Integració de diferents tècniques de monitorització ambiental i anàlisi de resultats per l'optimització de l'avaluació de riscos

Laboratori de Toxicologia i Salut Mediambiental
Departament de Ciències Mèdiques Bàsiques

Tesi Doctoral

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UNIVERSITAT ROVIRA I VIRGILI

Tarragona, 2008

UNIVERSITAT
ROVIRA I VIRGILI

Informe del director de la tesi doctoral

(art 11.3 del reial decret 56/2005 de Postgrau)

DADES IDENTIFICATIVES DE LA TESI DOCTORAL	
Títol de la tesi doctoral Integració de diferents de tècniques de monitorització ambiental i anàlisi de resultats per l'optimització de l'avaluació de riscos	
Doctorand/a Montserrat Mari Marcos	
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Programa de doctorat Neurotoxicologia i Psicofarmacologia	
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El(s) (co)directors sotasignats emeten el següent informe de la tesi doctoral presentada a tràmit de dipòsit		
	SI	NO
La tesi consisteix en un treball original de recerca	x	
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Les conclusions de la tesi corresponen a les hipòtesis i/o objectius formulats	x	
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D'aquesta tesi es deriven les següents aportacions científiques:

Mari M, Ferré-Huguet N, Nadal M, Schuhmacher M, Domingo JL (2007) Temporal trends in metal concentrations in soils and herbage collected near a municipal waste incinerator: Human health risks. Human and Ecological Risk Assessment 13: 457-472

Mari M, Nadal M, Ferré-Huguet, Schuhmacher M, Borrajo MA, Domingo JL (2007) Monitoring PCDD/Fs in soil and herbage samples collected near a hazardous waste incinerator: Health risks for the population living nearby. Human and Ecological Risk Assessment 13: 1255-1270

Mari M, Schuhmacher M, Feliubadaló J, Domingo JL (2008) Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers. Chemosphere 70: 1637-1643 *Mari M, Nadal M, Schuhmacher M, Domingo JL (2008) Monitoring PCDD/Fs, PCBs and heavy metals in ambient air of an industrial area of Catalonia, Spain. Chemosphere (En premsa)* *M Mari, MA Borrajo, M Schuhmacher, JL Domingo (2007) Monitoring PCDD/Fs and other organic substances in workers of a hazardous waste incinerator: A case study. Chemosphere 67: 574-581* *Kumar V, Mari M, Schuhmacher M, Domingo JL Partitioning total variance in risk assessment: Application to a municipal solid waste incinerator (2008) Environmental Modelling and Software (En premsa)*
Altres comentaris sobre la qualitat de la tesi

I en conclusió, s'emet l'informe favorable per tal que es pugui portar a terme tràmit de lectura i posterior defensa pública.

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Nom i cognoms: Marta Schuhmacher

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Codirector (si s'escau)

Als meus pares

Agraïments

Per començar, voldria agrair a totes les persones que m'han donat el seu suport durant la realització d'aquesta tesi.

En primer lloc voldria expressar el meu agraïment als directors de la meva tesi, la Dra. Marta Schuhmacher i el Dr. Domingo, per donar-me l'oportunitat de treballar al seu grup d'investigació i haver confiat sempre en mi. També voldria agrair molt especialment al Martí Nadal, que durant tot aquest temps m'hagi fet de "germà gran" professional i m'hagi guiat i ajudat sempre que ho he necessitat.

A totes les nenes del laboratori de "Tóxico". A la Núria que em va portar fins aquí . A la Silvia que és "un solet", per la seva bondat i espontaneïtat que sempre t'alegren el dia. A la Roser, que tants cops ha fet de conductora de la "furgo" i m'ha ajudat a moure els captadors amunt i avall. A la Diana per mostrar-me sempre la seva estima. A la Lolita ("floreta"), la Gemma, la Bea i la Isabel que ens han portat aire fresc i molt "bon rotllo". A la resta de nenes de Reus, la Tania, la Mery, l'Espe, el José Gregorio i l'Ingrid amb qui també he compartit bones estones, sobretot extralaborals. També a l'Ana, la Merche, la Teresa i la Paloma que des del principi m'han animat i ofert la seva ajuda.

A tots els membres de l'AGA, començant pel seu director el Dr. Fransesc Castells, que em van acollir com una més del grup. A l'Eva que em va ajudar en la meva "transició" a Tarragona, a la Isabela, el William, el Rafa, el Vikas, la Jennifer, la Jorgelina, la Guadalupe, l'Oscar, el Ronnie, la Miriam, la Tere, la Geogina, el Jordi, i especialment a l'Ana, que en els últims temps ha estat un gran suport. Gràcies per la vostra ajuda i sobretot pels bons moments que hem compartit junts fora del 213 a l'hora dels cafès o en les sortides a fer cervesetes i sopars amb plats internacionals. Haver-us conegut ha estat molt enriquidor.

A l'Ani i la Vicky per ser-hi sempre i per la vostra amistat. A la Delia, la Vanessa i la Sílvia. Espero la nostra amistat continui molts anys.

Per últim, voldria expressar el meu més profund agraïment a tota la meva família, i molt especialment als meus pares i germà, per donar-m'ho tot i estimar-me i cuidar-me tantíssim.

Gràcies a tots.

Índex

Abreviatures més comuns

ACP: Anàlisi de components principals

ATSDR: Agència americana pel registre de substàncies tòxiques i malalties

CLPs: Clorofenols

COPs: Compostos orgànics persistents

FHLS: Fuzzy latin hypercube sampling

HAPs: Hidrocarburs aromàtics policíclics

HCB: Hexaclorobenzè

HQ: Quocient de perill

HP: Hidroxipirè

HPLC: Cromatografia líquida d'alta pressió

HRMS: Espectrometria de masses d'alta resolució

HRGC: Cromatografia de gasos d'alta resolució

IARC: Agència internacional de recerca contra el càncer

ICP-MS: Espectrometria de masses de plasma acoblat inductivament

K_{ow}: Constant de partició octanol/aigua

LRAT: Long range atmospheric transport

NIOSH: Institut americà per la salut i seguretat ocupacional

OMS: Organització mundial de la salut

ONU: Organització de nacions unides

PCCD/Fs: Dioxines i furans policlorats

PCBs: Bifenils policlorats

PCNs: Naftalens policlorats

PCPs: Pentaclorofenols

PRGs: Preliminary remediation Goals

PDFs: Funcions de densitat de probabilitat

PM 10: Partícules ambientals (menors a 10 micres)

PUF: Escuma de poliuterà

RfD: Dosi de referència

SF: Factor de potència cancerígena
TDI: Ingesta diària tolerable
TEFs: Factors d'equivalència tòxica
TEQs: Equivalents tòxics
UE: Unió europea
US EPA: Agència de protecció ambiental americana

Resum

La gestió dels residus és un dels problemes amb que s'enfronta la societat actual. Els residus es generen constantment, cada vegada en major quantitat, essent la seva constitució variada i canviant en el temps. Això, fa que les administracions cerquin la millor forma de gestionar-los de manera que es garanteixi un mínim impacte sobre el medi ambient i sobre la salut de les persones. La incineració té molts avantatges davant d'altres sistemes de disposició de residus, ja que suposa una reducció del volum, la recuperació d'energia i l'eliminació d'agents patògens. Per altra banda, les potencials emissions de substàncies perilloses associades a la incineració, com les dioxines i furans (PCDD/Fs) i d'altres compostos orgànics persistents com els bifenils policlorats (PCBs) o els naftalens policlorats (PCNs), així com de metalls pesants, desperten preocupació a la gent que viu a les rodalies de les incineradores (síndrome NIMBY – "Not In My BackYard"). L'exposició crònica a aquestes substàncies s'associa a efectes adversos en òrgans com els pulmons, fetge o ronyons. A més, alguns metalls (com el crom, cadmi, beril·li i arsènic), així com alguns congèneres de PCDD/Fs són carcinògens. En aquest sentit, cal destacar que en els últims anys les emissions de les incineradores s'han reduït de forma molt notable degut a les estrictes disposicions reguladores actuals.

Per estudiar l'impacte de potencials fonts de contaminació és imprescindible monitoritzar, primer per establir els nivells base que representen l'estat inicial i, segon, per detectar canvis al llarg del temps. Per tant, cal definir estratègies de monitorització acurades en funció de la informació que es vulgui obtenir. Els monitors ambientals permeten conèixer l'existència de les fonts contaminants en el medi ambient. Per altra banda, el control biològic proporciona una avaluació més centrada i focalitzada del risc per a la salut que el control ambiental. Ara bé, cal l'aplicació de diferents tècniques d'anàlisi de resultats (en aquesta tesi s'han utilitzat bàsicament tècniques estadístiques com l'Anàlisi de Components Principals) per treure la màxima informació de les dades de la monitorització (determinar canvis, identificar fonts...) i poder fer una avaluació

acurada del risc. Així mateix, és també important tenir en compte la incertesa associada a les variables implicades en l'avaluació del risc ja que aquesta repercuteix en la fiabilitat dels resultats obtinguts i, per tant, en la presa de decisions en base als resultats.

L'objectiu d'aquesta tesi és l'aplicació de diferents tècniques de monitorització i d'anàlisi de resultats per avaluar els riscos generats per la incineració de residus. El treball s'ha dividit en sis Capítols que inclouen sis articles en els quals que s'avalua a través de diverses metodologies l'impacte ambiental i els riscos per la salut derivats de diferents incineradores.

El *Capítol I* inclou una breu introducció sobre la incineració de residus i els potencials riscos associats a les seves emissions. Aquest Capítol també conté una descripció dels contaminants de major interès, així com una breu explicació de la metodologia utilitzada en l'avaluació de riscos.

Al *Capítol II* s'utilitzen els sòls i les herbes com a monitors de contaminació ambiental a llarg i curt termini. Aquesta part consta de dos articles. En el primer, es va estudiar l'impacte d'una incineradora de residus industrials, mentre que en el segon es va avaluar una incineradora de residus sòlids urbans. Es van estudiar les variacions temporals/espacials de les concentracions de PCDD/Fs i metalls pesants a les rodalies d'ambdues d'incineradores. A més, es van analitzar els potencials riscos per la salut de la població que viu a les rodalies de totes dues instal·lacions. Es van calcular separadament els riscos carcinogènics i no carcinogènics. Els nens es van considerar separadament degut a la seva major sensibilitat als contaminants. En ambdós casos, els resultats van indicar que les incineradores estudiades no eren una font rellevant de PCDD/Fs i metalls.

Al *Capítol III* es presenten els nivells de PCDD/Fs, PCBs, PCNs i metalls pesants en aire als voltants d'una incineradora de residus sòlids urbans. Es van publicar dos articles en aquesta àrea. En el primer article, es va investigar la utilització captadors passius, en forma de discs de poliuretà (discs PUF), com a mètode complementari per la mesura dels nivells ambientals de PCDD/Fs, PCBs i PCNs. La tècnica convencional de captació d'aquest tipus de contaminants es basa en la utilització de captadors actius. Els múltiples desavantatges d'aquest sistema (com l'elevat cost dels equipaments o la necessitat d'una font de corrent elèctrica) fan que actualment s'estiguin cercant altres alternatives. A més, aquesta metodologia només permet conèixer concentracions puntuals/diàries. Els resultats van indicar que els discs de poliuretà són una bona alternativa per mesurar les concentracions ambientals de compostors orgànics persistents (COPs) durant períodes llargs de temps de forma barata i senzilla. En el segon article, es van presentar els resultats dels nivells en aire de PCDD/Fs i metalls pesants als voltants de la incineradora i es va analitzar la seva evolució temporal. També s'utilitzà l'Anàlisi de Components Principals (ACP) com a eina per obtenir informació sobre la relació entre les mostres, els contaminats i les possibles fonts. Els resultats van mostrar una diferència notable entre els perfils de les mostres ambientals i els de la incineradora, indicant que els nivells actuals de PCDD/Fs de la zona estarien més relacionats amb d'altres tipus de fonts (p.ex., el trànsit).

Al *Capítol IV*, s'estudia l'impacte d'una incineradora a partir d'un control biològic dels seus treballadors, el grup de població que, en cas que la instal·lació suposés un focus important de contaminants, en resultaria més afectat. En relació amb les substàncies que produeixen un efecte tòxic després de penetrar a l'organisme humà, el control biològic permet una avaluació més centrada i focalitzada del risc per a la salut que el control ambiental. Un paràmetre biològic que reflecteixi la dosi interna, permet entendre els efectes adversos sistèmics una mica millor que qualsevol determinació mediambiental. En aquest estudi es van mesurar les concentracions d'una sèrie de contaminats orgànics en mostres de plasma i orina de treballadors de la incineradora per establir les diferències temporals respecte als nivells control (determinats abans que la incineradora comencés a funcionar) i altres anys anteriors.

En les mostres de plasma es van determinar les concentracions d'hexaclorobenzè (HCB), bifenils policlorats (PCBs) i dioxines i furans (PCDD/Fs). Per altra banda es van determinar els nivells de pentaclorofenols (PCPs) i 1-hidroxipirè (1-HP) en mostres d'orina. Els resultats van indicar una disminució en els nivells de dioxines mentre que per la resta de compostos les concentracions van ser molt similars a l'estudi control. No es van trobar diferències entre les concentracions de compostos orgànics d'acord amb els diferents llocs de treball (planta, laboratori o administració). Els resultats van indicar que els treballadors de la incineradora no estan exposats a PCDD/Fs o altres substàncies orgàniques.

Al *Capítol V*, s'analitza la propagació de la incertesa i la variabilitat associades als diferents paràmetres implicats en l'avaluació de riscos. Per l'anàlisi es va utilitzar una nova aproximació, la Fuzzy Latin Hypercube Sampling (FLHS). Aquesta metodologia, tracta la variabilitat dels paràmetres utilitzant Funcions de Densitat de Probabilitat (en anglès: *probability density functions*, PDFs), mentre que per tractar la incertesa associada a cada paràmetre utilitza funcions de pertinència difuses (en anglès: *fuzzy membership functions*). Aquest mètode es va aplicar al cas d'estudi del risc produït per les emissions de dioxines i furans (PCDD/Fs) d'una incineradora. Primerament, es va utilitzar un model de dispersió multicompartimental per calcular les concentracions de PCDD/Fs, derivades de les emissions de la incineradora, en diferents compartiments ambientals (sòls, vegetals) i també com aquestes es transmetrien cap a la cadena alimentària (carn i llet). Posteriorment, es van aplicar models d'exposició i de risc (carcinogènic i no carcinogènic). El model FHLS va mostrar superioritat davant d'altres mètodes convencionals d'anàlisi de la incertesa com és l'Anàlisi de Monte Carlo. L'anàlisi de sensibilitat va indicar que en la deposició en sòls, la constant de pèrdua del sòl (ks) (55%), la velocitat de deposició seca (vd) 30%), i la proporció volumètrica de neteja de partícules (Wp) (14%) eren les variables que contribuïen majoritàriament a la incertesa. Pel que fa al model d'exposició, l'anàlisi de sensibilitat va mostrar que el 99% del risc era derivat de la dieta, mentre que menys de l'1% provindria de les emissions directes de la incineradora.

Finalment, al *Capítol VI* es presenten les conclusions generals. A través dels diversos monitors utilitzats i el posterior anàlisi dels resultats s'ha estudiat l'impacte de la incineració des de diferents punts de vista. L'Anàlisi de Components Principals ha resultat ser una eina efectiva a l'hora extreure la màxima informació de les dades de monitorització, mentre que a través del Fuzzy Latin Hypercube Sampling s'han identificat les principals fonts d'incertesa dins d'un model multicompartimental per l'avaluació del risc. Els estudis realitzats en diverses incineradores espanyoles han demostrat l'efectivitat de la legislació vigent, molt estricta en quant a les emissions de dioxines i furans i de metalls pesants. En cap dels casos, els resultats han indicat que les incineradores estudiades fossin una font rellevant d'aquests contaminats i, per tant un risc addicional per la gent que viu a les rodalies. A més, l'anàlisi dels resultats ha demostrat que els nivells actuals de PCDD/Fs estan més relacionats amb altres tipus de fonts (p.ex., el trànsit) que amb les pròpies emissions de les incineradores.

Capítol I

Introducció general, objectius i resum de la metodologia

1. Introducció

Un dels problemes més immediats amb que s'enfronta la nostra societat actual és l'adequada gestió dels residus que garanteixi un mínim impacte pel medi ambient i la salut de les persones. Per una banda, els residus urbans es generen constantment i en gran quantitat, essent la seva constitució variada i canviant en el temps. Tanmateix, la preocupació no solament es cenyeix als residus urbans, sinó també als residus industrials, els quals es generen en menor proporció que els urbans però acostumen a ser molt més tòxics. En relació a la gestió de residus, la Unió Europea ha publicat diferents directives amb l'objectiu de minimitzar el seu impacte sobre la salut de les persones i el medi ambient. Aquestes, es basen en tres principis: prevenció en la generació, reciclatge i re-ús, i finalment, millora de la disposició final. En aquest sentit la incineració amb recuperació d'energia sembla la millor alternativa. Tot i això, la implantació d'incineradores continua rebent fortes crítiques per part de certs sectors de la població que encara consideren que aquestes instal·lacions suposen un elevat risc per al medi ambient i per la salut de les persones.

Antigament, la quantitat de residus generats per la població era insignificant degut principalment a la menor quantitat població. En aquells temps, els residus eren dipositats directament al terra sense que això suposés cap problema pel medi ambient. A partir de la revolució industrial la gestió dels residus va esdevenir una qüestió crítica. L'augment de la població i el trasllat d'una població bàsicament rural a àrees urbanes durant el segle XVIII va fer que es produís un augment en la quantitat de residus urbans i industrials que suposava una amenaça per la salut de les persones i també pel medi ambient. No va ser fins a mitjans del segle XIX que es van començar a prendre mesures per la gestió dels residus.

1.1 La incineració

Les incineradores van començar a utilitzar-se a finals del segle XIX a Anglaterra. En aquest tipus de plantes es cremen continguts elevats de residus orgànics, aliments, plàstics, productes tèxtils, pells, cautxú, fusta, etc., en presència de clor, i amb continguts de metalls pesants. Això, fa que aquestes instal·lacions hagin estat tradicionalment una font important de formació de dioxines i furans (PCDD/Fs), i en menor mesura probablement també de bifenils policlorats (PCBs) i naftalens policlorats (PCNs), així com d'emissions de metalls (Tosine i col·ls., 1985; Fiedler i Hutzinger, 1990; Rappe, 1992; Uchida i col·ls., 1996; Schneider i col·ls., 1998). Tot i això, en els últims anys aquestes emissions s'han reduït de forma molt notable en aquells països on s'han adaptat a les noves tecnologies i disposicions reguladores.

L'any 2000, la UE va adoptar la Directiva 2000/76/CE (DOCE, 2000) relativa a la incineració de residus, que actualitza les anteriors, i la qual no fa distinció entre la incineració de residus municipals i especials. Aquesta directiva va entrar en vigor per a les noves instal·lacions al desembre de l'any 2002, i per a les instal·lacions preexistents al desembre del 2005. La directiva implica els límits d'emissió a l'atmosfera més exigents que hi ha avui dia a escala mundial per a qualsevol tipus d'instal·lació. Els valors límit relatius a metalls pesants i PCDD/Fs es mostren a la Taula 1.

D'acord amb aquests valors, es pot afirmar que la incineració de residus és l'activitat, tant industrial com d'infraestructura, que està sotmesa als límits d'emissió a l'atmosfera més exigents. Per contra, en l'actualitat les concentracions de PCBs i PCNs en les emissions encara no està regulada, malgrat que ja han estat reconegudes les seves característiques *dioxin-like* en quant a toxicitat i persistència en l'ambient (Safe, 1990; Kimbrough, 1995; Hayward, 1998; Blankenship i col·ls., 2000).

Taula 1

Concentracions límit d'emissió a l'atmosfera per a incineradores de residus en un període de 24 hores (mesurats en mg/m^3 a 273 ºK, 101.3 KPa, 11% O_2 i gas sec. Temperatura de combustió de comp. orgànics no halogenats: 850ºC. Temperatura de combustió de comp. orgànics halogenats: 1100ºC)

Contaminant	**2000/76/CE Incineració de residus**
Partícules totals	10
Cd + Tl	0.05
Hg	0.05
Sn + V + Sb + As + Pb + Cr + Co + Mn + Ni + Cu	0.05
Dioxines + Furans (ng TEQ/m^3)	0.1

FONT: http://www.gencat.net/mediamb/revista/rev29-4.htm

1.2 Contaminats d'interès

D'entre els contaminats emesos per les incineradores, els que tradicionalment han generat major preocupació degut a la seva toxicitat, persistència i capacitat de bioacumulació són les dioxines i furans (PCDD/Fs) i els metalls pesants. Els bifenils policlorats (PCBs) i naftalens policlorats (PCNs) són compostos organoclorats formats també en processos de combustió, amb caractrístiques similars a les PCDD/Fs. Per altra banda, les incineradores també poden emetre d'altres compostos organoclorats amb propietats tòxiques com l'hexaclorobenzè (HCB) o els clorofenols (CLPs). Els CLPs també s'utilitzen com a biomonitors indirectes a l'exposició actual a substàncies organoclorades. Pel que fa a l'hidroxipirè (HP), s'utilitza normalment en monitorització biològica com a marcador a l'exposició a hidrocarburs aromàtics policíclics (HAPs) ja que n'és un metabòlit format com a mètode de detoxificació.

1.2.1. Compostos orgànics

Dioxines i furans (PCDD/Fs)

El nom dibenzo-p-dioxines policlorades (PCDDs) agrupa a un conjunt de 75 congèneres, entre els que figura el més conegut i representatiu, la 2,3,7,8-tetraclordibenzo-p-dioxina o TCDD (Figura 1), mentre que els dibenzo-p-furans policlorats (PCDFs) agrupen 135 congèneres. Les dibenzo-p-dioxines i els dibenzo-p-furans policlorats són dos dels dotze compostos orgànics persistents (COPs) ("dirty dozen") inclosos a la Convenció d'Estocolm.

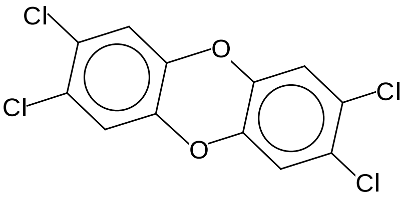

Figura 1. Estructura química de la TCDD.

Toxicitat i Efectes sobre la salut

Els 75 congèneres de les dioxines que hem esmentat abans es deuen a la diversa disposició i/o nombre d'àtoms de clor a l'anell aromàtic. Aquest nombre oscil·la entre 1 de les MCDD i 8 de les OCDD. Altrament, els dibenzofurans policlorats o PCDFs, tenen menys posicions de simetria que les PCDDs, posseint un total de 135 congèneres.

Són precisament el nombre i la posició dels substituents de clor a la molècula de PCDD/F el que determina la toxicitat dels diversos compostos. La toxicitat individual pot variar fins i tot amb un valor relatiu de 1000 vegades, el que evidentment complica l'avaluació del risc de l'exposició, ja que el més normal és que es trobin formant barreges complexes.

Per aquesta raó, i per tal de simplificar la tasca avaluadora de riscos, es va definir el concepte de factor d'equivalència tòxica (TEF) per a cadascun dels congèneres que configuren les barreges. El concepte de TEF, desenvolupat als anys 80, proporciona un mètode relativament senzill d'avaluar la toxicitat de barreges complexes de PCDD/PCDFs (Kutz i col·ls., 1990). S'han desenvolupat diversos sistemes per expressar la contribució tòxica total de les dioxines i furans. En cada sistema, la toxicitat de cada congènere és relativa a la de 2,3,7,8-TCDD (s'anomena Factor d'Equivalència Tòxica o TEF). Així, per calcular la toxicitat de la barreja els resultats de concentració de cada congènere es multipliquen pel valor corresponent de TEF de cada congènere. Quan aquests resultats es sumen, s'obté un total d'equivalència tòxica o TEQ de la barreja.

$$TEQ = \sum (TEF \times concentració)$$

Els dos sistemes més comuns per determinar els TEQs són els de l'Organització Mundial de la Salut (OMS-TEQ) i els de l'Organització del Tractat de l'Atlàntic Nord (OTAN), coneguts com els TEQ Internacionals (I-TEQ). En general tenen els mateixos valors, amb l'excepció de l'1,2,3,7,8-PeCDD, al que l'Organització Mundial de la Salut li assigna en factor d'1 mentre que el factor tòxic internacional és 0.5, i l'OCDD/F als que l'Organització Mundial de la Salut els assigna un factor de 0.0003 mentre que el factor tòxic internacional és 0.001. Pels 2,3,7,8-TCDF i 1,2,3,7,8-PeCDF , l'Organització Mundial de la Salut assigna un factor de 0.3 i 0.03 i mentre que el factor tòxic internacional és de 0.1 i 0.05, respectivament. Els factors tòxics internacionals són més comuns a Nord Amèrica, mentre que a Àsia i Europa es tendeix més a usar els OMS-TEQs. A la Taula 2 es mostren els diferents valors dels factors tòxics Internacionals i de l'Organització Mundial de la Salut.

Taula 2
Valors dels TEF Internacionals (OTAN, 1998) i dels TEF-OMS (Van den Berg i col·ls., 2006).

Congènere	**I-TEF**	**OMS- TEF**
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0003
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0003

Les dioxines produeixen un ampli ventall d'efectes bioquímics i tòxics en animals. Aparentment, els diferents congèneres acaben produint les mateixes alteracions encara que amb diferent grau de potència. Per la majoria, el mecanisme d'acció no acaba de ser clar, encara que sembla que el denominador comú que media l'efecte biològic de les PCDD/Fs sobre les cèl·lules, és la unió dels compostos al receptor de l'aril hidrocarboni (AhR).

En quant als efectes no carginogènics, el més remarcable produït per la intoxicació aguda a dioxines és el cloracné. Avui en dia, la toxicitat de la TCDD en humans només es coneix parcialment i a curt termini (toxicitat aguda). Els signes i símptomes aguts i subaguts més representatius són:

- *Cutanis*: cloracné, hiperqueratosi i hiperpigmentació
- *Sistèmics*: anorèxia i pèrdua de pes, lleugera fibrosi hepàtica, problemes digestius, dolors musculars i articulars, pielonefritis, cistitis hemorràgica, etc.;
- *Neurològics i psíquics*: disfunció sexual, problemes visuals, pèrdua de memòria, pèrdua d'audició, olfacte i tacte, depressió, irritabilitat, trastorns del son
- *Altres*: irritació ocular i conjuntivitis

Fins ara l'Agència de Protecció Ambiental Americana (US EPA són les sigles en anglès que s'utilitzaran a partir d'ara per identificar-la) no ha establert dosi de referència (RfD) per la 2,3,7,8 TCDD. Tot i això, els efectes no cancerígens normalment s'avaluen a través de la Ingesta Diària Tolerable (TDI) que marca la OMS (1-4 pg/kg pes corporal) (Van Leeuwen i col·ls., 2000).

Fonts

Les dioxines mai han estat produïdes/fabricades de forma voluntària sinó que es formen com a subproductes en certes síntesis químiques en les que hi intervé el clor, com la fabricació de paper, fabricació del PVC, o la fabricació d'herbicides, i en processos de combustió, com la incineració de residus urbans i hospitalaris, en la indústria cimentera, o la producció de metalls a alta temperatura, entre altres processos industrials.

Persistència

Les PCDD/Fs són extremadament persistents a l'ambient. A l'augmentar el grau de cloració augmenta tant l'estabilitat com la lipofilia (solubilitat en olis). La seva constant de distribució octanol/aigua (K_{ow}) (que indica la solubilitat relativa de lípid a aigua) és de l'ordre d'un a cent milions (log K_{ow} 6.5 a 8.8) cosa que suposa una elevada tendència a passar als lípids des de l'aigua. Els microorganismes del sòl o els animals no són capaços de trencar efectivament els clors en les posicions 2,3,7 i 8 de les PCDD/Fs i això fa que la seva eliminació sigui molt lenta.

Bioacumulació

Les PCDD/Fs són substàncies amb elevada persistència i a la vegada lipofíliques per la qual cosa es produeix un augment de la seva concentració a llarg de la cadena alimentaria, de forma que es troben presents en concentracions més elevades en organismes dels nivells més elevats de la cadena tròfica (mamífers i ocells). Es diu que es produeix bioacumulació i biomagnificació d'aquests compostos.

Long-Range Transport

El fet que les dioxines i furans siguin substàncies persistents i semivolàtils, fa que puguin ser transportades a grans distàncies per l'acció del vent, experimentant el que en anglès es coneix com a Long Range Atmospheric Transport (LRAT). És per això, que de vegades resulta possible trobar nivells diferents del "zero" a zones molt allunyades de cap font coneguda d'emissió.

Bifenils policlorats (PCBs)

Toxicitat i Efectes sobre la salut

Els PCBs comprenen un grup d'hidrocarburs clorats aromàtics format per 209 congèneres. El número i posició dels àtoms de clor determina les propietats biològiques i el comportament ambiental de cadascun dels bifenils policlorats (PCBs). Alguns PCBs amb menys de 4 àtoms de clor són bastant biodegradables. A tall d'exemple a la Figura 2 es mostra l'estructura química del PCB 28.

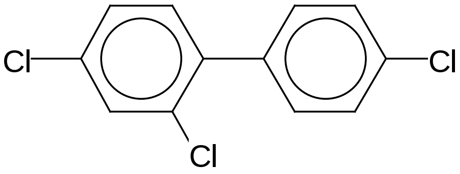

Figura 2. Estructura química del PCB 28.

Les mescles comercials de PCBs tenen un ampli espectre d'efectes tòxics. Molts d'aquests efectes tenen una gran similitud amb els causats per la 2,3,7,8- TCDD (Safe, 1990; Kimbrough, 1995). Alguns efectes adversos sobre la salut que han estat associats als PCBs són el cloracné en adults i canvis immunològics i en el neurocomportament en nens (ATSDR, 2000c).

Encara que no és conegut que els PCBs causin càncer a les persones, el Departament de Salut i Serveis Humans (DHHS), així com la IARC (Agència Internacional del Recerca en Càncer) i l'EPA (Agència Americana de Protecció

Mediambiental) han determinat que podrien ser precursors cancerígens (ATSDR, 2000c).

En animals d'experimentació, l'exposició a PCBs produeix disfuncions reproductives, immunosupressió i trastorns de comportament i aprenentatge (Lemesh, 1992; Kimbrough, 1995). L'exposició perinatal a aquests compostos s'ha associat amb dèficits cognitius tant en animals com en humans (Walkowiak i col·ls., 2001; Gilbert, 2003). Els nens nascuts de mares exposades a PCBs, tenen un pes més baix al néixer que els nascuts de mares no exposades, i presenten alteracions en el comportament durant els primers anys de vida. Alguns estudis realitzats a Suècia amb dones embarassades de famílies de pescadors mostren associació entre l'elevat consum de peix contaminat amb PCBs procedent del mar Bàltic i un baix pes al néixer dels nounats (Rylander i col·ls., 1996; Rylander i col·ls., 1998).

L'Organització de les Nacions Unides (ONU), a través de l'OMS, ha conclòs que segons el grau de cloració i el temps d'exposició, els PCBs produeixen efectes adversos tals com cloracné, increment de secrecions oculars, edemes i dolors abdominals (malaltia de Yusho) (Aoki, 2001).

Estudis realitzats amb persones exposades laboralment a aquests tòxics, mostren que els PCBs causen irritació nasal i pulmonar, així com alteracions gastrointestinals, hepàtiques i hematològiques, depressió i fatiga (ATSDR, 2000c). Alguns PCBs alteren l'acció d'hormones tiroidees i/o d'altres glàndules endocrines que poden afectar el creixement, el desenvolupament i la reproducció.

Els PCBs produeixen càncer en animals (ATSDR, 2000c). Encara que no està demostrat que aquestes substàncies causin càncer en humans, tant l'EPA (Agència Americana de Protecció Mediambiental), com la IARC (Agència Internacional del Recerca en Càncer), classifiquen els PCBs com a probables carcinògens en humans (categoria 2A), és a dir, són substàncies que tenen poca evidència de tenir relació causal de càncer en humans, però que presenten suficient evidència en estudis realitzats amb animals de laboratori (IARC, 1995). Altrament, alguns congèneres tenen efectes carcinogènics i poden estar associats amb un augment del risc de patir càncer de mama (Negri i col·ls., 2003).

Fonts

Els PCBs no es troben naturalment en l'ambient, sinó que són substàncies generades en els processos tecnològics. Es van sintetitzar per primera vegada en un laboratori a l'any 1929 als Estats Units. La seva fabricació produeix una mescla de compostos, les propietats dels quals depenen del grau de cloració. En general, són estables tèrmica, química i biològicament, amb una elevada constant dielèctrica, insolubles en aigua, podent mesclar-se amb olis i, sent altament resistents al foc. Per això, es van utilitzar com aïllants per equips elèctrics com transformadors i termòstats. Es van utilitzar durant anys en nombroses aplicacions industrials com la fabricació d'adhesius, vernissos, plastificadores, alguicides i molusquicides.

