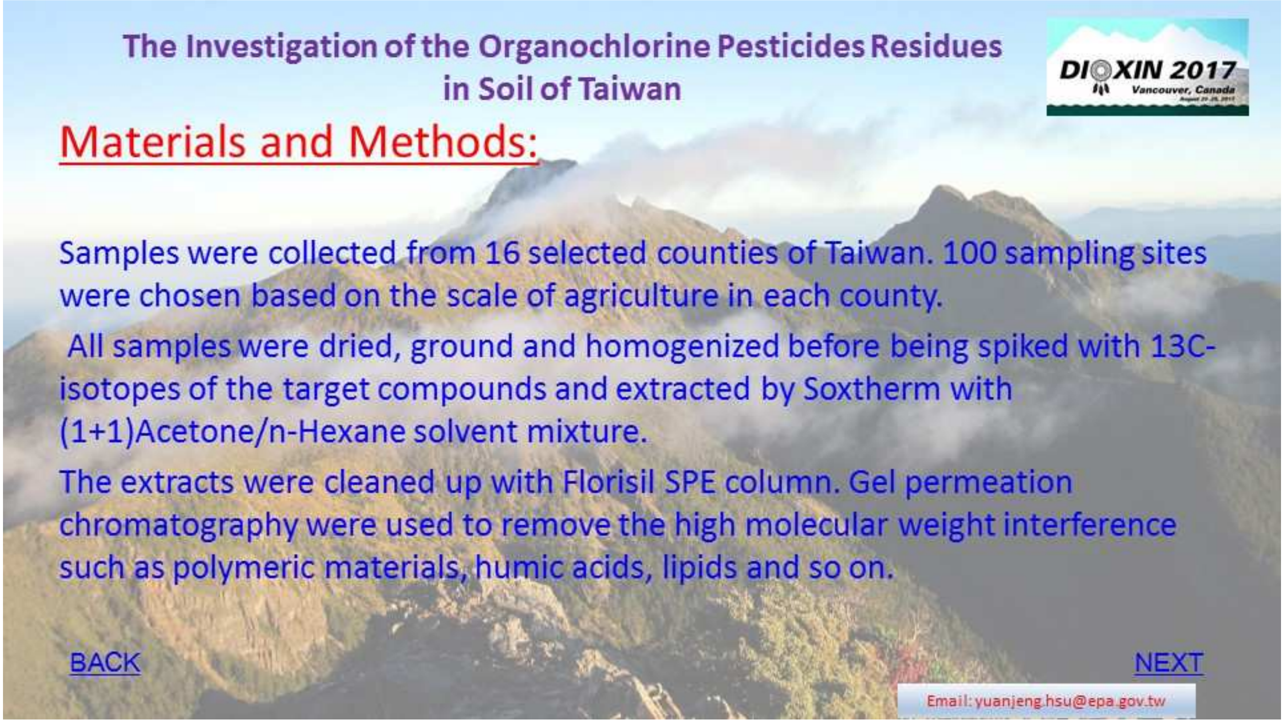

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DIOXIN 2017
Vancouver, Canada

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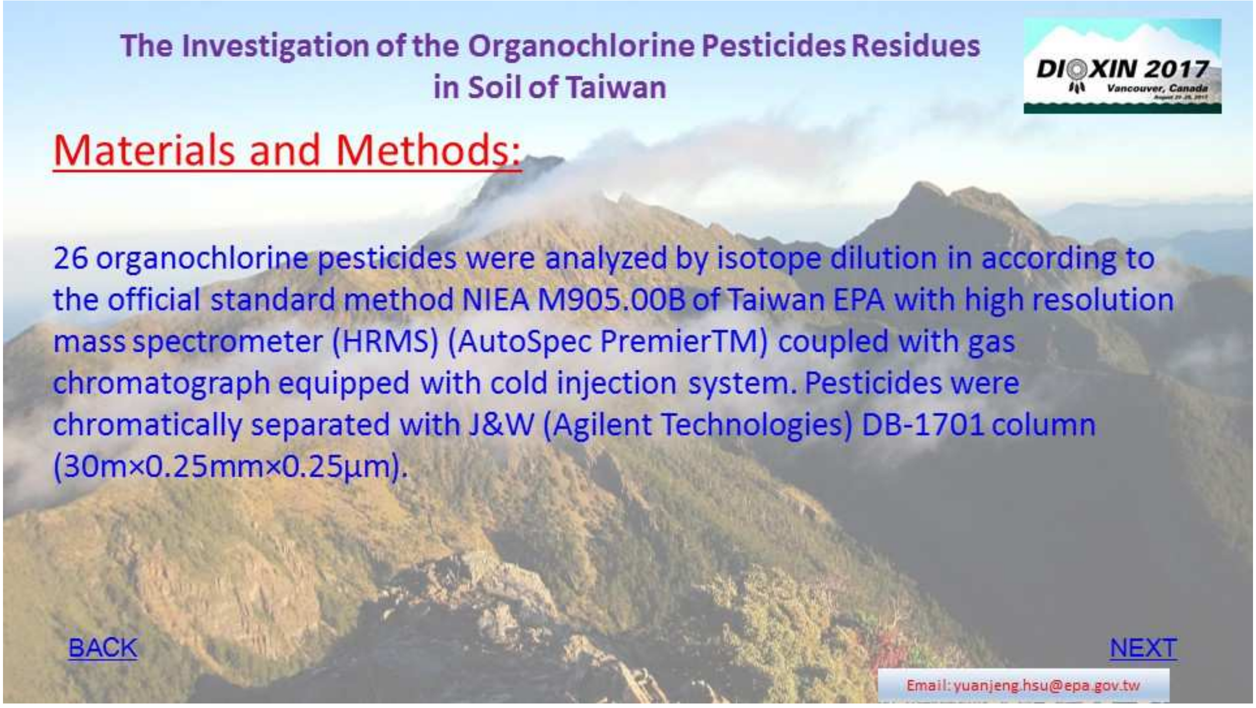

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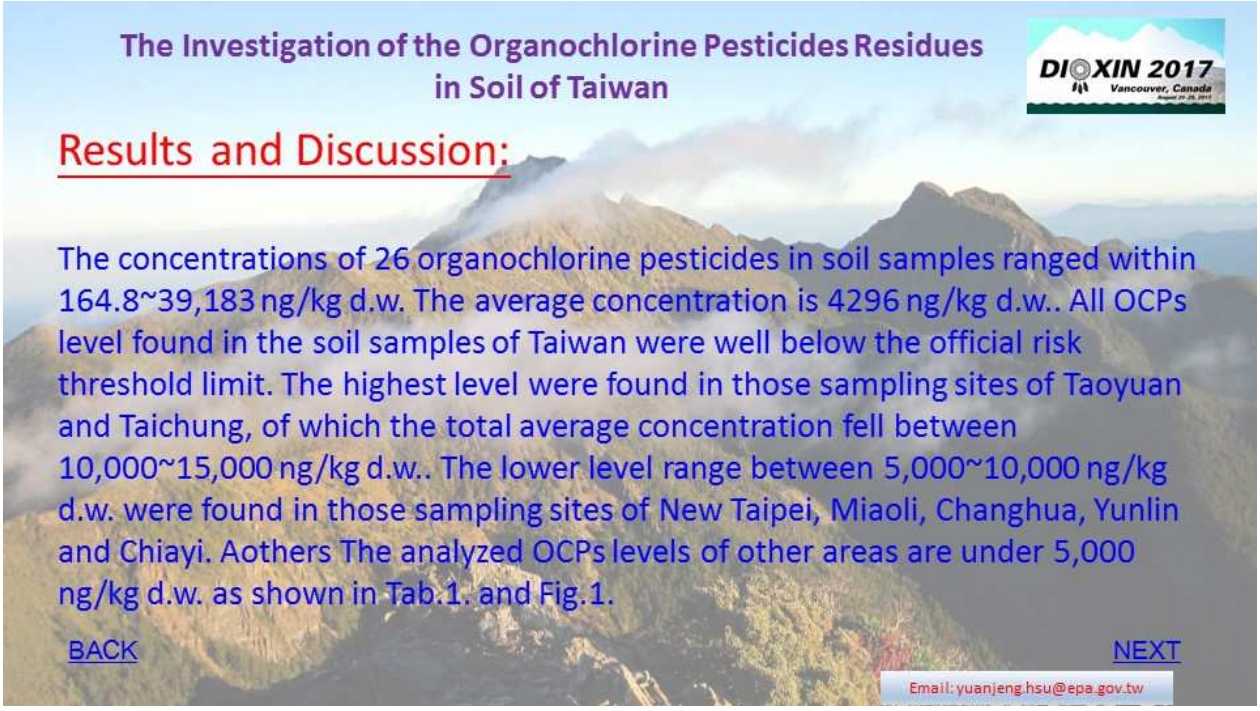

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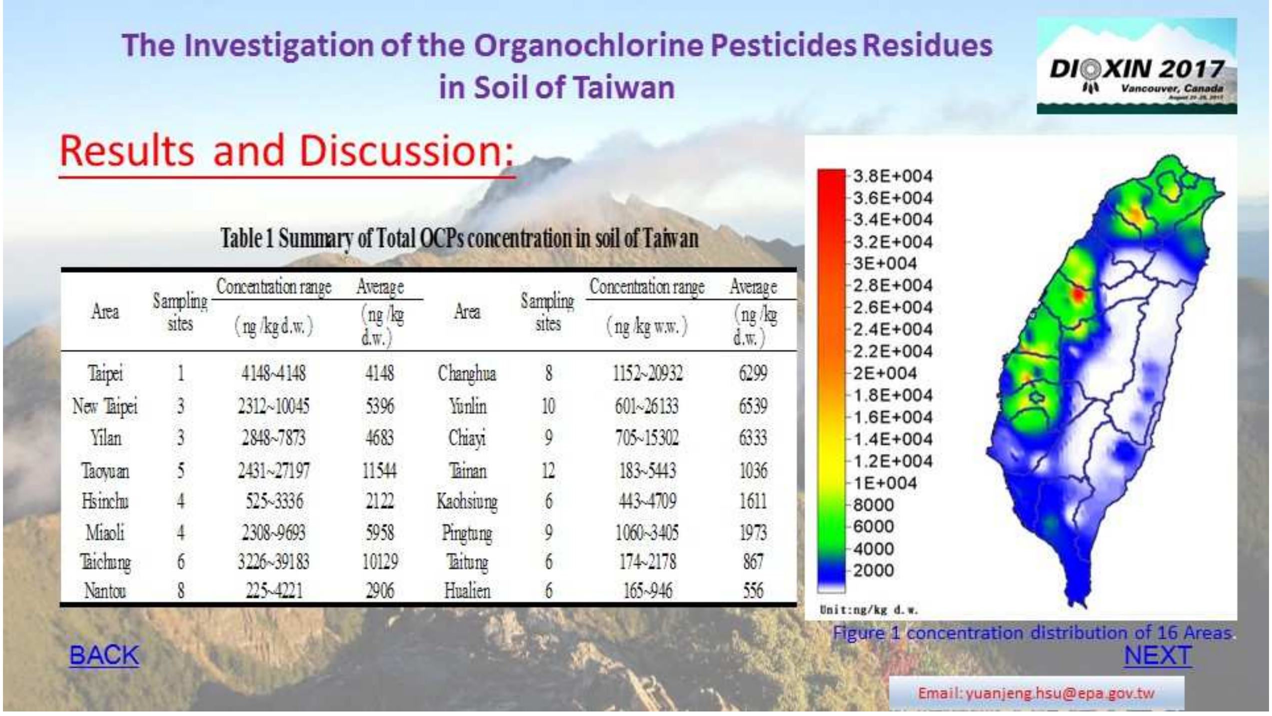

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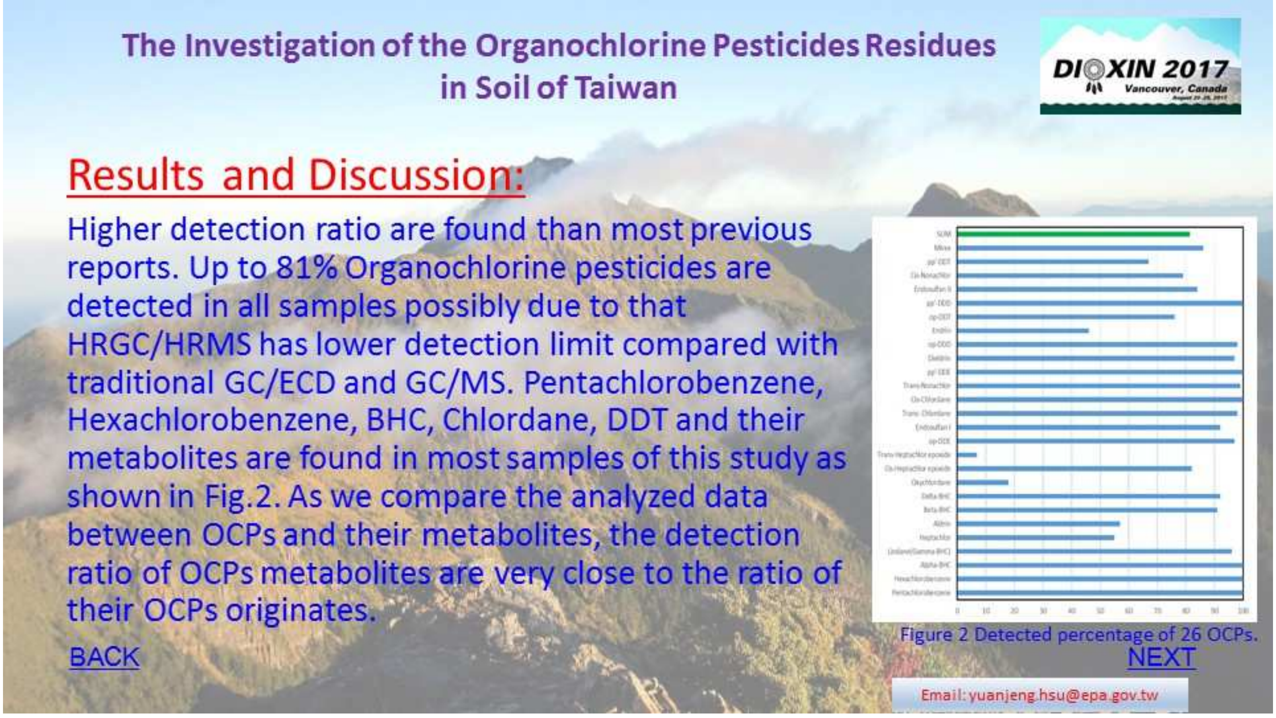

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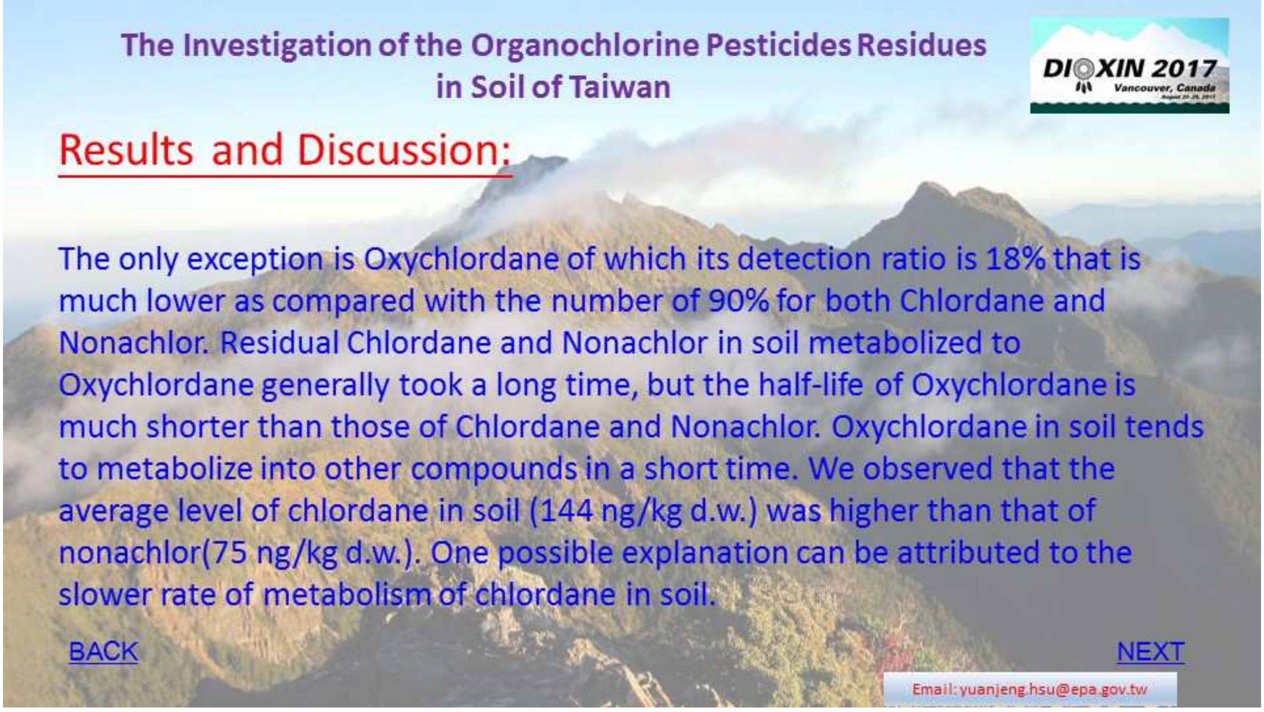

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

DIOXIN 2017 Vancouver, Canada

Results and Discussion:

The only exception is Oxychlordane of which its detection ratio is 18% that is much lower as compared with the number of 90% for both Chlordane and Nonachlor. Residual Chlordane and Nonachlor in soil metabolized to Oxychlordane generally took a long time, but the half-life of Oxychlordane is much shorter than those of Chlordane and Nonachlor. Oxychlordane in soil tends to metabolize into other compounds in a short time. We observed that the average level of chlordane in soil (144 ng/kg d.w.) was higher than that of nonachlor(75 ng/kg d.w.). One possible explanation can be attributed to the slower rate of metabolism of chlordane in soil.

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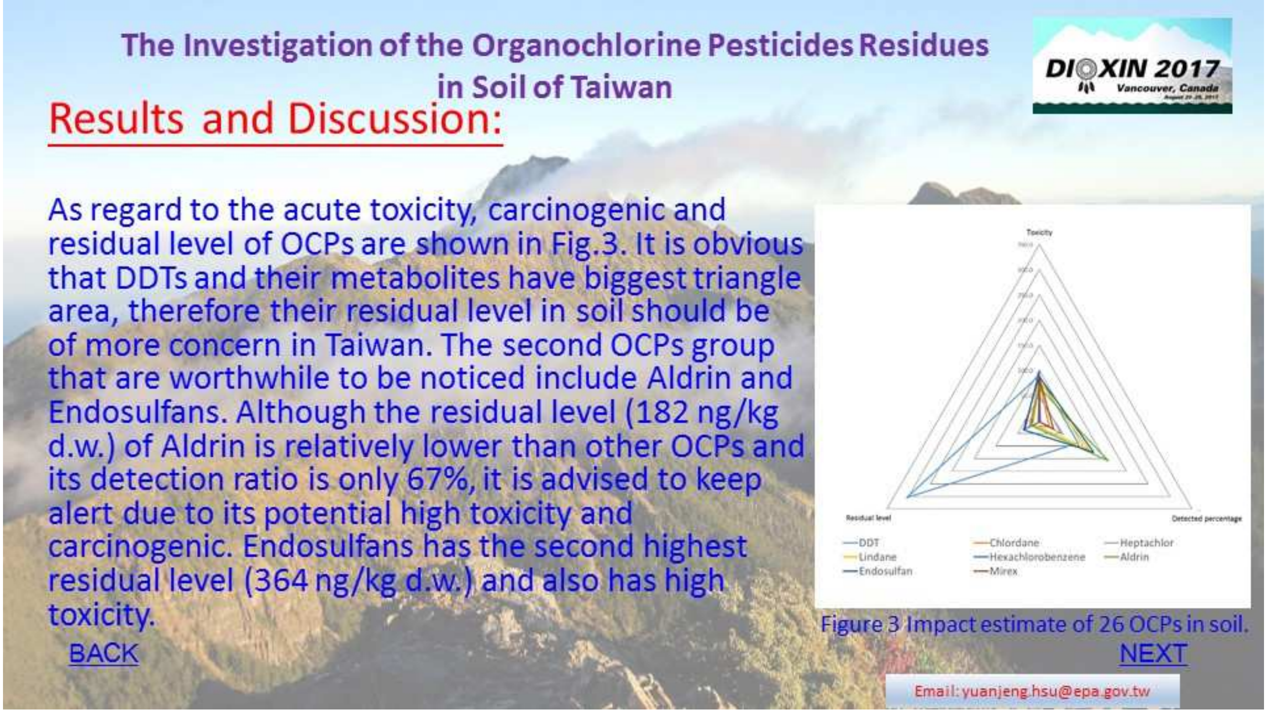

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

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Results and Discussion:

As regard to the acute toxicity, carcinogenic and residual level of OCPs are shown in Fig.3. It is obvious that DDTs and their metabolites have biggest triangle area, therefore their residual level in soil should be of more concern in Taiwan. The second OCPs group that are worthwhile to be noticed include Aldrin and Endosulfans. Although the residual level (182 ng/kg d.w.) of Aldrin is relatively lower than other OCPs and its detection ratio is only 67%, it is advised to keep alert due to its potential high toxicity and carcinogenic. Endosulfans has the second highest residual level (364 ng/kg d.w.) and also has high toxicity.

Figure 3 Impact estimate of 26 OCPs in soil.

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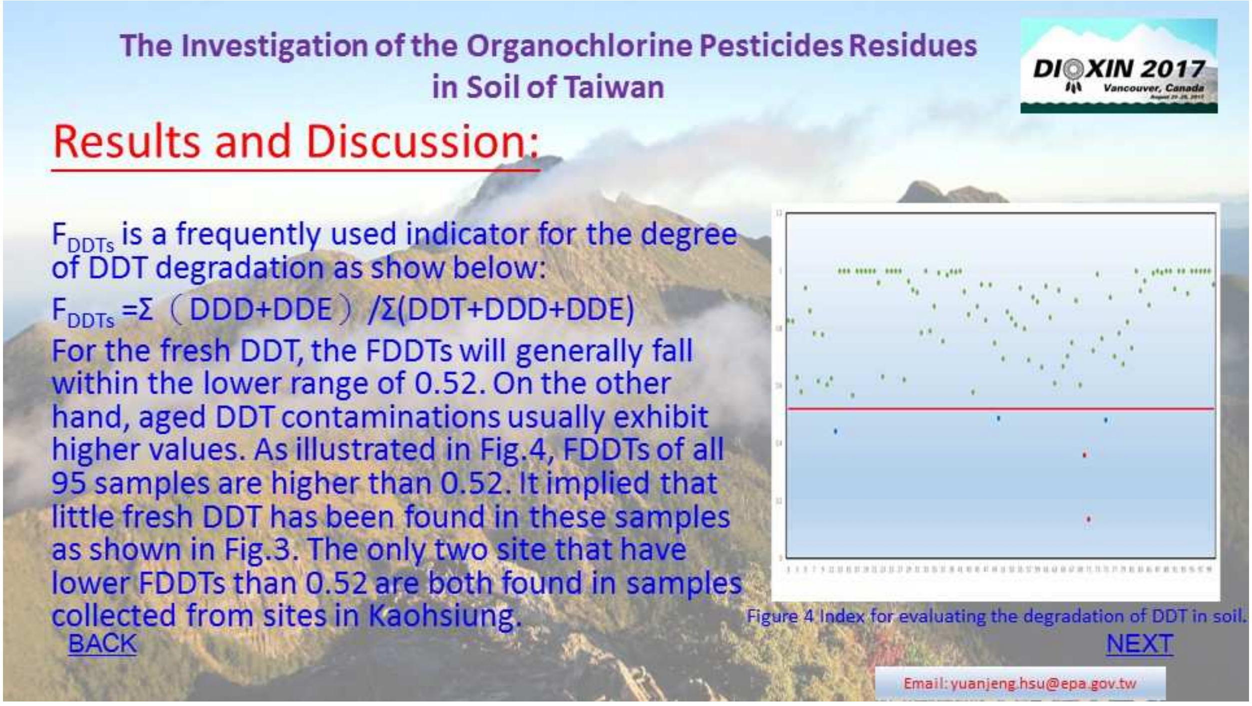

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

Results and Discussion:

F_{DDTs} is a frequently used indicator for the degree of DDT degradation as show below:

$F_{DDTs} = \Sigma（DDD+DDE）/\Sigma(DDT+DDD+DDE)$

For the fresh DDT, the FDDTs will generally fall within the lower range of 0.52. On the other hand, aged DDT contaminations usually exhibit higher values. As illustrated in Fig.4, FDDTs of all 95 samples are higher than 0.52. It implied that little fresh DDT has been found in these samples as shown in Fig.3. The only two site that have lower FDDTs than 0.52 are both found in samples collected from sites in Kaohsiung.

Figure 4 Index for evaluating the degradation of DDT in soil.

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The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

Results and Discussion:

The concentration distribution of the 26 targeted OCPs in Tainan, Yunlin and Chiayi counties are very similar possibly due to that the topographic features and their agriculture activitiese are quite similar in these three areas. However, the average total concentration of Tainan (1,035 ng/kg d.w.) is five times lower than the other two areas (6,539 and 6,333 ng/kg d.w.). One possible explanation is that due to Tainan is located in more south part of Taiwan. Average temperature in the year is higher and has generally more sunny days. It is possible that more and faster OCPs in soil will be metabolized. The average total concentration of Tainan is therefore lower and close to Kaohsiung (1,611 ng/kg d.w.) that are both located in the south ends of Taiwan.

