出國報告（出國類別：會議）

參加「第 32 屆含鹵素持久性有機污染物國際研討會(戴奧辛 2012)」

服務機關：行政院環境保護署
姓名職稱：空保處吳正道簡任視察
毒管處蔡秋美毒化物助理管理師
環境檢驗所翁英明組長
派赴國家：澳洲
出國期間：101 年 8 月 25 日～9 月 1 日
報告日期：101 年 11 月 30 日

摘要

為持續了解國際戴奧辛研究及發展趨勢、分析技術及收集最新研究成果，本署乃派員參加本（101）年於澳洲凱恩斯舉行第 32 屆國際鹵化持久性有機污染物研討會（即 2012 戴奧辛年會），期望藉此參與大會吸取先進國家之經驗，以提升本署對於持久性有機污染物管制成效。

參加本次大會之重要心得及建議如下：

一、 本次會議總計發表論文 483 篇（口頭報告 271 篇、海報展示 212 篇），其中持久性有機污染物之分析化學之論文有 60 篇（口頭報告 39 篇、海報展示 21 篇）；傳輸、流佈和監測之論文有 98 篇（口頭報告 53 篇、海報展示 45 篇）；來源、形成與轉化之論文有 47 篇（口頭報告 28 篇、海報展示 19 篇）；暴露於持久性有機污染物之論文有 72 篇（口頭報告 35 篇、海報展示 37 篇）；毒理學和健康之論文有 86 篇（口頭報告 46 篇、海報展示 40 篇）；法規、政策和生命週期管理之論文有 40 篇（口頭報告 23 篇、海報展示 17 篇）；其他議題之論文有 80 篇（口頭報告 47 篇、海報展示 33 篇）。

二、 本署（檢驗所）進行「SINK OF DIOXIN-LIKE CONPOUNDS AND PBDES IN RESERVOIR SYSTEMS IN NORTHERN AND CENTRAL TAIWAN」之口頭報告（Oral presentation）。分析台灣石門水庫及日月潭水庫底泥

PCDD/F, DL-PCB 及 PBDE 等戴奧辛及類戴奧辛化合物之不同時間濃度變化趨勢。

三、 本次研討會對於持久性有機污染物之採樣分析方法之開發與驗證有許多發展，在環境監測部分對於含氟化合物、溴化合物的類戴奧辛化合物的探討亦較往年多，尤其對於戴奧辛及類戴奧辛化合物之傳輸、流佈亦有許多探討。

四、 本次研討會對於鹵化持久性有機污染物之討論，除大氣環境與食物鏈外，亦開始著重在室內環境的影響，對於室內環境較易暴露之阻燃劑的應用及替代品，亦為所關心之議題。

五、 2013 年戴奧辛年會，將於 2013 年 8 月 25 日至 8 月 30 日在南韓 Daegu 舉行，屆時期望本署再派員與會，以收集各項發展之資訊，供國內施政之參考。

六、 本次會議是以鹵化持久性有機污染物之分析、傳輸流佈監測、來源、曝露和健康為討論之重點，並同時強調於法規和政策及風險評估管理和溝通之重要，其結果均可作為我國污染源防制之運用與借鏡。

目次

附錄九、FINGERPRINTS OF PBDEs, PCDD/Fs, AND dl-PCBs, IN RESIDENTIAL DUST OF WESTERN AUSTRALIA

附錄十、SOURCE EVALUATION OF DIOXINS/FURANS, PAHS, AND PENTACHLOROPHENOL IN SOIL SAMPLES NEAR A WOOD TREATING SITE IN THE SOUTHEASTERN USA

附錄十一、DIOXINS FORMED DURING FIRES, A THREAT TO THE FOOD CHAIN?

附錄十二、Environmentally Sustainable Management of Medical Waste in China, Dedicating to Reducing Dioxins—Progress and Impact

附錄十三、Substitutes of Persistent Organic Pollutant(POP) Pesticides in Bangladesh and The Need For a Sustainable Substitution Process

附錄十四、Environmental Health Research at NIEHS: Current Priorities and Plans For The Future

附錄十五、會議議程

壹、研討會簡介：

International Symposium on Halogenated Persistent Organic Pollutants，「含鹵素持久性有機污染物國際研討會」之前身為國際戴奧辛研討會，該研討會自1980年來每年於舉辦國舉行為期一周之研討會，吸引來自40多國家的800~1000名相關研究人員參與研討會。隨著國際對持久性(Persistent Organic Pollutants，POPs)有機污染物之關注，國際戴奧辛研討會會議名稱自2006年起改為「含鹵素持久性有機污染物國際研討會」，簡稱仍為戴奧辛研討會(Dioxin 20XX)。戴奧辛研討會至今已舉辦32屆，今年於澳洲凱恩斯(Cairns)舉辦，本屆總計發表超過450篇短論文(short papers)，其內容涵蓋分析及環境化學(analytical and environmental chemistry)、分子生物學(molecular biology)、人類健康(human health)、風險評估(risk assessment)、風險管理(risk management)等不同領域。

圖1　第32屆含鹵素持久性有機污染物國際研討會LOGO

貳、研討會研討重點

本次研討會分為 6 大主題，1.分析化學(Analytical chemistry)、2.污染物的傳輸、宿命及監測(Transport, fate and monitoring)、3.污染物的來源、形成及轉化(Sources, formation and transformation)、4.POPs 的暴露危害(Exposure to POPs)、5.毒理學及健康(Toxicology and health)、6.法規、政策及生命週期管理(Regulation, policy and life cycle management)。各大主題下有 4~6 項子題。各子題如下：

1. **Analytical chemistry**
   A1. Advances in instrument techniques
   A2. Non-target and emerging contaminant analysis
   A3. New screening and rapid methods
   A4. Sampling and sample preparation methods
   A5. QA/QC and interlaboratory studies
   A6. Development and validation of bioanalytical methods
2. **Transport, fate and monitoring**
   B1A.Environmental monitoring - brominated compounds
   B1B. Environmental monitoring - fluorinated compounds
   B1C. Environmental monitoring
   B2. Passive sampling approaches and applications
   B3. Modelling of environmental fate, transport and sources
   B4. Atmospheric monitoring, fate and sources
   B5. Indoor environments
   B6. Bioindicators, bioaccumulation and food web studies
3. **Sources, formation and transformation**
   C1: Source and emission inventories
   C2: Fingerprinting, sources and processes
   C3: Formation and degradation processes and products
   C4: Thermal sources and formation processes
   C5: Emission reduction methods and technologies
4. **Exposure to POPs**
   D1: Levels in food/feed

    - D2: Biomonitoring in humans
    - D3: Exposure assessments and pathways
    - D4: Industrial, occupational and accidental exposure
    - D5: Exposure and health of aquatic wildlife

5. **Toxicology and health**
    - E1: Epidemiology and burden of disease
    - E2: Mechanisms and pathways of toxicity, incl. mixture toxicity
    - E3: Toxicodynamics and toxicokinetics
    - E4: POPs and disease
6. **Regulation, policy and life cycle management**
    - F1: Regulation and policy of POPs
    - F2: Risk assessment, management and communication
    - F3: Sustainable production and use
    - F4: Remediation and assessment of contaminated areas

参、研討會內容摘要

針對本次研討會內容，特選與環境空氣戴奧辛及與管制方式及持久性有機污染物等相關 14 篇進行介紹。

1. 論文編號：A3.101

SIMPLIFYING MULTI-RESIDUE ANALYSIS OF FLAME RETARDANTS

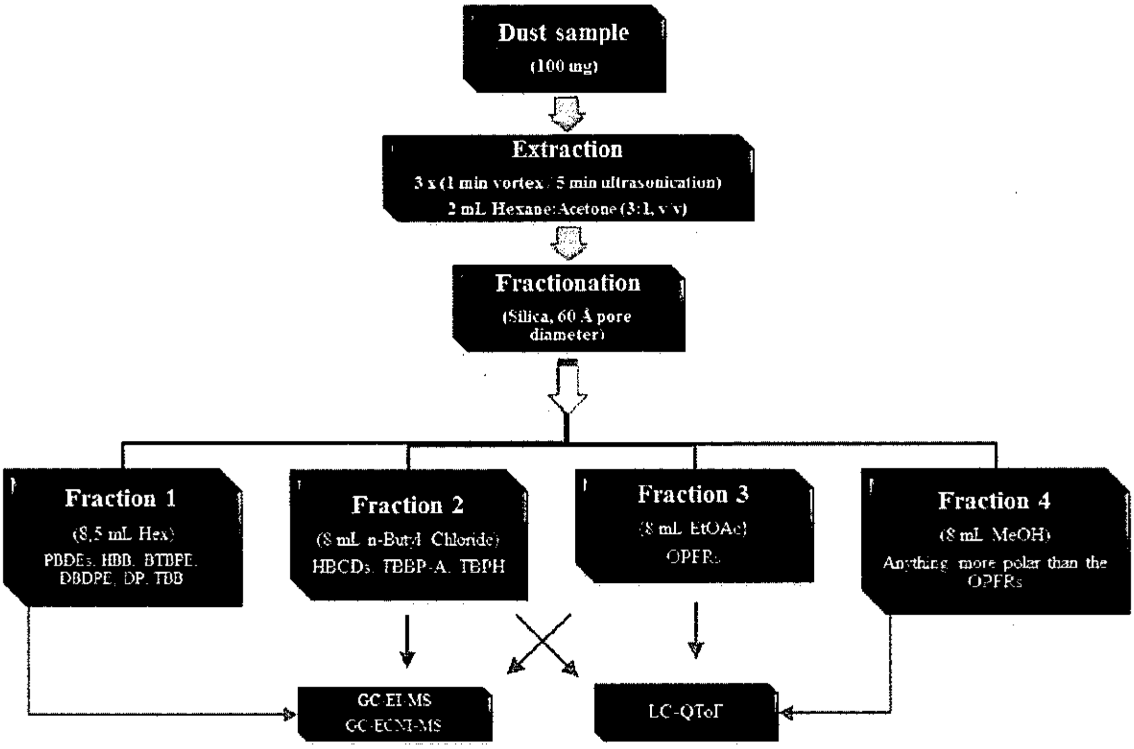
Ionas AC*, Covaci A

Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

為了降低可燃性，阻燃劑（FRS）經常被添加到消費類產品，軟墊家具、紡織、電子和建材。不幸的是，大多數這些化合物對環境和動物和人類健康的潛在危險有負面的影響。雖然阻燃劑已超過15年，我們對環境的流布和毒性作用的認識仍然有限。具選擇性功能的分析方法(如 GC-MS or LC-MS)同時測定不同類別的阻燃劑，如溴化（溴化阻燃劑）、有機磷（OPFRs）和氯化阻燃劑(如下表)。

表 不同類型流洗液所分析出之阻燃劑化合物

Fraction Nr.	Elution solvent	Compounds
1	Hexane	PBDEs, PBBs, α,β-TBCO, HBB, BTBPE*, syn,anti-DP, OBIND, DBDPE, TBA, ATE, DPTE, TBB, HCDBCO
2	*n*-Butyl Chloride (1-chlorobutane)	HBCDs and breakdown compounds, TBBP-A, MeTBBP-A, TBBPA-DBPE, TBPH
3	Ethyl Acetate	OPFRs including TDBPP
4	Methanol	None of the compounds in the standard mixtures; normally compounds more polar than the OPFRs



多重殘留阻燃劑之分析流程

2. 論文編號：A3.103

A RAPID METHOD FOR ANALYSIS OF PFAAs IN HUMAN SERUM USING 96-WELL PLATE-LARGE VOLUME INJECTION-UPLC-MS/MS

Samira Salihovic[1]*, Anna Kärrman[1], Gunilla Lindström[1], P. Monica Lind[2], Lars Lind[3], Bert van Bavel[1].

[1]MTM Research Centre, Örebro University, Örebro, Sweden; [2]Occupational and Environmental Medicine, Uppsala University, Uppsala, Sweden; [3]Acute and Internal Medicine, Uppsala University, Uppsala, Sweden

全氟烷基酸（Perfluoroalkyl Acids,PFAAs）已廣泛分佈於環境中。在瑞典PFAAs的流行病學研究中人體血液平均以全氟辛烷磺酸（PFOS）15.8 ng/mL，全氟辛酸（PFOA）4.5 ng/mL，全氟磺酸（PFHxS）5.5 ng/mL和全氟壬酸（PFNA）0.85 ng/mL檢出的濃度較高。研究顯示，在一般人群中即使

低劑量的的背景暴露於各種工業化學品，如PFAAs，亦可能對健康產生負面影響，為了能夠調查PFAAs之間的關聯性和健康的影響，以96孔板的高通量樣品製備和大體積注射UPLC-MS/MS分析技術，是一種快速、精確的分析方法。

3. 論文編號：B4.102

PCDD/F MEASUREMENT AT THREE HIGH-ALTITUDE STATIONS IN EASTERN ASIA: EVALUATION OF LONG-RANGE TRANSPORT OF PCDD/FS DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT

Chi KH[1]*, Chen YF[1], Lin CY[2], Sheu GR[3], Lin NH[3]

[1]Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei 112, Taiwan; [2]Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan; [3]Department of Atmospheric Sciences, National Central University, Chungli 320, Taiwan.

近年來長程傳輸所帶來之懸浮微粒中各污染物之組成特性也引起國內外學者的關注，其中持久性有機污染物（Persistent Organic Pollutants, POPs）即為最可能經由長程傳輸進入台灣境內的污染物之一。春季是中南半島生質燃燒季節，衛星遙測結果亦顯示觀測期間東南亞與南亞生質燃燒活動旺盛，所產生之大氣污染物可能隨西風帶傳送至鹿林山測站。該報告是由我國陽明大學紀凱獻博士研究團隊於2010年之研究，結果顯示鹿林山總大氣戴奧辛濃度介於1.25至6.09 fg I-TEQ/m^{3}之間，濃度變化相當顯著，同時間泰國清邁測站大氣戴奧辛濃度則介於3.88至12.1 fg I-TEQ/m^{3}之間，值得注意的是，兩測站大氣戴奧辛濃度日變化趨勢相當一致，明顯呈現受同一污染源之影響。為了進一步釐清東南亞生質燃燒事件對台灣大氣戴奧辛濃度變化之影響，於2011/3/16至2011/4/1針對鹿林山測站與越南西北部山區測站(Son La)進行生質燃燒事件大氣戴奧辛採樣，結果顯示，兩山區測站大氣戴奧辛濃度日變化趨勢相當接近，採樣期間鹿林山大氣戴奧辛濃度介於2.55~29.5 fg I-TEQ/m^{3}之間而越南西北山區Son La測站大氣戴奧辛濃度則介

於11.1~59.5 fg I-TEQ/m^3。值得注意的是，當地兩次生質燃燒事件日期間(2011/3/26~3/30)，兩測站大氣戴奧辛濃度明顯出現峰值，結合國際大氣戴奧辛聯合觀測數據與WRF/Chem模式模擬結果進行比對，在生質燃燒源區(泰國清邁與越南山蘿)大氣戴奧辛濃度之變化與衛星火點之發生頻率及強度面積相當吻合，反觀下風處鹿林山測站，其大氣戴奧辛濃度之變化則與生質燃燒源區所產生之污染氣團傳輸範圍及污染強度具相關性，進而驗證生質燃燒源區及下風背景測站之傳輸關係，並釐清戴奧辛污染物於生質燃燒事件期間之跨境傳輸特性。

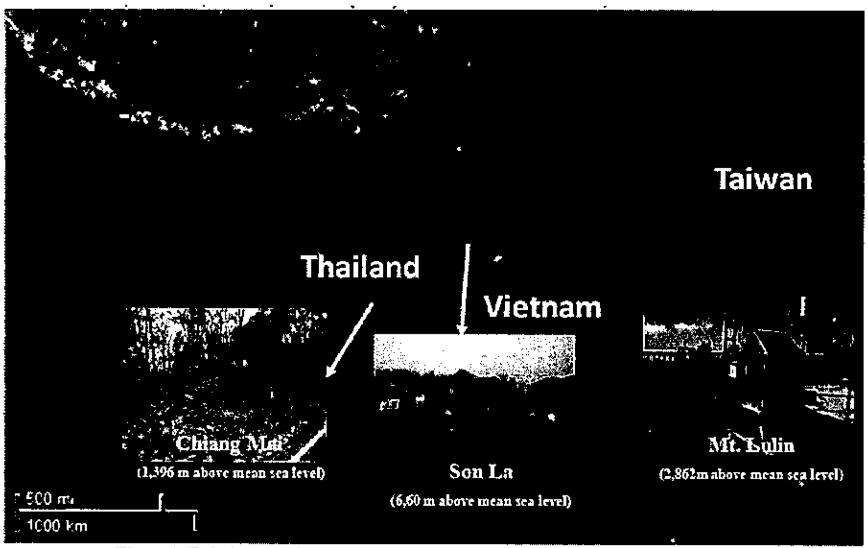


Figure 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

泰國清邁、越南山蘿與我國鹿林山測站相關位置圖

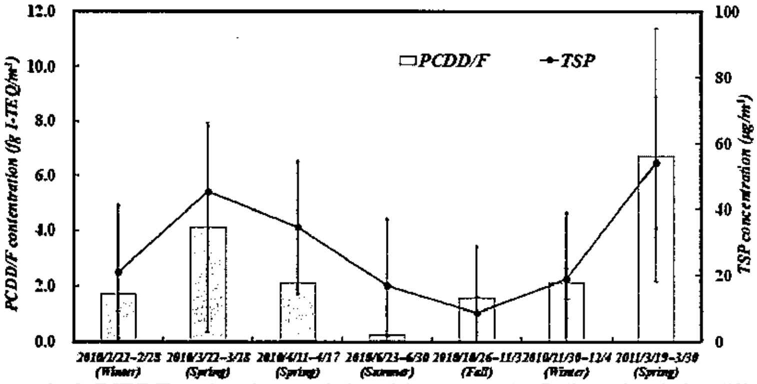


Figure 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during different periods.

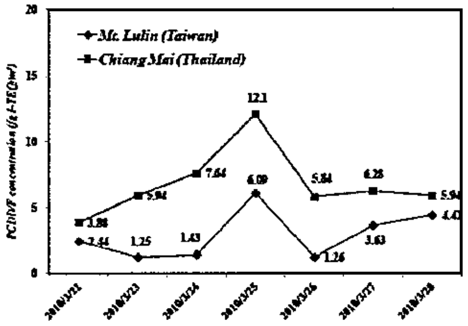


Figure 3 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Thailand during significant biomass burning event (2010/3/22-3/28).

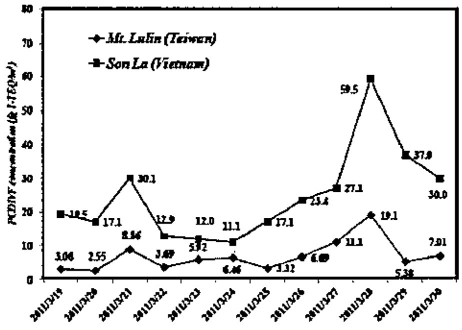


Figure 4 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Vietnam during significant biomass burning event and northern Vietnam (2011/3/19-3/30).

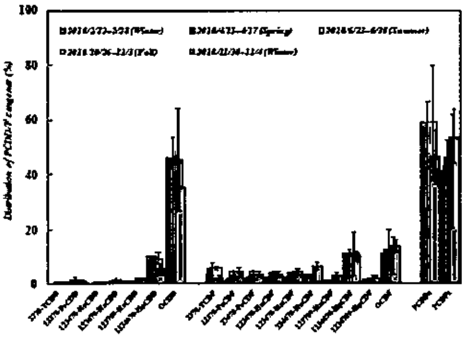


Figure 5 PCDD/F congener distribution in ambient air at Lulin station during regular sampling periods.

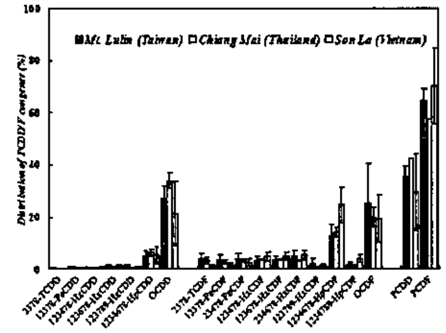


Figure 6 PCDD/F congener distribution in ambient air in central Taiwan, northern Thailand and Vietnam during Southeast Asia biomass burning event.

本研究各類型燃燒事件之戴奧辛特徵分布

4. 論文編號：B4.103

Persistent Organic Pollutants (PCDD/Fs, PCBs AND PBDEs) in Ambient Air from Barcelona (Catalonia, Spain). Seasonal Variation

Martínez A, Gasser M, Montaña MJ, Martí R, Díaz-Ferrero J

Environmental Laboratory, Institut Químic de Sarrià (University Ramon Llull), Barcelona, Spain.

本篇研究針對西班牙巴塞隆納之大氣PCDD/Fs、PCBs、PBDEs進行不同季節共13站次的監測，結果如表1，戴奧辛(PCDD/Fs+DL-PCB)環境空氣濃度為0.0157~ 0.0551 (平均0.0303) pg WHO$_{2005}$-TEQ/Nm^3。戴奧辛(PCDD/Fs)主要以粒狀存在，尤其在下雨過後會有明顯的降低(如圖2)。而PCBs則以氣態為主，夏天及白天濃度較高。PBDEs與PCDD/Fs相同以粒狀為主，夜晚的濃度較白天高。

表1　巴塞隆納大氣POPs監測結果

Table 2. Concentration of POPs in the samples analyzed.

Pollutants	Average	Minimum	Maximum
NDL-PCB (pg/m^3)	42.9	23.3	88.3
DL-PCB (pg/m^3)	5.55	2.00	11.5
TEQ*-DL-PCB (fg TEQ/m^3)	2.94	1.67	6.30
PCDD/F (pg/m^3)	0.63	0.13	3.30
TEQ*-PCDD/F (fg TEQ/m^3)	27.4	13.7	48.8
PBDE (w/o 209) (pg/m^3)	3.41	1.50	5.80
PBDE (w 209) (pg/m^3)	21.9	6.90	47.8

**TEQ concentration has been calculated by using 2005 TEF*[3]

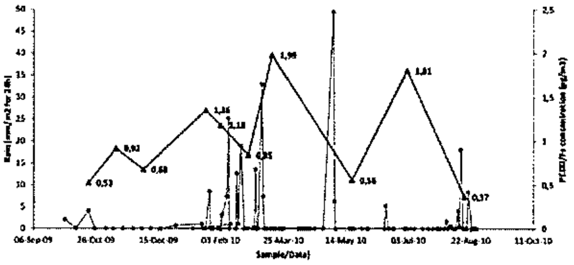


Figure 2. Rain deposition (mm/m^2 for 24h) and PCDD/F concentration during the studied period.

圖2　降雨與PCDD/Fs濃度之關係

5. 論文編號：B4.104.

Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Atmosphere Collected From Background Area in China in 2011-2012

Lirong Gao ,Lidan Liu, Bing zhang, Cheng Li, Minghui Zheng , Qiang Fu ; Yibing Lv
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China
Nationanal Environmental Monitoring Center of China, Beijing, China.

本篇研究團隊於中國6個背景站執行戴奧辛大氣監測(每站至少採3天)，測站相關位置如圖3，監測結果如表2所示，其結果為0.0047~0.3343 fg WHO-TEQ/m^3 最高值(C站)位於市區公園，最低值(E站)位於郊區。

Figure.1 sampling location

圖3　中國執行大氣戴奧辛監測背景站位置

表2　中國6背景站執行大氣戴奧辛監測結果

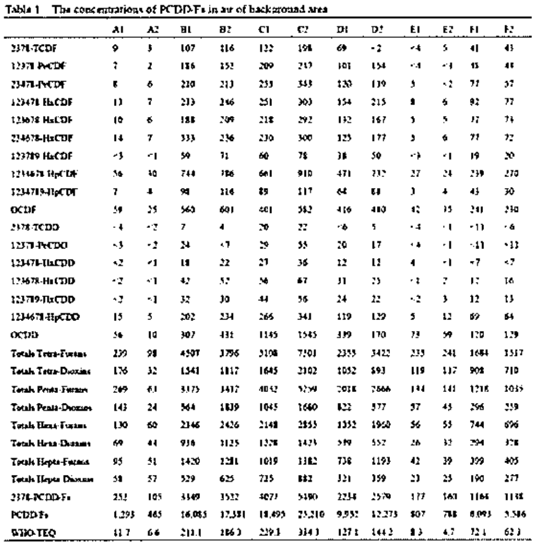


Table 1　The concentrations of PCDD-Fs in air of background area

	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2	F1	F2
2378-TCDF	9	3	107	116	122	198	69	<2	<4	5	41	43
12378-PeCDF	7	2	186	152	209	237	101	154	<4	<4	45	48
23478-PeCDF	8	6	210	213	233	343	120	139	3	<2	77	57
123478-HxCDF	13	7	213	246	251	303	154	215	8	6	92	77
123678-HxCDF	10	6	188	209	218	292	132	167	5	5	77	73
234678-HxCDF	14	7	333	236	230	300	125	177	3	6	77	72
123789-HxCDF	<3	<1	59	71	60	78	38	50	<3	<1	19	20
1234678-HpCDF	56	30	744	786	661	910	471	732	27	24	239	270
1234789-HpCDF	7	4	98	116	89	117	64	68	3	4	43	30
OCDF	59	25	560	601	401	582	416	480	42	35	241	230
2378-TCDD	<4	<2	7	4	20	22	<6	5	<4	<1	<11	<6
12378-PeCDD	<3	<2	24	<7	29	55	20	17	<4	<1	<11	<13
123478-HxCDD	<2	<1	18	22	27	36	12	13	4	<1	<7	<7
123678-HxCDD	<2	<1	42	57	56	67	31	23	<3	7	17	16
123789-HxCDD	<2	<1	32	30	44	56	24	22	<2	3	12	13
1234678-HpCDD	15	5	202	234	266	341	119	129	5	12	69	64
OCDD	56	10	307	431	1145	1545	339	170	73	59	120	129
Totals Tetra-Furans	239	98	4507	3796	3108	7301	2355	3422	233	241	1684	1317
Totals Tetra-Dioxins	176	32	1541	1817	1645	2102	1052	893	119	117	908	710
Totals Penta-Furans	269	61	3173	3417	4032	5759	2018	2666	144	141	1218	1035
Totals Penta-Dioxins	143	24	564	1839	1045	1660	822	577	57	43	296	259
Totals Hexa-Furans	130	60	2146	2426	2148	2855	1332	1960	56	53	744	696
Totals Hexa-Dioxins	69	44	916	1125	1328	1473	599	557	26	32	294	378
Totals Hepta-Furans	95	51	1420	1281	1019	1182	738	1193	42	39	399	405
Totals Hepta-Dioxins	58	57	529	625	725	882	321	359	23	25	190	277
2378-PCDD-Fs	252	105	3349	3522	4077	5490	2234	2579	177	160	1164	1138
PCDD-Fs	1,293	465	16,085	17,381	18,495	25,210	9,932	12,273	807	788	6,093	5,586
WHO-TEQ	41.7	6.6	211.1	186.3	229.1	334.3	127.1	144.2	8.3	4.7	72.1	62.3

6. 論文編號：B4.106

Levels of Persistent Organic Compounds in Ambient Air of Africa

Klánová J*, Kukučka P, Přibylová P, Borůvková J, Prokeš R

Research Centre for Toxic Compounds in the Environment

非洲之POPs主要來源為殺蟲劑的使用，如DDT、安殺番、氯丹、林丹、毒殺芬等，非洲地區面臨的重大問題在於囤積過時或已禁用之POPs殺蟲劑，當局也缺乏對禁用殺蟲劑的使用管制。圖4為針對非洲14國進行被動式

大氣採樣(為期共6個月)。其結果顯示剛果、蘇丹、塞內加爾之PCDD/Fs最高，質量濃度各為0.45、0.2、0.13 pg/m^3；PCBs最高為蘇丹，21 pg/m^3；PBDEs最高為蘇丹、剛果、加那利群島及模里西斯，為24 pg/m^3、10 pg/m^3、7 pg/m^3、7 pg/m^3。

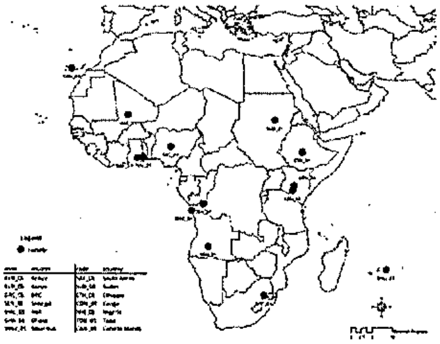


Figure 1. Passive air sampling sites monitored in the current campaign

圖4　非洲地區監測站位置

7. 論文編號：B4.109

PCDD/Fs Concentrations in the Atmosphere of Beijing, China

Zhou Z-G, Xu P-J, Qi L, Ren Y, Li N, Zheng S, Zhao H, Fan S, Zhang T, Liu A-M, Huang Y-R
State Environmental Protection Key Laboratory of Dioxin Pollution Control, Beijing, China

北京之工業排放源主要為電子、汽車製造、製藥、石油精煉及廢棄物燃燒，北京人口密度高，交通繁雜，因此北京之PCDD/Fs主要來源應為廢棄物燃燒及交通源。此研究針對4處交通繁忙點、1處公園、1處住宅區進行大氣採樣。監測結果為0.062~0.751 pg I-TEQ/Nm^3，超出日本0.6 pg WHO-TEQ/Nm^{3}之標準。最高值發生於冬天霾(haze)產生時，最低值於夏天發生。冬夏季別差異在於，冬季因使用暖氣，增加了石化燃料使用量且霾的產生增加了TSP，導致PCDD/Fs較夏季高(表3)。

表3　北京6站戴奧辛與TSP濃度

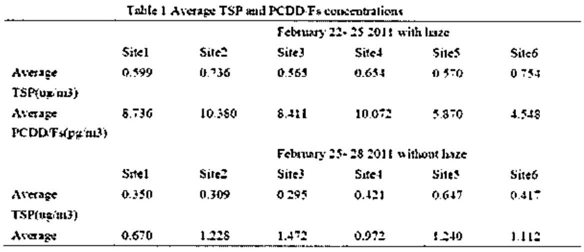


Table 1 Average TSP and PCDD/Fs concentrations

			February 22- 25 2011 with haze			
	Site1	Site2	Site3	Site4	Site5	Site6
Average TSP(ug/m3)	0.599	0.736	0.565	0.654	0.570	0.754
Average PCDD/Fs(pg/m3)	8.736	10.360	8.411	10.072	5.870	4.548
			February 25- 28 2011 without haze			
	Site1	Site2	Site3	Site4	Site5	Site6
Average TSP(ug/m3)	0.350	0.309	0.295	0.421	0.647	0.417
Average	0.670	1.228	1.472	0.972	1.240	1.112

8. 論文編號：C2.102

FINGERPRINTING PESTICIDES: EXPANDING DIOXIN SOURCE KNOWLEDGE

Holt EVA[1], Weber R[2], Stevenson G[3], Gaus C[1*]

[1]The University of Queensland (Entox), 39 Kessels Road, Coopers Plains, Australia; [2] POPs Environmental Consulting DE-73035 Göppingen, Germany; [3]National Measurement Institute, 1 Suakin Street, Pymble, 2073, Australia