Entre 1929 i 1977 es van produir mundialment un total d'un milió dos-centes mil tones de PCBs. Per les seves característiques ignífugues, la majoria dels olis dielèctrics amb PCBs es van utilitzar fonamentalment en llocs amb alt risc d'incendi, tals com plantes industrials i indústries petroquímiques (Helm i Bidleman, 2003).

L'any 1977 es va prohibir la fabricació i l'ús dels PCBs, degut a que les propietats que els feien tan útils (estables a la combustió normal, a les reaccions químiques i a la degradació biològica), produïa un gran impacte ambiental pel seu caràcter acumulatiu i persistència, la qual augmentava a mida que incrementava el grau de cloració. A més a més, els PCBs també podien produir subproductes tòxics com les PCDD/Fs (Aoki, 2001).

Degut a la seva potencial toxicitat en humans, el Departament d'Indústria, Comerç i Turisme de la Generalitat de Catalunya, seguint la Directiva 85/467 de la Unió Europea, dictà una Ordre (DOGC, 1986) en la que es prohibeix la utilització en instal·lacions industrials d'aparells o fluids que continguin PCBs (a excepció dels monoclorats i diclorats).

Persistència

Els PCBs són compostos amb una elevada solubilitat en lípids, per tant tenen tendència a acumular-se en el teixit adipós. Degut a les seves propietats físiques i químiques, els PCBs tendeixen a ser adsorbits en les partícules de l'aire, sòls i sediments. Encara que l'aire és el compartiment ambiental on es degraden més fàcilment, s'han suggerit unes vides mitjanes que oscil·len entre els 2 i els 6 anys depenent del grau de cloració (Sweetman i Jones, 2000; Meijer i col·ls., 2003). En aquest compartiment es considera que la fotodegradació és el mecanisme d'eliminació més important (Lin i col·ls., 1995). En aigua, els PCBs també s'adsorbeixen a les partícules on poden romandre durant anys (Gouin i col·ls., 2004). Finalment, degut a l'elevada afinitat pels sòls i els sediments, aquests actuen com a reservoris. S'observen elevades vides mitjanes en aquest medi especialment pels compostos més pesats (Sinkkonen i Paasivirta, 2000).

Bioacumulació

Els PCBs són compostos molt hidrofòbics amb elevada solubilitat en lípids, per tant, tendeixen a acumular-se en en el teixit adipós. La seva constant de distribució octanol/aigua varia de Log K_{ow} 5.6 a 7 dels tri- als hepta- PCBs (Mackay i col·ls., 1992). Degut a la seva capacitat de solubilitzar-se en lípids i l'elevada persistència es produeix bioacumulació i biomagnificació al llarg de la cadena alimentaria, augmentant els seus efectes toxicològics en els organismes. Pel que fa a les vides mitjanes biològiques, existeix una gran divergència sobre els diferents congèneres de PCBs. Es pensa que les vides mitjanes de barreges comercials de PCBs en el cos humà poden anar dels 2 als 6 anys (Shirai i Kissel, 1996). Tot i això, si es valoren els diferents congèneres individualment aquests valors poden variar molt. Per exemple, la vida mitjana del PCB- 153 s'estima en 12.4 anys, mentre que la del PCB-28 s'estima en 1.4 anys (Brown, 1994).

Long-range transport

Com les PCDD/Fs, els PCBs tenen molta tendència a ser adsorbits en les partícules de l'aire i per tant a desplaçar-se fins a distàncies molt llargues. Això, fa que s'hagin detectat concentracions de PCBs en aire i altres compartiments d'àrees molt remotes com a l'Àrtic i muntanyes allunyades de qualsevol font (Carrera i col·ls., 2001; Corsolini i col·ls., 2002; Evenset i col·ls., 2004; Grimalt i van Drooge, 2006; Nizzetto i col·ls., 2006).

Naftalens policlorats (PCNs)

Els naftalens policlorats (PCNs) són una família de 75 congèneres formats per un naftalè al que hi han units de un a vuit àtoms de clor. A tall d'exemple, es presenta a la Figura 3 l'estructura química del triclornaftalè. Les propietats físiques i químiques dels PCNs són molt semblants a les dels PCBs. Són hidrofòbics, i molt estables química i tèrmicament. A més a més, són bons aïllants elèctrics i retardants de flama (Falandysz, 1998).

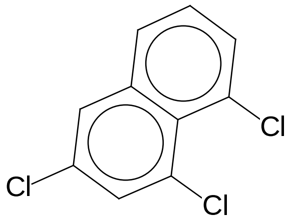

Figura 3. Estructura química del triclornaftalè.

Toxicitat i Efectes sobre la salut

Hi ha poca literatura referent a la toxicitat dels PCNs. Tot i això, el que sí s'ha determinat és que, com d'altres COPs, el mecanisme d'acció de la seva toxicitat es produeix a través del receptor de l'aril hidrocarboni (AhR) (Blankenship i col·ls., 2000). D'acord amb episodis d'intoxicació humana, els efectes que produeix l'exposició a PCNs són: cloracné, carcinogènesi, teratogènesi i inclús mortalitat (Hayward, 1998). Tot i això, el fet que sempre apareguin junt amb PCBs i PCDD/Fs pot haver fet que es sobreestimi el potencial de produir efectes adversos dels PCNs (Blankenship i col·ls., 2000).

Com en el cas de les PCDD/Fs i els PCBs, els PCNs generalment es troben en forma de barreges de diferents congèneres. Per caracteritzar la toxicitat dels PCNs, s'han establert valors de TEF per alguns congèneres. S'ha establert que els PCNs són de 3 a 6 ordres de magnitud menys tòxics que les PCDD/Fs, mentre que la seva potència és similar a la dels PCBs (Van den Berg i col·ls., 2000). Entre ells, alguns congèneres hexa-CNs són els més potents amb un TEF de 0.002 (Blankenship i col·ls., 2000). Tot i això, degut a la falta de dades suficientment fiables, la toxicitat dels PCNs s'ha classificat per només pocs congèneres (Kannan i col·ls., 2001; Eljarrat i Barcelo, 2003).

Fonts

Una de les fonts ambientals més importants de PCNs, especialment a l'hivern, són els processos tèrmics (Takasuga i col·ls., 2004). S'han trobat PCNs en els gasos i les cendres de diferents incineradores d'Espanya i Alemanya (Jarnberg i col·ls., 1993; Schneider i col·ls., 1998; Abad i col·ls., 1999). Al Canadà, les combustions suposen un 54 % de l'alliberament de PCNs a l'aire (Helm i Bidleman, 2003). També s'apunta als processos clor-àlcali com a fonts importants de PCNs (Jarnberg i col·ls., 1993; Kannan i col·ls., 1998). Altres fonts són les formulacions tècniques de PCBs en les quals s'estima que es produeixen 169 tones de PCNs com a subproducte (Yamashita i col·ls., 2000).

Històricament s'han produït diferents pics de residus de PCNs d'acord amb el seu grau de cloració. L''input" més elevat de penta i hexa-CNs es va produir abans del 1944, mentre que els pics dels tetra- i tri-CNs no es van produir fins als anys 50 i 70, respectivament (Meijer i col·ls., 2001). Malgrat això, s'ha observat un augment significatiu per molts dels congèneres associats amb combustions, cosa que fa pensar que avui en dia les fonts asociades a combustions són més importants que en el passat (Jarnberg i col·ls., 1993; Meijer i col·ls., 2001). A més, no s'ha observat cap descens en els nivells de PCNs des de l'inici dels 90 fins al 2001, a diferència del dels observats pels PCBs en el mateix període (Lee i col·ls., 2005).

Bioacumulació

De l'elevada constant de distribució octanol/aigua (K_{ow}) se'n pot deduir la seva capacitat de biomagnificació. La constant de distribució octanol/aigua, és especialment significativa pels homòlegs hexa- i hepta-CNs (Log K_{ow} està entre 3.90 i 8.3) (Harner i Bidleman, 1998).

Els experiments de bioacumulació s'han centrat bàsicament en la determinació dels factors de bioconcentració (BCF) d'algunes espècies aquàtiques (Domingo, 2004), on s'han sobrepassat valors de BCF de 20,000 (Opperhuizen i col·ls., 1985). Es pensa que els PCNs es biomagnifiquen al llarg de la cadena alimentària i que finalment s'acumulen en alguns teixits i fluids humans (Hanari i col·ls., 2004).

Persistència

Les dades sobre el temps de residència dels PCNs en aigua, sòls i sediments són molt limitades. De fet, les vides mitjanes només s'han establert pels mono- i di-CNs, amb valors de 38 a 104 dies (Crookes i Howe, 1993).

Long Range Transport

Durant la preparació del protocol de la Convenció Europea sobre *Long-Range Transboundary Air Pollution* de compostos orgànics persistents de la Comissió Econòmica de Nacions Unides (UN-ECE LRTAP-POPs Protocol) del 1998, els PCNs no van ser inclosos dintre de la llista dels "dirty dozen" degut a la falta de dades adequades (Van de Plassche i col·ls., 2002). Tot i això, els coneixements científics obtinguts els anys recents fan que els PCNs hagin esdevingut candidats a allargar la llista de químics a restringir (Domingo, 2004; Denier van der Gon i col·ls., 2007). Harner i. col·ls (1998) van dur a terme el primer estudi sobre els nivells de PCNs en aire a l'Àrtic. Per altra banda, també s'han publicat recentment els nivells ambientals determinats en dos estacions sueques properes al cercle polar (Egebäck i col·ls., 2004), així com en foques a Alaska (Wang i col·ls., 2007).

Hexaclorobenzè (HCB)

L'hexaclorobenzè (Figura 4) és un fungicida organoclorat introduït per primer cop al 1945, que s'utilitzà principalment per evitar que el blat fos atacat pel "carbó del blat" i pel tractament de sòls. Molts països en desenvolupament encara l'utilitzen per fumigar el blat.

Actualment, l'HCB s'utilitza com a plastificant i com a additiu de conservants per a la fusta, sent un producte bàsic important per a la síntesi de diferents compostos orgànics clorats. L'HCB no existeix en el medi ambient de forma natural, sinó que s'obté per la cloració de benzens poc clorats, sent la base per a la producció de pentaclorofenol. També es pot obtenir com a subproducte de la cloració industrial d'hidrocarburs. Per tant, l'HCB ingressa al medi ambient per combustió de productes que contenen clor (per exemple, la incineració), o mitjançant l'ús de pesticides contaminats amb aquesta substància (Breivik i col·ls., 2004; Lönnermark i col·ls., 2008).

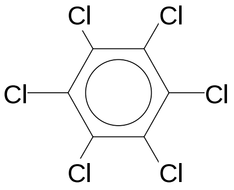

Figura 4. Estructura química de l'hexaclorobenzè.

L'HCB és absorbit en el tracte gastrointestinal, es metabolitza lentament i s'acumula en el teixit adipós. Quan es mobilitza el teixit adipós, l'HCB es remobilitza, i llavors es pot trobar en tots els òrgans. L'exposició prolongada a aquesta substància ha produït en alguns casos malalties cutànies, lesions hepàtiques i símptomes neurològics en rates. En ratolins, s'han observat efectes immunotòxics i infeccions virals pneumòniques i hepàtiques (ATSDR, 2002a).

El Departament de Serveis Humans i de la Salut (DHHS, USA) ha determinat que l'HCB podria ser potencialment cancerigen, ja que en estudis fets en animals intoxicats per HCB, ha causat càncer de fetge, ronyó i tiroides. Per tant, hi ha una evidència molt forta de que pugui causar càncer en les persones, encara que no s'han trobat efectes mutagènics ni teratogènics.

Un dels biomonitors més utilitzat en l'exposició a HCB és la sang (ATSDR, 2002a).

Clorofenols (CLPs)

Els clorofenols són una família de 19 compostos diferents, dels quals el pentaclorofenol (PCP) (Figura 5) és el més important del grup . Degut a l'ampli espectre de propietats antimicrobianes dels clorofenols, s'han utilitzat per la protecció de la fusta, pintures, fibres vegetals i cuir, i com desinfectants. També s'apliquen com a herbicides, fungicides i insecticides, així com agents intermediaris en la fabricació de productes farmacèutics i tintures.

La majoria dels clorofenols s'obtenen per cloració directa del fenol utilitzant gas de clor, havent-hi en el producte final impureses d'altres isòmers del clorofenol amb més o menys clor. Per tant, depenent de les condicions de procés, els clorofenols més pesats poden generar baixes concentracions de policlorfenoxifenols i PCDD/Fs, podent-se produir emissions en la seva fabricació, emmagatzematge, transport i aplicació (Messerer i col·ls., 1998).

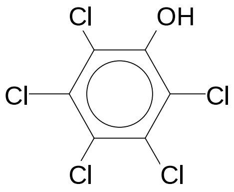

Figura 5. Estructura química del pentaclorofenol.

Els clorofenols poden ser absorbits pels pulmons, pel tracte gastrointestinal i per la pell. Aproximadament el 80% és expulsat pels ronyons sense haver sofert cap transformació. La seva toxicitat depèn del grau de cloració, de la posició dels àtoms de clor i de la puresa de la mostra, podent causar a dosis baixes irritacions en els ulls i les vies respiratòries. Les dosis tòxiques produeixen convulsions, coma i finalment la mort. Desprès de repetides administracions, les dosis tòxiques poden afectar als òrgans interns i la medul·la òssia. Respecte al pentaclorofenol (PCP), en experiments amb animals s'ha observat que aquest exerceix un efecte tòxic sobre els embrions, pels quals concentracions altes són letals.

Degut a estudis fets en animals, els quals demostren un increment de risc de càncer, especialment en el fetge, l'Agència Internacional de Recerca del Càncer (IARC) ha considerat que el PCP és un possible carcinògen humà, mentre que l'Organització Mundial de la Salut (OMS, 1977) no descarta el seu potencial mutagènic.

Els millors biomonitors utilitzats per l'exposició als clorofenols són els nivells a la sang i l'orina (ATSDR, 1994). Els CLPs també s'utilitzen com a biomonitors indirectes a l'exposició actual a substàncies organoclorades.

1-Hidroxipirè (1-HP)

Els HAPs es produeixen durant la combustió incompleta i piròlisi de matèria orgànica. Les majors emissions es produeixen en el fum dels tubs d'escapament dels automòbils, fum de tabac, combustions industrials, i un llarg etc. (Jongeneelen, 2001). L'1-hidroxipirè (1-HP) és un metabòlit urinari dels hidrocarburs aromàtics policíclics (HAPs),i per tant, és considerat un biomarcador de la seva exposició (Göen i col·ls., 1995; Li i col·ls., 2000).

En base a estudis epidemiològics l'Agència Internacional de Recerca sobre el Càncer (IARC) ha considerat que certs tipus d'exposicions industrials als HAPs són potencialment carcinogèniques per al ser humà, donant lloc a diferents tipus de càncer, principalment pulmonar i cutani (IARC, 1983).

El biomonitor més corrent utilitzat per l'exposició a HAPs és la concentració en l'orina d'1-hidroxipirè (Göen i col·ls., 1995; Li i col·ls., 2000).

1.2.2. Metalls pesants

Arsènic

L'Arsènic (As) és un element que es classifica com a metal·loide ja que presenta propietats de metall i de no-metall. Aquest element es troba de forma natural a l'escorça terrestre amb uns nivells entre 2 i 5 mg/kg (ATSDR, 2000a). Tot i això, normalment les fonts antropogèniques són molt més importants que les naturals. Una de les principals vies d'entrada d'aquest element als sòls primer, i després a l'aigua, és mitjançant la utilització de fertilitzants i pesticides en agricultura (Basu i col·ls., 2001). L'alliberament a l'aire es produeix principalment per la combustió de carbó i fusta, la mineria, al fondre metalls i en la incineració de residus.

L'arsènic es pot trobar tant en forma inorgànica com orgànica. Mentre que les formés inorgàniques, As_2O_3, As_2O_5 or AsH_3, són les més tòxiques, l'arsènic orgànic, molt menys tòxic, s'origina com a forma de detoxificació per la biotransformació a través de diferents organismes (Pongratz, 1998).

L'exposició no ocupacional a aquest compost es produeix bàsicament a través de la ingesta d'aliments, especialment de peix i marisc. Afortunadament el percentatge d'arsènic inorgànic (normalment en forma d'arseniobetaina) és notablement major en comparació amb l'As inorgànic (Fattorini i col·ls., 2004).

Els compostos d'As han estat reconeguts com a carcinògens en humans (Grup 1) en base a diferents evidències (IARC, 1987). Estudis epidemiològics han revelat una relació entre concentracions elevades d'As en aigua i elevades incidències de càncer de pell (Rossman i col·ls., 2004). Així mateix, s'ha establert una correlació positiva entre la inhalació d'As i el càncer de pulmó. També s'ha associat aquest element al desenvolupament de càncer de fetge, ronyó i bufeta (Huff i col·ls., 2000). Els factors de potència cancerígena oral i per inhalació s'han establert en 1.5 i 15 $(mg/kg/dia)^{-1}$, respectivament (US EPA, 2007). Els efectes no cancerígens a l'exposició a As inclouen desordres a la pell, així com problemes al sistema nerviós i cardiovascular. La dosi de referència estimada (RfD) per exposicions orals cròniques i subcròniques és $3{\cdot}10^{-4}$ mg/kg/dia (US EPA, 2007).

Beril·li

El beril·li (Be) és un metall que es troba de forma natural en roques, carbó, sòls i pols volcànica. La població general està exposada a nivells baixos de beril·li a través de l'aire, els aliments i l'aigua.

L'exposició a nivells elevats de Be (superiors a 1,000 µg/m³) pot produïr símptomes similars als de la pulmonia. En general, però, és improbable que la població general desenvolupi malaltia crònica per beril·li perquè els nivells ambientals d'aquest metall normalment són molt baixos (0.00003-0.0002 µg/m³) (ATSDR, 2002b).

No s'han descrit efectes després de la ingestió de beril·li en humans donat que molt poc Be és absorbit per l'estómac i els intestins. El contacte amb la pell pot causar úlceres i granellada (ATSDR, 2002b). La dosi de referència oral és $2{\cdot}10^{-3}$ mg/kg/dia i per inhalació $5.7{\cdot}10^{-6}$ mg/kg/dia (US EPA, 2007). L'Agència Internacional de Recerca sobre el Càncer (IARC) ha determinat que el Be és carcinogènic en humans. L'EPA ha determinat que el Be és probable carcinògen en humans (Grup 2) i li ha assignat un factor de potència cancerígena de 8.4 $(\text{mg/kg/dia})^{-1}$ (US EPA, 2007).

Cadmi

El cadmi (Cd) és un element no essencial des del punt de vista nutricional. Es genera com subproducte al fondre altres metalls com el zinc, el coure o el plom. Té una excel·lent resistència a la corrosió, i per això un gran percentatge de la quantitat que es consumeix s'utilitza per protegir (galvanitzar, etc.) altres metalls. Una quantitat respectable s'utilitza per preparar pigments per la fabricació de pintures i plàstics i com estabilitzant d'aquests últims. Les propietats mecàniques de certs aliatges de coure milloren amb l'addició de cadmi, i el seu ús és estès en la fabricació de bateries alcalines (Baldwin i Marshall, 1999).

L'absorció per la pell és mínima, mentre que l'absorció gastrointestinal és del 5% de la quantitat ingerida, encara que pot pujar fins el 20% en cas de deficiència de ferro o de poc aportament de calci. Per via pulmonar, pot arribar al 50% depenent de la grandària de la partícula i de la seva solubilitat (Robards i Worsford, 1991).

La dieta i el tabac juguen un paper important en l'exposició a Cd (McElroy i col·ls., 2006). Algunes gramínies, com l'arròs o el blat, concentren selectivament el cadmi present al sòl i a les aigües. Així doncs, la contaminació mediambiental pot arribar a l'home si aquests aliments són consumits. Un del majors episodis massius d'intoxicació per cadmi, va ser la malaltia Itai-Itai al Japó, a finals de la Segona Guerra Mundial, pel consum d'arròs i aigua contaminats (Kasuya, 2000).

El ronyó és l'òrgan principalment agredit per l'exposició crònica al cadmi. Els efectes de la inhalació inclouen també emfisema pulmonar, anèmia lleugera, disfunció del metabolisme hepàtic, del calci, del fòsfor i de la vitamina D. Aquests porten associats: osteoporosi, osteomalàcia i formació de càlculs renals càlcics (Satarug i Moore, 2004). Altrament, el fetge és l'òrgan diana pel cadmi a l'hora de dipositar-se, alterant la seva funció hepàtica subclínica, i cursant sovint amb lleugera elevació sèrica dels enzims hepàtics (Satarug i Moore, 2004).

Per últim, cal constatar que al llarg de nombrosos estudis epidemiològics, està comprovat que els individus exposats durant llargs períodes de temps a Cd tenen un risc més elevat que la població general de contraure càncer de pròstata, pulmó o pit (Elghany i cols. 1990; Collins i cols. 1992 (McElroy i col·ls., 2006) .

Les dosis de referència oral i per inhalació són $5{\cdot}10^{-4}$ i $5.7 \cdot 10^{-5}$ mg/kg/dia (US EPA, 2007). Aquest element ha estat classificat per la IARC com a cancerigen per humans (Grup 1), i probable cancerigen per humans per la US EPA (Grup B1). S'ha estimat un factor de potència cancerígena per inhalació de 6.3 (mg/kg/dia)$^{-1}$ (US EPA, 2007).

Cobalt

El cobalt (Co) es troba de forma natural en roques, sòls, aigua, plantes i animals. El Co s'utilitza per fer aleacions per la manufactura de motors d'avions, imans, eines per triturar i tallar, i en articulacions artificials de genoll i maluc. Els compostos de Co també s'utilitzen per acolorir vidres, ceràmiques i pintures i per assecar esmalts i pintures sobre porcellana.

Normalment el Co s'allibera a l'ambient des de fonts naturals i al cremar carbó o petroli, o durant la producció d'aleacions de cobalt. Un cop a l'aire, el cobalt s'associa a partícules que es dipositaran als sòls al cap d'uns dies.

El Co té efectes beneficiosos (forma part de la vitamina B_{12}) i perjudicials per a la salut humana. L'exposició a nivells alts de cobalt pot tenir efectes en pulmons i cor (Linna i col·ls., 2003). També pot produir dermatitis. En animals exposats a nivells elevats de cobalt també s'han observat efectes en fetge i pulmons (ATSDR, 2004b).

No s'ha observat que el cobalt no radioactiu produeixi càncer en humans o en animals després de l'exposició a través dels aliments o de l'aigua. Tot i això s'ha observat càncer en animals després de l'exposició a través de la respiració. Basant-se en dades de laboratori la IARC ha determinat que el Co i els seus compostos són possibles carcinogens en humans. Pel Co, l'EPA ha establert una dosi de referència oral de $2 \cdot 10^{-2}$ mg/kg/dia, per inhalació de $5.7 \cdot 10^{-6}$ mg/kg/dia i un factor de potència cancerígena per inhalació de 9.8 (mg/kg/dia)$^{-1}$ (US EPA, 2007).

Coure

El coure (Cu) és un metall que es troba de forma natural en roques, sòls, aigua i aire. El Cu és un element essencial pels animals i les plantes i per tant, necessari per a la vida. S'utilitza per fabricar molts productes com filferro o aixetes. S'usa també en agricultura per tractar malalties de les plantes. Un cop alliberat al medi ambient, el Cu s'adhereix a partícules de matèria orgànica dels sòls.

Nivells elevats de Cu poden ser perjudicials per la salut. La inhalació de concentracions elevades pot produir irritació del nas i la gola. La ingestió de nivells elevats de coure pot produir nàusees, vòmits i diarrea. Quantitats molt elevades poden danyar el fetge, ronyons i poden causar fins i tot la mort (ATSDR, 2004a). L'EPA ha establert una dosi de referència oral de $3.7 \cdot 10^{-2}$ mg/kg/dia (US EPA, 2007). No se sap si el Cu pot produir càncer en els humans. L'EPA ha determinat que el coure no és classificable en quant a carcinogeneitat en éssers humans (US EPA, 2007).

Crom

El crom (Cr) és un element natural que es troba a la superfície de les roques, els sòls, i el mar. Avui en dia, el crom està àmpliament difós a la indústria i el seu ús és força extens.

Com a metall no té toxicitat, però els seus productes d'oxidació (àcid cròmic, cromats, bicromats) són molt tòxics per la seva acció càustica. Els efectes tòxics més importants estan lligats a la presència de crom trivalent, i especialment l'hexavalent (més tòxic), els quals són agents desnaturalitzants de les proteïnes i precipitants dels àcids nuclèics, eliminant-se molt lentament per l'orina (Singh i col·ls., 1998; Vaglenov i col·ls., 1999).

Les manifestacions de la seva toxicitat cutània consisteixen en dermatosis, presentant-se en forma d'úlcera cutània o dermatitis al·lèrgica. També pot aparèixer, per inhalació, inflamació de les vies respiratòries (ATSDR, 2000b; Corbella, 2000).

En base a diferents estudis que mostraven evidències suficients de que l'exposició a Cr (VI) provoca càncer de pulmó, el Cr hexavalent ha esta classificat per la IARC (1990) com a carcinogènic per humans (Grup 1). L'EPA (1999) ha catalogat la forma hexavalent del Cr com a carcinogen humà conegut, i per tant ha establert un factor de potència cancerígena per inhalació de 42 $(mg/kg/dia)^{-1}$ (US EPA, 2007). L'exposició crònica a Cr (VI) pot produir efectes no cancerígens al fetge i ronyó i als sistemes gastrointestinal i immunològic. A més, després de l'exposició a aquest metall poden aparèixer efectes perjudicials en la pell (com dermatitis i ulceres). S'ha suggerit un valor de $3{\cdot}10^{-3}$ mg/kg/dia (US EPA, 2007).

Estany

L'estany (Sn) és un metall no soluble en aigua. Està present en el llautó, el bronze i en alguns materials per a soldar. L'estany metàl·lic s'usa per revestir llaunes d'aliments, begudes i aerosols. Compostos inorgànics d'estany s'usen en pastes dentals, perfums, sabons, additius per a aliments i colorants. Compostos orgànics d'estany s'usen per fabricar plàstics, envasos per a aliments, canonades plàstiques, plaguicides, pintures i repel·lents d'animals. L'estany és alliberat al medi per processos naturals i per activitats humanes com la mineria, la combustió de petroli i carbó i la producció i ús de compostos d'estany. A l'atmosfera, l'estany pot existir en forma vapor i també s'adhereix a partícules de pols i després als sòls. Els compostos orgànics de l'estany són bioacumulables, poden acumular-se en peixos i en altres animals i plantes.

L'estany metàl·lic no és gaire tòxic ja que s'absorbeix poc en el tracte gastrointestinal. Estudis en éssers humans han demostrat que la ingestió de grans quantitats de compostos inorgànics d'estany pot produir dolor d'estómac, anèmia i alteracions en el fetge i els ronyons. La inhalació de compostos orgànics d'estany pot produir efectes neurotòxics. En casos greus pot causar la mort (ATSDR, 2005a). Alguns compostos orgànics d'estany afecten al sistema immunitari en animals però no s'ha avaluat el seu efecte en humans. Alguns estudis en animals també han demostrat que aquests compostos afecten a la reproducció. Tampoc s'ha avaluat en humans. El contacte amb la pell o ulls de compostos orgànics o inorgànics d'estany pot produir irritació (ATSDR, 2005a). S'ha establert una dosi de referència oral de $6.0 \cdot 10^{-1}$ mg/kg/dia (US EPA, 2007). No hi ha cap evidència que l'estany o els seus compostos produeixi càncer en éssers humans. Els estudis de compostos inorgànics en animals han estat negatius. La IARC i l'EPA no han classificat l'estany metàl·lic ni els seus compostos inorgànics en quant a carcinogeneitat (US EPA, 2007).

Manganès

El manganès (Mn) és un element que es troba de forma natural a l'ambient, generalment en forma d'òxids. Es troba en sòls, aire, aigua i aliments. Les fonts antropogèniques de Mn inclouen plantes de producció de ciment, centrals elèctriques, incineració de residus i combustió de fuels fòssils (ATSDR, 2000d).

En humans, el Mn és un element essencial. La ingesta a través dels aliments és la principal via d'exposició no ocupacional. L'exposició ocupacional es produeix bàsicament per la inhalació de pols. La inhalació crònica de manganès provoca primerament efectes en el sistema nerviós (Josephs i col·ls., 2005).

Es recomana utilitzar una dosi de referència de $4.7 \cdot 10^{-2}$ mg/kg/dia. No hi ha dades que confirmin que el Mn causi càncer en humans. Per això, l'EPA, no el classifica com a metall cancerigen (US EPA, 2007).

Mercuri

Les fonts de mercuri (Hg) són tant naturals com antropogèniques. El Hg és un metall líquid a temperatura ambient, sent l'únic metall que es manté líquid a 0ºC. Per la seva alta volatilitat i baix punt d'ebullició es troba en fase gas en l'atmosfera (Chang i col·ls., 2000). La seva combinació amb altres elements com oxigen, sofre o clor poden originar formes de mercuri inorgàniques. El Hg també es pot combinar amb carboni formant compostos de mercuri orgànic. El més comú és el metil-mercuri, el qual és produït per microorganismes en el sòl i l'aigua (ATSDR, 1999).

Les incineradores de residus hospitalaris, les de residus municipals, les cimenteres i les plantes de clor-àlcali són importants causants de concentracions de vapor mercuri a l'atmosfera (Chang i col·ls., 2000). Per tant, moltes de les exposicions ocupacionals tenen lloc per inhalació de vapors de mercuri. Les exposicions cròniques a baixes concentracions de mercuri són més comuns (Karimi i col·ls., 2002).

La intoxicació més important per metil-mercuri es va produir per la ingesta de peix contaminat durant almenys 20 anys a la badia de Minamata al Japó. Els desordres neurològics ocasionats per aquesta intoxicació van rebre el nom de malaltia de Minamata (Ekino i col·ls., 2007).

En alguns països, l'ús de Hg com fungicida ha donat alguns problemes. Així mateix, l'ús de mercuri en les amalgames dentals ha estat causa de sobreexposicions, sobretot als operaris que les manipulen, més que als pacients que les porten. Afortunadament, les normes i costums dels dentistes i operaris dentals s'han modificat al llarg del temps, han après a manipular l'element de manera cada vegada més segura, i en els últims anys el risc ha estat molt menor que abans (King, 1988).

Els efectes del mercuri depenen altament de les seves diferents formes químiques. El sistema nerviós és molt susceptible a totes les formes de mercuri. El metil-mercuri i els vapors del mercuri metàl·lic són més nocius que d'altres formes, ja que una major quantitat d'aquestes formes de mercuri arriben al cervell. L'exposició a nivells alts de mercuri metàl·lic, inorgànic o orgànic poden causar danys als ronyons, el cervell i al fetus (ATSDR, 1999). L'expressió neurològica de la intoxicació per mercuri inclou tremolor involuntària de les extremitats, llengua i llavis; trastorns psicològics com nerviosisme, irritabilitat, comportament reservat patològic (eretisme), confusió mental, i polineuropatia perifèrica que afecta més a les extremitats superiors que a les inferiors (Horng i col·ls., 1999).

L'EPA ha classificat tant al mercuri inorgànic com al metil-mercuri dintre Grup C, és a dir possibles carcinògens humans, mentre que el mercuri metàl·lic seria no carcinogen humà (Grup D). Pel mercuri i els seus compostos s'ha establert una dosi de referència de $3 \cdot 10^{-4}$ mg/kg/dia (US EPA, 2007).

Níquel

Els principals usos del níquel (Ni) són industrials. Inclouen la fabricació d'acer i altres aliatges i superaliatges, i el galvanitzat. S'utilitzen, en menor quantitat, per la fabricació de ferro colat, productes químics, bateries, ceràmiques i com a catalitzador industrial. Així mateix, és considerat com a element essencial per l'home, encara que no s'ha caracteritzat la seva deficiència específica.

La major part de l'exposició laboral a Ni té lloc per via inhalatòria a partir dels fums o la pols, o bé per via dèrmica per contacte de la pell amb aliatges, sals o dissolucions (ATSDR, 2005b). Entre els treballadors de refinament de Ni es demostra una incidència més alta de càncer de pulmó i cavitats nasals. Alguns estudis diuen que aquests treballadors pateixen un risc superior de contraure altres tipus de processos malignes com el càncer de laringe, estómac, pròstata, ronyó i sarcoma de teixits tous. En el cas dels càncers més freqüents, el pulmonar i el nassal, sembla provat que indiquen el pas del flux d'aire i de deposició de partícules que en ell s'hi continguin

(Yokota i col·ls., 2007). La US EPA ha establert una dosi de referència per les sals solubles de níquel de $2 \cdot 10^{-2}$ mg/kg/dia (US EPA, 2007). Pels efectes carcinogènics, s'ha donat un factor de potència cancerígena per inhalació de la pols de níquel de refineria de $8.4 \cdot 10^{-1}$ $(mg/kg/dia)^{-1}$ (US EPA, 2007).

Plom

El plom (Pb) és un metall molt conegut des de l'antiguitat. Per la seva mal·leabilitat i el seu baix punt de fusió, els homes l'han usat des de la prehistòria per fer estatuetes, joies, canalitzacions d'aigua i gerres per beure. Així mateix, les seves sals són apreciades pels seus brillants colors. Actualment, és molt usat en la indústria per fabricació de pigments, recobriments, recipients, ungüents i piles elèctriques.