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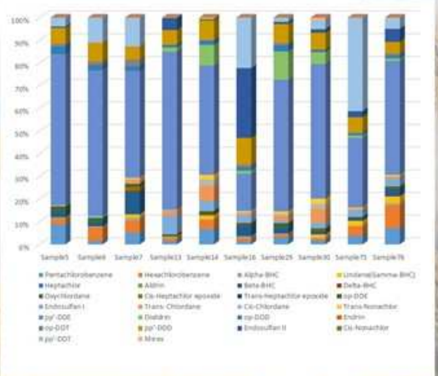
The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

Results and Discussion:



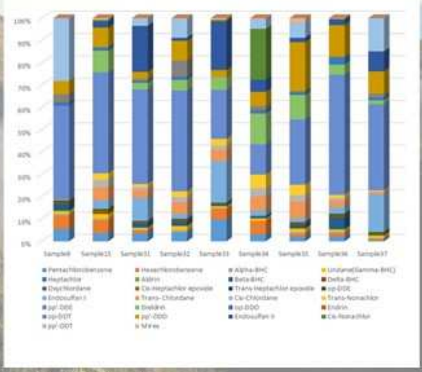


Figure 5 concentration distribution of 26 OCPs in Yunlin

Figure 6 concentration distribution of 26 OCPs in Chiayi

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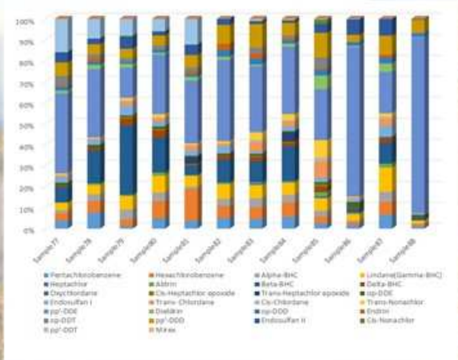
The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

Results and Discussion:



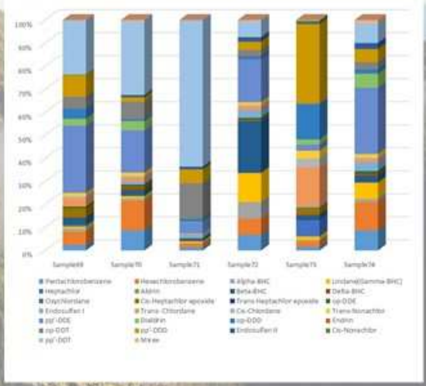


Figure 6 concentration distribution of 26 OCPs in Tainan

Figure 7 concentration distribution of 26 OCPs in Kaohsiung

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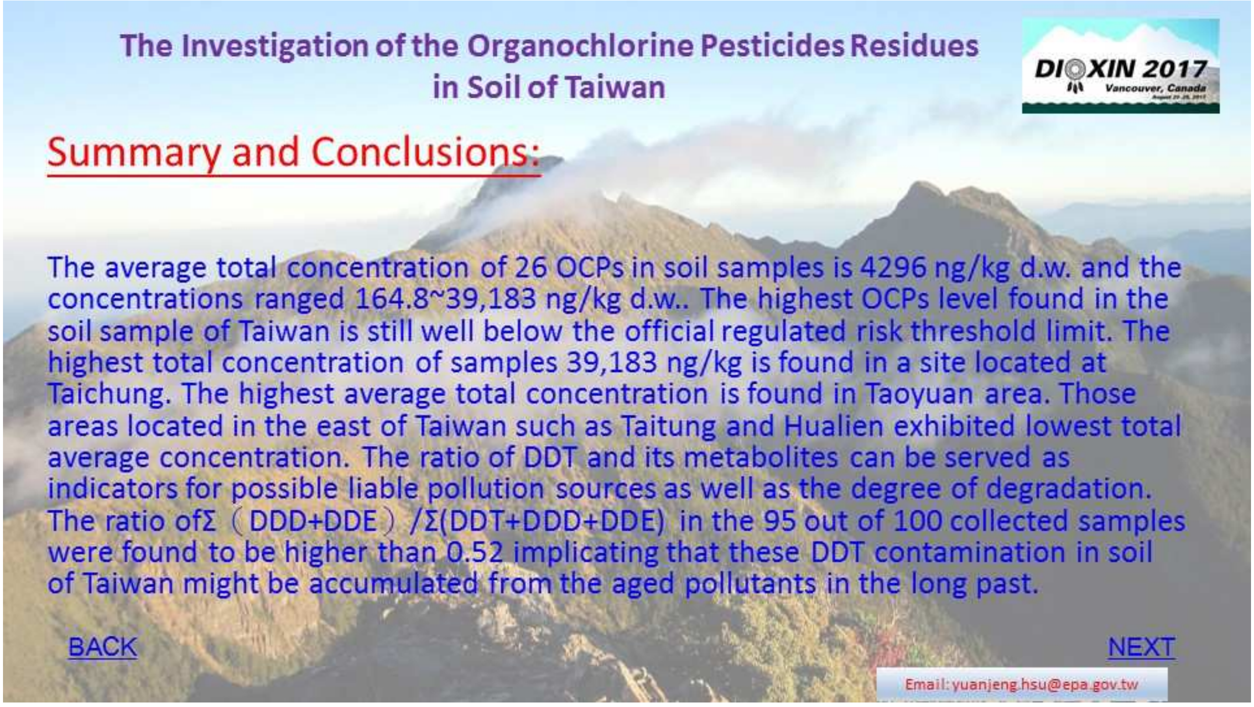

The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

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Summary and Conclusions:

The average total concentration of 26 OCPs in soil samples is 4296 ng/kg d.w. and the concentrations ranged 164.8~39,183 ng/kg d.w.. The highest OCPs level found in the soil sample of Taiwan is still well below the official regulated risk threshold limit. The highest total concentration of samples 39,183 ng/kg is found in a site located at Taichung. The highest average total concentration is found in Taoyuan area. Those areas located in the east of Taiwan such as Taitung and Hualien exhibited lowest total average concentration. The ratio of DDT and its metabolites can be served as indicators for possible liable pollution sources as well as the degree of degradation. The ratio ofΣ（DDD+DDE）/Σ(DDT+DDD+DDE) in the 95 out of 100 collected samples were found to be higher than 0.52 implicating that these DDT contamination in soil of Taiwan might be accumulated from the aged pollutants in the long past.

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Acknowledgements:

We would like to express our deep gratitude to the support from the Soil and Groundwater Fund Management Board of Taiwan EPA.

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附件四　大會演講論文摘要

Persistent, bioaccumulative and toxic contaminants in marine mammals: a legacy concern for conservationists

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The Stockholm Convention is a remarkable international treaty that was founded on good scientific research, concerns about health impacts in aquatic wildlife and on the safety of traditional seafoods for aboriginal communities, and the recognition that many persistent, bioaccumulative and toxic chemicals are travelling into remote regions of the world. Our work on marine mammals in Europe, the Arctic and the NE Pacific has shed light on the nature of food web bioaccumulation of POPs, and on the effects of PCBs on the endocrine and immune systems of different species. However, most troubling perhaps is our prediction that the Southern Resident Killer Whales frequenting the waters off Vancouver and Seattle will not be 'safe' from PCB-related health risks until the late 21st Century. This is one chemical among hundreds of thousands on the market. Such findings are highly relevant to conservationists dealing with real world threats to wildlife populations, but they also raise profound questions about the vulnerability of long-lived, high trophic level species, and about the effectiveness of chemical regulation and risk assessment paradigms. Simply put, short-term, lab-based toxicity testing with laboratory species fails to deliver the data needs of risk assessors, and we continue to conduct large-scale experiments in the natural world. A more precautionary approach to regulatory oversight would better capture such key considerations as trophic level, longevity, mobility and the relationship between endocrine disruption and the traditional measures of effects (growth, reproduction and mortality) before chemicals enter the marketplace.

DIOXIN AND THE AHR: THE BEGINNINGS AND NO END IN SITE

Safe S[1]

[1] Department of Veterinary Physiology and Physiology, Texas A&M University, College Station, TX 77843-4466

Otto Hutzinger – The Early Days

In the late 1960's, Otto Hutzinger was a newly hired Research Officer at the National Research Council (NRC) Regional Laboratory on the campus of Dalhousie University in Halifax, Nova Scotia. His interest in PCBs and Dioxins resulted from a conversation with Vlado Zitko, a scientist with the Fisheries Research Board in St. Andrews New Brunswick. Vlado indicated his concern regarding organochlorine environmental contaminants and suggested that environmental chemistry and impact of these compounds would be a "hot" area of research. I was also a Research Officer at NRC and Otto persuaded me to get involved in this new area of environmental research which would give us independence from our immediate supervisors and also be lots of fun. I reluctantly agreed, and from 1971-1974, we coauthored 35 refereed publications, at least 10 review articles, and two books, "The Chemistry of PCBs" (Hutzinger, Safe and Zitko) and "Mass Spectrometry of Pesticides and Pollutants" (Safe and Hutzinger) and founded a small company. Some of this early work described the first studies showing that PCBs could be photodegraded and metabolized (1-3), and these collaborative studies were continued after Otto was appointed Professor Environmental Chemistry at the University of Amsterdam in 1975 and I joined the University of Guelph in 1973. One of the lessons I learned from Otto was his attitude toward senior authorship and credit – he always favored his colleagues over himself.

After leaving NRC, Otto continued his studies on organohalogen pollutants and was the first to discover the formation and emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurants (PCDFs) from municipal waste incinerators. Otto was an original thinker and mentor to a generation of environmental scientists at the Universities of Amsterdam and Bayreuth, and he was continually organizing research conferences (starting with Dioxin 1 in Rome), editing journals (e.g. *Chemosphere*), and books (e.g. *The Handbook of Environmental Chemistry*). Otto was one of a kind and is greatly missed.

Dioxin and the Ah Receptor

The combination of several poisoning incidents due to occupational and accidental release of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and contaminated PCBs in Fukuoka (Yusho poisoning), Taiwan (Yucheng poisoning), and Seveso (TCDD) coupled with their widespread environmental contamination, stimulated scientific, regulatory and legal concerns about halogenated aromatics. All of these issues and their resolution were presented and discussed during the annual "Dioxin Symposia". Although some occupational exposures and the Seveso accident primarily involved a single toxicant, TCDD, other accidents and environmental exposures to persistent organic pollutants (POPs) involved TCDD and many other individual PCDD, PCDF and PCB congeners. The analytical approaches included development of high resolution separation and detection approach which are now routinely used to quantity POP congeners from multiple sources at the sub-parts-per-trillion level. Since human and other biota are exposed to complex mixtures of POPs, it was imperative to develop hazard and risk assessment paradigms that could quantitatively assess mixture-induced responses. Pioneering work by Dr. Alan Poland (4) showed that the mechanism of action of TCDD and structurally related PCBs, PCDDs and PCDFs involved initial binding to an intracellular protein designated as the aryl hydrocarbon receptor (AhR). This was later confirmed in AhR knockout mouse models where the characteristic AhR-mediated toxicities for TCDD and structurally related compounds were observed in wild-type but not AhR-knockout (AhRKO) mice. Thus, it was possible to develop a dioxin or toxic equivalents (TEQ) approach for risk assessment of TCDD- or dioxin-like compounds (DLCs), where

$$\mathrm{TEQ} = \sum[(\mathrm{DLC}_i) \times (\mathrm{RP}_i)]$$

the dioxin equivalents is equal to the summation of the individual concentrations of the DLC (DLC_i) times their relative potency (RP_i) compared to TCDD (arbitrarily set at 1.0) (5). This initial approach has been continually refined and modified as new data become available and has been used extensively by regulatory agencies to reduce emissions and environmental/human exposures to DLCs. The TEQ approach was invaluable for estimating the potential toxicity of an important sub-class of POPs (i.e. DLCs); however, evaluation of the potential adverse effects of non-DLCs is still a major regulatory problem

The AhR and Its Ligands: Health and Therapy

Although AhRKO mice are viable and reproduce, initial studies by Bradfield and others have identified an increasing number of defects in these animals, demonstrating that the receptor may play a role in organ/tissue homeostasis (6,7). For example, AhR-deficient mice exhibit a decreased liver size but only during development due to defects in closure of the ductus venosus. AhRKO mice have difficulty in maintaining pregnancy, they have an increased susceptibility to infection indicating a role for the AhR in the immune system function and the AhR also plays a role in stem cell development. Moreover, there is extensive evidence from transgenic animal studies that the AhR plays a critical role in intestinal health via interactions with microbiota-derived AhR metabolites and the AhR exhibits tissue-specific promotion or protection from cancer (8). Ongoing research continues to add to the growing list of AhR functions in animal models and to a lesser extent in humans and this makes the AhR an ideal target for drug development.

Receptors such as the estrogen receptor are among the most well developed targets for drug development since receptor-mediated adverse effects can be treated with receptor antagonists and receptor-mediated health benefits can be enhanced by receptor agonists. Although AhR-interactions with TCDD and related compounds lead to well characterized toxicities, the AhR also binds several endogenous biochemicals, health promoting phytochemicals, AhR-active pharmaceuticals, multiple microbiota-derived AhR ligands and synthetic AhR antagonists (9). These compounds are selective AhR modulators (SAhRMs) that exhibit tissue-specific AhR agonist or antagonist activities and can be exploited for treatment of multiple diseases including cancer, inflammatory bowel disease, immune and autoimmune diseases and expansion of stem cells. Development of AhR-active drugs has been a "cautionary tale" due to concerns of "dioxin-like" side effects; however, some of the current AhR-based drugs in clinical trials include Laquinimod for treatment of multiple sclerosis and StemReginin 1 (SR1), an AhR antagonist use for production of hemapoietic stem cells.

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Environmental Forensics of Persistent Organics Pollutants

Gwen O'Sullivan, David Megson, Court Sandau, Donald Patterson

Environmental forensics is a fast growing field of science which incorporates interdisciplinary knowledge to assess the source, age and timing of release of a contaminant(s). Environmental forensic investigations are methodical assessments of multiple lines of information, which may be used in litigation, to allocate responsibility for contamination. Environmental forensic studies can range in complexity; the simplest form may involve the identification of a source of contamination based on the presence or absence of chemical markers. More complex cases may involve mixed sources and environmental weathering which require advanced statistical interpretation to detangle distinctive signatures. Environmental forensics not only involves litigious matters but may also be applied to publicly disputed issues to support a particular claim or a position.

In toxicological studies it is important to separate the World Health Organisation 12 dioxin like polychlorinated biphenyls (WHO 12). However in environmental forensics studies a greater number of congeners are often needed to be separated to identify processes such as microbial degradation, volatilisation, and biotransformation in humans. Advancements in analytical techniques, including single and multidimensional time of flight mass spectrometry, has allowed for such congener profile development at trace levels. The amount of data generated from such analyses is vast and can require advanced multivariate statistical analysis techniques to discern patterns/source, differentiate background influences, and apportion contributions/liability.

This presentation will examine the development of environmental litigation including key treaties, statutes, regulations and case law pertaining to the control of persistent organic pollutants. A review of the interdisciplinary requirements of environmental forensic investigations including legal sampling techniques, analytical advancements, fate and transport, and statistical presentation in court will be provided. The presentation will conclude with discussions on advancements, limitations and recommendations for the development of the field of Environmental Forensics.

Science and Policy of POPs through Passive Air Sampling
Tom Harner

Abstract:

Since its inception in 2000, the polyurethane foam (PUF) disk passive air sampler has greatly advanced our understanding of the occurrence, transport and fate of persistent organic pollutants (POPs) and emerging chemicals. The ability to collect spatial information on both gas-phase and particle-associated POPs in a simple and cost-effective way has led to vast datasets for improving our understanding of regional and global-scale transport of POPs through models. This integration of passive air sampling data with models and emissions, coupled with the adoption of the PUF disk sampler by numerous research programs around the world, has led to the promulgation of the sampler under the Global Monitoring Plan (GMP) of the Stockholm Convention for addressing policy needs related to chemical risk assessment and risk management. The Global Atmospheric Passive Sampling (GAPS) network, which has been operating since 2005 at more than 50 sites on all seven continents, provides a unique global-scale picture on POPs. This plenary presentation will be a historical perspective of the PUF disk passive air sampler over the last 17 years. It will touch on the motivations for this technology, the early adoption that led to widespread use today, and the intersection of the science with policy needs at the international scale under the Stockholm Convention on POPs. We will also look to the future to some novel and exciting applications and approaches of passive air sampling.

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The role of environmental chemicals in obesity

Juliette Legler, Institute for Environment, Health and Societies, Brunel University London

The global incidence of obesity is one of the most serious public health challenges of our time. It is increasingly clear that environmental factors early in development, such as exposure to chemicals, play a role in the etiology of obesity. In recent years I have used an integrated toxicological and epidemiological approach to research the role of environmental chemicals in obesity. My research suggests that prenatal exposure to chemicals affects processes involved in obesity development, including increased differentiation of adipocytes, altered energy metabolism, and elevated weight in childhood. Current research in my lab is focused on unravelling the epigenetic mechanisms by which chemicals may perturb metabolic pathways and adipogenesis using in vitro and zebrafish models. I expect that by discovering novel gene regulatory mechanisms in obesity that can be disrupted by chemical exposure, novel risk factors involved in the etiology of obesity can be identified in order that preventative strategies be introduced to reduce obesity and the related drain on health care systems worldwide.

Contamination and human exposure to micropollutants including dioxin-related compounds in informal recycling sites for e-waste and end-of-life vehicles

Shin TAKAHASHI

Effective management of electronic waste (e-waste) has become a major issue of the modern world from both economic and environmental perspectives. Recently, end-of-life vehicles (ELV) has also become a matter of increasing concern because of their trade and management for reuse and recycling. E-waste and ELV contain valuable and reusable/recycable components and material but requires appropriate handling and recycling because of the high content of many hazardous substances, including toxic heavy metals as well as polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) and other toxic additives. However, informal recycling for e-waste/ELV using primitive techniques, which have been noted in developing or newly industrialized countires, results in environmental release of not only hazardous substances contained in these 'modern' wastes but also toxic secondary contaminants, including complex mixtures of dioxin-related compounds (DRCs), polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) and their brominated and mixed brominated/chlorinated analogues (PBDD/Fs and PXDD/Fs), as well as chlorinated/brominated polyaromatic hydrocarbons (Cl-/Br-PAHs). Assessing the environmental and human health impacts related to these pollutants from informal waste recycling activities is challenging due to the large number of compounds and the big data gap regarding their toxic potency. For the last several years, we conducted environmental and human monitoring in informal recycling sites for e-waste and ELV in northern Vietnam and Ghana, to evaluate environmental release of micropollutants including various DRCs and to assess their human health risk. I will present some details on the occurrence and contamination status of micropollutants in the e-waste/ELV recycling sites in northern Vietnam and discuss toxic identification and evaluation in view of dioxin-like toxicities using the dioxin receptor-CALUX *in vitro* bioassay. In addition, our recent results on targeted and non-targeted analysis for DRCs and Cl-/Br-PAHs in soil from an e-waste burning site in Ghana will be reviewed.

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附件五 **20** 篇口頭論文摘要

HIGH RESOLUTION ORIBITAL TRAPPING MASS SPECTROMETRY MEASUREMENT OF PERSISTENT ORGANIC POLLUTANTS IN COW's MILK

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are classes of related environmental pollutants produced through diverse sources or industrial use and are known to strongly bio-accumulate and produce multiple toxic endpoints in animals and humans[1,2]. The 2,3,7,8-tetrachlorodibenzobenzo-p-dioxin (TCDD) isomer has been classified as a group 1A human carcinogen by IARC[2]. PCBs with dioxin-like properties are often measured with the PCDD/Fs. These three classes of chemicals are listed as persistent organic pollutants (POPs) by the Stockholm convention designated for world-wide reduction in the environment[1].The primary route of non-occupational human exposure to PCDDs and PCDFs is foods and animal feeds[3-5]. Monitoring programs established are aimed to aid efforts to control contamination in foods and animal feeds[5]. Central to these efforts are confirmatory methods capable of measuring these chemicals at low concentrations in foods. We investigated an orbital trapping mass spectrometer for the measurement of PCDD/Fs and PCBs at low concentrations in whole cow's milk.

Materials and methods

Two calibration curves were constructed. One curve was prepared using Wellington Laboratory mixtures of all 17 native 2,3,7,8-substituted congeners and all 17 $^{13}C_{12}$ labeled standards at concentrations of 0.1, 0.2, 1, 5, 10, 20 and 40 ng/mL for PCDD/F along with PCBs 77, 81, 126 and 169 at 1, 2, 5, 20, 100, 1000 ng/mL used only with Maryland milks. The second curve uses the Cambridge Isotope laboratories (CIL) mixtures, EDF-9999-1-5, diluting them 10 fold resulting in concentrations of 0.25, 1, 5, 20 and 100 ng/mL. PCBs 77, 81, 126 and 169 were added at 0.25, 1, 5, 20 and 100ng/mL. Whole cow's milks from 3 commercial sources in Arkansas, USA were fortified 6 times near the maximum level allowable by EU (2.5 pg PCDD/F TEQ/g fat) and 6 unfortified milk portions (90-100g each) 2 each from the 3 sources were also analyzed. Whole milk samples from 3 commercial sources in Maryland USA, were collected and measured. The Arkansas whole milks were extracted using a Gerhardt Hydrotherm™/Soxtherm™ using 90-100g milk, 20 mL ethanol and 0.5g sodium oxalate and processed with 2M sulfuric acid using a Hydrotherm™/Soxtherm™ system. Fat obtained was removed by GPC followed by multi-layered silica columns. Final PCDD/F separation was performed with HPLC employing a 2-(1-pyrenyl)ethyl silica (PYE) column. The PCDD/Fs fraction was reconstituted in 10 µL of nonane[6]. Whole milks from Maryland were extracted using hexane/diethyl ether after addition of ethanol and sodium oxalate following a previously described method[4]. Whole milk extracts from Arkansas milks were measured using a Micromass AutoSpec Premier high resolution mass spectrometer a double focusing instrument (sector) with an Agilent 7890A gas chromatograph(GC) equipped with a 4 mm ID split/splitless liner with 1µL injections onto a 60 M x 0.25 mm ID DB-5ms column[6]. All milk extracts from Arkansas and Maryland, USA were measured using a TRACE 1300 GC coupled to a Q-Exactive mass spectrometer (QE) (ThermoFisher, San Jose, CA, USA). The GC column was a 40 M x 0.18 mm DB-5ms with a split/splitless injector, 4mm ID Restek sky liner. Two µLs were injected splitless at 300° C. GC was programmed from a starting temperature of 120 ⁰C which was held for 2 min prior to ramping at 20 ℃ /min. to 200 ℃. It was then ramped at 5 °C /min. to 240 °C and held for 12 min. before ramping at 10°/min. to 280° C with a final hold time of 10 min. The QE was operated in full scan SIM mode with 6 quadrupole filters. Settings used were 285-340, 300-340, 335-354, 335-380, 369-410, 435-480 *m/z*. An offset of -2 V was set between the source and the C-Trap. Other electron ionization source parameters were default including 70 eV, 50 µamps emission current, 1E6 target, AGC. No lock masses were used. Transfer line and source temperatures were 250 °C and 300 °C, respectively.

Results and Discussion

Table 1 provides the TEQs measured by the sector and QE for PCDD/Fs, PCB-81, 77, 126 and 169 in Arkansas milks. The TEQs for the PCBs agree closely with a range of 0.05-0.08 pg/g fat for the HRMS-sector and 0.05-0.07 pg/g fat for the QE. However, the PCDD/F TEQs were lower with the QE (0.06-0.22 pg/g fat upper bound) than the sector (0.19-0.38 pg/g fat). The sector identified PeCDD and 2,3,4,7,8-PeCDF in all milks, while QE found only 2 of 6 milks extracts with these congeners identified (ion ratios within ±15% of theoretical). The QE did not detect any signals for TCDD, TCDF or 1,2,3,7,8-PeCDF in the unfortified milk unlike the sector which measured these congeners in nearly all milks (data not shown). Five of the six Arkansas milks by QE failed the upper bound/lower bound criteria[7] of ±30% for the PCDD/F TEQ. For milks collected in Maryland, USA, PCDD/Fs and PCBs were measured using the QE only (**Table 2**). PCDD/F TEQs were 0.19-0.54 pg/g fat the QE (**Table 2**) in a similar range to Arkansas milks measured the by the sector (**Table 1**). All the PeCDD/Fs and HxCDD/Fs were measurable in all Maryland milk by the QE with isotope ratios ±15%, except 1,2,3,7,8,9-HxCDF(not detected). All these milks passed the upper bound/lower bound criteria. All milk PCDD/F TEQs from the Arkansas or Maryland were 5-12 times below the maximum limit set by the EU. The results from the two instruments were comparable for the milks fortified near the current EU maximum limit for PCDD/Fs (2.5 pg/g fat TEQ). Mean congener amounts were between 76-116% of theoretical with 1-28 relative standard deviations (RSDs) using the QE while the sector was 99-112% and 1.5-13 RSDs. TCDD, TCDF 1,2,3,7,8-PeCDF amounts by the QE were lower due to evaporation losses during and after multiple injections in the sector and APGC (**Table 3**). The mean amounts of PCDD/F TEQ measured in the fortified milks were nearly the same using either instrument (9.3 and 9.9 pg) (**Table 3**). The milk cleanup aided QE measurements in the fortified milks by maintaining low noise and interference in the TIC. Nevertheless, HpCDD was observed co-eluting with an unknown compound that produced a 0.8 minute wide response in the TIC of most milk samples. The peak was 1000 times larger than the labeled standard with a fragment ion at *m/z* 423.17 close to the native HpCDD mass of 423.7767. The presence of this compound may be responsible for a lower than expected result for one fortified HpCDD measurement increasing that congener's RSD.

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Table 1. Duplicate measurements for milks collected from three commercial sources (1, 2 and 3) in Arkansas (Ar), USA. Toxic equivalency (TEQ) expressed in pg/g fat for PCDD/F (D/F) and PCB-TEQ shown separately. TEQs are upper bound, split extracts.

	Sector			QE		
Milk IDs	**D/F-TEQ**	**PCB-TEQ**	**Total TEQ**	**D/F-TEQ**	**PCB-TEQ**	**Total TEQ**
Ar-S1	0.19	0.08	0.28	0.10	0.07	0.16
Ar-S1	0.22	0.09	0.31	0.09	0.07	0.13
Ar-S2	0.32	0.05	0.37	0.19	0.05	0.21
Ar-S2	0.32	0.05	0.37	0.17	0.05	0.20
Ar-S3	0.32	0.06	0.39	0.22	0.06	0.28
Ar-S3	0.38	0.06	0.44	0.16	0.05	0.19
Means	0.29	0.07	0.36	0.15	0.06	0.20

Table 2. Repeat measurements from whole milk collected from three commercial sources (A, B and C) in Maryland (MD), USA. Toxic equivalency (TEQ) expressed in pg/g fat for PCDD/F (D/F) and PCB-TEQ shown separately. PeCDD/Fs and HxCDD/Fs were measured in all milks with ion ratios ±15% of theoretical. TCDD/Fs were measurable in 4 of 7 milks with ion ratios ±15% of theoretical.

	QE		
Milk IDs	**D/F-TEQ**	**PCB-TEQ**	**Total TEQ**
MD-A1	0.36	0.22	0.57
MD-A2	0.33	0.10	0.43
MD-B1	0.40	0.17	0.57
MD-B2	0.33	0.09	0.39
MD-B3	0.19	0.07	0.24
MD-C1	0.34	0.10	0.43
MD-C2	0.54	0.17	0.71
Means	0.36	0.13	0.48

Table 3. Mean measurements for whole milk fortifications in pg, relative standard deviations (RSD) and % of theoretical spike (n=6) whole cow's milk from Arkansas, USA (90-100 g portions) fortified with 0.8, 4 or 8 pg/sample depending on the specific congener (see below) as measured by QE and Sector. For TCDD/F, PCB-77, 81 n=3 and 1,2,3,7,8-PeCDF n=4 with QE. Split extracts

	QE			**Sector**			
	Mean*	**RSD**	**% Theor.**	**Mean***	**RSD**	**% Theor.**	**Fortified Amount(pg)**
2,3,7,8-TCDF	0.61^	1.0	76	0.83	7.1	103	0.8
1,2,3,7,8-PeCDF	3.5^	17	86	4.3	2.2	108	4.0
2,3,4,7,8-PeCDF	4.3	4.4	109	4.2	2.1	105	4.0
1,2,3,4,7,8-HxCDF	3.9	3.1	97	4.3	2.3	108	4.0
1,2,3,6,7,8-HxCDF	3.9	3.4	97	4.2	3.8	104	4.0
2,3,4,6,7,8-HxCDF	4.2	1.7	104	4.3	2.7	109	4.0
1,2,3,7,8,9-HxCDF	3.8	5.0	95	4.1	2.8	102	4.0
1,2,3,4,6,7,8-HpCDF	4.0	11	100	4.2	2.2	104	4.0
1,2,3,4,7,8,9-HpCDF	4.0	2.5	99	4.4	1.5	110	4.0
OCDF	6.7	4.6	84	9.1	6.7	114	8.0
2,3,7,8-TCDD	0.64^	7.7	80	0.86	3.4	108	4.0
1,2,3,7,8-PeCDD	4.3	5.4	109	4.4	5.3	109	4.0
1,2,3,4,7,8-HxCDD	4.2	5.9	104	4.3	3.8	107	4.0
1,2,3,6,7,8-HxCDD	3.7	15	92	4.2	5.9	106	4.0
1,2,3,7,8,9-HxCDD	4.1	7.4	104	4.5	5.1	112	4.0
HpCDD	4.6	22	116	4.0	3.8	99	4.0
OCDD	7.7	28	96	8.5	7.7	106	8.0
TEQ pg spike	**9.3**			**9.9**			**9.1**
PCB-81	4.1^	21	102	4.6	4.3	114	4.0
PCB-77	4.0^	8.3	105	4.2	13	104	4.0
PCB-126	4.1	9.3	101	4.6	4.0	116	4.0
PCB-169	4.2	2.1	108	4.4	3.3	110	4.0

*Corrected for unfortified milk

^ n=4 1,2,3,7,8-PeCDF; n=3 for TCDD/F, PCB-81, 77

A GC×GC-HR-TOFMS with Enhanced Sensitivity: Targeted and Non-Targeted Analysis of Highly Complex Environmental Samples

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Gas chromatography coupled with mass spectrometry provides one of the best analytical tools which combine selectivity, sensitivity, reliability, and information capacity for both targeted and non-targeted methods of environmental analysis. The GC-MS identification of known compounds of interest and the structural elucidation of unknown compounds becomes considerably more reliable if accompanied by accurate mass measurements while using High Resolution Mass Spectrometry (HRMS). When analyzing real-life samples in a complex matrix, a high number of analytes of interest with a wide range of concentrations are likely present. Consequently, a significant increase in chromatographic peak capacity is required which can be realized by the use of comprehensive GCxGC.