減少或消除戴奧辛排放到環境中，來源確認是一個重要的步驟。而相關來源追踪研究卻很少，往往只有戴奧辛指紋的五氯酚（PCP）是用來描述農藥的使用來源，最近的研究發現，許多其他農藥中含有戴奧辛，它的使用可能是環境中戴奧辛重要的來源，新的信息也說明，形成從農藥之前驅物在環境中，可能會顯著改變原有的PCDD/ F指紋，本研究考慮之因素不只先前來源追蹤研究，在19個不同農藥產品的戴奧辛同源物特徵有更具體數據。在這項研究中的農藥製劑PCDD / Fs含量介於0.0043 - 1500奈克/克，值得注意的是，這些農藥的同源物的分佈相關性高（61 - 98%），主要是八氯數戴奧辛（OCDD），特別是五氯硝苯PCNB，金普施特，MECOPROP和可氯丹，文獻上同樣有高OCDD分布之農藥亦有五氯酚（PCP）和四氯苯醌。本研究對八氯數戴奧辛（OCDD）主要分布之農藥，亦列出<10%戴奧辛濃度的其他同系物，尤其經由不同來源及長期環境流布影響下，要藉由農藥中戴奧辛分布特徵，去區別環境中主要戴奧辛同源物OCDD是有難度

的，在長時間的環境曝露過程可能導致複雜的變化，當依靠小標記同源物指紋來源識別雖很重要，但是追溯性卻很難重建。有許多農藥的使用及其他來源的指紋導致PCDD/ F的污染，除了PCP外可能需要追查來源尚包括農藥前驅物的形成途徑。

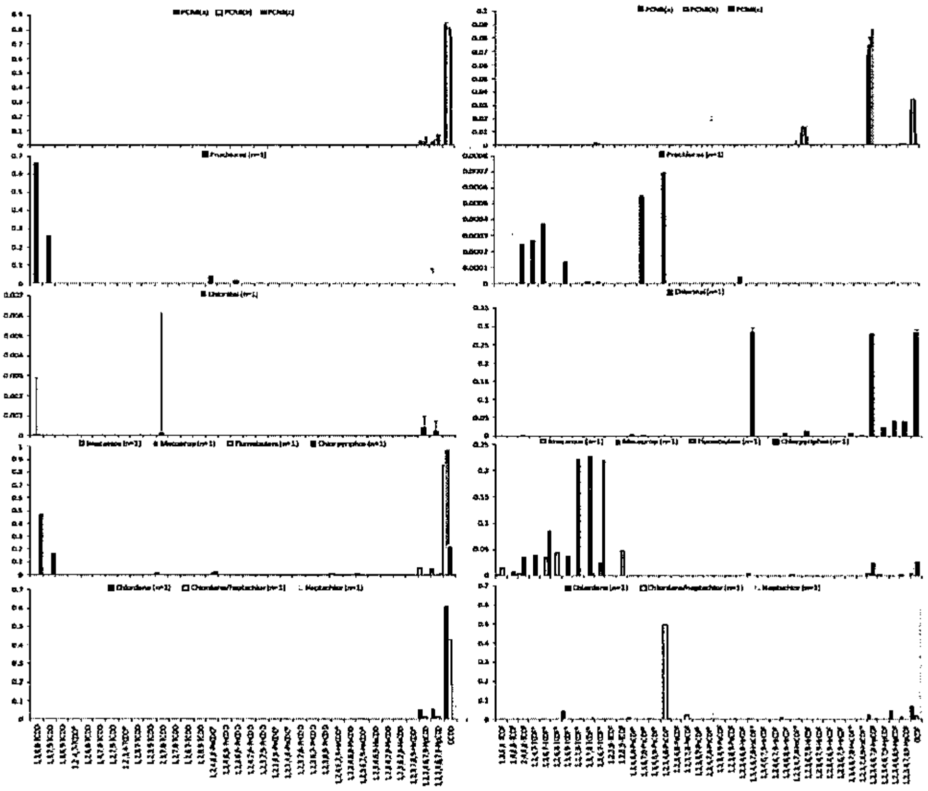


Figure 1. Congener profile (contribution to ∑PCDD/F) of PCNB; prochloraz; chlorthal [Average, minimum and maximum values of two replicates are presented for PCNB(a); PCNB(b) and chlorthal]; imazamox; mecoprop; flumetsulam; chlorpyriphos, and organochlorine pesticides - heptachlor and chlordane

不同農藥其PCDDs/PCDFs之同源物特徵分布亦不同

9. 論文編號：C2.103

FINGERPRINTS OF PBDEs, PCDD/Fs, AND dl-PCBs, IN RESIDENTIAL DUST OF WESTERN AUSTRALIA

Rogic D[1]*, Stevenson G[1], Yates A[1], Piro N[1], Crough R[1], de Araujo J[1], Mamahit G[1], Stasinska A[2], Reid A[2] ,Heyworth J[2] , Hinwood A[3], Callan A[3], Odland JO[4]

[1]National Measurement Institute, Riverside Corporate Park, 105 Delhi Road, North Ryde, NSW 2113, Australia; [2]University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia; [3]Edith Cowan University,270 Joondalup Drive, Joondalup WA 6027, Australia; [4]University of Tromso, NO-9037 Tromso, Norway

近年來，懷孕婦女、嬰兒和幼兒曝露在室內的污染物相當受到人們的重視，如多溴聯苯醚、鄰苯二甲酸鹽和農藥，用以評估和確定人類健康的風險。在許多室內灰塵中存在的有毒物質，我們把重點放在持久性生物蓄積性之毒性有機污染物，即多溴聯苯醚（PBDE）、戴奧辛（PCDDs/PCDFs）和戴奧辛類多氯聯苯（DL-PCBs）。本研究在建立西澳大利亞州的城市和農村灰塵的多溴聯苯醚、PCDD/ Fs和DL-PCBs的同源物的分佈，由特徵“指紋”以確定這些化合物的來源是背景污染或區域性活動所產生。包括比較各住宅粉塵樣品PBDE、PCDD / F與DL-PCB的同源物分佈型態和PCDD/ F和DL-PCB貢獻的TEQ值。雖然在1980年代以來，幾乎所有的工業國家，已禁止多氯聯苯的生產、加工和使用，而環境污染仍然發生，特別是由於處置不當的作法、使用中電氣設備和液壓系統洩漏，其他來源包括工業焚化爐、廢棄物焚燒、密封洩漏和舊建物油漆，由同源物特徵分布顯示，對於大多數家庭灰塵中PCDD/ Fs和DL-PCBs的污染可能是由類似的擴散源，由幾個樣品中可確定不同的分布型態所顯示不同區域的污染源特性。PBDE的多樣性分布型態更顯示多樣性的區域來源。

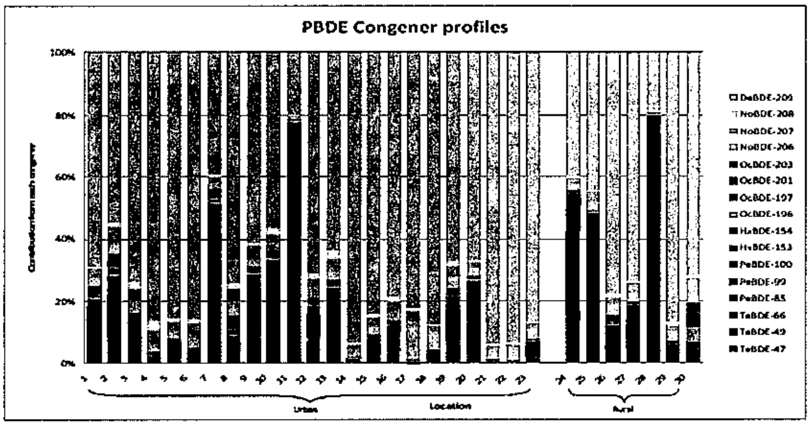


Figure 1 Contribution of major PBDE congeners to total mass of PBDEs

城市(NO.11)和農村(NO.28)室內灰塵的多溴聯苯醚具相似的分布特徵

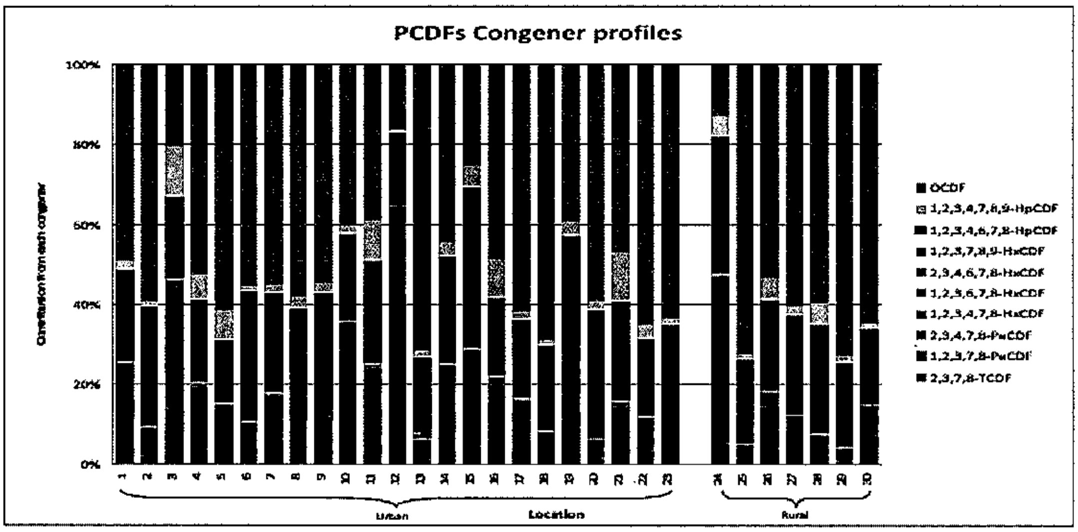


Figure 3 Contribution of PCDF congeners to total mass of PCDFs

特異性之PCDFs分布顯示城市和農村有區域性來源及工業排放源

10. 論文編號：C2.104

SOURCE EVALUATION OF DIOXINS/FURANS, PAHS, AND PENTACHLOROPHENOL IN SOIL SAMPLES NEAR A WOOD TREATING SITE IN THE SOUTHEASTERN USA

Shields WJ[1*], Edwards MR[1], Abrahams JA[2], Ferrara RA[3], Bollinger M[4], Paul LS[5]
[1]Exponent, 15375 SE 30th Place, Bellevue, WA, USA; [2]GeoTrans, Inc., 10860 Gold Center Dr., Rancho Cordova, CA, USA; [3]Omni Environmental LLC, 321 Wall Street, Princeton, NJ, USA; [4]Beazer East, Inc., 1910 Cochran Road, , Mt. Lebanon, PA, USA; [5]Koppers Inc., 436 Seventh Avenue, Pittsburgh, PA, USA

美國東南部(Mississippi)木材處理場附近土壤樣品中戴奧辛、PAHs及五氯酚的來源評估：土壤樣品收集來自排水窪地和、考伯斯公司附近的住宅區院子及美國的木材處理廠（本場址）。有關戴奧辛（與五氯酚使用有關）和多環芳香烴化合物(與木焦油使用有關)在地表水的主要傳輸路徑。OMNI公司進行過去和目前從現場傳輸到外圍地區表面排水特徵分析。

同時使用空間（地理）分析和化學指紋技術指數對來源進行評估。下游的樣品到上游現場樣品的相似性，說明PCDD/Fs的指紋圖譜確認（或排除）潛在來源是很有用的。在社區上對垃圾和庭院垃圾露天焚燒是一種常

見的做法，包括垃圾焚燒爐，這是PCDD/Fs和多環芳烴的來源，更容易與徑流或空氣污染的場址相比對。異常濃度的PCDD/Fs和五氯酚對居民常使用五氯酚已被證明是一個可能的解釋的，而不是場址的徑流。

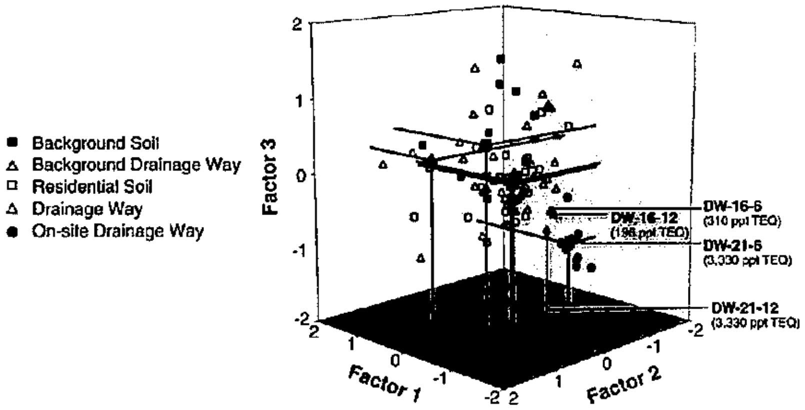


Figure 1. **Three-dimensional plot of PCA factor scores with the offsite drainage way samples from stations DW-16 and DW-21 indicated**

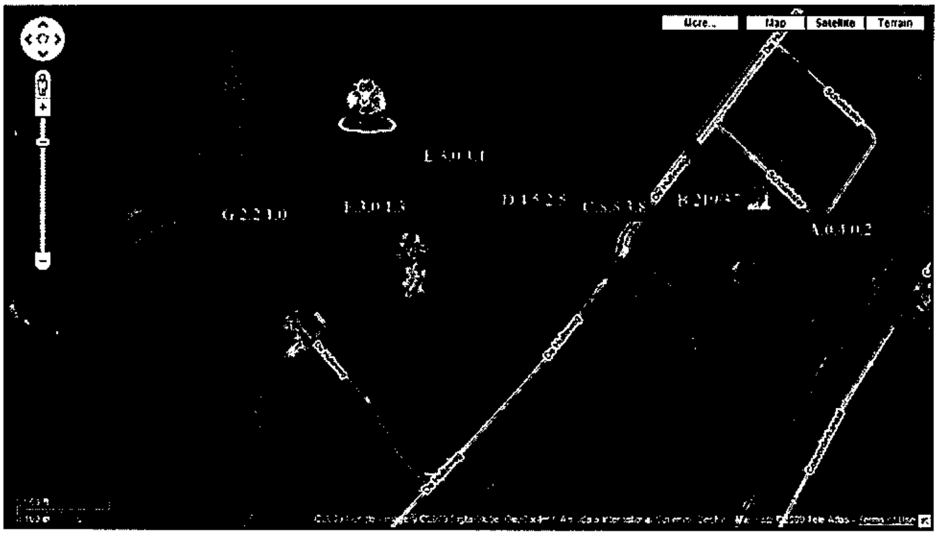
主成分分析三維相關因子分布圖

11. 論文編號：D3A.104

DIOXINS FORMED DURING FIRES, A THREAT TO THE FOOD CHAIN?

Hoogenboom L*, Hoffer S, Mennen M, Morgenstern P, Traag W
RIKILT Wageningen UR, Akkermaalsbos 2, 6708WB Wageningen, The Netherlands
RIVM National Institute for Public Health and Environment, Antonie van Leeuwenhoeklaan 9, 3721 MA Bilthoven, The Netherlands

意外火災導致戴奧辛的生成，並沉降在鄰近的農場，由空氣落塵而影響到牧草，本文介紹了一些火災潛在影響食物鏈的結果，這可能會增加飼料曝露，導致供人類消費性產品中戴奧辛含量的增加。



Coevorden舊金屬回收公司火災案戴奧辛監測結果，背景站(A)植物戴奧辛測值 0.2 ng TEQ/kg，火災現場附近(B)測值 219 ng TEQ/kg，往西0.2 (C), 0.3 (D), 0.5 (E), 0.6 (F) 和 0.8 公里處之測值分別為 8.8, 4.5, 3.0, 3.0 and 2.2 ng TEQ/kg. 從C到G站牧草含量一周後下降50%，但PCB下降則較慢只20%。

12. 論文編號：F1.103.

Environmentally Sustainable Management of Medical Waste in China, Dedicating to Reducing Dioxins—Progress and Impact

Ren ZY, Jiang C, Peng Z, Peng Y, Wang KX, Ding Q,Yu LF
Foreign Economic Cooperation Office, Ministry of Environmental Protection of China, Beijing, China

中國於2003年SARS發生後，廣設醫療廢棄物焚化爐。醫療廢棄物於2006年已達670,000公噸，根據統計2004年之醫療廢棄物焚化爐戴奧辛排放量達427.4g TEQ/年，佔當年總排放量之11.5%。因此，中國政府希望可透過「中國醫療廢棄物環境永續管理」方案降低醫療廢棄物所衍生之污染問題。透過監督、執行、包裝和標示、儲存、運輸、掩埋設施、新技術、污染控制等辦法管理整個醫療廢棄物之生命周期。推動成功後預計可將醫療廢棄物之戴奧辛排放量降至22.66 g TEQ/年。根據本方案，接近半數的醫療廢棄物處理廠將由焚化處理轉為非焚化技術處理；共計將推動18項國家法

案、技術指導方針及標準，10項管理辦法(含BAT)及相關政策(如圖5)，排放標準預計從0.5 ng TEQ/m^{3}下修至0.1 ng TEQ/m^3。

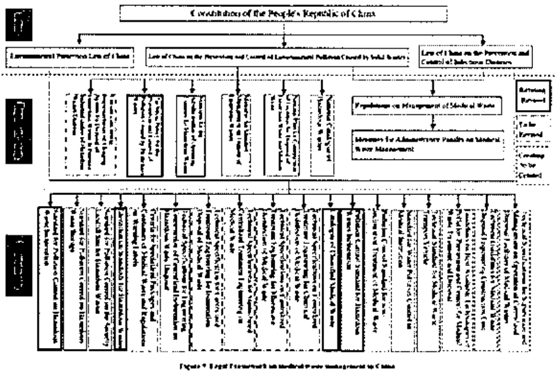


圖5　中國醫療廢棄物管理架構

13. 論文編號：F3.103.

SUBSTITUTES OF PERSISTENT ORGANIC POLLUTANT (POP) PESTICIDES IN BANGLADESH AND THE NEED FOR A SUSTAINABLE SUBSTITUTION PROCESS

Rahman MM*1, Weber R2, Tennekes HA3, Sanchez-Bayo F4.

孟加拉，有超過160萬人的區域147570平方公里，農業（作物和園藝）貢獻在2010年國內生產總值約11.16%，水稻是最重要的農作物，其他重要的作物包括其他穀物，茄果類，豆科植物，葫蘆科植物。其他經濟作物有黃麻，甘蔗，茶和棉花。此外，水果的主要作物包括香蕉，芒果，菠蘿，菠蘿蜜，番石榴，棗等所有這些作物常被病蟲害嚴重破壞。自1957/58左右正式使用農藥”安特靈(endrin)”約10年，包括持久性有機污染物（POPs）像阿特靈(aldrin), 地特靈(dieldrin), 可氯丹(chlordane), 靈丹(BHC/lindane)及飛佈達(heptachlor)，但為符合其法律並支持世衛組織和多邊環境協定，孟加拉開始陸續停止，禁止，註銷極為危險的農藥，1998年終於禁止的持久性有機污染物是飛佈達(heptachlor)。此外，瘧疾在孟加拉是一個嚴重的問題，防止瘧疾仍需要使用DDT，所以唯一的例外DDT是被允許限制使用在緊急

情況下防止蚊子的持久性有機污染物。最重要的結果，這樣的禁令或停止使用持久性有機污染物，以致農業害蟲防治改以普遍使用有機磷，氨基甲酸酯類，合成除蟲菊，新菸鹼類殺蟲劑等替代品。

Table 3. Properties of some pesticides replacing or having replaced POPs pesticides in Bangladesh

Insecticide	Acute (48h) LD_{50} honey bee (in nanogram per bee)	Soil degradation	Leaching potential
Imidacloprid	3.7 (oral)*	**persistent**	**high**
Carbosulfan	180 (oral)	non-persistent	low
Chlorpyrifos	59 (contact)	moderately persistent	low

* exposure route in parentheses

14. 論文編號：G7.101

ENVIRONMENTAL HEALTH RESEARCH AT NIEHS: CURRENT PRIORITIES AND PLANS FOR THE FUTURE

Birnbaum LS1* , Jung P1
1National Institute of Environmental Health Sciences and National Toxicology Program, 111 T.W. Alexander Parkway, Research Triangle Park, North Carolina, USA

本文介紹，美國國家環境健康科學研究所（NIEHS）在全球擁有校內研究實驗室和校外資助計劃，是最大的環境健康科學的研究機構。因此，NIEHS在美國和海外進行的環境健康研究有相當大的影響力。在2011年年底，NIEHS訂定了一個新的戰略計劃，研擬未來5年具研究潛力的環境健康研究所方向和優先。

長程策略規劃的程序結果如下：

(1) 美國國家環境健康科學研究所(National Institute of Environmental Health Sciences)的使命為發現環境對人類的影響以促進更健康的人類生活。

(2) 美國國家環境健康科學研究所的願景是提供全球一個領導性的創新研究，於預防環境性疾病及殘疾領域，以促進公共衛生。

(3) 支持該研究所之使命及願景的6個主題：

a.基礎研究：了解生物學基本機制的定義以對應環境壓力對人類健康的影響。

b.暴露研究：了解在個體及群題層級的暴露複雜性以促進健康。

c. 轉化科學：跨學科的環境健康科學，以告知促進健康的個體、臨床及公共衛生決策。

d. 健康差距及全球環境衛生研究：了解環境對全球衛生及健康差距的影響。

e.訓練與教育：發展及保持環境衛生相關專業的永續管道，包括基礎科學、暴露科學、翻譯、政策等，進而延伸至教育、訓練及職能發展，以提高一般民眾及其它NIEHS利益相關者對環境衛生認知的層次。

f.溝通與承諾：進階的科學知識翻譯及傳播對環境及人體健康層面的作用為：追求適當且有效的方式，使廣大的環境衛生研究及公共衛生推動的利益相關者共同參與。

(4) 兩個交叉理論涵括了所有其它主題：

a.知識管理：環境對於衛生及疾病的影響是複雜的，必須先透過綜合性的資料庫管理進而了解這些影響。環境衛生科學資料庫的產生遠超過現有的資訊的搜集、管理、分析、可視化和傳播。各種不同的問題包括資訊、數據、知識管理等是所有的戰略規劃主題與意義的首要問題。

b.合作及綜合方法：確立環境衛生科學之合作及綜合方法為NIEHS策略規劃程序的重要主題。在整個複雜系統中多項的負面影響將導致疾病的產生，其中多來自於多重暴露及不同的生命階段。環境衛生科學的研究事業需要利用所有相關學科的協調統一來解決這些複雜的問題。環境衛生科學須要與其它相關領域互相合作：如細胞和分子生物學、

結構生物學、生物化學、遺傳學、藥理學、毒理學、流行病學、生物統計學、行為科學、工程學及其它。系統生物學，計算生物學，以及其他新方法是建立於跨學科的合作之上。除了以跨學科合作方法來滿足其科學使命外，NIEHS仍須與其它相關當局、團體及其他夥伴發展創新合作，以有效傳播預防等相關知識，並引導利益相關者做出各種決策。

肆、心得與建議

本署於86年率先針對大型垃圾焚化爐發布排放標準進行管制，爾後陸續針對中小型焚化爐、煉鋼業電弧爐、鋼鐵業燒結工場、煉鋼業集塵灰高溫冶煉設施及一般性固定源全數納入管制。台灣為國際間第一個將所有固定污染源排放戴奧辛均納入管制之國家，在本署積極推動各項管制下，自91年開始，我國戴奧辛排放量呈逐年下降趨勢，以91年為基準年(327 g I-TEQ/year)，至100年止，戴奧辛排放減量已達83% (55.7 g I-TEQ/year)，顯示管制工作已相當具有成效。環境空氣部分，國內戴奧辛環境空氣監測始於91、92年度，當時監測平均濃度為0.089 pg I-TEQ/m^3，自95年開始本署空保處將空品監測列為例行性執行工作，95年~100年間，環境空氣戴奧辛濃度介於0.035 ~ 0.051 pg I-TEQ/m^3，均低於日本環境空氣戴奧辛標準0.6 pg WHO-TEQ/m^3。

參加本次會議，使本署團隊更加了解國際研究POPs之趨勢及政策動向。與他國環境空氣戴奧辛濃度進行比較，北京之環境空氣戴奧辛濃度高出台灣許多，由其冬季之測值超過日本之環境空氣戴奧辛標準，值得日後密切注意中國未來之減量情形。而中國針對醫療廢棄物之管理亦提出相關配套措施，希望藉由監督、執行、包裝和標示、儲存、運輸、掩埋設施、新技術、污染控制等辦法管理整個醫療廢棄物之生命周期，計畫推動18項國家法案、技術指導方針及標準，10項管理辦法(含BAT)及相關政策。雖我國之醫療廢棄物焚化爐在經歷數年的執行後，已有相當的控制，但中國針對醫療廢棄物之管理方式仍值得我國參考其管理之精神與方式。

本次參加會議亦發現，中國、非洲等區之基礎背景研究資料開始增加，顯示開發中國家漸漸建立起相關機制。然非洲國家因含鹵素殺蟲劑的管制仍不完善，在管制執行上應還有一段路要走。

超過半世紀的持久性有機人造化學品（persistent organic chemicals ,POCs）對環境的污染已成為全球性嚴重的議題。 POCs在空氣、水、土壤、生物及世界各地的野生動物和人類中普遍存在且不易降解，並在生物體造成長期的影響。對環境和生物樣品之研究議題，範圍包括大氣、水、土壤、沉積物、雙殼類軟體動物、魚類、海洋哺乳類動物、陸生哺乳動物和人類乳汁，由空間和時間分布趨勢已涵蓋舊有和新興的污染物，包括多氯聯苯、有機氯農藥、多氯化萘、多氯戴奧辛/呋喃、多溴聯苯醚、六溴環十二烷(HBCDs)、全氟化合物（PFCs）、合成麝香、（PAHs）、三氯蔗糖和辛基與壬基酚，以預測未來全球的典型污染趨勢和新興的持久性有機化學品清單，將是未來值得關注的永續環境議題。

參加國際研討會除可增加相關研究領域之最新知識，並可與國際同領域之研究學者進行互動，獲益良多。建議參與會議時多與他國與會人員進行互動交流，各國所遇到問題皆不一樣，不同的思考方式，可能為未來的突破口。

SIMPLIFYING MULTI-RESIDUE ANALYSIS OF FLAME RETARDANTS

Ionas AC*, Covaci A

Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

Introduction

To decrease flammability, flame retardants (FRs) are frequently added to consumer products ranging from upholstered furniture to textiles, electronics and building materials. Unfortunately, most of these compounds have a negative impact on the environment and a potential risk for animal and human health. Although FRs have been investigated for more than 15 years, our understanding of their environmental fate and toxic effects still remains limited.

In order to address these issues, it is important to employ sensitive and selective analytical methods (e.g. GC-MS or LC-MS) which allow the simultaneous determination of various classes of FRs, such as brominated (BFRs), organophosphorous (OPFRs) and chlorinated FRs. Still, the routine analysis suffers due to the complexity of the matrices (e.g. dust) and moreover, several target compounds may coelute (e.g. TBBP-A with BDE-153 or the degradation products of HBCD with BDE-49 and BDE-99)[1].

This study is part of the INFLAME Marie Curie Initial Training Network, an EU funded project. The aim of this work was to develop a fractionation procedure that would reduce the sample complexity, prevent coelutions and thus facilitate FR analysis. This was done by dividing the target compounds (FRs) in several fractions according to their polarity. A combination of ultrasonic-assisted extraction (UAE)[2] and solid phase extraction (SPE) was applied for household dust. FRs were eluted from the SPE cartridge by using different solvents of increasing polarity. In this way, PBDEs were separated from HBCD and TBBP-A, which in turn were separated from OPFRs, eliminating coelutions and allowing for the simultaneous determination of these classes of FRs.

Materials and methods

All solvents used during analysis were of analytical or pesticide grade. *n*-Hexane was purchased from Acros Organics (Geel, Belgium). Acetone, *n*-butyl chloride, ethyl acetate, methanol and *iso*-octane were purchased from Merck (Darmstadt, Germany). Supelclean™ ENVI™- Florisil® SPE cartridges (500 mg/3mL) were purchased from Supelco (Bellefonte, PA, USA), Bond Elut-Si from Agilent (Santa Clara, CA, USA) and Oasis HLB from Waters (Milford, MA, USA). Empty polypropylene filtration tubes (3 mL) SPE cartridges were also purchased from Supelco and Aluminium oxide 60 from Merck (active basic, activity stage I, particle size 0.063-0.2 mm).

Standards of BDE 28, 47, 66, 85, 99, 100, 153, 154, 183 and 209, α-HBCD, β-HBCD, γ-HBCD, BTBPE, DBDPE, HCDBCO, TBB, TBPH, HBB, TBBPA-dbpe, TBBPA, TBECH isomers, ATE, BATE, DPTE, TBCO isomers, OBIND, dechlorane plus (DP) isomers were purchased from Wellington Laboratories (Guelph, ON, Canada). Standards of PBBs were purchased from Dr. Ehrenstorfer (Augsburg, Germany). BDE 77 was obtained from AccuStandard Inc. (New Haven, CT, USA). Standards of tri-isobutyl phosphate (TiBP), tri-n-butyl phosphate (TnBP), triphenyl phosphate (TPhP), tris(2-chloroethyl) phosphate (TCEP), ethyl-hexyl-diphenyl phosphate (EHDPhP), triscresyl phosphate (TCP, mixture of 4 isomers) and tris(1,3-dichloropropyl) phosphate (TDCPP, mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway). Tris(2-butoxyethyl) phosphate (TBEP) were purchased from Sigma Aldrich. Tris(1-chloro-2-propyl) phosphate (TCPP, mixture of 3 isomers) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards was >98%, except for TBEP (>94%). SRM 2585 was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

The extraction method used was based on the method described by van den Eede et al. (2011)[3]. For method development, a dust sample collected from a carpenter shop containing all the major classes of FRs and a mixture of standards were used. The solvent mixture employed in the extraction was hexane/acetone (3:1, *v/v*). The process consisted of consecutive steps of vortexing (1 min) and ultrasonication (5 min) with 2 mL of the aforementioned solvent mixture. This cycle was repeated 3 times and after each cycle, the supernatant was transferred to a clean tube. The extracts were evaporated to near dryness using a gentle nitrogen stream and the solvent was exchanged to hexane (1 mL).

No destructive clean-up method was applied to insure that no analytes of interest are degraded. The PBDEs and non-polar NBFRs were eluted with 8 mL of hexane, the HBCDs, TBBP-A, TBPH and related compounds with 8 mL of *n*-butyl chloride, the OPFRs with 8 mL of ethyl acetate and compounds more polar than the OPFRs with 8 mL of methanol.

The fractions obtained were injected on a GC-MS system (Agilent 6890 GC coupled to an Agilent 5973 MS), operated in electron capture negative ionization (ECNI) mode. The GC system was equipped with a programmable-temperature vaporizer inlet (PTV) which was run in the pulsed splitless mode. One μL of extract was injected on a DB-5 column (15 m × 0.25 mm × 0.10 μm). The GC temperature program was 90 °C, hold 1.5 min, ramp 10 °C/min to 300 °C, hold 4 min, ramp 40 °C/min to 310 °C, hold 15 min. Helium (purity 5.9) was used as a carrier gas with a ramped flow. Methane was used as moderating gas (purity 4.5). The initial flow was 1 mL/min (for 19 min), and then ramp 10 mL/min to 2 mL/min. The ion source, quadrupole and interface temperatures were set at 250, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V.