Els efecte tòxics del Pb són els mateixos si s'ingereix o s'inhala. El plom pot afectar quasi tots els òrgans i sistemes del cos, però el més sensible és el nerviós, tant en adults com en nens. L'exposició prolongada en adults pot deteriorar algunes funcions del sistema nerviós (Finkelstein i col·ls., 1998). L'exposició crònica en nens, s'associa a problemes de comportament, dificultat en l'aprenentatge i hiperactivitat (Torrente i col·ls., 2005). També pot produir debilitat als dits, canells i turmells. L'exposició a plom produeix un augment de la pressió sanguínia, pot causar anèmia (Navas-Acien i col·ls., 2008) i danys als ronyons (dos Santos i col·ls., 1994). La IARC ha classificat el plom com a possible carcinogènic en humans (Grup 2B) (IARC, 1987).

Tal·li

El tal·li (Tl) és un metall que es troba en quantitats molt petites a l'escorça terrestre. S'utilitza principalment en la fabricació d'articles electrònics, interruptors i terminals, principalment en la indústria dels semiconductors. També s'utilitza, encara que de forma limitada, en la fabricació de vidres especials i en certs procediments mèdics. El Tl entra al medi ambient principalment al cremar carbó i des de fundicions, en ambdós casos com a contaminant de la matèria crua. El tal·li es bioacumula, és a dir, és absorbit per les plantes i entra a la cadena alimentària.

L'exposició a nivells elevats de Tl pot produir efectes perjudicials per la salut. En un estudi en treballadors exposats durant diversos anys a la inhalació de tal·li es van observar efectes en el sistema nerviós (Saha, 2005). En estudis de població que ha ingerit grans quantitats de tal·li durant un període breu s'han descrit vòmits, diarrea, caiguda temporal del cabell i efectes en el sistema nerviós, els pulmons, cor, fetge i ronyons (Saha, 2005). El Tl també ha causat la mort. Els efectes a la ingestió de tal·li durant períodes llargs de temps no es coneixen. En estudis amb rates exposades a alts nivells de tal·li es van observar alteracions en el desenvolupament. No hi ha informació disponible, ja sigui en humans o en animals, sobre els efectes del contacte del tal·li amb la pell (ATSDR, 1992b). La US EPA ha establert una dosi de referència oral de $7.0 \cdot 10^{-5}$ mg/kg/dia (US EPA, 2007). No hi ha estudis en humans o animals sobre els efectes carcinogènics de la inhalació, ingestió o contacte dèrmic del tal·li. Ni la IARC ni la US EPA han classificat al tal·li en quant a carcinogènesi en éssers humans (US EPA, 2007).

Vanadi

El vanadi (V) és un metall de color gris clar o blanc brillant. El vanadi i els seus compostos es troben a l'escorça terrestre i les roques, i es recupera com subproducte de mineria d'altres metalls. L'utilització més abundant del metall és en aliatges amb ferro, molibdè i alumini, i per formar part del bronze i del llautó. Quantitats més modestes són utilitzades com a catalitzadors, per fer ceràmiques, en processos de tenyit, insecticides, revelat fotogràfic, televisors en color i per la producció de vidre. El petroli n'és relativament ric, i la combustió de grans masses representa un aportament considerable al medi ambient. La inhalació de pols o fums, particularment de pentòxid, és la forma més freqüent d'exposició laboral (ATSDR, 1992a).

S'absorbeix principalment per via respiratòria i es distribueix per tots els teixits, a través de la sang, per on circula unit a la transferrina. Es troba sobretot en teixit ossi, en forma de metavanadat, més soluble. També s'uneix al fetge i al pulmó, i s'elimina lentament. La major quantitat de vanadi és eliminada pel ronyó. El patró de resposta més clàssic a l'exposició laboral a pols amb alt contingut de vanadi és la irritació del tracte respiratori superior. Depenent de la concentració en l'aire, els símptomes apareixen al cap d'unes hores de l'exposició. La resposta específica inclou: tos, respiració forçada, irritació dels ulls, nas i gola, bronquitis hemorràgica i més rarament pneumonitis química (Corbella, 2000).

S'ha definit una dosi oral de referència de $5 \cdot 10^{-3}$ mg/kg/dia. Per altra banda, el vanadi no s'ha vist implicat en processos carcinogènics (US EPA, 2007).

1.3 Avaluació de riscos

Per avaluació de riscos s'entén el procés o procediment utilitzat per estimar la probabilitat que es produeixin efectes adversos sobre la salut humana o sistemes ecològics per l'efecte d'agents químics o físics sota una sèrie de condicions (Paustenbach, 2002). D'acord amb Friess, (1987) el que coneixem per avaluació de riscos va començar aproximadament cap als anys 30. En aquesta època es va establir als Estat Units i Europa la necessitat de protegir als éssers humans dels efectes adversos produïts per productes químics en el lloc de treball, o a través dels aliments o del medi ambient.

Des dels anys 70 el camp de l'avaluació de riscos ha rebut molta atenció entre la comunitat científica i la reguladora, així com per la població general (Starr, 1969). A la dècada dels 80, va començar a incrementar-se l'interès donat que l'avaluació del risc podia ajudar a posar ordre al que fins al moment semblava una quantitat de dades científiques i mèdiques no manejable (referents als potencials perills d'agents físics i químics al medi ambient). A més, s'esperava que les metodologies d'avaluació de riscos ajudessin als reguladors a prendre millors decisions. Es pretenia obtenir una millora significativa en la formulació de decisions sobretot respecte als anys 50, quan els científics només donaven el "blanc o negre", "sí, ho és", "no ho és" com a resultat dels tests de toxicitat. L'avaluació de riscos va guanyar popularitat perquè oferia un rang d'opcions, cadascuna amb el seu cost i benefici específic, tant als gestors del risc, com als legisladors i a la població (Graham i Hartwell, 1997).

Des dels anys 90, el camp de l'avaluació de riscos ha madurat de forma significativa. S'han fet avaluacions de riscos d'incineradores, de vessaments en aigües, de sòls contaminats, sediments contaminats... La qualitat d'aquestes avaluacions ha anat millorant degut a la millora en les dades d'exposició, a caracteritzacions del risc més equilibrades, a l'ús de tècniques de Monte-Carlo (que incorporen la variabilitat i la incertesa) i a la disseminació de la informació.

El procés d'avaluació de riscos es pot dividir en quatre etapes principals (NRC, 1983): identificació de perill, avaluació de la dosi-resposta, avaluació de l'exposició i finalment caracterització de risc.

- **Identificació de perill** es defineix com el procés per determinar si l'exposició humana a un agent pot causar un increment en l'incidència de la condició de salut (càncer, defectes de naixement, etc.), o si l'exposició d'un receptor no humà (peixos, ocells, etc.) pot ser afectada de forma adversa. Implica la caracterització de la natura i la intensitat de les evidències de la causa. Encara que la qüestió de si una substància causa càncer o altres efectes sobre la salut és teòricament una pregunta amb resposta "sí" o "no", hi ha pocs agents físics o químics per als que les dades en humans siguin definitives (NRC, 1983). Per tant, sovint la qüestió es replanteja en termes d'efectes sobre animals de laboratori o altres tipus de tests: l'agent indueix càncer en animals? Respostes positives a aquesta qüestió sovint es prenen com a evidències que l'agent en qüestió pot causar càncer als humans exposats. En certes circumstàncies, informació de proves "in vitro" a curt termini i la similitud estructural a químics perillosos pot ser considerat com a informació adequada d'identificació d'un perill.

Respecte als efectes carcinogènics l'Agencia Internacional de Recerca sobre el Càncer (en anglès: International Agency for Research on Cancer, IARC) té com a objectiu identificar les causes que provoquen càncer. Per altra banda l'Organització mundial de la Salut OMS es l'autoritat de dirigeix i coordina la salut dintre del sistema de les Nacions Unides.

- **Avaluació de la dosi-resposta** és el procés de caracteritzar la relació entre la dosi d'un agent administrat o rebut i l'incidència d'un efecte advers en poblacions exposades a l'agent en qüestió. Aquest procés considera factors importants com la intensitat de l'exposició, el patró d'edat i la possibilitat d'altres variables que poden afectar la resposta, com el sexe i l'estil de vida. Una avaluació dosi-resposta sovint requereix de l'extrapolació d'altes a baixes dosis i l'extrapolació d'animals a humans, o d'una espècie de laboratori a una espècie salvatge. Una avaluació dosi-resposta hauria de descriure i justificar els mètodes d'extrapolació utilitzats per predir l'incidència, i hauria de caracteritzar l'incertesa estadística i biològica en aquests mètodes. Quan sigui possible, l'incertesa s'hauria de descriure numèricament més que qualitativament.

- **Avaluació de l'exposició** és el procés de mesura o estimació de l'intensitat, freqüència i duració de l'exposició animal o humana a un agent present a l'ambient. En la seva forma més completa, l'avaluació de l'exposició hauria de descriure la magnitud, duració i via d'exposició; mida, natura, i classes de poblacions exposades; i l'incertesa en totes les estimacions.

- **Caracterització del risc** és el procés d'estimació de l'incidència d'efecte sobre la salut sota diverses condicions d'exposició descrites en l'avaluació de l'exposició. Es realitza combinant l'exposició i la dosi-resposta. El resum dels efectes de la incertesa en les etapes prèvies s'ha de descriure en aquesta etapa.

Les diferents etapes del procés d'avaluació de riscos porten associades diferents nivells de incertesa i variabilitat que s'han de tenir en compte a l'hora d'analitzar els resultats.

1.4 Hipòtesi

Si els gasos formats no es tracten adequadament, la incineració pot ser una font de compostos orgànics persistents com les PCDD/Fs, els PCBs o els PCNs (formats com a subproductes de la combustió) i de metalls pesants (presents en els residus). Tots aquests compostos són tòxics i molt bioacumulatius. Per tant, les emissions de les incineradores són un risc potencial per la salut de les persones que viuen al voltant.

En els últims anys, les emissions de les incineradores s'han reduït de forma molt notable en aquells països on s'han adaptat a les noves tecnologies i disposicions reguladores, les quals són molt restrictives en comparació amb d'altres tipus d'activitats industrals. Per tant, avui en dia l'impacte ambiental de les incineradores no és tan significatiu com ho va ser en el passat. És per això, que la incineració és l'opció que la UE anteposa davant dels abocadors, per la disposició dels residus que no poden ser reciclats i reutilitzats. Per altra banda, altres activitats de tipus industrial, o fins i tot el trànsit, estan passant a tenir un paper cada vegada més significatiu en l'alliberament d'aquests contaminants al medi ambient.

Tot i això, la implantació d'incineradores continua generant gran controversia, especialment entre la població que viu al voltant d'aquestes instal·lacions (síndrome NIMBY – "Not In My BackYard"). Així, molta gent les continua veient com una font de contaminants perillosos que suposa un elevat risc pel medi ambient i la salut dels habitants del seu entorn.

Davant de tot això es planteja la hipòtesi que les emissions de les incineradores, les quals poden contenir concentracions elevades de metalls pesants, PCDD/Fs i altres subproductes de combustió com els PCBs i PCNs, puguin produïr un augment d'aquests contaminants al medi ambient i afectar la salut de les persones.

1.5 Objectius

Objectiu general

Aplicar diferents tècniques de monitorització i d'anàlisi de resultats per avaluar els riscos derivats de les emissions de metalls pesants i compostos orgànics persistents (PCDD/Fs, PCBs i PCNs) de diferentes incineradores de residus.

Objectius específics

- Monitoritzar els nivells de compostos orgànics persistents i metalls pesants en diferents matrius ambientals (aire, sòls, herbes) i biològiques (sangs i orines) i establir les variacions espacials/temporals d'aquests contaminants.
- Avaluar els riscos per la salut deguts a l'exposició a dioxines i metalls pesants
- Avaluar la utilització dels discs de poliuretà (PUFs) com a mètode de monitorització passiva de compostos orgànics persistents.
- Establir correlacions entre diferents contaminants.
- Identificar les principals fonts que afecten a les concentracions ambientals de cada contaminant.
- Analitzar la propagació de la incertesa dintre del models de dispersió de contaminats, i d'exposició i d'avaluació del risc.

2. Materials i Mètodes

Quan hi ha una font de contaminants, aquests poden arribar als possibles receptors (animals, humans...) a través del diferents medis (aire, sòls, aigua...). El terme monitorització es refereix a la mesura continua utilitzada com a mitjà de control. A través de la monitorització es pretén en primer lloc, establir els nivells base que representen l'estat actual i, segon, detectar canvis al llarg del temps. Junt amb aquestes raons, també hi ha el desig de definir la causa d'aquests canvis observats.

2.1 Presa de mostra

Monitors ambientals

Sòls

Es van prendre uns 500 g de sòls en submostres corresponents a una àrea d'aproximadament 5 x 5 m. Un cop al laboratori, les mostres es van assecar a temperatura ambient. Seguidament, es van passar per un tamís de 2 mm de diàmetre per tal d'homogeneïtzar la mida de les partícules.

Herbes

Es van prendre uns 500 g d'herbes (*Pipatherum paradoxum* L.) en submostres corresponents a una àrea d'aproximadament 5 x 5 m. Les mostres es van obtenir tallant a aproximadament 5 cm del terra. Un cop al laboratori es van assecar a temperatura ambient.

Aire

La presa de mostra es va realitzar a una alçada d'entre 1.5 i 4 m del terra, a una distància mínima de 0.5 m de l'edifici més proper, i almenys a 25 m dels punts de tràfic abundant, seguint la Directiva sobre Qualitat de l'Aire 1999/30/EC.

Per la presa de mostra de COPs s'utilitzà el captador d'alt volum TE-1000 de la casa Tisch Environmental (Figura 6), d'acord amb el mètode US EPA TO-9. La fase lligada a partícules de les dioxines i furans es va recollir sobre filtres de microfibra de quars (100 mm), mentre que la fase gasosa de les dioxines i furans es va recollir en espumes de poliuretà (PUF), que prèviament havien estat netejats amb diclorometà amb un Soxhlet durant 24 hores. L'aparell es va calibrar a 0.225 m^3/min abans d'iniciar la presa de mostres. Aquest flux es va comprovar al lloc de presa de mostra mitjançant lectures de la pressió a l'inici i final de cada període de mostreig. El volum d'aire de les mostres va ser de 600-700 m^3, i la presa de mostra va durar aproximadament unes 48 hores. Els PUFs i el filtre de microfibra de quars es van guardar junts en un recipient hermètic de vidre amb tap de tefló i de color ambre per evitar la fotodegradació dels compostos. Un cop al laboratori les mostres es van mantenir a –20 ºC fins al moment de l'anàlisi.

En quant als metalls de la fase lligada a partícula PM_{10}, per a la presa de mostra s'utilitzà un captador d'alt volum model 6070-DV de la casa Tisch Environmental (Figura 6), d'acord amb el mètode US EPA IO-2.1. Aquest aparell té un control de flux volumètric i un inlet selectiu de partícules menors a 10 micres quan treballa a un flux de 1.13 m^3/min. Aquest flux es va comprovar al lloc de presa de mostra mitjançant lectures de la pressió a l'inici i final de cada període de mostreig. El volum d'aire total per mostra va ser d'aproximadament 1600 m^3 durant un temps de 24 hores. Es van utilitzar filtres de fibra de quars Whatman (20.3 x 25.4 cm). Un cop acabada la presa de mostra, els filtres es van guardar protegits per un full de paper de seda. Un cop al laboratori les mostres es van mantenir en un lloc sec i fresc fins al moment de l'anàlisi.

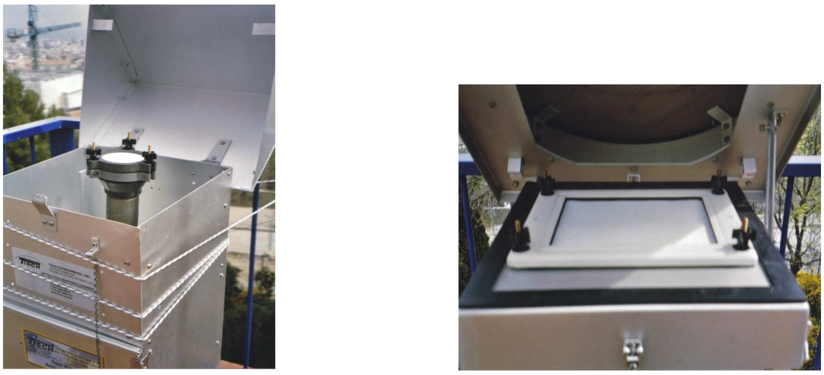

Figura 6. A la imatge de l'esquerra s'observa el capçal del captador TE-1000. Es pot veure el filtre sobre el que queden les partícules mentre que a l'interior del cilindre hi ha el PUF on queda retinguda la fase gasosa. A la imatge de la dreta hi ha el captador de partícules amb l'inlet pujat de manera que queda a la vista el filtre.

Per la presa de mostra de dioxines, també es van utilitzar captadors passius com a mètode complementari. Enfront dels clàssics captadors actius, vàlids per conèixer l'estat de contaminació puntual, els captadors passius permeten avaluar els nivells de pol·lució durant llargs períodes de temps (3 mesos). Aquest tipus de captadors consisteixen en un filtre de poliuretà (en el qual queden retinguts els contaminants orgànics semivolàtils com les dioxines) el qual està envoltat per un dispositiu metàl·lic que el protegeix del sol, la pluja i la deposició directa, mentre es permet el moviment d'aire al voltant del filtre. Aquests captadors es van deixar penjats durant tres mesos, de juliol a l'octubre de 2007 i de desembre de 2007 a març de 2008. A la Figura 7 es pot veure l'estructura d'aquests captadors.

Figura 7. Detall dels captadors passius.

Monitors biològics

Sangs

Les mostres de sang van ser extretes a cadascun dels treballadors per personal sanitari especialitzat, a la Mútua d'Accidents de Treball de Tarragona (MATT), i dipositades en contenidors estèrils amb anticoagulants. Posteriorment, es centrifugaren per tal de separar el plasma.

Orines

A la mateixa MATT, es van recollir en contenidors estèrils mostres d'orines per cadascun dels treballadors.

2.2 Determinacions analítiques

Compostos orgànics

En les mostres d'aire, sòls i herbes, les concentracions de PCDD/Fs, PCBs i PCNs es van analitzar seguint els procediments descrits pel mètode de validació alemany VDI 3499.

En les mostres de plasma, la determinació de PCDD/Fs, PCBs i PCNs es va portar a terme d'acord amb els mètodes alemanys VDI 3499 (1993) i dels procediments descrits per la "Environmental Protection Agency" (EPA USA Method 1625).

Les etapes fonamentals que caracteritzen la metodologia són:

a.- Extracció

A les mostres se'ls va afegir una quantitat coneguda de patró de recuperació, marcats amb $^{13}C_{12}$. Després es realitzà una extracció segons les característiques particulars de cada mostra, amb el sistema d'extracció accelerada DIONEX ASE 300.

b.- Purificació o "clean-up" mitjançant cromatografia de columna

L'objectiu d'aqueta etapa fou l'eliminació dels diferents compostos interferents que s'havien extret conjuntament amb els compostos d'interès. Aquest procés de purificació es realitzà mitjançant cromatografia d'absorció sòlid-líquid en columnes obertes eluïdes per gravetat. L'extracte obtingut es va sotmetre a l'acció de dos tipus de columnes:

- Columna mescla de sílica gel activada bàsica, neutra i àcida. Aquesta conté llana de vidre, 20 g de silica gel basica 33% NaOH, 20 g de silica gel neutra 33%, 200 g amb silica gel àcida amb 44% de d'àcid sulfuric i sulfat de sodi. Aquesta colunmna es va netejar amb 400 ml d'hexà. L'hexà es va reduir posteriorment a 1ml.
- Columna d'alumina. La solució es traspassà a una columna amb 25 g d'aluminai 20 g de sulfat de sodi. Lacolumna s'eluei primer amb 80 ml de benzè (fracció de PCBs i PCNs) i després amb 150 ml d'hexà/diclormetà 50/50 (v/v). Les solucions amb les fraccions de PCBs/PCNs i PCDD/Fs respectivament, es concentren a 1 ml.

c.- Anàlisi de l'extracte purificat

L'anàlisi de les mostres es va realitzar per cromatografia de gasos d'alta resolució (HRGC) acoblat a espectrometria de masses d'alta resolució (HRMS). L'extracte final s'analitzà mitjançant cromatografia de gasos d'alta resolució acoblada a espectrometria de masses d'alta resolució (HRGC/HRMS). El cromatògraf de gasos utilitzat per les determinacions va ser un GC HP 5890 amb una columna de sílica fosa, 30mx 0.25 mm ID. Espessor: 0.15 µm per PCDD/Fs i 0.25 µm per PCBs i PCNs. La detecció es va efectuar per espectrometria de masses d'impacte electrònic (EI) en modus positiu (35-45 eV), i amb monitorització de l'ió seleccionat (SIM) amb una resolució de 6.000 a 10.000 amu.

L'anàlisi de clorofenols (CLPs) en orina es va realitzar pel mètode NIOSH (National Institute of Occupational and Safety Health) núm. 8001. El pentaclorofenol en orina es va determinar mitjançant el mètode Henschler (determinació de PCP en orina o sèrum després de l'acetilació: Henschler, Analytische Methoden, Analysen in biologischem Material, 5. Lieferung, 1981). L'extracció dels CLPs es va realitzar mitjançant un procés d'hidròlisi obtenint-se els diferents derivats. Aquests van ser analitzats per HRGC/HRMS (cromatografia de gasos/espectrofotometria de masses d'alta resolució), fent servir un Fisons CE 8000 GC acoblat a un sistema VG Autosepc Ultima. La detecció s'efectuà per espectrometria de masses d'impacte electrònic a una resolució mínima de 10.000. L'anàlisi es va realitzar en un medi polar amb una columna DB-XLB. La quantificació es va portar a terme utilitzant estàndards interns de CLP, marcats amb ^{13}C.

La determinació d'1-hidroxipirè es va realitzar utilitzant el mètode DFG, Anàlisi de Substàncies Pelilloses en Matrius Biològiques (Analyses of Hazardous Substances in Biological Matrices, Vol.3, S.151, 1990). Aquest mètode s'utilitza per la determinació d'1-hidroxipirè lliure o conjugat. Després d'una hidròlisi enzimàtica s'allibera part del conjugat d'1-hidroxipirè, que és separat de la matriu i purificat per una extracció líquid/sòlid en una columna de fase reversa. Els components de l'eluït van ser separats per cromatografia líquida d'alta pressió (HPLC) i l'1-hidroxipirè es va determinar amb detector de fluorescència.

Metalls pesants

Pel tractament de les mostres previ a l'anàlisi de metalls, s'utilitzaren digestors de tefló. Aquests digestors tenen una capacitat de 100 ml i una tapa hermètica amb rosca per evitar pèrdues per esquitxos o vaporització. Això és especialment apropiat per la preparació de mostres destinades a la determinació de metalls amb alta pressió de vapor (p.ex., mercuri), a més de ser especialment resistents a l'atac dels àcids.

Per a l'extracció dels metalls en sòls i herbes, es van digerir 0.5 g de mostra amb 5 ml de HNO_3 65% Suprapur (E. Merck, Darmstadt, Alemanya) durant 8 h a temperatura ambient, i durant 8 h més a 80º C, en bombes hermètiques de tefló Les mostres es van filtrar i es van portar fins a un volum de 25 ml amb aigua desionitzada. Finalment, es van guardar congelades a -20º C fins al moment de les anàlisis. La determinació d'As, Cd, Cr, Hg, Mn, Pb, Ni i V en les mostres de sòls es va realitzar també per ICP-MS (Perkin Elmer Elan 6000). En el cas de les herbes, l'As, Cd, Hg, Mn i Pb també es van analitzar per ICP-MS (Perkin Elmer Elan 6000), mentre que el Cr, Ni i V es van analitzar per AAS.

Per l'extracció dels metalls dels filtres de partícules ambientals PM10, es tractà una vuitena part del filtre (50.3 cm^2) amb 2 ml d'àcid nítric 65% Suprapur (E. Merck, Darmstadt, RFA) i 3 ml d'àcid fluorhídric (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Espanya) a l'interior de la bomba de tefló. Es predigerí durant 8 h a temperatura ambient, i després les bombes es van escalfar a 80ºC a l'estufa durant 8 h més. La digestió àcida es va dur a sequedat al bany de sorra a 250ºC. El residu es redissolgué en 2.5 ml d'HNO_3. Posteriorment, es va filtrar i es va portar fins a 25 ml amb aigua desionitzada. Els 25 ml resultants van separarar en dues alíquotes que es van conservar congelades a -20 ºC fins el moment de les anàlisis. Les concentracions de Cd, Cr, Hg, Pb, Ni i As es van mesurar amb espectrometria de masses acoblada a una font de plasma (ICP-MS, Perkin Elmer Elan 6000).

En tots els casos s'utilitzà un material de referència *(Soil, Loamy clay, Resource Technology Corporation US, CRM 052),* com a control intern per poder calcular el percentatge de recuperació dels diferents metalls.

2.3. Avaluació de riscos

Per l'estudi comparatiu d'exposició per a la població i anàlisi de riscos es van considerar dos grups de població: nens (fins 6 anys) i adults.

Metalls

Per avaluar els riscos no carcinogènics, les concentracions de metalls en sòls es van comparar amb els nivells considerats com a segurs per la gent que viu en àrees residencials (Preliminary Remediation Goals, PRGs) (US EPA, 2004). Els riscos no carcinogènics també es van avaluar calculant el Hazard Quotient (HQ), que es defineix com el quocient entre l'exposició i la dosi de referència oral (RfDo). El criteri pels càlculs es va prendre de la US EPA. També es va calcular la inhalació per tots els elements.

Respecte als riscos carcinogènics, els nivells dels metalls carcinogènics (As, Cd i Cr) es van comparar amb els PRG. Així mateix, els riscos carcinogènics per ingestió i inhalació es van calcular multiplicant l'exposició pel corresponent factor de potència cancerígena.

PCDD/Fs

Per l'avaluació del risc per PCDD/Fs, es va aplicar la metodologia VLIER-HUMAAN desenvolupada per Nouwen i col·ls (2001). Les vies d'exposició considerades van ser la inhalació d'aire, l'absorció dèrmica i la ingestió de sòls.

Els riscos no carcinogènics es van calcular a través del Hazard Quotient, comparant l'exposició ambiental (suma de les diferents vies d'exposició considerades) amb la ingesta diària tolerable (TDI) (Van Leeuwen i col·ls., 2000).

Pel que fa als riscos carcinogènics es van calcular multiplicant l'exposició ambiental (suma de les diferents vies d'exposició considerades) pel corresponent factor de potència cancerígena.

2.4. Anàlisi de resultats

Estadística

L'anàlisi estadística dels resultats es va dur a terme amb el paquet estadístic SPSS. Per comprovar l'homogeneïtat de les variàncies es va aplicar el test de Levene. A fi d'avaluar les diferències significatives com a tests no paramètrics es van utilitzar el tests estadístics Kruskal-Wallis i la U de Mann-Whitney. Es va considerar significativa una probabilitat igual o menor a 0.05 ($p<0.05$).

Anàlisi de Components Principals (ACP)

L'ACP va ser introduït a principis dels 1900s (Pearson, 1901; Hotelling, 1933) i és una de les eines d'anàlisi multivariant més popular. L'objectiu de l'ACP és reconvertir les variables inicials en uns pocs components que són una combinació lineal de les variables originals (Components Principals), les quals donen una descripció molt àmplia amb una pèrdua molt petita d'informació. A cada mostra se li dona una puntuació per a cadascun dels components, la qual cosa permet una ràpida classificació i fàcil visualització. Tots els càlculs es van fer mitjançant el software del programa estadístic SPSS.

En aquest estudi l'ACP es va aplicar amb diferents objectius:

a) comparar els perfils de les mostres de diferents recollides al voltant d'una mateixa incineradora per determinar possibles canvis entre les fonts passades i les actuals
b) comparar els perfils de mostres properes i llunyanes a la font (incineradora)
c) trobar correlacions entre diferents contaminants
d) identificar les principals fonts que afecten a les concentracions ambientals de cada contaminant

Anàlisi de la incertesa: Fuzzy Latin Hypercube Sampling (FHLS)

En l'avaluació de riscos és important caracteritzar i quantificar la incertesa i la variabilitat per prevenir raonaments erronis. Per incertesa s'enten el coneixement incomplet sobre el sistema que s'està estudiant, per tant és reduible a través d'estudis addicionals. En canvi, la variablitat fa referència a l'heterogeneitat dels paràmetres, i per tant no és pot disminuir.

La tècnica del Fuzzy Latin Hypercube Sampling (FLHS) permet la caracterització de la incertesa i la variabilitat en els paràmetres d'entrada del model de distribució de contaminants i d'avaluació dels riscos. Aquesta tècnica, tracta la incertesa i la variabilitat dels paràmetres separadament. Parteix de la premissa de que els paràmetres poden ser incerts, variables o totes dues coses alhora. Així, la variabilitat dels paràmetres es tracta a través de funcions de densitat de probabilitat (PDFs), mentre que la incertesa s'associa utilitzant funcions de pertinència. El mètode pot donar un anàlisi detallat de la contribució de la incertesa i variabilitat de cada paràmetre al resultat final, cosa que permet ajudar al modelador a prendre la desició de recollir més informació o a millorar l'observació per tal de millorar els resultats en cas que sigui necessari.

Es va desenvolupar una "toolbox" amb Matlab pel seu ús en avaluació de riscos.

Capítol II

Herbes i sòls com a monitors ambientals. Avaluació de riscos

Articles 1 i 2:

Mari M, Ferré-Huguet N, Nadal M, Schuhmacher M, Domingo JL

Temporal trends in metal concentrations in soils and herbage collected near a municipal waste incinerator: Human health risks

Human and Ecological Risk Assessment, 13: 457-472 (2007)

Mari M, Nadal M, Ferré-Huguet, Schuhmacher M, Borrajo MA, Domingo JL

Monitoring PCDD/Fs in soil and herbage samples collected near a hazardous waste incinerator: Health risks for the population living nearby

Human and Ecological Risk Assessment, 13: 1255-1270 (2007)

Article 1: "Temporal trends in metal concentrations in soils and herbage collected near a municipal waste incinerator: Human health risks"

Abstract

Emissions of metals by municipal solid waste incinerators (MSWIs) are still an issue of concern for the health of residents in the vicinity of these facilities. Since 1991 a MSWI has been operating in Tarragona (Spain). In 1997, a modernization of the flue gas cleaning systems of the MSWI was carried out. Since then, periodically soil and herbage samples have been collected near the facility and the concentrations of the following elements determined: As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Tl and V. In 2002, a 4-year environmental surveillance program was initiated. The mean concentrations of these elements in various surveys performed between 1997 and 2005, as well as the spatial and temporal trends are here reported. On the other hand, human health risks, carcinogenic and non-carcinogenic, were also assessed. Risks for adults and children were separately evaluated. Children were chosen because they are one of the most susceptible groups of population. According to the current results, in principle, no significant health risks for the population living in the neighbourhood of the facility can be expected due to metal emissions from the stack. However, a continuous environmental surveillance program is recommended because the As levels in soils of Tarragona are slightly higher than the US EPA Preliminary Remediation Goals.

Key Words: Municipal solid waste incinerator, metals, soils, herbage, health risks.

1. Introduction

In recent years, among the different options of management of municipal solid waste, incineration has been one of the preferred strategies. The main advantages of incineration are volume and weight reduction of the wastes (about 90 and 75%, respectively), energy recovery and eradication of disease causing bacteria (Ferreira i col·ls., 2003). Unfortunately, if the gas stream is not properly treated, important amounts of toxic pollutants such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and heavy metals may be emitted to the atmosphere (Bache i col·ls., 1991; Rappe, 1992). Therefore, municipal solid waste incinerators (MSWIs) may have a negative influence on the surrounding environment, as well as on the health of the individuals living in the vicinity of these facilities (Glorennec i col·ls., 2005; Lee i col·ls., 2005).

Municipal solid wastes typically contain metals such as mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), manganese (Mn), chromium (Cr) or cobalt (Co), among others. Although some of these elements (Co, Cu, Mn, Zn) are essential for the normal growth and development of mammals, they may also become toxic at high concentrations (Domingo, 1994; Chang i col·ls., 2000). Moreover, municipal waste also contains elements such as mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As), which are typically associated with adverse health effects (Chang i col·ls., 2000). Metals show a tendency to accumulate in the food chain (Bocio i Domingo, 2005; Notten i col·ls., 2005) and bioaccumulate in plants (Efroymson *et al.* 2004). Although some elements are released by natural sources (Garrett 2000), toxic metals may appear in the effluents of different combustion processes. In recent years, their release into the environment has become under regulatory scrutiny (Linak i Wendt, 1993). Nowadays, modern incinerators observe very strict emission limit values in accordance to new legislations (OJEC, 2000). These legislative strategies are aimed at preventing and limiting the negative environmental effects, as well as reducing the potential risks on human health (Grant *et al.*2002). In spite of legislation efforts, waste incineration still remains generating considerable public concern.