A ultrahigh resolution TOF mass spectrometer with a Folded Flight Path TOF Mass Analyzer was used in this study. This instrument has resolving power up to 50,000 and is capable of acquiring up to 200 full spectra/s, which matches the requirements for optimal GCxGC analysis [1]. The novel data acquisition technique, Encoded Frequent Pushing (EFP™), was implemented to significantly increase sensitivity of the instrument.

Several sample sets were analyzed, including Arctic ice and city snow. The environmental samples were prepared in according to EPA Method 8270. The analysis was performed using 1D GC and GCxGC methods, and the data were processed using ChromaTOF software which includes features such as High Resolution Deconvolution, Advanced Spectra Analysis Tool and others which provide detailed and accurate results. GCxGC allowed significant (~10 times) increase of peak capacity and improved chromatographic separation of analytes, which are known to be difficult to separate by single dimension GC. But even when analytes were coeluting, accurate mass information allowed reliable elucidation [2].

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Variable energy electron ionization enhances the sensitivity and selectivity of brominated flame retardant analysis by GC/MS and GC x GC TOF/MS

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Introduction

In the last few years, several studies have reported on the identification, detection and quantification of several "novel" brominated flame retardants (NBFRs) used as replacements for the banned PBDE formulations [1]. Quantitative methods for analysis of PBDEs and NBFRs in different environmental matrices are based mainly on GC/MS or LC/MS. Currently, GC/MS methods apply mainly negative chemical ionization (NCI) for analysis of a broad range of BFRs due to the inherent lack of sensitivity associated with electron ionization (EI) for the heavier, highly brominated compounds (e..g. BDE-209 and DBDPE). This mainly attributed to extensive fragmentation of the highly brominated compounds under EI conditions resulting in low intensity fragments. However, the use of NCI for analysis of BFRs relies mainly upon monitoring the most intense bromine fraction (*m/z* = 79, 81) resulting in a lack of selectivity and increased dependence on chromatographic separation. Moreover, this precludes the use of ^{13}C-labelled isomers as internal standards for the compounds monitored at $[Br]^-$ [2].

To address this issue, we investigated the application of variable energy electron ionization accompanied with enhanced ion focusing to achieve softer (i.e. less fragmentation) ionization of the heavier brominated compounds using the EI source. The optimized source parameters were then applied for determination of 25 tri- to deca- brominated BFRs (including 12 PBDEs) in standard mixtures and indoor dust samples.

Materials and methods

25 legacy and novel BFRs were analyzed using a ThermoFisher Trace 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS) operated in electron ionisation mode. 1 µL of sample was injected using a programmable temperature vaporiser (PTV) onto a Restek Rxi-5Sil MS column (15 m x 0.25 mm x 0.25 µm film thickness). The injection temperature was set at 92 °C, hold 0.04 min, ramp 11.7 °C /sec to 295 °C, hold 20 mins. Injection was performed under a pressure of 0.19 bar until 1 min and purge flow to split vent of 50 mL/min. The GC temperature program was 50 °C, hold 0.50 min, ramp 20 °C/min to 250 °C, ramp 5 °C /min to 270 °C, ramp 20 °C/min to 305 °C, hold 12 min. Helium was used as a carrier gas with a flow rate of 1.5 mL/min.

For the GC x GC TOF/MS platform, samples were also analyzed on an Agilent 7890B GC equipped with a Zoex ZX2 thermal modulator. The 1st column was a 30 m SGE BPX5, followed by a shorter 4 m SGE BPX50 column in the 2nd dimension. This system was interfaced to a Markes BenchTOF-Select platform. Data files were processed using GC Image™ Version™ 2.5.

Results and discussion

1- Tuning source parameters

The low sensitivity of highly brominated compounds (i.e. more than 6 Br atoms) on GC-EI-MS was mainly attributed to extensive in-source fragmentation resulting in low intensity molecular $[M]^{\cdot}+$ or major fragment $[M\text{-}2Br]^{\cdot}$ peaks [3]. Such extensive fragmentation is directly associated with the electron ionization energy set at 70 eV by default. The use of this default value is explained by a maximum total ion current (TIC) produced due to the matching between the *de Broglie* wavelength of the electrons and the length of typical bonds in organic molecules (about 0.14 nm) leading to the strongest possible ionization and fragmentation [4]. However, a high TIC is not beneficial with multiple low intensity fragments as observed with higher PBDEs. Therefore, we used the advanced tuning tools to study the effect of lower electron ionization energy (70-30 ev) on the fragmentation pattern. It should be noted that a decrease in the ionization energy is accompanied by an undesirable scatter of the produced ions [4]. Hence, our method involved simultaneous adjustment of the applied positive potential (15-35 KV) on the focusing lens to improve the ion path and enhance the overall detector gain.

Representative results for 4 compounds with various levels of bromination are shown in Figure 1. While no significant increase in the chromatographic peak area was observed for the tetrabrominated BDE-47 (monitored at m/z = 483.7), substantial improvements in sensitivity were observed for the higher brominated BDE-183, BDE-209 and DBDPE. Interestingly, both BDE-183 and BDE-209 were monitored at the major fragment [M-2Br]$^{-}$, while DBDPE was monitored at [$C_7H_2Br_5$]$^{-}$. This allows for the use of ^{13}C-labelled isotopes as internal standards for improved accuracy of quantification of these BFRs in real samples.

The GC x GC TOF/MS platform applies preset values to adjust the lens voltage according to the reduced ionisation energy setup. However, similar results were obtained with an optimum setup of 35 eV and 30 KV for all the studied BFRs.

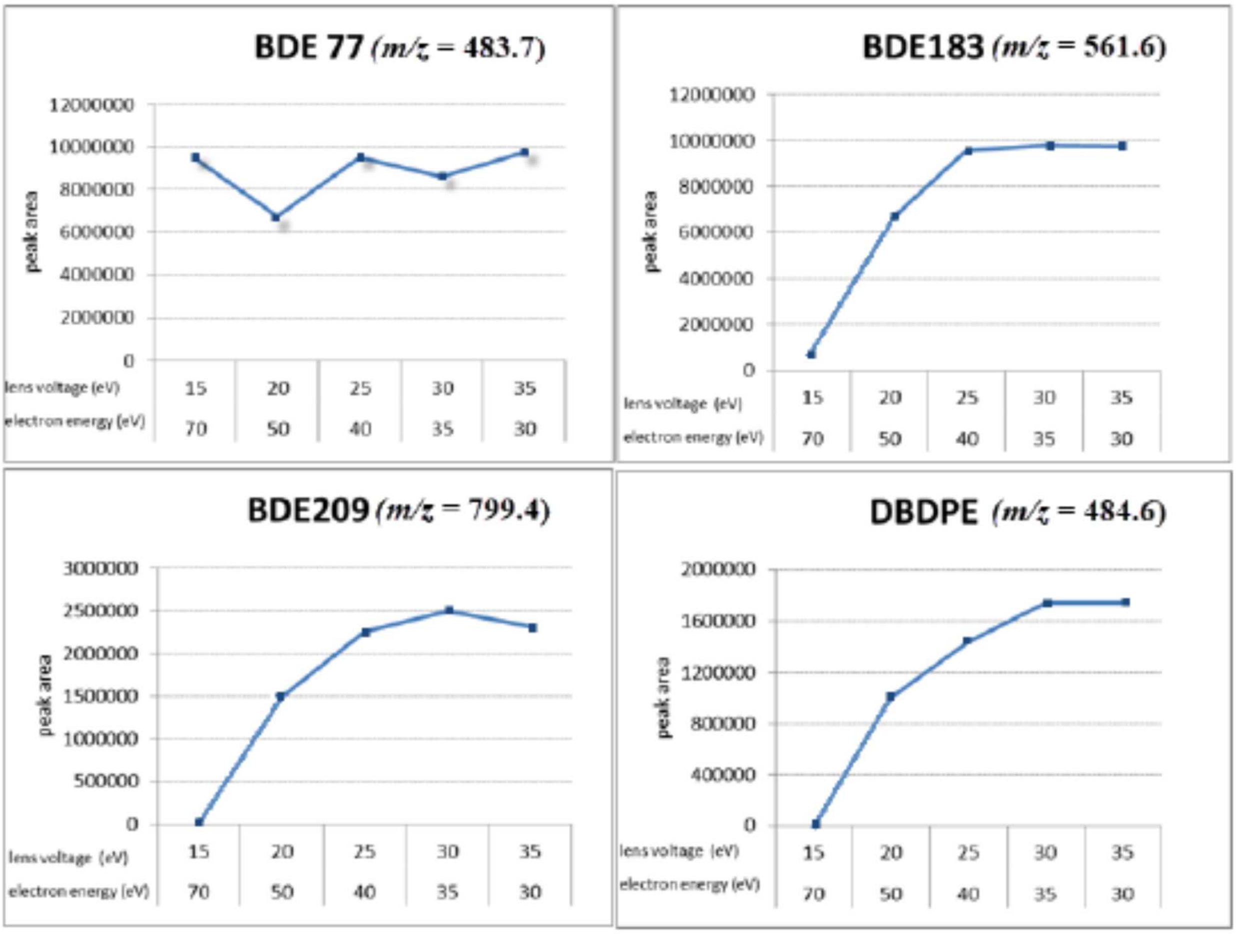


Figure 1: Comparison of peak areas of four brominated compounds (BDE-47, BDE-183, BDE-209, DBDPE) at different electron energy and lens voltage.

2- Fragmentation pattern

A significant change in the fragmentation pattern was observed under the optimised source conditions compared the standard setup. A representative example is provided in figure 2. At 70 eV, the sensitivity for the nona-brominated BDE-207 is so low that a mass of 5 ng on column was needed to obtain a clear mass spectrum (Fig 2a) showing extensive fragmentation with a very low intensity at the molecular ion peak and higher intensity for the lower molecular weight ion clusters. However, at 35 eV, much softer fragmentation is observed with higher intensity ion clusters at the molecular ion and [M-2Br]$^{-}$ peaks with only 50 pg on column. While the ion cluster at [M-2Br]$^{-}$ was used for subsequent quantification, the molecular ion peak can be used to confirm identity of the analyte. The enhanced sensitivity is accompanied with improved selectivity which is beneficial for identification and determination of NBFRs which might co-elute with PBDEs in complex environmental matrices (e.g. BDE-28 and pentabromotoluene or BEHTBP and BDE-197). This provides an advantage over GC-NCI/MS methods which only monitor the [Br]$^{-}$ fraction and rely mainly on chromatographic separation and retention time for identification of the studied BFRs.

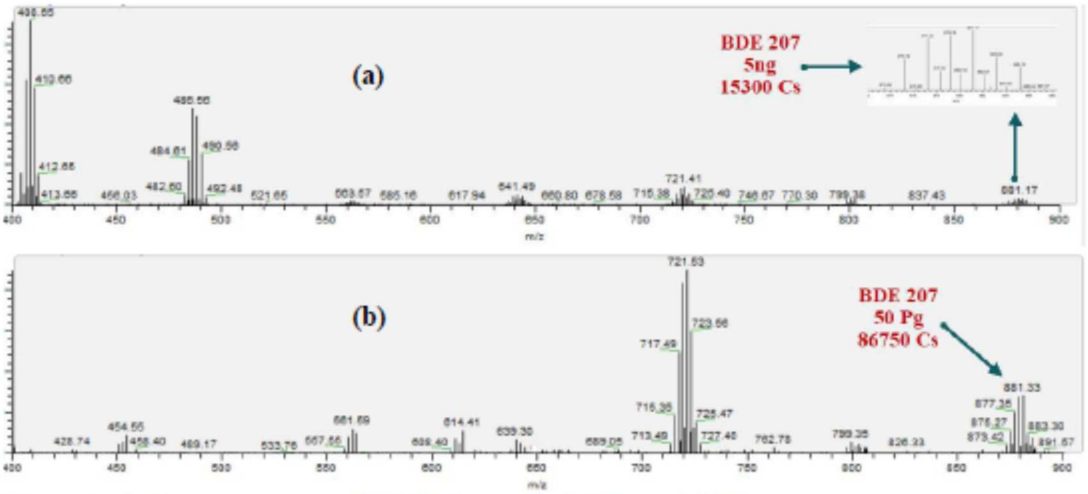
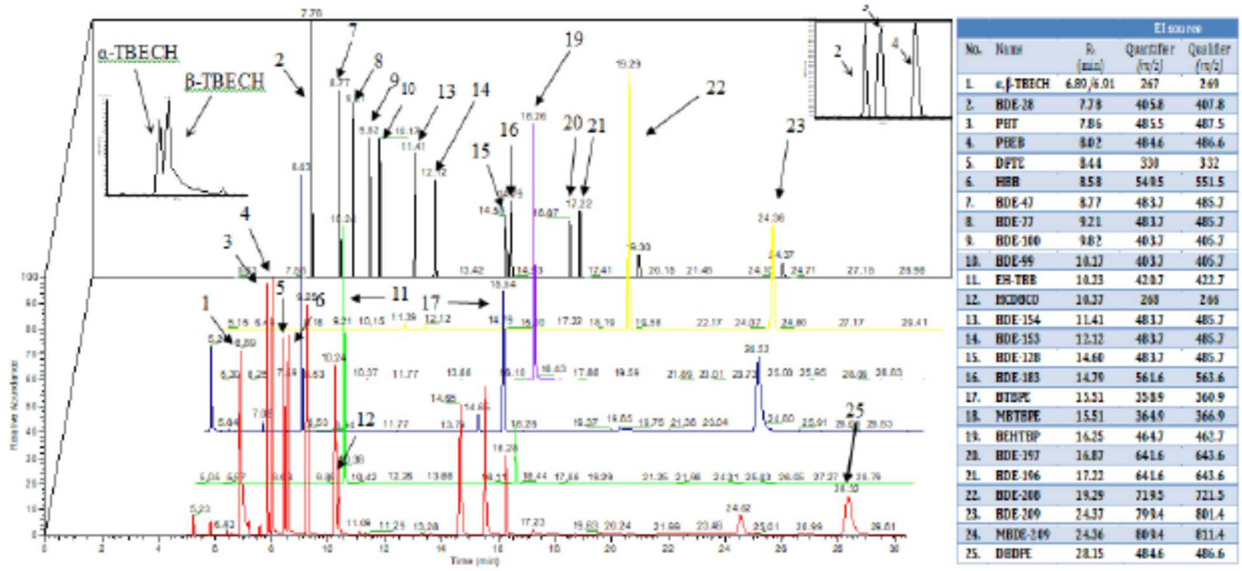


Figure 2: Electron inonisation mass spectrum of BDE-207 acquired at (a) 70 ev and (b) 35 ev.

3- Separation and determination of PBDEs and emerging BFRs

The efficiency of the separation and determination of PBDE and novel BFRs using the variable energy electron ionization GC-MS technique was examined using a standard mixture of 25 compounds. Simultaneous separation of the 25 compounds and the internal standards was achieved in 29 min. The dwell time parameter was optimized between 0.03 and 0.2 s in order to obtain good chromatographic peaks (with at least 15 points per peak) securing satisfactory sensitivity for all compounds. The results of separation of all the compounds are shown in Figure 3. The confirmation of analyte identity was established from GC retention times and the most abundant ion cluster from the full scan mass spectra. The retention times, quantifier and qualifier ions (m/z) for the studied 25 analytes are presented in Figure 3.



			EI source	
No.	Name	R_t (min)	Quantifier (m/z)	Qualifier (m/z)
1.	α,β-TBECH	6.80/6.01	267	269
2.	BDE-28	7.78	405.8	407.8
3.	PBT	7.86	485.5	487.5
4.	PBEB	8.02	484.6	486.6
5.	DPTE	8.44	330	332
6.	HBB	8.58	549.5	551.5
7.	BDE-47	8.77	483.7	485.7
8.	BDE-77	9.21	483.7	485.7
9.	BDE-100	9.82	403.7	405.7
10.	BDE-99	10.17	403.7	405.7
11.	EH-TBB	10.23	420.7	422.7
12.	HCDBCO	10.37	268	266
13.	BDE-154	11.41	483.7	485.7
14.	BDE-153	12.12	483.7	485.7
15.	BDE-128	14.60	483.7	485.7
16.	BDE-183	14.79	561.6	563.6
17.	BTBPE	15.51	358.9	360.9
18.	MBTBPE	15.51	364.9	366.9
19.	BEHTBP	16.25	464.7	463.7
20.	BDE-197	16.87	641.6	643.6
21.	BDE-196	17.22	641.6	643.6
22.	BDE-208	19.29	719.5	721.5
23.	BDE-209	24.37	799.4	801.4
24.	MBDE-209	24.36	809.4	811.4
25.	DBDPE	28.15	484.6	486.6

Figure 3: Chromatographic separation and characterisation of 25 BFRs (250 pg/µL mixture in isooctane).

The sensitivity of the developed method was compared to the more commonly applied GC-NCI/MS analysis via comparison of the peak areas obtained for each target analyte. Results revealed comparable sensitivities for the lower brominated compounds. However, the peak area of DBDPE increased nearly fivefold in EI mode compared to NCI. For other highly brominated compounds, the peak area also increased more significantly such as BTBPE, 8 times increase in the peak area, compared to twofold for BDE28. Interestingly, the peak area for BDE-209 was less (0.8) than that obtained with NCI analysis. Nevertheless, the signal to noise (S/N) ration was higher for all the studied analytes in EI mode due to less background interference at higher masses compared to the low masses monitored in NCI.

The method was finally applied for the analysis of NIST SRM 2585 dust using a previously reported extraction procedure [5]. The obtained results in generally in good agreement with certified and previously reported levels for the target BFRs in this SRM (Table 1).

Table 1: Average concentrations (ng/g) of BFRs in NIST SRM 2525.

	EI results (n=6)	SD	NIST certified values	Ali et al. n=2[6] (NCI/MS)	Sahlstrom et al. n=5[7] (NCI/MS)	Cristale et al. n=4[8] (GC-EI-MS/MS)	Van den Eede et al. n=6[9] (NCI/MS)
BDE28	55	3	46.9				
BDE47	568	11	497				
BDE99	916	19	892				
BDE100	139	3	145				
BDE153	130	6	119				
BDE154	95	4	83.5				
BDE183	38	2	43				
BDE209	2368	211	2510				
TBB	33	4		40	36(2.4)	35(6)	26(2)
BTBPE	57	7		32	39(4.9)	76(4)	39(14)
TBPH	618	25		652	1300(94)	857(73)	574(49)

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NATIONAL AND CONTINUOUS DIOXIN AIR MONITORING NETWORK IN TAIWAN (2006-2016): SPATIAL, TEMPORAL VARIATION AND EMISSION SOURCES APPORTIONMENT VIA POSITIVE MATRIX FACTORIZATION

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are formed and released unintentionally from anthropogenic sources, and may be transported long distances to other environmental compartments, so the atmosphere is a major pathway for the transport and deposition[1]. Due to the reasons, it is important to monitor the atmospheric PCDD/Fs concentrations and evaluate the potential sources. The Environmental Protection Administration of Taiwan established the ambient dioxin air monitoring network in 2006. The objective was to determine the concentrations of PCDD/Fs of different regions in Taiwan. Recently, the monitoring of atmospheric dioxin is just in the representative areas, including the industrial areas and adjacent areas. Furthermore, the winter monsoon and dust storm event not only brings cold air but also transports air pollutants and dust over long distances from mainland China to Taiwan[2, 3]. Receptor models are statistical methods to analyze the relationship between receptor sites and emission sources. Positive Matrix Factorization (PMF) is a multivariate receptor method and it was developed by Paatero and Tapper in 1994[4]. The PMF statistical results can be interpreted quantitatively and estimate the relative contribution of the various possible sources. Applications of PMF receptor modeling have been widely employed in air pollution and sediment pollution studies [5,6]. The objective of this study is to determine the concentrations and congener profiles of atmospheric PCDD/Fs and to identify the spatial and temporal characteristics, moreover, estimate the relative contribution of various emission sources by applying the PMF receptor modeling to apportion of PCDD/Fs in atmospheric in Taiwan.

Materials and methods

The Environmental Protection Administration of Taiwan established the ambient dioxin air monitoring network in 2006. Ambient air sampling was conducted from 2006 to 2016, and there are 86 air monitoring stations at different regions in Taiwan (Fig.1), 26 stations in northern, 8 stations in northwestern, 14 stations in central, 12 stations in southwestern, 19 stations in southern, 3 stations in northeastern, 3 stations in eastern and one background station in Mt. Lulin (2,862 m above mean sea level). Based on the Taiwan EPA standard method (NIEA A809.11B), ambient air samples for both PCDD/F compounds and total suspended particles were collected using high-volume sampling trains equipped with quartz fiber filters for collecting solid-phase PCDD/Fs. Polyurethane foam (PUF) plugs were used to retain PCDD/F compounds in the vapor phase. In this study, the analysis tool was used to reconstruct plausible contamination source of PCDD/F fingerprint patterns and calculate fraction contribution of plausible sources with PMF that is a receptor model and a multivariate method. The PMF 5.0[7] was used in this study which is provided by US EPA, to establish and analysis of the data set.

Results and discussion

Annual variations (2006-2016) in atmospheric PCDD/Fs I-TEQ concentrations measured at all stations in Taiwan were shown in Fig.2. The mean concentrations decreased gradually, particularly during 2010-2013. The annual mean concentrations were 48.1±44 and 31.7±31 fg I-TEQ/m^3 in 2007 and 2016, respectively, decreasing of 35% in ten years. From 2006 to 2016, the annual mean concentrations of PCDD/Fs for all regions was shown in Fig.3. At different regions, there was the highest and lowest concentrations in central Taiwan and background station at Mt. Lulin, respectively. The median concentrations of dioxin for other regions were 16.0 (n=195), 24.0 (n=116), 38.0 (n=165), 41.0 (n=190), 40.0 (n=147), 13.5 (n=38), 11.0 (n=69) and 1.47 (n=185) fg I-TEQ/m^3 in northern, northwestern, entral, southwestern, southern, northeastern, eastern and background station, respectively. The average concentrations of PCDD/Fs at all regions in Taiwan were lower than the Japanese annual standard (600 fg WHO-TEQ/m^3)[8] and the national Germany target value (150 fg I-TEQ/m^3)[9]. The seasonality of PCDD/Fs in atmospheric in Taiwan, where the levels in autumn and winter were higher than which in spring and summer (Fig.3). The mean concentrations were 31.5±28.5, 26.5±23.0, 37.3±33.2, and 61.5±48.3 fg I-TEQ/m^3 in spring, summer, autumn, and winter, respectively. Due to the increase of industrial activities and the seasonal variations were the likely causes. Fig. 4 demonstrated that the distribution of OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF at all regions in Taiwan, which accounted for 50-60%. The factor numbers of PMF model in Taiwan and in the different regions are presented in Table 1, respectively. The factor numbers selected could adequately reproduce the data set. The PCDD/F fingerprint patterns of the plausible sources (factors) in Taiwan was generated by PMF model. In Taiwan, the dioxin emissions from different stationary sources had been monitored by Taiwan EPA since 1999. The results indicated that the high abundances of PCDFs in the stack gas were observed in sinter plant and electric arc furnace (EAF), moreover, the difference between them were the amounts of PCDDs which were significantly higher in EAF compared to sinter plant emission. The difference between the municipal solid waste incinerator (MSWI) and the industrial waste incinerator (IWI) were the proportion of PCDFs. Generally, the abundances of PCDFs in IWIs were higher than in MSWIs in Taiwan. On the other hand, the secondary aluminum smelt plant (SAS) was characterized by higher amounts of OCDD, OCDF and 1,2,3,4,6,7,8-HpCDD, and the amount of PCDFs were higher than PCDDs. In contrast to SAS, the secondary zinc smelting plant (SZS) was characterized by higher amounts of OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and the amount of PCDDs were higher than PCDFs[10]. The PCDD/Fs in stack gases from cement kilns (CK) wearcharacterized by higher amounts of 1,2,3,4,6,7,8-HpCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF, and the amount of PCDFs were higher than PCDDs. Kuo[12] investigated the characteristics of PCDD/Fs in stack-flue gases from coal-fired power plants in Taiwan, indecated that characterized by higher amounts of OCDF, OCDD, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD, and the amount of PCDFs were also higher than PCDDs. Based on the previous atmospheric measurements during the long-range transport (LRT) events such as winter monsoon and dust storm event[2,3], the similar features of the atmospheric PCDD/F profiles can be observed. The results indicated mainly dominated by the high-chlorinated PCDD/F congeners of OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF, moreover, the fraction of total PCDFs were higher than the total PCDDs. Black et al.[12] indicated the characteristics of PCDD/Fs from open burning and biomass burning (BB), indecated that characterized by higher amounts of PCDFs and PCDDs, respectively. Considering these observations, in this present study, those factors were hypothesized to describe the individual contributions. The result indicated that the major contributors were EAF (50.8%), LRT (25.0%), MSWI/IWI (14.2%), BB (9.2%), and sinter plant (0.81%) in Taiwan. From 2006 to 2013, the major contributors were EAF (33.3%~67.5%), MSWI/IWI (9.1%~44.1%), LRT (1.7%~36.7%) in Taiwan. In addition, the candidate sources contributed to atmospheric PCDD/Fs at different regions in Taiwan were listed in Table 1. For different regions, the major contributors were MSWI (62.9%), EAF (60.1%), EAF(69.5%), IWI (62.6%), EAF (55.7%), LRT (51.9%), and co-combustion (86.1%) in northern, northwestern, central, southwestern, southern, northeastern, eastern and background station in Taiwan, respectively. The PCDD/F concentrations tended to decrease, but there were high concentration observed particularly in central Taiwan. It is important to continuous monitoring at the regular and futher control in industrial areas.

Acknowledgements
The authors gratefully acknowledge the financial support provided by the Environmental Protection Administration (100-EPA-F-001-001 and 102-EPA-F-006-001) and Ministry of Science and Technology (MOST 103-2628-M-010-001 and MOST 104-2628-M-010-001-MY3) of Taiwan.