Each fraction was also injected in an identical GC-MS system operated in the electron ionisation (EI) mode. The PTV was run in the pulsed splitless mode. One μL of extract was injected on a SGE-HT8 column (25 m × 0.22 mm × 0.25 μm). The GC temperature program was 90 °C, hold 1.50 min, ramp 10 °C/min to 310 °C, hold 20 min. Helium (purity 5.9) was used as a carrier gas with a constant flow (1 mL/min). The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V.

Results and discussion

Development and optimisation. To determine which sorbent is most adequate for obtaining clear-cut fractions, the same dust sample (containing all the major classes of FRs) was extracted, fractionated using different sorbent types and injected in both the aforementioned instruments. The chromatograms of the individual fractions were analysed and the FR compounds detected were logged. On this basis, a comparison between different sorbents was done and the most adequate one was determined to be underivatised silica (Table 1), with a particle size of 40 μm and an average pore diameter of 60 Å^2.

Table 1: Fitness for purpose of different sorbent types

Sorbent	Signal/noise in chromatograms	Clear-cut fractions	Unwanted coelutions	Other issues	Fitness for purpose
Florisil	+++	No	Yes	HBCDs in two fractions	+
Silica	++	Yes	No	-	+++
Alumina	++	No	No	TPhP present in n-BC fraction	++
Oasis HLB	++	No	Yes	HBCD degradation	-

To get a better idea about what compounds are to be expected in which fractions, two mixtures of standards were prepared. The first mixture contained lower PBDEs (tri-hepta), HBCDs, TBBP-A, MeTBBP-A, α,β-TBCO, OBIND, α,β-TBECH, syn-DP, anti-DP, HBB, BTBPE, DBDPE and BDE-209. The second mixture contained PBBs (153, 155, 103, 80, 209), ATE, BATE, DPTE, TBA, γ,δ-TBECH, OPFRs, BTBPE, HCDBCO, TBB, TBPH and TBBPA-BDPE. These mixtures were fractionated on Silica SPE and logged for future reference (Table 2).

Table 2: Compounds per fraction

Fraction Nr.	Elution solvent	Compounds
1	Hexane	PBDEs, PBBs, α,β-TBCO, HBB, BTBPE*, syn,anti-DP, OBIND, DBDPE, TBA, ATE, DPTE, TBB, HCDBCO
2	*n*-Butyl Chloride	HBCDs and breakdown compounds, TBBP-A, MeTBBP-A, TBBPA-DBPE, TBPH
3	Ethyl Acetate	OPFRs including TDBPP

4	Methanol	None of the compounds in the standard mixtures; normally compounds more polar than the OPFRs

*A small part of the BTBPE is in the *n*-Butyl Chloride fraction. This can be easily corrected by increasing the hexane elution volume by 0.5 mL.

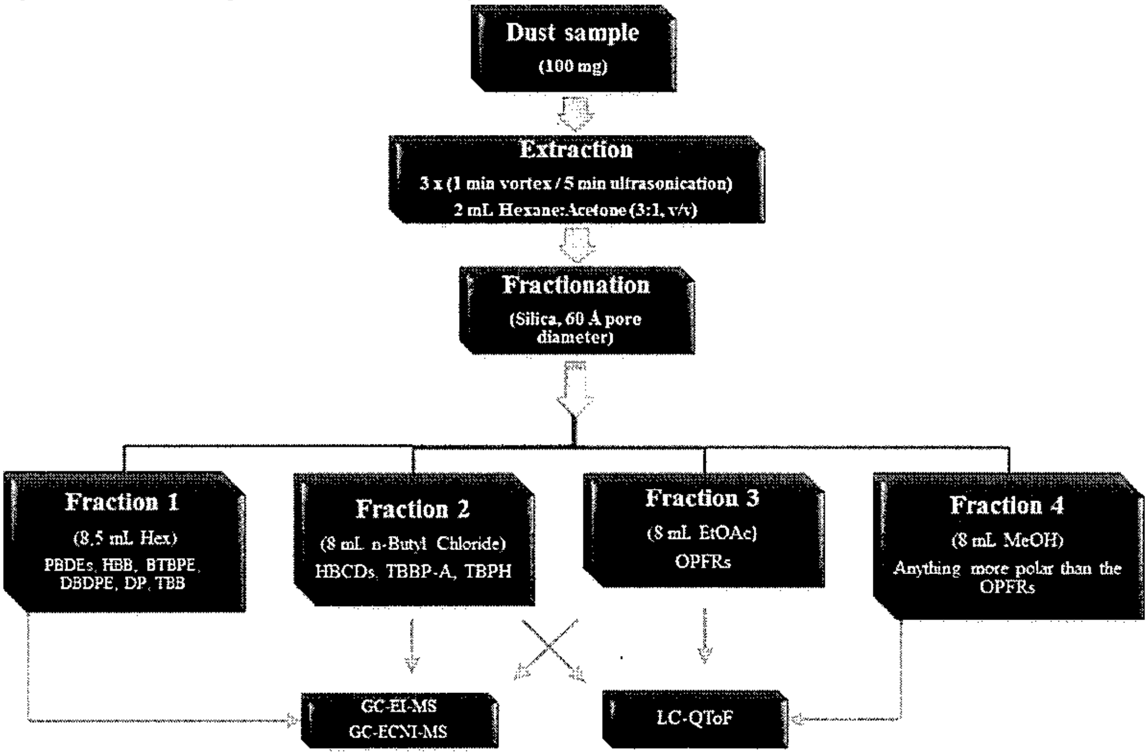
The only compound that is not entirely in one of the fractions is TBECH, which is found in both the hexane fraction and in the n-Butyl Chloride fraction.

Fractionation of SRM 2585. For the purpose of confirming the distribution of compounds for each fraction, the NIST SRM 2585 reference material for organic contaminants in house dust was analysed using the developed procedure. The same solvents and volumes were used for the elutions from the SPE cartridge.

The reference material used is not certified for NBFRs or OPFRs, but in other publications[3,5] these compounds have been reported and quantified. Upon analysis of the obtained chromatograms, it was found that the distribution of the analytes in the fractions was consistent with our previous observations from the method development stages.

When applying this procedure to generic samples, all but the non-polar fraction are also injected on a LC instrument (Figure 1) – a LC-QToF to screen for and identify unknown compounds or a LC-MS/MS for the quantification of known analytes. Through fractionation, the sample complexity is significantly decreased and the compounds fall into known intervals of polarity. This further information can prove very valuable in identifying unknown compounds or at the very least narrowing down the number of possibilities.

Figure 1: Schematic representation of the analysis workflow



Acknowledgements

ACI acknowledges the funding of his PhD scholarship through the Marie Curie ITN INFLAME and Dirtu AC for valuable discussions.

References

1. Korytar P, Covaci A, de Boer J, Gelbin A and Brinkman UATh. (2005) *J. Chromatogr. A,* 1065:239–249
2. Covaci A, Dirtu AC, Voorspoels S, Roosens L and Lepom P. (2011) *The Handbook of Environmental Chemistry*, 16: 55-94
3. Van den Eede N, Dirtu AC, Neels H, Covaci A. (2011) Environ Int. 37(2):454-61
4. www.chem.agilent.com/en-US/Products/columns-supplies/samplepreparation/spe/bondelutSI
5. Ali N, Harrad S, Muenhor D, Neels H, Covaci A. (2011) *Anal Bioanal Chem*, 400(9): 3073-83.

A RAPID METHOD FOR ANALYSIS OF PFAAs IN HUMAN SERUM USING 96-WELL PLATE-LARGE VOLUME INJECTION-UPLC-MS/MS

Samira Salihovic[1*], Anna Kärrman[1], Gunilla Lindström[1], P. Monica Lind[2], Lars Lind[3], Bert van Bavel[1].

[1]MTM Research Centre, Örebro University, Örebro, Sweden; [2]Occupational and Environmental Medicine, Uppsala University, Uppsala, Sweden; [3]Acute and Internal Medicine, Uppsala University, Uppsala, Sweden

Introduction

Perfluoroalkyl acids (PFAAs) are widely distributed in the environment. In humans perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), and perfluorononanoic acid (PFNA) are typically found in the highest concentrations[1]. Recently epidemiological studies have indicated that even the low-dose background exposure to various industrial chemicals, such as the PFAAs, might be related to negative health effects in the general population[2]. To be able to investigate the associations between the PFAAs and various health effects in the general population there is a need for targeted epidemiological studies.

A rapid and sensitive analytical method, based on 96-well plate sample preparation and large volume injection UPLC-MS/MS, for epidemiological studies on PFAA is presented. The method was developed and used in the prospective investigation of the vasculature in Uppsala seniors (PIVUS).

Materials and methods

Chemicals

Ammonium acetate (>99%, p.a. for HPLC), was purchased from Fluka (Steinheim, Germany). Methanol and water (LC-MS grade) were from Fisher Scientific (Leicestershire, UK) Acetonitrile (HPLC) was purchased from Scharlau (Barcelona, Spain). Formic acid (98-100%) was purchased from Sigma Aldrich (Steinheim, Germany).. Standards and ^{13}C-labeled standards (PFCAs and PFSAs) were acquired from Wellington Laboratories (Guelph, Ontario, Canada).

Sample preparation

Briefly, frozen serum was allowed to thaw at room temperature and then vortex mixed for 10 s. Internal standards and 150 µL serum were added to a Ostro Sample Preparation 96-well plate 25mg (Waters Corporation, Milford, USA) followed by 450 µL 1% formic acid in acetonitrile. The sample was mixed thoroughly by aspirating three times with a pipette. Samples were filtered using a 15' vacuum manifold for 5 minutes. The extract was transferred to vials containing recovery standard and evaporated down to 250 µL using nitrogen. Finally, 750 µL 0.1 M formic acid in water was used to dilute the sample prior to the instrumental analysis.

Instrumental analysis

Analyses were performed on a UPLC-MS/MS (Waters Corporation, Milford, USA) system by injecting a 250 µL aliquot of the sample onto a C18 (2.1×20mm, 2.5µm) trap column connected to a C18 (2.1×100 mm, 1.7 µm) analytical column by a 6-port column switch valve. Analytes were analyzed on a MS/MS system run in electrospray ionization mode (ESI). Quantitative analysis of the PFAAs was performed using the internal standard method .

Results and discussion

In order to meet the demands of epidemiological studies a rapid and sensitive method for the analysis of selected PFAAs in human plasma was developed. A low contaminated quality control (QC) reference serum sample was used for the method development in this study. The variation of spiked QC samples (n=7) analyzed on three different days was determined to be below 20% relative standard deviation (RSD) except for PFPeA, PFBuS, and PFTDA as shown in Table 1. Recovery of native compounds was satisfactory and ranged between 74-122%.

Table 1. Recoveries and RSDs of 12 native PFAA standards spiked at 1ng/mL in human serum (n=7, reproducibility from day to day).

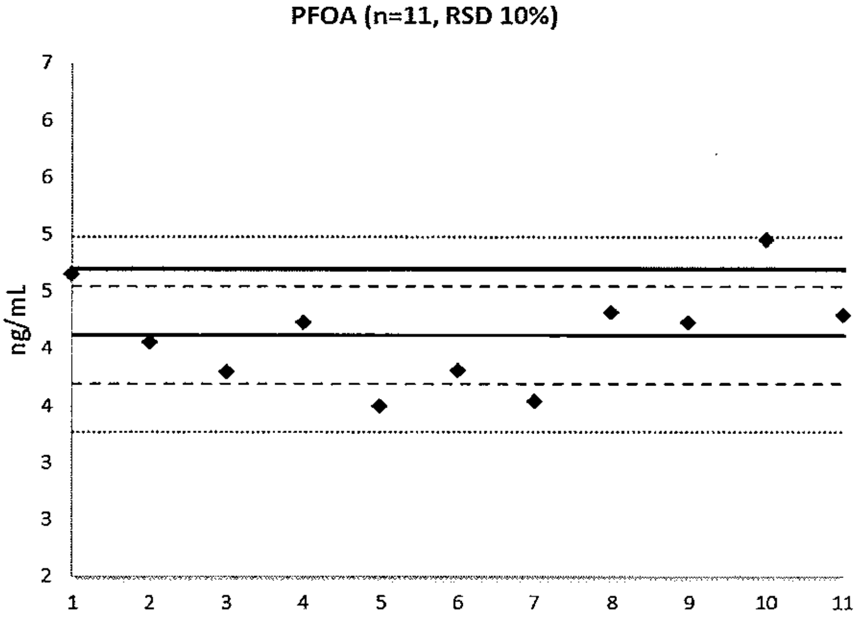
Analyte	*Recovery (%)*	*RSD (%)*
PFPeA	81	33
PFBuS	74	28
PFHxA	102	14
PFHpA	94	16
PFHxS	119	7
PFOS	122	8
PFOA	106	14
PFNA	105	16
PFDA	106	15
PFUnDA	109	12
PFDoDA	99	8
PFTrDA	81	19
PFTDA	74	33

The method was successfully confirmed using a serum sample from the 2nd worldwide interlaboratory study on PFAAs performed in 2006. The RSD of serum samples (n=11) analyzed on different occasions was below 20% for all compounds except PFBuS and PFHxA. Conformity between the developed method and the median result reported in the interlaboratory study is shown in Figure 1 and 2 for the most occurring PFAAs (PFNA, PFOA, PFHxS, and PFOS). The median concentrations reported by the participating laboratories are represented by the solid red line in the chart. Good conformity (± 2SD) between our method and the 2006 interlaboratory study is shown for all PFAAs. The systematic deviation showing lower results for PFOS in our method and the ILS is likely an effect of different standards used and treatment of linear vs. branched PFOS isomers in the ILS.

The method proved sensitive with a method detection limit of 1-10 pg/mL serum for the most occurring PFAAs in human serum, based on calculated S/N of 3 for spiked QC samples. The developed method is a powerful tool for analysis PFAAs in human serum or plasma in studies requiring high sample throughput and precision.

References:

1. Calafat, A.M., Wong, L-Y, Kuklenyik, Z. et al. 2007. Environ Health Perspect 115(11) 1596-1602.
2. Grandjean, P., Wreford Andersen, E., Budtz-Jörgensen, E. et al. 2012. JAMA 307(4) 391-397



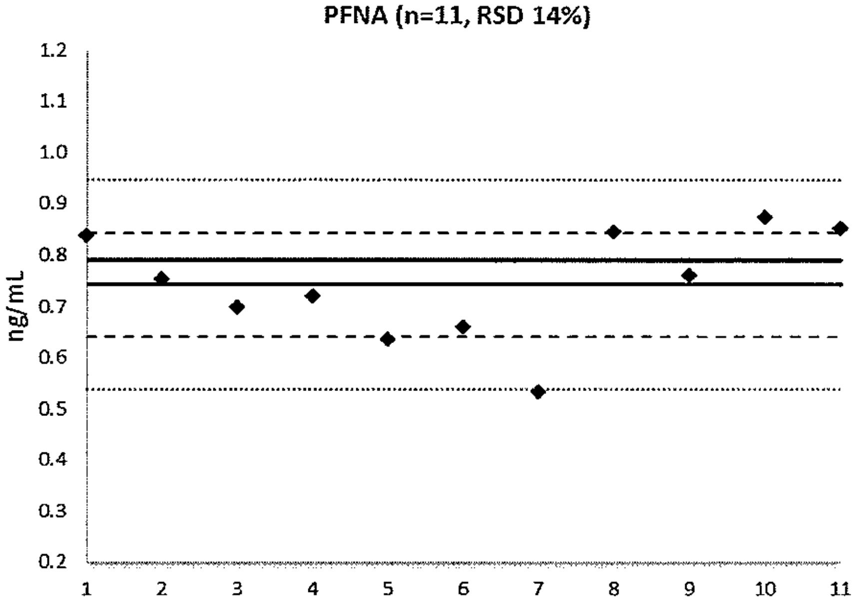


Figure 1. Control chart of PFOA and PFNA in human serum samples from the 2nd worldwide interlaboratory study on PFAAs performed in 2006. The solid black lines show the average concentration of our method and the solid red lines show median concentrations reported in the interlaboratory study. Confidence intervals are represented by the dashed lines (1SD) and dotted lines (2SD).

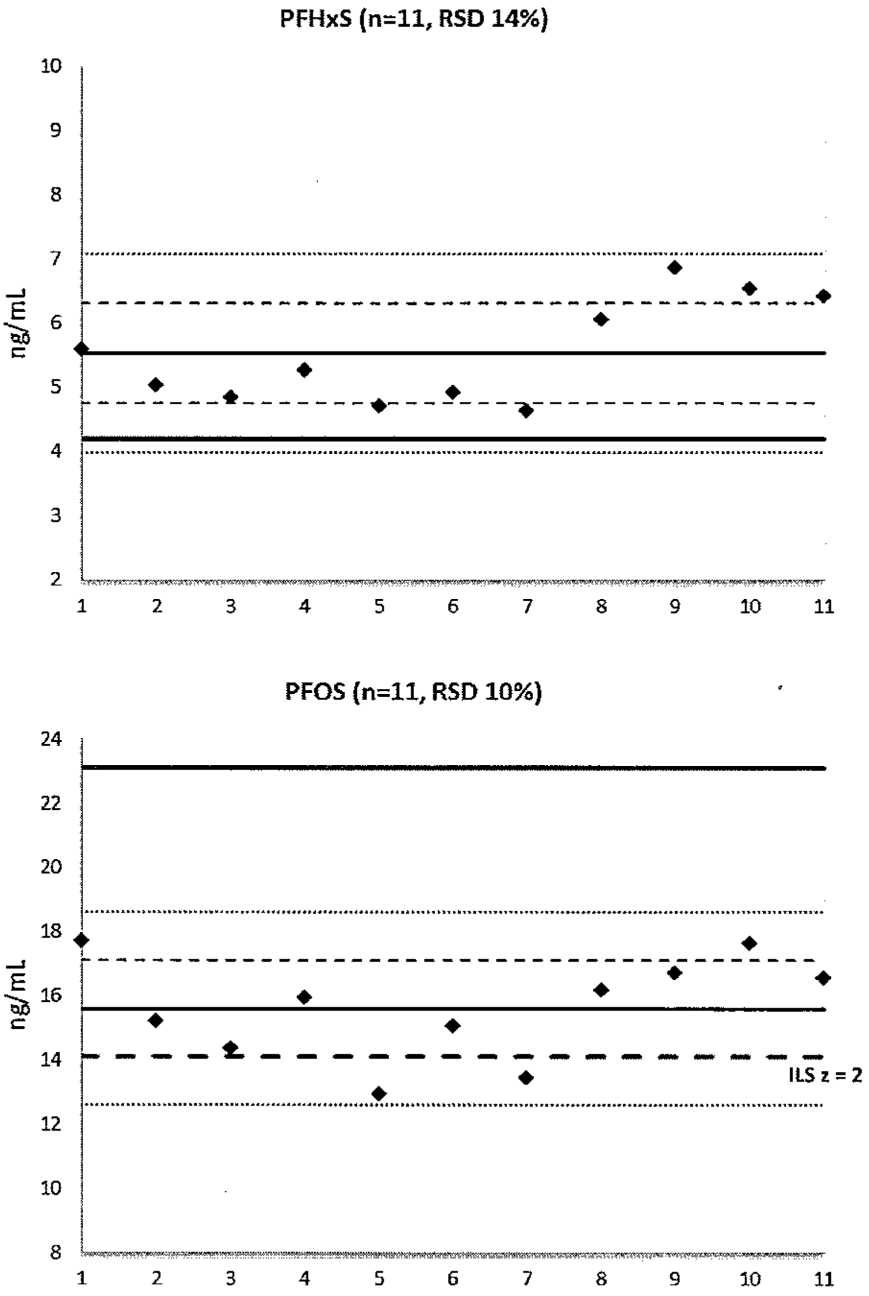


Figure 2. Control chart of PFHxS and PFOS in human serum samples from the 2nd worldwide interlaboratory study on PFAAs performed in 2006. The solid black lines show the average concentration of our method and the solid red and dashed lines show median and 2SD concentrations reported in the interlaboratory study (ILS). Confidence intervals are represented by the dashed lines (1SD) and dotted lines (2SD).

PCDD/F MEASUREMENT AT THREE HIGH-ALTITUDE STATIONS IN EASTERN ASIA: EVALUATION OF LONG-RANGE TRANSPORT OF PCDD/FS DURING THE SOUTHEAST ASIA BIOMASS BURNING EVENT

Chi KH[1*], Chen YF[1], Lin CY[2], Sheu GR[3], Lin NH[3]

[1]Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei 112, Taiwan; [2]Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan; [3]Department of Atmospheric Sciences, National Central University, Chungli 320, Taiwan.

Introduction

Limited data suggest that field burning of agricultural crops can result in formation and emission of PCDD/Fs[1]. The year 2000 draft United States inventory of PCDD/F sources indicates that about 6% of the estimated total annual emissions come from forest fires[2]. It is further unclear whether PCDD/F emissions are mainly from combustion of the biomass itself, or simply due to the volatilization of compounds on the biomass surface that had previously been ''scrubbed'' from the atmosphere[3]. In recent years, Eastern Asia biomass burning has caused global concerns due to its adverse effects on visibility, human health and global climate by emitting particulate matter and other gaseous pollutants such as CO, SO_x, NO_x and VOCs. A previous study[3] also indicated that the PCDD/F emission factor via biomass burning ranged from 15 to 25 ng TEQ/kg burned. The mass-specific emissions are about 20 times higher than the concentration of the extracted biomass, suggesting that PCDD/F emissions are not simply a result of vaporization of cuticle-bound PCDD/F but are formed predominantly during the biomass combustion. Relevant epidemiological study[4] reveals that suspended particle considerably influences respiratory health. A previous study[5] indicated that around 70 to 80% PCDD/F concentrations in the atmosphere were essentially bound to particles. The solid-phase PCDD/Fs are brought into the atmosphere through wind blowing, and eventually settle to water bodies or other receptors in the environment via either dry or wet deposition mechanism. To our knowledge, few studies have been conducted toward examining the relationship between the Eastern Asia biomass burning and the concentrations of atmospheric PCDD/Fs. In this study, the concentrations of particulate matter and seventeen 2, 3, 7, 8-substituted PCDD/F were monitored in central Taiwan (Mountain Lulin), northern Vietnam (Son La) and Thailand (Chiang Mai) using high volume ambient air samplers during 2010 and 2011. The objective of this study is to evaluate the effects of Southeast Asia biomass burning on the atmospheric concentration variation of dioxin compounds.

Materials and methods

In order to measure the long-range transport of PCDD/Fs, three high-altitude sampling sites were selected based on the meteorological information and location relative to the biomass burning in Eastern Asia (Fig. 1). In central Taiwan, the sampling station is located at the peak of Mt. Lulin (23.51-°N, 120.92-°E; 2,862 m above mean sea level). Its high elevation means it is generally free from local pollution. Mt. Lulin generally lies in the free troposphere (especially during the winter months) and is free from boundary layer pollution. Frontal mechanisms, which frequently occur in winter and spring of Taiwan, have been reported to be able to transport pollutants from the boundary layer to the free troposphere. Chiang Mai, with an elevation of 310 m, is located in the mountainous northern Thailand. This city is a shipping center for agricultural products of the surrounding region, but also produces silver and wood articles, pottery, and silk and cotton goods. The sampling site is located at Suthep Mountain under the jurisdiction of the Doi Suthep-Pui National Park Protection Unit (1,396 m above mean sea level). It is located to the west of Chiang Mai, about 20 km away. Fires, which were several hundred meters away from the site, were occasionally observed during the experiment. In northern Vietnam, the sampling station is located at the National hydro-meteorological service of Vietnam, northeastern regional hydro-meteorological observatory(103.91-°E 21.32-°N; 660 m above mean sea level) in Son La province. No significant PCDD/F emission sources existed in the vicinity of these three high-altitude stations. In central Taiwan, all PCDD/F samples were taken during the regular sampling periods (Febuary, March, April, June, Octobor, December, 2010 and March 2011) for the analysis of PCDD/Fs with 4 to 6 samples taken each month. During a special long range transport season (2010/3/22-3/28 2011/3/19-3/30), one sample was taken everyday for 24 hours at Mt. Lulin, Son La and Chiang Mai in the meantime. Ambient air samples for both vapor phase and particle phase of dioxin-liked compounds were collected using high volume sampling trains (Shibata HV-1000F). The HV-1000F samplers were equipped with Whatman quartz fiber filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs were used for retaining PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 1,000 m^3 for a typical sampling duration of 1 day. The PUF and filter samples were than Soxhlet extracted with toluene for 24 hrs, treated with concentrated sulfuric acid, and then passed through a series of clean-up columns containing sulfuric acid-silica gel, acidic aluminum oxide and celite/carbon. The detailed information regarding the extraction and clean-up procedure of PCDD/F samples is provided elsewhere[6]. In this study, only the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed with high-resolution gas chromatography (HRGC)/high-resolution mass spectrometry (HRMS) (Thermo DFS) equipped with a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25μm, J&W).

Results and discussion

During the regular sampling periods, the atmospheric PCDD/F and TSP concentrations measured at Lulin station in 2010 and 2011 range from 0.232±0.02-6.76±4.6 fg I-TEQ/m^3 and 8.6±2.6-54.2±29 μg/m^3, respectively (Fig. 2). The lowest concentrations were measured during the summer season (23-30 June, 2010). Atmospheric PCDD/F concentrations measured at Lulin Mountain in central Taiwan were significantly lower than those measured at other background stations. The low atmospheric PCDD/F concentration can be attributed to the lack of dioxin emissions and combustion sources within almost 50 km of the station at Lulin Mountain. However, a significant increase of PCDF compounds in ambient air is measured during the spring, and the highest concentration of atmospheric PCDD/Fs and TSPs was observed at Lulin station during the spring season. In addition, the average concentrations of CO, ozone and PM_{10} measured at Lulin station in 2010 are about 144±67 ppb, 33±15 ppb and 11.2±10 μg/m^3, respectively. The background concentrations of CO, ozone and PM_{10} are estimated 82 ppb, 28 ppb and 6.0 μg/m^3, respectively. Especially in March, the concentrations of above three pollutants (CO: 215±92 ppb, ozone:51±17 ppb and PM_{10}: 25±15 μg/m^3,) show twice higher than their background values. These results imply that the higher atmospheric PCDD/F and TSP concentrations observed at Lulin station in the spring could be attributed to the effects of long-range transport of Southeast Asia biomass burning. Based on meteorological data, the southwest and west winds predominated since March at Lulin Mountain. To analyze the effects of the Southeast Asia biomass burning event in Taiwan during the period of March, 2010 and 2011, on the levels of ambient PCDD/F compounds, the atmospheric PCDD/F samples were also collected at the source regions in northern Thailand on 2010/3/22-3/28 and northern Vietnam on 2011/3/19-3/30. The five-day back trajectory analyses are calculated using HYSPLIT at the altitudes of 3 km from the location of Lulin station in central Taiwan for the events of March 2010 and 2011, respectively, suggested that the air masses in central Taiwan originated from Indochina on those periods at a lower elevation than the trace layer. Moderate Resolution Imaging Spectroradiometer (MODIS) satellite (1 km resolution) data shows significant active fire detections occurred during 2010/3/24-3/25, 2011/3/20-3/21 and 2011/3/27-3/28. At Mt. Lulin,our measurements indicated that the CO and ozone concentration observed at Lulin station during the Southeast biomass burning events (2010/3/24-3/25, 2011/3/20-3/21 and 2011/3/27-3/28) ranged from 105-298 ppb and 33-82 ppb, respectively. The satellite data and air mass paths revealed that the air masses of the PCDD/F peak layer possibly came from biomass-burning regions for these episodes. An intensive observation program was carried out at the same time at Lulin station. Figures 3 and 4 show the atmospheric PCDD/F concentrations measured in Taiwan and the source regions in northern Thailand (2010/3/22-3/28) and northern Vietnam (2011/3/19-3/30) during biomass burning events and reveal that the variations of atmospheric PCDD/F concentrations at these three sites were quite similar. The highest PCDD/F content (579 pg I-TEQ/g-TSP) was measured in northern Vietnam during the burning event (2011/3/27-3/28). In the same period, PCDD/F contents in suspended particles of around 399 pg I-TEQ/g-TSP were measured at Mt. Lulin. Interestingly,, the atmospheric PCDD/F concentration decreased dramatically 2 days after those biomass burning event. Backward trajectories calculated for Mt. Lulin and Son La showed similar paths during (2011/3/27-3/28), implying that the higher PCDD/F concentrations measured at Mt. Lulin originated from the source regions of biomass buring in northern Vietnam. Figure 5 shows the PCDD/F congener distributions in ambient air measured at Lulin station during the regular sampling periods. The results indicate that PCDFs account for 41~53% of total PCDD/Fs. The distribution of PCDD/F congeners measured at Lulin station is quite different from those measured at urban and industrial area in Taiwan with high PCDF distribution (>60%) conducted[7]. However, Figure 6 shows that the PCDFs account for 65% of the total PCDD/Fs measured during the Southeast Asia biomass burning event (March, 2010 and 2011). Interestingly, Figure 6 also shows that the distribution of PCDD/F congener observed in the source regions of biomass burning in northern Thailand and Vietnam was similar to the measurement at Mt. Lulin in Taiwan during the significant biomass burning event. Gullett et al.[8] indicated that raw biomass is dominated by PCDDs, particularly OCDD, whereas the emissions are dominated by PCDFs, primarily PeCDFs. These observations suggest that the emissions are not simply a result of target volatilization and dechlorination, but represent in situ formation. Hence, the measurements conducted in this study demonstrate that the increase in PCDF compounds could be attributed the long-range transport of the Southeast Asia biomass burning event.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the National Science Council (NSC 101-2111-M-010-001-) and Environmental Protection Administration (EPA-98-FA11-03-D020) of the Republic of China. Assistance provided by Prof. Moo Been Chang and Mr. Shu Hao Chang of National Central University in analyzing the samples and in valuable discussions is also acknowledged.

References:

1. Meyer C, Mueller J, Beer T, Marney D, Bradbury G. (2004) *Organohalogen Compd. 66*, 913-19.
2. US EPA, Sources of dioxin-like compounds in the United States. (2001) Draft (external) Final Report; EPA/600/P-00/001Cb.
3. Gullett B K, Touati A. (2003) *Atmos. Environ.* 37, 803-13.
4. Husar R B et al. (2001) *J. Geophys. Res.* 106, 18317.
5. Dockery D W, Pope C A, Xu X, Spengler J D, Ware J H, Fay M E, Ferris B G, Speizer F E. (1993) *New England Journal Medicine* 329, 1753.
6. Chi KH, Lin TY, Ou Yang CH, Wang JL, Lin NH, Sheu GR, Lee CT. (2010) *Environ. Sci. Technol.* 44, 2954-60.
7. Chang M B, Chi K H, Chang S H, Chen Y W. (2004) *Atmos. Environ.* 38, 2535-44.
8. Gullett B K, Touati A, Huwe J, Hakk H. (2006) *Environ. Sci. Technol.* 40, 6228-34.