Since 1991, a MSWI (aprox. 145.000 tones/year) has been operating in Tarragona (Catalonia, Spain). The plant is located at 2.5 km from the city center and at 1.5 km from inhabited areas. It is situated in an industrial region in which other potential pollution sources (i.e., a hazardous waste incinerator (HWI) and a big oil refinery) are also placed. In 1994, a wide surveillance program was initiated in order to provide information on the environmental impact and the health risks of metals and PCDD/Fs in the surroundings of the MSWI (Schuhmacher i col·ls., 1999; Llobet i col·ls., 2002). Soils and herbage were chosen as indicators of long-term and short-term environmental pollution, respectively. In 1997, in accordance to the EU Waste Incineration Directive emission limits (OJEC, 2000), in order to reduce the emissions of acid gases (HCl/SO_2), metals and PCDD/Fs, a new cleaning system was installed in the facility. A 700-fold decrease of the PCDD/F levels was observed, , whereas the subsequently found concentrations of metals released to air were also notably lower than the maximum allowed levels regulated in the legislation. In 1999, a new survey was carried out to detect the temporal trend of metal concentrations in soils and herbage collected near the plant (Llobet i col·ls., 2002). According to those results, the impact of the MSWI was not remarkable in comparison to other potential emission sources of metals located in the same area.

In 2002, a 4-year environmental surveillance program was again started. During this period, soil and herbage samples were periodically monitored for metals and PCDD/Fs. In this paper, the levels of metals in soils and herbage collected in the vicinity of the MSWI between 2002 and 2005 are reported. They are compared with the concentrations found in the 1997 and 1999 surveys (just before and after the technical modernization of the MSWI). Moreover, the potential health risks for the local population potentially exposed to metals were also assessed and are here reported.

2. Materials and methods

2.1. Sampling

In 2002 and 2004, 24 herbage (*Pipatherum paradoxum* L.) samples were collected at different sampling points in the neighbourhood of the MSWI of Tarragona (Catalonia, Spain). A wide description of the facility and surroundings was previously reported (Schuhmacher i col·ls., 1996; Schuhmacher i col·ls., 1997; Schuhmacher i col·ls., 1998; Domingo i col·ls., 2001). The sampling points were the same than those of the surveys carried out in 1997 and 1999: distances of 250, 500, 750, 1000, 1250 and 1500 m from the MSWI stack, and 4 wind directions (NE, NW, SE and SW) (Figure 1). Samples were obtained by cutting at about 5 cm from the ground. They were immediately stored in a double-aluminum fold, and dried at room temperature until the analyses.

On the other hand, in 2003 and 2005, duplicate soil samples were also collected at the same points. Soil samples were taken from the upper 3 cm and stored in polyethylene bags. They were dried at room temperature until constant weight. Subsequently, they were sieved through a 2-mm mesh screen to get a homogeneous grain distribution.

2.2. Analytical Procedure

Approximately 0.50 g of dried soil or herbage were treated with 5 ml of 65% HNO_3 (Suprapur, E. Merck, Darmstadt, Germany) in teflon bombs. Samples were pre-digested at room temperature for 8 h, and then heated at 80ºC for other 8 h. After cooling, solutions were filtered and made up to 25 ml with deionized water. The concentrations of As, Cd, Cr, Hg, Mn, Pb and V in soils were determined by inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000), while atomic absorption spectrophotometry with graphite furnace atomization (AAS, Varian spectrophotometer, Spectra A-30) was used to determine the levels of Ni. The levels of

As, Cd, Hg, Mn and Pb in herbage were determined by ICP-MS, whereas those of Cr, Ni and V were analysed by AAS (Schuhmacher i col·ls., 1996; Meneses i col·ls., 1999; Llobet i col·ls., 2002).

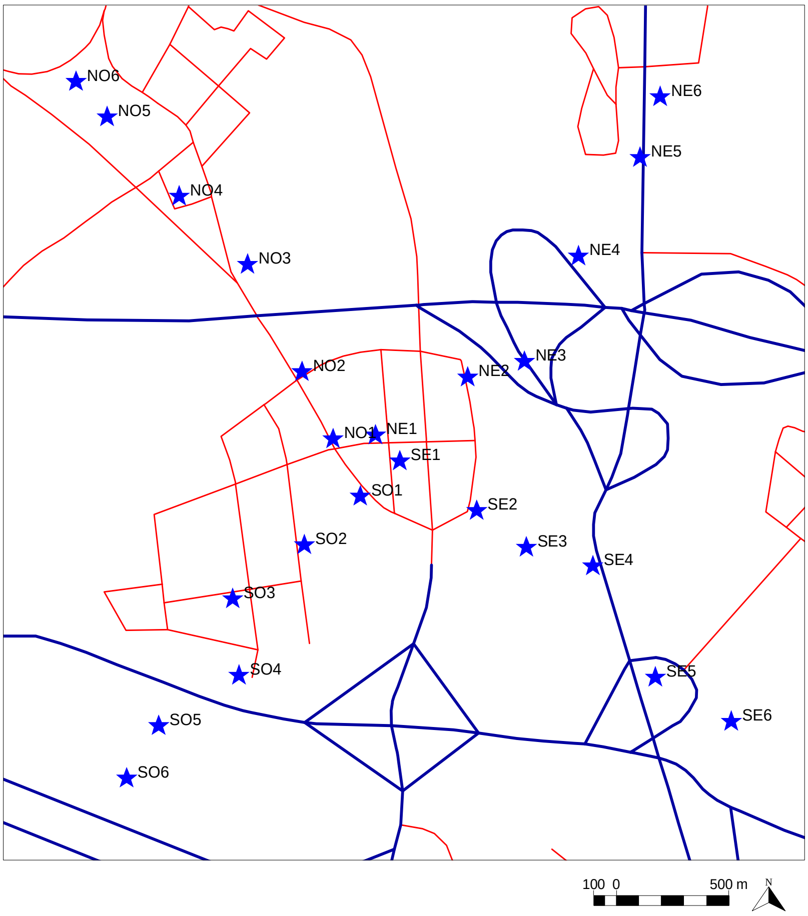

Figure 1. Sampling points in the area of study.

The accuracy of the instrumental methods and analytical procedures was checked by triplicate. Blanks were used as controls. Furthermore, a reference material (*Lobster hepatopancreas*, *NRC Canada, TORT-2*) was run every 7 samples to check the potential drift in the instrument sensitivity. For each element, quantification was based on the most abundant isotope of that element free of analytical interferences. Detection limits in soils were the following: 0.1 μg/g for As, 0.25 μg/g for Be, Cr and V, 0.03 μg/g for Mn, Cd, Pb and Tl, 0.01 μg/g for Ni, and 0.05 μg/g for Hg. In herbage, the limits of detection were 0.02 μg/g for Pb, Mn, Cr and Cd, 0.01 μg/g for Ni, 0.1 μg/g for As, 0.03 μg/g for Tl and V, 0.05 μg/g for Hg, and 0.25 μg/g for Be.

2.3. Human Health Risks

The exposure of the local population to metals was estimated by considering two different routes: oral (ingestion) and inhalation (Abrahams, 2002; Granero i Domingo, 2002; Nadal i col·ls., 2004). The daily metal intake was evaluated for two groups of population: adults and children. Non-carcinogenic and carcinogenic risks were assessed.

2.4. Statistics

For calculations, when an element showed a value under its detection limit, the concentration was assumed to be one-half of that limit of detection (ND = 1/2 LOD). Statistical significance was computed by one way analysis of variance (ANOVA) followed by Student's t-test or by the Kruskal-Wallis test. Probabilities of 0.05 or lower were considered as significant. Statistical analysis was carried out using the SPSS-13.0 Statistical Software Package.

3. Results and discussion

3.1. Metal Concentrations in Soils and Herbage

The mean concentrations of a number of metals in soil and herbage samples collected in the vicinity of the MSWI of Tarragona in various surveys between 1997 and 2005 are summarized in Table 1. The temporal trends (expressed in percentages of variation) between the samplings are also shown. In soils, the highest concentrations corresponded to Mn and Pb. In the 2005 survey, Be was the only element which showed a concentration below the limit of detection. In the period 1997-2005, a significant decrease of all analyzed elements (excepting Be and Cd) was observed, while the concentrations of As, Cr, Hg, Mn, Ni, Tl and V showed a significant reduction between 1999 and 2005. Only Cd and Pb concentrations notably (but not significantly) increased during this period.

Although a significant reduction in the levels of Pb was noted in soils between 1997 and 2005, a decrease was not observed during the 1999-2005 and 2003-2005 periods. However, in comparison to the values obtained in the previous surveys, a significant reduction was observed for As, Cr, Mn, Ni, Tl and V concentrations in soils collected near the MSWI in 2005. In contrast, the increased concentrations noted for some elements did not reach the level of statistical significance ($p < 0.05$). Furthermore, for most metals, the current (2005) concentrations were even lower than those found in previous surveys performed near the HWI of Tarragona (Llobet i col·ls., 2002; Nadal i col·ls., 2004), as well as in other industrial areas of Catalonia (Schuhmacher i col·ls., 1998; Meneses i col·ls., 1999; Llobet i col·ls., 2002; Nadal i col·ls., 2004). Recently, Rimmer *et al.* (in press) found notable higher concentrations of heavy metals in soils sampled near the Byker MSWI (Newcastle, England). In fact, the levels here reported are similar or lower than those recently found by a number of authors in various soils worldwide (Mesilio i col·ls., 2003; Hanari i col·ls., 2004; Loska i col·ls., 2004; Ferreira-Baptista i De Miguel, 2005; Ruiz-Cortés i col·ls., 2005; Wilcke i col·ls., 2005).

Table 1. Metal concentrations (µg/g ± SD) in soil and herbage samples collected near the MSWI of Tarragona (Catalonia, Spain).

Soil	1997[a]	1999	2003	2005	% 1997-1999	%1997-2005	%1999-2005	%2003-2005
As	4.66 ± 1.83	5.56 ± 3.45	5.99 ± 1.26	1.71 ± 0.62	19.39	-63.28**	-69.24**	-71.47***
Be	0.17 ± 0.18	0.33 ± 0.12	0.34 ± 0.15	ND	97.01	---	---	---
Cd	0.27 ± 0.07	0.15 ± 0.06	0.20 ± 0.11	0.22 ± 0.09	-42.68*	-19.00	41.30	8.11
Cr	7.75 ± 4.50	11.30 ± 4.25	14.37 ± 5.67	4.57 ± 2.44	45.76	-41.05**	-59.55**	-68.19***
Hg	0.13 ± 0.06	0.06 ± 0.02	0.03 ± 0.02	0.03 ± 0.01	-55.67	-73.67**	-40.60**	6.76
Mn	182.4 ± 125.5	223.96 ± 72.13	241.17 ± 56.01	158.70 ± 45.49	22.80	-12.98**	-29.14**	-34.20***
Ni	7.39 ± 4.25	8.75 ± 2.87	10.39 ± 6.17	2.06 ± 0.64	18.43	-72.18**	-76.51**	-80.20***
Pb	138.3 ± 56.4	25.68 ± 21.44	29.66 ± 14.54	33.74 ± 34.76	-81.43***	-75.60**	31.41	13.76
Tl	0.07 ± 0.03	0.06 ± 0.02	0.12 ± 0.04	0.02 ± 0.01	-13.58*	-72.84**	-68.57**	-84.72***
V	12.67 ± 4.82	16.00 ± 4.20	20.48 ± 5.10	7.55 ± 1.83	26.29	-40.42**	-52.86**	-63.13***

Herbage	1999	2002	2004	% 1999-2002	%1999-2004	%2002-2004
As	0.13 ± 0.01	0.08 ± 0.05	0.09 ± 0.04	-34.65***	-32.34**	3.54
Be	ND	ND	ND	---	---	---
Cd	0.03 ± 0.02	ND	ND	---	---	---
Cr	0.27 ± 0.15	0.68 ± 1.32	ND	153.70***	---	----
Hg	0.10 ± 0.00	ND	ND	---	---	---
Mn	36.20 ± 1.32	31.54 ± 10.97	28.12 ± 13.57	-12.87	-22.32	-10.86
Ni	1.02 ± 0.65	0.80 ± 2.83	0.40 ± 0.59	-21.45***	-61.01***	-50.37
Pb	1.22 ± 0.92	0.73 ± 0.42	0.48 ± 0.37	-40.37	-60.69***	-34.03**
Tl	ND	ND	ND	---	---	---
V	0.60 ± 0.34	0.22 ± 0.15	0.39 ± 0.19	-62.97***	-35.10	75.23***

ND= not detected

[a] The 1997 data correspond to levels obtained before the modernization of the flue gas cleaning systems was carried out in the facility.

Asterisks indicate significant differences at: * $p< 0.05$; ** $p< 0.01$; *** $p< 0.001$.

In all surveys, the levels of Be and Tl in herbage were below their respective analytical detection limits (0.25 and 0.03 µg/g, respectively), while the highest levels corresponded also to Mn. Between 1999 to 2004, the concentrations of all analysed elements significantly diminished ($p < 0.001$). These reductions would be an indicator of the general decreasing tendency found in recent years for the atmospheric concentrations of a number of metals (Schuhmacher i col·ls., 2002a). Because of the ban on the use of leaded gasoline (Bellés i col·ls., 1995; Schuhmacher i col·ls., 1996), herbage would reflect a reduction of the atmospheric Pb levels. The differences found between different surveys in metal concentrations in herbage samples would be probably due to the heterogeneity of the samples rather than to the potential differences in the atmospheric concentrations of metals in the area under study. On the other hand, although in the period 2002-2004, most metals (Cr, Mn, Ni, Pb) showed lower concentrations in herbage, the level of statistical significance for these decreases was only reached by Pb ($p<0.01$). In contrast, in 2004 the concentrations of As were higher than those found in the previous survey (2002). However, V levels showed a significant increase between both surveys (75.2%, $p<0.001$). Anyhow, the 2005 metal concentrations in herbage samples collected near the MSWI of Tarragona seemed to be similar or even lower than those reported by a number of authors in various vegetal species (Schuhmacher i col·ls., 2003; Bosco i col·ls., 2005; Sardans i Peñuelas, 2005).

3.2. Human Risk Assessment

3.2.1. Non-cancer risk evaluation

The predicted oral exposure for adults and children is shown in Table 2. Children were chosen as target populations because they are one of the most sensitive groups of population. In fact, they are especially vulnerable to ingestion due to the hand-to-mouth activity. The criteria used for calculations were taken from Nadal *et al.* (2004). The oral predicted exposure for each element was calculated using the following equation:

Oral Predicted Exposure = (Metal concentration in soil x Soil intake) / Body weight

A soil intake of 50 mg/day and 200 mg/day, and a body weight of 70 and 15 kg was considered for adults and children, respectively (US EPA, 2000).

The oral reference dose (RfDo) of a chemical is defined as a numerical estimate of a daily oral exposure to the human population (including sensitive subgroups such as children) that is not likely to cause harmful effects during a lifetime (U.S. Environmental Protection Agency, 1997). The Hazard Quotient (HQ) was calculated by comparing the predicted exposure through ingestion and the oral reference dose for each element. The values of HQ for adults and children living in the vicinity of the MSWI are depicted in Figure 2. The maximum HQ corresponded to Pb in 1997 with levels of $2.8 \cdot 10^{-2}$ and 0.57 for adults and children, respectively. In any case, the quotient was below the safety level of 1. Similar results were also found in recent investigations performed in a petrochemical zone and close to a HWI, which are both located near the MSWI here evaluated (2004).

The estimated inhalation exposure to metals resuspended from soils is presented in Table 3. For calculations, it was assumed that 50% of air particles came from local resuspended soils (Hawley, 1986). Following this criterion, the mean levels of total suspended particulates (TSP) in the airborne of this area were taken into account (Generalitat de Catalunya, 1997; 2000; 2003; 2005). The TSP in the area ranged between 35 and 60 µg/m^3, corresponding to 1997 and 2003, respectively. The Limit Value (LV) was calculated in accordance to the threshold limit established by the Spanish legislation: 150 µg/m^3 (BOE, 2002). An inhalation rate of 20 and 10 m^3/day for adults and children was considered (US EPA 2004). The predicted exposure for most metals was lower than the LV, although inhaled As slightly overpasses that value.

Table 2. Predicted oral daily exposure to metals from soils for adults and children in four surveys carried out in the vicinity of the MSWI of Tarragona (Catalonia, Spain).

	RfD$_0$	**Adults**				**Children**			
	(mg/kg day)	**1997** [a]	**1999**	**2003**	**2005**	**1997** [a]	**1999**	**2003**	**2005**
As	3.00E-04	3.33E-06	3.97E-06	4.28E-06	1.22E-06	6.21E-05	7.41E-05	7.99E-05	2.28E-05
Be	2.00E-03	1.20E-07	2.36E-07	2.43E-07	9.29E-08	2.23E-06	4.40E-06	4.53E-06	1.73E-06
Cd	5.00E-04	1.91E-07	1.10E-07	1.43E-07	1.55E-07	3.57E-06	2.04E-06	2.67E-06	2.89E-06
Cr	3.00E-03	5.54E-06	8.07E-06	1.03E-05	3.26E-06	1.03E-04	1.51E-04	1.92E-04	6.09E-05
Hg	3.00E-04	8.93E-08	3.96E-08	2.20E-08	2.35E-08	1.67E-06	7.39E-07	4.11E-07	4.39E-07
Mn	2.40E-02	1.30E-04	1.60E-04	1.72E-04	1.13E-04	2.43E-03	2.99E-03	3.22E-03	2.12E-03
Ni	2.00E-02	5.28E-06	6.25E-06	7.42E-06	1.47E-06	9.86E-05	1.17E-04	1.39E-04	2.74E-05
Pb	3.50E-03	9.88E-05	1.83E-05	2.12E-05	2.41E-05	1.84E-03	3.42E-04	3.95E-04	4.50E-04
Tl	6.60E-05	4.82E-08	4.17E-08	8.57E-08	1.31E-08	9.00E-07	7.78E-07	1.60E-06	2.44E-07
V	1.00E-03	9.05E-06	1.14E-05	1.46E-05	5.39E-06	1.69E-04	2.13E-04	2.73E-04	1.01E-04

[a] The 1997 data correspond to levels obtained before the modernization of the flue gas cleaning systems was carried out in the facility.

The non-carcinogenic risks for Be, Cd, total Cr, Hg, Mn, Ni, Tl and V in soils are shown in Figure 3A. These risks were calculated by comparison between the metal concentrations in soil and the Preliminary Remediation Goals (PRG) developed by the US EPA (2004), which are considered as safe levels for people. Although V and Mn showed the highest risks, their values were below the safe level of 100%. Because of the high levels of Pb in soils sampled in 1997, a risk of this element reached then a 35% soil screening level. However, this value was notably reduced in the following surveys, remaining constant during the period 1999-2003. In general, non-carcinogenic risks for all metals increased between 1997 and 2003, although they diminished in the last survey (2005). These risk fluctuations were basically due to little variations of the metal concentrations. However, considering that none of them were statistically significant, the reason would be found more in the fact that the environmental levels of the elements change continuously, rather than in the impact of the facility here assessed.

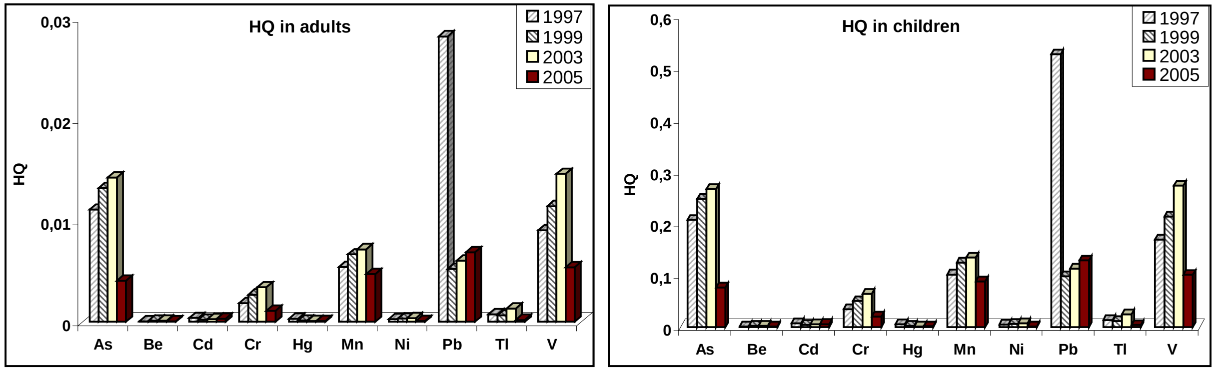

Figure 2. Hazard quotients for adults (A) and children (B) living near the MSWI of Tarragona (Catalonia, Spain).

Table 3. Predicted inhalation exposure to metals from residential and industrial soils (mg/kg/day) collected in the vicinity of the MSWI of Tarragona (Catalonia. Spain). Data for adults and children. Limit Value according to the PRG and the maximum level of TPS. for the period 1997-2005.

	Adults						Children					
	1997 [a]	1999	2003	2005	Limit Value		1997 [a]	1999	2003	2005	Limit Value	
					Residential	Industrial					Residential	Industrial
As	2.33E-08	3.26E-08	5.14E-08	1.27E-08	8.35E-09	3.41E-08	5.43E-08	7.60E-08	1.20E-07	2.96E-08	1.95E-08	7.95E-08
Be	8.38E-10	1.93E-09	2.91E-09	9.66E-10	3.31E-06	4.16E-05	1.95E-09	4.51E-09	6.80E-09	2.25E-09	7.72E-06	9.70E-05
Cd	1.34E-09	8.98E-10	1.72E-09	1.61E-09	7.94E-07	9.67E-06	3.12E-09	2.10E-09	4.01E-09	3.76E-09	1.85E-06	2.26E-05
Cr	3.88E-08	6.62E-08	1.23E-07	3.40E-08	4.51E-06	9.61E-06	9.04E-08	1.54E-07	2.87E-07	7.92E-08	1.05E-05	2.24E-05
Hg	6.25E-10	3.25E-10	2.64E-10	2.45E-10	5.03E-07	6.57E-06	1.46E-09	7.57E-10	6.17E-10	5.71E-10	1.17E-06	1.53E-05
Mn	9.12E-07	1.31E-06	2.07E-06	1.18E-06	4.17E-04	3.78E-05	2.13E-06	3.06E-06	4.82E-06	2.75E-06	9.73E-04	8.81E-05
Ni	3.70E-08	5.13E-08	8.91E-08	1.53E-08	3.35E-05	4.38E-04	8.62E-08	1.20E-07	2.08E-07	3.56E-08	7.82E-05	1.02E-03
Pb	6.91E-07	1.50E-07	2.54E-07	2.51E-07	8.57E-06	1.71E-05	1.61E-06	3.51E-07	5.93E-07	5.85E-07	2.00E-05	4.00E-05
Tl	3.38E-10	3.42E-10	1.03E-09	1.36E-10	1.11E-07	1.45E-06	7.88E-10	7.97E-10	2.40E-09	3.18E-10	2.58E-07	3.37E-06
V	6.34E-08	9.37E-08	1.76E-07	5.61E-08	1.68E-06	2.19E-05	1.48E-07	2.19E-07	4.10E-07	1.31E-07	3.91E-06	5.11E-05

[a] The 1997 data correspond to levels obtained before the modernization of the flue gas cleaning systems was carried out in the facility.

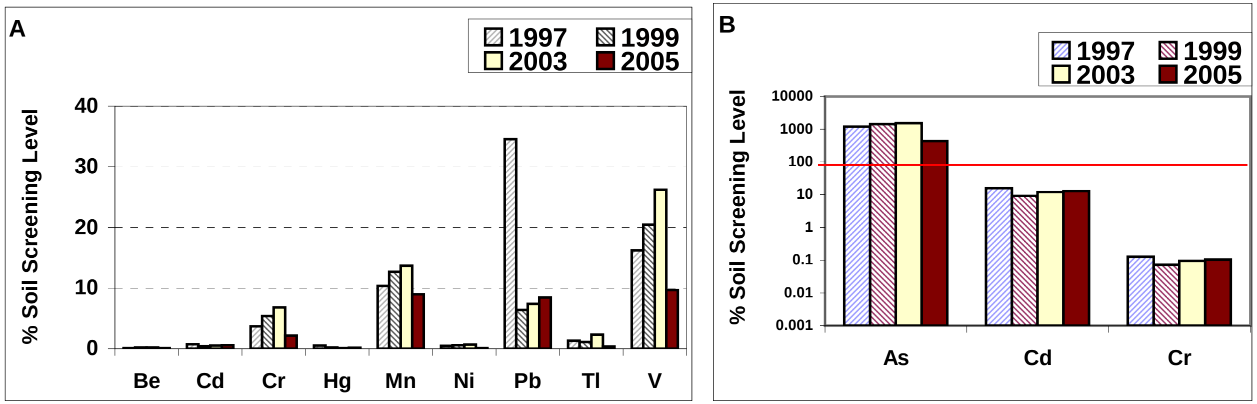

Figure 3. Non-carcinogenic (A) and carcinogenic (B) risks for the population living near the MSWI of Tarragona (Catalonia, Spain). Comparison between the metal concentrations in soils and the Preliminary Remediation Goals.

3.2.2. Cancer risk evaluation

Cancer risks are expressed in terms of the probability to develop cancer at a given lifetime exposure level (U.S. Environmental Protection Agency, 2005). The cancer risk probability is determined from the slope factor (SF) of the dose-response curve in the low-dose region where the relationship between the exposure dose and response (measured in terms of probability of developing cancer) is assumed to be linear (Lee i col·ls., 2005). The estimated oral daily intake of metals from soil, as well as the risk index for adults and children is shown in Table 4. The criteria used for calculations were taken from Granero and Domingo (2002). Slope Factors through inhalation (SF_i) were calculated by multiplying the unit risk factors (URF, in m^3/mg) given by the US EPA (1999) by the body weight (in kg), and dividing the result by the inhalation rate (m^3/day). Since only slope factors through ingestion of As and inhalation of As, Be, Cd and total Cr have been established (US EPA, 2004), cancer risks were only calculated for these elements.

The carcinogenic risk for the population living near the MSWI is summarized in Table 4. Considering a maximum acceptable risk of 10^{-6}, only As ingestion exceeded this value. However, it is important to remark that the threshold value for As has been often exceeded in soil samples from a number of countries (Nadal i col·ls., 2004). Although the levels of As in soil samples collected in the industrial area of Tarragona were generally within the ranges previously reported for soils, these were higher than the USEPA values used in PRG. The results for the remaining elements showed values lower than 10^{-6}.

To assess carcinogenic risks, the metal concentrations in soil samples corresponding to the period 1997-2005 were compared to the PRG for As, Cd and Cr (US EPA, 2004) (Figure 3B). The carcinogenic risks for Cd and Cr were clearly below 100%, while As levels in soils were approximately 10 times higher than the cancer endpoint in the PRG (0.39 µg/g). Soil screening levels for As were 1200, 1430 1540 and 440%, in 1997, 1999, 2002 and 2005, respectively. Although in soil samples As concentration was higher in the last survey (2005), its levels were lower than those found in the previous survey, which means an important decrease of the carcinogenic risk. Similar results were showed in studies performed in a petrochemical area and a HWI near to the MSWI here examined (Nadal i col·ls., 2004).

Table 4. Risk of cancer due to oral and inhalation exposures to metals from soils of the levels for adults and children living in the vicinity of the MSWI of Tarragona (Catalonia. Spain). Data are given for four surveys performed between 1997 and 2005.

		Adults					**Children**				
		SF (kg day/mg)	**1997**	**1999**	**2003**	**2005**	**SF (kg day/mg)**	**1997**	**1999**	**2003**	**2005**
Oral	**As**	1.5[a]	2.1E-06	2.6E-06	2.8E-06	7.9E-07	1.5[a]	8.0E-06	9.5E-06	1.0E-05	2.9E-06
Inhalation	**As**	15.1	1.5E-07	2.1E-07	3.3E-07	8.2E-08	6.5	3.0E-08	4.2E-08	6.6E-08	1.6E-08
	Be	8.4	3.0E-09	7.0E-09	1.0E-08	3.5E-09	3.6	6.0E-10	1.4E-09	2.1E-09	7.0E-10
	Cd	6.3	3.6E-09	2.4E-09	4.6E-09	4.3E-09	2.7	7.2E-10	4.8E-10	9.3E-10	8.7E-10
	Cr	42.0	7.0E-07	1.2E-06	2.2E-06	6.1E-07	18.0	1.4E-07	2.4E-07	4.4E-07	1.2E-07

SF: Cancer Slope Factor by oral (ingestion) and inhalation exposure.

[a] US EPA (2004)

In conclusion, the relatively low metal concentrations in soils and herbage here found indicate that the MSWI of Tarragona is not a relevant source of metals for the surrounding environment. However, as it has been suggested in previous investigations carried out in the vicinity of various MSWIs, metal contamination resulting from these facilities is rather difficult to detect in environments with other metal pollution sources (Llobet i col·ls., 2002; Capuano i col·ls., 2005; Rimmer i col·ls., in press). Because of the notable reductions observed in the last surveys in the levels of some elements here analysed, it seems that in recent years the importance of other potential metal pollution sources in the zone under evaluation has also decreased. With respect to the human health risks, the presence of the MSWI here assessed should not mean, in principle, significant non-carcinogenic or carcinogenic risks for the population living in the neighbourhood. However, as it has been concluded in previous investigations carried out in the same sampling area (Nadal i col·ls., 2004), some efforts should be focused on reducing the environmental levels of As in the industrial zone of Tarragona.

4 Acknowledgement

This study was financially supported SIRUSA, Tarragona, Spain.

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Article 2: "Monitoring PCDD/Fs in Soil and Herbage Samples Collected Near a Hazardous Waste Incinerator. Health Risks for the Population Living Nearby"

Abstract

In 1998, we started a wide environmental surveillance program focused on evaluating the environmental impact of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) emitted by a new hazardous waste incinerator (HWI) (Tarragona County, Catalonia, Spain) and assessing the potential health risks for the population living near the facility. The HWI initiated regular operations in 1999. Since then, periodical surveys have been performed. We here report the results concerning PCDD/F levels in 40 soils and 40 herbage samples collected in 2004 and 2005, respectively, in the vicinity of the HWI. The human health risks derived from exposure to PCDD/Fs were also assessed. PCDD/F concentrations in soils ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. In herbage, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. A comparison with these results with those of the baseline survey show that, after 6 years of regular operation, the HWI did not significantly increase PCDD/F levels in soils and herbage of the surrounding environment. Moreover, PCDD/F emissions from the HWI do not mean additional significant risks for the health of the individuals living in the vicinity of the facility. The results of the current study together with those of recent investigations in municipal waste incinerators indicate that, when adequately controlled for PCDD/F emissions, the modern waste incinerators should not mean any special concern for the population living in the neighborhood.

Key Words: Hazardous waste incinerator, dioxins and furans (PCDD/Fs), soils, herbage, health risks

1. Introduction

It is well known that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDD/Fs), especially the 2,3,7,8-substituted congeners, are toxic to humans and animals, being also bioaccumulative (Kogevinas 2001; Cole et al. 2003). These chemicals are formed unintentionally in different industrial processes of combustion, such as incinerators, metal processing and chemical manufacturing plants. In addition, they may be also released to the atmosphere by accidental forest fires and vehicle traffic (Alcock and Jones 1996; Fuster et al. 2001). Among environmental PCDD/F sources, until recent years waste incinerators had a preponderant role as emitters (Fiedler 1996; Meneses et al. 2004; Kim et al. 2005; Schuhmacher and Domingo 2006). However, nowadays only PCCD/F emissions from municipal solid (MSWI) and hazardous waste incinerators (HWI) are regulated in the European Union by the 2000/76/CE Directive to maximum levels of 0.1 ng TEQ/Nm3. In Spain, as a consequence of the regulatory co-ntrol, an important number of studies concerning the PCDD/F emission by combustion processes has been carried out in recent years (Abad et al. 2003, 2004, 2006; Schuhmacher and Domingo 2006). However, in spite of these strict regulations, incineration remains continues to generate great controversy and concern among the general population (Domingo 2002a, b; Meneses et al. 2004).

Due to the physico-chemical properties of PCDD/Fs, once these pollutants are emitted to the atmosphere they are dispersed through the environment and accumulated in soils and plants, reaching easily the food chain (Wuthe et al. 1993; Muller et al. 1994; Harrad and Smith 1997). Following atmospheric deposition, soils are natural sinks for PCDD/Fs (Huang and Batterman, 2003). When absorbed to the organic material of the soil, PCDD/Fs remain quite immobile. Therefore, soil is a typical long-term accumulating matrix for PCDD/Fs (Ferré-Huguet et al. 2006). In turn, vegetation receives inputs of airborne PCDD/Fs via gas phase and particulate dry matter as well as wet deposition (Meneses et al. 2002). Concentrations of PCDD/Fs in vegetation are a more suitable indicator of the atmospheric emissions of contaminants during short periods of time (Domingo et al. 1999, 2002b).