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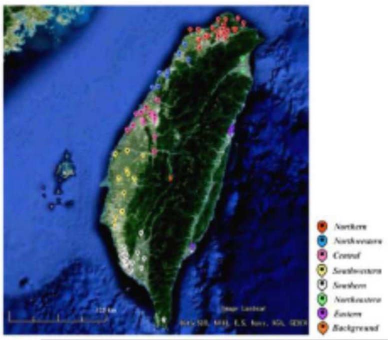

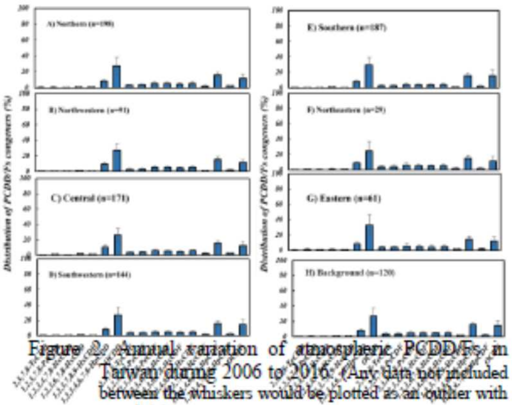

Figure 2. Annual variation of atmospheric PCDD/Fs in Taiwan during 2006 to 2016. (Any data not included between the whiskers would be plotted as an outlier with ○ and ★.)

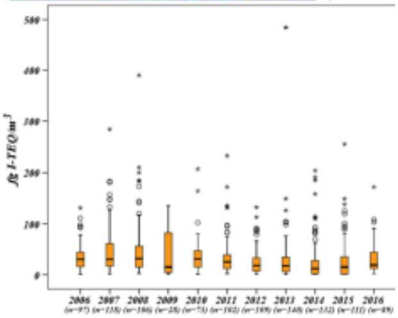

Figure 1. Ambient air monitoring network stations in Taiwan.

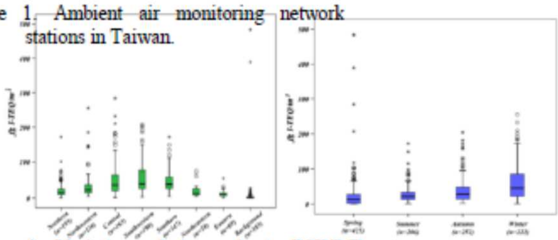

Figure 3. Variation of Atmospheric PCDD/Fs at different regions and season in Taiwan.

Figure 4. Congener profiles for PCDD/Fs in atmospheric of different regions in Taiwan.

(Any data not included between the whiskers would be plotted as an outlier with ○ and ★.)

Table 1. The possible sources contributed to atmospheric PCDD/Fs at different regions in Taiwan.

Regions	Factor	Candidate source	Contribution (%)	Regions	Factor	Candidate source	Contribution (%)
Northern	A	MSWI	62.9	Southwestern	A	BB	23.2
	B	EAF	19.6		B	Power plant	14.1
	C	LRT	17.5		C	IWI	62.6
Northwestern	A	EAF	60.1	Northeastern	A	LRT	51.9
	B	MSWI	17.5		B	EAF	4.2
	C	LRT	22.4		C	MSWI	33.7
Central	A	Power plant	15.3	Eastern	A	Co-combustion	86.1
	B	EAF	69.5		B	CK	8.4
	C	MSWI	15.1		C	BB	5.5
Southern	A	SAS	21.9	Background	A	BB	52.4
	B	SZS	21.3		B	Open-B	25.4
	C	EAF	55.7		C	Unknown	22.2
	D	Sinter plant	1.2				

High throughput GC-HRMS acquisition methods for the analysis of PCDD/Fs and PCBs in biological matrices

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) have been recognized as highly toxic and ubiquitous environmental contaminants. They have structure-related toxicity at low exposures and hence sample preparation and instrumental quantification requires determination of individual congeners at very low levels (ppb and ppt). For this reason sample preparation involves sophisticated and delicate multistage steps, which can also require several days. In the last few years a lot of effort has been expended in the development of high throughput methods to increase lab productivity and food safety, in the context of enhanced capacity to cope with potential dioxin crises [1]. In this paper, two Gas Chromatography coupled with High Resolution Mass Spectrometry (GC-HRMS) alternative acquisition methods have been developed for confirmatory analysis of Dioxins and PCBs in biological samples (food, feed and serum). The first method proposed uses a classical GC method and Dual Data Acquisition, a new system developed by Thermo Fisher Scientific, (Bremen, Germany). The second method is based on Fast GC using smaller and narrower chromatographic columns. Both methods increase lab productivity while maintaining similar performance of our ISO17025 validated method for the confirmatory analysis of Dioxins and PCBs in biological matrices. When coupling one of these acquisition methods with high throughput sample preparation already available in our lab [1], the quantitative analysis of one sample can be completed within 4 hours.

Materials and methods

Sample preparation in our laboratory provides two fractions per sample, one containing regulated PCDDs, PCDFs and coplanar-PCBs (co-PCBs, #77, 81, 126, 169), here referred to as "Dioxin fraction", and the other one containing mono-*ortho* (MO-, #105, 114, 118, 123, 156, 157, 167, 189) and indicator (I-, #28, 52, 101, 138, 153, 180) PCBs, here referred to as "PCB fraction". Analytical methods were developed accordingly. Nonane puriss analytical-reagent grade standard for GC, purchased from Fluka (Steinheim, Germany) was the injection solvent. A six point calibration curve for PCDD/Fs and co-PCBs, ranging from 0.05 to 10 pg/µL for Tetra- and Penta-congeners, was prepared from the following standard solutions: native PCDD/Fs and native co-PCBs standards were respectively the NK-ST-B4 and the BP-CP81 solutions, both purchased from Wellington (Wellington Laboratories, Guelph, Canada); ^{13}C-labelled internal standard (ISTD) for PCDD/Fs and co-PCBs was the EDF-4144 solution and ^{13}C-labelled recovery standard (RS) was the EDF-4145, both obtained from CIL (Cambridge Isotope Laboratories, Tewksbury, Massachusetts, United States). The EDF-4144 standard was also diluted and used as spiking solution for the quantification of native congeners with Isotope Dilution (ID) mass spectrometry; while the EDF-4145 was diluted and used to assess recoveries. An eight point calibration curve for MO- and I-PCBs, ranging from 0.4 to 140 pg/µL, was prepared using the following standards: EC-4987 (native MO-PCBs), EC-5179 (native I-PCBs), EC-4058 (^{13}C-labelled ISTDs for I-PCBs) and EC-1414 (^{13}C-labelled PCB 80 RS) were purchased from CIL, and MBP-MXK ^{13}C-labelled ISTDs for MO-PCBs was obtained from Wellington. ^{13}C-labelled ISTD solutions and ^{13}C-labelled PCB 80 RS solution were diluted and used to quantify the native compounds and assess recoveries for this fraction. GC-HRMS was used for the identification and quantification of all the congeners. For all the experiments in this study, a Double Focusing Sector (DFS) mass spectrometer from Thermo was connected by two heated transfer lines (270°C) to two GCs (Trace 1310 Series), each one provided with Split/Splitless (SSL) injector and connected to a TriPlus RSH autosampler. The HRMS instrument was operated in selected ion monitoring (SIM) mode with mass resolution at least 10,000 at a 10 % valley, using Perfluorotributylamine (PFTBA or FC-43) as the reference compound. The ion source was maintained at 260°C. Each chromatographic peak was defined by the acquisition of a minimum of 10 mass spectra. For part of this study, Dual Data Acquisition modules were installed on each GC. A DB-5ms 60 m × 0.25 mm × 0.25 µm column from Agilent (Agilent Technologies, Santa Clara, California United States) was used to separate PCDD/Fs and co-PCBs. Injection volume was 1 µL and the SSL injector was operated in splitless mode at 290 °C, with split flow 70 mL/min for 2 minutes and purge flow 5 mL/min. Helium carrier gas was maintained at constant flow rate of 1 mL/min. The oven temperature was maintained at 120 °C for 5 min, ramped at 25 °C/min to 250 °C and held for 5 minutes, then ramped at 2.5 °C/min to 285 °C for 16 minutes, and eventually at 10°C/min to 300°C for 5 minutes. The total temperature program took 51.7 min. An HT-8 25 m × 0.22 mm × 0.25 µm column from SGE (by Trajan Scientific and Medical, Ringwood, Victoria, Australia) was deployed for the separation of MO- and I-PCBs. A volume of 1 µL was injected in splitless mode at 290 °C, with split flow 70 mL/min for 2 minutes and purge flow 5 mL/min. Helium was used as the carrier gas at constant flow rate of 0.8 mL/min. The oven temperature was maintained at 140 °C for 2 min, ramped at 15.0 °C/min to 220 °C held for 7.5 min, ramped at 6.0 °C/min to 250 °C, ramped at 2.0 °C/min to 265 °C, and finally ramped at 28 °C/min to 320 °C, for a total separation time of 30 min. In this instance, mass spectrometric traces of two ions, for each native, ^{13}C-labelled ISTD and RS compounds were recorded in SIM. For the Fast GC experiments, both Dual Data modules were disconnected from the GCs. An Rtx-5 20 m × 0.18 mm × 0.20 µm column from Restek (Bellefonte, Pennsylvania, United States) was used for PCDD/Fs and co-PCBs. A volume of 0.7 µL was injected on the SSL injector in splitless mode at 290 °C, with split flow 70 mL/min for 2 minutes and purge flow 5 mL/min. Helium carrier gas was maintained at constant flow rate of 1 mL/min during all the temperature program reported in Table 1 (left side), for a total run time of 17 minutes. For the PCB fraction, an HT-8 10 m × 0.10 mm × 0.10 µm column from SGE was deployed. Injection volume for this narrow bore column was 0.3 µL. SSL injector was heated at 290 °C and working in splitless mode at 70 mL/min for 2 minutes and purge flow of 5 mL/min. Helium carries gas flow was 0.45 mL/min during the temperature program reported in Table 1 (right side), for a total run time of 11.5 minutes.

Table 1: Temperature programs for the analysis of Dioxins (left) and PCBs (right) in Fast GC

Dioxin fraction	Rate (°C/min)	Temp (°C)	Hold time (min)
Initial		120	1.3
1	60	225	2.8
2	20	232	1.6
3	30	245	0.8
4	2.5	253	0
5	20	283	2.5
6	80	310	0.5

PCB fraction	Rate (°C/min)	Temp (°C)	Hold time (min)
Initial		60	0.35
1	45	200	0
2	5	215	0
3	7	235	0
4	20	255	0
5	40	300	0

Results and discussion

Dual Data Acquisition**:** The Dual Data module consists of a switching valve where two columns are connected: the chromatographic column and a restriction, where only Helium as the carrier gas is flowing. The valve is able to divert the flow entering the ion source: during method waiting time (from the injection to the elution of the first analyte) pure Helium enters the ion source and column flow is directed to the purge. As soon as the first eluting compound approaches, the Dual Data valve switches and diverts column flow into the ion source for MS acquisition (measuring time), and Helium from the restriction to the purge. DFS equipped with two GCs, both with Dual Data modules, allows optimization of the acquisition rate, as the waiting time of one method overlaps with the measuring time of the other method, and *vice versa*. As described in the Materials and Methods section, in this case, the DB-5 60 m column and HT-8 25 m column were used for the analysis of Dioxins and PCBs respectively. The two chromatographic methods used in these experiments were part of an already validated procedure for the analysis of Dioxins and PCBs in biological matrices in our laboratory with proved chromatographic performances for biological matrices [2]. In particular, our Reference chromatographic method for the Dioxin fraction was divided into ~15 minutes waiting time and 37 minutes acquisition time; while the method for PCBs consisted of 7.5 minutes waiting time and 17.5 minutes acquisition time. Thus the total run time required per sample (two fractions) was around 76.7 minutes and 18 samples could be run per day. The introduction of the Dual Data Module allowed the measurement of one sample in 54.5 minutes and 26 samples per day, with almost 45 % productivity increase (Table 2). The Dual Data modules did not exert a discernible effect on peak shape and calibration curves, while procedural blanks and Quality Control samples (QCs, prepared in house) injected when modules were installed gave comparable results to our classical acquisition method. Full validation of the method involving Dual Data modules was not carried out, but our results showed that this new technology is valuable tool for faster quantification of Dioxins and PCBs in biological matrices.

Fast GC: Fast GC methods, using a shorter and narrower column, were developed for high throughput analysis of PCDD/Fs and PCBs. No Dual Data module was installed in this set of experiments, because preliminary results showed poorer peak shape quality for these sharper peaks. Chromatographic resolution with such columns was lower in comparison with our classical acquisition method, but it was still fit-for-purpose. Possible MS interferences were resolved chromatographically, making sure that all ^{13}C-labelled PCDFs were separated from all native Dioxins, as well as co-PCBs (#126 from Tetra compounds and #169 from Pentas). GC separation of 1,2,3,4,7,8- HexaCDF and 1,2,3,6,7,8-HexaCDF isomers was better than 25 % peak to peak, as required by the EU Regulation for food and feed matrices [3] (Figure 1). The method developed for PCB fraction assured the separation of tri-chlorinated CBs, like #31 and 28, as well as of Penta-chlorinated congeners such as #163 and 138, and 123 and 118. Also the hexa-chlorinated CBs #156 and 157 were completely resolved. The DFS analyzer was required to work with high acquisition frequency because of peak squeezing. To assure the acquisition of at least 10 points for each chromatographic peak, two ions were recorded for each native compound, but only one for the ^{13}C-labelled ISTD and RS, as their concentration was between 5 to 50 times higher than native compounds in the calibration range. Dwell times for each congener were optimized to achieve the highest sensitivity while retaining good peak shape. Peak squeezing also improved the Signal-to-Noise ratio (S/N), allowing the detection of 19 fg TCDD on column, with S/N 202 (Figure 2). LOD and LOQ calculation is still ongoing, but they are expected to be lower than for our reference method. A six point calibration curve was injected for both fractions, and Relative Response Factor (RRF) relative standard deviation (RSD) was lower than 15 % for all the congeners, as required by EU Regulation. Fast GC methods allowed the analysis of a single sample, both fractions, in 28.5 min, and hence 50 samples per day. Productivity increase using Fast GC could be up to 177 % (Table 2).

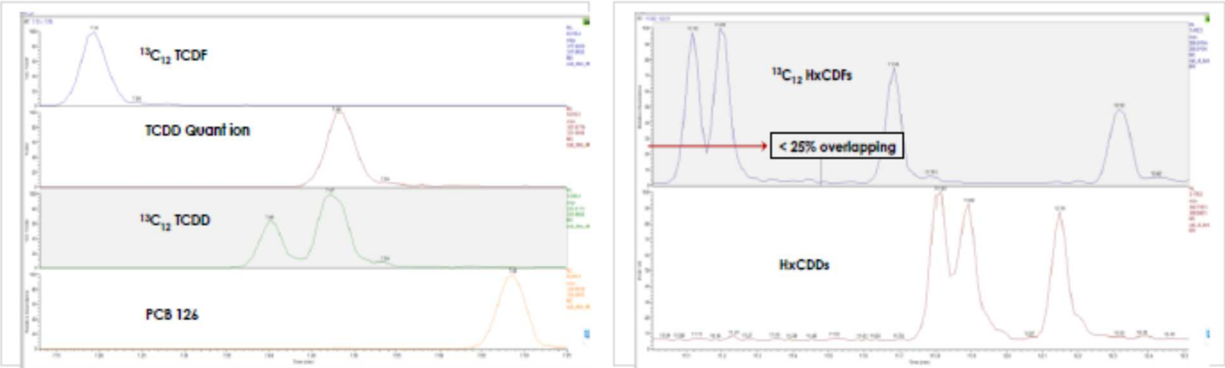

Figure 1: Chromatographic separation of Tetra- and Hexa-CDD/Fs using Fast GC

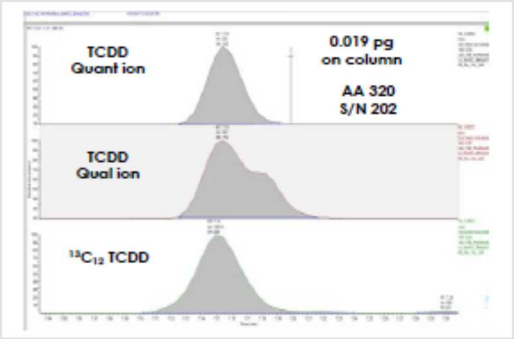

Figure 2: Signal of 19 fg of TCDD on Rtx-5 column analysed in Fast GC

Table 2: Comparison between productivity using our Reference method, Dual Data method, and Fast GC method

	Time/single sample(min)	Number of samples/day	Productivity increase
Reference method	76.7	18	
Dual Data method	54.5*	26	~45 %
Fast GC method	28.5	50	~177 %
* First sample of the series 62 min (waiting time of the first injection, 7.4 min, cannot be saved)			

Full validation of the Fast GC method is still ongoing, but these results show this technique could be used for the confirmatory analysis of Dioxins and PCBs in biological matrices.

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Integration of polybrominated diphenyl ethers (PBDE) and other brominated compounds into the automated sample preparation for dioxines and PCBs.

Introduction

Polybrominated diphenyl ethers (PBDE) are almost omnipresent persistent contaminants of the environment and subsequently food and feed. Due to their physico-chemical properties, they have been used as flame retardants. Different to other persistent organic pollutants (POPs) like dioxins and PCBs, overall PBDE concentrations have been increasing within the last years. Historically, the use of PBDE as flame retardants has tremendously increased since the early 1970s but their commercial production and use of PBDE mixtures has been banned in the EU since 2004 by the EU Restriction of Hazardous Substances (RoHS). In 2008 the use of BDE-209 in electronics was stopped. Although, the ban on PBDE and other brominated flame retardants (BFR) has been in place for some years, the continuous use of brominated substitutes as well as the gradual disposal of old products containing BFRs ensure a significant source of these contaminants for the future years. The global material cycle inevitably spreads PBDE and other brominated compounds into the environment. This subsequently lead to human consumption and intoxication of liver, thyroid hormone homeostasis, as well as the reproductive and nervous system [1, 2]. Moreover, many questions regarding ecotoxicological relevance have not been answered yet [3]. According to the 2011 European Food Safety Authority (EFSA) report [1] milk and dairy products belong to the most contaminated food categories, yet, also baby food contains a vast variety of ingredients of different origins and is under extraordinary control. Although, the eight BDE-congeners are of interest, only four of them derived a benchmark dose by EFSA. As PBDD/Fs, the brominated counterparts of PCDD/F, can be subsequent decomposition products of PBDEs further surveillance is urgently required. Besides the analytical questions of accuracy and precision, also economic factors e.g. working time, solvent consumptions and consumables are important aspects in daily laboratory work. Hence, a wide-range of matrices covering and reliable but cheap method had to be developed, to analyse a broad variety of PBDE congeners and other brominated compounds simultaneously to PCB, PCDD/F but also PBDD/F compounds. The first step of developing an automated sample preparation system used a classical four column set-up (multilayer sulphuric acid column, Florisil® column and two activated carbon columns) to clean-up PBDEs in addition to PCDD/F and PCBs [4]. Although, all chlorinated compounds were cleaned up adequately, the approach showed a rather insufficient performance for brominated molecules [5]. A replacement of the Florisil® column by alumina was tested. As the results for brominated substances improved, the alumina column method marked the starting point to reduce the system technically to a three-column approach as shown in figure 1. This reduction of one column lead to a variety of advantages. Most importantly, high quality results were achieved, yet, the run-time as well as the solvent consumption were minimized. This automatically made the method more cost saving, too.

Material and methods

Chemicals and Standards

PBDE-Standards (EO-5320-A) and solvents were obtained from LGC (Wesel, Germany). Basic alumina B for dioxin analysis (Cat.No. 04569) was delivered by MP Biomedicals (Eschwege, Germany). All columns for the DEXTech Plus device (silica gel with sulfuric acid, alumina and active carbon) were provided by LCTech (Obertaufkirchen, Germany).

Fat-Extraction

To receive the fat fraction the breast milk samples were separated by centrifugation. This procedure was repeated twice with the aqueous phase. The collected fat fractions were mixed with sodium sulfate and extracted by n-hexane/acetone (2/1). After drying and weighing the obtained fat internal standards were added for the determination of PBDE and PBDD/F.

Clean-up

Automated sample preparation was done by using a DEXTech Plus device (figure 1a). The automated clean-up method was originally developed to analyse polychlorinated dioxins and furans (PCDD/Fs) as well as polychlorinated biphenyls (PCBs) in food and feed [4]. Besides mono-ortho- and ndl-PCBs, PBDEs are eluted in fraction 1 by a n-hexane/Dichloromethane-mixture (1/1, v/v). (figure 1b). Recovery standards were added to extracts for analysing by GC-HRMS (see figures 2a (^{13}C12-labelled PBDE-Standard) and 2b (native PBDEs)). The second fraction containing non-ortho PCBs as well as PCDD/Fs and PBDD/Fs (figure 1b) was only partly taken into account for this study.

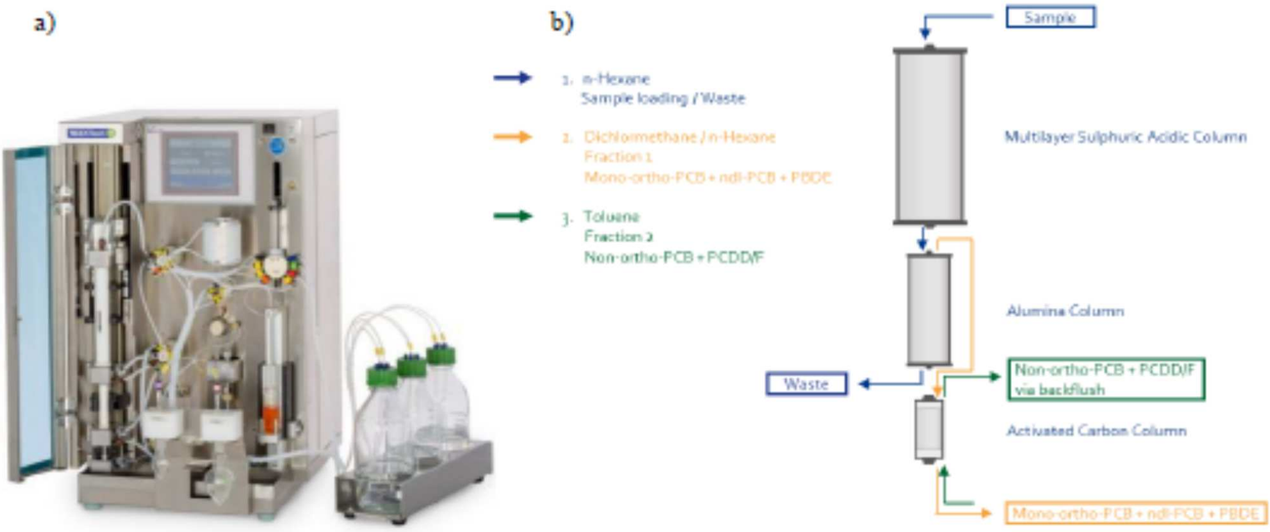


Figure 1a: The current Dextech Plus system. Figure 1b: Flowpath of the Dextech Plus. The Sample is loaded with hexane on the alumina column after lipid degradation on the acidic silica column.Degradation products go to waste while interesting compounds are trapped on the alumina column. Mono-ortho-, non-dioxine-like-PCBs and PBDEs are separated from the planar compounds and collected as Fraction 1 by a 1:1 mixture of dichloromethane and n-hexane.PCDD/F and coplanar-PCBs are retained on the top of the carbon column and collected in backflush elution with toluene.

Instrumentation

A Thermo DFS 2-GC/HRMS in EI+ mode with MID at resolution 10,000 was applied for measuring all fractions, using FC 5311 as internal mass reference. One GC was fitted with two columns (Rtx-Dioxin2, 60 m x 0,25 mm x 0,25 µm to analyse PCDD/Fs, non-ortho-PCBs and PCB-11 as well as DB-5ms, 15 m x 0,2 mm x 0,1 µm for PBDEs and PBDD/Fs). The other GC was used for measuring mono-ortho- and ndl-PCBs with one column (SGE-HT8-PCB, 60 m x 0,25 mm). All separation columns are provided with a 5 m deactivated guard columns with next higher diameter to ensure better evaporation, to avoid contamination of the separation columns and to maintain retention times. The MS-source had the inlet of three columns all the time. If one column is active, both others are in a stand-by-mode with less carrier gas flow. All injectors are PTVs.

Quantification

PBDEs and PBDD/Fs were separated on a short column (15 m), to reduce risk of on column degradation of higher brominated diphenylethers, with thin film (0,1 µm) to obtain sufficient separation. The PTV-injector is also essential to avoid degradation especially of higher brominated diphenylethers. As most intensive ion M+ is used for Tri- to Penta-BDE and [M-2Br]+ for Hexa- to Deca-BDE as a function of GC temperature [6]. It must be pointed out that the blank values of PCB-11 have to be subtracted from the measured sample-values.

Quality control

In general each sample is spiked with ^{13}C12-labeled internal standard solutions at the beginning of the fat-clean-up. At the end of the sample preparation a ^{13}C12-labeled recovery standard solutions was added to determine the recoveries for each congener. According to Commission Regulation (EU) 2017/644 [7] recoveries were in the screening range of 30 to 140%, almost all of them in the confirmatory range of 60 to 120%. To ensure correct measure conditions a diluted calibration solution was embedded in every sequence.

LOD/Q

LOD level was defined as S/N 3:1 and LOQ as S/N 10:1 and automatically determined by Thermo TargetQuan software.

Results and discussion

The complete approach was run with various samples and matrices. Besides the results for breastmilk preparation and analysis in this study also bovine milk and infant food was tested in another study (Bernsmann et al., unpublished data) focussing on matrix-specific difficulties and subsequent overall comparability of achieved results. Looking at breast milk, the recoveries of PBDEs we reached are comparable to the recoveries for PCBs and PBDD/Fs (table 1).

Table 1: Average percentage recoveries from all internal standard congeners over five breast milk samples from one analytic series determined in each particular DEXTech Plus-fraction.

DEXTech-Fraction	mono-ortho-PCB	recovery [%]	ndl-PCB	recovery [%]	PBDE	recovery [%]	DEXTech-Fraction	PCDD	recovery [%]	PCDF	recovery [%]	PBDD	recovery [%]
1	PCB 123	94	PCB 28	62	BDE-28	57	2	2,3,7,8-TCDD	72	2,3,7,8-TCDF	84	2,3,7,8-TBDD	89
	PCB 118	79	PCB 52	68	BDE-47	72		1,2,3,7,8-PeCDD	69	1,2,3,7,8-PeCDF	73	1,2,3,7,8-PeBDD	82
	PCB 114	83	PCB 101	78	BDE-100	96		1,2,3,4,7,8-HxCDD	84	2,3,4,7,8-PeCDF	77	1,2,3,4,7,8-HxBDD	92
	PCB 105	94	PCB 153	74	BDE-99	70		1,2,3,6,7,8-HxCDD	88	1,2,3,4,7,8-HxCDF	90	1,2,3,6,7,8-HxBDD	92
	PCB 167	82	PCB 138	71	BDE-154	80		1,2,3,4,6,7,8-HpCDD	99	1,2,3,6,7,8-HxCDF	92	1,2,3,4,6,7,8-HpBDD	122
	PCB 156	94	PCB 180	87	BDE-153	76		OCDD	101	2,3,4,6,7,8-HxCDF	90	OBDD	144
	PCB 157	88			BDE-183	90				1,2,3,7,8,9-HxCDF	92		
	PCB 189	90			BDE-197	99				1,2,3,4,6,7,8-HpCDF	93		
					BDE-203	97				1,2,3,4,7,8,9-HpCDF	100		
					BDE-208	82		non-ortho-PCB	recovery [%]	lower chlorinated	recovery [%]	PBDF	recovery [%]
					BDE-207	76		PCB 81	103	PCB 11	40	2,3,7,8-TBDF	82
					BDE-206	97		PCB 77	103			2,3,4,7,8-PeBDF	84
					BDE-209	35		PCB 126	120			1,2,3,4,7,8-HxBDF	91
								PCB 169	134			1,2,3,4,6,7,8-HpBDF	127
												OBDF	28

Moreover, also lower chlorinated PCBs as 3,3′-Dichlorobiphenyl (PCB11) were recovered in a range suitable within the screening level [7]. Figures 2-3 show distinct peaks for spiked internal standards but also for native congeners. They proof the cleanliness of the sample fractions after preparation, thus, successful implementation of the alumina column into the three column approach of the DEXTech Plus system. In summary, this instrumental and methodical setup allows to provide brominated flame retardants PBDE and their thermal decomposition products PBDD/F in addition to chlorinated compounds PCDD/F, dl- and ndl-PCB for measurement via HRMS.