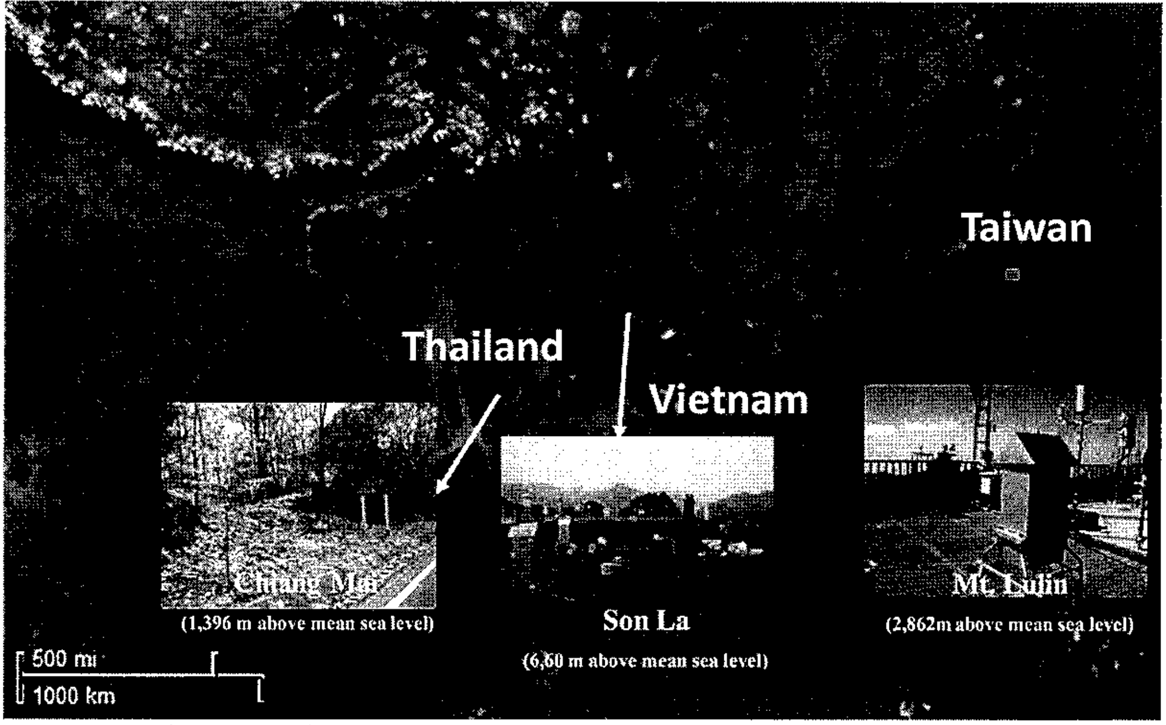


Figure 1 Relative locations of three high-altitude sampling sites in Southeast Asia.

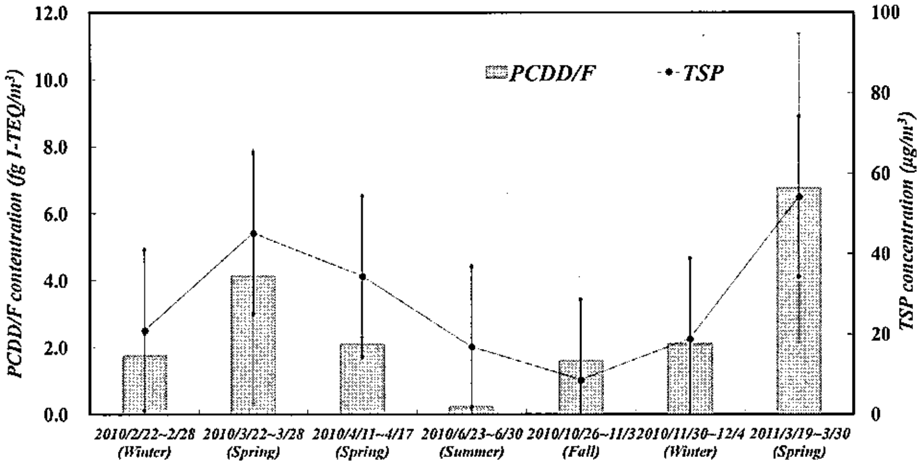


Figure 2 Atmospheric PCDD/Fs and total suspended particles measured at Lulin station during different periods.

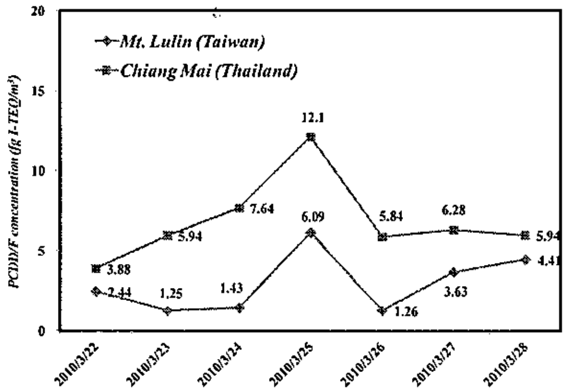


Figure 3 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Thailand during significant biomass burning event (2010/3/22-3/28).

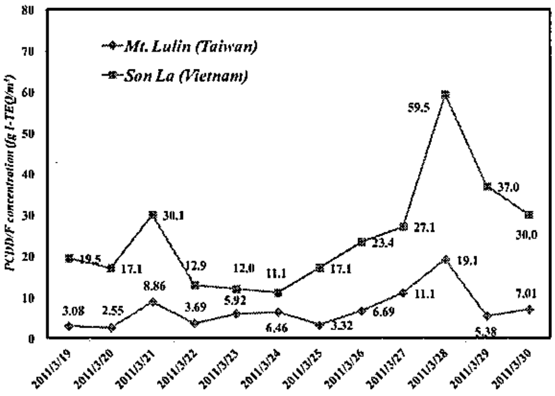


Figure 4 Variation of atmospheric PCDD/F concentrations measured in Taiwan and Vietnam during significant biomass burning event and northern Vietnam (2011/3/19-3/30).

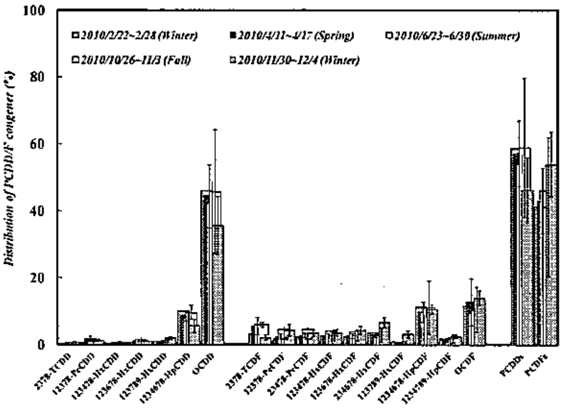


Figure 5 PCDD/F congener distribution in ambient air at Lulin station during regular sampling periods.

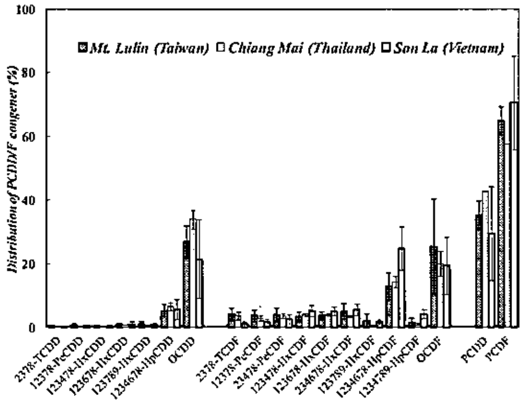


Figure 6 PCDD/F congener distribution in ambient air in central Taiwan, northern Thailand and Vietnam during Southeast Asia biomass burning event.

PERSISTENT ORGANIC POLLUTANTS (PCDD/Fs, PCBs AND PBDEs) IN AMBIENT AIR FROM BARCELONA (CATALONIA, SPAIN). SEASONAL VARIATION

Martínez A, Gasser M, Montaña MJ, Martí R, Díaz-Ferrero J*

Environmental Laboratory, Institut Químic de Sarrià (University Ramon Llull), Via Augusta 390, 08017 Barcelona (Spain). jordi.diaz@iqs.edu

Introduction

Barcelona is a city located in central coast of Catalonia (Spain) with more than 1.5 million people living there. The city spreads out from the Mediterranean Sea to Collserola Mountains for 100 km^2. The surrounding area is highly industrialized and, additionally, the impact of traffic is very high. Our study was focused on the characterization of POPs (PCDD/Fs, DL-PCBs, NDL-PCBs and PBDEs), both in the vapor and the particulate phase. Since some authors have detected seasonal influence on the levels of these compounds in air[1-3], the study considered this factor and, also, the possible influence of climatological conditions.

Materials and methods

Sampling

The sampling station was located in the upper part of Barcelona, in the neighborhood of Sarrià. Two main roads (the road that crosses Collserola Mountains starting in Sarrià, and the road that surrounds Barcelona) were close to the sampling point. Sampling was carried out between October 2009 and August 2010. Sampling was performed with a high volume sampler (MCV, Barcelona, Spain). Particle phase was retained by a quartz-fiber filter, followed by a polyurethane foam (PUF) block for vapor phase absorption. Table 1 shows sample codes and some of their characteristics.

Table 1. Codes and characteristics of samples analysed.

Code	Date	Sampling time (hours)	Volume sampled (m^3)	Comments
A1	19/10/09	11	751	---
A2	10/11/09	24	1564	---
A3	02/12/09	24	1644	---
A4	21/01/10	24	1645	---
A5	02/02/10	24	1633	---
A6n	10/02/10	12	859	Night sampling
A7n	24/02/10	13	921	Night sampling
A7d	25/02/10	10	743	Day sampling
A8n	15/03/10	13	849	Night sampling
A8d	16/03/10	10	653	Day sampling
A9	18/05/10	24	1742	---
A10	01/07/10	24	1605	---
A11	16/08/10	24	1639	---

Analysis

Following compounds were analysed in the samples: NDL-PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180), DL-PCBs (PCB 81, PCB 77, PCB 123, PCB 118, PCB 114, PCB 105, PCB 126, PCB 167, PCB 156, PCB 157, PCB 169, PCB 189), PCDD/Fs (2,3,7,8-chlorosubstituted congeners) and PBDEs (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209).

Analytical procedure was based on international methods (US EPA 1613, US EPA 1614, UNE-EN 1948) and consisted of following steps: (1) pre-treatment of different parts of the sample, (2) spiking with $^{13}C_{12}$-labelled extraction standards (Wellington Laboratories, Canada), (3) Soxhlet extraction with toluene for 48 h (4) extract clean-up in multilayer silica column (5) fractionation of the extract by HPLC equipped with a pyrenyl column[4] (6) concentration of each fraction under nitrogen stream and addition of $^{13}C_{12}$-labelled recovery standards (7) instrumental determination of PCDD/F, DL-PCB, NDL-PCB and PBDEs by HRGC-HRMS and quantitation by the isotopic dilution method. For each sample, filter and PUF were analysed separately in order to evaluate pollutant concentrations in particulate and vapour phase. Particulate matter was measured gravimetrically according to the method UNE-EN 12341. In addition, climatological conditions were measured by an Advanced Weather Station Model WMR100 (Oregon Scientific) located in the sampling point.

Results and discussion

Total concentrations

Table 2 shows the concentrations (average, minimum and maximum) of NDL-PCBs, DL-PCBs, PCDD/Fs and PBDEs (with and without BDE 209) obtained in the samples. Each concentration is the sum of the different congeners analyzed and it is expressed as upperbound.

Table 2. Concentration of POPs in the samples analyzed.

Pollutants	Average	Minimum	Maximum
NDL-PCB (pg/m^3)	42.9	23.3	88.3
DL-PCB (pg/m^3)	5.55	2.00	11.5
TEQ*-DL-PCB (fg TEQ/m^3)	2.94	1.67	6.30
PCDD/F (pg/m^3)	0.63	0.13	3.30
TEQ*-PCDD/F (fg TEQ/m^3)	27.4	13.7	48.8
PBDE (w/o 209) (pg/m^3)	3.41	1.50	5.80
PBDE (w 209) (pg/m^3)	21.9	6.90	47.8

**TEQ concentration has been calculated by using 2005 TEF[5]*

As it is usual in air samples, concentrations of NDL-PCBs and PBDEs are higher than those of PCDD/Fs. In general, concentrations of POPs detected in the samples are similar or lower than those found by other authors in areas close to Barcelona [3, 6-7] or in other cities around the world [8-12].

Seasonal variation

Graphics in Figure 1 show the seasonal variation for the concentrations of the pollutants studied in the vapor phase (PUF), particulate phase (filter) and total concentration.

NDL-PCB and DL-PCB were found mainly in the vapor phase, even in winter. However, if individual congeners are studied, some differences are observed. While less chlorinated congeners (PCB 28, PCB 52, PCB 77) were found in the vapor phase (more than 75%) in all the samples, other congeners with more chlorine atoms (PCB 180, PCB 189) showed important variations in the proportion detected in the PUF in the different seasons: from 30-50% in winter to 80-90 % in summer. Total concentrations of NDL-PCB and DL-PCB increased during the summer, probably due to the evaporation of those pollutants from terrestrial environment at higher temperatures.

For PCDD/F, an opposite trend was observed: the concentration in the vapor phase was, proportionally, very low compared to particulate phase. In addition, while the PUF concentration remained almost constant during the year, the PCDD/F concentration in particulate showed important variations. They can be explained by changes in the sources (e.g. domestic heating in winter, differences between traffic load in winter and summer), but also by particle deposition due to rain (Figure 2) or degradation due to sun UV-light. Some differences are also observed in the congener profile between samples collected in the winter and those sampled in the summer.

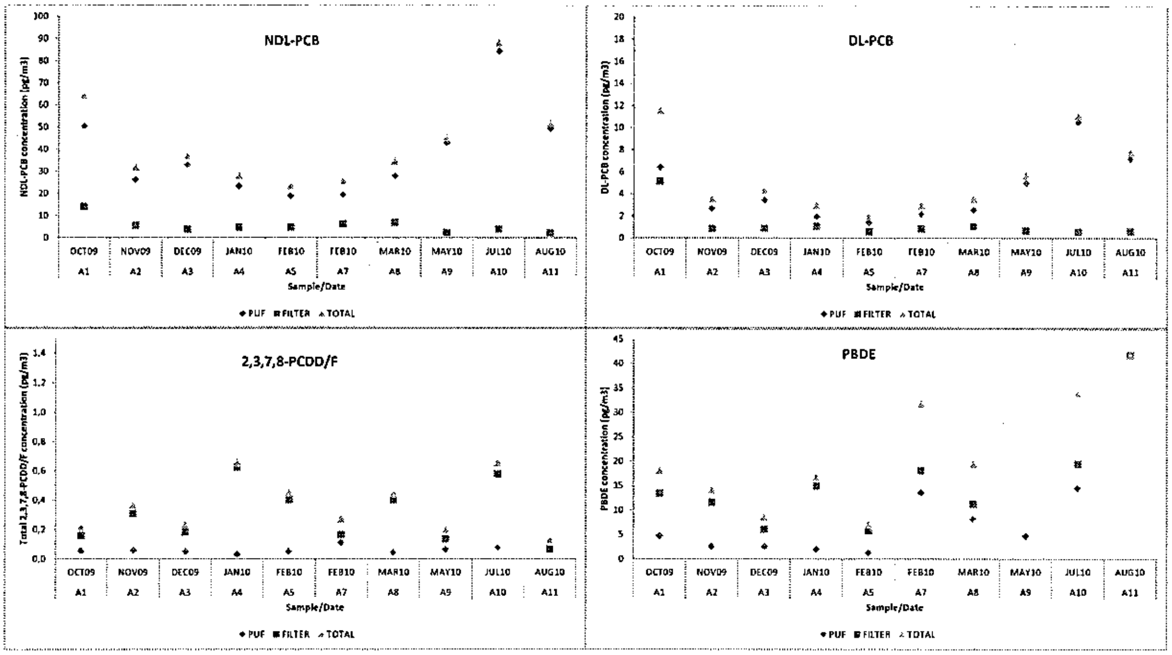


Figure 1. Seasonal variation of POP concentration in vapor and particle phase.

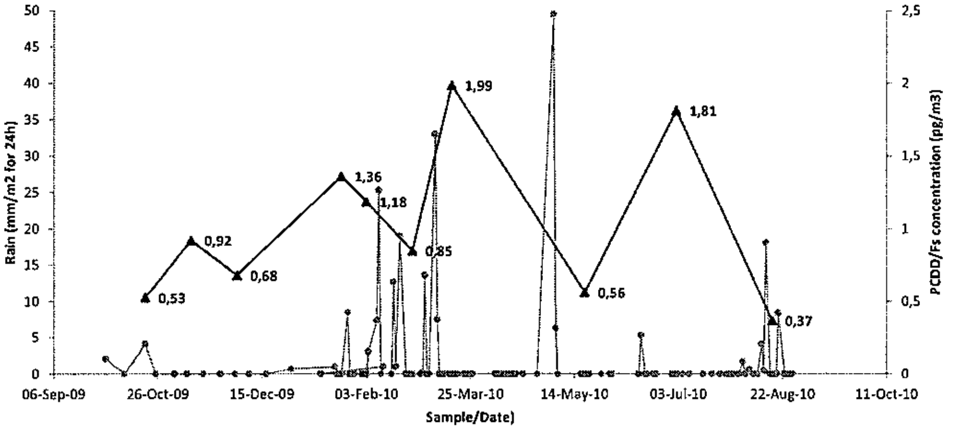


Figure 2. Rain deposition (mm/m^2 for 24h) and PCDD/F concentration during the studied period.

For total PBDE, concentration in particle phase was higher than in vapor phase, due to the presence of BDE 209 (most predominant congener) mainly in particle phase. For the other congeners, at much lower levels of concentration, the proportion detected in PUF increased in summer months until 70-80%. Total PBDE concentration increased from winter to summer, with levels of 47.8 pg/m^3 in August sample.

Daily variations

Differences in concentration between day and night were evaluated by collecting 12-h samples. Although the variability between samples made difficult to state a conclusion, for PCBs (NDL and DL), day samples seemed to present higher concentrations, while for PCDD/Fs and PBDEs concentrations seemed to be higher during the night (Figure 3).

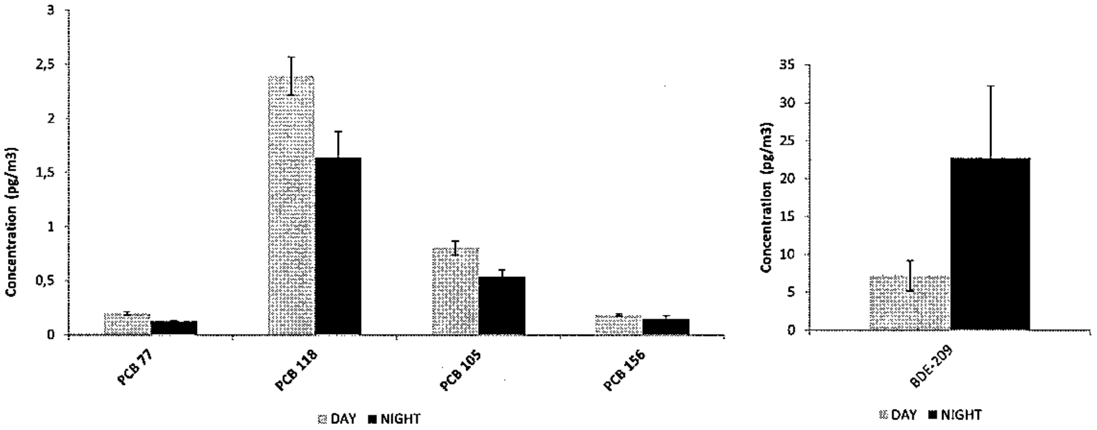


Figure 3. Concentration of PCB 77, PCB 118, PCB 105, PCB 156 and BDE 209 in day and night samples.

Acknowledgements

Authors gratefully acknowledges the collaboration of Environment Department of Catalan Government (Departament de Medi Ambient i Habitatge, Generalitat de Catalunya) in sampling processes.

References:

1. Kim DG, Min YK, Jeong JY, Kim GH, Kim JY, Son CS, Lee DH. (2007) *Chemosphere* 67:1722.
2. Cleverly D, Ferrario J, Byrne C, Riggs K, Joseph D, Hartford P. (2007) *Environ Sci Technol* 41:1537.
3. Gasser M, Martí R, Montaña MJ, Díaz-Ferrero J. (2008) *Organohalogen Compounds* 70:2416.
4. Ortiz X, Marti R, Montaña MJ, Gasser M, Margarit L, Broto F, Díaz-Ferrero J. (2010) *Anal Bioanal Chem* 398:985.
5. Van den Berg M, Birnbaum L, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D. (2006) *Toxicol. Series* 93:223.
6. Mari M, Schuhmacher M, Feliubadaló J, Domingo JL. (2008) Chemosphere 70:1637.
7. Abad E, Martínez K, Gustems L, Gómez R, Guinart X, Hernández I, Rivera J. (2007) *Chemosphere* 67:1709.
8. Helm PA, Bidleman TF. (2003) *Environ Sci Technol* 37:1075.
9. Chen TL, Li XD, Yan JH, Lu SY, Cen KF. (2011) *Atm. Environ* 45:6567.
10. Shin SK, Jin GZ, Kim WI, Kim BH, Hwang SM, Hong JP, Park JS. (2011) *Chemosphere* 83:1339.
11. Hoh E, Hites RA. (2005) *Environ Sci Technol* 39:7794.
12. Moeckel C, Gasic B, Macleod M, Scheringer M, Jones KC, Hungerbühler K. (2010) *Environ Sci Technol* 44:4225.

POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN ATMOSPHERE COLLECTED FROM BACKGROUND AREA IN CHINA IN 2011-2012

Lirong Gao [1],Lidan Liu[1], Bing zhang[1], Cheng Li[1], Minghui Zheng [1], Qiang Fu [2] ; Yibing Lv [2]

[1]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China
[2]Nationanal Environmental Monitoring Center of China, No 8 Dayangfang Road Changyang District, Beijing, China.

Introduction

The Stockholm Convention on POPs under the United Nations Environment Program (UNEP) identified a group of POPs termed the "dirty dozen" to be removed from the global environment. Article 16 of the Stockholm Convention on POPs requires the Conference of the Parties to perform an effectiveness evaluation starting four years after entry into force of the Convention and then at periodic intervals. To assist member countries with this task, UNEP Chemicals published a guidance document for the global monitoring of POPs (UNEP,2007). In this document, air is recommended for investigating POP levels in the environment. The guidance also suggests collect air samples from background with high volume air samplers with a size-selective inlet for collecting only those particles smaller than 10 micrometers diameter.

Monitoring of dioxins by this method maybe helpful to know the usually pollutions of POPs in background air and the long range transport of POPs. Only china followed this method in the first time global monitoring of POPs in background area. The aim of this study was to investigate the concentrations and profiles of background atmospheric PCDD/Fs in China. Samples were collected between 2011 and 2012 at 6 background sites in different provinces. This study implements the national monitoring plan for POPs, and provides data to assess regional and global environmental transport of POPs. Nonetheless, this study is also helpful for monitoring trends and making an assessment of the effectiveness of source reduction measures.

Material and Methods

Two samples and a field blank were collected from 6 background area (Site A and E located in remote, Site B, C loacted in a park of urban area, Site D loacted in suburb area and site F loated in coastal area) in 2011-2012. So 12 samples were collected. Air samples were collected using high-volume samplers designed to collect both vapor and particle bound phases. A typical air sampling high volume sampler with a size-selective inlet for collecting only those particles smaller than 10 micrometers diameter was used for sample collection for more than 3 days. In these samplers, air is first drawn through a Whatman 102-mm binderless quartz micro-fiber filter where atmospheric particles of <10μm in diameter are trapped. Air then passes through a polyurethane foam plug (PUF) used to remove the vapors from the air stream. The airflow rate was calibrated to 0.220 m^3/min prior to initiation of the sampling and checked at the conclusion of each sampling event. An average flow rate of 0.220 m^3/min was recorded during the period sampled. A total volume of air about 1000m^3 was processed. According to the US EPA method TO-9A (EPA, 1999a), GMFs were heated in a muffle at 450 °C for 12 h before sampling and then stored in aluminum foil until use. Filters and PUFs were pre-treated to ensure to be free of contamination and volatilization losses.PUF plugs were rinsed with water and then Soxhlet extracted for 24 h with acetone, dried in a vacuum desiccator, and stored in solvent rinsed aluminum cans. After sampling, PUF plugs were resealed in their original containers while GMFs were placed in aluminum foil. Samples were then returned to the laboratory and stored at –20 °C until extraction.

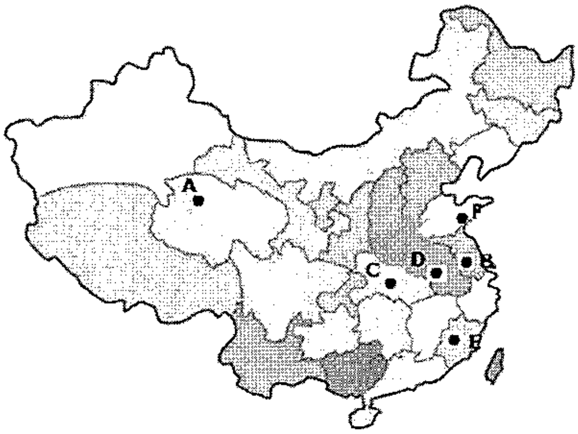


Figure.1 sampling location

The entire analytical process was performed according to US EPA method 1613B The filter and PUF were combined for sample preparation and spiked with ^{13}C-labeled compound solution (Wellington Laboratories, Canada). The sample was then extracted with dichloromethane and hexane (1:1, v/v) using accelerated solvent extraction (ASE 300, Dionex, USA).After concentration, an automated sample preparation system (Power-Prep™, Fluid Management System, USA) was employed for sample cleanup. This cleanup process included a series of three columns: multilayer acid/base/neutral (ABN) silica, basic alumina, and carbon columns. Then the fraction obtained was concentrated under a gentle stream of purified nitrogen and the solvent was changed to nonane (10 μL) in a minivial. For quantification of recovery, the sample extract was spiked with ^{13}C-labeled internal standard (Wellington Laboratories, Canada) immediately prior to instrumental analysis.PCDD/Fs were analyzed by an Agilent 6890 gas chromatograph coupled with Micromass Autospec Ultima high-resolution mass spectrometry by tracing the M+,(M+2)+, or the most intensive ions of the isotope cluster. PCDD/F congeners were analyzed by a 60 m DB5 MS column (60 m * 0.25 mm i.d. *0.25 μm). The carrier gas was helium at 1.2 mL/min. Injection volume was 1 μL in splitless mode with a 60 s splitless period. The MS was operated over 10 000 resolution with EI (35 eV), and data were obtained in the selected ion monitoring (SIM) mode. The instrument stability and relative response factor variance were obtained from the analysis of calibration standard solutions during each sample batch. For quality control, the retention times of the analytes in a sample had to be within 2 s of the retention times of the internal standards. Isotope ratios of the two monitored ions for each compound had to be within 15% of the theoretical chlorine values.

Several steps were taken to assure that the data collected in this study are of high quality including collection of field and lab blanks, duplicates from collocated samplers and breakthrough samples. Field and laboratory blanks were taken with each set of samples and processed in an identical manner to the samples. The method detection limit (MDL) is determined by the background amounts on these blanks rather than the instrumental detection limit. None of the lower chlorinated congeners were detected in the blanks. OCCD was the most prevalent congener in the blanks. However, their concentrations in the blanks corresponded to less than 8% of the concentrations found in the air samples. Concentrations of duplicates obtained at the collocated sites were in good agreement with each other. Of the 17 congeners, 2,3,7,8-TCDD was the most difficult to measure because the concentrations are extremely low. Recoveries of each chemical during clean-up procedure were calculated separately from surrogates and were also determined. The average recoveries for the $^{13}C_{12}$-PCDD/PCDFs were in the range of

56-122%.

Results and discussion

Table 1 summarizes the full data set of over 12 air samples collected from 6 background areas in 2011-2012. Total (gas +particle) concentrations of ΣPCDD/Fs ranged from 435-25210 fg/m^3. The (gas +particle) concentrations of Σ2,3,7,8-PCDD/Fs were 105 fg/m^3 and 5490 fg/m^3 in air samples The highest Σ2,3,7,8-PCDD/Fs concentration were found at location C and the lowest concentration were found at location. During the regular sampling periods, major contributors of atmospheric PCDD/Fs measured at background area include 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD.

Table 1 The concentrations of PCDD/Fs in air of background area

	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2	F1	F2
2378-TCDF	9	3	107	116	122	198	69	<2	<4	5	41	43
12378-PeCDF	7	2	186	152	209	247	101	154	<4	<3	48	44
23478-PeCDF	8	6	210	213	253	343	120	139	5	<2	77	57
123478-HxCDF	13	7	233	246	251	303	154	215	8	6	92	77
123678-HxCDF	10	6	188	209	218	292	132	167	5	5	77	73
234678-HxCDF	14	7	333	236	230	300	125	177	5	6	77	72
123789-HxCDF	<3	<1	59	71	60	78	38	50	<3	<1	19	20
1234678-HpCDF	56	30	744	786	661	910	471	732	27	24	239	270
1234789-HpCDF	7	4	98	116	89	117	64	88	3	4	43	30
OCDF	59	25	560	604	401	582	416	480	42	35	241	230
2378-TCDD	<4	<2	7	4	20	22	<6	5	<4	<1	<11	<6
12378-PeCDD	<3	<2	24	<7	29	55	20	17	<4	<1	<11	<11
123478-HxCDD	<2	<1	18	22	27	36	12	12	4	<1	<7	<7
123678-HxCDD	<2	<1	42	52	56	67	31	25	<1	2	12	16
123789-HxCDD	<2	<1	32	30	44	56	24	22	<2	3	12	13
1234678-HpCDD	15	5	202	234	266	341	119	129	5	12	69	64
OCDD	56	10	307	431	1145	1545	339	170	73	59	120	129
Totals Tetra-Furans	239	98	4507	3796	5108	7501	2355	3422	235	241	1684	1517
Totals Tetra-Dioxins	176	32	1541	1817	1645	2102	1052	893	119	117	908	710
Totals Penta-Furans	269	63	3375	3437	4032	5259	2018	2666	134	141	1218	1035
Totals Penta-Dioxins	143	24	564	1839	1045	1680	822	577	57	45	296	259
Totals Hexa-Furans	130	60	2346	2426	2148	2855	1352	1960	56	55	744	696
Totals Hexa-Dioxins	69	44	936	1125	1228	1423	539	552	26	32	294	328
Totals Hepta-Furans	95	51	1420	1281	1019	1382	738	1193	42	39	399	405
Totals Hepta-Dioxins	58	57	529	625	725	882	321	359	23	25	190	277
2378-PCDD/Fs	252	105	3349	3522	4077	5490	2234	2579	177	160	1164	1138
PCDD/Fs	1,293	465	16,085	17,381	18,495	25,210	9,952	12,273	807	788	6,093	5,586
WHO-TEQ	11.7	6.6	211.1	186.3	229.3	334.3	127.1	144.2	8.3	4.7	72.1	62.3

To normalize concentrations and the toxicity of the different PCDD and PCDF congeners, World

Health Organization (WHO) toxicity equivalent factors (WHO-TEFs) (Van den Berg et al., 2006) were used to calculate the WHO toxicity equivalent for the samples. The WHO-TEQ were calculated where the measurement results were below the limits of detection, their concentrations were taken as 0.5 of the value. The dioxin levels varied from 4.7 to 334.3fg WHO-TEQ/m^3. The dioxins levels in site A and E in this study were in the same magnitude with those analyzed in previous study and site D were much higher than previous data (Wu et al., 2009). The highest levels were observed in site C located in a park of urban area and the lowest levels were observed in Site E located in a remote area which is far away from city. Among all PCDD/F congeners, 1,2,3,4,7,8,9-HpCDF, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were the major contributors of total WHO-TEQ.