In 1999, the first HWI in Spain initiated its regular operations in Constantí (Tarragona County, Catalonia). The plant is located in an active industrial zone, with a number of important chemical/petrochemical industries and a MSWI, which is also crossed by a highway and two motorways with heavy traffic. Because of the potential environmental and health risks, the construction of the facility generated an important concern among the local population. In 1998, we started a wide environmental surveillance program mainly focused on evaluating the impact of the HWI on the environment and assessing the potential health risks for the population living in the vicinity of the facility (Agramunt et al. 2002, 2005; Nadal et al. 2002a, 2004a; Schuhmacher et al. 2002, 2004a,b). Soils and herbage were collected in 40 different sampling points in the surrounding of the HWI. PCDD/F levels were determined in the samples. In 2003, in order to study the temporal trend of the PCDD/F levels, soil and herbage samples were again collected at the same sampling points. The health risks for the local population derived from PCDD/F exposure were also evaluated (Ferré-Huguet et al. 2006).

Although in terms of PCDD/F exposure, the HWI did not mean, in principle, a negative impact on the environment or additional risks on the population (Ferré-Huguet et al. 2006), it was decided to continue the monitoring program to get data on the environmental trend of those pollutants. In the present study, we report PCDD/F concentrations in soil and herbage samples collected around the HWI between 2003 and 2005. These results were compared with those obtained in the baseline survey. Moreover, the human health risks derived from exposure to PCDD/Fs were also assessed.

2. Materials and methods

2.1. Sampling

In April 2004, 40 soil samples, were collected around the HWI of Constantí (Catalonia, Spain). The sampling sites were from the same locations as the baseline and the subsequent studies (Schuhmacher et al., 1997, 1998a,b, 2000, 2002) . These sites were chosen at different distances and wind directions (E, N, NW and S) within a radius of 7 km from the stack. Thirty sampling sites were located in zones considered as rural, whereas the remaining 10 were located in areas considered as urban. At each sampling site, soil samples, 500 g approximately, were taken from the upper 5 cm of ground and stored in polyethylene bags. The bulked samples were dried at room temperature and sieved with a 2 mm mesh seive until analysis. About 50 g (dry weight) were used for analysis.

In April 2005, samples of vegetation (Piptatherum paradoxum L.) were collected at the same points. Approximately 150 g were obtained by cutting at a height of approximately 4 cm from the soil. When samples were collected, the plants were about 25 cm high. All samples were immediately packed in aluminum foils. Subsequently, they were dried at room temperature, kept in a double aluminum foil and packed in labeled plastic bags until analysis. About 50 g (dry weight) were used for analysis.

2.2. Analytical Procedure

The 2,3,7,8-substituted congeners of PCDDs and PCDFs in soil and herbage samples were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), following the US EPA method 1613. A mixture of 13C12-marked standards were added prior to Soxhlet extraction with toluene for 24 h. The extract was subsequently subjected to an acid/base clean-up procedure followed on micro columns of silicagel and alumina. HRGC/HRMS analysis was carried using a Fisons CE 8000 GC coupled with a VG Autospec Ultima system (EI and multiple ion detection mode, resolution 10000). Two GC columns were used: DB 5-MS for hepta- and octaCDD and CDF, and CP-Sil 88 for tetra- through hexaCDD and CDF, including the 2,3,7,8-substituted isomers. For detection, at least two masses (M+ and M2+; M2+ and M4+, respectively) were used for each native and labeled dioxin and furan homologue group. Quantitative determinations of PCDD/Fs were performed using internal standards.

2.3. Data Analysis

Toxic Equivalents (I-TEQ) were calculated using the NATO/CCMS factors. In the case of PCDD/F congeners whose levels were under the respective detection limit, the concentration of that congener was assumed to be one-half of the detection limit (ND = ½ LOD). For statistical comparison of data between different years, the significance of the differences was computed by the non-parametric Kruskal-Wallis test and the parametric ANOVA test, depending on the sample distribution. A probability of 0.05 or less was considered as significant ($P < 0.05$). All statistical analyses were carried out using the SPSS-13.0 Statistical Software Package for Windows.

3. Results and discussion

3.1. Environmental Concentrations of PCDD/Fs

The individual concentrations of PCDD/Fs (I-TEQ) of the 40 soil and herbage samples (urban and rural) collected during the period 2003-2005 around the HWI, as well as those obtained in the baseline survey (1998) are summarized in Tables 1 and 2. The temporal variation (%) between the 1998 study (before the HWI initiated its regular operations) (Schuhmacher et al. 2002b) and subsequent surveys (four, five and six years after starting operations) are also shown for each sample. In turn, the box plots of soil and herbage samples collected in the vicinity of the facility during the same period

(1998-2005) are depicted in Figure 1. Moreover, a summary of the concentrations of PCDD/Fs, depending on the year and the year/distance of collection are presented in Tables 3 and 4, respectively. In 1998, PCDD/F soil concentrations ranged from 0.12 to 17.2 ng I-TEQ/kg with median and mean values of 0.75 and 1.59 ng I-TEQ/kg , respectively. In 2003, PCDD/F concentrations ranged from 0.10 to 3.66 ng I-TEQ/kg, with median and mean values of 0.56 and 0.77 ng I-TEQ/kg, respectively. In 2004, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. The highest concentrations were observed in the SV sites, located in urban areas at different directions from the facility and at a distance >4 km from the facility. The soil sample SV9 (12.60 ng I-TEQ/kg) was placed in an area presumably affected by a waste spill with an unknown scope (Schuhmacher *et al.* 2004c). The temporal changes observed in that zone could be the result of variations in SV sampling sites (moved within an area), since this zone has been subject of an important urban development expansion.

PCDD/F levels in soils increased during the period 2003-2004 in 22 of the 40 samples, whereas in the other 18 a reduction was observed. The median value increased 16%. Between 1998 and 2003, a reduction of 13% was detected. Probably, these variations are due to the standard deviations in the analytical determinations concurrently with small variations in the collection sites. However, the Mann-Whitney U-test did not show significant differences between 1998 and 2004 in none of the scenarios considered (500, 2500 and >4000 m from the HWI).

Most tetra- to octa-PCDD/Fs were detected in all soil samples. In 2003, the most toxic congener 2,3,7,8-TCDD was detected in 14 of the 40 samples (detection limit: 0.05 ng/kg), 0.13 ng/kg being the highest concentration found. In the 2004 survey, 2,3,7,8-TCDD was detected in 36 of the 40 samples with a mean value of 0.05 ng/kg (detection limit: 0.03 ng/kg). OCDD was the most abundant congener with concentrations ranging between 4.07 and 527 ng/kg, 0.38 and 460 ng/kg, and 2.50 and 415.8 ng/kg in the 1998, 2003 and 2004 surveys, respectively.

Table 1. PCDD/F concentrations (ng I-TEQ/kg dry matter) in soil samples collected around the HWI in 1998, 2003 and 2004.

Sample Code	**Distance to the HWI**	**Area**	**1998**	**2003**	**2004**	**Temporal variation**	
						% 1998-2004	**% 2003-2004**
E1	500	R	1.22	0.89	1.43	*17*	*61*
E2	1000	R	0.52	0.78	0.5	*-4*	*-36*
E3	1500	R	0.41	0.53	1.79	*337*	*238*
E4	2000	R	0.65	0.60	0.8	*23*	*33*
E5	2500	R	5.11	0.10	0.31	*-94*	*210*
E6	3000	R	0.40	0.10	1.00	*150*	*900*
E7	3500	R	0.12	0.16	1.35	*1025*	*744*
E8	4000	U	1.99	0.72	0.7	*-65*	*-3*
E9	>4000	R	0.16	0.15	0.65	*306*	*333*
N1	500	R	0.34	0.28	0.51	*50*	*82*
N2	1000	R	0.23	0.47	0.32	*39*	*-32*
N3	1500	R	0.26	0.28	2.53	*873*	*804*
N4	2000	R	0.75	0.22	0.99	*32*	*350*
N5	2500	R	0.13	2.39	0.18	*38*	*-92*
N6	3000	R	0.51	0.82	0.57	*12*	*-30*
N7	3500	R	0.60	0.59	0.38	*-37*	*-36*
NW1	500	R	0.64	0.26	0.23	*-64*	*-12*
NW2	1000	R	0.22	0.53	0.75	*241*	*42*
NW3	1500	R	0.43	0.73	1.74	*305*	*138*
NW4	2000	R	3.68	0.24	0.46	*-88*	*92*
NW5	2500	R	0.66	0.26	0.64	*-3*	*146*
NW6	3000	R	1.07	0.43	0.75	*-30*	*74*
NW7	3500	R	2.34	0.59	1.81	*-23*	*207*
S1	500	R	1.10	0.91	1.02	*-7*	*12*
S2	1000	R	1.02	0.23	0.14	*-86*	*-39*
S3	1500	R	0.75	0.53	0.38	*-49*	*-28*
S4	2000	R	0.45	1.14	0.65	*44*	*-43*
S5	2500	R	1.01	1.24	2.13	*111*	*72*
S6	3000	R	1.00	0.61	0.10	*-90*	*-84*
S7	3500	R	0.35	0.42	0.38	*9*	*-10*
S8	4000	R	1.94	1.00	3.15	*62*	*215*
SV1	>4000	U	0.15	0.36	0.51	*240*	*42*
SV2	>4000	U	2.00	0.43	0.34	*-83*	*-21*
SV4	>4000	U	3.43	0.74	1.55	*-55*	*109*
SV6	>4000	U	3.61	2.70	0.32	*-91*	*-88*
SV7	>4000	U	2.42	3.66	0.74	*2*	*-80*
SV8	>4000	U	17.2	2.30	0.06	*-100*	*-97*
SV9	>4000	U	3.06	0.35	12.6	*312*	*3500*
SV10	>4000	U	0.84	0.93	0.25	*-70*	*-73*
SV11	>4000	U	0.75	1.20	1.05	*40*	*-13*
			0.75[a]	**0.56**[a]	**0.65**[a]	*-13*	*16*

R= Rural; U= Urban; E= East; N= North; NW= Northwest; S= South; SV= urban sites at different directions; [a]Median values.

Table 2. PCDD/F concentrations (ng I-TEQ/kg dry matter) in herbage samples collected around the HWI in 1998, 2003 and 2005.

Sample code	**Distance to the HWI**	**Area**	**1998**	**2003**	**2005**	**Temporal variation**	
						% 1998-2005	**% 2003-2005**
E1	500	R	0.21	0.23	0.41	*95*	*78*
E2	1000	R	0.32	0.22	0.16	*-50*	*-27*
E3	1500	R	0.19	0.16	0.19	*0*	*19*
E4	2000	R	0.22	0.21	0.17	*-23*	*-19*
E5	2500	R	0.18	0.32	0.33	*83*	*3*
E6	3000	R	0.17	0.29	0.29	*71*	*0*
E7	3500	R	0.14	0.93	0.55	*293*	*-41*
E8	4000	U	0.51	0.20	0.75	*47*	*275*
E9	>4000	R	0.43	0.23	0.59	*37*	*157*
N1	500	R	0.25	0.14	0.63	*152*	*350*
N2	1000	R	0.19	0.11	0.75	*295*	*582*
N3	1500	R	0.24	0.19	0.56	*133*	*195*
N4	2000	R	0.28	0.17	0.56	*100*	*229*
N5	2500	R	0.30	0.21	0.60	*100*	*186*
N6	3000	R	0.27	0.14	0.49	*81*	*250*
N7	3500	R	0.19	0.21	0.26	*37*	*24*
NW1	500	R	0.52	0.32	0.60	*15*	*88*
NW2	1000	R	0.20	0.24	0.29	*45*	*21*
NW3	1500	R	0.21	0.23	0.24	*14*	*4*
NW4	2000	R	0.32	0.23	0.23	*-28*	*0*
NW5	2500	R	0.32	0.21	0.31	*-3*	*48*
NW6	3000	R	0.21	0.19	0.41	*95*	*116*
NW7	3500	R	0.48	0.22	0.24	*-50*	*9*
S1	500	R	0.18	0.24	0.37	*106*	*54*
S2	1000	R	0.34	0.07	0.30	*-12*	*329*
S3	1500	R	0.23	0.05	0.21	*-9*	*320*
S4	2000	R	0.17	0.20	0.24	*41*	*20*
S5	2500	R	0.19	0.14	0.81	*326*	*479*
S6	3000	R	0.19	0.10	0.17	*-11*	*70*
S7	3500	R	0.21	0.44	0.29	*38*	*-34*
S8	4000	R	0.32	0.28	0.29	*-9*	*4*
SV1	>4000	U	0.18	0.33	0.76	*322*	*130*
SV2	>4000	U	2.01	0.44	1.57	*-22*	*257*
SV4	>4000	U	0.17	0.20	0.22	*29*	*10*
SV6	>4000	U	0.24	0.16	0.39	*63*	*144*
SV7	>4000	U	0.21	0.11	0.33	*57*	*200*
SV8	>4000	U	0.45	0.15	0.03	*-93*	*-80*
SV9	>4000	U	0.32	0.21	0.09	*-72*	*-57*
SV10	>4000	U	0.36	0.16	0.19	*-47*	*19*
SV11	>4000	U	0.25	0.13	0.13	*-48*	*0*
			0.23[a]	**0.21**[a]	**0.31**[a]	*35*	*48*

R= Rural; U= Urban; E= East; N= North; NW= Northwest; S= South; SV= urban sites at different directions; [a]Median values.

Table 3. Summary of PCDD/F concentrations (ng I-TEQ/kg) in soil and herbage samples collected around the HWI.

Sample	Year	Mean	SD	Minimum value	Maximum Value
Soil	1998	1.59	2.79	0.12	17.20
	2003	0.77	0.75	0.10	3.66
	2004	1.11	1.98	0.06	12.60
Herbage	1998	0.31^{ab}	0.29	0.14	2.01
	2003	0.22^{a}	0.14	0.05	0.93
	2005	0.40^{b}	0.28	0.03	1.57

Values showing different superscripts (a,b) are significantly different at $P < 0.05$. For both soil and herbage, the number of samples was 40 in each collection.

Table 4. Summary of PCDD/F concentrations (ng I-TEQ/kg) in soil and herbage samples taken at different distances from the HWI.

	Distance (m)	500 (n=4)	2500 (n=4)	>4000 (n=10)
Sample	**Year**			
Soil	**1998**	0.83 ± 0.41	1.73 ± 2.28	3.36 ± 5.03
	2003	0.59 ± 0.36	1.00 ± 1.06	1.28 ± 1.20
	2004	0.90 ± 0.41	0.40 ± 0.20	1.81 ± 3.81
Herbage	**1998**	0.29 ± 0.16	0.25^{a} ± 0.07	0.49 ± 0.58
	2003	0.20^{a} ± 0.06	0.20^{a} ± 0.25	0.22 ± 0.10
	2005	0.50^{b} ± 0.13	0.51^{b} ± 0.24	0.45 ± 0.48

Mean ± St. Deviation. Values showing different superscripts (a,b) are significantly different at $P < 0.05$.

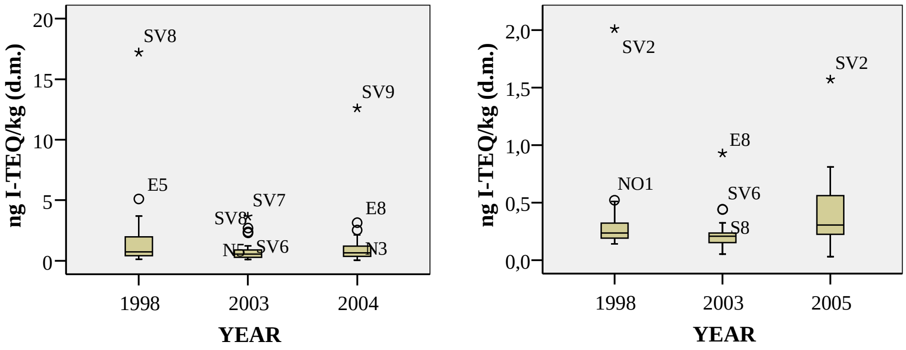

Figure 1. Box plot of soil (A) and herbage (B) samples collected in the vicinity of the HWI during the period 1998-2005.

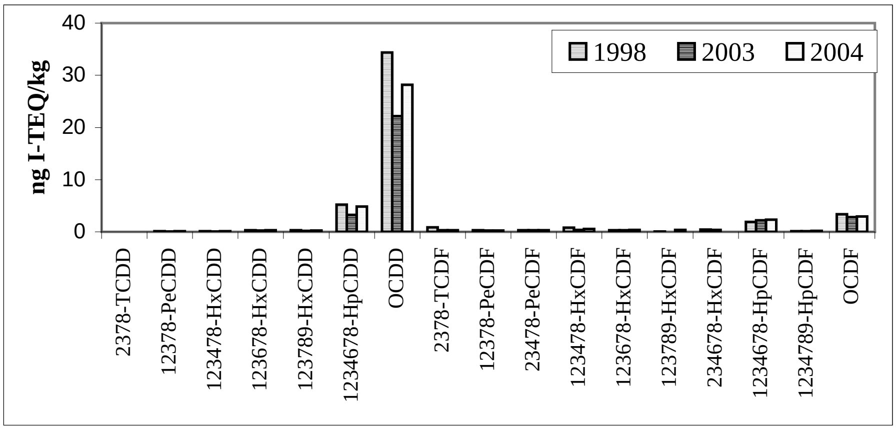

Figure 2. PCDD/F profile (median values) of soil samples collected around the HWI during the period 1998-2004.

Figure 2 shows the PCDD/F congener profiles in soil samples during the period 1998-2004. In most of the samples, OCDD was the most abundant congener, followed by 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDDF. Similar PCDD/F profiles were observed for the three years. Although in 2004, OCDD concentrations were slightly higher than those found in 2003, the differences were not statistically significant.

Most air pollutant sources emit trace element combinations that are characteristic to their specific source type. A Principal Component Analysis (PCA) was carried out to identify possible changes in congener profiles corresponding to each sampling period. The scatterplot of the component scores on both principal components showed that most soil samples were located in a main cluster with only a few samples appearing as outliers (Figure 3). The first Principal Component (PC) was correlated with the hexa-CDFs and OCDF, while the second PC was mainly correlated with OCDD, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,7,8,9-HxCDD. The main cluster shows a lack of differences in emission sources of the current survey with respect to the baseline study. On the other hand, some samples of the last survey (SV9 and S8) showed elevated values of the second component (related to PeCDD). The different profile of these samples reflects that they could have been affected by punctual

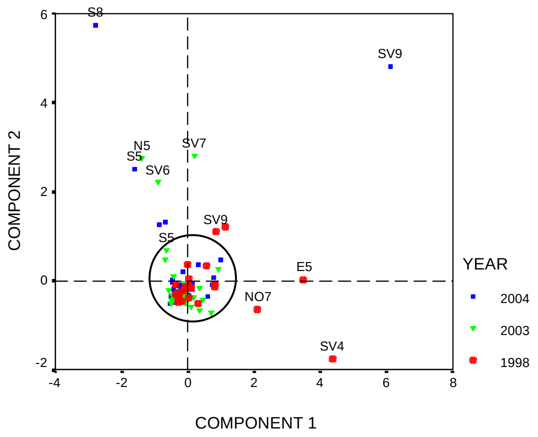

Figure 3. Principal Component Analysis for soil samples collected in the vicinity of the HWI.

pollution sources, such as traffic and agricultural burning.

Nowadays, in Spain there is no guideline for PCDD/F levels in soils. However, the concentrations here reported are, in general terms, below 5 pg TEQ/g, the threshold limit established for the Germany soils guideline corresponding to soils used for agricultural purposes (Bassler 1994). On the other hand, all samples were notably below the 100 and 1000 pg TEQ/g established in the same guideline for children's playgrounds and residential areas, respectively. Furthermore, PCDD/F soil concentrations here reported are of the same order of magnitude as those recently found in other studies around municipal waste incinerators in Taiwan and Italy (Cheng *et al.* 2003; Caserini *et al.* 2004), as well as in background areas (Caserini *et al.* 2004; Martinez *et al.* 2006).

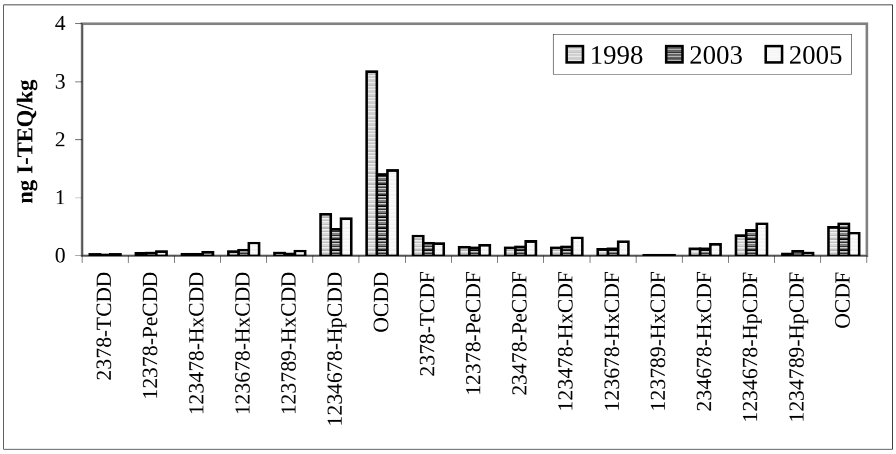

Figure 4. PCDD/F profile (median values) of herbage samples collected around the HWI during the period 1998-2005.

In 1998, PCDD/F concentrations in herbage samples ranged from 0.14 to 2.01 ng I-TEQ/kg with a median value of 0.23 ng I-TEQ/kg and a mean value of 0.31 ng I-TEQ/kg. In 2003, PCDD/F concentrations ranged from 0.05 to 0.93 ng -TEQ/kg, with median and mean values of 0.21 and 0.22 ng I-TEQ/kg, respectively. In the 2005 study, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. The temporal variation between 1998 and 2005 showed that PCDD/F levels diminished in 14 of the 40 samples, whereas in the remaining 26 different increments were noted. The median value increased 35% between the baseline (1998) and the 2005 survey. Analyzing only the two last surveys (2003/2005), it can be seen that PCDD/F concentrations decreased in 6 herbage samples, increased in 27, and remained nearly unchanged in 7 samples. In general, PCDD/F herbage levels of the different surveys are similar, with the exception of samples collected in the north direction, which slightly increased. On the other hand, PCDD/F concentrations in SV samples, collected in urban areas at different directions from the facility, diminished. Significant differences ($P < 0.05$) were found when the 2003 and 2005 values were compared. When samples were compared taken into account the different distances to the HWI for the same period of time, only rural samples (500 and 2500 m) showed a significant increase. On contrary, urban levels (>4000 m) remained similar. In spite of the inclusion of the PCDD/Fs in the "dirty dozen" list of the Stockholm Convention on Persistent Organic Pollutants, the importance of other non-regulated industrial, as well as diffuse sources could be increasing in recent years (Alcock *et al.* 2001; Quass *et al.* 2004).

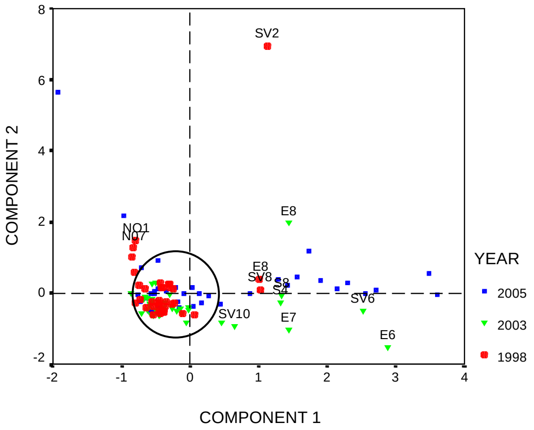

Figure 5. Principal Component Analysis for herbage samples collected in the vicinity of the HWI.

Most tetra- to octa-PCDD/F were detected in herbage samples. In the 1998 survey, the 2,3,7,8-TCDD highest concentration was 0.21 ng/kg, with median and mean values of 0.02 and 0.03 ng/kg, respectively. In 2003, 2,3,7,8-TCDD was detected in 15 of the 40 samples with a mean value of 0.02 ng/kg. In the last study, 2,3,7,8-TCDD mean value was 0.03 ng/kg. OCDD mean values were 3.93 ng/kg , 1.78 ng/kg and 2.05 ng/kg for the 1998, 2003 and 2005 surveys, respectively (median values of 3.17, 1.40 and 1.47 ng/kg, respectively).

Figure 4 shows the PCDD/F profile for herbage samples collected around the HWI during the period 1998-2005. OCDD was the most abundant congener, followed by 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDF, respectively. That pattern fits well with that found for soil samples.

In 1998, PCDD/F significant differences between urban and rural samples were noted, levels in urban samples being higher than those found in rural samples ($P < 0.05$). In the last study, PCDD/F levels in herbage diminished lightly in urban samples (-3%), with a median value of 0.28 ng/kg. In rural samples, PCDD/F concentrations increased (41%), the median value being 0.31 ng/kg of dry weight. These results reflect a reduction in the urban areas, whereas in rural areas, the levels of PCDD/F increased. The reduction was probably caused by the increasing use of unleaded fuel for motor vehicles, as well as other changes in PCDD/F emissions such as the use of new cleaning systems in incinerators. On the other hand, increased PCDD/F levels in rural areas could be caused by herbage burning. In 2005, no significant differences were found when PCDD/F levels in rural and urban herbage samples were compared ($P > 0.05$).

When a PCA was carried out on herbage samples, a single two-dimensional model that accounted for 62.1 % of the variance was obtained (Figure 5). The first main PC (48.8 % of the variance) was correlated with the HpCDDFs, while the second PC (13.3 % of the variance) was correlated with TCDFs and PeCDFs. Most samples were clustered together. However, 2003 and 2005 samples showed higher values of the first PC than that corresponding to the 1998 samples.

3.2. Human Health Risks

Data from the last survey of the environmental monitoring program (2004) were used to evaluate human health risks. The exposure to PCDD/Fs was divided into two pathways: environmental and dietary. Two groups of population, adults and children, were assessed according to their different sensitivity (Dourson *et al.* 2004). Three exposure routes were considered to assess the environmental exposure to PCDD/Fs: inhalation, dermal absorption through soil and dust, and ingestion of soil and dust. PCDD/F concentrations in air and ventilation rates of 20 m^3/day and 7.6 m^3/day for adults and children, respectively, were used to calculate inhalation through air , whereas dermal absorption and ingestion of soil and dust were determined on the basis of PCDD/F concentrations in soils (Nouwen *et al.* 2001; Nadal *et al.* 2004b). The skin coverage with soil outside, the skin coverage with dust inside, the soil fraction inside the dust and the exposed skin surface area for forehands and hands were the parameters used to evaluate the dermal exposure through soil and dust. The ingestion of soil particles, the sleeping time, the exposed time fractions and the soil fraction inside the dust were the parameters used to evaluate the dermal exposure through soil and dust. Further details on the calculations of environmental exposure such as parameters and equations, were previously reported (Domingo *et al.* 2002a; Nadal *et al.* 2004b). On the other hand, exposure to PCDD/Fs through the diet was calculated from 2003 data concerning PCDD/F concentrations and consumption of various groups of foodstuffs (Bocio and Domingo 2005). Finally, exposure was evaluated in three receptors according to the distance to the HWI: 500 m, 2500 m (rural sites) and >4000 m (urban sampling point).

Table 5. PCDD/F exposure for adults and children living at 500, 2500 and >4000 m from the HWI in 2004.

	500 m		**2500 m**		**> 4000 m**	
	Adults	**Children**	**Adults**	**Children**	**Adults**	**Children**
Environmental exposure						
PCDD/F C_{air} (ng I-TEQ/m^3)[a]	4.47E-06		4.53E-06		2.43E-04	
PCDD/F C_{soil} (ng I-TEQ/kg d.m.)	0.798		0.815		1.807	
PCDD/F *Inh* (ng I-TEQ/kg/day)	5.90E-07	7.76E-07	5.98E-07	7.87E-07	3.21E-05	4.23E-05
PCDD/F *Der total* (ng I-TEQ/kg/day)	4.89E-07	4.26E-07	5.00E-07	4.35E-07	1.11E-06	9.65E-07
PCDD/F *Ing total* (ng I-TEQ/kg/day)	1.71E-07	1.21E-06	1.73E-07	1.22E-06	2.63E-07	1.73E-06
Total environmental exposure (ng I-TEQ/kg/day)	1.25E-06	2.41E-06	1.27E-06	2.44E-06	3.35E-05	4.50E-05
Dietary exposure						
Intake of PCDD/F (ng I-TEQ/kg/day)	8.52E-04	3.24E-03	8.52E-04	3.24E-03	8.52E-04	3.24E-03
Total Exposure (ng I-TEQ/kg/day)	**8.54E-04**	**3.24E-03**	**8.54E-04**	**3.24E-03**	**8.86E-04**	**3.28E-03**

[a] PCDD/F concentrations in air particulate matter (samples collected in March 22, 2004).

The results of the human health risk assessment are summarized in Table 4. With respect to the direct exposure of PCDD/Fs, air inhalation was the main pathway in adults, especially in the urban area ($5.90\cdot10^{-7}$, $5.98\cdot10^{-7}$ and $3.21\cdot10^{-5}$ ng I-TEQ/kg/day at 500, 2500 and >4000 m, respectively). It would be due to the great difference in air concentration of PCDD/Fs between rural and urban zones (4.5 and 243 fg I-TEQ/m^3, respectively). In children, air inhalation was also the most important contributor to PCDD/F exposure at >4000 m, while the ingestion of soil and dust was the main pathway in those points located near to the HWI. In spite of the importance of air inhalation in the urban zones, in the current study exposure of PCDD/Fs through this route was of the same order of magnitude than that recently reported by Yu *et al.* (2005) in Guangzhou (China). These authors calculated inhalation of particulated PCDD/Fs of $1.38\cdot10^{-5}$, $5.68\cdot10^{-5}$, and $10.15\cdot10^{-5}$ ng I-TEQ/kg/day for adults in a forest park, a residential area, and a strongly industrialized zone, respectively. In our study, the high levels of PCDD/Fs in soil and air found in the urban areas, as well as the associated environmental exposure of the population, suggest that traffic is a very important pollution source of PCDD/Fs (Lee *et al.* 2004).

The levels of the total environmental exposure for subjects living in rural zones did not show significant differences depending on the distance to the HWI. Thus, direct exposures of $1.3 \cdot 10^{-6}$ and $2.4 \cdot 10^{-6}$ ng I-TEQ/kg/day were estimated for adults and children, respectively, independently of the distance to the stack. These levels were lower than those reported in our previous study (2003). In that survey, the environmental exposure values were $6.78 \cdot 10^{-6}$ and $9.66 \cdot 10^{-6}$ ng I-TEQ/kg/day, for adults and children, respectively, living at 500 m. These values were $5.00 \cdot 10^{-6}$ and $7.37 \cdot 10^{-6}$ ng I-TEQ/kg/day for individuals living at 2500 m. By contrast, in the 2003 survey, a lower total direct exposure was noted for adults and children living in Tarragona city (Ferré-Huguet *et al.* 2006). In the present study, environmental exposure accounted only for 0.1% of total PCDD/F exposure for adults and children living in the rural area closer to the HWI (500 and 2500 m). It increased up to 3.8 and 1.4% of total exposure for adults and children, respectively, in the urban area (>4000 m). Consequently, it seems quite evident that dietary intake of PCDD/Fs is, by far, the main pathway of PCDD/F exposure. This is not new, as the importance of the diet as the main route of PCDD/F intake has been shown in a number of studies (Domingo *et al.* 2002a,b; Karademir, 2004; Nadal *et al.* 2004b; Schuhmacher and Domingo 2006).

The non-carcinogenic risk was assessed by comparing total PCDD/F exposure with the tolerable daily intake suggested by the World Health Organization (WHO): 1-4 pg I-TEQ/kg/day (van Leeuwen *et al.* 2000; Pohl *et al.* 2002). The risk index range at the rural sites (500 and 2500 m from the HWI) was the same as that calculated in 2003: 0.21-0.85 and 0.81-3.24 for adults and children, respectively. In the urban area, the risk was slightly higher in both groups of population (0.22-0.89 in adults, and 0.82-3.28 in children). However, the upper-threshold value of 4 pg I-TEQ/kg/day was not exceeded in any scenario. The carcinogenic risk derived from the exposure to PCDD/Fs by adults was evaluated by considering an upper-bound risk of $1{\cdot}10^{-3}$ (US EPA 2000). The calculation of the total PCDD/F exposure was carried out by assimilating inhalation and dermal contact to oral exposure. Cancer risks of 850 and 890 were estimated for areas close to and far away the HWI, respectively. Considering a mean lifetime of 70 years, it would mean 12 and 13 cases of cancer for a population of 1 million inhabitants in rural and urban zones of Tarragona, respectively.