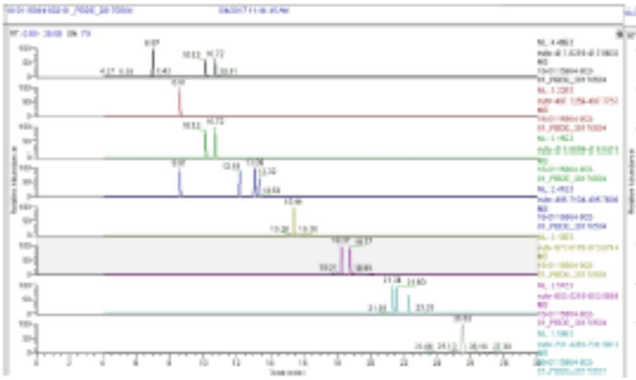
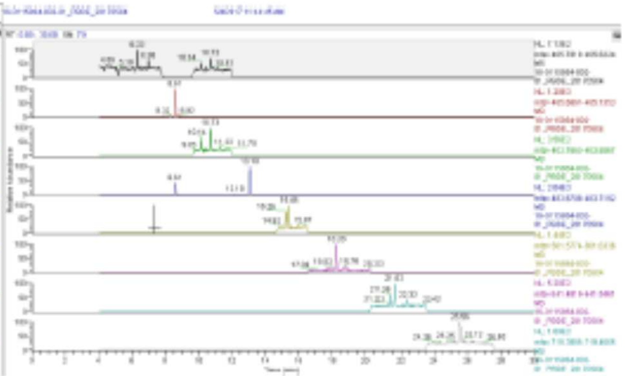


Figure 2a: HRMS-chromatogram from internal PBDE-standards



2b: HRMS-chromatogram from native PBDE-congeners in one particular breast milk sample

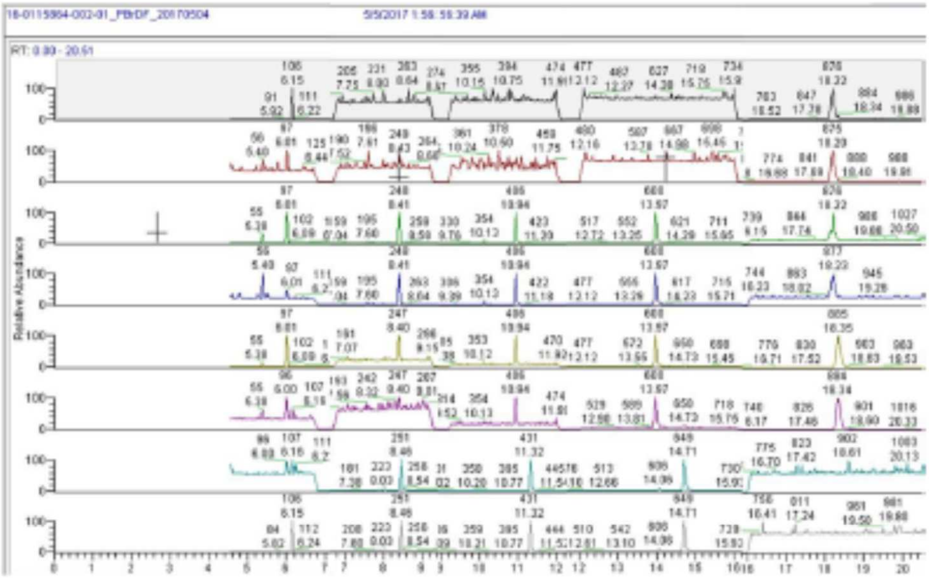


Figure 3: Framed PBDD/F-chromatogram from HRMS-measurement with 5 recorded functions

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Organic and inorganic persistent pollutants monitoring: emission source identification

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Introduction

Air quality and human health are closely bound: among the exposure paths, the inhalation of contaminated air and dusts is probably the major route of exposure to xenobiotics, second only to diet [1]. Air pollution is the result of the contribution of different emission sources and anthropogenic activities and is of high concern for international, national and local governments. The potential hazard of some toxic elements such as PCDD/Fs, PCB, PAH and metals (As, Cd, Cr, Ni, Hg and Pb) is well known [2,3].

In the present study, ambient air samples were simultaneously collected at six locations in Brescia, a city in the North of Italy whose large scale industrial development has resulted in an impact on the surrounding environment. Seven sampling points were chosen in the proximity of a chemical factory - the only Italian PCB producer operating from 1930 to 1984 - indicated as the principal responsible for PCDD/Fs and PCBs soil concentrations- that are higher than legal limits in surrounding areas [4]. The purpose of this study is to identify other source emissions different than the chemical factory that are accountable for air pollution in the considered site, using Principal Component Analysis (PCA).

Materials and methods

Heavy metals (As, Cd, Cr, Ni and Pb) were quantified on one tenth of each filter using an atomic absorption spectrometer equipped with a transversely heated graphite atomizer furnace (Analyst 600, Perkin Elmer, MA USA), after microwave acid digestion [5]. PAHs, PCBs and PCDDFs were extracted from the filters and the PUFs as previously reported [6]. The extract was injected into an automated clean up system consisting of a gel permeation chromatography (GPC) module (AccuPrep™ J2 Scientific, Columbia, MI, USA) coupled to an evaporator (AccuVap™) and three solid phase modules able to manage the acid silica/neutral silica, basic alumina and active carbon columns SPE purification. The extract, at a volume of 5 ml, was injected into the GPC system using dichloromethane as the mobile phase. The system used a 5 mL sample loop and a flow rate of 5 mL/min. The GPC column was calibrated according to US-EPA Method 3640A. The eluate was collected between 23 and 45 minutes and concentrated to a final volume of 5 ml. Ten percent of sample collected was than concentrated under nitrogen flow to 100 µL and submitted to instrumental analysis for PAHs. The remaining 90% was concentrated to 0.5 ml and then diluted with n-hexane to 5ml. The sample was submitted to an automated clean up using acid silica/neutral silica, basic alumina and active carbon columns [7]. PAHs were analyzed using a HRGC-NICI-LMRS equipped with a fused silica capillary column. PCDD/Fs and PCBs were quantified using a TRACE GC2000 coupled with a Mat 95 XP Mass spectrometer (Thermoquest, Bremen, Germany) operating in the electron impact ionization (EI+) mode.

Results and discussion

Ambient air was sampled (58 samples) at seven sites: CR, CR30, SPG, SK, IVC, QIM and SE. Table 1 shows the pollutants air concentration. Municipal solid waste incinerator (MSWI), chemical, metallurgical and steel plants, cement factories, thermoelectric power station and vehicular traffic are the main emission sources in the study area. They have direct relationships with the analyzed contaminants [8,9] as reported in Table 2.

Table 1. PCDD/F, PCB, PAH and metals concentrations

Location	Hg ng/m^3	Cd ng/m^3	As ng/m^3	Pb ng/m^3	Cr ng/m^3	Ni ng/m^3	PCDD/Fs[1] pg/m^3	PCBs[2] pg/m^3	PAH[3] ng/m^3
CR	29.76	3.86	18.29	6.56	28.63	20.54	0.04	0.02	0.06
CR30	23.03	3.15	29.66	13.54	19.68	14.18	0.04	0.02	0.17
SPG	27.67	1.81	13.15	24.44	20.80	20.94	0.04	0.13	0.06
SK	40.77	3.21	23.06	14.07	23.03	21.35	0.05	0.02	0.08
IVC	31.44	2.05	9.44	17.04	18.79	10.98	0.03	0.03	0.11
QIM	24.06	2.89	20.33	28.63	16.77	27.37	0.05	0.14	0.05
SE	22.11	2.20	69.38	2.12	47.86	19.22	1.49	0.01	0.09

1 I-TEF WHO 2005; 2 I-TEF WHO 2005; 3 B(a)P EPA equivalent

Table 2. Relationships between emission sources and contaminants

Emission source	Typical emissions
Thermoelectric power stations	Ni
Municipal solid waste incinerators	Cd, Hg, PAH, PCB, PCDD/F
Vehicular traffic	Pb, PAH
Metallurgical and steel plants	As, PCDD/F
Carbon combustion plants	As, Cr, PCDD/F
Chemical plants	Hg, PCB

PCA technique was used to identify the different pollutant sources in the seven considered sites. Table 3 describes the analytical results. Four PCs have been calculated, identifying four different emission sources. PCs accounted for 69.3% of the cumulative variance. PC1 show a high positive correlation with As, Cr and PCDD/Fs, PC2 presents high positive correlation with Cd and PAH, PC3 "saturates" Ni, while PC4 is positively correlated with Hg and negatively correlated with PCBs. Pb shows a low negative correlation with PC3. Some of relationships between original variables and PCs are graphically represented in Fig. 1-4

Relationships shown in Table 2 and in Figures 1-4 suggest four pollutant's emission typologies:

PC1: Carbon combustion plants, characterized by Cr, As and PCDD/F; PC2: Municipal solid waste incinerators, characterized by Cd, PAH; PC3: Thermoelectric power stations, characterized by Ni; PC4: Chemical farm, PCBs producer, characterized by Hg and PCB.

In addition, a score plot of the sampling sites with respect to PC1 (Fig. 5) shows that carbon combustion plants are the main emission sources for the SE site, while the other six locations are subjected to multisource atmospheric pollution.

Table 3 – Principal Components Analysis: rotated component matrix and variance explained

Element	PC1	PC2	PC3	PC4
Hg	-0,310	-0,214	0,072	0,769
Cd	0,055	0,836	-0,004	-0,021
As	0,760	0,322	0,001	-0,025
Pb	-0,312	0,054	-0,633	0,144
Cr	0,766	0,082	0,341	-0,147
Ni	-0,025	0,044	0,861	0,190
PCDD/F	0,836	-0,233	0,067	0,141
PCB	-0,368	-0,229	0,010	-0,729
PAH	0,018	0,764	0,006	0,012
% variance	*24,4*	*17,2*	*14,1*	*13,6*
% Cum. variance	*24,4*	*41,6*	*55,7*	*69,3*

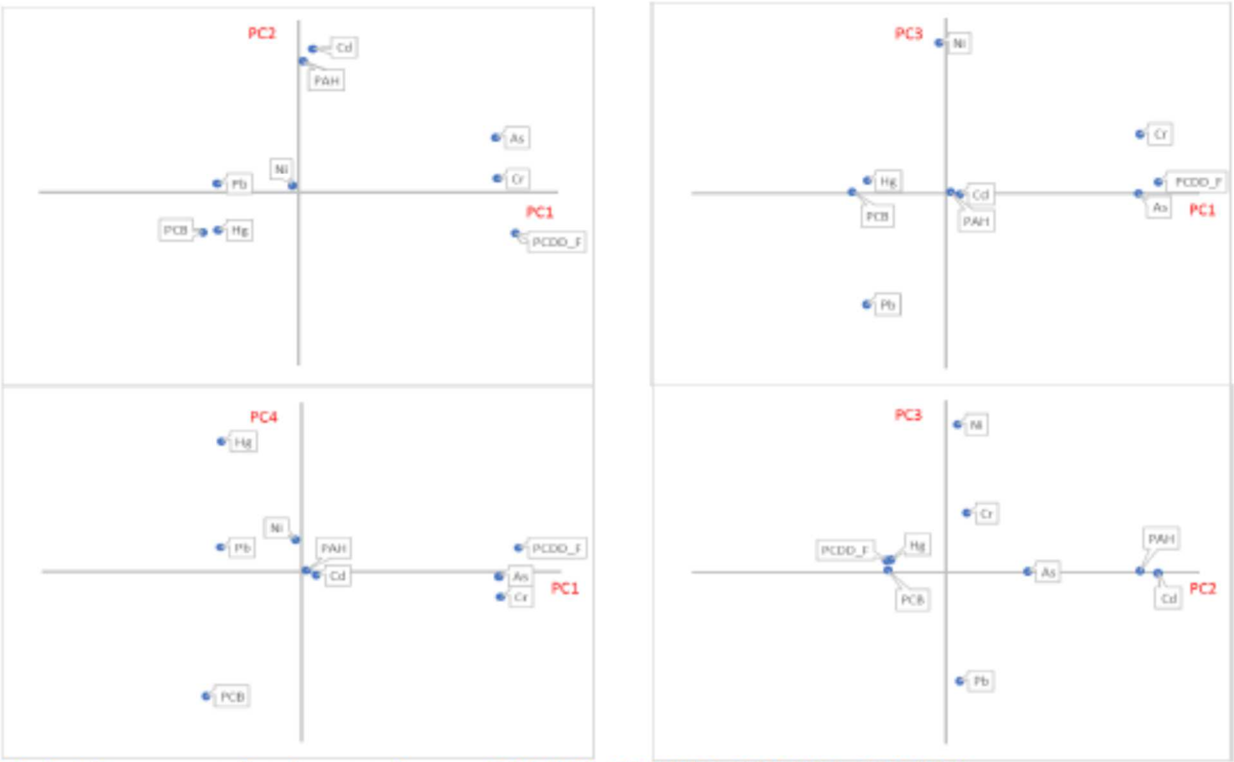

Fig 1-4 Component plots in rotated space: PC1-PC2; PC1-PC3; PC1-PC4; PC3-PC4

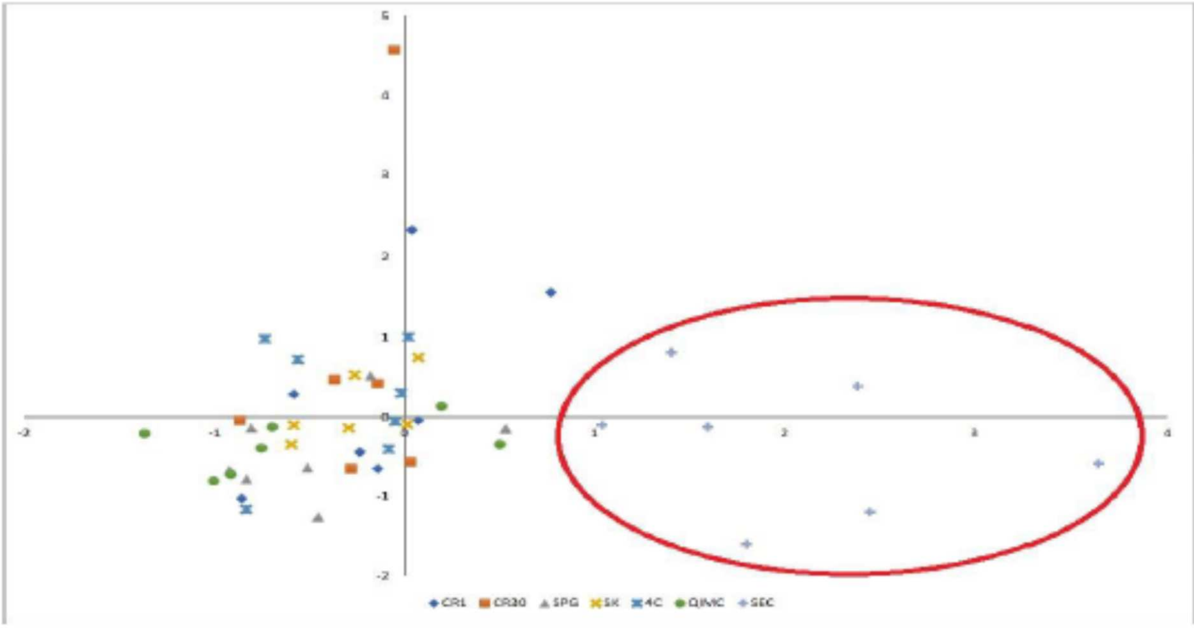

Fig. 5 Score plot in PC1 space: cluster identify PC1 (carbon combustion plants) such as a source *fingerprint* for SE

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Target, Suspect and Non-Target Screening of Dioxin-Like Compounds in Sediment and Fish Using A Sensitive High-Resolution Time-of-flight Mass Spectrometer

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and planar PCBs (pPCBs) are highly toxic and present at very low concentrations (ppt-ppq) in environmental samples. Highly sensitive and selective gas chromatography sector high-resolution MS (GC-HRMS) systems have therefore been the gold standard for measurement of these compounds. In the last decade, GC triplequadrupole MS systems have become sufficiently sensitive to offer an alternative to GC-HRMS. Recent developments in ion source, analyzer and detector design of high-resolution GC quadrupole time-of-flight MS (GC/Q-TOF) systems has resulted in improved sensitivity and resolution. Such instruments may now be feasible alternatives to GC-HRMS, offering high sensitivity, high selectivity and verification of identity through full-spectrum EI spectra. The performance of such a system was evaluated in the current study for the analysis of both biotic (fish) and abiotic (sediment) samples.

The utility of the GC/Q-TOF systems extends beyond trace-analysis of target compounds, such as PCDD/Fs and pPCBs. The entire full-spectrum data is written to disc and is available for various post-acquisition tasks, such as suspect and non-target screening. To illustrate this we have screened a sediment sample for dioxin-analogues such as polychlorinated naphthalenes (PCNs), polychlorinated dibenzothiophenes (PCDTs) and polychlorinated thianthrenes (PCTAs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs). We also used non-target screening workflows to find additional planar halogenated compounds.

Materials and methods

Samples were spiked with ^{13}C-internal standards and extracted by Soxhlet (sediment) or column extraction (salmon) in Umeå. Extracts were cleaned up using sulfuric acid treatment and carbon column fractionation using ISO/IEC 17025 accredited methods. The planar halogenated aromatic compound fraction from the carbon column was shipped (coded) to Agilent, CA; data were acquired using a novel 7250 GC/Q-TOF system equipped with a novel ion source. The GC analysis was performed by split-less injections (1 µL) onto an Agilent DB-5MS column (60m long, 0.25 mm ID, 0.25 µm film thickness). The oven temperature program was 90 °C (2 min), raise at 15 °C/min to 190 °C, raise at 3 °C/min to 300 °C. Helium was used as carrier at a constant flow of 1.2 mL/min. Electron ionization was used at an electron energy of 70 eV. Centroid and profile data was collected over the m/z range 50 to 1200. The mass resolution was 25,000 or better.

To aid the data analysis, an accurate mass library containing spectra of PCDD/Fs and pPCBs (natural and 13C-labelled analogs) was created in a .cdb format. The data were processed using MassHunter Qualitative Analysis Find-by-Fragment screening workflow for quick detection of the target compounds, which were later quantified using MassHunter Quantitative Analysis software. The quantification was based on calibration curves and internal standard normalization.

Results and discussion

The accurate mass PCDL (Personal Compound Database and Library) that was created using spectra of 46 native and labeled PCDD/Fs and pPCBs proved highly useful in both qualitative screening and quantitative workflows. The new Find-by-Fragment screening workflow was effective in extracting target compound features from the complex data and provided a comprehensive overview of the results.

The sensitivity was good with the lowest point of the calibration graph generally below 100 fg (even lower for tetra- and penta-congeners). Two sets of comparison data were available: one small set from GC-HRMS analyses of the sample extracts prior to shipment to CA, and one large set from previous analyses of the samples (in-house reference materials, RMs). There was good agreement between the GC-HRMS data and the average RM values (Table 1). The GC/Q-TOF data for the toxicologically most relevant congeners (PCB126, 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8- and 2,3,4,7,8-PeCDF) were within ± 25 % of the GC-HRMS and RM values. Similarly, the dioxin toxic equivalency values (TEQs) were within ± 19 % of the comparison data. Larger deviations between the GC/Q-TOF and the comparison data were observed for hexa- and hepta-CDD/Fs and octa-CDD/F that were present at levels close to the limit-of-quantification. All congeners with good signal quality, i.e. a signal-to-noise ratio equal to or better than 10, were within +/– 40 % of the RM values.

Table 1: Comparison of GC-QTOF-HRMS and GC-Magnetic Sector-HRMS results.

Congener	**Sediment**			**Salmon**		
	QTOF	Sector	RM mean	QTOF	Sector	RM mean
PCB-77	32	37	36	1125	900	910
PCB-81	3.5	1.8	1.8	23	23	26
PCB-126	8.8	8	7.3	464	410	430
PCB-169	3.9	1.8	1.6	53	53	58
2,3,7,8 -TCDD	**1.8**	**1.5**	**1.5**	**2.3**	**2.6**	**2.7**
12378 -PeCDD	**3.2**	**3.2**	**2.8**	**4.7**	**4.4**	**4.6**
123478 -HxCDD	6.4	1.8	2.1	0.4	0.3	0.3
123678 -HxCDD	14	11	11	3	1.7	1.9
123789 -HxCDD	8.2	7	6.8	0.2	0.1	0.2
HpCDD	40	34	36	0.7	0.3	0.3
OCDD	137	100	113	1.9	0.9	1.2
2378 -TCDF	**13**	**14**	**17**	**26**	**23**	**23**
12378 -PeCDF	**4.7**	**4.1**	**4.2**	**4.2**	**5.4**	**5**
23478 -PeCDF	**11**	**10**	**9.4**	**29**	**26**	**25**
123478 -HxCDF	7	7.1	9.1	1.3	0.9	0.9
123678 -HxCDF	10	5.1	4.5	2.7	1.2	1.2
234678 -HxCDF	8.5	6.1	6.1	1.5	1	0.9
123789 -HxCDF	3.7	1.9	2.3	ND	0.2	0.2
1234678 -HpCDF	95	76	77	0.2	0.3	0.3
1234789 -HpCDF	8	3.1	3.4	ND	0.1	0.1
OCDF	130	94	105	1.6	0.2	0.3
TEQ	**18**	**15**	**15**	**67**	**60**	**63**

Suspect screening revealed PCNs, PCDTs, and PBDDs in the sediment samples, with PCNs as the most abundant class of dioxin-like compounds. The PCN levels were slightly higher than those of PCDFs. Non-target screening showed that Polycyclic Aromatic Compounds (PACs), incl. PAHs, dominated the dioxin fraction, and also revealed many halogenated PAHs (halo-PAHs) (**Figure 1**). The abundances (area units) of halo-PAHs were about 100-fold lower than those of the parent PAHs, and were declining with increasing degree of halogenation.

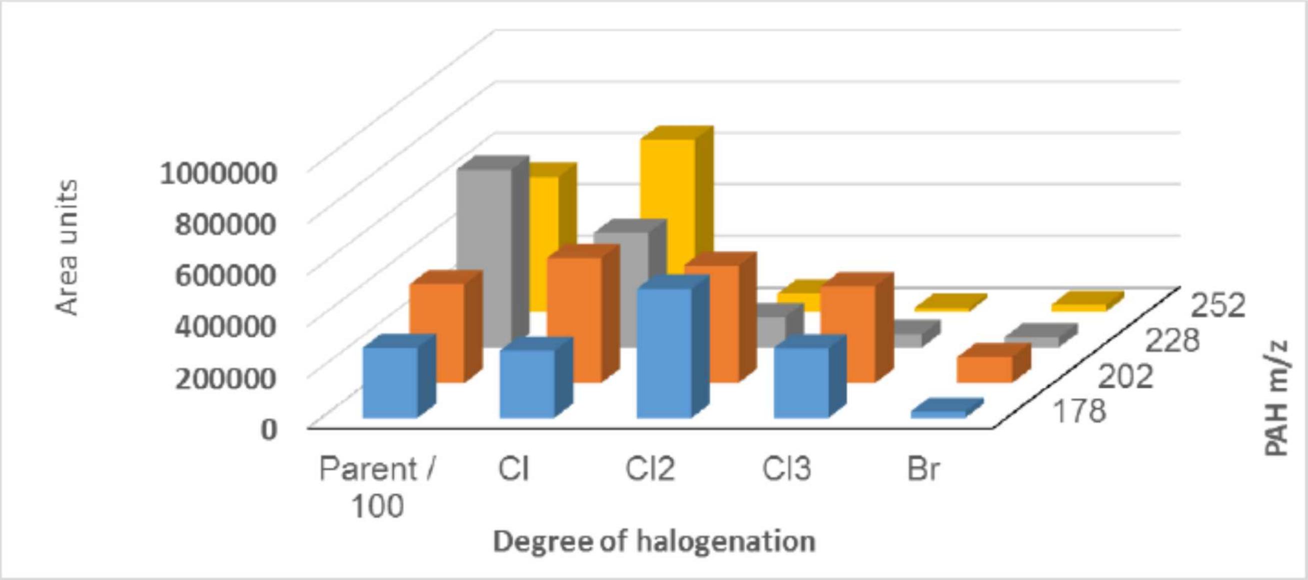

Figure 1. Abundances (peak heights) of parent PAHs and their halogenated derivatives in Baltic Sea sediment.

No PCTAs were found in the sediment, but an interfering signal was noted during octa-CTA screening. Its spectrum displayed a tetrabromo isotope cluster at (monoisotope) m/z 492.730, and another tetrabromo cluster at [M-15], likely corresponding to a methyl loss (**Figure 2**). Molecular formula generation returned C13 H7 N Br4 as the most likely formula and a ChemSpider search returned only one candidate, 1,3,6,8-tetrabromo-9-methyl-carbazole (TB-Me-CZ). A likely origin may be *in-situ* methylation of an halogenated natural product 1,3,6,8-tetrabromocarbazole (TB-CZ), which has been reported in Great Lakes sediment [1]. TB-CZ was also present in the investigated sediment at about twice the abundance of TB-Me-CZ (as expected at a slightly shorter retention time, 51.21 min).

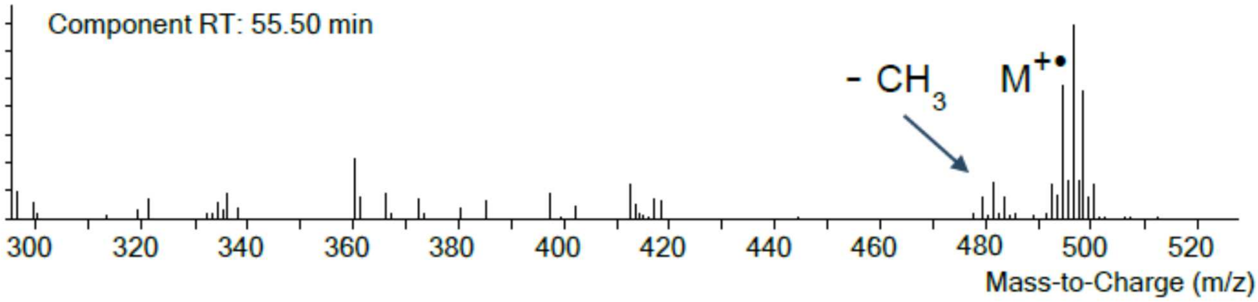

Figure 2. EI-MS spectrum of C13 H7 N Br4 unknown.