Acknowledgements

This study was supported by Knowledge Innovation Program of the Chinese Academy of Sciences (KZCX2-YW-JS40) and National Natural Science Foundation of China (21007084).

Reference

M Van den Berg, L Birnbaum, M Denison et al., The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds Toxicol. Sci. 2006, 93 (2): 223-241.

United Nations of Environment Programme Guidance on the Global Monitoring Plan for Persistent Organic Poutants 2007 http://chm.pops.int/DNNADMIN/HiddenModulesforMandeepsPublications/tabid/222/ctl/Download/mid/5232/Default.aspx?id=0&ObjID=4342

Wu JJ, Gao LR , Zheng MH et al., Polychlorinated dibenzo-p-dioxins and dibenzofurans in background air in China Organohalogen Compounds 2009,71, 2741-2743

LEVELS OF PERSISTENT ORGANIC COMPOUNDS IN AMBIENT AIR OF AFRICA

Klánová J*, Kukučka P, Přibylová P, Borůvková J, Prokeš R

Research Centre for Toxic Compounds in the Environment
klanova@recetox.muni.cz

Background

Application of persistent organic pollutants (POPs) in the African countries is closely connected to pesticides. They were used in the agricultural production of food crops such as maize, sorghum and millet as well as cash crops for export such as cocoa, rubber, cotton and timber. They were applied also for disease vector control, especially for mosquito (malaria) and tsetse fly (trypanosomiases). POP pesticides have been generally imported and not produced in Africa, but pesticide formulation plants exist in many countries. DDT, endosulfan, chlordane, lindane (HCH), heptachlor, toxaphene, HCB and aldrin were identified as most frequently used pesticides. The most serious problem the African region faces is the issue of stocks and reservoirs of obsolete discarded and banned POP pesticides. In addition, banned pesticides continue to be used in practice without any control of the authorities.

Sampling sites

Based on the results of the first African air monitoring project (MONET AFRICA) from 2008 in frames of which selected sites have been monitored for 6 months using passive air sampling technique, sites in 14 countries on the African continent (Congo, Democratic Republic of Congo, Egypt, Ethiopia, Ghana, Kenya, Mali, Nigeria, Senegal, South Africa, Sudan, Togo, Tunis, Zambia) plus Mauritius and Canary Islands were selected for the follow up project (Figure 1).

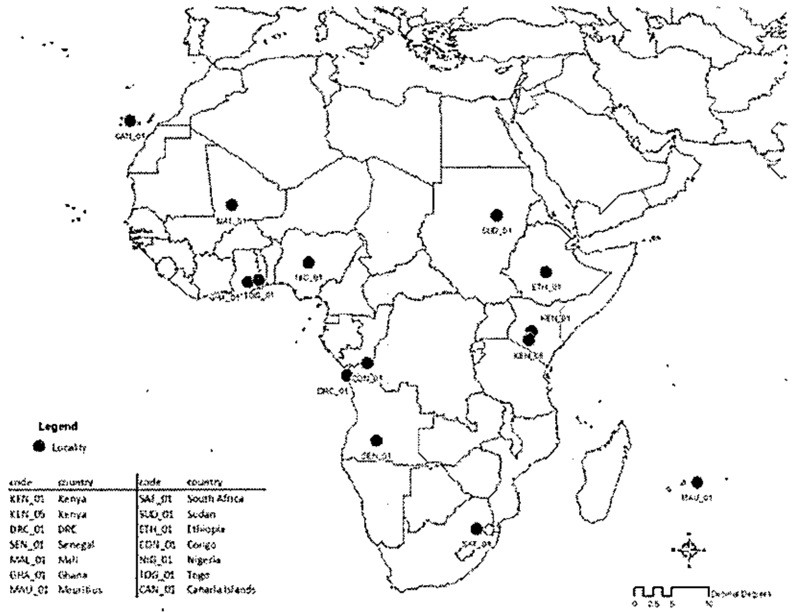


Figure 1. Passive air sampling sites monitored in the current campaign

Compounds of interest

Target compounds of the Stockholm Convention as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and furans (PCDDs/Fs), or organochlorine pesticides (OCPs) (DDT including metabolites, hexachlorobenzene, aldrin, dieldrin, endrin, heptachlor, methoxychlor, mirex, chlordane) were among the compounds of interest together with newly listed chemicals as isomers of hexachlorocyclohexane (HCHs), pentachlorobenzene, endosulfan, chlordecone, hexabromobiphenyl, tetra-, penta-, hexa- and hepta-bromodiphenyl ethers, and hexabromocyclododecane as a candidate chemical.

Design of the sampling campaign

Two polyurethane foam passive air samplers were deployed at each site. First sampler was exposed for 28 days and used to assess temporal variations of PCBs, HCHs, DDTs, HCB, and PeCB. Second sampler was exposed for 84 days and used to assess concentrations of aldrin, dieldrin, endrin, heptachlor, isodrin, methoxychlor, mirex, *cis*-chlordane, *trans*-chlordane, nonachlor, endosulfan, and polychlorinated dibenzodioxins and furans.

Air sampling

Passive air samplers consisting of the polyurethane foam (PUF) disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm^{-3}, type N 3038; Gumotex Breclav, Czech Republic) housed in the protective chambers were employed in this study. Theoretical sampling volume of 7 m^3/day was determined by co-location of active and passive samplers and used for calculation of the air concentrations. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All PUF disks were prewashed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane for PCBs and OCPs, 8 hours extraction in acetone and 8 hours in toluene for PCDDs/Fs), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. Exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported in cooler at 5 °C to the laboratory where they were kept in the freezer at –18 °C until the analysis. Field blanks were obtained by installing and removing the PUF disks at all sampling sites.

Sample analysis

All 4-week samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. One laboratory blank and one reference material were analyzed with each set of ten samples. Surrogate recovery standards (PCB 30 and PCB 185 for PCBs analysis) were spiked on each filter prior to extraction. PCB 121 was used as an internal standard for PCBs/OCPs analyses. Volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a sulphuric acid modified silica gel column. Samples were analyzed using GC-MS/MS (Quattro Micro GC – Watters) supplied with a J&W Scientific fused silica column DB-5MS for PCBs and OCPs.

12-week samples were spiked with the isotopically labeled standards and extracted with toluene in a Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) with toluene in a B-811 extraction unit (Büchi, Switzerland). Prior to extraction, the samples were spiked with ^{13}C PCDDs/Fs (according to EN-1948), ^{13}C dl-PCBs and ^{13}C BDEs. The concentrated extracts were cleaned-up on a H_2SO_4 modified (30% w/w) silica gel column, eluted with 40 mL DCM/*n*-hexane mixture (1:1). Fractionation was achieved in a micro column (6 mm i.d) containing from bottom to top: 50 mg silica gel, 70 mg charcoal/silica gel (1:40) and 50 mg of silica gel. The column was prewashed with 5 mL of toluene, followed by 5 mL of DCM/cyclohexane mixture (30%), then the sample was applied and eluted with 9 mL DCM/cyclohexane mixture (30%) in fraction 1 (PBDEs, mono-ortho dl-PCBs) and 40 mL of toluene in fraction 2 (PCDDs/Fs, non-ortho dl-PCBs). Each fraction was concentrated using stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. The syringe standards (^{13}C PCDDs, ^{13}C PCBs 70, 111, 138 and 170, ^{13}C BDEs 77 and 138) were added to all samples, the final volume was 50 uL. HRGC/HRMS instrumental analysis (PCDDs/Fs, dl-PCBs) was performed on an 7890A GC (Agilent, USA) equipped with a 60m x 0.25mm x 0.25um DB5-MS column (Agilent J&W, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at the resolution of >10 000. BDEs were analyzed on the same system using 15m x 0.25 mm x 0.10 um DB5 column (Agilent J&W, USA). For BDE 209, the MS resolution was set to >5 000.

Quality Assurance / Quality Control

Recoveries of PCBs and OCPs were determined for all samples by spiking with the surrogate standards prior to extraction. Amounts were similar to detected quantities of analytes in the samples, and recoveries were higher than 76 %.Recovery factors were not applied to any of the data. Recovery of native analytes measured for the reference material varied from 88 to 103 % for PCBs, and from 75 to 98 % for OCPs. Laboratory blanks were under the detection limits for selected compounds. Field blanks consisted of pre-extracted PUF disks and they were taken on each sampling site. They were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 3% of quantities detected in samples for PCBs, and 1% for OCPs, indicating minimal contamination during the transport, storage and analysis.

For PCDDs/Fs, recoveries of the isotopically labelled standards were 55-90%. For dl-PCBs, recoveries ranged between 60 and 90%. For BDEs, recoveries ranged between 60 and 110%. All data are recovery corrected. Laboratory blanks were under the quantitation limits for all compounds. Field blanks consisted of pre-extracted PUF disks and were taken on each sampling site. These were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 3% of quantities detected in samples for PCDDs/Fs, 5% for dl-PCBs and 10% for BDEs, indicating minimal contamination during the transport, storage and analysis.

Results

The air samples from 13 sampling sites in 12 countries were collected during two years of the African follow-up study. Sampling sites ranged from continental through rural to urban backgrounds. Levels of various chemicals ranged over several orders of magnitude. Congo, Sudan and Senegal had the highest levels of PCDDs/Fs (up to 262, 120 and 80 pg/sample, i.e. 0.45, 0.2 and 0.13 pg/m^3, of 17 EPA congeners, respectively) while they never exceeded 1 pg/sample at Mount Kenya. The highest concentrations of PCBs were found in Sudan (4.2 ng/sample, 21 pg/m^3) and highest concentrations of PBDEs in Sudan (14.3 ng/sample, 24 pg/m^3), Congo (5.8 ng/sample, 10 pg/m^3), Canary Islands and Mauritius (both up to 4 ng/sample, 7 pg/m^3). For pesticides, the highest levels of DDTs were determined in Ethiopia (78 ng/sample, 390 pg/m^3), HCHs in Togo (2.4 ng/sample, 12 pg/m^3), and endosulfane in Ethiopia (75 ng/sample, 120 pg/m^3).

This study is an important contribution to our current knowledge on the levels and distribution of POPs in the African continent. As such, it also significantly contributes to successfull realization of the Global Monitoring Plan, an important tool for effectiveness evaluation of the Stockholm Convention.

Aknowledgement

The air monitoring activities in Africa are based on the Memorandum of Understanding signed between the United Nations Environment Programme represented by the Secretariat of the Stockholm Convention and Masaryk University represented by the Research Centre for Toxic Compounds in the Environment (RECETOX). This project was also supported by the CETOCOEN project

(CZ.1.05/2.1.00/01.0001) granted by the European Union and administrated by the Czech Ministry of Education, Youth and Sports.

References

Klanova J., Cupr P., Holoubek I., Boruvkova J., Pribylova P., Kares R., Tomsej T., and Ocelka T. (2009) Monitoring of persistent organic pollutants in Africa. Part 1: Passive air sampling across the continent in 2008. Journal of Environmental Monitoring, 2009, 11, 1951-1953.

Lammel G., Dobrovolný, P., Dvorská, A., Chromá, K., Brázdil, R., Holoubek, I., Hošek, J. (2009) Monitoring of persistent organic pollutants in Africa. Part 2: Design of a network to monitor the continental and intercontinental background. Journal of Environmental Monitoring, 2009, 11, 1964-1972.

PCDD/FS CONCENTRATIONS IN THE ATMOSPHERE OF BEIJING, CHINA

ZHOU Zhi-guang*, XU Peng-jun, QI Li, REN Yue, LI Nan, ZHENG Sen, ZHAO Hu, FAN Shuang, ZHANG Ting, LIU Ai-min, Huang Ye-ru

State Environmental Protection Key Laboratory of Dioxin Pollution Control, Beijing 100029, China

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have aroused big concerns of the public and government for a few decades. More attention is paid than any other persistent organic pollutant (POPs) due to the fact that they are highly toxic and bioaccumulative in ecosystem. Moreover, PCDD/Fs can transport over long distances from their sources of emission. Ambient air is the most important pathway for PCDD/Fs transfer. Many countries (including China) have conducted PCDD/Fs monitoring studies in ambient air[1].

Beijing, as the capital of China, is one of the largest cities throughout the country. It is characterized with a high population density and heavy traffic. Industries mainly consist of electronics, automobile manufacture, pharmaceutical synthesis, petroleum refining and waste burning. As a result, traffic and waste burning may be the primary source for PCDD/Fs in Beijing. The goal of this paper is to report the atmospheric PCDD/Fs pattern in Beijing. Measurements of these toxic pollutants were carried out in winter, and summer. Four sample sites were chosen near the Fourth Ring Road with intense traffic, where the traffic flow comprises heavy duty diesel buses and light duty gas vehicles. Vehicular emissions are expected to make significant contributions since there are no industrial activities in the immediate vicinity. Additional two sample sites, one in Tian Tan Park and the other in residential area, are selected as comparisons to those along the Fourth Ring Road. PCDD/Fs concentration, and their relationship with meteorological conditions, seasonal variations, as well as the potential emission sources are also discussed.

2. Materials and Methods

2.1 Sampling

Ambient samples were collected according to US EPA Method TO-9A using a SIBATA HV-1000F sampler, equipped with quartz fiber filter (QFF), and followed by a glass cartridge containing two polyurethane foam (PUF) plugs. Before sampling, the PUF plugs were spiked with 1 ng of $^{13}C_{12}$ labeled surrogate standards. About 2160 m^3 ambient air were sampled during a 72 h sampling period, with a flow rate of 0.5 m^3 min^{-1}. After sampling, the samples were placed in a glass container wrapped with aluminum foil. The QFF was weighed before and after sampling to obtain total suspended particle (TSP) mass concentration. The sample period was between February 22-28 in winter and between July 7-13 in summer in 2011.

2.2 Analysis

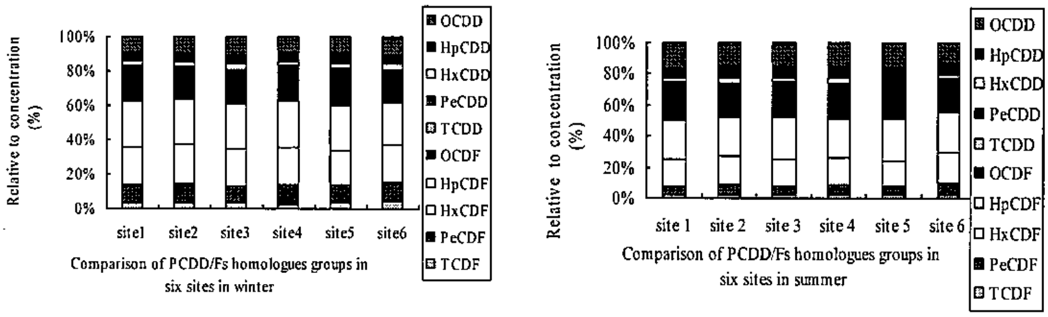
All the organic solvents are pesticide residue grade from J. T Baker (USA). Silica was purchased from Wako (Osaka Japan). Calibration standard solutions, $^{13}C_{12}$ labeled surrogate standards and $^{13}C_{12}$ labeled injection standards were purchased from Wellington Laboratories (Guelph, Canada).

Analysis of PCDD/Fs followed HJ 77.2-2008 in China.

3. Results and discussion

3.1 PCDD/Fs mass concentrations

The highest mass concentration of total seventeen 2,3,7,8-substituted PCDD/Fs was found at site with the concentration of 10.38 pg/m^3 in winter. The lowest concentration is 1.31 pg/m3 at site 16 in summer. Similar homologue profiles were observed in both winter and summer for all the sampling sites that HpCDF predominated furan concentrations. The main contributors to the PCDD/Fs were HpCDF, followed by HxCDF and OCDF, which account for 27%, 22% and 20% of PCDD/Fs mass concentration on average, respectively. Additionally, an increase in the concentration was observed as chlorination level increased ($Cl_4 < Cl_5 < Cl_6 < Cl_7 < Cl_8$) for PCDDs. The same trend was also found for PCDFs, with an exception of OCDF whose concentrations were between PeCDFs and HxCDFs ($Cl_4 < Cl_5 < Cl_8 < Cl_6 < Cl_7$).



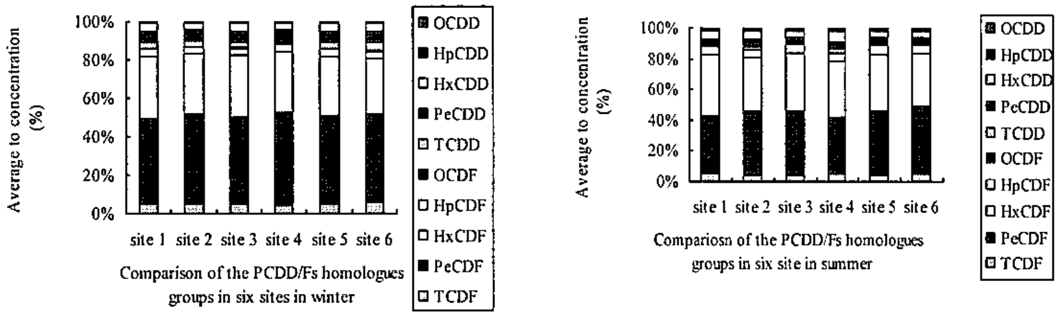
Comparison of PCDD/Fs homologues groups in six sites in winter

Comparison of PCDD/Fs homologues groups in six sites in summer

Fig. 1 Comparison of the PCDD/Fs congeners in samples

3.2 Toxicity equivalency (TEQ) concentrations of PCDD/Fs

The TEQ concentrations of the seventeen congeners of PCDD/Fs are calculated using I-TEF (International Toxicity Equivalency Factor). The I-TEQ concentrations of PCDD/Fs range from 0.062-0.751 pg I-TEQ. m^{-3}with the highest concentration found in a haze day in winter and the lowest found in summer. PeCDF contributed most to the total TEQ concentration, with an average contribution of 45.5%. Other important contributors were HxCDF (30%), PeCDD (5%), TCDF (4.5%), and HxCDD (4.0%). OCDD and OCDF contribute <1% to the TEQ concentration. The ∑PCDF concentrations were higher than that of ∑PCDDs and all the ∑PCDDs/∑PCDFs ratios were <1. The concentrations of 2,3,7,8-substitued PCDD/Fs in Beijing air in winter were higher than those reported by Joao et al. (2005) and exceeded the ambient air standard of 0.6 pg TEQ m^{-3} regulated in Japan (http://www.env.go.jp/en/air/aq/aq.html) for some samples, but in summer the concentrations were lower than other cities and below 0.6 pg-TEQ/m^{-3}.[2]



Comparison of the PCDD/Fs homologues groups in six sites in winter

Compariosn of the PCDD/Fs homologues groups in six site in summer

Fig. 2 Comparison of the PCDD/Fs homologues in samples

3.3 Seasonal variation

Seasonal variation was characterized with higher concentrations in winter and lower concentrations in the summer, which was consistent with observations in previous studies[3]. The seasonal variation can be explained by the extensive fossil fuel combustion for heating and haze weather resulting in worse dispersion in winter. During summer sampling period, light rains and good dispersion conditions during the whole sampling period were observed. Lower concentrations of PCDD/Fs were found when compared to those in winter samples. As wet deposition is the major removal mechanism for suspended particles, rainfall lead to a lower environmental concentration of PCDD/Fs[4]. And low TSP concentrations were also observed during the same sampling period.

3.4 TSP vs. PCDD/Fs

A haze occurred on February 22-24 in 2011 during the sample period, which indicated heavy air pollution by the data released by Beijing Environmental Monitor Station. During the haze period, the level of PCDD/Fs increased dramatically with the highest mass concentration of 10.38 pg/m^3, which is about ten times higher than those during non-haze periods. In the following four days, the concentration of PCDD/Fs decreased to about one tenth of the highest concentration with snow occurring. When haze occurred, the TSP concentration increased by two times, but the concentration of PCDD/Fs increased by 4-10 times. This indicted that fine particles were increase in haze, and fine particles absorbed PCDD/Fs, so the concentration of PCDD/Fs increased more than TSP.

Table 1 Average TSP and PCDD/Fs concentrations

			February 22- 25 2011 with haze			
	Site1	Site2	Site3	Site4	Site5	Site6
Average TSP(ug/m3)	0.599	0.736	0.565	0.654	0.570	0.754
Average PCDD/Fs(pg/m3)	8.736	10.380	8.411	10.072	5.870	4.548
			February 25- 28 2011 without haze			
	Site1	Site2	Site3	Site4	Site5	Site6
Average TSP(ug/m3)	0.350	0.309	0.295	0.421	0.647	0.417
Average	0.670	1.228	1.472	0.972	1.240	1.112

PCDD/Fs(pg/m3)						
Difference between with and without haze in TSP(ug/m3)	0.249	0.427	0.256	0.233	0.244	0.337
PCDD/Fs(pg/m3)	8.036	9.152	6.940	9.100	4.630	3.436

3.5 Principal component analysis

In order to identify the potential emission sources of PCDD/Fs, and to compare the differences and similarities in the congener profiles, principal component analysis (PCA) was performed on the relative intensity of ten homologues of each sample. The first principal component (PC1, explaining 56% of the total variance) was strongly and positively correlated with HxCDF, TeCDF, and PeCDF, yet strongly and negatively with OCDF. The second principal component (PC2, explaining 18% of the total variance) was negatively correlated with OCDF, yet positively with OCDD. All the samples were divided into three groups. Combining with the meteorological conditions, we found that: The samples in group 1 were collected in haze day in winter, and group 2 were sampled after snowing in winter, and group 3 were sampled in summer. The analysis indicated that PCDD/Fs in haze day were attributable to multiple emission sources, such as waste burning, vehicle exhaust and domestic heating. The pattern in group 2 differed due to the washout effect by snow. The profiles for group 3, of which the samples were collected in summer without domestic heating, were expected to be mainly influenced by waste burning and vehicle exhaust.

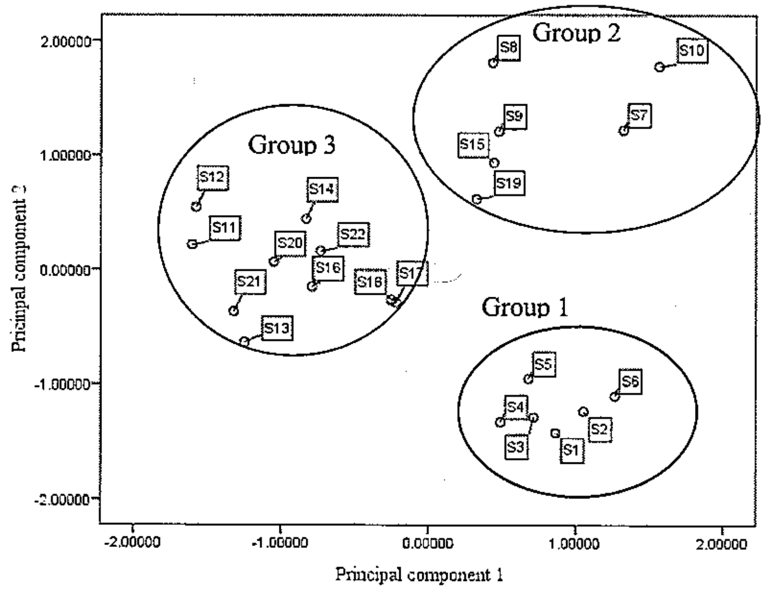


Fig.3 Principal component analysis for samples

4. Acknowledgements

This works was supported by "State Environmental Protection Administration, research and public service industry, a special (Grant No. 200909095)", and "National Key Fundamental Research Project (973) (Grant No. 2009CB421602)".

5. Reference

1. Tong Chen, Xiaodong Li, Jianhua Yan, Shengyong Lu, Kefa Cen. (2011) *Atmospheric Environment* 45: 6567-6575
2. Joao V, Celia R, Pesquero, Roy E. Bruns, Lilian R.F, Carvalho. (2005) *Chemosphere* 58: 1391–1398
3. Lee R G., Green N J, Lohmann R, Jones K C. (1999) *Environ Sci Technol* 33: 2864–2871
4. Chang M B, Weng Y M, Lee T Y, Chen Y W, Chang S H, Chi KH. (2003) *Chemosphere* 51: 1103–1110

FINGERPRINTING PESTICIDES: EXPANDING DIOXIN SOURCE KNOWLEDGE

Holt EVA[1], Weber R[2], Stevenson G[3], Gaus C[1]*

[1]The University of Queensland (Entox), 39 Kessels Road, Coopers Plains, Australia; [2] POPs Environmental Consulting DE-73035 Göppingen, Germany; [3]National Measurement Institute, 1 Suakin Street, Pymble, 2073, Australia

Introduction

Source identification is an important step to reduce or eliminate polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) emissions to the environment. Pesticide sources are poorly represented in source tracing studies where often only the PCDD/F fingerprint of pentachlorophenol (PCP) is used to characterize pesticide use. Recent studies show that many other pesticides contain PCDD/Fs[1], the use of which may represent an important source of PCDD/Fs to the environment. New information also suggests that formation from pesticide derived precursors in the environment may significantly alter the original PCDD/F fingerprint in pesticide products[2] a consideration not previously made in source tracing studies. Detailed congener-specific data on the PCDD/F levels in nineteen different pesticide products are presented in this study.

Materials and methods

Sampling and chemical analysis

For the present study, HRGC-HRMS raw data files of samples previously analysed and reported for the seventeen 2,3,7,8-substuted PCDD/F congeners and homologues were integrated to determine concentrations for all congeners (73 after data treatment, see below). These samples included a total of 21 pesticide formulations (13 active ingredients)[1] .

Identification and quantification of congeners

Congener-specific PCDD/F concentrations were determined as previously reported[1,2,3]. Results for some congeners were combined to enable direct comparison between source (pesticides from the present study and those analysed previously[2]) and receptor (e.g. Australian soils[4]) profiles, the analysis of which were carried out on different columns (DB-5 or ZB-5MS). Congeners that were combined or coeluted are marked with an asterix (*) throughout the text (Table 1). Where congeners were combined, the lower bound concentrations were summed and where all combined congeners were <LOQ, maximum LOQs were used.

Table 1. Abbreviations for combined or co-elutioned congeners

PCDDs: 1,2,4,7-TCDD* (1,2,4,7/1,2,4,8/1,3,7,8/1,4,6,9/1,2,4,6/1,2,4,9-TCDD); 1,2,3,4-TCDD* (1,2,3,4/1,2,3,6/1,2,6,9-TCDD); 1,2,3,6,9-PnCDD* (1,2,3,6,9/1,2,4,6,7/1,2,4,8,9-PnCDD); 1,2,3,7,8,9-HxCDD* (1,2,3,4,6,7/1,2,3,7,8,9-HxCDD)	PCDFs: 1,2,6,8-TCDF* (1,2,6,8/1,4,6,7/1,4,7,8-TCDF); 1,2,7,8-TCDF* (1,2,7,8/1,3,4,9/1,2,6,7-TCDF) 2,3,6,7-TCDF* (2,3,6,7/3,4,6,7/1,2,6,9-TCDF); 1,3,6,7,8-PnCDF* (1,3,6,7,8/1,2,4,6,7/1,3,4,6,7/1,3,4,7,8/1,2,3,6,8/1,2,4,7,8/1,4,6,7,8/1,3,4,7,9-PnCDF); 1,2,3,4,6-PnCDF* (1,2,3,4,6/1,2,4,6,9/2,3,4,6,8/1,2,3,4,7-PnCDF); 2,3,4,7,8-PnCDF* (2,3,4,7,8/1,2,4,8,9/1,2,6,7,9/1,2,3,6,9/2,3,4,6,7-PnCDF); 1,2,3,4,7,8-HxCDF* (1,2,3,4,6,7/1,2,3,4,7,8-HxCDF); 1,2,3,7,8,9-HxCDF* (1,2,3,4,8,9/1,2,3,7,8,9-HxCDF)

Results and discussion:

PCDD/F congener profiles in current use pesticides

Levels of PCDD/Fs in pesticide formulations included in this study ranged from 0.0043 – 1,500 ng ∑PCDD/F g^{-1} as reported previously[1]. Notably, the congener profiles of several of these pesticides were characterised by relatively high (61 - 98%) contributions of octachlorodibenzo-*p*-dioxin (OCDD), particularly PCNB, imazamox, mecoprop and chlordane (Figure 1). Similarly high OCDD contributions have previously been known for pentachlorophenol (PCP)[5,6] and *p*-chloranil[7]. Other congeners in the OCDD dominated pesticides included in the present study, which may provide additional congeners (markers) contributed <10% to ΣPCDD/F concentrations. These congeners include traces of 1,2,3,4,6,7,9-heptachlorodibenzo-p-dioxin (HpCDD), 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF) and octachlorodibenzofuran (OCDF) for PCNB; 1,2,3,4,6,7,9-HpCDD and 1,2,3,4,6,7,8-HpCDD for imazamox and OCDF for mecoprop. The chlordane formulation, analysed for the present study, contained 1,2,3,4,6,7,9-HpCDD, 1,2,3,4,6,7,8-HpCDD, OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,8,9-HpCDF it also contained 1,3,6,9-tetrachlorodibenzofuran (TCDF). In the past many of the congeners (1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF) detected in the OCDD dominated pesticides (PCNB, MCPA, chlordane and imazamox) from the present study were previously only observed in PCP formulations and hence are used to identify PCP usage as a source of PCDD/Fs[5]. The contributions of PCDD/Fs via these pesticides may thus be difficult to distinguish based on congener profiles in environmental matrices dominated by OCDD, in particular in aged deposition matrices influenced by various fate processes and source mixtures.