The above results show that, after 6 years of regular operation, the HWI did not significantly increase PCDD/F levels in soils and herbage of the surrounding environment. Moreover, PCDD/F emissions from the HWI do not mean additional significant risks for the health of the individuals living in the vicinity of the facility. In recent years, we have performed various studies concerning the environmental impact and human health risks near several waste incinerators of Catalonia (Schuhmacher *et al.* 1998b; Domingo *et al.* 1999; Nadal *et al.* 2002b; Ferré-Huguet *et al.* 2006; Schuhmacher and Domingo 2006). We found that those incinerators whose emission levels of PCDD/Fs compared with those regulated by the European Union, did not constitute in general terms any relevant source of PCDD/Fs. Additional health risks due to PCDD/F exposure for the population living in the vicinity were not observed. Therefore, taking together the results of the current study with our investigations in MSWI indicate that when adequately controlled for PCDD/F emissions, waste incinerators should not represent any special concern for the population living in the neighborhood. To establish the role of non-regulated and diffuse sources, especially traffic and certain industrial activities, is important in order to get comparative data with PCDD/F emissions from modern incinerators.

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Discussió conjunta dels articles del Capítol II

Nivells de metalls en herbes i sòls de les rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona

En sòls, les concentracions més elevades van correspondre al Mn i el Pb. En el període 1997-2005 es va observar una disminució de tots els metalls estudiats (excepte pel Cd i Cr), mentre que les concentracions d'As, Cr, Hg, Mn, Ni, Tl i V van mostrar una reducció significativa entre el 1999-2005. Només pel Cd i Pb es va observar un augment notable, però no significatiu. En el període 1997-2005, es va notar una disminució dels nivells de Pb en sòls. Per la majoria de metalls, les concentracions actuals (2005) van ser inferiors a les d'altres estudis fets prèviament als voltants de la incineradora de Tarragona i d'altres àrees industrals de Catalunya (Llobet i col·ls., 2002; Nadal i col·ls., 2004).

En herbes, les concentracions de Be i Tl es van trobar per sota del seu corresponent límit de detecció (0.25 i 0.03 μg/g, respectivament) en totes les mostres, mentre que les concentracions més elevades es van trobar pel Mn. Les concentracions de tots els elements analitzats van disminuir significativament ($p<0.001$) entre el 1999 i el 2004. Aquesta disminució podria indicar la tendència general a la baixa de les concentracions ambientals de molts metalls (Schuhmacher i col·ls., 2002b). Les concentracions de Pb en herbes van reflexar la reducció ambiental dels nivells de Pb causada per la prohibició de les gasolines amb plom (Bellés i col·ls., 1995; Schuhmacher i col·ls., 1996). Les diferències trobades entre les concentracions de metalls en herbes dels diferents anys estarien probablement causades per l'heterogeneïtat de les mostres, més que per les potencials diferències entre les concentracions ambientals de metalls en l'àrea estudiada. En tot cas, les concentracions de metalls en herbes trobades al 2005 als voltants de la incineradora de Tarragona van ser similars o inferiors a les detectades per altres autors en diferents espècies vegetals (Schuhmacher i col·ls., 2003; Bosco i col·ls., 2005; Sardans i Peñuelas, 2005).

Avaluació de riscos per exposició a metalls pesants a rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona

La relació entre les concentracions de metalls en sòls i els Preliminary Remediation Goals, va ser en tots els casos inferior a 100%, indicant que els nivells són segurs per la població. Així mateix, per tots els metalls el Hazard Quotient calculat a partir de l'exposició oral diària va estar per sota del valor d'1, considerat com a segur, tant per adults com per nens.

Només la ingestió d'As va superar el màxim risc carcinogènic acceptable de 10^{-6}. Per altra banda, cal destacar que aquest límit ha estat superat per sòls de diferents països (Nadal i col·ls., 2004). De la mateixa manera, quan es va comparar la concentració d'As en sòls amb el corresponent PRG (0.39 μg/g) es va superar el valor límit del 100% (amb un valor de 440), tal i com ja ho havia fet els anys anteriors 1997, 1999 i 2002 (amb valors de 1200, 1430 i 1540, respectivament). Tot i això, l'any 2005 es va observar una important disminució en els riscos carcinogènics.

Nivells de PCDD/Fs en herbes i sòls de les rodalies de la Incineradora de Residus Industrials de Tarragona

El 2004, després de cinc anys de funcionament de la planta incineradora de residus especials, les concentracions de PCDD/Fs en sòls van estar compreses entre 0.06 a 12.60 ng I-TEQ/kg, amb una mitjana i mediana de 0.65 i 1.14 ng I-TEQ/kg, respectivament. Les concentracions més elevades es van observar en punts urbans. En el període 2003-2004, es va observar un augment de les concentracions en 22 de les 40 mostres. El valor mitjà va augemntar un 16%. Aquestes variacions van ser causades probablement per desviacions en les determinacions analítiques junt amb petites variacions en els punts de mostreig. Tot i això, el test U-Mann Whitney no va mostrar diferències significatives entre el 1998 i el 2004 per cap dels escenaris considerats (500, 2,500 i > 4,000 m de la incineradora). En general, el patró de les mostres va ser similar per tots els anys estudiats, sent l'OCDD el congènere més abundant, seguit de 1,2,3,4,6,7,8-HpCDD, OCDF i 1,2,3,4,6,7,8-HpCDF. Tot i això, l'ACP va mostrar un perfil diferent per algunes mostres que podrien haver estat afectades per fonts de contaminació puntuals com la crema de rostolls.

Pel que fa a les herbes, al 2005 les concentracions de PCCD/Fs van anar de 0.03 a 1.57 ng I-TEQ/kg, amb una mitjana i una mediana de 0.31 i 0.40 ng I-TEQ/kg, respectivament. L'evolució temporal entre el 1998 i el 2008 va mostrar que els nivells van disminuir en 14 de les 40 mostres. El valor de la mediana va augmentar en un 35%. En general es va observar un augment en les concentracuions de PCCD/Fs de mostres rurals en la direcció nord, mentre que en les mostres urbanes preses en les diferents direccions es va notar un descens. La reducció podria ser causada pel nou sistema de depuració de gasos de la incineradora. Per altra banda, l'augment en les mostres rurals podria ser causat per la crema de rostolls. Els perfils de les mostres van ser semblants als trobats pels sòls, sent l'OCDD el congènere més abundant, seguit de 1,2,3,4,6,7,8-HpCDD, OCDF i 1,2,3,4,6,7,8-HpCDF. En l'ACP, com en el cas dels sòls, es va observar un cluster on s'agrupen la majoria de mostres la qual cosa indicaria que les fonts que contribueixen als nivells ambientals de PCDD/Fs de la zona han estat les mateixes els diferents anys.

Avaluació de riscos per exposició a PCDD/Fs a rodalies de la Incineradora de Residus Industrials de Tarragona

Es va calcular l'exposició ambiental a PCDD/Fs a partir de les dades d'aquest estudi. Per altra banda, es va calcular l'exposició a PCDD/Fs a través de la dieta a partir de dades d'un estudi anterior (Bocio i Domingo, 2005). Es va avaluar l'exposició d'acord amb la distància a la planta incineradora: 500 m, 2,500 m (punts rurals) i >4,000 m (punts urbans) diferenciant els grups de nens i d'adults.

Respecte a l'exposició directa a PCDD/Fs, la principal via d'exposició en adults va ser la inhalació, especialment en l'àrea urbana ($5.90 \cdot 10^{-7}$, $5.98 \cdot 10^{-7}$ i $3.21 \cdot 10^{-5}$ ng I-TEQ/kg/dia a 500, 2,500 i >4,000 m de la planta, respectivament). La raó, és la gran diferència en les concentracions de PCCD/Fs trobades en aire per la zona rural i urbana (4.5 i 243 fg I-TEQ/m^3, respectivament). Pels nens a >4,000 m de la planta, la principal via d'exposició també va ser la inhalació, mentre que a la zona rural la principal via d'exposició seria la ingesta de sòls. Per les zones rurals, els nivells d'exposició total no van mostrar diferències significatives depenent de la distància a la incineradora.

Pels adults i els nens de l'àrea més propera a la planta incineradora (500 i 2,500 m), l'exposició ambiental només va representar un 0.1% de l'exposició total (ambiental més la dieta). En l'àrea urbana (>4,000 m), aquest percentatge va pujar fins a un 3.8 i 1.4% de l'exposició total per adults i nens, respectivament.

A la zona rural (500 i 2,500 m) l'exposició va ser 0.21-0.85 i 0.81-3.24 pg/kg/dia per adults i nens, respectivament. A l'àrea urbana l'índex de risc va ser 0.22-0.89 i 0.82-3.28 per adults i nens, respectivament. A l'àrea urbana, el risc va ser lleugerament superior per ambdós grups de població (0.22-0.89 per adults i 0.82-3.28 per nens). En cap cas es va sobrepassar el valor límit (4 pg I-TEQ/kg/dia). Es van estimar rics de càncer de 850 i 890 per les àrees propera i llunyana a la incineradora, respectivament. Considerant una vida mitjana de 70 anys, això suposaria un excés de risc de càncer de 12 i 13 per una població d'1 milió en les zones rural i urbana, respectivament.

Els resultats van indicar que les emissions de la incineradora no suposaven riscos addicionals per la salut de la gent que viu a les rodalies de la instal·lació.

Capítol III

Nivells de compostos organoclorats i metalls pesants en aire

Articles 3 i 4:

Mari M, Schuhmacher M, Feliubadaló J, Domingo JL

Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers

Chemosphere 70: 1637-1643 (2008)

Mari M, Nadal M, Schuhmacher M, Domingo JL

Monitoring PCDD/Fs, PCBs and heavy metals in ambient air of an industrial area of Catalonia, Spain

Chemosphere (En premsa)

Article 3: "Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers"

Abstract

The concentrations of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) were determined in air samples collected at four sampling sites located in two zones of Barcelona (Spain): near a municipal solid waste incinerator (MSWI) and a combined cycle power plant (3 sites), and at a background/control site. Samples were collected using high-volume active samplers. Moreover, 4 PUF passive samplers were deployed at the same sampling points during three months. For PCDD/Fs, total WHO-TEQ were 27.3 and 10.9 fg WHO-TEQ m^{-3} at the urban/industrial and the background sites, respectively. The sum of 7 PCB congeners and the ΣPCN levels were also higher at the industrial site than at the background site. In order to compare active and passive sampling, the accumulated amounts of PCDD/Fs, PCBs and PCNs in the four passive air samplers, as well as the total toxic equivalents in each sampling site were also determined. To assess the use of PUF passive samplers as a complementary tool for PCDD/F, PCB and PCN monitoring, sampling rates were calculated in accordance with the theory of passive air samplers. PUF disks allowed establishing differences among zones for the POP levels, showing that they can be a suitable method to determine POP air concentrations in areas with various potential emission sources. Although both particle and gas phase were sorbed by the PUFs, data of gas phase congeners are more reproducible.

Keywords: PCDD/Fs; PCBs; PCNs; Air; High-volume samplers; PUF disks

1. Introduction

In recent years, a number of monitoring studies have been performed in order to investigate sources and levels in environmental compartments of the persistent organic pollutants (POP) PCDD/Fs, PCBs and PCNs, as well as to analyze behavior and fate (Harner i Bidleman, 1997; Harrad i Mao, 2004; Nadal i col·ls., 2004; Bakoglu i col·ls., 2005; Hung i col·ls., 2005; Schuhmacher i Domingo, 2006; Schuhmacher i col·ls., 2006). For air monitoring of POP, high-volume samplers are used as conventional sampling techniques. The relative high cost of the equipment, as well as the requirement of a pump and source electricity are important disadvantages of this sampling method. Moreover, only daily concentrations can be determined. Meteorological variations and punctual emissions of POP can also modify their concentrations in air during short time periods. A potential alternative is the use of passive samplers. These devices allow semi-quantitative comparisons of the atmospheric POP levels (Harner i col·ls., 2004). Semipermeable membrane devices (SPMDs), XAD resin samplers, tristearin-coated fiberglass, polymer-coated glass samplers (POG) and polyethylene based samplers have been used as different types of passive samplers**.** Taking into account their low cost and simple manipulation, polyurethane foam (PUF) disks are especially attractive (Jaward i col·ls., 2004a; Pozo i col·ls., 2004; Wilford i col·ls., 2004; Harner i col·ls., 2006).

In recent years, we established an environmental surveillance program in the neighborhood of a municipal solid waste incinerator (MSWI) of Sant Adrià del Besòs (Barcelona, Catalonia, Spain) (Domingo i col·ls., 2000; Schuhmacher i col·ls., 2000; Domingo i col·ls., 2002a; Domingo i col·ls., 2002b). However, due to important recent changes in town-planning, numerous soil movements have been performed in the zone under evaluation. Therefore, the characteristics of the surveillance program previously established, which involved sampling of soils and herbage, needed an important modification. The aim of the present study was to determine the atmospheric concentrations of PCDD/Fs in the same zone, an active industrial area of Barcelona with two potentially important emissions sources of PCDD/Fs and other POP: the MSWI and a combined cycle power plant. PCBs and PCNs were also included in the current survey. A second goal of the present investigation was to assess the use of passive air samplers as a complementary tool for monitoring the levels of these POP in potentially contaminated areas.

2. Methods

2.1. Sampling sites

In March-April 2005, air samples were collected using high-volume active samplers at four sampling locations of Barcelona. Three sampling sites were placed in the area above indicated and were situated at different wind directions from the two main pollutant sources. A fourth sampling site was placed in a semi rural area close to a large park with no direct pollutant sources (background/control sampling site). On the other hand, four passive samplers were deployed at the same four sampling points for approximately 3 months (between March-June 2005). The average temperature and the most frequent wind directions in Barcelona during the sampling period were 14.1ºC (range: 0.2ºC-28.9ºC) and SW, NE and NW, respectively.

2.2. Active and passive samplers

Ambient air samples of PCDD/Fs, PCBs and PCNs were collected using high-volume samplers (Tisch TE-1000) complying with US EPA TO-9 (USEPA, 1999). Passive samplers consist of a PUF disk (14 cm diameter, 1.35 cm thick) purchased from PacWill Environmental (Stoney Creek, ON, Canada) contained within a stainless steel shelter made up of two dishes (30 and 25 cm diameter, respectively). The gap between the two dishes is 2.5 cm.

2.3. Analytical methods

Concentrations of PCDD/Fs, PCBs and PCNs in air were determined by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) according to the VDI 3499 method. $^{13}C_{12}$-isotopic recovery internal standards were added to the samples. Subsequently, the filter and PUF plugs were extracted by ASE (Accelerated Solvent Extraction) from Dionex 300. Toluene was used as solvent under the following conditions: heat 5 min to 100ºC, and a pressure of 100 bars during 5 min. The volume of the sample extract was reduced to about 1 ml by means of a Zymark-Turbovap. The extract was subsequently subjected to an acid/base clean-up procedure followed on micro columns of silica gel and alumina. For clean-up step 1, the solution was transferred to the first column with glass wool, 20 g alkaline silica gel 33% NaOH, 20 g neutral silica gel with 44% sulfuric acid and 20 g sodium sulfate. This column was washed with 400 ml of hexane, being the solution then reduced to 1 ml. For clean-up step 2, the solution was transferred to a column with 25 g of alumina and 20 g of sodium sulfate. The column was firstly eluted with 150 ml of hexane/dichloromethane 50/50 (v/v). The solution was subsequently reduced to 1 ml. The PCDD/F fraction (or the PCB/PCN fraction) was concentrated near to dryness by a gentle stream of dry nitrogen. The final extract was spiked with the isotopic labeled internal standard and then analyzed with HRGC-HRMS (GC HP 5890 or Varian GC coupled with HR MS VG Autospec or Finnigan MAT95) to determine the recovery efficiencies achieved for the $^{13}C_{12}$-labelled internal standards. The mass spectrometer operated under electron impact (EI) positive mode (35-45 eV) and selected ion monitoring (SIM) mode, at resolving power range from 6.000 to 10.000 amu. The mass range available was 0-2.000 amu. The selected PCBs were quantified via the internal recovery standard, whereas PCNs were quantified by means of $^{13}C_{12}$-PCB standards (Halowax standards). For analytical quality control, clean PUF disks (blanks) were pre-extracted and similarly analyzed. Samples were spiked with isotopic labeled internal standard and then analyzed to determine the recovery efficiencies achieved for the $^{13}C_{12}$-labeled internal standards.

3. Results and Discussion

3.1. PCDD/F, PCB and PCN concentrations

Table 1 shows the PCDD/F, PCB and PCN concentrations of the high-volume air samples collected in four sampling sites of Barcelona. The major contributor to total WHO-TEQ was 2,3,4,7,8-PeCDF (13-27%). According to various international studies, this congener accounts for 20-40% of total TEQ (Lohmann i Jones, 1998). Probably, the current contribution percentages were slightly lower because of the new WHO-TEF (Van den Berg i col·ls., 2006) value for this congener is smaller. The most abundant congener was OCDD (44% of the total concentration), followed by 1,2,3,4,6,7,8-HpCDD (14%) and OCDF (10%). The homologue concentrations found at the urban/industrial and background sites are depicted in Fig. 1. An ambient pattern of decreasing concentrations of PCDFs and increasing concentrations of PCDDs with increasing chlorination level could be observed in both zones (urban/industrial and background). Different ratios between 2,3,7,8-PCDDs and 2,3,7,8-PCDFs might reflect differences in local emissions, and/or different atmospheric conditions (Correa i col·ls., 2004). Taking this into account, ratios were calculated for each sampling site. Site 4 (background/control) showed the lowest ratio (1.1), whereas site 1 (urban/industrial area), showed the largest value (3.2), being the ratios at sites 2 and 3 comparatively similar (1.6 and 1.3, respectively).

Table 1

Atmospheric concentrations of PCDD/Fs (fg m^{-3}), PCBs and PCNs (pg m^{-3}) determined by high-volume air sampling in four sites of Barcelona (March-April 2005).

	Urban/Industrial			**Background**
	S1	**S2**	**S3**	**S4**
2,3,7,8-TCDD	<1.5	<1.5	<1.8	<1.5
1,2,3,7,8-PeCDD	3.6	2.7	3.5	1.5
1,2,3,4,7,8-HxCDD	3.7	2.8	3.5	1.5
1,2,3,6,7,8-HxCDD	12.1	11.9	11.8	4.4
1,2,3,4,7,8-HxCDD	9.1	7.5	7.6	2.1
1,2,3,4,6,7,8-HpCDD	149.6	94.3	92.9	30
OCDD	705.9	234.5	242.0	79.8
2,3,7,8-TCDF	12.9	14.8	21.5	11.0
1,2,3,7,8-PeCDF	10.6	13.3	16.8	9.1
2,3,4,7,8-PeCDF	17.2	14.9	21.8	9.8
1,2,3,4,7,8-HxCDF	17.0	14.2	19.5	7.6
1,2,3,6,7,8-HxCDF	19.7	17.4	24.4	10.6
2,3,4,6,7,8-HxCDF	1.9	1.8	1.6	1.5
1,2,3,7,8,9-HxCDF	18.8	15.3	23.4	9.7
1,2,3,4,6,7,8-HpCDF	64.2	52.4	69.5	22.7
1,2,3,4,7,8,9-HpCDF	5.7	6.6	7.9	4.5
OCDF	108.3	66.1	77.4	21.6
Ratio PCDD/PCDF	3.2	1.6	1.3	1.1
fg WHO-TEQ^{a} m^{-3}	38.7	18.5	24.6	10.9
PCB 28	66	60	56	28
PCB 52	42	36	26	16
PCB 101	24	22	30	22
PCB 118	<10	<10	13	<10
PCB 138	13	16	24	25
PCB 153	14	18	24	26
PCB 180	<10	<10	<10	<10
∑PCB	169	162	178	127
Sum of MonoCNs	272.8	122.7	140.1	219.1
Sum of DiCNs	218.9	122.7	99.1	208.7

Sum of TriCNs	90.9	52.0	30.8	62.6
Sum of TetraCNs	26.9	37.2	10.3	24.3
Sum of PentaCNs	2.0	3.7	1.7	2.4
Sum of HexaCNs	<1.7	<1.7	<1.7	<1.7
Sum of HeptaCNs	<1.7	<1.7	<1.7	<1.7
OctaCN	6.7	14.9	<1.7	<1.7
∑ PCN	621.8	356.9	288.8	522.4

[a]To calculate total WHO-TEQ values, for those congeners below the limit of detection (LOD), concentrations were assumed to be half of the LOD.

The sum of the PCB congeners was higher at the urban/industrial zone (mean: 170 pg m^{-3}) than at the background site (127 pg m^{-3}). These values are in the range of a number of reported levels concerning urban areas over the world (Brunciak i col·ls., 2001; Garcia-Alonso i col·ls., 2002; Mandalakis i col·ls., 2002; Yeo i col·ls., 2004). However, it must be noted that in most studies some congeners were determined as mixtures. In the present study, PCB 180 was under its detection limit in all samples, whereas PCB 118 could be detected only at site 3 (13 pg m^{-3}). Both PCB congeners are typical of MSWI and coal power emissions (Biterna i Voutsa, 2005). Decreasing concentrations with rising chlorination degree were observed in the urban/industrial sites. Similar results were also previously reported in both urban and rural areas (Mandalakis i col·ls., 2002; Yeo i col·ls., 2004).

Mono- and dichloronaphthalenes were the predominating PCN homologues (78% of the total contribution). However, when the most frequently analyzed homologues, tri- to octaCNs, were taken into account, the highest sum of homologues corresponded to triCNs followed by tetraCNs, which is in agreement with results of previous studies (Dorr i col·ls., 1996; Harner i col·ls., 2000). When compared with literature data (Dorr i col·ls., 1996; Harner i col·ls., 2000; Jaward i col·ls., 2004a; Manodori i col·ls., 2006), the current values seem to be enormous. Notwithstanding, it must be noted that in those studies only some PCN congeners or homologues (tri- to octaCNs) were analyzed.

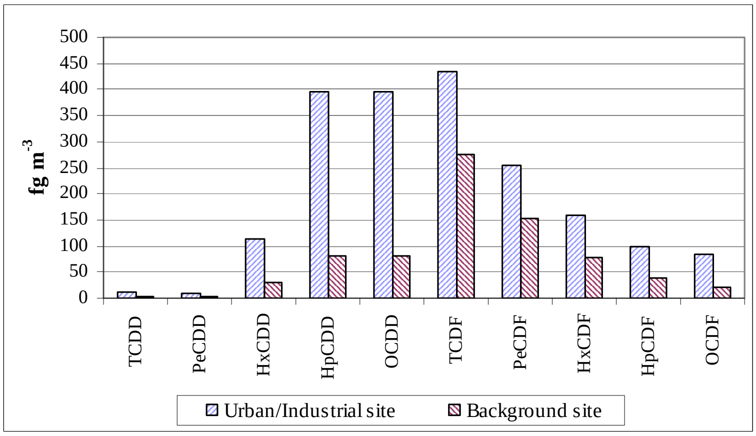

Fig. 1. Homologue concentrations of PCDD/Fs in the high-volume air samples of the urban/industrial area (mean values) and the background site.

In general terms, we found low air levels of the analyzed POP. It would reflect the global decrease of these chemicals worldwide as result of the use of new technologies in the flue gas cleaning systems of incinerators, the increasing use of unleaded fuel motor vehicles, as well as other important environmental improvements (Schuhmacher i col·ls., 2002b; Yeo i col·ls., 2004). A similar reduction was also recently observed in studies performed in the same area, when soil and herbage samples were used as environmental monitors (Domingo i col·ls., 2002a). Clean marine air could also contribute to dilute the effect of those emission sources, which are located at a few meters from the Mediterranean Sea (Gao i col·ls., 2002; Gambaro i col·ls., 2004).

3.2. PCDD/F, PCB and PCN concentrations in passive air samplers

The accumulated amounts of PCDD/Fs, PCBs and PCNs in the four passive air samplers, as well as the total toxic equivalents in each sampling site are shown in Table 2. Total tetra- and penta-CDFs and tetra-CDDs were the main contributors to total PCDD/Fs. These homologues are predominant in the gas phase, tending PCDDs to be more associated with the particulate than the equivalent PCDF homologues. OCDD was the predominant congener, 62% of the total, followed by 1,2,3,4,6,7,8-HpCDD, 7%, of the total. With respect to PCDFs, OCDF accounted for 3-5% of the total 2,3,7,8-substituted congeners. These results show that most compounds associated with particles are also sequestered by the samplers. Similar findings were reported in a recent study in which PUF passive air samplers were also used (Jaward i col·ls., 2005).

With respect to PCBs, because of analytical problems no data from site 3 are reported. PCB 28 was the most abundant congener in the remaining three sites. Sites 1 and 2, situated at the urban/industrial zone, showed decreasing concentrations with the increasing number of chlorine atoms. As also observed in the active sampling, at the background site hexa- and heptaCBs (No. 138, 153 and 180) were found at higher quantities than tetraCBs (No. 52 and 101). With regard to PCNs, as for active samplers, the homologue pattern was dominated by the lower chlorinated PCNs. A very notable difference was found between the concentrations of the mono- and diCNs, which are more volatile and prone to undergo LRAT (Pribylova i col·ls., 2006), and those concerning the rest of homologues.

Table 2

Accumulated amounts of PCDD/Fs (pg), PCBs and PCNs (ng) by passive air samplers in four sites of Barcelona during March-June 2005.

	Urban/Industrial			**Background**
	S1	**S2**	**S3**	**S4**
Sampling period (days)	97	91	97	97
2,3,7,8-TCDD	<0.5	<0.5	<0.6	<0.6
1,2,3,7,8-PeCDD	0.5	<0.5	0.9	<0.6
1,2,3,4,7,8-HxCDD	0.5	<0.5	<0.6	<0.9
1,2,3,6,7,8-HxCDD	1.5	<0.5	<0.6	<0.9
1,2,3,4,7,8-HxCDD	1.1	<0.5	<0.6	<0.9
1,2,3,4,6,7,8-HpCDD	23.3	6.8	7.2	4.2
OCDD	195.0	32.2	69.9	32.7
2,3,7,8-TCDF	4.1	2.8	2.1	<2.7*
1,2,3,7,8-PeCDF	2.7	2.6	2.7	0.9
2,3,4,7,8-PeCDF	2.4	2.9	3.3	1.8
1,2,3,4,7,8-HxCDF	3.6	2.2	2.4	2.4
1,2,3,6,7,8-HxCDF	3.4	2.6	3.6	1.8
2,3,4,6,7,8-HxCDF	<0.5	<0.5	<0.6	<0.9
1,2,3,7,8,9-HxCDF	1.8	1.3	0.9	<0.9
1,2,3,4,6,7,8-HpCDF	10.0	7.5	5.4	4.2
1,2,3,4,7,8,9-HpCDF	0.7	<1.0	<1.5	<0.9
OCDF	10.5	3.3	3.3	<6.0*
pg WHO-TEQ	3.6	2.6	3.4	2.0
PCB 28	16.4	17.2	-	12.3
PCB 52	9.6	11.0	-	7.5
PCB 101	7.3	8.6	-	6.9
PCB 118	2.0	3.0	-	<3.0
PCB 138	4.6	6.1	-	8.4
PCB 153	5.0	6.7	-	9.9
PCB 180	2.0	2.6	-	8.4
Sum of MonoCNs	105	93	85	69

Sum of DiCNs	122	114	101	82
Sum of TriCNs	4	5	5	3
Sum of TetraCNs	3	4	2	2
Sum of PentaCNs	0.4	0.4	0.3	0.3
Sum of HexaCNs	<0.1	<0.1	0.2	<0.1
Sum of HeptaCNs	<0.1	<0.1	<0.1	<0.1
OctaCN	0.2	0.1	0.2	0.2
Σ PCN	236	218	194	158

* Increased LOD because of matrix interferences.

3.3. PCDD/F and PCB passive sampling rates

To evaluate the use of PUF passive air samplers as a potential complementary tool for environmental monitoring of PCDD/Fs, and PCBs and PCNs, sampling rates were calculated in accordance with the theory of passive air samplers (Harner i col·ls., 2004; Pozo i col·ls., 2004). Passive air samplers accumulate chemicals via diffusion (Shoeib i Harner, 2002). The chemical exchange between uptake and elimination processes is described using mass transfer coefficients and rate constants:

$$V_{PUF}\left(\frac{dC_{PUF}}{dt}\right) = k_A \cdot A_{PUF}\left(C_A - \frac{C_{PUF}}{K_{PUF-A}}\right) \quad (1)$$

where:

V_{PUF} is the volume of the sampling medium (cm^3)

C_{PUF} is the passive sampler concentration (ng)

C_A is the air concentration (ng cm^{-3})

k_A is the air side mass transfer coefficient (cm s^{-1})

A_{PUF} is the planar area of the exposed portion (cm^2)

K_{PUF-A} is the passive sampler medium-air partition coefficient (dimensionless)

It has been shown that K_{PUF-A} is well correlated with $K_{OA,}$ being the time required for a chemical to reach saturation inversely proportional to K_{PUF-A} (Pozo i col·ls., 2004). It has been also demonstrated that sampling rates of chemicals with $K_{OA} > 10^{8.5}$ remained linear (and defined by the mass transfer coefficient) over 100 days at few $m^3 day^{-1}$ (Shoeib i Harner, 2002). Under these conditions of linearity, sampling rates for the target compounds can be calculated according to the following simple expression:

$$R_{cal} = \frac{C_{PUF}}{C_A} \cdot t \quad (2)$$

where R_{cal} is the sampling rate (m^3 day^{-1}) measured at the calibration site, C_{PUF} is the amount of pollutant accumulated in the sampler (ng), C_A is the concentration of that contaminant in the vapor phase (ng m^{-3}), and t is the time of exposure (days). It is important to note that this analysis considers only the gas phase transfer of contaminants, being the mass transfer coefficient strongly related to wind speed (Bartkow i col·ls., 2005). Therefore, PUFs are housed in a chamber which protects them from precipitation and sunlight, also diminishing the effect of wind. The rates can be used to estimate air concentrations using the same kind of devices.

Table 3

Sampling rates (m^3 day^{-1}) for each PUF passive air sampler.

Congeners	PS 1	PS 2	PS 3	PS 4
2,3,7,8-TCDD	-	-	-	-
1,2,3,7,8-PeCDD	4.0 (1.4)	-	7.2 (2.7)	-
1,2,3,4,7,8-HxCDD	9.7 (1.5)	-	-	-
1,2,3,6,7,8-HxCDD	8.3 (1.3)	-	-	-
1,2,3,4,7,8-HxCDD	9.8 (1.4)	-	-	-
1,2,3,4,6,7,8-HpCDD	24.2 (2.1)	7.5 (0.6)	7.5 (0.7)	16.4 (1.4)
OCDD	224.8 (5.1)	39.6 (0.8)	80.6 (1.8)	186.2 (4.2)
2,3,7,8-TCDF	3.4 (3.3)	2.5 (2.1)	1.7 (1.0)	-
1,2,3,7,8-PeCDF	3.9 (2.6)	4.0 2.1)	3.9 (1.7)	2.0 (0.5)
2,3,4,7,8-PeCDF	3.0 (1.4)	3.9 (2.1)	4.2 (1.6)	4.2 (1.9)
1,2,3,4,7,8-HxCDF	9.4 (2.2)	6.1 (1.4)	6.2(1.5)	13.9 (3.3)
1,2,3,6,7,8-HxCDF	7.6 (1.7)	6.2 (1.4)	8.0 (1.8)	7.7 (1.8)
2,3,4,6,7,8-HxCDF	-	-	-	-
1,2,3,7,8,9-HxCDF	1.5 (0.9)	1.1 (0.7)	0.7 (0.5)	-
1,2,3,4,6,7,8-HpCDF	10.5 (1.7)	8.4 (1.3)	5.7 (0.9)	12.0 (1.9)
1,2,3,4,7,8,9-HpCDF	11.6 (1.1)	-	-	-
OCDF	40.6 (1.3)	13.6 (0.4)	12.8 (0.4)	-
PCB 28	2.8	3.1	-	4.5
PCB 52	2.9	3.5	-	4.9
PCB 101	3.8	4.8	-	4.2
PCB 118	1.6	2.6	-	-
PCB 138	3.4	4.8	-	4.4
PCB 153	3.4	4.9	-	4.9
PCB 180	-	-	-	-
Sum of MonoCNs	3.8	7.8	6.3	3.2
Sum of DiCNs	5.5	9.6	10.5	4.1
Sum of TriCNs	0.4	1.0	1.7	0.5
Sum of TetraCNs	1.1	1.1	2.0	0.8

Sum of PentaCNs	2.0	1.1	1.8	1.3
Sum of HexaCNs	-	-	-	-
Sum of HeptaCNs	-	-	-	-
OctaCN	-	-	-	-

In parentheses, sampling rates calculated using total air concentrations (c_v+c_p).