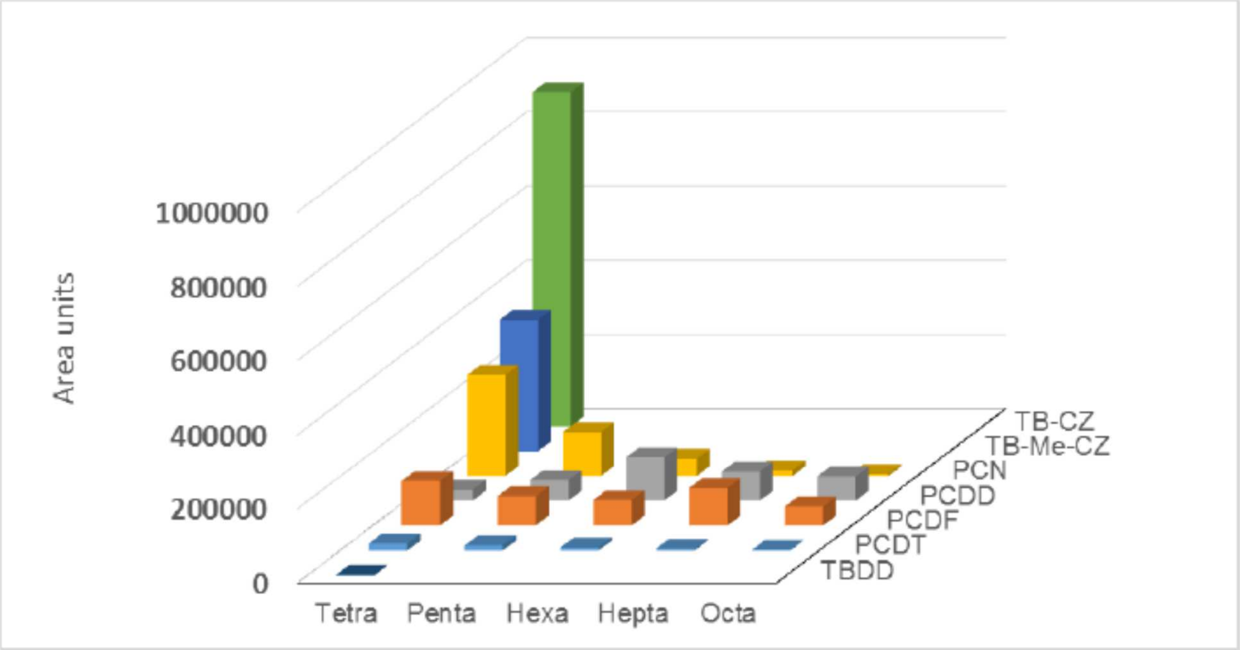

Figure 3. Abundances of bi- and tri-cyclic dioxin like compounds detected in the Baltic Sea sediment sample.

The relative abundances of the bi- and tri-cyclic planar halogenated compounds that were detected in sediment are summarized and compared in **Figure 3.** The halogenated natural products (TB-CZ and TB-Me-CZ) was the most abundant group of dioxin-like compounds. They are N-analogues of PCDFs, and their total abundance was similar to the combined abundances of the anthropogenic compound groups PCNs, PCDDs, and PCDFs. The S-analogues of PCDFs, PCDTs, was much less abundant than the TB-CZs and the PCDFs. Least abundant was PBDD/Fs of which only two early eluting tetrabromo dioxin congeners (TBDDs) were found, likely corresponding to 1,3,6,8- and 1,3,7,9- TBDD. These are considered to be of natural origin, just like TB-CZ. Further work is needed to positively identify the TB-Me-CZ and investigate if it is of natural or anthropogenic origin.

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Comparison of International Quality Assurance and Quality Control Standards for High Resolution Mass Spectrometry Dioxin Analysis

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The analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in environmental media, foods and tissues by high resolution gas chromatography-high resolution mass spectrometry (HRMS) is frequently used as the reference methodology against which other candidate analytical approaches are measured. Official methods based in this technology, employing isotopically labeled standards for recovery correction have been established in the European Union[1], the United States[2,3], Japan[4] and other nations for decades and international standards for such methods have been established by ISO (Standards 13914 and 18073, for example)[5,6].

It is perhaps the working assumption among data users that all methods employing these powerful instrumental and quantitative techniques will produce data of similar quality and that data sets from various countries with robust regulatory requirements may be integrated with minimal consideration given to differences in analytical method quality requirements. However a formal comparison to verify the basis for the assumption of data coherence has not been conducted to the authors' knowledge.

In order to identify achievable best practices and to understand differences in the precision, accuracy and qualitative certainty for data produced from wide-ranging sources, an examination of the requirements of these methods is being conducted. A concise review identifying critical differences and areas of agreement with regard to qualitative criteria, precision and accuracy will be presented, along with perspectives on the degree of impact differences may have on the application of data from researchers conducting analyses under different protocols.

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PAHs in Chinese atmosphere: Concentration, source and gas-particle partitioning

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As we known, polycyclic aromatic hydrocarbons (PAHs) have been received frequent attention in the past decades in the world due to their potential hazard to ecosystem and human health. China is one of the highest PAH emissions countries due to the rapid economic growth and energy consumption. In addition to local and national impact over China, the outflow of PAHs emitted from China can reach the neighbor countries and regions through long-range atmospheric transport. Therefore, the national study on atmospheric PAHs in China has regional and global significance to understand the large scale atmospheric transport of PAHs.

In this study, based on one year monitoring data from 11 urban sites across China, atmospheric PAHs on the national scale were comprehensively studied. Air samples in gaseous and particle phases were simultaneously collected from August, 2008 to July, 2009 using high volume air samplers. 16 US EPA priority PAHs were analyzed in more than 500 pairs of gas and particle phase samples. The average total concentration of the 16 PAHs was 239 ± 329 ng/m^3 and 165 ± 164 ng/m^3 for the Northern Chinese cities and the Southern Chinese cities, respectively. For Northern Chinese cities, the atmospheric PAHs concentrations were in the order of winter > autumn > spring > summer. However, the seasonal variation in Southern Chinese cities was not uniform. The different seasonal variations of atmospheric PAHs across China was mainly caused by the influences of residential energy consumptions in winter. Identified by principal component analysis, coal combustion and vehicle exhaust were the major sources of atmospheric PAHs in northern and southern cities of China, respectively. The temperatures dependences of atmospheric PAHs were different between Northern China and Southern China, which were caused by the different influences of ambient temperature on identified sources. The sub-cooled liquid vapor pressure ($\log P_L^o$)-based model and octanol-air partition coefficient (Koa)-based model were applied based on the monitoring database. The results of both models indicated that atmospheric PAHs had not reached equilibrium between gas and particle phases based on the theory of equilibrium state.

To our knowledge, this is the first comprehensive study to report the difference with concentrations, seasonal variations, sources and gas-particle partitioning of atmospheric PAHs in China on the national scale. The results of this study presented a whole picture of the occurrence, spatial and temporal variations of atmospheric PAHs over China, which will be helpful for further studies on large scale atmospheric transport of PAHs.

OCCURRENCE AND DISTRIBUTION OF PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN MULTI-ENVIRONMENTAL MATRICES AROUND TWO FLUOROCHEMICAL MANUFACTURING PARKS IN FUXIN, CHINA

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Introduction

As a class of good-quality surfactant, perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used in numerous industrial and household products such as textile finishing agents, leather treatment agents, coatings, and pesticides [1,2]. Due to their wide use, PFASs, including ionic perfluoroalkyl sulfonic acids (PFSAs) and carboxylic acids (PFCAs) and neutral fluorotelomer alcohols (FTOHs) and fluorotelomer iodides (FTIs), have been detected in various environmental media, including air, water, soils, dusts, sediments, wildlife and human beings [3-7]. Due to the ubiquitous occurrence, along with the persistence, global and national legislations have been established to control the manufacture and use of long-chain PFASs ($C\geq6$), especally C8-PFASs and some long-chain PFASs were gradually replaced by short-chain (C4-C7) congeners [8,9]. However, the manufacture of C8 substances had shifted to China [10].

Multiple processes have been involved in the distribution and fate of PFASs, and many of processes are still poorly understand. It has been revealed that once released in the environment, fluorotelomer-based precursors (e.g., FTOHs and FTIs) can be degraded to metabolites including PFCAs via (photo)chemical and biological degradations [11-13], which is recognized an important source of ionic PFASs in the environment. Besides, the transport way of PFASs is still unclear, and it was recently found that outdoor dusts play an important role in the global transportation of ionic PFASs (i-PFASs) [7].

Since 2004, two fluorochemical manufacturing parks (FMPs) have been developed in Fuxin, which makes the city as a fluorine industrial centre in China [14]. Both electrochemical fluorination and telomerization were implied to produce PFASs products. Previous studies reported that short-chain PFAAs were the predominant PFASs in FMPs [14-16]. In this study, multiple environmental matrices, including air, precipitation, surface river water, shallow underground water, outdoor dust, soil, river and reservoir sediment and leaves were taken around the two FMPs. The objectives were to investigate the occurrence and distribution of PFASs in multi-environmental matrices around two FMPs, to discuss the transportation of PFASs via air and water, to make comprehensive understanding of the PFASs fate around the two FMPs, and to evaluate the potential exposure risks to local inhabitants.

Materials and methods

Air (n=8), precipitation (n=3), surface river water (n=15), surface reservoir water (n=2), shallow underground water (n=4), outdoor dust (n=12), soil (n=21), surface river and reservoir sediment (n=13), leaves of the willow (*Salix babylonica*, n=7), leaves of the maize (*Zea mays*, n=7), and needles of pyramidalis (*Sabina chinensis*, n=2) samples were collected from the ambient environment around two FMPs in Fuxin, China in September and

October 2016. Air samples were collected using passive air samplers employed sorbent-impregnated polyurethane foam (SIP) disks. The SIP disk samplers were deployed from 1st September to 15th October 2016 (45 days). Precipitation samples were collected using stainless steel basin and stored in 500 mL PP bottles. Shallow underground water samples were collected from the hand pressed well and stored in 500 mL PP bottles. Surface water samples were collected from river and reservoir using a 5 L organic glass hydrophore and then stored in 500 mL PP bottles. At the same time, surface river and reservoir sediment samples (about 0-5 cm deep) were collected using a grab sampler and stored in 500 mL PP bottles. At each sampling site, outdoor dust samples were collected from out wall surface of a building 1 m above the ground using a disposable wool brush and a polypropylene (PP) tube. Surface soil samples (0-5 cm) were collected with a stainless steel trowel and sealed in polyethylene bags. Leaves were collected using stainless steel scissors, wrapped in aluminium foil and stored in polyethylene bags. All sampling tools were precleaned with MeOH and Milli-Q water.

After being spiked with mass-labelled internal standards (10 μL of 500 pg/μL; containing mass-labelled 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), PFSAs, PFCAs, FTOHs, perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs)) and the SIP disks were Soxhlet extracted by ethyl acetate (S1) and methanol (S2) each for 24 h, successively. The extracts were concentrated by rotary evaporation followed by gentle nitrogen blow down to 0.5 mL and cleaned up by EnviCarb (50 mg, 100-400 mesh, Supelco, USA). A 100-μL aliquot of S1 was analysed for neutral PFASs (n-PFASs). Another 100-μL aliquot of S1 was evaporated to dryness by gentle nitrogen and dissolved with 100-μL aliquot of S2, and this combination was analyzed for i-PFASs [17]. After being spiked with mass-labelled internal standards (10 μL of 500 pg/μL; containing mass-labelled 8:2 FTUCA, PFSAs and PFCAs), the water samples were solid phase extracted (SPE) using Oasis weak anion exchange (WAX) cartridges (6cc, 500 mg, Waters, USA). After being spiked with mass-labelled internal standards (10 μL of 500 pg/μL; containing mass-labelled 8:2 FTUCA, PFSAs, PFCAs, FTOHs, FOSAs and FOSEs) and the outdoor dust, soil, sediment and leaves were sonicated using methanol [18]. The analytical quantification of the samples was done using gas chromatography mass spectrometry (GC-MS; Agilent Technologies GC 7890A series coupled to 5975C Triple-Axis detector, Palo Alto, CA, USA) for n-PFASs and high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS; Agilent Technologies LC 1260 series coupled to 6460 Triple Quad system, Palo Alto, CA, USA) for i-PFASs.

Results and discussion

FTOHs and FTIs were the predominant n-PFASs in air with the sum concentrations ranging from 122 to 7870 pg/m^3 and 4.48 to 922 pg/m^3 (Figure 1a), respectively. Perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS) and perfluorooctanoic acid (PFOA) were the predominant i-PFASs in air (Figure 1b), surface river water (Figure 1c), surface reservoir water (Figure 1c), shallow underground water (Figure 1c), outdoor dust and sediment. PFBA (0.228-131 ng/g) and perfluoroheptanoic acid (PFHpA) (0.0293-135 ng/g) were the predominant i-PFASs in soil. PFBA was the predominant PFASs in leaves from Fuxin (50.5-99.5%). Downstream of the effluent from the FMPs, PFBA and PFBS concentrations up to 11900 and 5810 ng/L were detected in the River Xi. Short-chain i-PFASs (C4-C7) predominated in the surface river water (14.8-98.7%), while long-chain PFASs (C8-C12) prevailed in the surface sediment. Field-based sediment-water distribution coefficients of PFCAs increase linearly ($R^2=0.99$, $p<0.01$) with the chain length increasing from C4 to C12, while decreased from C2 to C4. Trifluoroacetic acid (TFA) were detected in all environmental matrices. TFA concentrations were 1 or 2 orders of magnitude higher than other individual i-PFASs in most samples. The levels of PFASs in surface river water, air (Figure 2), and outdoor dust decreased exponentially with increasing distance from the FMPs (significantly in the first 5 km), thus, FMPs were the point sources in the studying area. Concentrations of 8:2 FTUCA in air and outdoor dust significantly correlated with those of long-chain PFCAs (C9-C12) and 8:2 FTOHs, suggesting the degradation of precursors (e.g., FTOHs and FTIs). For residents around the two FMPs, potential health risks existed, due to high concentrations of PFASs in air, outdoor dust, water and soil. Adults around the FMPs were exposed to 2.73×10^{-3}-0.177 ng/kg/d of FTOHs and 5.97×10^{-3}-0.143 ng/kg/d of PFOA through air inhalation, which were significant higher than those via dust and soil ingestion.

Acknowledgements

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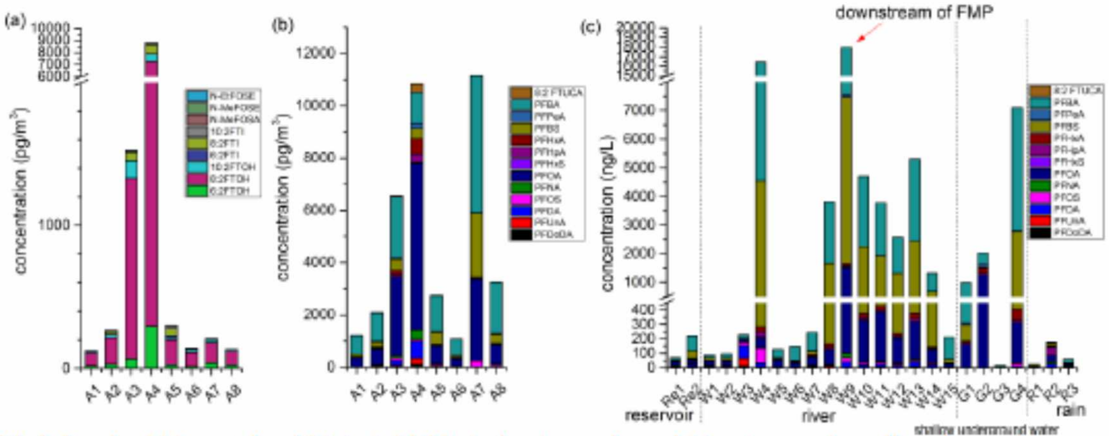

Fig.1. Levels of (a) neutral and (b) ionic PFASs in the air samples and (c) water samples collected around two fluorochemical manufacturing parks, Fuxin, China.

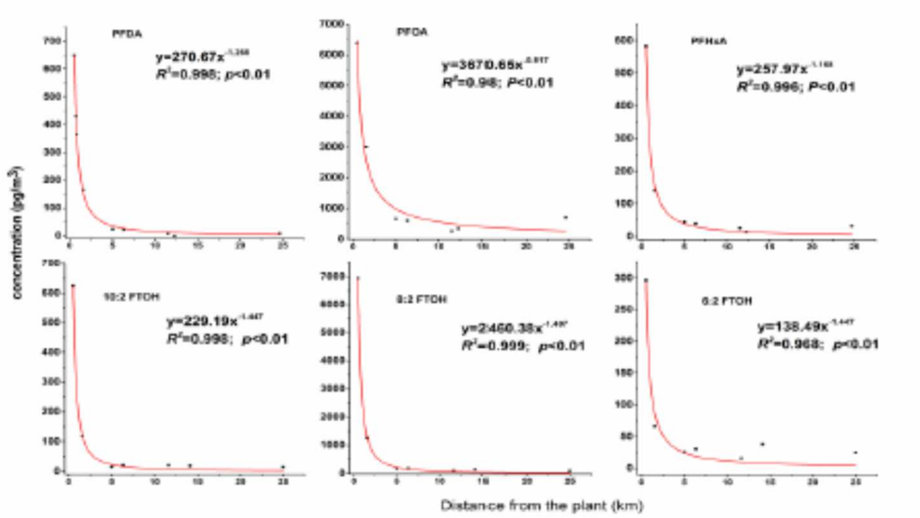

Fig.2. Decline of PFASs concentrations in air with the distance from the fluorochemical manufacturing parks, Fuxin, China.

Environmental impact of biomass and polyethylene waste co-firing: emissions of particulate matter, PCDD/Fs and DL-PCBs

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Introduction

Biomass is fuel derived from organic materials, a renewable and sustainable source of energy used to create electricity or other forms of power. It is a CO_2-neutral fuel which offers an attractive renewable alternative for power plants. Biomass generally has a lower heating value than coal and this is due to its higher moisture and volatile matter (VM) content. High moisture content of biomass is one of the predominant factors in affecting the energy output and combustion performance [1, 2]. Rice husk is the most prolific agricultural residue in rice producing countries around the world. It is one of the major by-products from the rice milling process and constitutes about 20% of paddy by weight. Rice husk and rice straw are an attractive source of energy due to their chemical and physical properties [3]

Co-combustion of biomass with solid waste offers a number of economical and environmental benefits, such as alleviation of the problem of solid wastes disposal and recovery of their energy content [4].

The average EU recycling, reuse and recovery rate of plastics is about 20%, markedly lower than for other materials [5]. Polyethylene (PE) has the highest share of production of any polymer type; the percentages of non-recycled PE waste is allocated between three disposal options: landfill, incineration and mechanical biological treatment. In a study done by Eriksson and Finnveden [6], the swedish scientists concluded that burning plastic can give off less carbon dioxide equivalent than burying it in landfills.

The combustion or incineration of various wastes or natural materials containing chlorine can lead to the formation and emission of polynuclear aromatic hydro-carbons (PAHs), dioxins (PCDDs), furans (PCDFs), PolyChloroBiphenils (PCBs), chlorohydrocarbons and other species [7].

In this study, the emissions of particulate matter, dioxins and dioxin-like PCBs from a thermal power plant, feeded with biomass residues (i.e. rice husks), partially substituted by polyethylene waste , were investigated.

Materials and methods

Weekly tests were carried out in a 4-MW thermal power plant, that uses locally-obtained rice husks as feed and an Integrated Environmental Authorization allows the plant to use polyethylene waste for energy recovery. The power plant includes a bed combustion system with moving grate technology incineration furnace and a boiler, and a system consisting of a steam turbine, condenser and generator for the production of electricity. The plant is equipped with: i) a system of control of NOx emissions through proper temperature control and the injection of a solution of urea (SNCR), ii) a system of injection of sodium bicarbonate upstream of the dust collection system for reducing emissions of acid, and iii) a high-efficiency dust collection system (bag filter).

Particulate matter, PCDD/Fs and dl-PCBs were investigated; triplicate sampling followed UNI EN 13284-1:2003 and UNI EN 1948-1:2006, UNI EN 1948-4:2007, respectively. Before sampling the fumes at the emissions, the linearity of the continuous monitoring system at the plant was verified for macropollutants (CO_2, CO, O_2, SO_2, NO, NO_2, HCl, TOC).

Organic micropollutants were analyzed according to EN 1948-2, -3 and -4. Briefly, they were 36-h Soxhlet extracted with toluene. Clean-up was performed by an automated system (J2 Scientific, Columbia, USA), based on Gel Permeation Chromatography, followed by an in-line automated concentrator and alumina column, as described by Rossetti et al. [8, 9]. The extracts were then concentrated and PCDD/Fs and DL-PCBs were analyzed by HRGC-HRMS on a GC 8000 series gas chromatograph (Fisons Instruments) coupled to an Autospec mass spectrometer (Micromass, Manchester, UK) in SIM mode. The GC-MS identification and quantification were made by the isotope dilution method. The particulate matter was evaluated via gravimetric analysis.

Results and discussion

The amount of plastic waste introduced into each campaign was defined taking into account the lower heating value (LHV) of each fuel (in consideration of moisture of the material), since the percentage of PE is referred to the energy content. Table 1 shows the average concentrations (n=3) of particulate, total PCDD/Fs and total dl-PCBs, referring to 11% oxygen, and the amount of PE waste added in each campaign.

An analysis of the distribution of the congeners of both PCDD/Fs and DL-PCBs, shows a similar fingerprint for each sampling campaign, with Tetra- and Penta-chlorinated furans and PCB-126 and PCB-169 predominant contribution on the total TEQ concentration (data not shown).

A correlation between PM and total TEQ chlorinated pollutants has been investigated, taking into account the contribution of PCDD/Fs and PCBs in each campaign. Figure 1 shows the mean distribution of PCDD/Fs and PCBs with respect to the PM concentration. It can be observed that the contribution of PCDD/Fs is predominant: 70-80% up to 10% of PE. DL-PCBs contribution became 50% when rice husk is substituted with 15% of PE.

As a further step, the determined concentrations were combined with data of consumption of plastic waste (kg over 24 hours total) and flow rate on days when the samples were performed, provided by the plant owner. Therefore, it was possible to estimate an "emission factor" (EF), defined by the Italian Legislative Decree 152/06 as "the amount of pollutant emitted referred to the production process considered in its totality and in its technological phases, expressed in terms of mass of pollutant emitted, compared to the mass of product or raw material, or any other parameters suitable for representing the production sector concerned". Figure 2 shows the average emission factor of each class of pollutant, expressed in pg TEQ/kg PE, in each experimental campaign. It can be observed an inversely proportional trend: the emission factor is lower with PE increasing rate, and it is more evident with PCDD/Fs .

Conclusions

The study allowed us to outline the environmental impact in the use of polyethylene waste in a biomass (rice husks) fueled plant, aimed at energy recovery. It is reasonable to assume that concentrations of pollutants have remained almost unchanged by introducing PE in feed for low halide halides and metals contained in the waste itself.

The combustion of polyethylene waste presents a profile of environmental sustainability higher that of the other plastic compounds (eg PVC), as these materials are made up of straight chain hydrocarbons free of halogens.

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	PE	**PM**	**PCDD/F**	**dl-PCB**
	[%]	**[mg/Nm^3 ref. 11% O$_2$]**	**[pg TEQ/Nm^3 ref. 11% O$_2$]**	**[pg TEQ/Nm^3 rif. 11% O$_2$]**
I	0	16	0.614	0.174
II	5	11	0.882	0.427
III	10	24	1.242	0.122
IV	15	12	0.747	0.645
V	10	15	0.759	0.235
VI	5	29	0.765	0.225

Table 1. concentration of PM, PCDD/Fs and dl-PCBs with respect to PE rate

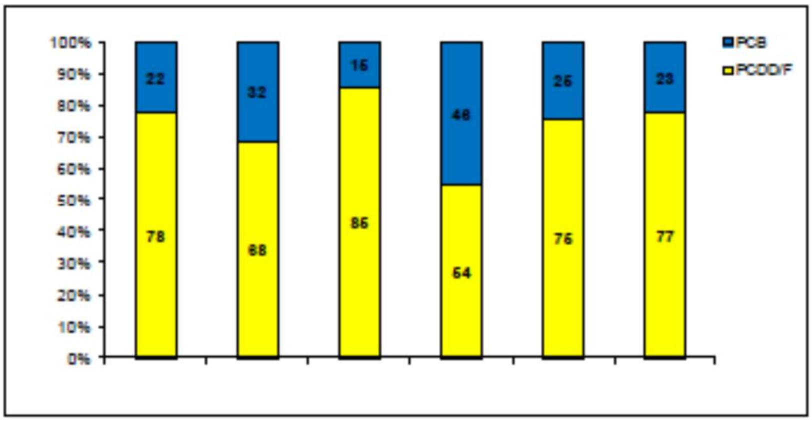

Figure 1 – Average contribution of PCDD/Fs and dl-PCB to the PM concentration

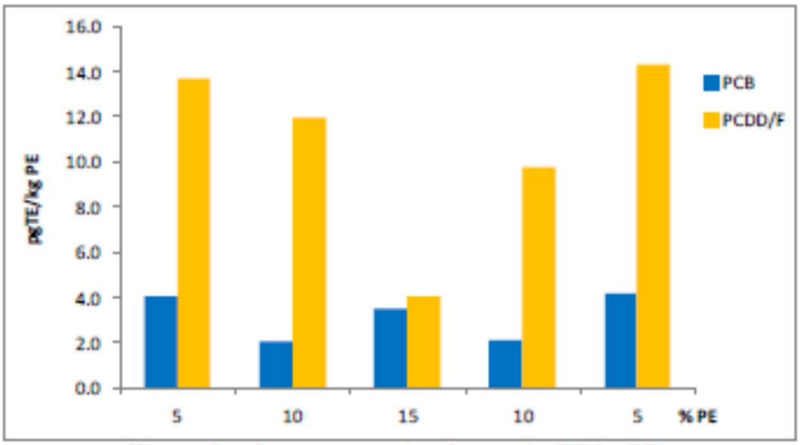

Figure 2 – Average emission factors (pgTE/kg PE)

Non-target and suspect screening of organic chemicals in indoor dust from five countries

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Introduction

Indoor air quality and human exposure assessment of chemicals have become subject of multiple studies during the last decade, because people reside for a large part of their life indoors. People in Europe and the US spend on average around 90% of their time indoors (homes, workplaces, cars and public transport means, etc.)[1]. The role that dust plays in human exposure assessment is, therefore, of paramount importance. Previous studies have shown that dust can carry organic contaminants[2] such as brominated (BFRs) and organophosphate flame retardants (OPFRs), perfluorinated compounds, phthalates, polychlorinared biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides and drugs[3]. Most of these chemicals are released through evaporation, leaching and ageing of common consumer goods present indoors such as electronic devices, furniture, textiles, cleaning and health care products and building materials. A combination of various analytical techniques in combination with suspect and non-target screening and multivariate statistics approaches made it possible to identify a large range of chemicals including flame retardants, pesticides, plasticizers, drugs, and perfluorinated compounds in indoor dust. We applied this approach to dust samples from five countries (Norway, Sweden, the Netherlands, United Kingdom, and Japan).

Materials and methods

A total of 48 dust samples from vacuum cleaner bags were collected in Norway, Japan, the Netherlands and the UK between 2014 and 2016, and in Sweden in 2008. The collected dust was sieved with a 250 µm sieve.

A sub-sample of 100 mg of sieved dust from each sample was spiked with an internal standard mixture and extracted with n-hexane/acetone in an ultrasound bath. Samples were then centrifuged and the supernatant was transferred into a clean glass tube. The extraction process was repeated two times and after addition of isooctane evaporated under a gentle steam of nitrogen. The extracts were evaporated to almost dryness and re-suspended in 100 µL isooctane for injection in GC (not reported here), or methanol for LC analysis. The methanol extracts were analyzed using the ESI source and the APCI source, both in the positive and negative mode. A high resolution time-of-flight MS (Compact QTOF, Bruker Daltonics, Bremen, Germany with mass accuracy <2ppm and resolution >22,000) connected to an LC was used for this analysis. Internal mass calibration was used resulting in an accuracy below 5 ppm. For the LC analysis a Kinetex core shell LC C18 column was used with eluents H_2O and CH_3OH.