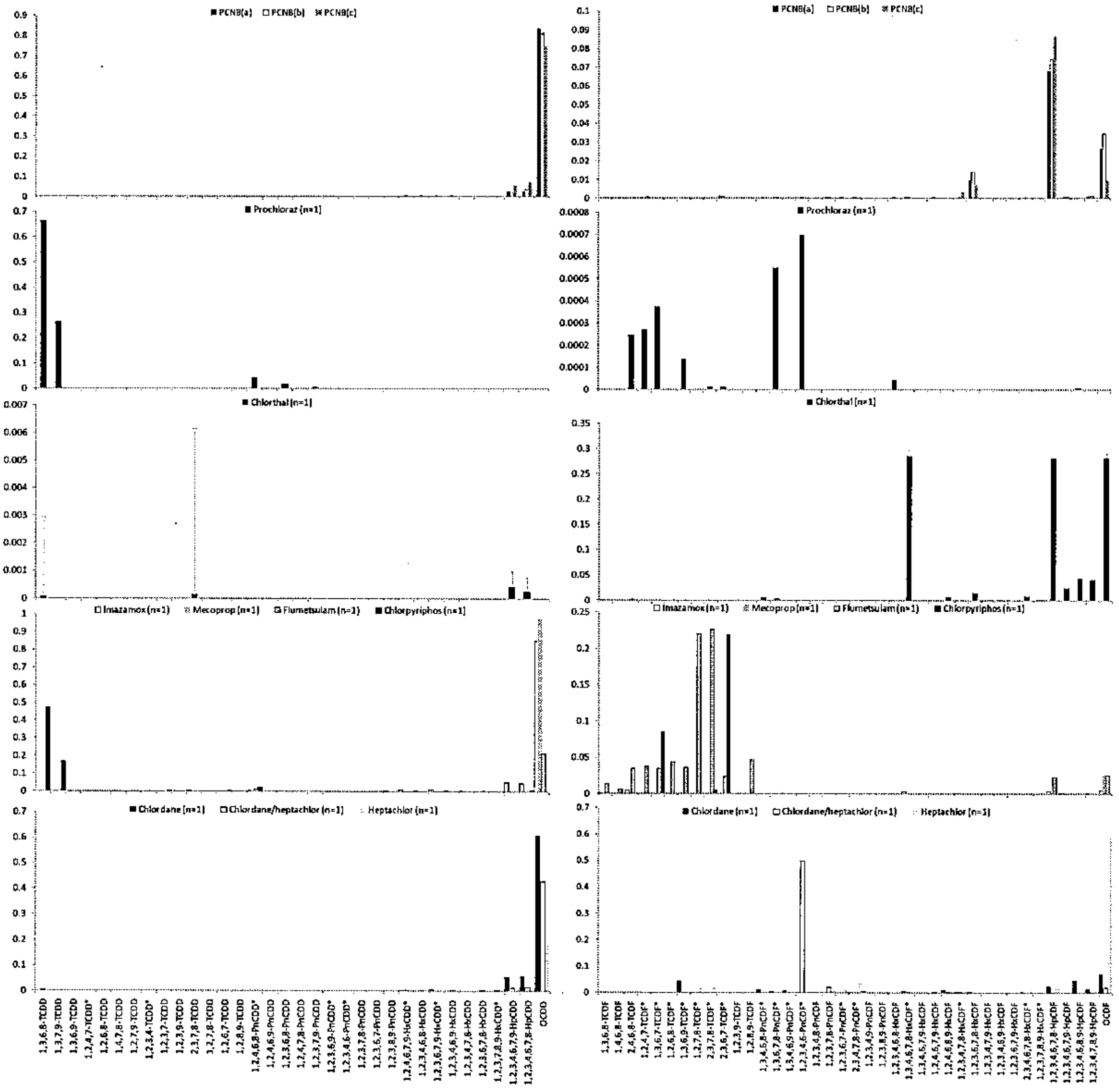


Figure 1. Congener profile (contribution to ∑PCDD/F) of PCNB; prochloraz; chlorthal [Average, minimum and maximum values of two replicates are presented for PCNB(a); PCNB(b) and chlorthal]; imazamox; mecoprop; flumetsulam; chlorpyriphos, and organochlorine pesticides - heptachlor and chlordane

PCDD/F congener profiles of the herbicides chlorpyriphos and flumetsulam and the fungicide prochloraz (Figure 1) were characterised by the lower chlorinated congeners 1,3,6,9-TCDD (47%), 1,3,7,9-TCDD (17%), 1,3,6,7-

TCDF* (9%) and 2,3,6,7-TCDF* (22%) in chlorpyriphos, TCDFs (including 1,2,7,8-TCDF* and 2,3,7,8-TCDF* with 22 and 23% contribution to the ∑PCDD/F, respectively) in flumetsulam, and 1,3,6,9- (67%) and 1,3,7,9-TCDD (26%) in prochloraz. In contrast, chlorthal and heptachlor formulations contained mainly higher chlorinated PCDD/Fs, including 1,3,4,6,7,8-hexacchlorodibenzofuran (HxCDF), 1,2,34,6,7,8-HpCDF and OCDF (with % contributions of 29, 28 and 28 to the ∑PCDD/F, respectively), for chlorthal, and 1,2,3,4,6-PnCDF* (50%) and OCDD (43%) in heptachlor/chlordane formulation.

Phenoxy herbicides 2,4-dichlorophenoxyacetic acid (2,4-D); 2,4-dichlorophenoxybutyric acid (2,4-DB) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)/2,4-D were characterized by the presence of lower chlorinated PCDDs (in 2,4-DB) or lower chlorinated PCDFs (in 2,4-D and 2,4,5-T/2,4-D) (Figure 2). Fingerprints in these pesticides could be clearly distinguished, with relatively high contribution of 1,2,4,6,8-pentachlorodibenzo-p-dioxin (PnCDD)* (~50%) in 2,4-DB, 2,4,6,8-tetrachlorodibenzofuran (TCDF) (~25 - 30%) in 2,4-D, and 2,3,7,8-TCDF*(~50%) in 2,4-D/2,4,5-T, respectively. Other phenoxy herbicides analysed included two formulations containing 2-methyl-4-chlorophenoxy-acetic acid (MCPA) as an active ingredient (although dicamba was also present as a secondary active constituent); these were characterised by ~30% contribution of OCDD to the congener profile and both contained similar and distinctive contributions of 1,3,6,8-tetrachlorodibenzo-p-dioxin (TCDD), 2,4,6,8-TCDF, 1,3,4,6,8- pentachlorodibenzofuran (PnCDF) and OCDF (5 - 10% each).

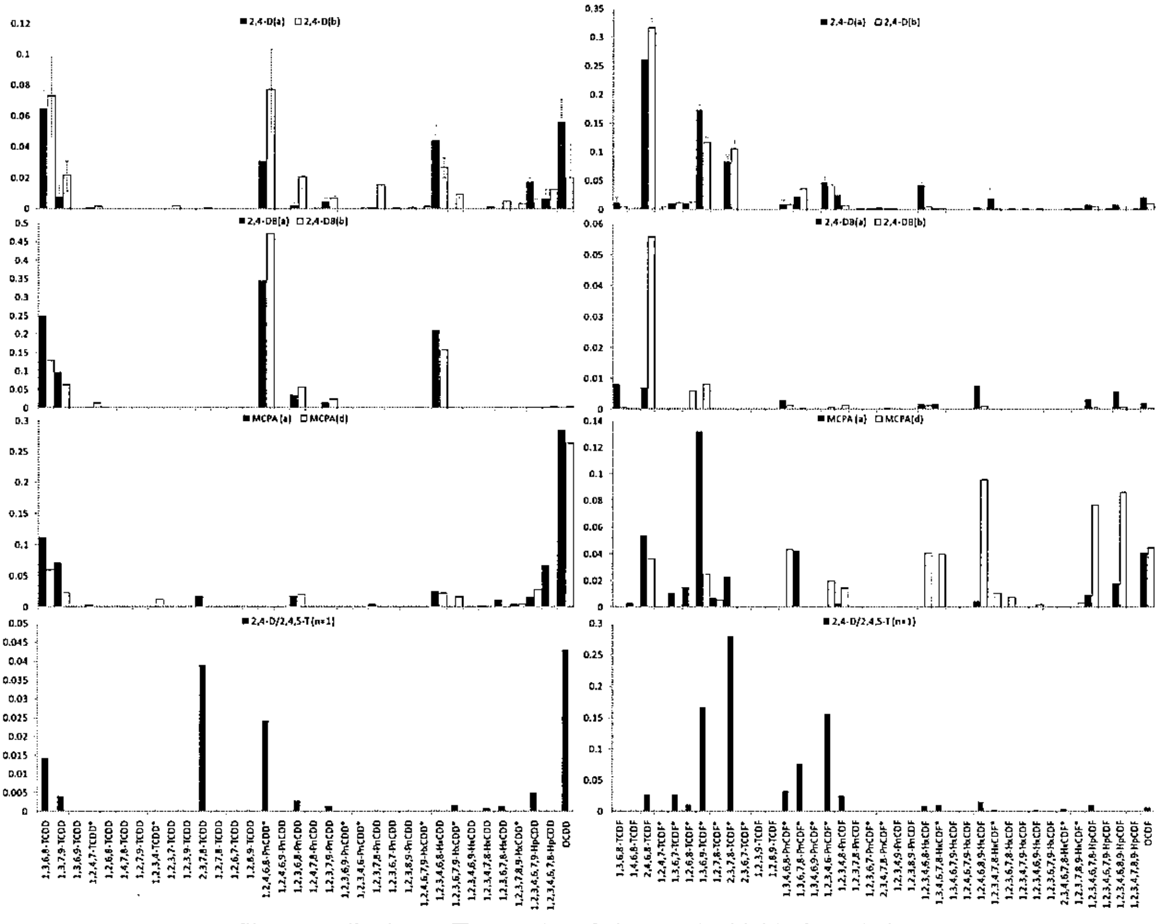


Figure2. Congener profiles (contribution to ∑PCDD/F) of phenoxy herbicide formulations: MCPA; 2,4-DB; 2,4-D & 2,4-D/2,4,5-T [Average, minimum and maximum values of two replicates are presented for 2,4-D(a) and 2,4-D(b)]

Among the congener profiles identified in the present study, only 2,4-D and MCPA have previously been reported, comprising formulations obtained in Japan[5]. While the PCDD/F congener profiles of these formulations are comparable, the contribution of some congeners show marked differences between 2,4-D sourced from Japan and Australia. Most notably, 2,4,6,8-TCDF and 1,3,6,9-TCDF contributed the highest proportions to the ΣPCDD/F concentrations in both 2,4-D formulations analysed for the present study, while 1,2,3,8-, 2,3,4,8- and 2,4,6,8-TCDF dominate (in descending order) the profile of 2,4-D from Japan[5]. Differences in congener profile were also evident for MCPA formulations analysed in the present study, where OCDD dominates amongst all congeners, as opposed to Japanese MCPA, which contains mainly 1,3,6,8-TCDD[5]. These examples indicate that source identification based on one or few source fingerprints, as typically necessitated by the sparse data available for pesticide impurities to date, is likely associated with some uncertainties as a result of changes in PCDD/F profiles /patterns (and concentrations) between pesticide production years, batches, manufacturers and/or countries.

Generally, pesticides of the same active ingredient are manufactured using similar production processes, and are thus likely to contain in similar PCDD/F impurity profiles but there is potential for variation in the PCDD/F fingerprints due to changes in pesticide production processes over time or differences between manufacturers, as well as fluctuations in process conditions[9,10] or during the variety of subsequent pesticide formulation processes[10]. In addition to pesticide production processes and conditions, relatively small congener-specific changes of PCDD/F profiles are expected to occur after their release to the environment, for example, diffuse atmospheric PCDD/F patterns from mixed sources are typically dominated by the most stable congener OCDD[11]. Furthermore, a recent study[2] has shown that PCDD/F congener profiles in pesticides may undergo considerable changes via PCDD/Fs formation from precursors when exposed to natural sunlight. For example, predominantly OCDD was formed in PCNB formulations, associated by an increase of its contribution to ΣPCDD/F concentration from 85 to 99%, as well as considerable increase in the ratio of PCDD to PCDFs (DF ratio) (from 8 to 220)[2]. Similarly, photolytic formation of particular PCDD/F congeners (2,4,6,8-TCDF, 1,3,6,8-TCDD; 1,2,3,6,8-PnCDD; and 1,3,6,8-TCDF) has been observed in sunlight exposed 2,4-D, resulting in marked changes to the PCDD/F congener profile (e.g. contribution of 2,4,6,8-TCDF increased from 29 to 93%)[2]. Over long time periods, such concurrently occurring processes may result in complex changes of fingerprints that may be important when relying on minor marker congeners for source identification, but are difficult to reconstruct retrospectively.

The results from the present study show that there are numerous other source fingerprints representative of PCDD/F contamination from pesticide use, apart from PCP, that may need to be considered in future source tracing, including consideration of a pesticide precursor formation pathway.

Acknowledgements:

This research was funded through an Australian Research Council Discovery grant (DP0665316). EnTox is co-funded by Queensland Health.

References:

1. Holt E, Weber R, Stevenson G, Gaus C. (2010); *Environ. Sci. Technol.* 44(14): 5409-15
2. Holt E, Weber R, Stevenson G, Gaus C. (2012); *Chemosphere* 88(3): 364-70
3. Grant S, Stevenson G, Malcom D, Gaus C. (2010); *Environ. Sci. Technol.* 45(2): 406-11
4. Müller J, Muller R, Goudkamp K, Shaw M, Mortimer M, Haynes D, Burniston D, Symons R, Moore M. (2004); NDP: Technical Report No. 5: http://www.environment.gov.au
5. Masunaga S, Takasuga T, Nakanishi J. (2001); *Chemosphere* 44(4): 873-85
7. Seike N, Otani T, Ueji M, Takasuga T, Tsuzuki N. (2003); *J. Environ. Chem.* 13(1): 117-31
8. Ni Y, Zhang Z, Zhang Q, Chen J, Wu Y, Liang X. (2005); *Chemosphere* 60(6): 779-84
9. Esposito M, Tiernan T, Dryden F. (1980); *Dioxins*: http://nepis.epa.gov/
10. Ambrus A, Hamilton D, Kuiper H, Racke D. (2003); *Pure Appl. Chem.* 75(7): 937-73
11. Sundqvist K, Tysklind M, Geladi P, Hopke P, Wiberg K. (2010); *Environ. Sci. Technol.* 44(5): 1690-97

FINGERPRINTS OF PBDEs, PCDD/Fs, AND dl-PCBs, IN RESIDENTIAL DUST OF WESTERN AUSTRALIA

Rogic D[1]*, Stevenson G[1], Yates A[1], Piro N[1], Crough R[1], de Araujo J[1], Mamahit G[1], Stasinska A[2], Reid A[2], Heyworth J[2], Hinwood A[3], Callan A[3], Odland JO[4]

[1]National Measurement Institute, Riverside Corporate Park, 105 Delhi Road, North Ryde, NSW 2113, Australia; [2]University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia; [3]Edith Cowan University, 270 Joondalup Drive, Joondalup WA 6027, Australia; [4]University of Tromso, NO-9037 Tromso, Norway

Introduction

In recent years, considerable attention has been paid to the exposure of pregnant women, infants and toddlers to indoor contaminants such as PBDEs, phthalates and pesticides in order to assess and identify human health risks. This has led to the identification of house dust[1] as a significant exposure medium. Results available on the basic composition of house dust suggest that the composition varies throughout the home as well as between homes among various locations within a given country.

Among many toxicants being present in house dust we have focused on the most persistent, bioacumulative and toxic organic pollutants, namely polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxin (PCDDs), polychlorinated dibenzo-p-furans (PCDFs) and dioxin like polychlorinated biphenyls (dl-PCBs). Fire retardants in many consumer products are sources of PBDEs contamination. PCDD/Fs are by-products of natural and industrial processes including waste incineration, forest fires, diesel exhaust and the production and disposal of herbicides and fungicides[2]. They increased public concern due to their occurrence in the environment and the potential for human exposure through foods and consumer products.

Many studies of umbilical cord blood, breast milk and children's blood find that children are exposed to these chemicals through early life, including during pregnancy, infancy and childhood. Some studies show the significance of dust as a pathway to exposure of young children[3]. A limited number of studies that examine PBDEs in residential dust in Australia and other Countries found that BDE-209 was to be the dominant PBDE congener and that Australian dust also contained higher levels of lower-brominated PBDEs than European dust, although still much lower than those found in the U.S [4].

This study establishes congener profiles of PBDEs, PCDD/Fs and dl-PCBs in residential dust from urban and rural sites in Western Australia. It looks at qualitative "fingerprints" to identify if sources of these compounds are widespread background contamination or active localised sources. Objectives included a comparison of selected PBDE, PCDD/F, dl-PCB congener profiles and the comparison of contributions from total PCDD/F and dl-PCB congeners to the TEQ for each residential dust sample.

Materials and methods

Thirty residential dust samples (23 urban and 7 rural) were collected from residential home vacuum cleaners in urban and rural areas across Western Australia as part of the Australian Maternal Exposure to Toxic Substances (AMETS) Study. Samples were analysed at the National Measurement Institute for concentrations of PBDEs, PCDD/Fs and dl-PCBs. Chemical analysis was performed in accordance with USEPA methods 1613, 1614 and 1668.

20g of the sieved dust samples were accurately weighed and homogenized with hydromatrix (Varian USA) drying agent and packed into an ASE cell prior to spiking with fifteen ^{13}C isotopically labeled PBDEs, fifteen ^{13}C isotopically labeled PCDD/Fs and twelve ^{13}C isotopically labeled dl-PCBs to act as surrogate standards. The cell contents were then extracted using an Automated Solvent Extraction (ASE, Dionex USA) System with toluene at 150°C and 1700 psi. The extract was evaporated under a vacuum using Büchi Evaporation Unit and reconstituted in hexane. After concentration and splitting, the samples underwent a cleanup process with concentrated sulfuric acid, washing the extract until both layers were clear. The extracts were concentrated using clean nitrogen then solvent exchanged into dichloromethane (DCM). 2ml of the DCM extract was then injected into a Waters Envirogel multi column Gel Permeation Chromatography (GPC) Cleanup System to remove sulfur contamination and high molecular weight biomolecules co-extracted from the sample. DCM was used as the mobile phase at a constant flow rate of 5.00ml/min. Samples were then solvent exchanged back into hexane for subsequent cleaning using the Power-Prep (Fluid Management Systems (FMS), Waltham, MA, USA) Automated liquid column chromatography by elution through three different columns.

Two different fractions were produced. The first fraction of PBDEs and mono-ortho PCBs were collected in DCM/Hexane solvent mixture. The second fraction of non-ortho PCBs and PCDD/Fs were collected later in toluene. Two PCDD/F, four PCB and four PBDE ^{13}C isotopically-labeled internal standards were added to the corresponding sample extracts immediately before high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis to allow the quantification of surrogate standard recovery. All analyses were conducted on a Finnigan MAT 95XL HRMS coupled to a HP 6890 GC equipped with a Finnigan Mat A200S autosampler. A ZB-5 Gas Chromatograph Column (60 m x 0.25 mm x 0.25 µm) was used as the primary analytical column for PCDD/Fs and PCBs. For confirmation of the mono-ortho substituted PCBs and several PCDD/Fs congeners that have possible co-elutions on the ZB5-MS column, samples were also analysed using a J&W DB-dioxin Gas Chromatograph column (60m x 0.25mm x 0.15 µm). For the analysis of PBDEs, J&W DB-5 Gas Chromatograph column (10m x 0.1mm x 0.1µm) was used. Individual congeners were identified using the GC retention time and ion abundance ratios with reference to surrogate standards and quantified by isotope dilution.

Standards, ^{13}C isotopically labeled surrogates and internal standards were sourced from Wellington Laboratories (Ontario, Canada) and were used for calibration, quantification and determination of recovery of PBDEs PCDD/Fs and dl-PCBs. Solvent were purchased as pesticide-grade and used as received. Preparatory chromatographic columns were purchased from Fluid Management Systems (Waltham, MA, USA) and were used without any further treatment. Quality assurance was maintained through blanks, duplicate samples, reproducible calibration and use of ^{13}C isotopically labeled internal standards.

Results and discussion

Pregnant women living in Western Australia, aged 18 years or older, not occupationally exposed to POPs, non-smokers, were recruited between 2008 and 2010 to the Australian Maternal Exposure to Toxic Substances study. At 38 week gestations, participants were asked to provide a dust sample from their home vacuum cleaners. Thirty residential dust samples were analysed for concentrations of PBDEs, PCDD/Fs and dl-PCBs. When producing the graphs all congener values below LOR were treated as equal to the LOR, including all those contribution in the TEQ result as upper bound.

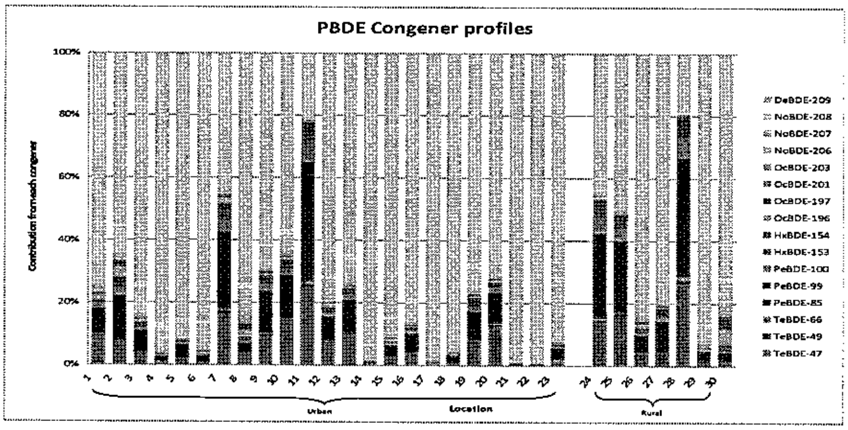


Figure 1 Contribution of major PBDE congeners to total mass of PBDEs

The PBDE congener profiles (Fig.1) show the most varied congener patterns with sample No 11 (urban) and No 28 (rural) having very similar patterns. DeBDE-209 makes up the highest proportion of major16 PBDEs in residential dust of urban (19-93%) and rural (17-86%) sites. PBDE congener profile in dust for both sites is dominated with BDE-209, followed by BDE-99, BDE-47 and BDE-100. This is consistent with previously reported Australian data[5]. Most samples show predominately Deca formulation patterns, but a few samples such as No 8 (urban) and No 30 (rural) show Penta and Octa formulation patterns. This shows that the PBDE sources are likely to be localised.

Over time, exposure to PBDE flame retardants should decline in the United States as production of Penta and OctaBDE were voluntarily discontinued by December 2004 and the last type DecaBDE is planned for phase out at the end of 2013. Exposures will continue from consumer products, furnishings and existing building materials that contain PBDEs. The use and production of PBDEs continues in other parts of the world so they may still be in imported products[6].

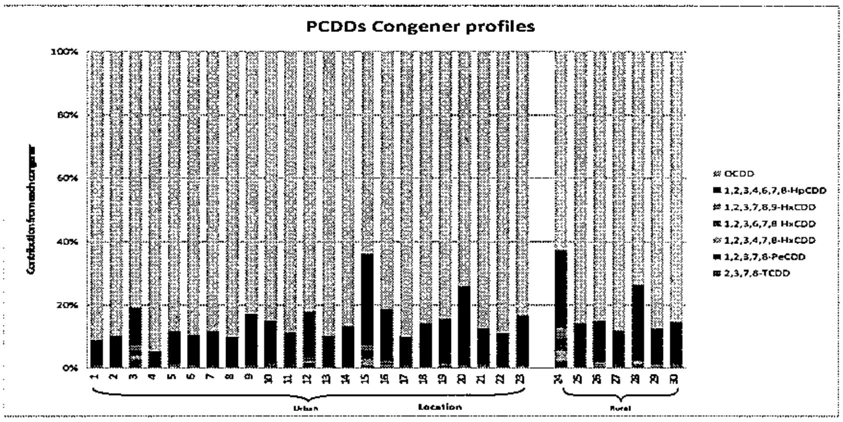


Figure 2 Contribution of PCDD congeners to total mass of PCDDs

The PCDD congener profiles (Fig. 2) are similar for all dust samples across the urban and rural sites pointing to similar contamination sources. It is dominated by OCDD (62-94 %) followed by 1,2,3,4,6,7,8-HpCDD (5-29 %) congeners. There are two slightly different samples; No 15 (urban) and sample No 24 (rural). They have additional congeners (0.1-24%), of 1,2,3,6,7,8-HxCDD,1,2,3,7,8,9-HxCDD, 1,2,3,4,7,8-HxCDD and 1,2,3,7,8-PeCDD suggesting they may have a local source. The sample No 3 has a similar pattern but all congeners were below the limit of reporting so it does not differ from other samples.

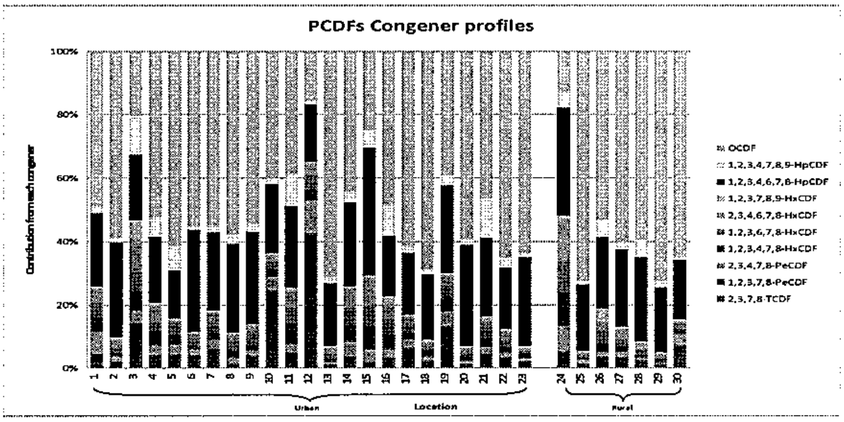


Figure 3 Contribution of PCDF congeners to total mass of PCDFs

PCDD/F congener profiles of soil samples around Australia are dominated by OCDD, contributing 60-90% of total PCDD/F congener profiles with HpCDD the next most predominant congener[7].

The PCDF congener profiles (Fig. 3) have more variety in the patterns, which may indicate several local sources such as combustion or industrial emissions. The PCDF congener profile is dominated by OCDF congener (13-72%), followed by 2,3,4,6,7,8-HxCDF (2-10%).Sample No 24 (rural) once again differs from the rest of dust samples having lowest OCDF congener (13%).

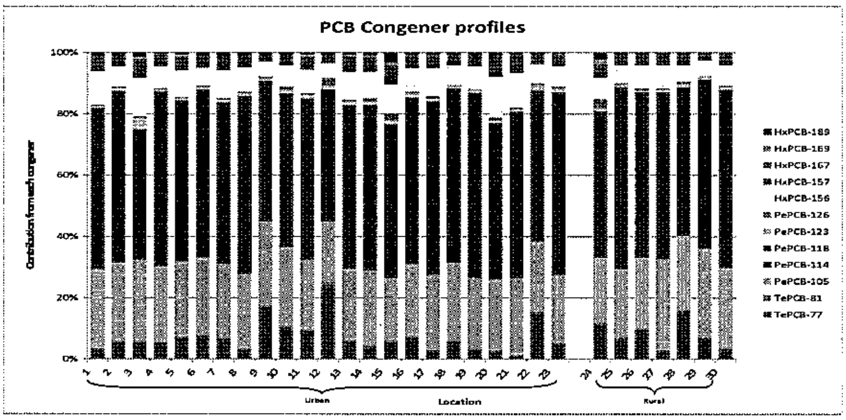


Figure 4 Contribution of PCB congeners to total mass of dl-PCBs

The dl-PCB congener profiles (Fig. 4) had similar patterns across all sites indicating widespread sources across Western Australia. The PCBs profile is dominated by Mono-ortho PCB congeners namely PePCB-118 (42-59%), PePCB-105 (20-30%), followed by HxPCB-156 (3-13%). TePCB-77 was the most dominant Non-ortho PCB with some variation (2-17%) due to no-detect in some dust samples.

Although the manufacture, processing and distribution of dl-PCBs has been prohibited in almost all industrial countries since 1980s, their entry into the environment still occurs, especially due to improper disposal practices or leaks in electrical equipment and hydraulic system in use. Other sources include the burning of waste in industrial incinerators, leakage from sealants and paint in older buildings[8].

This interpretation of the congener profiles has shown that for most homes tested, the PCDD/Fs and dl-PCBs contamination may be from similar diffuse sources, but identified several samples with different profiles indicating local sources. The PBDE profiles showed much more variation between samples which is consistent with varied local sources of PBDEs with homes. Our colleagues are reporting the concentrations found.

References:

1. Mercier F, Glorennec P, Thomas O. Le Bot B. (2011) Environ Sci Technol. 45: 6716-6727
2. Holt E, Weber R, Stevenson G, Gaus C. (2010) Environ Sci Technol. 44(14): 5409-5415
3. Harrad S, Goosey E, Desborough J, M, Covaci A, *et al.* (2010b) Environ Sci Technol. 44: 4198-4202
4. Sjödin A, Päpke O, *et al.* (2008) Chemosphere 73: 131-136
5. Environmental Working Group (2008) (www.ewg.org)
6. Stapleton HM, Dodder NG, Offenberg JH, Schantz MM. *et al.* (2005) Environ Sci Technol. 39: 925-931
7. Müller J, Müller K, Goudkamp M, Mortimer M, Haynes D. (2004) Technical report 5: 1-42
8. Tlustos C, Sheridan M, Sullivan D, *et al.* (2012) Food Additive Contamination 29(1): 128-138

SOURCE EVALUATION OF DIOXINS/FURANS, PAHS, AND PENTACHLOROPHENOL IN SOIL SAMPLES NEAR A WOOD TREATING SITE IN THE SOUTHEASTERN USA

Shields WJ[1]*, Edwards MR[1], Abrahams JA[2], Ferrara RA[3], Bollinger M[4], Paul LS[5]

[1]Exponent, 15375 SE 30th Place, Bellevue, WA, USA; [2]GeoTrans, Inc., 10860 Gold Center Dr., Rancho Cordova, CA, USA; [3]Omni Environmental LLC, 321 Wall Street, Princeton, NJ, USA; [4]Beazer East, Inc., 1910 Cochran Road, , Mt. Lebanon, PA, USA; [5]Koppers Inc., 436 Seventh Avenue, Pittsburgh, PA, USA

Introduction

A source evaluation was conducted to evaluate potential sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs),and pentachlorophenol in soil samples collected in drainage swales and residential yards near the Koppers Inc., wood treatment plant (the Site) in Tie Plant, Mississippi, USA.

Materials and methods

Soil samples were collected[1] by GeoTrans, Inc. from 59 locations in residential yards (0- to 15-cm and 15- to 30-cm depths) and drainage pathways (0- to 15-cm and 15- to 30-cm depths) in the Site vicinity, from 6 locations onsite to establish source fingerprints, and from 20 locations within Grenada and Montgomery Counties to provide regional background congener compositions. The interpretation of these sample results was augmented with analytical results for soils sampled from 43 offsite locations in the Tie Plant vicinity in 2004 and 2005.

The PAH and pentachlorophenol analyses were performed by Columbia Analytical Services in Kelso, Washington, USA. PAH analysis used U.S. Environmental Protection Agency (EPA) Method 8270 SIM and included 38 alkylated PAHs in addition to the 17 priority pollutants. Pentachlorophenol was analyzed by EPA Method 8151M. Analytical Perspectives Laboratory in Wilmington, North Carolina, USA, performed the PCDD/F analyses using EPA Method 8290.

The primary transport pathway of concern was surface water transport of PCDD/Fs (associated with pentachlorophenol use) and PAHs (associated with creosote use). Omni Environmental LLC (Omni) conducted a surface water drainage pattern analysis of historical and current transport from onsite areas to offsite areas. The Site lies within the Batupan Bogue watershed and is adjacent to a residential neighborhood known as Carver Circle. The focus of the analysis was whether drainage from the Site flows or has flowed into (a) Carver Circle, and/or(b) other residential areas in the Tie Plant area. In this regard, a detailed evaluation of drainage patterns between 1937 and the present was completed.

Source evaluation was conducted by Exponent using both spatial (geographic) analysis and chemical fingerprinting techniques.