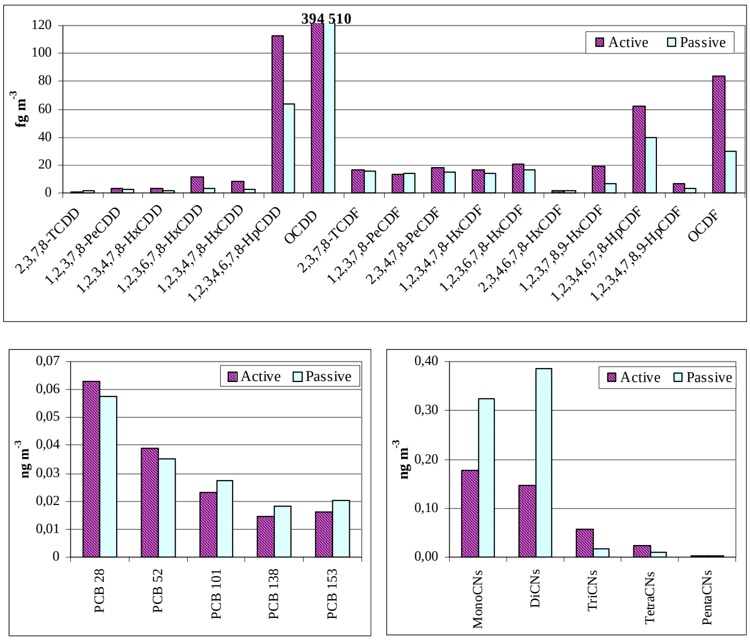

Fig. 2. Concentrations of PCDD/Fs (top) and PCBs and PCNs (bottom) in active and passive samples calculated using rates of 2 and 3 $m^3 day^{-1}$ for PCDD/Fs, and for PCBs and PCNs, respectively.

In the current study, sampling rates (m^3 day^{-1}) were calculated according to this theory. Passive sampler amounts of each congener were used and the corresponding vapor phase concentration determined separately in the active sampling. This approach resulted in very high rates for the heaviest PCDD/Fs, which are almost exclusively associated to the particle phase. However, as previously found in the concentrations in the PAS, they were also trapped (at least part of them) by the passive samplers (Table 2). Therefore, for rate estimation of PCDD/Fs, the total air concentration (Cv+Cp) was also considered and a linear uptake was assumed throughout exposure time (91-97 days). The uptake/rate results for each PCDD/F and PCB congener and PCN homologues are also shown in Table 3. High substituted PCDD/F congeners resulted in very high rates when only the gas phase was considered. However, when total air concentrations were taken into account, the rates (0.4-5.1 m^3 day^{-1}) were lower than those obtained for most gas phase congeners (tetra- and penta- congeners) (1.7-7.2 m^3 day^{-1}). Data for hepta- and octa- congeners were rather heterogeneous, which could be due to the particle size in each site. The finer the particle, the more easily it is sorbed by the passive sampling device. The current results are in agreement with those of Lohmann et al. (1998), who found SPMD efficient samplers for vapor phase species with good reproducibility between samplers, but with a poorer reproducibility for particle associated species. In general terms, rates obtained for tetra- and pentaCDD/F substituted congeners were homogeneous, with a mean value of 3.7 m^3 day^{-1}. Otherwise, when total air concentrations were taken into account a mean value of 1.7 m^3 day^{-1} was obtained. Because part of the particles were sequestered by the PAS, it seemed more appropriated to use a 2 m^3 day^{-1} value for PCDD/F estimations. PCB uptake/rates ranged from 1.6 to 4.9 m^3 day^{-1}, with a mean value of 3.8 m^3 day^{-1}. These values are similar to those reported by Shoeib and Harner (2002), 3-4 m^3 day^{-1}, in indoor conditions. An uptake rate of 3-4 m^3 day^{-1} has been used in field-studies to assess PCB levels (Gouin i col·ls., 2004; Jaward i col·ls., 2004b). PCNs rates ranged from 0.4 to 10.5 m^3 day^{-1}, with the highest rates belonging to the most abundant air homologues. The mean value for PCNs was 3.3 m^3 day^{-1}. In order to validate these mean rates, PAS concentrations were calculated and compared with those of the active samples (Fig. 2). The results indicate that the concentrations obtained with the passive samplers fit quite well with the levels obtained with the active samplers. It suggests that these devices might be used as complementary tools in environmental air monitoring.

In summary, in agreement with data of other recent studies (Gouin i col·ls., 2004; Harner i col·ls., 2006), the current results show that PUF disks may be a suitable tool to estimate POP levels in air, mainly in those areas where a number of potential emission sources are located. Both particle and gas phases are sorbed by the PUFs. However, data of most gas phase congeners are more reproducible. Consequently, estimations of low log K_{OA} species are more accurate.

Acknowledgments

This study was financially supported by the Metropolitan Entity of the Environment, Barcelona, Catalonia, Spain.

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Article 4: "Monitoring PCDD/Fs, PCBs and heavy metals in ambient air of an industrial area of Catalonia, Spain"

Abstract

In 2005 and 2006, the levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and metals (As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Tl and V) were measured in air samples collected in an industrial area of Sant Adrià del Besòs (Barcelona, Catalonia, Spain) where a municipal solid waste incinerator (MSWI) is placed, and in a background/control area. In general terms, concentrations of all environmental pollutants were higher at the industrial site. No significant seasonal/temporal variations were observed in any of the areas. No Pearson correlation was found between the PCDD/F concentrations and the environmental conditions of the two sampling periods considered. Principal Component Analyses (PCA) were performed to get information on the relationship among samples, pollutants, and emission sources. The results indicate that the MSWI of S. Adrià de Besòs is not a significant emission source of the above compounds for the area under its direct influence. Moreover, a notable difference in the PCDD/F congener profiles was found between ambient air and stack gas emissions, indicating that the current levels of PCDD/Fs are more related to other potential emissions sources rather than to those from the MSWI.

Keywords: PCDD/Fs; PCBs; Metals; Air; Municipal solid waste incinerator; Principal Component Analysis

1. Introduction

In recent years, a number of studies have demonstrated that emissions of toxic pollutants from modern municipal solid waste incinerators (MSWIs) have a relatively low environmental impact in comparison with other alternatives of waste disposal or different industrial activities (Schuhmacher i Domingo, 2006; Kao i col·ls., 2007; Wang i col·ls., 2008). However, waste incinerators in general, and MSWIs in particular, continue to generate a notable concern in the public opinion based mainly on the potential risks associated with the emission of hazardous substances (Domingo, 2002). Among these substances, special attention has been paid to polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), and polychlorinated biphenyls (PCBs), taking into account the toxicity, environmental persistence, and capacity for bioaccumulation. The human exposure to these chlorinated contaminants mainly occurs via consumption of food, and more specifically, the ingestion of fatty foodstuffs (Llobet et al., 2008). However, the environmental exposure to PCDD/Fs must not be neglected. Among the different pathways of direct exposure, inhalation seems to be the most important route (Nadal et al., 2004b).

Chronic (long-term) inhalation of those substances is associated with damage to organs such as lungs, liver or kidney. In addition, some metals (i.e. chromium, cadmium, beryllium and arsenic), as well as some PCDD/F congeners are carcinogens (IARC, 1997; Ekino i col·ls., 2007).

Although environmental policies are becoming more and more stringent with respect to the emission limits of different pollutants, monitoring surveys are important in order (1) to ensure the proper working of cleaning systems, (2) to control the environmental levels, (3) to assess environmental exposure to and health risks associated with different pollutant sources, and (4) to identify the relative importance emission sources into the atmosphere to adopt the necessary measures to protect the environment and the human health. In that context, ambient air monitoring is crucial to estimate the current emissions (Raun i col·ls., 2005).

Sant Adrià de Besòs (3.87 km^2 and 32,600 inhabitants) is a town situated at the NE of Barcelona (Catalonia, Spain), being part of its metropolitan area. Since 1975, a MSWI which handles 300,000 tones per year is operating there. In addition, a combined cycle power plant (783 MW) is located at only 1 km from the MSWI. Both facilities have been eventually integrated in the town landscape due to the urban expansion.

In Spring 2005, we performed a survey focused on determining the concentrations of PCDD/Fs and PCBs in air samples collected at four sampling sites in Sant Adrià de Besòs, three were located near the MSWI and one at a control site (Ekino i col·ls., 2007). The main goal of the present study was to assess the temporal trend in the ambient air levels of PCDD/Fs and PCBs near the MSWI of Sant Adrià del Besòs, as well as to obtain data on the levels of heavy metal in the area under assessment. Moreover, the influence of the MSWI and other potential emission sources was evaluated by means of the comparison with a control site using Principal Component Analysis (PCA).

2. Materials and methods

2.1. Sampling

In 2005 and 2006, air samples were collected at four sampling sites by using high-volume active samplers (TE-1000 PUF for organic compounds ($N_{PCDD/Fs}$=16; N_{PCBs}=16) and TE-6070DV Air Sampler for PM10 particulate matter (N_{PM10}=16), Tisch Environmental, Cleves, OH, USA). Three sampling sites (SAB-1, SAB-2 and SAB-3) were located within the S. Adrià de Besòs area under the influence of a MSWI and a power plant. SAB-1 and SAB-2 were both situated at 500 from the MSWI, while SAB-3 was placed at 1 km. A fourth sampling site (BK) was located in a suburban area near a green space of Barcelona, with no direct industrial pollutant sources (Fig. 1). It was considered as background/control sampling site. Samples were collected during two different periods of the year: spring (temperature range: 6.7-23.7 ºC) and autumn (temperature range: 11.9-30.1 ºC). The prevailing wind directions during the sampling periods were SW, NW and W.

2.2. Analytical procedure

PCDD/F and PCB concentrations were determined by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) following the German VDI 3499 method (VDI, 2003). Quartz fiber filters and polyurethane foam (PUF) plugs were used to collect separately the particle and the gas phases, respectively. Prior to the extraction, $^{13}C_{12}$-PCDD/F congeners were added as internal standards to compensate for any potential loss during the extraction and clean-up process. Quartz fiber filters and PUF plugs were extracted with toluene by Accelerated Solvent Extraction (ASE). The extract was subsequently subjected to an acid/base clean-up procedure followed on micro columns of silica gel and alumina. The final extract was spiked with isotopically labeled recovery standards and then analyzed by HRGC-HRMS (GC HP 5890 or Varian GC coupled with HR MS VG Autospec Finnigan MAT95, depending on the chemical). For analytical quality control, clean PUFs (blanks) were pre-extracted and similarly analyzed. Recovery percentages ranged between 60% and 130%. A quality assurance/quality control (QA/QC) process was carried out during the calibration and quantification. The sensitivity of the method was determined by checking that the HRMS signal of 1 pg of TCDD presented a signal to noise ratio higher than 10:1. Thereby, 5 ions were simultaneously monitored. The compound identification required the following criteria: a) the ratio of 2 ions obtained by the GC/MS matched the theoretical ration of the ratio obtained from the calibration standard run within ±15%; b) monitored ions to a given congener had to maximize within 2 s. Finally, the limit of

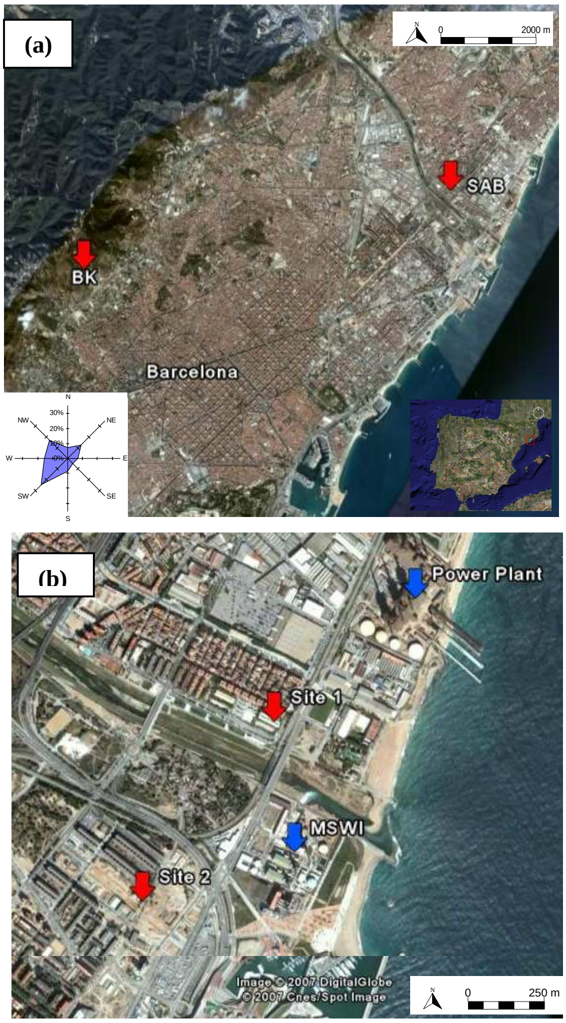


Fig. 1. Sampling locations (a) Areas of S.Adrià de Besòs (SAB) and background/control area (BK); (b) Sites of the SAB area, together with the MSWI and the power plant. Wind rose in the area of study, indicating the prevailing wind direction (coming from).

detection (LOD) for each PCDD/F congener was calculated as 3-times the signal to noise ratio.

Metal (As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Tl and V) concentrations were measured by inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000) after filter digestion. One eighth part of each filter (surface: 50.3 cm^2) was digested with HNO_3 (65% Suprapur, E. Merck, Darmstadt, Germany) and HF (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Spain) in hermetic teflon bombs. Blank and control samples, as well as reference materials (Soil, Loamy clay, Resource Technology Corporation, Laramie, WY, USA, CRM 052), were used to check the accuracy of the instrumental methods. The recovery percentage of this reference material ranged from 84% to 134% for Pb and As, respectively.

2.3. Data analysis

For calculations, when a result was below the LOD, the value was assumed to be half of that limit (ND = 1/2 LOD). Data analysis was carried out by means of the SPSS 15.0 statistical package. The statistical significance was established by applying the Levene test to analyze whether or not the data followed a parametric distribution. Subsequently, an ANOVA test was applied. Toxic equivalents for PCDD/Fs were calculated according to the 2005 WHO-TEF system (Van den Berg i col·ls., 2006).

3. Results and discussion

3.1. PCDD/Fs

The concentrations of the 2,3,7,8-substituted PCDD/F congeners in air samples collected in S. Adrià de Besòs (SAB-samples) and the background/control site (BK-samples) in 2005 and 2006 are summarized in Table 1. The mean concentrations in the SAB industrial and BK control areas were 0.018 and 0.012 pg WHO-TEQ m^{-3}, respectively. The highest concentrations corresponded to sample SAB-3.1 (0.024 pg WHO-TEQ m^{-3}) in the industrial area, while the lowest levels were found in sample BK-4.4 (0.008 pg WHO-TEQ m^{-3}) belonging to the background/control area.

Tetrachlorodibenzo-p-dioxin (TCDD), the most toxic congener of dioxins and furans, was found under its detection limit (<0.002 pg m^{-3}) in all samples except SAB-3.4 (0.006 pg m^{-3}) and BK-4.4 (0.002 pg m^{-3}). This last sample showed a quite different profile, with very low values for all the remaining congeners. The most abundant congeners in all samples were the highest chlorinated: OCDD, whose concentration ranged between 0.027 and 0.706 pg m^{-3}, followed by 1,2,3,4,6,7,8-HpCDD (range: 0.014-0.150 pg m^{-3}) and OCDF (range: 0.011- 0.108 pg m^{-3}). In terms of contribution to total WHO-TEQ, OCDF was the congener showing the lowest contribution to total WHO-TEQ in all samples (< 1%). In contrast, 2,3,4,7,8-PeCDF was the most important contributor in most samples (22-25%), with the exception of BK-4.2 (where 1,2,3,7,8-PeCDD contributed 22%) and SAB-3.4 (where TCDD contributed 31%). Notwithstanding, mean PCDD/F congener profiles of both SAB and BK areas were similar (Fig. 2). The mean profile of four emission samples recently collected in the MSWI stack gas is also shown in Fig. 2. It can be noted that ambient and source profiles were quite different, with respect to the OCDD/HpCDD ratio with OCCD and 1,2,3,4,6,7,8-HpCDD being the most abundant PCDD/F congeners in immission and emission air samples, respectively. Although the different PCDD/F congeners may undergo different reactions and/or deposition processes, by comparing source and ambient samples it seems evident that the MSWI is not primarily responsible for the environmental levels of PCDD/Fs in the area under evaluation.

Table 1. PCDD/F concentrations (pg m^{-3}) in active air samples collected near the MSWI of S. Adrià del Besòs in 2005 and 2006.

	SAB-1.1	**SAB-2.1**	**SAB-3.1**	**SAB-1.2**	**SAB-2.2**	**SAB-3.2**	**SAB-1.3**	**SAB-2.3**	**SAB-3.3**	**SAB-1.4**	**SAB-2.4**	**SAB-3.4**	**BK-4.1**	**BK-4.2**	**BK-4.3**	**BK-4.4**
2,3,7,8-TCDD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	<LOD	<LOD	<LOD	0.002
1,2,3,7,8 PeCDD	0.004	0.003	0.004	0.004	0.002	0.004	0.002	0.004	0.004	0.002	0.002	0.002	0.002	0.002	0.003	<LOD
1,2,3,4,7,8-HxCDD	0.004	0.003	0.004	0.003	<LOD	0.003	0.002	0.003	0.002	0.002	0.001	0.001	0.002	0.004	0.003	<LOD
1,2,3,6,7,8-HxCDD	0.012	0.012	0.012	0.009	0.005	0.008	0.007	0.009	0.01	0.004	0.005	0.004	0.004	0.007	0.011	0.002
1,2,3,7,8,9-HxCDD	0.009	0.008	0.008	0.006	0.003	0.007	0.005	0.004	0.006	0.002	0.003	0.003	0.002	0.006	0.005	0.001
1,2,3,4,6,7,8-HpCDD	0.150	0.094	0.093	0.056	0.040	0.055	0.038	0.046	0.045	0.023	0.033	0.026	0.030	0.044	0.042	0.014
OCDD	0.706	0.235	0.242	0.192	0.106	0.140	0.143	0.092	0.087	0.067	0.070	0.071	0.080	0.084	0.083	0.027
2,3,7,8-TCDF	0.013	0.015	0.022	0.017	0.010	0.016	0.01	0.016	0.014	0.009	0.008	0.021	0.011	0.006	0.01	0.007
1,2,3,7,8 PeCDF	0.011	0.013	0.017	0.015	0.005	0.011	0.006	0.010	0.014	0.007	0.009	0.015	0.009	0.006	0.016	0.003
2,3,4,7,8 PeCDF	0.017	0.015	0.022	0.018	0.007	0.019	0.009	0.018	0.017	0.014	0.010	0.017	0.010	0.006	0.017	0.009
1,2,3,4,7,8-HxCDF	0.017	0.014	0.020	0.016	0.007	0.015	0.008	0.017	0.017	0.013	0.014	0.007	0.008	0.005	0.015	0.004
1,2,3,6,7,8-HxCDF	0.020	0.017	0.024	0.018	0.008	0.018	0.008	0.02	0.019	0.013	0.011	0.008	0.011	0.005	0.022	0.004
1,2,3,7,8,9-HxCDF	0.002	0.002	0.002	0.003	<LOD	<LOD	<LOD	0.003	0.002	<LOD	0.001	<LOD	0.002	<LOD	0.003	<LOD
2,3,4,6,7,8-HxCDF	0.019	0.015	0.023	0.016	0.007	0.015	0.008	0.018	0.019	0.019	0.013	0.007	0.010	0.007	0.018	0.003
1,2,3,4,6,7,8-HpCDD	0.064	0.052	0.070	0.05	0.024	0.043	0.031	0.051	0.052	0.051	0.057	0.020	0.023	0.021	0.062	0.013
1,2,3,4,7,8,9-HpCDF	0.006	0.007	0.008	0.006	<LOD	0.007	<LOD	0.01	0.007	<LOD	0.010	<LOD	0.005	<LOD	0.011	<LOD
OCDF	0.108	0.066	0.077	0.052	<LOD	0.038	0.039	0.036	0.038	0.036	0.048	0.014	0.022	<LOD	0.035	0.011
Mean WHO-TEQ	0.022	0.018	0.024	0.020	0.010	0.020	0.011	0.020	0.020	0.014	0.012	0.019	0.011	0.009	0.019	0.008

LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: TCDD and 1,2,3,7,8,9-HxCDF: 0.002 pg m^{-3}; 1,2,3,7,8 PeCDD and 1,2,3,4,7,8-HxCDD: 0.001 pg m^{-3}; 1,2,3,4,7,8,9-HpCDF: 0.003 pg m^{-3} and OCDF: 0.020 pg m^{-3}. WHO-TEQ calculated according to the 2005 WHO-TEF system (Van den Berg et al., 2006).

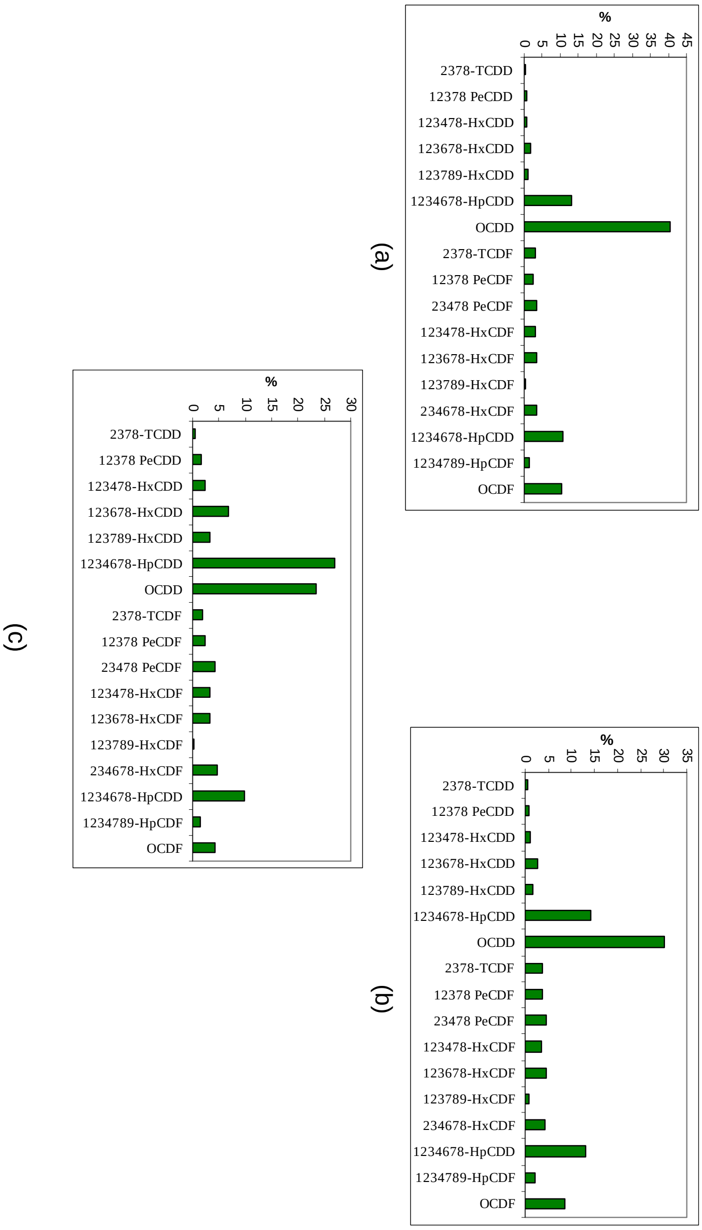


Fig. 2. PCDD/F congener profiles of air samples collected in (a) S.Adrià de Besòs (SAB), (b) background/control area (BK) and (c) emissions of the MSWI.

In our previous survey (spring 2005), mean PCDD/F concentrations of 27.3 and 10.9 fg WHO-TEQ m^{-3} were found at the urban/industrial and the background sites, respectively (Ekino i col·ls., 2007). A detailed study of the temporal trend in each sampling point did not reveal statistically significant seasonal/temporal variations in any of the studied areas. However, the current results are in the lower range of those reported by Abad et al. (2007) in a ten year (period 1994-2004) ambient air monitoring in Catalonia. The range of values presented in that comprehensive study were: 0.013-0.357 pg I-TEQ m^{-3} in urban/traffic sites, 0.010-0.138 pg I-TEQ m^{-3} in suburban/traffic sites, 0.042-0.406 pg I-TEQ m^{-3} in urban/industrial sites, 0.007-1.196 pg I-TEQ m^{-3} in suburban/industrial sites, and 0.005-0.045 pg I-TEQ m^{-3} in rural/industrial sites, whereas concentrations in background areas were 0.008-0.028 pg I-TEQ m^{-3} (Abad i col·ls., 2007). The PCDD/F levels found in air of S. Adrià del Besòs fit well into the less polluted categories (urban/industrial, rural/industrial or even background areas). When compared with worldwide levels, those found in the S. Adrià de Besòs area are also relatively low. In Porto (Portugal), Coutinho et al. (2007) evaluated the effects of a MSWI through an ambient monitoring program whose median PCDD/Fs concentration was 0.130 pg I-TEQ m^{-3}. In turn, Shih et al. (2006) reported a mean total PCDD/F concentrations in the outdoor air of 2 Taiwanese MSWIs of 0.0783 pg I-TEQ/Nm^3 (0.0828 pg WHO-TEQ/Nm^3), ranging from 0.0216 to 0.155 pg I-TEQ/Nm^3. On the other hand, the PCDD/Fs concentrations in ambient air samples collected near a MSWI in Bucheon, Korea, ranged from 0.22 to 1.16 pg I-TEQ m^{-3}, with an average of 0.66 pg I-TEQ m^{-3} (Van den Berg i col·ls., 2006), while Tung et al. (2005) reported an annual average (2000/2001) concentration of 0.052 pg I-TEQ m^{-3} in Hong-Kong. Recently, ambient levels of PCDD/Fs were analyzed in different areas of Croatia by Krauthacker et al. (2006) and mean values of 0.1656 and 0.0486 pg I-TEQ m^{-3} were found at industrial and landfill sites, respectively. In the industrial environment of Houston (TX, USA), the measurements of atmospheric PCDD/F levels over a year showed a mean concentration of 0.016 pg WHO-TEQ m^{-3} (Raun i col·ls., 2005).

The ambient levels of PCDD/Fs are also determined by meteorological conditions. Thus, the fact that the current samples were collected in coastal sites and the most prevailing wind directions during the diverse sampling periods (W, NW and SW) blew towards the sea (away from the sampling sites) could contribute to the low levels obtained (Fig. 1.). In relation to the seasonal variation, a number of studies have reported higher concentrations in winter than in summer (Cheng i col·ls., 2003; Raun i col·ls., 2005; Tung i col·ls., 2005; Krauthacker i col·ls., 2006; Van den Berg i col·ls., 2006; Coutinho i col·ls., 2007), or in autumn (Kim i col·ls., 2007). According to Lohmann and Jones (1998), there are some seasonal factors that may affect PCDD/F ambient concentrations: (1) heating combustion sources, (2) mixing layer (temperature dependent), and (3) loss processes through deposition or chemical reactions (temperature dependent). However, as the same authors noted, the industrial and vehicular sources, which may be the most important, are not seasonally conditioned. In the present study, no Pearson correlation was found between the PCDD/F concentrations and the environmental conditions of the two sampling periods considered. The reason could be that both seasons (spring and autumn) were characterized by mild temperatures (mean: 15 ºC) and/or because combustion of coal or wood are usually not used as domestic home heating methods in the area under study.

3.2. PCBs

The concentrations of the 7 indicator PCBs congeners in air samples collected in S. Adrià de Besòs (SAB-samples) and the background/control site (BK-samples) in 2005 and 2006 are shown in Table 2. Total PCB concentrations ranged from 0.076 to 0.297 ng m^{-3} (mean value: 0.159 ng m^{-3}) in the SAB area, and from 0.062 to 0.127 ng m^{-3} (mean value: 0.095 ng m^{-3}) in the BK area. In this study, concentrations were lower than those recently found in different urban and industrial areas of Turkey (Cetin i col·ls., 2007), but similar to those found in urban areas of Rome (Menichini i col·ls., 2007). The lowest chlorinated congener, PCB 28, was the most abundant in all samples, with mean values of 0.055 and 0.024 ng m^{-3} in the SAB and BK areas, respectively. Its average contribution to total PCBs was 32%. On the other hand, the levels of PCBs 118 and 180 were scarce, with concentrations under its detection limit (0.005 ng m^{-3}) in certain cases. The highest concentration of PCB 118 was 0.013 ng m^{-3}, while that of PCB 180 was 0.012 ng m^{-3}. In the two areas, not only total PCB concentrations, but also PCB congener profiles were rather different. In the SAB zone, PCBs 28 and 52 were more abundant than the more chlorinated congeners, whereas in the BK area all PCB congeners showed similar concentrations. Although relatively higher levels of the lowest chlorinated PCBs than those of higher chlorinated congeners have been reported, there is not a homogeneous tendency. On the other hand, similarities of PCB congener levels have also been reported in air of background areas, such as a Mediterranean coastal lagoon (Castro-Jiménez et al., in press). As for PCDD/Fs, no correlation between PCB concentrations and the two different sampling periods considered could be noted.

Table 2. PCB concentrations (ng m^{-3}) in active air samples collected near the MSWI of S. Adrià del Besòs in 2005 and 2006.

	SAB-1.1	**SAB-2.1**	**SAB-3.1**	**SAB-1.2**	**SAB-2.2**	**SAB-3.2**	**SAB-1.3**	**SAB-2.3**	**SAB-3.3**	**SAB-1.4**	**SAB-2.4**	**SAB-3.4**	**BK-4.1**	**BK-4.2**	**BK-4.3**	**BK-4.4**
PCB 28	0.066	0.060	0.056	0.117	0.043	0.036	0.033	0.048	0.023	0.046	0.055	0.076	0.028	0.016	0.014	0.039
PCB 52	0.042	0.036	0.026	0.063	0.020	0.024	0.021	0.038	0.015	0.027	0.038	0.074	0.016	0.012	0.010	0.017
PCB 101	0.024	0.022	0.030	0.028	0.013	0.022	0.015	0.025	0.010	0.017	0.024	0.055	0.022	0.016	0.011	0.019
PCB 118	<LOD	<LOD	0.013	0.012	0.004	0.008	0.005	0.010	0.004	0.004	0.005	0.012	<LOD	0.003	0.003	<LOD
PCB 138	0.013	0.016	0.024	0.014	0.010	0.016	0.010	0.018	0.009	0.006	0.012	0.028	0.025	0.011	0.009	0.015
PCB 153	0.014	0.018	0.024	0.019	0.011	0.018	0.012	0.020	0.010	0.016	0.016	0.040	0.026	0.014	0.011	0.019
PCB 180	<LOD	<LOD	<LOD	0.004	0.003	0.006	0.003	0.006	0.005	0.005	0.005	0.012	<LOD	0.003	0.003	0.006
Sum PCB	0.169	0.162	0.178	0.256	0.105	0.130	0.098	0.167	0.076	0.121	0.155	0.297	0.127	0.074	0.062	0.117

LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: PCB 118: 0.002 ng m^{-3}; PCB 180: 0.005 ng m^{-3}

In the previous study (spring 2005), the sum of the PCB congeners was higher at the urban/industrial zone (mean: 170 pg m^{-3}) than at the background site (127 pg m^{-3}) (Ekino i col·ls., 2007). PCB levels fluctuated through the time, and a clear trend was not found. As far as it is known, there is still considerable uncertainty with respect to the relative importance of different industries as sources of PCBs (Breivik et al., 2004). However, a number of other sources, such as leakage from old equipment, building materials, stockpiles and landfill sites, are still generating even a greater concern than combustion and industrial processes (Vallack et al., 1998). Anyhow, studies on PCB profiles of potential emission sources are very scarce. For instance, Biterna and Voutsa (2005) reported that PCB 180 was predominant in particles from traffic emissions, as well as in those from residential heating and refuse burning. Other authors found this congener was also abundant in emissions from open burning (Breivik i col·ls., 2004) and MSWIs (Dyke i col·ls., 2003). However, Kim et al. (2004) found PCB 180 to be representative of Kanechlor in spite of incineration samples. In the same study, PCB 118 was found to be predominant in MSWI emissions (Yeo i col·ls., 2004). Therefore, it is rather difficult to establish relationships between PCB levels and the contribution of potential sources.

3.3. Metals

Table 3 shows the average concentrations of some trace elements (Mn, Pb, Cu, Sn, Tl, Cd, Be, Co, As, V, Cr and Ni) associated with PM_{10} particulate matter in samples from S. Adrià de Besòs (SAB-samples) and background/control sites (BK-samples) collected in 2005 and 2006. Levels are in the same range of those found in other urban areas of Barcelona (Viana i col·ls., 2005) and in other cities (Monaci i col·ls., 2000; Gao i col·ls., 2002; López i col·ls., 2005). In general terms, concentrations in the BK zone were lower than those of the SAB area. Copper showed the highest concentrations, with mean values of 69.4 and 29.8 ng m^{-3} in the SAB and BK areas, respectively. Copper is characteristic of emissions of automobile traffic, industrial activities and coal-fired power generation (Monaci i col·ls., 2000; Viana i col·ls., 2005;

Wang i col·ls., 2006). Thallium (mean: 0.08 and 0.20 ng m^{-3} in the SAB and BK areas, respectively) and Be (mean: 0.04 and 0.03 ng m^{-3} in the SAB and BK areas, respectively) showed the lowest concentrations, followed by Co (mean: 0.37 and 0.28 ng m^{-3} in the SAB and BK areas, respectively) and Cd (mean: 0.20 and 0.31 ng m^{-3} in the SAB and BK areas, respectively). Due to the use of unleaded gasoline, in recent years ambient Pb levels have dramatically decreased worldwide (López i col·ls., 2005). In the present study, Pb mean values were 11.50 and 8.25 ng m^{-3} in the SAB and BK areas, respectively, notably lower than the limit established by EU Council Directive 1999/30/EC (0.5 µg m^{-3} expressed as annual mean). Chromium levels ranged from 0.09 to 7.77 ng m^{-3}. Although Cd, Pb and Cr are characteristic elements of waste incinerator emissions (Gao i col·ls., 2002), the levels found in the SAB area were even comparable with concentrations reported in rural and semirural areas (López i col·ls., 2005). Nickel levels ranged from 1.09 to 11.9 ng m^{-3} in the SAB area, and from 1.34 to 2.61 ng m^{-3} in the BK area. In turn, the levels of V ranged from 3.65 to 36.75 ng m^{-3} in the SAB area, and from 1.95 to 6.40 ng m^{-3} in the BK zone, respectively. These two elements are associated with combustion of fuels (Nadal i col·ls., 2004; López i col·ls., 2005). Arsenic levels ranged from 0.14 to 1.31 ng m^{-3}. Although this element can be released to the atmosphere from natural sources such as natural erosion, in urban areas the concentrations mainly come from the burning of fuels (especially coal) and waste incineration (Wang i Mulligan, 2006).