The software Data analysis 4.0 from Bruker Daltonics (Bremen, Germany) was used to process data. Internal calibration was performed on all the spectra with the enhanced quadratic mode and chromatograms were processed with the Find Molecular Feature (FMF) algorithm which combines isotopes, charge state, adducts and common neutral losses belonging to the same compound into one feature. Retention time, m/z value and intensity define each molecular feature. Parameters were set as follows: S/N = 5, correlation coefficient threshold = 0.8, minimum compound length = 10 spectra. The molecular features were then aligned by retention time using an algorithm (non-linear retention time shift), processed in bucketing and normalization with the software Profile Analysis 2.1 (Bruker Daltonics, Bremen, Germany). The generated bucket table was imported to SIMCA-P+ 13.0 (Umetrics, Umeå, Sweden) and processed for multivariate data analysis (MVDA). Principal component analysis (PCA) and Partial

Least Square discriminant analysis (PLS-DA) were performed using Pareto scaling (the intensity of each variable was scaled by the square root of that variable's standard deviation).

All calibrated spectra were also processed with the Metaboscape 2.0 software (Bruker Daltonik, Bremen, Germany) using a self-built suspect database of around 9,000 compounds. Results from the Metaboscape and Multivariate data analysis were combined in order to identify chemicals including identification of unknown compounds based on exact mass and isotope pattern. Multivariate data analysis was also performed for the non-target screening using all molecular features.

Results and discussion

Samples were sorted by source and ionization mode. Hundreds to up to more than 6800 molecular features were found. About a third of the molecular features found in APCI could be identified as suspects (Table 1). For ESI this was only roughly 10%. Partial Least Square discriminant analysis (PLS-DA) was performed on all molecular features to evaluate the clustering of dust from different countries for each ionization source and mode. Two score plots of the samples analyzed are shown in Fig. 1. Loading plots in which the PLS-DA of the compounds (not shown) together with the score plots were used to further investigate the chemical profile of compounds in the dust from the various countries. Analyses are ongoing to identify as many as possible compounds. Figure 1 shows three main country groups in the APCI (+) PLS-DA score plot, whereas the ESI (-) PLS-DA plot shows a much more scattered picture. Interestingly, all four plots (APCI (-) and ESI (+) not shown here) show a distinct clustering of the Japanese dust samples. Some Dutch samples overlap with the Swedish samples in both pictures in Fig.1, while other Dutch samples can clearly be distinguished from the Swedish samples.

Table 1. The number of molecular features and the number of suspects found in the dust samples analyzed by LC-TOF-MS with positive and negative APCI and ESI.

Source/mode	Number molecular features	Number suspects
APCI neg	745	198
APCI pos	1276	403
ESI neg	3768	334
ESI pos	6868	578

Table 2 shows only some examples of organic chemicals tentatively identified such as flame retardants, plasticizers, stabilizers, and drugs. Many different types of organophosphorous flame retardants were found. Interestingly, common drugs as Lovastin a statin drug used for lowering cholesterol levels, and non-steroidal anti-inflammatory drugs such as Flurbiprofen were found. This is probably due to the fact that human skin cells are part of house dust and it seems that the drugs levels are high enough to be detected.

The combined approach of molecular features and multivariate data analysis is an interesting tool for identifying chemicals in dust samples. It appears that chemical signatures in dust samples are highly complex. The software packages are extremely helpful in the identification of the chemical compounds. A confirmatory analysis based on analytical standards can further help to elucidate the identity of unknown compounds. This multivariate approach also offers possibilities for making correlations with information from questionnaires when recorded during time of sampling. In addition, an interesting combination is also possible with the results of direct probe analysis of consumer products, which already has shown the presence of a multitude of chemicals including flame retardants, their degradation products and by-products[4,5]. Therefore, this approach will further help to fill the gap between the vast number of chemicals in consumer good and human exposure.

Table 2. Examples of tentatively identified organic chemicals, including flame retardants, plasticizers, stabilizers, and drugs.

Suspect	**Mol. formula**	**Use/Application**
Tripentyl phosphate	$C_{15}H_{33}O_4P$	Flame retardant
Tris(2-butoxyethyl) phosphate	$C_{18}H_{39}O_7P$	Flame retardant
Diphenyl Phosphate	$C_{12}H_{11}O_4P$	Flame retardant
Tri(isopropylphenyl) phosphate	$C_{27}H_{33}O_4P$	Flame retardant
Triphenyl phosphate	$C_{18}H_{15}O_4P$	Flame retardant
Cresyldiphenylphosphate	$C_{19}H_{17}O_4P$	Flame retardant
Diisodecyl phenylphosphate	$C_{26}H_{47}O_4P$	Flame retardant
Phosflex 418	$C_{26}H_{39}O_4P$	Flame retardant
Fyrol 6	$C_9H_{22}NO_5P$	Flame retardant
DOPO	$C_{12}H_9O_2P$	Flame retardant
1-2-3-Propanetricarboxylic acid- 2-hydroxy-tributyl ester (Citroflex 4)	$C_{18}H_{32}O_7$	Plasticizer
Dioctyl sebacate	$C_{26}H_{50}O_4$	Plasticizer
Irganox1076	$C_{35}H_{62}O_3$	Antioxidant/stabilizer
Lovastin	$C_{24}H_{36}O_5$	Drug
Flurbiprofen	$C_{15}H_{13}FO_2$	Drug

Acknowledgements

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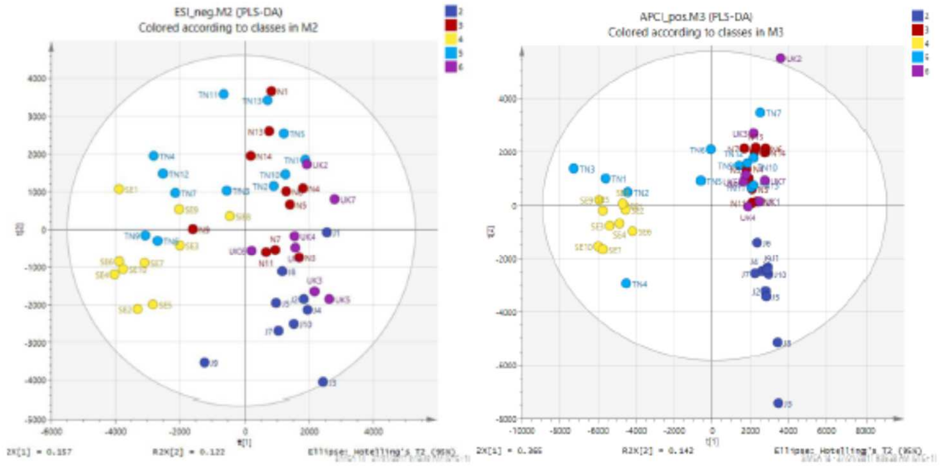

Figure 1. PLS-DA score plots of APCI (+) (above) and ESI (-) (below) results. 2: Japan, 3: Norway, 4: Sweden, 5: The Netherlands, 6: UK.

Screening halogenated contaminants in the marine environment based on high resolution mass spectrometry profiling

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Introduction

Polyhalogenated chemicals constitute a wide sub group of organic environmental contaminants and many of them are subjected to restrictions or bans due to the risks for the environmental and human health. Monitoring environmental contaminants is a major scientific activity supporting risk assessments. Highly specific and sensitive targeted analytical methods involving chromatography and mass spectrometry couplings are available for a wide range of known substances. Most of the time, however, only the pieces of information required to maximize the specificity and sensitivity for the targeted substance(s) are acquired. With the broad variety of polyhalogenated compounds, unknown substances (*e.g.* unidentified substances, transformation products) are likely to occur in the environment as additional potential contaminants. Investigating unknowns proactively and efficiently is challenging, targeted available methods being unfitted for this purpose.

Based on two specific physical-chemical properties of bromine and chlorine, we previously developed an innovative analytical strategy using high-resolution mass spectrometry (HRMS) data fingerprints to seek unknown polyhalogenated substances in complex matrices[1]. The first property takes advantage of the discriminant mass defect (MD) engendered by heavy heteroatoms such as bromine and chlorine compared to usual atoms composing organic substances, typically C, H, O, N. An elegant way to visualize and interpret the signals is to plot the *m/z* fractional part versus *m/z* (MD plot). In 2010, Taguchi et al. [1] suggested a mass-scale based on an exact mass of 34.00000 for the substitution of a hydrogen by a chlorine, -H/+^{35}Cl,. Thus, polychlorinated homologues series (as well as polybrominated series) exhibit the same fractional part and are aligned horizontally on an H/Cl-scale MD plot. The second property involves characteristic isotopic pattern, due to the presence of two natural and stable isotopes with specific abundances for both halogens. Isotopic patterns allow determining the number of halogen atoms in the ions, which decrease the number of potential chemical formula.

Acquiring data in HRMS full scan of complex samples leads however to a huge number of signals. In order to support and facilitate the data processing step, bioinformatics tools were developed under the open source programming R environment. It involves two main steps (i) the automated integration of chromatograms using *xcms* package and (ii) a script, which pairs signals according to retention time and MD between C, Cl and Br isotopes.

In the present work, we applied the approach to two selected samples, a sediment and mussels from the river Seine mouth (France). Sediment is known to act as a reservoir for environmental contaminants, hydrophobic ones binding strongly with it. Mussels are filter feeder organisms that accumulate contaminants present in the water, often considered as a sentinel species for the marine environment.

Materials and methods

Sample preparation

Sediment sample was collected in 2002 and mussel samples in 2017, both from the river Seine mouth (France) a highly industrialized and urbanized area. Lipophilic compounds were extracted from 1 g freeze-dried matter by

Pressurized Liquid Extraction (ASE, Dionex Corp., CA, USA) pending two consecutive extractions, using dichloromethane, at 100 °C and 100 bar. The organic extracts were evaporated until 3 mL with a rotary evaporator. The extracts were transferred into hexane (5 mL) by evaporating dichloromethane under a gentle stream of nitrogen. Activated copper was added to the sediment extract to remove sulfur-containing compounds. The mussel extract was treated by successive liquid-liquid partitioning with concentrated sulfuric acid (2 × 3 mL) to remove lipids. The organic layer was neutralized with 2 × 5 mL ultrapure water and dried with anhydrous sodium sulfate. The purified extracts were spiked with 2.5 ng of $^{2}H_{18}$-β-HBCDD in toluene, evaporated to dryness under a gentle stream of nitrogen, reconstituted in a MeOH/H_2O 1:1 mixture (v/v, 50 µL) and were centrifuged prior to analysis.

LC-HRMS data acquisition

Extracts were analyzed with an UltiMate 3000 UHPLC pumping system coupled to an Orbitrap Q-Exactive mass spectrometer fitted with a heated Electrospray source (Thermo Fischer Scientific, San José, CA, USA). Instrument control and data processing were carried out by Chromeleon Xpress and Xcalibur softwares (Thermo Fischer Scientific). Chromatographic separation was achieved using reversed phase chromatography on a Hypersil Gold analytical column (100 mm × 2.1 mm, 1.9 µm) (Thermo Fischer Scientific) kept at 45 °C. Mobile phases consisted of 10 mM ammonium acetate in water (A) and in acetonitrile (B). The gradient began with (A/B) 95:5 (v/v) for 2 min, then ramped linearly to 50:50 over 10 min and to 0:100 over 2 min to be maintained for 5 min, and returned to 95:5 over 2 min. The flow rate was set at 0.4 mL min^{-1} and the sample injection volume to 10 µL. HRMS data were acquired in negative mode in full scan mode over the *m/z* range 120-1000 at a resolving power of 140,000 full width half maximum at *m/z* 200.

Post-acquisition data treatment

The open access msConvert software (ProteoWizard) was used to convert raw data (*.raw*) to the open format *.mzXML*. Datasets were then processed by the *xcms* package using centWave peak detection algorithm to extract chromatographic features. Peak picking parameters were as follows: method, "centWave"; ppm, 5; snthresh, 10; prefilterstep, 5; prefilter level, 10000; peakwidth, 5-60; noise, 0; mzdiff, 0.001. A table report in *.csv* file format was created where each features was defined by an exact mass (*m/z*), a retention time (min) and an intensity (area). Features were paired according to a method developed by Cariou et al. [1]. Paired isotopic clusters were manually investigated (pattern, extracted ion chromatograms) allowing to deduce the number of halogen atoms. Elemental composition assignments were performed *via* Xcalibur, considering usual elements (C, H, O, N, P, S, Cl and Br). Then, structural hypotheses were suggested.

Results and discussion

Sediment

The centWave function resulted in the detection of 11,940 features, among them 775 paired clusters were suspected to exhibit at least one chlorine or bromine atom. A total of 183 paired clusters were manually investigated (Figure 1a). It resulted in 111 elemental composition hypotheses (61%) and 77 chemical structure propositions (40%). External standard mass deviation was 0.80 mmu. Particular attention was paid to two remarkable series.

- On Figure 1b, series potentially corresponding to hydroxylated polychlorinated biphenyls (OH-PCBs, 3 occurrences), hydroxylated polychlorinated diphenyl ethers (OH-PCDEs, 6 occurrences) and hydroxylated and methoxylated polybrominated diphenyl ethers (OH-PBDEs, 2 occurrences; MeO-PBDE, 1 occurrence) are presented in orange, blue and purple, respectively. Some of these compounds were suggested as potential biotransformation products of the related parent compounds

- Three clusters exhibiting the same H/Cl-scale fractional part and being separated by the characteristic vector -H/+Br were suspected to form a series of homologous polybrominated compounds (Figure 1b, in red). The chemical formula suggested was $C_{16}H_{12-x}Br_xN_2$, with x ∈ [4–6] (Figure 2). Extracted ion chromatograms show a logical increasing in retention time with bromine increments as well as possible presence of isomers for Br_4- and Br_5-containing compounds.

Mussel

The centWave function resulted in the detection of 6,416 features, among which 385 paired clusters were identified. A total of 34 clusters were manually investigated. It resulted in 28 elemental composition hypotheses (82%) and 4 chemical structure propositions (12%). External standard deviation was 0.23 mmu. Particular attention was paid to two remarkable series.

- A set of three series of homologous polybrominated compounds with a general formula of $C_{18}H_{14-x}Br_xO_3$, with x ∈ [5–7] was suggested. Only the pentabrominated cluster appeared with several isomers. The formula may match the tetradecabromodiphenoxybenzene ($C_{18}Br_{14}O_2$) pending debromation and hydroxylation. Further investigation is needed to confirm such hypothesis.
- A group of 11 clusters, possibly mixed halogenated compounds (–Cl/+Br, –H/+Cl and –H/+Br vectors), appeared to form 3 series, penta- to heptahalogenated, with chemical formulas being $C_8Br_xCl_yO$ (4 clusters), $C_8HBr_xCl_y$ (4 clusters) and a $C_8H_2Br_xCl_yO$ (2 clusters), with x ∈ [1–4] and y ∈ [2–6].

Conclusion and perspectives

The analytical strategy succeeded in highlighting - in both biotic and abiotic samples - numerous polyhalogenated compounds representative of different class of contaminants, confirming the relevance of the proposed strategy to offer global detection of emerging contaminants. Such approach fully answers current risk assessment expectations. Further experiments, including MS^2, derivatization and/or standard injections, will be necessary to gain structural information. Complementary analytical approaches such as gas chromatography and/or Atmospheric Pressure Chemical Ionization could also allow investigating different sample fractions, thus increasing the range of compounds properties. Finally, a homemade friendly-user application is being developed to manage efficiently the complete post-acquisition data treatment processing.

Acknowledgements

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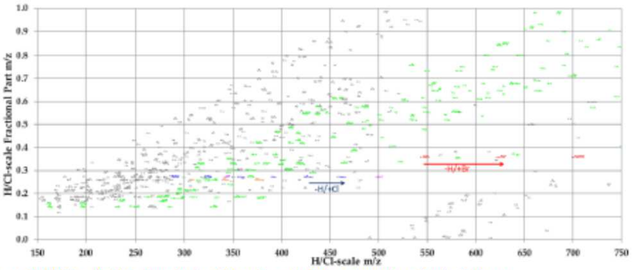

Figure 1: *H/Cl-scale MD plots obtained for sediment). Colors: investigated paired clusters.*

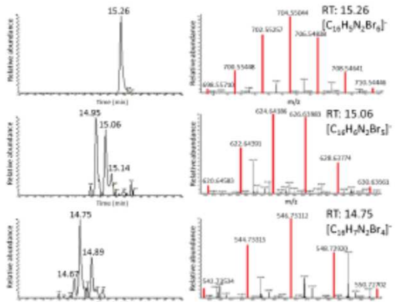

Figure 2: *Extracted ion chromatograms of base peaks (± 20 ppm) and mass spectrums (bromine isotopic contributions in red) of selected polybrominated series observed in the sediment sample.*

Non-Target Analysis of Ambient Air Using Cryogenic Air Sampler

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Introduction

Non-target analysis using Time of Flight Mass Spectrometry (TOF-MS) seems to be the recent movement of analytical chemistry. Several reports attempted to establish this concept with modern development of the instruments, application of data analysis and with relatively simple sample preparation. Unexpectedly, the last one is most important, because different standard operation protocols (SOPs) of sample preparation may only extract "selected chemicals" to be measured in the whole sample. Water, sediment and biological samples might be possible to use for non-target analysis because of their well reported sample preparation procedure, such as solid phase extraction and others.

On the other hand, the most difficult part in non-target analysis of ambient air is the air sampling devices that are generally specific to their target chemicals. Many adsorption cartridges for most common volatile organic compounds are Benzene/Toluene/Xylene, acid gas, styrene and so on. These VOCs are collected using specific commercially available sampling tube. However, there is no such single sampler for sampling both particle and gaseous phases in air. In spite of numbers of sampling devices for hundreds of chemicals in air, it is supposed to be impossible to develop non-target analysis of ambient air, because till today sampling devices like adsorption tube can only analyze "Selected Chemicals - target".

New technology, the Cryogenic Air Sampler (CAS), is a breakthrough on this issue. Concept of cryogenic collection of air has already known for non-selective collection of nitrogen and carbon dioxide using liquid helium (-269 °C). However, there is no such technology to collect wide variety of organic gases including highly volatile compounds, volatile organic gases, semi-volatile and non-volatile (partly particulate) organic chemicals in ambient air using cryogenic collection because of several industrial limitations to manufacture this sampler.

AIST and Sibata Scientific Technology Ltd. innovated a cryogenic moisture sampler (CMS) for collection of water soluble gas and particulate matter in ambient air in 2013 [1, 2]. After the industrial innovation for the last five years, most comprehensive cryogenic sampling device, namely cryogenic air sampler (CAS) for POPs (CAS-02) was manufactured and introduced to market at the Pittsburg conference (Chicago, USA) in March 2017. CAS-02 is the first available instrument to enable comprehensive collection of wide variety of organic chemicals in ambient air using single sampling device.

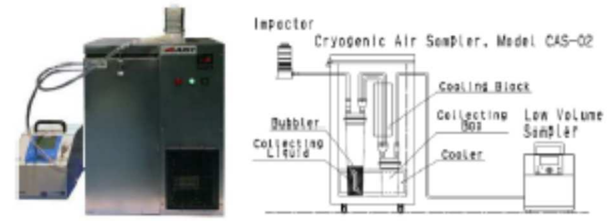
In this report, preliminary trial of non-target analysis of POPs in ambient air using CAS-02 and TOFMS is described.

Materials and methods

The Cryogenic Air Sampler for POPs (CAS-02) is a device to collect both gases of high/low boiling points and particle matters in the air simultaneously. It is also designed with a new concept which is effective for sampling of Fluorinated organic toxic substances (such as PFOS, which was the limitation of collection rate by the conventional methods) and light/temperature sensitive Brominated flame retardant (such as PBDEs) at the same time.

CAS-02 can collect different types of chemicals ranging from high & low-boiling gases (e.g., VVOC, VOC and SVOC) to particle matter (e.g., POM, PM10 and PM2.5) in work environment and ambient air. A comprehensive air sampler when connected to a classified impactor, it can collect hazardous air pollutants including both high & low-boiling gases and particle matters simultaneously. Specifications and dimensions are shown below.

After sample collection by CAS-02, liquid sample were analyzed using TOF-MS scan and Information Dependent Acquisition (IDA) by TripleTOF®4600 system equipped with Agilent 1100 HPLC.



Setting temp. range	-20 to 0 ℃
Display	Digital (℃)
Joint hose diameter	O. D. φ8 (inlet, decompression)
Safety function	Electrical leakage breaker (with overcurrent prevention)
Alarm function	Exhaust heat warning for excess heat increase, Sensor short circuit
Dimensions	460 (W) x 340 (D) x 625 (H) mm
Weight	19 kg
Power supply	AC 100V to 240V

Figure: 1. Specifications of the Cryogenic Air Sampler for POPs (CAS-02).

Results and discussion

PFASs were chosen as test chemicals to evaluate the performance of CAS-02 because of their specific physicochemical properties. Figure 2 shows the results of recovery experiments using glass traps (similar to conventional air sampler such as high volume air sampler) and polypropylene traps used for CAS-01 (previous version). Glass traps showed poor recoveries; in contrast, polypropylene traps showed good recoveries for most PFASs. This is remarkable and indicates clear adsorption of PFASs onto glass surface as expected. Very low recovery of longer chains compared to C4 (PFBS and PFBA) suggests "unsuitability of glass apparatus for atmospheric sampling of PFSAs and PFCAs".

On the other hand, some of volatile precursors showed better recoveries for cold trap and mist trap of glass apparatus compared to polypropylene. Although the reason for this is not known, CAS-02 can be useful not only for atmospheric sampling of PFASs but also enable useful "chamber study" that may provide some insight into environmental kinetics of PFASs at various temperatures and humidity in the environment.

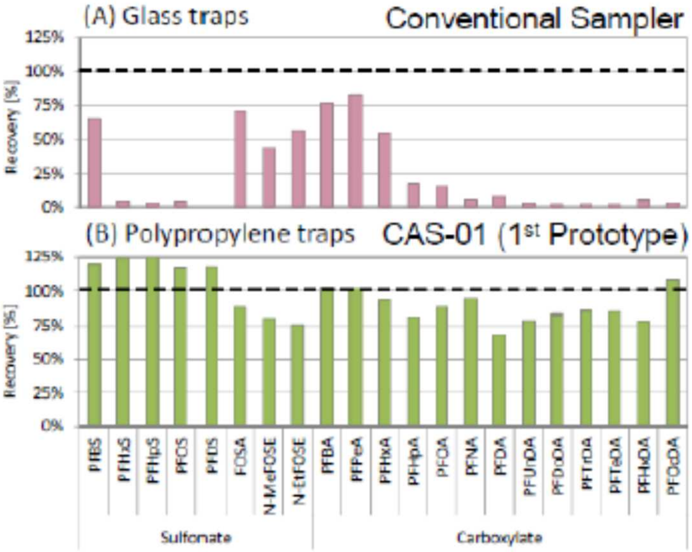


Figure: 2. Recovery results for PFASs using "CAS-01" for glass traps (upper) and polypropylene traps (below).

Several parameters for TOF-MS were optimized to obtain the higher intensities using comprehensive analysis of most PFASs in liquid extraction of ambient air collected by CAS-02. The parameters of Ion Source Gas 1 (GS1 (psi)), Ion Source Gas 2(GS2 (psi)), Curtain Gas (CUR (psi)), Temperature (TEM (°C)), Ion Spray Voltage Floating (ISVF (V)) and Declustering Potential (DP (V)) were optimized. After optimization, intensities of selected PFAS were 7.4 to 43.8 times higher than original values of parameters. In brief, liquid sample collected from ambient air using CAS-02 contained not only well-known PFASs but also several unidentified chemicals in air. including C_6HF_{11} (m/z 280.9830 as [M-H]-), proposed structure was 1,1,2,3,3,4,4,5,5,6,6-Undecafluoro-1-hexene, undecafluorocyclohexane. $C_6H_2F_{10}O_2$ (m/z 294.9822 as [M-H]-), proposed structure was 1,2,3,3,4,4,5,5,6,6-decafluoro-1,2-cyclohexanediol, 2,2,3,3,3-pentafluoropropyl pentafluoropropanoate, 1,1,1,3,5,5,5-heptafluoro-4-(trifluoromethyl)-3-pentene-2,2-diol or 2,2,2-trifluoroethyl heptafluorobutanoate. This result showed that the combination of CAS-02 and TOF-MS identification seems to be very useful technique for non-targeting analysis of chemicals in ambient air.

Conclusion: CAS-02 has several features suitable to "non-target analysis of ambient air" as below:

A) Comprehensive sampling device – capable to collect both particulate matter and gaseous materials at the same time in one compact equipment;

B) Highly accurate fine analysis - by using a functionalized resin, the CAS-02 is capable for sampling of fluorinated organic toxic substance and brominated flame retardant, which seems difficult to collect with current glass or Teflon based sampling methods;

C) LC-MS analysis ready - direct measurement is possible without further extraction, because ambient chemicals are collected in freeze/liquid sample;

D) Convenient to use at different sites - the cooling part doesn't require optional coolant such as liquid-nitrogen;

E) Applicable to humid environment - the CAS-02 does not require the removal of moisture from the atmosphere and can work in humid and foggy environment, but conventional samplers cannot; and

F) Compliance with ISO methods - the CAS-02 complies with ISO25101 (PFOS/PFOA) and on-going international standard of ISO method, TC147/SC2/WG74 "PFAS LC-MS/MS".

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PAHs depositions in the environment of a waste incinerator

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Introduction

In 2011 the most modern waste incinerator of the Netherlands was built in Harlingen. Several studies show this so called "state of the art' incinerator as an unexpected important source of emissions of Unintentionally produced Persistent Organic Pollutants (UPOPs) to the environment, not only during failures (shutdowns) but also under normal operation conditions (1). A risk for human health and an ongoing pollution of the surrounded environment, including the UNESCO Wadden Sea, to which the waste incinerator directly is located. In this research a screening test for analysis of PAH is applied to estimate the amount of PAH in the environment of the waste incinerator.

Methods

Samples were taken from different outdoor objects; installations, roofs and window framework. Scrapping multi-increments composite sampling from these objects; dust 1- 10 gram/object, and roof dust 100 gram/object. The analytical test is performed by the bioassay PAH Calux, BioDetection Systems BV (BDS), Amsterdam, the Netherlands (2).

Summary

The analyzed dust samples are collected from buildings (some located directly near the waste incinerator) in Harlingen region. PAHs have been analyzed in significant amount by PAH CALUX. This indicates that further investigations are needed to know more about which kinds of PAHs does play a significant contamination role, about the potential sources and the risk assessment for environmental, wildlife and human health.

Acknowledgements

Citizens concerned about industrial pollution in their environment fund NGO ToxicoWatch Foundation. Government of the Netherlands funds continuous long-term sampling of waste incinerator, Harlingen.

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Organohalogen pollutants in surface particulates from workshop floors of four major e-waste recycling sites in China and implications for emission lists

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Because of the primitiveness of e-waste recycling activities, the environmental effects of e-waste disposal are attracting increasing attention[1]. Concerns focus not only on the volume of e-waste generated but also on the list of e-waste-associated contaminants. Organohalogen pollutants (OHPs) are one of the most concerning classes because of their significant levels in e-waste[2]. Thus, the pollution status of OHPs in the e-waste recycling sites is particularly concerning. In addition, the levels and patterns of OHPs found in e-waste largely depend on the type of items being dismantled[2]. However, little is known about the types and possible sources of OHP contamination associated with the dismantled e-waste items.

The surface particulates on workshop floors can provide information about the concentration and distribution of contaminants in e-waste because a large number of OHPs may end up concentrated in the surface environment. China appears to be the largest dumping site for e-waste because of the dual pressure illegally imported and domestically generated e-waste. Therefore, the primary objective of the present study was to gain an overview of the levels, compositions and congener group profiles of OHPs (including short- and medium-chain chlorinated paraffins (SCCPs and MCCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and several other halogenated flame retardants (OHFRs)) in surface particulates from four major e-waste recycling areas (Taizhou, Guiyu, Qingyuan and Dali) in China. An effort was also made to characterize the types and possible sources of contamination present in the particulate matter found on workshop floors in e-waste recycling sites.