Results and discussion

Surface water drainage patterns—Analysis demonstrated that only a limited opportunity existed for drainage from the Site to have entered Carver Circle. Drainage from approximately 10% of the Site had the opportunity to flow along an open primary drainage channel through a small area on the northwest corner of Carver Circle for a limited period of time. No other portions of Carver Circle were ever subject to drainage from the active Koppers Site. Chemical analyses of ditch sediment samples, discussed below, were consistent with this hydraulic analysis.

Spatial evaluation of contaminant concentration data—The spatial distribution of PCDD/F concentrations (as indicated by toxicity equivalents [TEQ_{WHO-05}]), pentachlorophenol, and PAH concentrations (as indicated by benzo[a]pyrene toxicity equivalents [BaP-TE]) were evaluated using "dot maps" and bar charts. These maps and charts will be presented at the conference. Data from the earlier sampling events (2004 and 2005) were also included in the spatial analysis.

This analysis had two significant findings. First, the heterogeneity of concentrations within the community is more likely attributable to area-specific sources rather than a large regional source (i.e., surface water or aerial discharges from the Site), which would result in more uniform concentrations with much less variability between residential yards. Second, elevated concentrations downstream of the primary stormwater outfall (Outfall 6) indicate historical transport of these constituents along the historical drainage pathways. This is consistent with the analysis of historical surface drainage patterns.

Chemical fingerprinting—The PCDD/F congener composition for the onsite samples was, with several notable exceptions, distinct from the offsite samples based on a principal component analysis (PCA) as shown in Figure 1. The factor loadings and percent variability accounted for by the first three factors from the PCA are shown in Table 1. Congener compositions of samples from the Carver Circle area (shown as residential soils and drainage way samples in Figure 1) were more similar to regional (i.e., background) samples than to the onsite samples, with the exception of the drainage way samples historically downstream from Outfall 6. The fingerprint of these samples (from locations DW-16 and DW-21) were more similar to the fingerprints of the onsite drainage way samples. The similarity of these downstream drainage way samples to upstream onsite samples demonstrates that the PCDD/F fingerprinting method was robust and useful in identifying (or eliminating) potential sources.

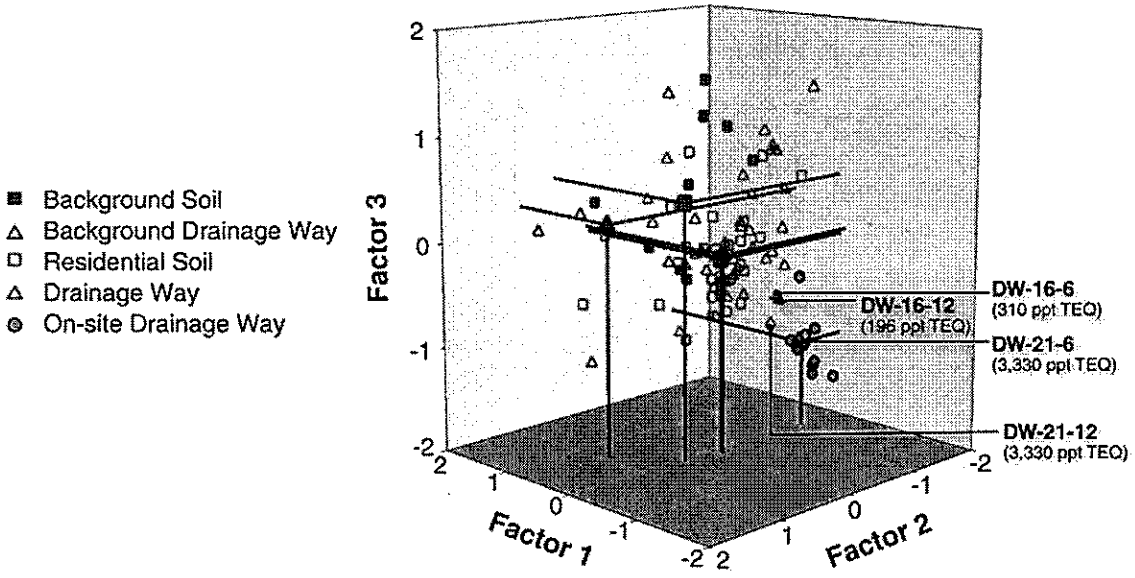


Figure 1. **Three-dimensional plot of PCA factor scores with the offsite drainage way samples from stations DW-16 and DW-21 indicated**

PAH fingerprinting was less informative than PCDD/F fingerprinting in identifying or eliminating potential sources. This was because the PAH compositions of the onsite samples were similar to those of some background samples. Also, the PAH compositions of the onsite samples were more variable (i.e., not as uniform) than those of the PCDD/F congeners.

Table 1. Factor loadings and percent of variability explained for first three factors in the PCDD/F principle components analysis

Congener	Factor 1	Factor 2	Factor 3
Dioxins			
2,3,7,8-TCDD	0.25	**0.72**	-0.39
1,2,3,7,8-PeCDD	0.39	**0.71**	-0.41
1,2,3,4,7,8-HxCDD	0.46	0.52	-0.41
1,2,3,6,7,8-HxCDD	**0.78**	0.04	-0.20
1,2,3,7,8,9-HxCDD	0.54	0.64	-0.43
1,2,3,4,6,7,8-HpCDD	0.20	0.04	**-0.62**
OCDD	**-0.62**	0.56	0.54
Furans			
2,3,7,8-TCDF	0.58	0.38	0.45
1,2,3,7,8-PeCDF	**0.75**	0.27	0.35
2,3,4,7,8-PeCDF	**0.87**	-0.14	0.35
1,2,3,4,7,8-HxCDF	**0.92**	-0.15	0.29
1,2,3,6,7,8-HxCDF	**0.92**	-0.12	0.23
2,3,4,6,7,8-HxCDF	**0.92**	-0.20	0.19
1,2,3,4,6,7,8-HpCDF	**0.83**	-0.36	0.17
1,2,3,4,7,8,9-HpCDF	0.40	-0.55	**-0.61**
OCDF	0.15	**-0.65**	**-0.64**
Variance Explained (%)	42.7	19.9	17.7
Cumulative Variance (%)	42.7	62.7	80.3

Note: 1,2,3,7,8,9-HxCDF was excluded from the PCA because of a high percentage of non-detect results.

Factor loadings greater than 0.6 or less than -0.6 are shown in bold.

Spatial analysis and chemical fingerprinting indicate that alternate sources (aside from the Site) were the cause of several anomalous concentrations of PCDD/Fs, PAHs, and pentachlorophenol found in the Carver Circle community soils. These elevated concentrations were not subject to surface water runoff from the Site. They could not have been a result of aerial deposition from the Site because that would have resulted in more uniform concentrations and could not account for the high yard-to-yard variability. Open burning of trash and yard waste was a common practice in this community, including a trash incinerator, which were more likely sources of PCDD/Fs and PAHs than runoff or aerial emissions from the Site. Resident-specific use of pentachlorophenol has been documented and is a more probable explanation of the anomalous concentrations of both PCDD/Fs and pentachlorophenol, rather than runoff from the Site.

Acknowledgements

This study was funded by Beazer East, Inc. and Koppers Inc.

References

1. GeoTrans, Inc. (2010) Final Draft Sampling Report, Additional Sampling, Koppers Inc., Tie Plant Facility, Tie Plant, Mississippi; Prepared for Beazer East, Inc. and Koppers Inc. and submitted to U.S. Environmental Protection Agency, Atlanta, Georgia, USA on December 22, 2010.

DIOXINS FORMED DURING FIRES, A THREAT TO THE FOOD CHAIN?

Hoogenboom L*, Hoffer S, Mennen M, Morgenstern P, Traag W

RIKILT Wageningen UR, Akkermaalsbos 2, 6708WB Wageningen, The Netherlands
RIVM National Institute for Public Health and Environment, Antonie van Leeuwenhoeklaan 9, 3721 MA Bilthoven, The Netherlands

Introduction

Burning of certain materials like PVC-plastics, PCB-containing materials and certain pesticides is a well-known source of dioxins. This means that also incidental fires may result in the formation of dioxins, which may deposit at adjacent agricultural farm land[1,2]. This may cause increased exposure of food-producing animals and subsequently increased levels in animal-derived products for human consumption. In the EU, products exceeding the limits are not fit for consumption and can lead to the temporary closure of farms with huge financial impact. In the Netherlands a rapid emergency team, called BOT-mi and consisting of experts from various institutes, is involved in advising on the potential consequences of larger fires. Depending on the materials involved in the fire, additional samples of air, dust and grass are taken and investigated for dioxins, PAHs and heavy metals. The present paper describes the outcome of a number of fires and their potential impact on the food chain.

Materials and methods

Samples of air, dust and grass were in most cases collected by the MOD (Environmental Incident Service), a mobile emergency team that is part of RIVM, at locations near the fire. Based on a first assessment and measurements in the smoke, it was decided whether samples should be analysed by RIKILT for dioxins and dl-PCBs. If so, grass samples were homogenized under liquid nitrogen and GC/HRMS analysis was carried out as described previously[3] based on the extraction with ASE and clean-up on a Powerprep system (FMS). Results are expressed in TEQ based on the application of the TEFs from 1998 which were applicable at that time according to EU-legislation[4]. According to the legislation, levels in grass used as feed should be expressed on 88% dry matter. The maximum levels for dioxins and the sum of dioxins and dl-PCBs in feed of plant origin were 0.75 and 1.25 ng TEQ/kg (until April 2012). In some cases also CALUX analysis was performed to investigate the potential use of the bioassay during incidents. The assay was carried out as described previously[5]. In short, samples were mixed with methanol/water and extracted with hexane/diiethylether and subsequently cleaned-up over an acid silica column. The eluate was evaporated, dissolved in a small amount of DMSO and mixed with the culture medium used to expose the 1.1 pGudLuc transfected H4IIE-cells.

Results and discussion

Cases

In the past years there were a number of fires where a substantial amount of grass samples were investigated just after the fires and a week or more later. The most important incidents are described below.

Coevorden

Half of May 2009, there was a fire at a company recycling old metals near the city of Coevorden. The smoke of the fire went over a number of farms with cows and goats (Figure 1). The day after the fire a number of grass samples were collected and analyzed for dioxins with GC/HRMS. A sample next to the fire (B) showed a dioxin level of 219 ng TEQ/kg, whereas a background sample taken from the other side of the fire (A) showed a level of 0.2 ng TEQ/kg. Levels of dl-PCBs at these two locations were 37 and 0.2 ng TEQ/kg. Samples taken at 0.2 (C), 0.3 (D), 0.5 (E), 0.6 (F) and 0.8 km west of the fire showed dioxin levels of 8.8, 4.5, 3.0, 3.0 and 2.2 ng TEQ/kg. The levels of dl-PCBs were lower at all locations but showed a relatively high contribution when compared to the level at site B. Levels of the 6 indicator-PCBs (ndl-PCBs) were also analysed and showed levels of 0.8, 35.3, 8.9, 4.9, 3.1, 2.4 and 1.5 µg/kg (for comparison, new EU-limit valid since April 2012 is 10 µg/kg). As a precautionary measure, cows and goats were kept inside but during the fire farmers were harvesting the grass for the winter period. One sample was analysed and showed dioxin and dl-PCB levels of 3.1 and 1.1 ng

TEQ/kg. This is one of the major concerns since such grass will be fed during a prolonged period, whereas grass in the pasture will continue to grow resulting in decreased levels.

One week after the fire, during which there was considerable rain fall, new samples were collected at locations C and G showing decreased dioxin levels of 1.8 and 0.5 ng TEQ/kg (about 50% decline). Strange enough, dl-PCB levels declined much less being respectively 2.8 and 0.8 ng TEQ/kg (20% decline) and being higher than the dioxin levels. This suggests either another source of the dl-PCBs, or, maybe more likely, a more rapid decline of dioxins compared to dl-PCBs. There was no other industrial activity close to this site. At both sites also soil samples were taken, showing dioxin and dl-PCB levels of 1.7 and 0.5 ng TEQ/kg dm at location C and 1.2 and 0.2 ng TEQ/kg dm at location F. The pattern in the soil samples was similar to that in the grass but the question is how specific this pattern is (see below).

Grass samples were also analysed with the CALUX-assay and showed a good correlation with the GC/HRMS data. The response measured at the various locations A to F was 58 (A), 5950 (B), 2226 (C), 1735 (D), 2181 (E), 1034 (F) and 765 (G) RLUs. This demonstrates that the bioassay can be used to make an inventory of the potentially affected area, allowing the analysis of 20-40 samples within 2-3 days.

Figure 1. Levels of dioxins and dl-PCBs in grass samples taken 1 day after the fire. Wind came from the east.

Weurt

End of October 2010, a fire occurred at a meat packaging company in Weurt. Although initially unsuspected, chlorine levels on air filters were rather high and warranted the analysis of grass samples for dioxins and dl-PCBs. It turned out that a huge amount of plastic materials was present at the company for transport and packaging of the meat. Burned debris was found even at 1.6 km from the fire. The nearest agricultural area affected by the smoke was about 0.6 km away and levels in samples taken during the final stage of the fire revealed a dioxin level of 1.9 ng TEQ/kg (88% dm) in grass (about 2.5 times the EU-limit for grass used as animal feed). The level of dl-PCBs was 0.3 ng TEQ/kg. At a reference location south of the fire, the levels for dioxins and dl-PCBs were 0.4 and 0.3 ng TEQ/kg. A week after the fire various locations were resampled, including one at 1.6 km from the fire (point most far away from the fire), a dioxin level of 1.3 ng TEQ/kg was measured with a very similar pattern. Also at other locations levels were still increased.

Follow-up during several weeks did not show a significant decline in the levels despite the large amount of rain during this period. In a sample taken one month after the fire (end of November), the dioxin level at the location at 0.6 km even increased to 2.4 ng TEQ/kg. However, at this time also the reference location showed an increased level of 0.9 ng TEQ/kg. This increased level is observed more often in winter time and can be explained by deposition during the winter and the lack of growth of the grass during this period. At this time point also a sample was collected from grass near a ditch at about 0.1 km from the fire. The dioxin level was 11.3 ng TEQ/kg, the dl-PCB level 0.8 ng TEQ/kg. It seems essential to collect samples close to the fire in order to strengthen a possible relationship with the fire.

Moerdijk

One of the largest incidents during the last decade occurred in the beginning of January 2010. A company with large volumes of all kinds of chemicals burned down completely with a large number of explosions. The fire was covered broadly by Dutch television and caused a major concern for possible consequences for inhabitants and farms downwind of the fire. Fortunately, the nearest farms were 2.5 km or further away due to the Hollands Diep, a broad river directly north of the fire. A large number of grass samples were collected in the potentially affected area shortly after the fire. A sample opposite of the fire at 2.5 km showed dioxin and dl-PCB levels of 7.1 and 0.9 ng TEQ/kg. Many other samples collected in an area up to 10 km from the fire showed dioxin levels between 1.1 and 2.4 ng TEQ/kg and dl-PCB levels of 0.2 to 0.4 ng TEQ/kg. Samples were also collected at two other locations at the unaffected side of the fire. A first sample, taken on the industrial site, showed dioxin and dl-PCB levels of 4.6 and 9.5 ng TEQ/kg. Two other samples, taken West of the fire in a more agricultural area but close to a road showed dioxin levels of 3.5 and 4.3 ng TEQ/kg, and dl-PCB levels of 0.9 and 0.9 ng TEQ/kg. Five farms in this area were resampled, taking samples in pastures. The average dioxin level was 1.9 ng TEQ/kg (range 1.5-2.5). The levels of dl-PCBs was 0.4 ng TEQ/kg (range 0.4-0.6). This demonstrates that it is tricky to conclude whether increased levels are really due to a fire, especially in winter time. A large number of Brussels sprouts and curly kale were also analysed but none of these showed an elevated dioxin or dl-PCB level.

The incident opened up the discussion on the potential consequences of feeding grass with levels 2-3 times the limits to cows and especially sheep. A major question is whether carry-over factors for dioxins from fires are similar to those from other incidents with feed. This will be part of future studies.

Lith

In September 2011, a storage facility of a company supplying silos and plastics for farms burned down completely. The materials included a large amount of PVC. Being a known source of dioxins, samples of grass and corn from fields adjacent to the fire were sampled one day after the fire. A grass sample from a lawn next to the fire showed a dioxin level of 43.6 and dl-PCB level of 5.5 ng TEQ/kg. A corn sample taken at 0.1 km from the fire showed dioxin and dl-PCB levels of 1.8 and 0.4 ng TEQ/kg. The grass was not intended to be used as feed but the corn was turned into silage for feeding of dairy cows. Regarding the relatively high level, exceeding the feed limit, it was recommended not to use the material as feed. Part of the material was used to perform a carry-over study with dairy cows.

Congener patterns

Figure 2 shows the congener patterns of the samples with the highest observed dioxin levels in each of the four cases, expressed as relative contribution to the TEQ-level. It is clear that patterns are remarkably similar, with the exception of Moerdijk. In the other 3 cases PCDFs and in particular 2,3,4,7,8-PeCDF contribute most to the TEQ-level. When applying the new TEFs of 2005, the contribution of 2,3,4,7,8-PeCDF will slightly decrease to around 30%. The quite different pattern in the case of Moerdijk, which also differed from other samples taken during this incident, implies that the fire may not be the cause of the elevated level in this sample. The actual location was a small shipyard and other sources seem possible.

The relative high contribution of 2,3,4,7,8-PeCDF and other lower chlorinated PCDD/Fs is of importance since these show relatively high absorption and carry-over rates to milk and eggs. This was confirmed by preliminary results from a carry-over study with contaminated corn silage from the fire in Lith. Levels in the corn were around 1 ng TEQ/kg (88% dm) and within 5 weeks resulted in milk levels around the limit.

Conclusions

The present data show that levels in grass taken close to a fire (<0.2 km) can contain very high levels of dioxins which would certainly cause increased levels in e.g. milk, eggs and meat when fed to animals. At somewhat higher distances, up to 1-2 km, levels may still be elevated compared to the normal background levels and even exceed the EU-limits for feed. Prolonged feeding of such materials like grass and corn could certainly result in an increase in the levels in e.g. milk and eggs. If the materials are not harvested and are still growing, there will be a gradual dilution of the levels and this will counteract the gradual increase in the levels in milk and eggs observed when feeding material with a constant level of dioxins. Precipitation does not seem to affect the levels in grass which may be explained by the lipophilic nature of these compounds.

A particular issue is the situation in late autumn and winter. At this time of the year, dairy cows are normally kept inside and grass in pastures is not a feed commodity for these animals. The situation is different for certain types of meat cows and especially for sheep which in principle are kept outside during the whole year. The elevated levels in the winter grass may be one of the reasons that sheep meat and especially livers often show relatively high levels of dioxins. The carry-over of dioxins and PCBs in both lactating sheep and meat sheep is currently under investigation, partly within the EU-project QSAFFE.

It can be concluded that fires may cause an increase in dioxin levels in grass and other feed commodities in the direct surroundings and that measures to prevent increased levels in animal derived food products are warranted. Rapid analyses of samples by GC/HRMS, possibly supported by screening assays, is required to reduce the potential effects on both consumer and animal health and economics of affected farms.

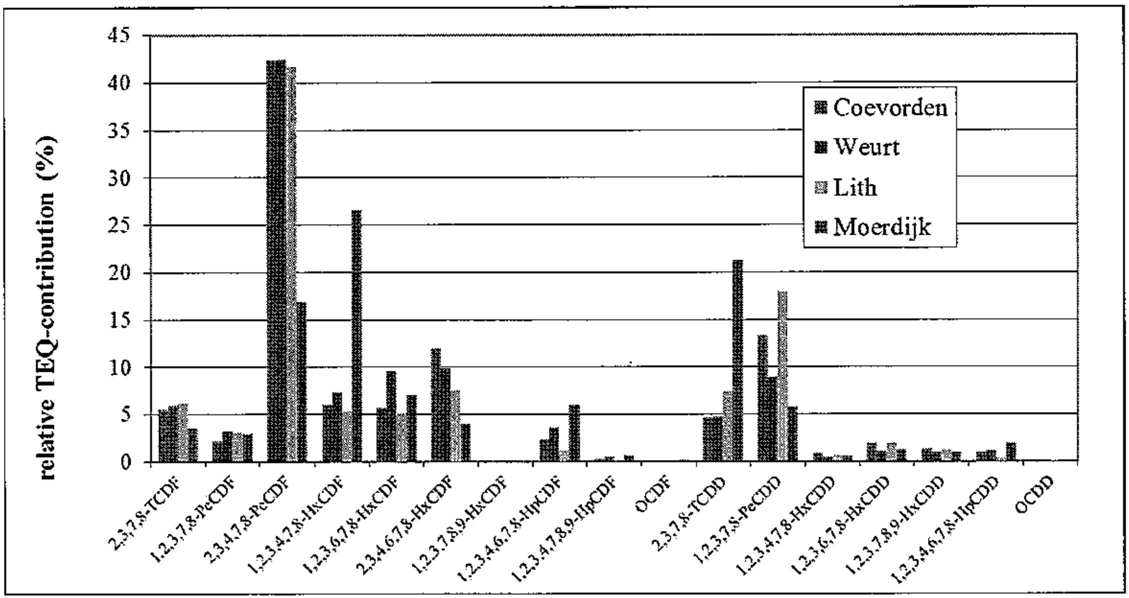


Figure 2. Congener patterns of dioxins in grass samples with the highest observed levels during the incidents in Coevorden (219 ng TEQ/kg), Weurt (11.3 ng TEQ/kg), Lith (43.6 ng TEQ/kg) and Moerdijk (7.1 ng TEQ/kg). Levels are expressed as relative contribution to the TEQ-level using TEFs 1998.

Acknowledgements

The work was financed by the Dutch ministry of Economics, Agriculture and Innovation (EL&I) and the ministry of Infrastructure and the Environment. The authors would also like to thank the analysts and the people involved in the MOD for their valuable contribution.

References

1. Marklund S, Anderson R, Tysklind M, Rappe C (1989) *Chemosphere.* 18; 1031-8.
2. Draper W, Phillips J, Harnly M, Stephens (1988) *Chemosphere* 17; 1831-50.
3. Hoogenboom L, Van Eijkeren J, Zeilmaker M, Mengelers M, Herbes R, Immerzeel J, Traag W (2007) *Chemosphere* 68; 814-23.
4. EC (2006) *Off. J. Eur. Union.* L32, 44-53.
5. Hoogenboom L, Bovee T, Portier L, Bor G, van der Weg G, Onstenk C, Traag W (2004) *Talanta* 63; 1249-53.

ENVIRONMENTALLY SUSTAINABLE MANAGEMENT OF MEDICAL WASTE IN CHINA, DEDICATING TO REDUCING DIOXINS—PROGRESS AND IMPACT

Ren ZY[1*], Jiang C[1], Peng Z[1], Peng Y[1], Wang KX[1], Ding Q[1] ,Yu LF[1]

[1]Foreign Economic Cooperation Office, Ministry of Environmental Protection of China, 5 Houyingfang Hutong, Xicheng District, Beijing, 100035, China

Introduction

Medical waste (MW) incineration is one of the most important PCDD/PCDF(dioxins) release sources[1]. The net amount of MW produced in China was approximately 670,000 tonnes in 2006, with a daily average output of 1,780 tonnes. Following the outbreak of Severe Acute Respiratory Syndrome (SARS) epidemic in 2003, Chinese Government moved quickly to establish the National Plan for Construction of Facilities for Disposal of Hazardous Waste and Medical Waste, in which China is committed to construct about 300 dedicated MW disposal facilities across the country[2]. According to the survey of dioxins inventory in 2004, the total amount of dioxins releases from MW incinerators in China reached 427.4 g TEQ, accounting for 11.5% of the total releases from all sources listed in the Toolkit[3]. As a key emission source of dioxins, MW incinerations should be given the application of best available techniques and best environmental practices (BAT/BEP) in priority, required by Article 5 of Stockholm Convention[4-5]. Under such a circumstance, a project concerning the supervision, operation, packaging and labeling, construction, storage, landfill sites, transportation, new technical, pollution control and etc of MW, was developed as "Environmentally Sustainable Management of Medical Waste in China" project, with the concept of improving overall process and whole life cycle on MW management. Based on the project design, dioxins releases will be avoided and reduced up to 22.66 g TEQ annually after its successful implementation[6-10].

Concepts and objectives

The overall objective of the project is to reduce and ultimately eliminate the releases of unintentionally produced POPs and other globally harmful pollutants into the environment, and assist China in implementing its relevant obligations under the Stockholm Convention. The project is to interact with the Nationwide Investment Plan and promote the widespread adoption of BAT/BEP in the evolving MW management infrastructure and industry in a manner that reduces adverse environmental impacts and protects human health[9-10].

Conceptually, the overall objective will be achieved through combined strategies of reducing and modifying the materials to be disposed of, the optimization of incineration technologies, the introduction of non-combustion technologies, the raising of awareness and the dissemination of know-how, the incorporation of management systems, the innovation and adaptation of appropriate technologies and techniques, the integration of economic and financial systems and the enhancement of relevant laws and regulations[9-10]. The project conceptual framework is given in Figure 1[10] and Figure 2[11].

To continuously reduce dioxins releases, the project is determined to carry out the demonstration and replication of BAT/BEP in the environmentally sound management of MW by upgrading the incineration equipment and air pollution control systems to the BAT level and replacing outdated or over-capacity incineration facilities with alternative, non-incineration techniques that avoid the release of dioxins as shown in Figure 3 and Figure 4. Accordingly, demonstrations on the application of integrated MW management among institutions and the coordinated MW treatment among the dedicated MW facilities are to be carried out at the municipal level and the provincial level respectively[9-10].

While China has established a relatively complete regulatory framework for the MW management given in Figure 5[11], there are important articles in the laws and regulations, which may be absent or impractical. The regulatory framework requires practical application and fine-tuning to assure its effectiveness[9-10].

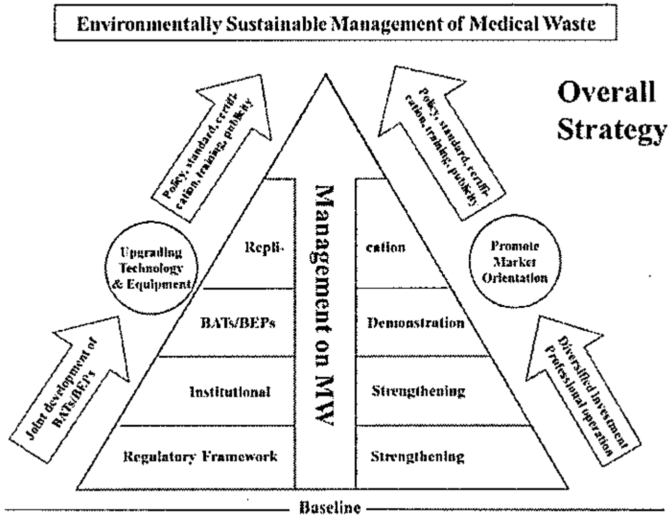


Figure 1. Overall strategy on medical waste management in China

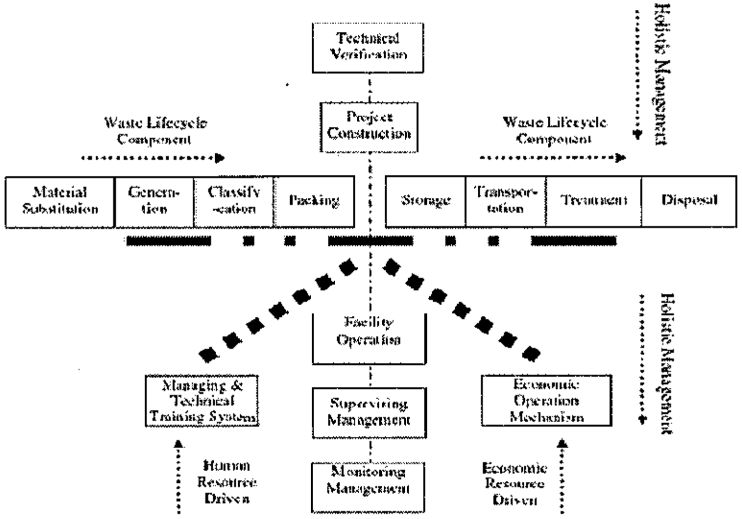


Figure 2. Concept of overall process and whole life cycle on medical waste management

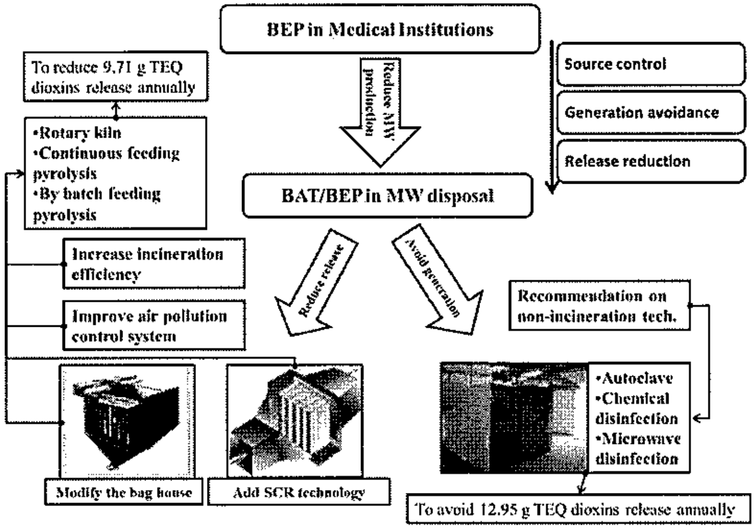


Figure 3. Logical relationship between BAT/BEP application and dioxins reduction on medical waste

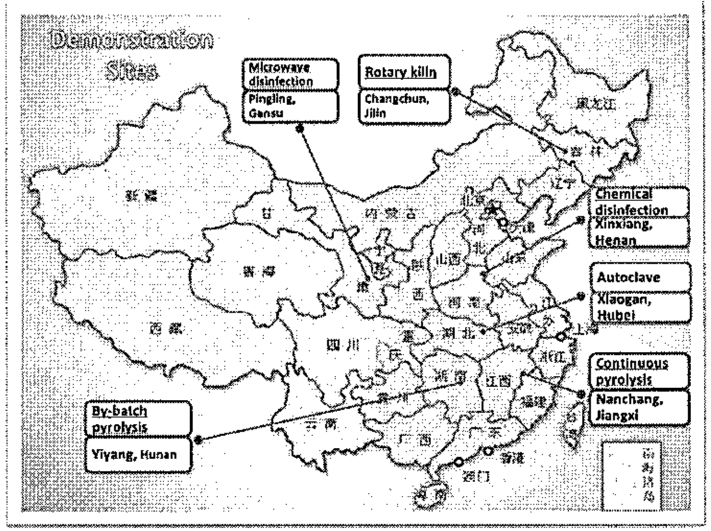


Figure 4. Distributions of BAT/BEP demonstrations on various medical waste disposal techonologies

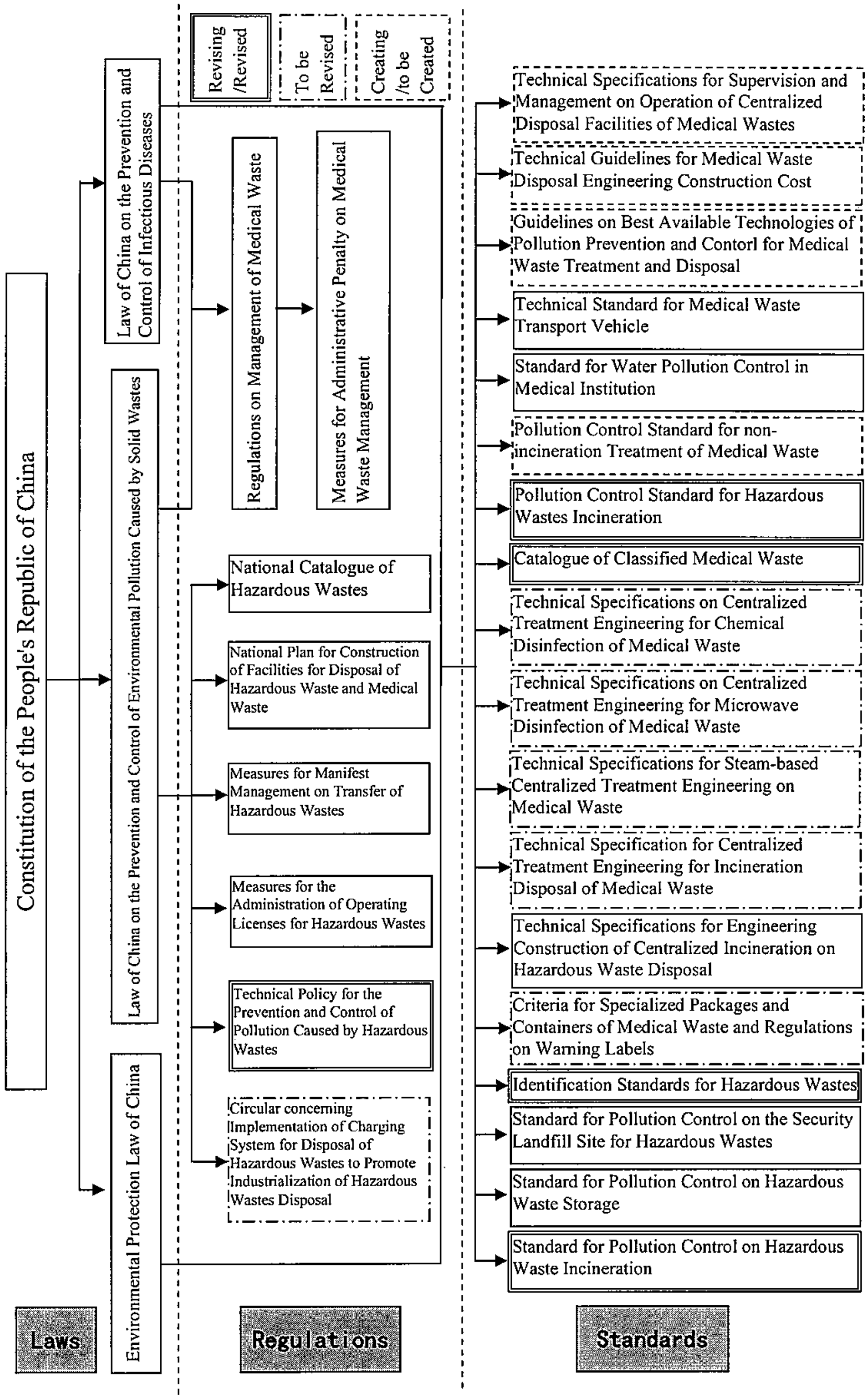


Figure 5. Legal Framework on medical waste management in China

Progress and impacts

Through the development of this project, awareness at central governmental level has been further raised for the need to properly manage MWs in order to minimize the formation and release of dioxins. As a result of this, nearly half of the MW disposal centers are turning from using incineration techniques into using non-incineration techniques, avoiding 12.95 g TEQ dioxin release annually as shown in Figure 3. Another important impact is the inclusion of the BAT/BEP guidelines for the management of MWs in the 12th Five Year Plan[12].