Generally, CPs were the predominant OHPs in the particulate samples, followed by PBDEs, OHFRs (including decabromodiphenyl ethane, dechlorane plus (DP), 1,2-bis(2,4,6-tribromophenoxy) ethane, tetrabromobisphenol A, hexabromocyclododecanes (HBCDs), polybrominated biphenyls, hexabromobenzene, pentabromotoluene, and pentabromoethylbenzene,), and PCBs. The composition of OHPs varied depend on the e-waste items processing in different regions. Guiyu and Dali were typical sites contaminated by HFRs and CPs, respectively, while Qingyuan, and Taizhou were representative PCB-polluted regions. Different DP isomer and HBCD diastereoisomer profiles were observed among different regions. The evidence produced by this preliminary study indicated that electronic devices and plastics may account for the high content of HFRs and the metal products are likely the major source of CPs in these e-waste sites.

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Medium-chain and long-chain chlorinated paraffin products predominate in Swedish coastal sediment cores over the past 50 years.

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated straight alkanes. They have been commonly used as lubricants, plasticizers, flame retardants and metal cutting fluids for decades. CPs are divided into short chain (C_{10-13}, SCCPs), medium chain (C_{14-17}, MCCPs), and long chain (C_{18-}, LCCPs) products, according to the alkane-chain-length range [1]. SCCPs, MCCPs and LCCPs are considered toxic to many aquatic organisms such as invertebrates [2]. SCCPs were proposed to be included in the Stockholm Convention list of persistent organic pollutants (POPs) [3]. MCCPs meet the criteria for substances of very high concern as defined by REACH [4].

Compared to SCCPs, MCCPs and LCCPs have received less attention. However, recent studies showed that MCCPs and/or LCCPs were predominant CPs in sewage sludge [5], soil [6] and indoor dust [7] in many countries. Whether these CPs, especially LCCPs, are "new" contaminants in the environment is unclear. In this study, we measured CPs with alkane-chain lengths ranging from C_9 to C_{36} in a sediment core collected from the Baltic Sea coast for a historical profile of CP pollution in Sweden.

Materials and methods

Wastewater treatment plants are typical sinks and sources of CPs.[8] Sediment cores from the Baltic Sea were collected in September 2016 near Himmerfjärden wastewater treatment plant (59°04'03.6"N 17°42'25.9"E) at a depth of c.a. 20 – 50 m using a gravity corer with a diameter of 58 mm. The wastewater treatment plant serves about 340 000 persons of the sourthern Stockholm's metropolitan area. One core was used for analytical method validation and preliminary testing. Then a 1.2-m core was used to rebuild a historical profile of CP pollution. The cores were cut into 2.5 cm slices and stored in Whirl-Pak® sampling bags in a -20 °C freezer before dating. The sediment cores were dated by ^{137}Cs and ^{210}Pb analysis [9]. The average sedimentation rates were 0.82 – 0.98 cm per year. The extraction and cleanup process for CP analysis was adopted from previous studies [7, 10]. Briefly, approximately 10 g of freeze-dried samples was spiked with $^{13}C_{10}$-1,5,5,6,6,10-hexachlorodecane as the internal standard and extracted using accelerated solvent extraction (ASE 300; Dionex Europe, Leeds, UK). The extracts were blown to near dryness with nitrogen, sulfur was removed using activated copper and then cleaned-up on a multilayer SPE column. The eluent was reconstituted in 100 µL isooctane. 20 ng Dechlorane-603 was used as volumetric standard.

Instrumental Analysis: Samples were directly injected into APCI-QTOF-MS (QTOF Premier, Waters, UK). Instrument settings have been described previously [11] and were applied with several adjustments [12]. The observed resolution was 8000 – 9000. CP congener groups from C_9Cl_3 to $C_{36}Cl_{15}$ were considered to form a congener group pattern.

Quantification: CP congener group patterns of a set of CP technical products ($n = 65$) were initially analyzed, and a sub-set of 16 products were selected for quantification in this study, consisting of 5 SCCPs, 6 MCCPs and 5 LCCPs. The CP congener group pattern of each sample was reconstructed by a deconvolution algorithm from

CP patterns of the selected products. In this study, CP patterns in the sediment samples were satisfactorily reconstructed ($R^2 > 0.80$). Relative contributions of the products were then used to calculate instrument response factors of SCCPs, MCCPs and LCCPs in the sample. A detailed deconvolution procedure has been given in Bogdal et al [11]. The limits of quantification (LOQ) was defined based on the blank plus ten times the standard deviation (SD), which is 1.4 and 6.5 ng/g dry sediment for SCCPs and MCCPs, respectively. LCCPs were undetectable in the blank.

Results and discussion

Total CP concentrations (∑CPs) in the sediment core are shown in Figure 1. ∑CPs were above LOQ in the sediment section representing the year 1960 and increased to the maximum concentration of 48 ng/g d.w. in 1991. ∑CPs decreased to 15 ng/g d.w. in the surface sediment (representing the year 2015). ∑CPs were, in general, lower than in sediment from Switzerland [13], China and Japan [14], which may be due to comparably lower use of CPs in the studied area. The historical trend of ∑CPs in the sediment core is consistent with statistics on imported amounts of CPs to Sweden, which showed that the highest annual import of ∑CPs was 4800 tons in 1991 [15]. Since there is no CP production in Sweden [15], the import amount indicates the amounts of CPs in use.

LCCPs were the predominant CPs before 1991, making up c.a. 60 % of total CPs. After 1991, MCCPs became predominant, making up c.a. 70 % of total CPs. The results were also supported by a recent study in which CPs in dust from Sweden were predominated by LCCPs [7]. In all sections of the sediment cores, SCCPs were less than 20 % of total CPs with an average of 10 %. This is consistent with the importof CPs in Sweden, where SCCPs were on average 10 % of total CPs imported between 1990 – 2014 [15]. CP compositions in the sediment core show that large amounts of MCCPs and LCCPs have been emitted into the local environment for a long time.

Figure 2 shows a congener group pattern of CPs in a sediment section representing the year 1960. C_9 – C_{36} CPs were identified in the section, with C_{24} as the dominant alkane-chain-length group. These CPs, consisting of SCCPs, MCCPs, LCCPs and C_9 CPs, appear to have persisted in the sediment for c.a. 50 years.

This study indicates that CP pollution in Sweden is predominated by MCCP and/or LCCP products. Whether MCCPs and LCCPs pose a risk to the environment, in particular marine sediment ecosystem, is not clear, and requires further study.

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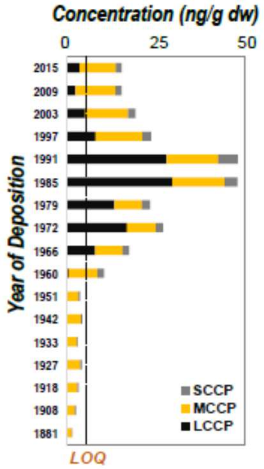

Figure 1. Historical time trend of SCCP, MCCP and LCCP concentrations in a sediment core from the Baltic Sea.

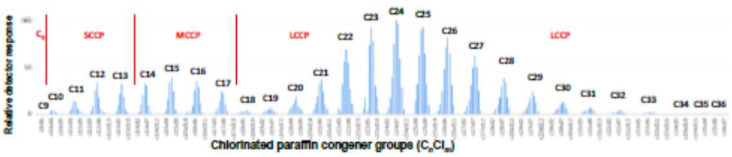

Figure 2. Chlorinated paraffin congener group pattern in a 50-year-old sediment section.

Short-Chain Chlorinated Paraffins (SCCPs), a Toxic Industrial Chemical Included for Global Prohibition, Contaminate Children's Toys

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Introduction

Short-chain chlorinated paraffins (SCCPs) are widely used as industrial lubricants and coolants in metalworking applications. However, they are also present in consumer products when used as plasticizers and flame retardants, especially in polyvinyl chloride (PVC) plastic, as well as in rubber, textiles, and polymers. Additionally, they are used as plasticizers in such applications as sealants, adhesives, and paints [1]. According to a recent scientific study "*no other persistent anthropogenic chemical has been produced in such quantities* [as chlorinated paraffins]" [2] Production and use of SCCPs is increasing [3]. In 2016, a Stockholm Convention expert committee recommended listing SCCPs in the treaty for global elimination [4]. The expert committee noted that SCCPs are ubiquitous in the global environment, wildlife, and humans [5]. They also fulfill key treaty characteristics as they are persistent, bioaccumulative, and transported long distances to remote locations, including the Arctic and Antarctic. SCCPs were listed under provisions of the Stockholm Convention for global elimination with the allowance of time-limited exemptions for certain industrial uses at the 8th Conference of the Parties in April 2017 [6]. SCCPs are toxic to aquatic organisms at low concentrations; adversely affect the kidney, liver, and thyroid; and disrupt endocrine function [7, 8, 9]. SCCPs are classified in the 13th Edition of the Report on Carcinogens by the U.S. National Toxicology Program as *"reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity from studies in experimental animals* [10]." SCCPs are found in fish, seals, walrus, and whales of the Arctic that serve as traditional foods of Indigenous peoples [11, 12, 13]. SCCPs are also found in the breast milk of Arctic Inuit women [14]. The Stockholm Convention review of SCCPs found reports of contamination in consumer products – including children's products and food contact materials. This study investigated the levels of SCCPs in children's toys purchased in 10 countries and in hand blenders used to make baby food because we hypothesized that they are ubiquitous in a range of consumer products, including toys.

Materials and methods

One gram of sample (cryogenically milled) was extracted by shaking with the solvent mixture *n*-hexane:dichloromethane (4:1; v/v) for 3 h. The crude extract was purified using gel permeation chromatography in the Bio-Beads S-X3 column with the mixture cyclohexane-ethylacetate (1:1, v/v). The fraction corresponding to elution of SCCPs was evaporated, residues were dissolved in cyclohexane and transferred into the vial for final instrumental analysis. The instrumental measurement was performed on an Agilent 7890B gas chromatograph coupled with a 7200 QTOF mass spectrometer (both Agilent Technologies, USA) in negative chemical ionization

(NCI). A capillary column DB-5MS (30 m x 0.25 mm x 0.25 µm, Agilent Technologies, USA) was used for separation of target compounds. The following instrumental settings were applied: He flow (carrier gas) - 1 ml/min; Inlet temperature - 280°C; Injection - 1 µl pulse splitless (206.7 kPa, 30 psi); Temperature program - 140°C (held 1 min) - 30°C / min to 310°C - 2°C / min to 325°C (held for 2 min), total analysis time 16.2 min; Transferline temperature - 280°C; Reaction gas – methane; Ion source temperature - 150°C; Acquisition rate - 5 spectra/s; HRMS - 12,500 FWHM . The quantification method is based on the calculation of the chlorine content within the SCCPs fraction. Six standard mixture (technical mixtures) of the same concentration (10 µg/ml), but with different average chlorine contents, were measured. 48 masses (24 quantification and 24 confirmation ions) corresponding to [M Cl] - ions representing individual congener groups (each characterized by the compound formula) were monitored. A total response factor (TRF) was calculated. This quantification method is based on a study by Xia et al. 2016 [15].

Results and discussion

Laboratory analyses of 60 toys and other children's articles from 10 countries (Brazil, Canada, China, Czech Republic, India, Japan, Kenya, Netherlands, Russia, and United States) found that 45% (27) of the samples contained SCCPs at concentrations ranging from 8.4 to 19,808 parts per million (ppm). Toys and children's articles analyzed in this survey included plastic animals, jump ropes, sandals, rain boots, plastic balls, pendants, and swim gear. A majority of the labeled products containing SCCPs were manufactured in China. SCCPs are pervasive in a broad range of household products that may contribute to human exposure. Children are more vulnerable because their physiology and behavior may cause higher exposures through skin absorption, inhalation, and ingestion. This study found a hand blender which contained SCCP contamination, with a level measured in leachate of 3.3 ppb. This product can contaminate prepared foods and is commonly used to prepare baby food. None of the product labeling indicated that they contained substances of current global concern.

The levels of SCCPs found in this study were similar to those observed in previous studies. SCCPs exceeded permitted levels in children's products tested in Norway, with concentrations ranging from 1,600 – 107,000 ppm (0.16-10.7%) [16]. When conducting tests on household articles, the Swedish Chemicals Agency found that of 62 articles tested, 16 contained SCCPs in high concentrations; and 11 of the articles contained lower concentrations of SCCPs that were thought to have resulted from contamination in the manufacturing or delivery process [17]. In Germany, 19 of 84 plastic products contained SCCPs, with concentrations ranging from 440-50,000 ppm [18]. Levels of SCCPs ranging from 4,000 – 69,000 ppm (0.4-6.9%) were found in mats tested in Austria [19]. In Sweden, a recent study demonstrated that hand blenders used in food preparation for babies and infants are unexpected and serious sources of exposure to SCCPs. Eight out of twelve hand blenders leaked SCCPs into prepared food. The scientists concluded: *"the presence of chlorinated paraffins in household appliances that contaminate food during preparation is unacceptable and actions have to be taken immediately* [20]."

In 2015, the European Commission set a weak regulatory limit of 0.15% by weight (1,500 parts per million) for SCCPs in articles [21]. Six of the toys in this study (10%) significantly exceeded this standard with levels of 4,376 ppm (a baby bib purchased in India), 4,866 ppm (a baby bib purchased in Kenya), 6,918 (beach ball purchased in Kenya), 9,715 ppm (a gym ball purchased in the Czech Republic), 13,973 ppm (a plastic duck purchased in Brazil), and 19,808 ppm (a jump rope purchased in Japan). Several countries where SCCPs are banned (including Austria, Germany, Norway, and Sweden) have taken enforcement actions when inspections revealed that SCCPs exceeded permitted levels in household products.

The Stockholm Convention expert committee (known as the POPs Review Committee or POPRC) recommended listing SCCPs in Annex A of the treaty for global elimination. The Conference of the Parties of the Stockholm Convention listed SCCPs in Annex A of the Convention in April 2017 with specific time-limited exemptions [22]. Listing SCCPs in Annex A of the treaty prohibits production, use, import, and export of SCCPs, except for purposes of environmentally sound disposal in accordance with Convention provisions. The Stockholm Convention also includes measures to address releases from stockpiles and wastes in Article 6. This includes establishment of hazardous waste limits known as low POP content levels (LPCLs). These limits define the value at which wastes are considered to be POPs wastes and therefore must be *"Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed"* (Stockholm Convention Article 6.1 d ii.) Thus, LPCLs are crucial for defining which wastes are hazardous according their POPs content. The provisional LPCLs for most POPs listed in the treaty have been set at 50 ppm. However, lower limits have been proposed for some substances [23]. For example, PCBs have had a provisional LPCL of 50 ppm, but a limit of 10 ppm has been proposed. If SCCPs are listed in the Convention, then an expert group will study the matter and make a proposal for LPCL for consideration at the Conference of the Parties in 2019. Using 50 ppm as a "typical" LPCL for comparison reveals that a significant proportion of the products in this study would be considered hazardous waste. Eighteen toys (67%) exceeded 50 ppm SCCPs. If a lower LPCL of 10 ppm is used for comparison, then 96% of the samples (26 of 27) exceeded this limit and would be classified as hazardous waste and subject to treaty waste provisions.

SCCPs are substances of global concern and now included for world-wide elimination under the Stockholm Convention. Surprisingly, SCCPs are widely present in children's toys made of plastic. Ninety-six percent of the toys with measureable concentrations of SCCPs contained levels of 10 ppm or greater. These results compare with other studies that found SCCPs in consumer products, even though they are banned—often in high concentrations and above permitted levels. Products containing SCCPs are likely to be a significant pathway for human exposure and particularly harmful for infants and children. It will be important to monitor levels of SCCPs in consumer products as a measure of the effectiveness of the Stockholm Convention.

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Characterization of placental transfer of short- and medium-chain chlorinated paraffins in paired maternal and cord serum

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1.Introduction

Chlorinated paraffins (CPs), or named polychlorinated alkanes (PCAs), are a class of complex mixtures containing thousands of different isomers, enantiomers, and diastereomers [1]. According to the carbon chain length, they can be subdivided into short-chain CPs (SCCPs, C_{10}–C_{13}), medium-chain CPs (MCCPs, C_{14}–C_{17}), and long-chain CPs (LCCPs, $C_{>17}$). Considering the potential for long-range transport [2], persistence [3], bioaccumulation [4] and toxicity [5], SCCPs have been listed as persistent organic pollutants (POPs) in the Stockholm Convention in May 2017. Although multiple studies have demonstrated the occurrence of SCCPs and MCCPs in environmental matrices, including air [6], water [7], soil [6] and sediment [8], studies about human exposure of SCCPs and MCCPs are very limited. To date, only a few studies have investigated the level of CPs in human milk [9, 10], and just one study has focused on the human blood [11]. More data on internal exposure, including human blood concentrations and congener profiles, are needed to access the health risk posed by CPs.

POPs have been reported to also penetrate into the fetal system, despite the protective role of placenta. In fast growing stages of life, fetuses are more vulnerable than adults to the potential harmful effects of chemicals. The prenatal exposure to chemical contaminants via placental transfer may even result in irreversible adverse effects on growth and development of fetuses. The potential toxicity of the compounds in this case highlighted the necessity to understand CP contaminant levels in umbilical cord blood, placental transport mechanisms as well as health effects of prenatal exposure. However, to the best of our knowledge, there has been no related study due to the difficulty in analytical technique of CPs.

In this study, SCCPs and MCCPs were analyzed in fifteen paired maternal and umbilical cord serum using two-dimensional gas chromatography coupled with time-of-flight mass spectrometer (GC×GC–TOFMS). The contamination levels and congener group profiles were investigated at the first step to gain a better understanding of the mechanisms of the placental transfer and neonatal exposure risk of CPs.

2.Materials and methods

2.1 Sample collection

15 pairs of maternal and cord serum samples were collected from women and their neonates in 2012. From February to May, volunteers of the pregnant women were randomly recruited. For the aim to investigate the prenatal exposure in Beijing general population and to exclude other influencing factors, volunteers were required as healthy local resident women who gave birth to a single live-born child without congenital anomalies. These women agreed to participate in the present study at Haidian Maternal & Child Health Hospital in Beijing, capital

city of China. For each participant, information such as maternal age, BMI, maternal previous live births, neonatal sex, neonatal type of delivery, gestational weeks, neonate's birth weight and birth length was collected from medical records since 13–16 weeks of pregnancy. Cord blood samples were collected immediately after delivery, while maternal blood samples were collected within one or two days before delivery. Then the sera were transferred to prescreened 3 mL polypropylene containers and stored at −80 °C for analysis.

2.2 Sample extraction and cleanup

Each 1mL of serum sample was spiked with 2.5 ng of $^{13}C_{10}$-trans-chlordane, and then extracted with 10mL mixed solvent of n-hexane and dichloromethane (1:1, v/v) by ultrasonic for five times. The extract was evaporated to about 1 mL, and fractionated on a multi-layer silica gel column containing 3 g of Florisil, 2 g of neutral silica gel, 5 g of 30% acidified silica gel, and 4 g of anhydrous sodium sulfate from the bottom to top. The column was rinsed with 50 mL of n-hexane. Afterwards, the sample was added and eluted with 40 mL of n-hexane as well as 100 mL of n-hexane/dichloromethane (1:1, v/v). The second fraction was collected, concentrated to near dryness, and solvent-exchanged with 50 µL of cyclohexane. Before analysis, 2.5 ng of ε-HCH was added as an injection internal standard.

2.3 Instrumental analysis

Analysis of SCCPs (C_{10}–C_{13} with 5–10 chlorine atoms) and MCCPs (C_{14}–C_{17} with 5–10 chlorine atoms) in the serum samples were carried out by a GC×GC–TOFMS instrument. Briefly, each 1-µL sample was injected in splitless mode, and the injector was set at 280 °C. The GC oven temperature started at 140 °C for 1 min, then increased at 10 °C/min to 200 °C, increased at 1.5 °C/min to 310 °C, and finally maintained at 310 °C for 5 min. The modulation period was set to 8 s. The mass spectrometer was performed in ECNI mode with methane as the reagent gas. Twelve groups of ordered structures were shown on the two-dimensional chromatogram, and those congeners with the same number of carbon plus chlorine atoms (e.g., $C_{10}H_{13}Cl_9$, $C_{11}H_{16}Cl_8$, and $C_{12}H_{19}Cl_7$, $C_{13}H_{22}Cl_6$) were divided into the same group. The two most abundant $[M-Cl]^-$ m/z were selected as the quantification and qualification ions. The calibration curves between total response factors and chlorine contents of prepared CP solutions were established, so that differences of the chlorine contents between the experimental samples and referenced CP standards can be corrected. The GC×GC data were processed via GC Image® R2.5 Software (GC Image, Lincoln, NE).

3.Results and discussion

3.1 Occurrences of SCCPs and MCCPs in maternal and cord serum.

SCCP and MCCP concentrations in collected serum samples were all reported basing on the wet weight (ww). The concentrations of SCCPs in the maternal serum ranged from 20.1 to 178.3 ng/g ww, and the range for the chlorine contents was 60.7−61.6%. The MCCP concentrations ranged from 5.6 to 24.7 ng/g ww, and the chlorine contents of MCCPs were 54.9–56.6%. The concentrations of MCCPs were lower than those of SCCPs in all of the investigated samples. Compared with one previous studies of CPs in human blood [11], the concentrations in the present samples were lower to those found in a general population from Shenzhen, China. Concentrations of total SCCP and MCCP in cord serum were estimated to be 6.2−40.5 and 3.2−8.7 ng/g ww, respectively. The findings clearly demonstrated that SCCPs and MCCPs can cross the placenta and accumulate in fetal blood. Besides, concentrations of these compounds studied were all ordered maternal serum > cord serum, suggesting an effective placental barrier and possible dilution during fetal growth.

3.2 Congener group profiles of SCCPs and MCCPs in maternal and cord serum.

The homolog patterns of SCCP and MCCP in maternal and cord serum were both analyzed (Fig.1). For SCCPs in the maternal serum, C_{10}-CPs was the most abundant, followed by C_{11}-CPs. The dominant chlorine homolog groups were Cl_6- and Cl_7-CPs. For MCCPs, Cl_7- and Cl_8-CPs were the major chlorine homolog groups, and C_{14}-CPs was the main carbon chain. The homolog patterns of SCCP were different from those found in Shenzhen [11], in which C_{13}-CPs dominated most, followed by C_{12}, C_{11}, C_{10} compounds. The reason may be the different contamination source between different places. In addition, the congener patterns of SCCP and MCCP in cord serum were similar with that in maternal serum, but with an increasing percentage of long-chain compounds.

3.3 Placental transfer of SCCPs and MCCPs.

Average concentration ratios of SCCPs and MCCPs between maternal blood and cord blood were calculated and shown in Fig.2. All values were less than one but varied among different homologs. In particular, the ratio increased as carbon chain became longer to a certain extent, and the value was highest for C_{16}-CPs. Similarly, the ratio was highest for Cl_8-CPs not Cl_{10}-CPs. It has been reported that passive diffusion often governs transport mechanism for drugs crossing the placental barrier. Important properties of the chemicals that determine the rate and extent of placental transfer by passive diffusion include molecular weight, ionization, lipid solubility, and protein binding. Toxic chemicals that are lipophilic and not protein-binding transfer more easily through the placenta. In this case, CPs with longer carbon chain are more easily to cross the placental. Obviously, the actual process was more complicated than only this based on the above data. There are other possible transmission mechanisms at the same time, such as facilitated diffusion and transporter mediated transport. The process of placental transfer of SCCPs and MCCPs may be governed by some different factors concurrently.

To our knowledge, this is the first study to report the occurrence of SCCPs and MCCPs in cord serum and the maternal-fetal ratios of each congener. While the sample size in the present study is relatively small, the results can provide insights into the placental transfer behavior of these chemicals. The mechanisms elucidated by which SCCPs and MCCPs are transferred from mother to fetus through the placenta could give us important implications for assessing infant health risks associated with maternal exposure to the compounds.

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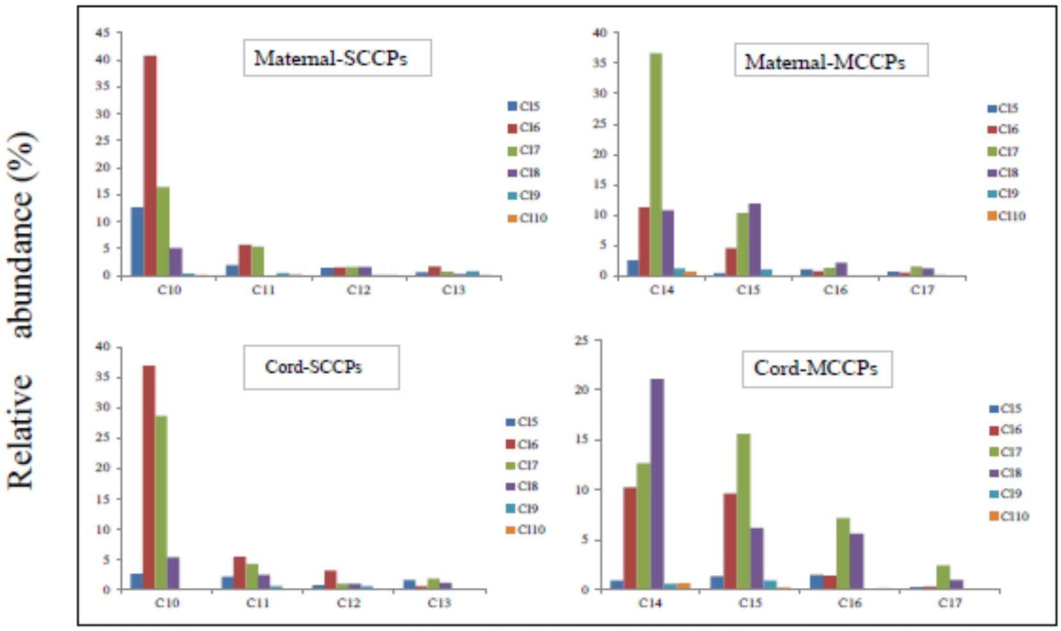

Fig.1. Congener group profiles of SCCPs and MCCPs in maternal and cord serum

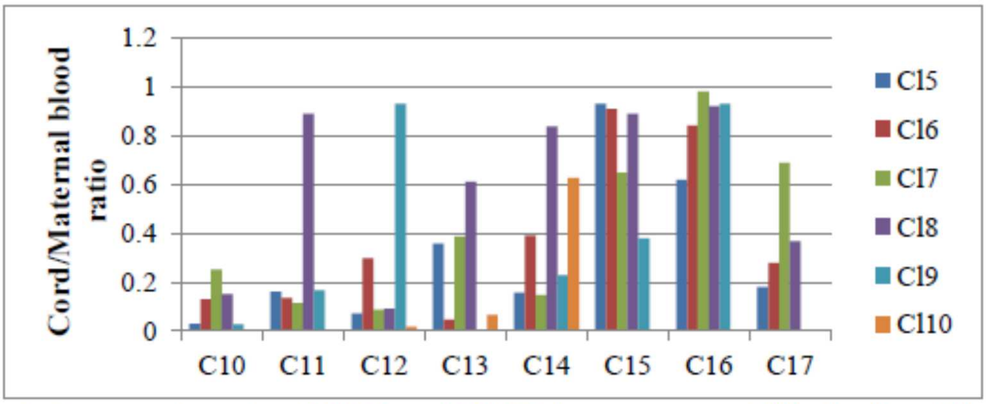

Fig.2. Concentration ratios of SCCPs and MCCPs between maternal blood and cord blood