The gaps of the existing regulatory framework and their consequences are analyzed by reviewing and bringing forward recommendations for the creation of an enabling regulatory environment[11]. Currently, a total of 18 national policy, technical guidelines & standard and 10 management measures and booklets have been developed including BAT/BEP guidelines and related policies[13]. It is particularly worth noting that the MW incineration pollution standard of dioxins release is hopeful promoted from 0.5 ng TEQ/m^3 to 0.1 ng TEQ/m^3.

6 MW disposal centers, 3 for incineration techniques and 3 for non-incineration techniques, were selected as demonstrations to retrofit equipments to meet the requirements of BAT/BEP, whose experience will be replicated amongst disposal centers nationwide. In the 6 demonstration cities of integrated MW management, a proper system for collection, transportation and disposal of MW, as well as a fee system to be paid by Medical institutions to MW disposal centers have been established[13]. Furthermore, the coordinated MW treatment demonstrations are ready to set off at the provincial level.

At all levels and for all stakeholders, awareness regarding the need to soundly manage medical waste has been aroused during the execution of the project. Based on the existing administrative structure and training system of the health administration, a 4-tier personnel training system covering national, provincial, municipal, and county medical institutions, including establishment of 7 training bases for training of high-level managerial and technical staff in health agencies and medical institutions has been established. 3 training bases for training of dedicated MW treatment staff will be established on the basis of the existing environmental technical training and research system[10].

In the joint efforts of all stakeholders, the MW management in China has made tremendous progress under the promotion of the project. Although there is still a long way to go to realize environmentally sustainable management on MW, China has formed a set of internationally compatible management system.

Acknowledgements

This work was supported by GEF project (Project No.: GF/CPR/07/008, Environmentally Sustainable Management of Medical Waste in China).

References:

1. UNEP Chemicals. Stockholm Convention on Persistent Organic Pollutants. (2001)
2. SEPA, Hazardous Waste and Medical Waste Treatment Facility Construction Plan. (2003)
3. UNEP Chemicals. Standardized Toolkit for Identification and Quantification of Dioxins Releases. (2005)
4. UNEP Chemicals. Revised edited draft guidelines on BAT and guidance on BEP. (2006)
5. P.R. China. National Implementation Plan for the Stockholm Convention on POPs. (2007)
6. Deng Z, Zhang W. (2006) *China Environment Industry*. 3: 32- 35.(in Chinese)
7. Chen Y, Wang K, Liu F. (2005) *EIA Issue for Medical Waste Projects*. 7: 57- 58, 63.(in Chinese)
8. Chen Y, Li P, Sun Y, Chen G, Jiang C. (2008) *Environmental Science & Technology*. 31(3). (in Chinese)
9. UNIDO. Environmentally Sustainable Management of Medical Waste in China (PDF-B). (2005)
10. UNIDO. Environmentally Sustainable Management of Medical Waste in China (Project Document). (2007)
11. SAES, IHEP/CAS, CAEP. (2009) Research on MW disposal pollution control specifications of BAT/BEP (Final Report)
12. MEP. 12th 5 Year Plan on POPs Control and Prevention. (2012)
13. MEP. Final Reports of the 3rd Tripartite Meeting and the Relevant Reports for 2010. (2010)

SUBSTITUTES OF PERSISTENT ORGANIC POLLUTANT (POP) PESTICIDES IN BANGLADESH AND THE NEED FOR A SUSTAINABLE SUBSTITUTION PROCESS

Rahman MM*[1], Weber R[2], Tennekes HA[3], Sanchez-Bayo F[4]

[1]Department of Entomology, Bangabandhu Sheikh Mujibur Rahman Agricultural University (BSMRAU), Gazipur 1706, Bangladesh, [2]POPs Environmental Consulting, Ulmenstrasse 3, 73035 Göppingen, Germany, [3]Experimental Toxicology Services (ETS) Nederland bv, Frankensteeg 4, 7201KN Zutphen, The Netherlands, [4]Centre for Ecotoxicology, University of Technology Sydney, Office of Environment & Heritage Department of Premier & Cabinet, NSW, 480 Weeroona Road, Lidcombe, NSW 2141, Australia

Introduction

Bangladesh, with more than 160 million people in an area of 147,570 km^2 and with agriculture (Crops and horticulture) contributing with about 11.16% to the national GDP (BBS 2010)[1], is located in the north eastern part of South Asia between 20°34' and 26°38' north latitude and 88°01' and 92°41' east longitude. Bangladesh enjoys a subtropical monsoon climate with a temperature range from a minimum of 7°C-13°C to average of 24°C-31°C and up to 40°C in winter, autumn and summer seasons respectively. Rice is the most important crop grown in three seasons almost year-round. Further important crops include other cereals (wheat, maize), Solanaceae (e.g. eggplant, potato, tomato, okra), Leguminosae (e.g. country bean, mungbean, blackgram, chickpea, yard long bean), Cucurbitaceae (e.g. pumpkin, cucumber, bitter gourd, snake gourd, ribbed gourd, sponge gourd and pointed gourd, and Cruciferaceae (e.g. mustard, radish). Other cash crops include jute, sugarcane, tea (grown in some specialized areas only) and cotton. Besides, the major fruit crops include banana, mango, pineapple, jackfruit, guava and jujube. All these crops are seriously damaged by insect pests and diseases. Under farmers' field conditions, in certain years and places, yield losses range from 35% to 80% – Up to 100% loss has been recorded due to a single insect or disease, especially in the case of rice. Similar estimates apply to wheat, jute, sugarcane, pulses, oilseeds, vegetables and fruits. Therefore, the use of pesticides in Bangladesh has increased over the last 4 decades (Figure 1). Among the insect pests, cutworm, termite, mole cricket, white grub, grasshopper etc., are major soil insect pests of many crops. All these necessitated the use of pesticides formally including persistent organic pollutant (POPs) like aldrin, dieldrin, heptachlor, chlordane, etc. For storage pests HCH/lindane was used. Moreover, vector-borne diseases, particularly malaria, were a serious problem in Bangladesh. Malaria is still a serious problem in some areas. This necessitated the use of DDT. But in compliance with the WHO specifications as well as other relevant multilateral environmental agreements like the Stockholm Convention, Rotterdam Convention and Montreal Protocol, Bangladesh banned and/or discontinued the use of the most hazardous pesticides including POPs by 1998. The only exception was DDT allowed for restricted use in case of emergency against mosquito, the vector of malaria. The most important consequence of such ban and/or discontinuation of the POPs and other hazardous pesticides has been the predominant use of other classes of pesticides like organophosphates, carbamates, synthetic pyrethroids, neonicotinoids, avermectin, spinosad etc. due to the absence of adequately effective integrated pest management (IPM) packages with or without insecticides.

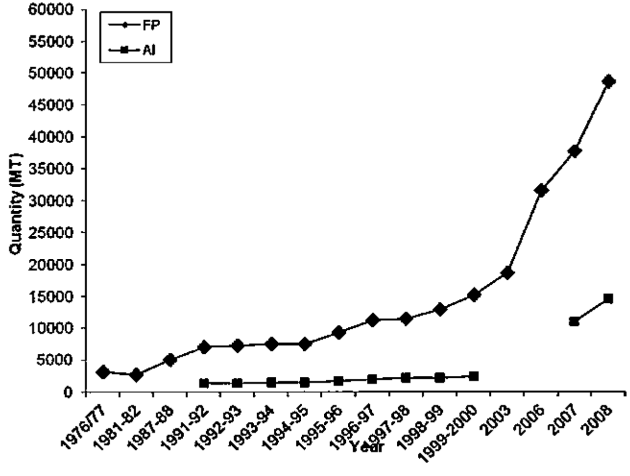


Figure 1. Pesticide consumption trend Bangladesh (1976 to 2008)[2] (FP: formulation product, AI: active ingredient)

Materials and methods

The article has been prepared based on information on past and current pesticide use in Bangladesh collected from regulatory authority, students research work for MS/PhD theses/ dissertation, association of pesticides companies and data collections from some sample farmers.

Results and discussions

POPs Pesticides history in Bangladesh

Three tons of endrin were received through barter and applied in modern rice cultivation in around 1957/58 land marked the use of pesticides in Bangladesh (former East Pakistan). The use of endrin continued for 10 years. Meanwhile, other POP pesticides like aldrin, dieldrin, chlordane, BHC/lindane and heptachlor were largely imported and used for agricultural purposes. DDT was received initially through WHO, then was imported, and from 1972 was manufactured locally. DDT was used exclusively for mosquito control for preventing/combating malaria. But in compliance with its legislation supported by WHO and MEAs, Bangladesh started discontinuing, banning, deregistering extremely hazardous pesticides in the 70's, and lastly banned heptachlor in 1998. The POPs pesticides, which have been discontinued, banned or deregistered include endrin and HCH/lindane (1970), aldrin (1975), chlordane (1985), dieldrin (1997), and heptachlor (1998)[3]. The government imposed only restricted use permission for DDT in 2005. Other POPs pesticides such as toxaphene and mirex were never imported and used in Bangladesh. However endosulfan is produced in Bangladesh by two producers and is still the most commonly used insecticide for different crops.

Substitutes of POPs Pesticides

With the exception of endosulfan, no POP pesticide has been imported or produced in Bangladesh since 1998. A very limited quantity of DDT is received through WHO and/or imported under the malaria control program. Therefore, the total consumption of pesticides in Bangladesh since 2000 shown in Figure 1 truly reflects the consumption of non-POP pesticides, which include 2,443 active ingredients (AIs) and 15,160 formulated products (FP) marketed (BCPA 2010)[2]. This total quantity includes the POPs' substitutes registered for specific crops in addition to the quantity used for crops other than for which they are basically registered. The crops, their target pests, substituted POPs pesticides, their POPs pesticides substitutes and adoption are shown in Table 1. In addition, Table 2 shows the consumption of the three most common POPs substitutes listed in Table 1, namely carbosulfan, chlorpyrifos, and imidacloprid (a neonicotinoid).

Table 2 shows the quantity of the use of newer pesticides, such as imidacloprid as a substitute of POPs with possibly increasing trends for imidacloprid and carbosulfan. They are applied at different crop stages including flowering stage, when pollinators including bees visit the crop. There is a high risk of bee decline, since imidacloprid has been proven to be highly toxic to bees[6] (Table 3). Moreover, imidacloprid is persistent in soil and water, and has high leaching potential[6]. Imidacloprid may be washed out of the soil into water bodies and groundwater[7]. The chemical is then further distributed into the environment.

Imidacloprid is absorbed by and translocated through the plant system and is poisonous to pollinating insects[5-11] through contamination of nectar and pollen. In Bangladesh, *Apis melifera* is a very common and efficient commercially cultivated pollinator collecting pollen and nectar from different flowering crops including mustard, rapeseed, linseed, mungbean, cucurbits etc. for which imidacloprid-containing formulations are registered for aphid and white fly control.

Table 1: Substitutes of POPs Pesticides in Bangladesh (Source: PPW 2011)[4]

Crops/Public Health	**Pests**	**Replaced POPs Pesticides**	**POPs Substitute Pesticides**	**Widely adopted Alternative to POPs pesticides**
Potato	Cutworm	Dieldrin, Heptachlor	Bifenthrin, Carbofuran, Cartap, Chlorpyrifos, Chlorpyrifos methyl, Lambda Cyhalothrin, Diazinon, Imidacloprid	Carbofuran, Chlorpyrifos, Lambda Cyhalothrin, Imidacloprid
Sugarcane	White Grub & termite	Heptachlor Dieldrin	Bifenthrin, Cadusafos, Carbofuran, Imidacloprid	Carbofuran, Imidacloprid
	Termite	Heptachlor, Dieldrin	Carbofuran, Chlorpyrifos, Chlorpyrifos + Alpha-Cypermethrin, Permethrin, Imidacloprid, Thiamethoxam	Carbofuran, Chlorpyrifos, Imidacloprid, Thiamethoxan
Tea	Termite	Chlordane Dieldrin	Bifenthrin, Chlorpyrifos, Permethrin, Imidacloprid, Thiamethoxam	
Maize	Cutworm		Chlorpyrifos, Lambda Cyhalothrin, imidacloprid	Chlorpyrifos, Imidacloprid
Rice	Stored Grain insects		Fenitrothion, Pirimiphos methyl, Aluminium Phosphide	
Public Health	Mosquito	DDT	Cypermethrin, Malathion, Malathion + Permethrin, Lambda Cyhalothrin, d-allethrin, Permethrin, Tetramethrin, Temephos, Phenthoate, Alpha Cypermethrin, Deltamethrin, S. Bioallethrin + Permethrin, d-transallethrin, Allethrin, Esbiothrin, S. Bioallethrin + permethrin + PBO, ETOC (Prallethrin), ETOC & Sumithrin (d-Pheothrin)	Bed nets Impregnated bed net Coils, Aerosols (Limited use)

Table 2. Consumption of three pesticides used partly as POPs pesticide substitutes in 2009 and 2010 (Source: BCPA 2010)[2]

Name of Insecticides	2009 (metric tonne)		2010 (metric tonne)	
	FP*	AI**	FP*	AI**
Carbosulfan	170.4	34.08	213.69	42.74
Imidacloprid	87.65	17.5	94.83	18.94
Emamectin Benzoate	13.58	0.68	10.72	0.54

***FP – Formulation Product **AI- Active Ingredient;**

Table 3. Properties of some pesticides replacing or having replaced POPs pesticides in Bangladesh

Insecticide	Acute (48h) LD_{50} honey bee (in nanogram per bee)	Soil degradation	Leaching potential
Imidacloprid	3.7 (oral)*	**persistent**	**high**
Carbosulfan	180 (oral)	non-persistent	low
Chlorpyrifos	59 (contact)	moderately persistent	low

* exposure route in parentheses

Risk assessment need for substitutes of POPs pesticides

The substitutes of POPs pesticides have been introduced in Bangladesh largely without a particular risk assessment. The main driver for the selection of a pesticide substitute was/is the cost of the pesticide and the effectiveness against the respective pest. However, of the three listed pesticides, imidacloprid is known to be highly toxic to bees[5-11] and considered as an important factor for the massive bee decline observed in the US and in Europe over the last 15 years threatening harvest yields of bee pollination-dependent crops. The decrease in bees and other pollinators have important economic implications[12,13]. In addition, very recent studies indicate that neonicotinoids may adversely affect human health, especially the developing brain[14]. It is in particular worrisome that main patents for imidacloprid have finished and therefore companies in particular in developing countries might increasingly produce this persistent and toxic neonicotinoid.

POPs pesticides have been banned in Bangladesh, but adequate information about the safety of their substitutes now in use have not been duly considered. Therefore, before the large-scale adoption of any substitute for POPs pesticides a proper investigation with respect to their safety for the ecosystem including bees and other pollinators and for human health aspects should be carried-out. International collaboration in this respect would be highly useful and urgently needed for Bangladesh and most probably also for other developing countries.

Acknowledgements:

The authors acknowledge gratefully the AusAID support, which has enabled the first author to participate in the conference. Appreciations are also due to BCPA, which has provided the latest information about the pesticide usage in Bangladesh.

References:

1. BBS (Bangladesh Bureau of Statistics) (2010) GDP of Bangladesh at 2007-08 to 2010-11. Bangladesh Statistics Bhaban. Agargaon. Dhaka.http://www.bbs.gov.bd/WebTestApplication/userfiles/Image/BBS/GDP_2011.pdf
2. BCPA (Bangladesh Crop Protection Association) (2010) Sales and Consumption of Pesticides in Bangladesh during 2008-2009.
3. Rahman, MM (2009) Latest developments on obsolete and POPs pesticides after finalization of National Implementation Plan in Bangladesh. Section 3. Pesticides Waste management. In Proceedings/Presentations: 10th International HCH and Pesticides Forum held on 06-10 September 2009, Kounicova 6, Brno, Czech Republic.
4. PPW (Plant Protection Wing of Department of Agricultural Extension) (2011) List of Registered Agricultural Pesticides & Public Health Products in Bangladesh (up to 61 PTAC & 88 PTASC meeting).
5. T.CFO.054 (1997) Chlorpyrifos Technical – Acute toxicity to honey bees (Apis mellifera)
6. Akca I, Tuncer C, Guler A, Saruhan I (2009) *Bioassays Journal of Animal and Veterinary Advances* 8: 2380-2382
7. IUPAC FOOTPRINT Pesticides Properties database. http://sitem.herts.ac.uk/aeru/iupac/index.htm
8. Gupta S, Gajbhiye VT, Agnihotri N (2002) *Bull Environ Contam Toxicol* 68: 502-508
9. Tennekes HA, Sánchez-Bayo F (2011) *J Environment Analytic Toxicol* S4:001. doi:10.4172/2161-0525.S4-001.
10. Tennekes HA (2010) The systemic insecticides: the disaster in the making. ISBN/EAN: 978-90-79627-06-6
11. Kindemba V (2009) The impact of neonicotinoid insecticides on bumblebees, Honey bees and other nontarget invertebrates ISBN 978-1-904878-9642009 October 2009. http://www.buglife.org.uk/Resources/Buglife/revised%20neonics%20report.pdf
12. The Economist (2012) Subtle poison - Evidence is growing that commonly used pesticides, even when employed carefully, are bad for bees. Mar 31st 2012.
13. Pesticide Action Network North America. (2012) Economic Value of Commercial Beekeeping. http://www.beyondpesticides.org/pollinators/EconomicValueCommercialBeekeeping.pdf
14. Kimura-Kuroda J, Komuta Y, Kuroda Y, Hayashi M, Kawano H (2012) *PLoS ONE* 7(2): e32432. doi:10.1371/journal.pone.0032432

ENVIRONMENTAL HEALTH RESEARCH AT NIEHS: CURRENT PRIORITIES AND PLANS FOR THE FUTURE

Birnbaum LS[1]*, Jung P[1]

[1]National Institute of Environmental Health Sciences and National Toxicology Program, 111 T.W. Alexander Parkway, Research Triangle Park, North Carolina, USA

INTRODUCTION

The National Institute of Environmental Health Sciences (NIEHS) is the premier environmental health sciences research institution in the world with both intramural research laboratories and extramural funding programs. As such, NIEHS and its priorities have considerable influence on environmental health research conducted in the U.S. and abroad. In late 2011, NIEHS embarked on a new strategic plan to capture the future research potential in environmental health and prioritize Institute directions for the next 5 years.

MATERIALS AND METHODS

The strategic planning process utilized four distinct steps:

1. A public, open-access website to acquire input from a broad base of constituents to generate "Visionary Ideas" for the strategic plan. This process permitted all interested parties, from employees to grantees to the general public, to submit ideas for the strategic plan. The website also allowed visitors to nominate attendees for the next step, an in-person community workshop. The ideas generated through the website were cataloged and provided to the attendees of the comunity workshop.

2. An in-person Strategic Planning Stakeholder Community Workshop, held over 3 days with nearly 200 participants, including a mixture of scientists, public health policy, regulatory experts, management of scientific research, communication experts, and non-scientific staff. Utilizing "Open Space Technology" participants quickly filled a blank agenda with 124 topics. After consolidating topics, attendees held breakout discussions and produced reports of highlights and recommendations. A total of 97 discussion groups met and submitted reports. These reports were then collated and clustered such that strategic themes emerged from the wide variety of topics. Participants then had the opportunity to vote for the reports that they felt were crucial to the strategic plan. Thirteen reports received the most votes, and remaining topics were clustered around the primary 13 topics, forming the final 8 themes that best supported the mission of the strategic plan. All 97 discussion group reports and subsequent 13 topics continue to be available on the NIEHS Strategic Plan website.

3. A second, in-person meeting of approximately 50 stakeholders who represented the broad expertise of environmental health science, held over two days, to review all the compiled input from the website and the 97 published reports from the first in-person community workshop. This group of participants drafted a mission statement, a vision for the Institute, and supporting themes that would comprise the actual content of the strategic plan. Public review and comment were also offered on drafts of these items on the NIEHS website.

4. Using the mission, vision and themes, Institute leadership spearheaded the process of developing strategic goals by leading divisional retreats to obtain broad-based input. All strategic goals were collected and coalesced into a single list, from which Institute leadership organized and developed a set of 11 institutional goals.

Transparency was a primary consideration throughout the strategic planning process. All documents were (and still are) made available on the public NIEHS website, the public was afforded opportunity for input, and updates at all stages were provided to the National Advisory Enviornmental Health Sciences Council, an oversight body for the Institute.

RESULTS AND DISCUSSION

The lengthy Strategic Planning process resulted in the following:

1. The mission of the National Institute of Environmental Health Sciences is to discover how the environment affects people in order to promote healthier lives. This mission statement provides a concise statement of why the Institute exists, what it works to achieve, its purpose and unique identity. It describes how the Institute will serve those affected by its work and defines the Institute's values and aims.

2. The vision of the National Institute of Environmental Health Sciences is to provide global leadership for innovative research that improves public health by preventing disease and disability from our environment. This vision statement tells us where the Institute is going as an organization. It creates a mental image of where the Institute wants to be in the future, and is a source of inspiration, setting a standard to strive toward.

3. Six themes that support the Institute's mission and vision:

a. Fundamental Research: Understanding the biology that defines basic mechanisms of response to environmental stressors and the implications for human health.

b. Exposure Research: Understanding how the complex nature of exposures, at the individual and population levels, contributes to health outcomes.

c. Translational Science: Transdisciplinary environmental health science to inform individual, clinical, and public health decision making to improve health.

d. Health Disparities and Global Environmental Health: Research to understand environmental contributors to global health and health disparities.

e. Training and Education: Developing and retaining a sustainable pipeline of environmental health professionals across a range of related disciplines including fundamental science, exposure science, translation, policy, and outreach through efforts in education, training, and career development; raising the level of environmental health literacy of the general population and all other NIEHS stakeholders.

f. Communications and Engagement: Advancing translation and dissemination of scientific knowledge on the role of the environment and human health; pursuing appropriate and effective means of engagement of the broad range of institute stakeholders in environmental health research and public health promotion.

4. Two cross-cutting themes that serve as overarching ideas that traverse all the other themes:

a. Knowledge Management: Environmental effects on health and disease are complex, and understanding these effects requires an integrated and comprehensive approach to data management. The pace of data generation in environmental health sciences has outstripped the existing infrastructure for information acquisition, management, analysis, visualization and dissemination. The various issues around information/data/knowledge management comprise an overarching issue with implications applicable to all the Strategic Planning Themes.

b. Collaborative and Integrative Approaches: An overarching theme identified during the NIEHS strategic planning process is the importance of collaborative and integrative approaches to environmental health sciences. Adverse effects leading to disease occur at multiple points throughout complex systems, often from multiple exposures, and across various life stages. The research enterprise for environmental health sciences needs to be positioned to exploit all relevant disciplines in a coordinated, integrated fashion to solve these complex problems. Environmental health scientists need to be enabled to work across a wide array of fields: cell and molecular biology, structural biology, biochemistry, genetics, pharmacology, toxicology, epidemiology, biostatistics, behavioral sciences, engineering, and many others. Systems biology, computational biology, and other promising new approaches are dependent on interdisciplinary collaborations. In addition to interdisciplinary approaches to fulfilling its science mission, NIEHS must also work to develop innovative collaborations with sister agencies, communities, and other partners to effectively translate this knowledge to inform prevention and interventions, as well as to guide stakeholder decision making at all levels.

By seeking and accepting input from a broad array of internal and external stakeholders, NIEHS is poised to confront modern and future challenges in environmental health with its new strategic plan.

ACKNOWLEDGEMENTS

This abstract has been reviewed by the National Institute of Environmental Health Sciences, and approved for publication. Approval does not signify that the contents necessarily reflect the views of the Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use. The opinions expressed in this manuscript are those of the authors and do not necessarily reflect the official opinion of the National Institutes of Health.

32^{nd} International Symposium on Halogenated Persistent Organic Pollutants

Sunday 26 August—Friday 31 August 2012, Cairns, Australia

**please note program is subject to change*

DIOXIN | 2012 | CAIRNS

Sunday 26 August 2012	
1600–1900	Registration
1700–1900	Informal reception

Monday 27 August 2012	
0900–0945	Opening ceremony
0945–1030	Plenary session—Martin Van den Berg & Mike Denison
1030–1100	Coffee break & exhibition
1100–1220	Development and validation of bioanalytical methods (I)
	New screening and rapid methods
	Fingerprinting, sources and processes
	Emission reduction methods and technologies (I)
	Passive sampling approaches and applications
1220–1330	Lunch & exhibition Lunch seminar presented by Agilent
1330–1450	Development and validation of bioanalytical methods (II)
	Exposure assessments and pathways (I)
	Atmospheric monitoring, fate and sources (I)
	Emission reduction methods and technologies (II)
	Bioindicators, bioaccumulation and food web studies (I)
1450–1520	Coffee break & exhibition
1520–1700	Endocrine disruptor chemicals and effects (emphasis on POPs)
	Exposure assessments and pathways (II)
	Atmospheric monitoring, fate and sources (II)
	POPs in developing and transition countries
	Bioindicators, bioaccumulation and food web studies (II)
1700–1800	Happy Hour poster session
1900–2200	Welcome Reception

Tuesday 28 August 2012	
0830–0915	Plenary session—Shin-ichi Sakai
0915–0945	Coffee break & exhibition
0945–1145	Industrial, occupational and accidental exposure
	Integrating toxicology and epidemiology for risk assessment
	Advances in instrument techniques
	Metabolism of flame retardants in biota
	Thermal sources and formation processes
1145–1300	Lunch & exhibition Lunch seminar presented by Waters
1300–1500	Remediation and assessment of contaminated areas
	Mechanisms and pathways of toxicity, incl. mixture toxicity
	Modelling of environmental fate, transport and sources
	Levels in food/feed
	Formation and degradation processes and products
1500–1530	Coffee break & exhibition
1530–1710	Risk assessment, management and communication
	Dioxins and other POPs in Vietnam
	Sampling and sample preparation methods
	Indoor environments (I)
	Source and emission inventories
1710–1810	Happy hour poster session

Wednesday 29 August 2012	
0830–0915	Plenary session—Katharina Fabricius
0915–0945	Coffee break & exhibition
0945–1145	Regulation and policy of POPs
	Toxicodynamics and toxicokinetics
	Non-target and emerging contaminant analysis
	Indoor environments (II)
	Biomonitoring in humans
1200–1730	Symposium tours
1800–2330	Gala in the Rainforest dinner

Thursday 30 August 2012	
0830–0915	Plenary session—Aiqian Zhang
0915–0945	Coffee break & exhibition
0945–1145	POPs and disease
	Sustainable production and use
	From Bayreuth to Cairns-progress in 20 years
	Environmental monitoring—brominated compounds
	QA/QC and interlaboratory studies (I)
1145–1300	Lunch & exhibition Lunch seminar presented by Shimadzu & BUCHI Lunch seminar presented by AB Sciex
1300–1440	Epidemiology and burden of disease
	Flame retardants alternatives
	Exposure and health of aquatic wildlife (I)
	Environmental monitoring—fluorinated compounds
	QA/QC and interlaboratory studies (II)
1440–1510	Coffee break & exhibition
1510–1650	Exposure and effects of POPs in children
	Unintentional formation of POPs from chemical manufacturing and use
	Exposure and health of aquatic wildlife (II)
	Environmental monitoring
	Ongoing interlaboratory comparison studies on POPs
1650–1800	Happy hour poster session

Friday 31 August 2012	
0830–1030	Plenary series: State-of-the-art and Future Challenges (core topics A–F)
1030–1100	Coffee break
1100–1200	Symposium close: Hutzinger award presentations Introduction to Dioxin 2013 – Jae-Ho Yang