Table 3. Concentrations of heavy metals (ng m^{-3}) associated with PM_{10} particulate matter.

	SAB-1.1	**SAB-2.1**	**SAB-3.1**	**SAB-1.2**	**SAB-2.2**	**SAB-3.2**	**SAB-1.3**	**SAB-2.3**	**SAB-3.3**	**SAB-1.4**	**SAB-2.4**	**SAB-3.4**	**BK-4.1**	**BK-4.2**	**BK-4.3**	**BK-4.4**
Mn	8.60	13.8	13.8	20.6	30.0	13.1	4.75	-	3.22	5.61	18.9	4.44	18.4	8.30	4.61	2.14
Pb	10.8	12.4	12.2	22.7	12.9	12.1	10.0	6.30	8.84	0.34	12.8	17.2	6.38	10.8	12.3	3.52
Cu	44.2	114.3	62.0	123.9	75.8	57.6	60.1	94.6	23.0	44.4	75.3	57.6	22.8	13.0	15.3	68.0
Sn	1.30	3.10	2.39	7.28	5.93	4.52	5.88	4.83	3.34	1.85	4.82	5.67	1.69	5.29	1.78	1.60
Tl	< LOD	0.06	0.09	0.15	0.06	0.08	0.05	0.10	< LOD	0.02	0.09	0.11	< LOD	0.06	0.48	0.07
Cd	0.12	0.33	0.30	0.49	0.27	0.18	0.31	0.14	0.07	0.04	0.08	0.12	0.28	0.45	0.16	0.34
Be	< LOD	< LOD	< LOD	0.01	0.01	< LOD	0.12	0.02	0.09	0.04	0.04	0.02	< LOD	0.04	0.04	0.02
Co	0.20	0.35	0.27	0.45	0.47	0.36	0.55	0.30	0.41	0.10	0.53	0.49	0.50	0.13	0.29	0.19
As	0.42	0.30	0.18	0.73	0.40	0.38	1.30	0.55	1.31	0.34	0.79	0.91	0.20	0.14	0.40	0.44
V	12.0	13.6	19.4	21.0	10.0	13.8	12.7	36.8	3.65	4.79	16.0	22.4	6.40	2.85	1.95	3.92
Cr	3.20	7.7	6.8	7.22	6.62	4.96	6.41	0.09	1.69	0.16	4.06	5.43	3.60	2.59	1.77	0.89
Ni	3.40	7.40	5.8	9.37	6.50	6.22	4.95	11.9	2.34	1.09	5.49	9.24	-	2.61	1.34	1.79

LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: V: 0.147 ng m^{-3}; Ni and Cr: 0.074 ng m^{-3}; Mn, As, Co, Sn, Be, Cu: 0.015 ng m^{-}3; Pb,Cd i Tl: 0.007 ng m^{-3}.

3.4. PCA analysis

Although in the current survey the number of samples was relatively low, two Principal Component Analyses (PCAs) were executed to get some information about the relationship among samples, pollutants and sources. The objective of a PCA is to derive a few new components (Principal Components) as a linear combination of the original variables, which provides a description of the data structure with a minimum loss of information. These analyses were here applied with a double objective: a) to compare the samples from S. Adrià de Besòs with those collected outside the direct influence of the MSWI and the power plant (background/control samples), as well as find out correlations between the different pollutants, and b) to identify the main sources affecting the ambient PCDD/F levels around the MSWI.

Firstly, a PCA was performed using the different pollutant concentrations (PCDD/Fs, PCBs and heavy metals) available for each site and sampling period. Those pollutants with concentrations below the detection limit in more than 40% of the samples were removed. The PCA provided a 3-dimensional model with 3 principal components (PC1, PC2 and PC3), explaining 36%, 21% and 12% of the variance, respectively. The scores plots of PC1 vs. PC2, and PC1 vs. PC3 are depicted in Fig. 3a and Fig. 3b, respectively. In turn, Fig. 4a and Fig. 4b show the loading plot of PC1 vs. PC2, and PC1 vs. PC3, respectively. The score plot did not show differences

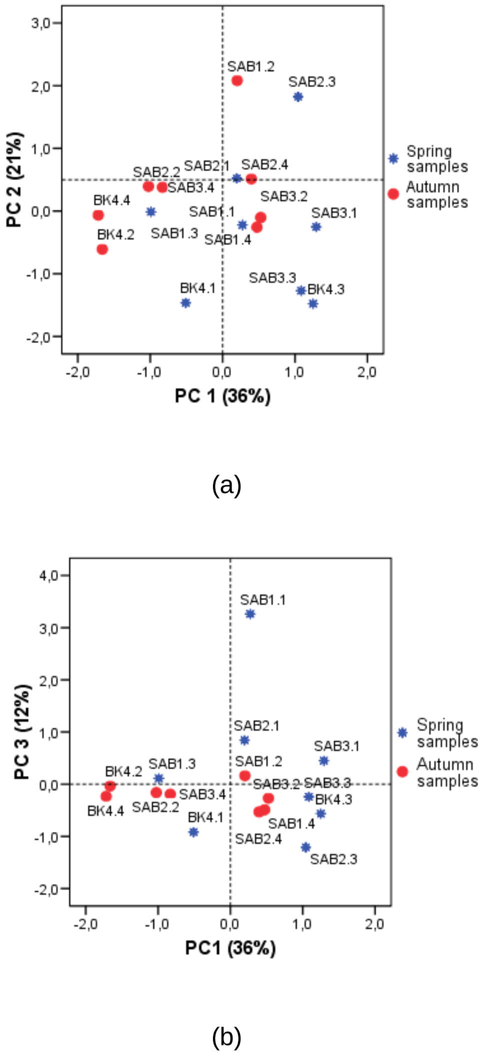
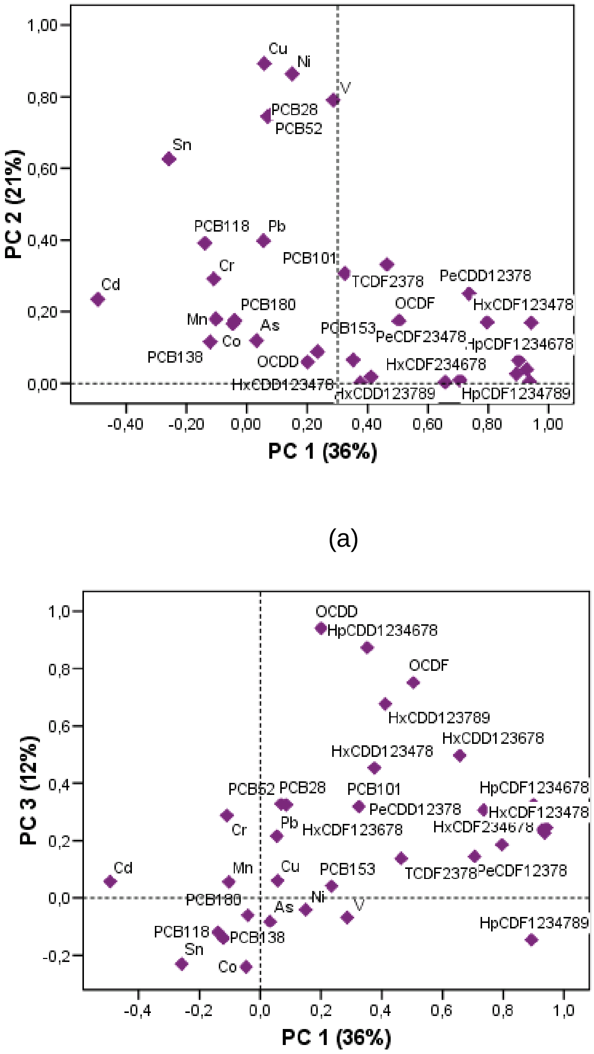


Fig. 3. Score plot of samples showing (a) PC1 vs. PC2, and (b) PC1 vs. PC3.

SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).



(a)

(b)

Fig. 4. Loading plot of samples showing (a) PC1 vs. PC2, and (b) PC1 vs.PC3.

SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1,2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).

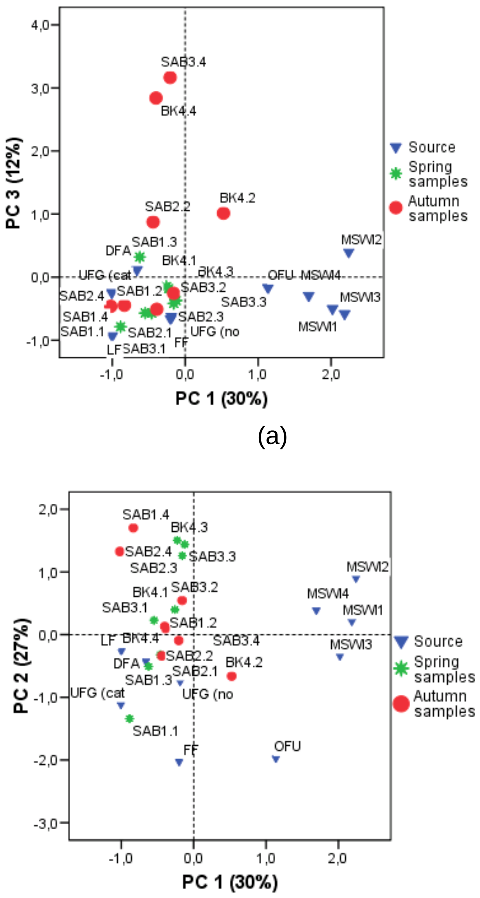


Fig. 5. Score plot of ambient samples and source profiles showing (a) PC1 vs. PC2 and (b) PC1 vs. PC3.

DFA: Diesel fuelled Automobile; UGF (no): Unleaded Gasoline-Fuelled-without catalytic converters; UFG (cat): Unleaded Gasoline-Fuelled-with catalytic converters; MSWI: Municipal Solid Waste Incinerator; OFU: Oil Fired Utility; FF: Forest Fires; LF: Landfill Flares. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).

between areas and periods, and all samples formed a single cluster. This indicates that the industrial sources in the SAB area do not affect significantly the profiles of those pollutants. Therefore, the diffuse sources, which also affect the BK area, seem to have a great influence over total concentrations. The loading plots resulting of the PCA allow establishing the correlation between each PC and the different pollutants. Chemicals associated to the same PC, and then clustered together, are likely to have a similar environmental behavior and/or to come from the same emission source. In the loading plot, PC1 showed a positive correlation with the most-substituted PCDFs (excepting OCDF), whereas PC2 did it with Cu, Ni, V, CB-28 and CB-52, and finally, PC 3 with the highest chlorinated congeners OCDD**,** 1,2,3,4,6,7,8-HpCDD and OCDF. The strong correlation between PC2 and several metals (Cu, Ni and V) as well as the lowest chlorinated PCB congeners would indicate that the emission sources for those pollutants would be the same. In fact, Ni and V have been pointed out as markers of anthropogenic emission sources, such as burning of fuel oil or coal (Yatkin and Bayram, 2008).

PCDD/Fs source emission profiles have been widely studied and are available as emission factors (EF) (USEPA, 2005). Therefore, a second PCA was performed to determine the most influential PCDD/Fs sources by characterizing the air samples in a set of fingerprints. For this, the emission factors (EF) of the potential sources were included in a PCA analysis in order to find similarities with the ambient samples. For each air sample and EF, a score was assigned in each component, thus allowing a further analysis and plotting of summarized data. Each PCDD/F source is characterized by its own congener profile. According to the definition given by the US EPA (USEPA, 2007), an emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Such factors facilitate the estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category. However, the particular profile of certain sources may change depending on diverse operational parameters, such as the waste composition and the conditions of the combustion causing the emission. Moreover, as it has been previously mentioned, the concentrations at sampling sites are strongly dependent on the meteorological conditions. The emission factors considered for the PCA analysis were: (1) different kinds of vehicle emissions: Diesel fuelled Automobile (DFA), Unleaded Gasoline-Fuelled-without catalytic converters (UGF (no)), and Unleaded Gasoline-Fuelled-with catalytic converters (UFG (cat)); (2) Oil Fired Utility (OFU) representing the adjacent power plant; (3) Forest Fires (FF), and (4) Landfill Flares (LF). The MSWI was represented by 4 emission samples obtained in the facility stack.

In this case, PCs 1, 2, and 3 were responsible for 30%, 27%, and 12 % of the variance, respectively. Figures 5a and 5b represent the scores plot of PC1 vs. PC2, and PC1 vs. PC3. No difference was observed between BK and the SAB samples, all being grouped in a same cluster. These results indicate that the PCDD/Fs patterns of ambient samples were similar, and therefore, influenced by the same sources in both areas and periods. The four MSWI profiles appeared apart from the samples (with a high PC1), indicating a low contribution to ambient PCDD/F concentrations. On the other hand, vehicles, the unleaded fuelled gasoline with and without catalytic converters, as well as the diesel fuelled, were associated with the field samples indicating its influence on the ambient patterns. In Spain, the car density is approximately 456 per 1,000 population (ACEA, 2007), being characterized by a high diesel penetration. According to data from the Spanish DGT (Dirección General de Tráfico), in 2004 the registration of diesel vehicles surpassed those of petrol-engine vehicles (66% vs. 34%) (DGT, 2004). PCDD/Fs from light-duty diesel vehicles are approximately twice those from catalyzed cars run on unleaded gasoline (Turrio-Baldassarri i col·ls., 2005). Although there is no landfill near the area here evaluated, landfill fires, probably caused by the uncontrolled combustion of agriculture/domestic wastes, seem also influence the total ambient patterns. It must be taken into account that the power plant may actually work with either natural gas or fuel oil. However, because no emission factors for natural gas were found in the literature, oil fired utility profiles were included in the PCA analysis. It seems that the results of PCDD/Fs in ambient samples were not affected by the oil-fired utility and forest fires. Anyhow, light fuel oil and natural gas are always fired in specially designed burners. It is rather unlikely they generate large amounts of PCDD/F, as both are very high-calorific, clean-burning fuels leaving little ash. Increased gas use for power generation (as a replacement fuel for coal and oil) results in reductions of PCDD/F from the generation sector (UNECE, 1998). In the present survey, PC1 was highly correlated with penta-, hexa-, and heptadioxins while PC2 did with penta-, hexa-, and heptafurans. PC3 was correlated with TCDD and 1,2,3,4,7,8,9-HpCDF.

In conclusion, the results of the current study suggest that the MSWI of S. Adrià de Besòs is not a strong emission source of PCDD/Fs, PCBs and heavy metals and does not contribute significantly to the air pollution in its immediate surrounding. No significant temporal, seasonal and spatial variations have been observed. Moreover, a notable difference of the PCDD/F congener profiles has been found between ambient air and emission gas, indicating that the current levels of PCDD/Fs are more related to other potential sources (e.g., traffic) rather than to emissions from the MSWI.

Acknowledgements

This study was financially supported by the Metropolitan Entity of the Environment, Barcelona, Catalonia, Spain.

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Discussió conjunta dels articles del Capítol III

Nivells de PCDD/Fs, PCBs i PCNs en aire

Les concentracions de PCDD/Fs, PCBs i PCNs determinades en les mostres d'aire de la zona industrial del Besòs (Barcelona) (on es situen una incineradora i una central tèrmica) van ser superiors a les trobades en la zona control. Tot i això, en termes generals les concentracions trobades van ser més baixes del que en principi es podria esperar en una zona industrial. Els nivells serien un reflexe de la disminució dels nivells d'aquests compostos a nivell mundial causat per la millora en els sistemes de neteja en incineradores i d'altres millores ambientals (Schuhmacher i col·ls., 2002b; Yeo i col·ls., 2004). A més, les baixes concentracions trobades podrien ser resultat de la proximitat al mar dels punts de mostreig, ja que les masses d'aire marí net poden produir un efecte de dilució (Gao i col·ls., 2002; Gambaro i col·ls., 2004) i pel fet que les direccions predominats a la zona fossin (Oest, Nord-Oest, i swd-Oest) en direcció cap al mar.

Fluxe (m^3/dia) a través dels captadors passius

Quan pel seu càlcul només es va tenir en compte la fase gasosa de cada congènere es van obtenir un fluxes alts pels PCDD/Fs més substituïts. En canvi, quan es va considerar la concentració total (gas + particulada) es van obtenir un fluxes de 0.4-5.1 m^3/dia. En general, els fluxes calculats van ser més reproduïbles pels congèneres més volàtils. Per PCDD/Fs es va concluir que el més apropiat seria utilitzar un fluxe de 2 m^3/dia. Per PCBs es va obtenir un fluxe mitjà de 3.8 m^3/dia, valor similar al que han determinat altres autors en condicions indoor (Shoeib i Harner, 2002). Pels PCNs el fluxe obtingut va ser 3.3 m^3/dia.

Variació temporal dels nivells de PCDD/Fs, PCBs i metalls pesants

Les concentracions mitjanes de PCDD/Fs el 2005 i 2006 a la zona industrial del Besòs i a la zona control van ser 0.018 i 0.012 pg OMS-TEQ/m^3, respectivament. La mitjana dels perfils d'immissió de PCDD/Fs de les dues àrees van ser similars entre ells, i a la vegada diferents al perfil d'emissió de la planta incineradora del Besòs. No es van trobar diferències estadísticament significatives quan es van estudiar les variacions temporals/estacionals. Els resultats trobats estan a la part baixa del rang trobat en altres àrees de Catalunya (Abad i col·ls., 2007).

Les concentracions de PCBs van anar de 0.076 a 0.297 ng/m^3 (valor mitjà: 0.159 ng/m^3) a la zona industrial del Besòs i de 0.062 a 0.127 ng/m^3 (valor mitjà: 0.095 ng/m^3) a la zona control. Els tant les concentracions com els perfils dels congèneres de PCBs corresponents a les dues àrees estudiades van ser força diferents. Tampoc es va trobar correlació entre els diferents períodes estudiats.

Els nivells de metalls pesants en aire van ser similars als trobats en altres àrees de Barcelona (Viana i col·ls., 2005) i d'altres ciutats (Monaci i col·ls., 2000; Gao i col·ls., 2002; López i col·ls., 2005). En termes generals, els nivells de metalls a la zona industrial del Besòs van ser superiors als trobats a la zona control. El coure va mostrar les concentracions més elevades. Per altra banda, el tal·li, el beri·li i el cadmi van presentar els nivells més baixos. La concentració de plom va ser notablement inferior a l'establerta per la directiva europea.

Capítol IV

Monitorització biològica

Article 5:

Mari M, Borrajo MA, Schuhmacher M, Domingo JL

Monitoring PCDD/Fs and other organic substances in workers of a hazardous waste incinerator: A case study

Chemosphere 67: 574-581 (2007)

Article 5: "Monitoring PCDD/Fs and other organic substances in workers of a hazardous waste incinerator: A case study"

Abstract

The aim of this study was to measure, 6 years after regular operations, the concentrations of a number of organic substances in blood and urine of 19 workers employed at a hazardous waste incinerator (HWI) in Spain, and to establish the temporal variation with respect to baseline data and previously performed surveys. This facility was the first, and so far the only HWI in that country. The levels of hexachlorobenzene (HCB), polychlorinated biphenyls (PCB 28, 52, 101, 138, 153 and 180) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were analyzed in 6 composite plasma samples, while concentrations of di-, tri, and pentachlorophenols, as well those of 1-hydroxypyrene were measured in the urine of these workers. The current mean PCDD/F concentration, 10.4 ng I-TEQ/kg lipid, was significantly lower than that found in the baseline survey, 26.7 ng I-TEQ/kg lipid and similar to that found in the previous (2004) study (7.7 ng I-TEQ/kg lipid). PCDD/F levels in plasma were similar or even lower than those recently reported for various non-exposed populations. For the remaining analyzed substances in plasma and urine, there was not any significant increase in comparison with the levels found in the baseline survey. On the other hand, no marked differences between the concentrations of organic substances in plasma or urine were found according to the respective workplace (plant, laboratory and administration). The results of the present survey indicate that after 6 years of regular operation, the workers at the HWI are not occupationally exposed to PCDD/Fs and other organic substances in their workplaces.

Keywords: Hazardous waste incinerator; Biomonitoring; Workers; PCDD/Fs; Organic substances

1. Introduction

It is well established that among the potential methods and systems of waste management incineration is an effective way of treating municipal solid waste (MSW), hazardous waste (HW) and medical waste (MW). In comparison with other treatments for processing MSW, HW and MW, incineration has multiple advantages such as volume reduction, energy recovery, elimination of pathogen agents, and chemical-toxicity destruction, which is of particular interest for HW (Oppelt, 1990; Dempsey, 1993). However, waste management facilities in general and incinerators in particular, have been traditionally affected by the syndrome known as NIMBY (Not In My Back Yard) (Kuhn and Ballard, 1998). Thus, in many countries the potential health risks associated with stack emissions, specially those of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), have become a cause of great controversy and concern (Domingo, 2002a,b; Lothgren and van Bavel, 2005; Oh et al., 2006). However, although PCDD/Fs, especially the 2,3,7,8-substituted congeners, are probably the most hazardous pollutants released by incinerators, an important number of other different activities are also known sources of PCDD/F emissions (Alcok and Jones, 1996; Fiedler, 1996; Anderson and Fisher, 2002; Meneses et al., 2004; Quass et al., 2004), exceeding some of them (i.e., traffic emissions) those from incinerators (Fuster et al., 2001).

With respect to HW, incineration is often chosen as an ultimate disposal method for this kind of waste that can not be recycled, reduced, or safely deposited in secured landfill sites. Incineration of HW is a thermal oxidation process in which it is converted into gases and incombustible solid residues. In 1996, the construction of a HW incinerator (HWI) was initiated in Constantí (Tarragona County, Catalonia, Spain). Regular operations started in 1999. This facility was the first, and up until now the only HWI in Spain. Therefore, the interest and concern on its potential environmental impact and human health risks have been considerable. In response to it, a wide preoperational monitoring program was designed to assess the potential impact of

PCDD/F emissions from the new HWI on the neighborhood, as well as to establish the health risks on the population living near the facility (Schuhmacher et al., 1997,1998,1999a,b,c). This program also included the assessment of internal exposure of workers to a number of organic substances such as PCDD/Fs and polychlorinated biphenyls (PCBs). Baseline levels of these substances were determined in the future workers of the HWI during the period of construction of the facility (Domingo et al., 2001).

In occupational medicine, biological monitoring is an important tool to assess the levels of exposure to potentially harmful substances taken up from the occupational environment (Angerer et al., 1992; Hardt and Angerer, 2003; Bolt and Their, 2006). It is also useful to evaluate temporal changes in individuals environmentally or occupationally exposed to a defined contaminant. Since the baseline data were obtained (Domingo et al., 2001), we have annually measured in the workers of the HWI the concentrations of the organic substances that were also determined in the baseline survey (Schuhmacher et al., 2002; Agramunt et al., 2003,2004). The aim of the present study was to determine, after approximately 6 years of regular operations in the HWI, the concentrations in blood and urine of the organic substances and to establish which is the temporal variation of these compounds in relation to the baseline survey (Domingo et al., 2001) and the previous monitoring studies (Schuhmacher et al., 2002; Agramunt et al., 2003,2004).

2. Subjects and methods

2.1. Subjects

Nineteen workers (15 men and 4 women) participated voluntarily in this study. As in the previous surveys, individuals were divided into three groups according to their respective workplace and task in the facility. Group I (plant workers) included 12 subjects aged from 30 to 40 years, whose occupations were incinerator operators, boiler maintenance, furnace maintenance, control panel, and waste-gas-washing operators; Group 2 (laboratory workers) included 5 individuals aged from 27 to 41 years with analytical jobs, and Group 3 (administration workers) included 2 subjects (28 and 31 years) with administrative tasks.

Blood samples were drawn from each individual into thoroughly cleaned glass bottles. Approximately 50 ml were centrifuged for getting plasma. Urine samples were also collected and centrifuged. To determine the concentrations of organic substances in plasma (hexachlorobenzene (HCB), PCDD/Fs, PCBs 28, 52, 101, 138, 153, and 180) and urine (2,4- and 2,5-dichloropehnol, 2,4,5- and 2,4,6-trichlorophenol, pentachlorophenol and 1-hydroxypyrene), as in the previous surveys (excepting the baseline survey) we pooled the 19 individual samples into 6 composite samples (approximately 80 ml per sample for plasma and 60 ml for urine) corresponding to plant (four samples), laboratory (one sample) and administration (one sample). Samples were mixed by equal volume per subject. The criteria used for pooling was previously reported (Schuhmacher et al., 2002). Information about each participant concerning health status and lifestyle, potential environmental exposure sources, dietary habits, as well as drinking and smoking habits were obtained using a specific questionnaire.

2.2 Analytical methods

The analytical determination of PCDD/Fs, PCBs and HCB in plasma was performed in accordance with the US ESPA method 1625. Samples were homogenized and subsequently extracted (liquid/liquid extraction). After evaporation of the solvent, the amount of lipid was determined and spiked with a mixture of $^{13}C_{12}$-PCDD/PCDF standards and a set of $^{13}C_{12}$-PCB and $^{13}C_6$-hexachlorobenzene. The clean-up procedure and fractionation of the crude extract was carried out by adsorption chromatography as a multi-step clean-up using silica and alumina columns. The final step was reduction of the PCDD/PCDF-containing fraction to the analytically needed volume. The cleaned extract was analyzed by HRGC/HRMS using an Agilent HP 6890

GC coupled to a VG Autospec Ultima HRMS (with selected ion recording at resolution 10 000). The analysis of the PCDD/F congeners took place using a non polar column of a DB5-type. The quantification was carried out using internal standards. As an indication of the uncertainty of the analysis, the relative standard deviation (RSD) of the control sample was used. The RSD of the control sample is less than 10 %. In addition to the quantification of the PCDD/F congeners, the toxic equivalents (TEQ) of the analysed PCDD/F were calculated according to the international NATO/CCMS system.

For the analysis of chlorophenols in urine, the samples were spiked with ^{13}C-marked chlorophenols. This was followed by an acid hydrolysis and an extraction with dichloromethane. The concentrated extract was analyzed by HRGC/HRMS using an Agilent HP 6890 GC coupled to a VG Autospec Ultima HRMS (with selected ion recording at resolution 10 000). The analysis of the chlorophenols took place on a non-polar column of a DB1-type. The quantification was carried out using the ^{13}C-marked internal standards. On the other hand, the analysis of 1-hydroxypyrene (1-HP) was performed after enzymatic hydrolysis to release the conjugated part of the 1-HP. To determine the conjugated and free 1-HP, the extract of the hydrolyzed urine was cleaned using a C18-SPE cartridge and the analyte was eluted with methanol. After concentration, the extract was analyzed by HPLC/Fluorescence using a Waters 600E-HPLC together with a Waters 774 fluorescence detector and a Microsphere RP18 EC reverse phase column.

2.3. Statistical analysis

The Leven test was used to compare the homeogeneity of the variances. Significance of the data was computed by the Kruskal-Wallis and the Mann-Whitney U-test. The statistical software SPSS version 12.0 was used for the analyses. A probability of 0.05 or less was considered as significant.

3. Results

Table 1 shows the current concentrations of HCB, PCBs and PCCD/Fs in plasma of the workers of the HWI. Mean and median levels, standard deviations and the minimum and maximum values are given. A comparison of the current mean concentrations of these organohalogenated compounds with those obtained since 1999 are shown in Table 2. The ratios between the results from the baseline survey (1999) and those of the present study, as well as between the previous (2004) and the present surveys, are also shown. It can be seen that although the concentrations of HCB decreased notably since the baseline survey (ratio 1999/2005: 2.1), the difference did not reach the level of statistical significance. The current HCB concentration was statistically similar to that of the previous (2004) survey (ratio: 0.9). With respect to PCBs, the current concentrations were significantly lower that the baseline levels for the congeners 28, 101, 138 and 153, while were apparently lower (but not significantly different) for the congeners 52 and 180. There were some variations between the concentrations of PCBs found in 2004 and 2005. Thus, while the current levels of PCB-28 and PCB-153 were significantly higher, those of PCB-138 were significantly lower. A detailed observation of the PCB levels obtained in the studies carried out between 1999 (baseline) and 2005 (current) show an important number of fluctuations, with increases or decreases depending on the year and the specific PCB congener. However, in comparison with the baseline concentrations a general tendency to the reduction of PCB concentrations in plasma seems to be evident.

The current mean PCDD/F concentration, 10.4 ng I-TEQ/kg lipid, was significantly lower than that found in the baseline survey, 26.7 ng I-TEQ/kg lipid. However, it was statistically similar to the concentration found in the previous study (7.7 ng I-TEQ/kg lipid), as well as to the levels detected since the 2000 survey.

Table 1. Concentrations of organohalogenated compounds in plasma of workers at a HWI. Data concerning to the 2005 survey.

	Mean	Median	Standard deviation	Minimum	Maximum
HCB	71.0	57.0	43.4	39.0	150.0
2,4,4'-Tri-PCB28	2.4	1.6	1.5	1.4	4.9
2,2',5,5'-Tetra-PCB52	0.8	0.3	0.9	0.2	2.2
2,2',4,5,5'-Penta-PCB101	1.5	0.9	1.1	0.8	3.3
2,2',3,4,4',5'-Hexa-PCB138	48.0	46.5	14.6	29	71
2,2',4,4',5,5'-Hexa-PCB153	110.8	105.0	34.4	65	170
2,2',3,4,4',5,5'-Hepta-PCB180	114.8	110.0	33.8	71	170
PCDD/Fs	10.4	8.3	6.1	6.3	22.5

Results are given in µg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ/kg de lipid.

Notwithstanding, the mean PCDD/F concentration in the 2000 survey was, in absolute value, remarkably higher than the current one (16.9 vs. 10.4 ng I-TEQ/kg lipid). The fact that the difference between these concentrations was not statistically significant ($P > 0.05$) is probably due to the reduced number of composite samples (six) analyzed in both studies, in contrast to the comparatively higher number of samples analyzed in the baseline survey (28 individual samples). Thus, in the current study a very remarkable difference between the minimum and maximum PCDD/F concentrations, 6.3 and 22.5 ng I-TEQ/kg lipid, respectively, was noted (Table 1). It might explain the lack of significant differences among the annual studies performed between 2000 and 2005. With regard to the distribution of PCDD/F congeners, in the baseline survey OCDD, followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,6,7,8-HxCDD, were the PCDD congeners showing the highest contribution to TEQ, tendency that was maintained in all the remaining studies including the present one (data not shown). In contrast, PCDF congeners showed some changes. OCDF, followed by 1,2,3,4,6,7,8-HpCDF, were the main contributors to TEQ in the baseline survey, while in the remaining studies the main contributor was 1,2,3,4,6,7,8-HpCDF, being the second position variable

(1,2,3,4,7,8-HxCDF in the current study). When PCDD/Fs were determined in plasma of the non-exposed population living in the vicinity of the HWI, the same PCDD/F congeners than those found in the baseline survey were the main contributors to TEQ (Schuhmacher et al., 1999). In 2002, the last time that the general population was monitored, among the five main contributors to TEQ, only the fifth position was different, corresponding to 2,3,4,7,8-PeCDF (Agramunt et al., 2005). This congener occupied also this position in the 2001, 2002 and 2004 studies (data not shown).

On the other hand, the levels of these organohalogenated compounds in plasma of the HWI workers classified according to the specific workplace are summarized in Table 3. Data show the baseline and current results, as well those concerning to the annual monitoring studies performed between both surveys. Statistical comparison of the results according to the year could be only carried out for plant workers, as only one composite sample was annually analyzed for each group of laboratory and administration workers. Consequently, the statistical comparison among the three groups of workers was non-viable. Despite of this, a detailed observation of the data allows to note that for these organohalogenated compounds, a similar annual tendency to that found for all HWI workers (Table 2) is also seen for plant workers. Moreover, the visual (no statistical) comparison of the current data shows that the concentrations of HCB, PCB-138, PCB-153, and PCB-180 were lower in plant workers than those corresponding to the other 2 groups, while the levels of the remaining PCBs and those of PCDD/Fs were higher in that group of workers. However, it is important to remark that these differences could not be statistically evaluated, and therefore, the significance of the comparison is not scientifically relevant. Notwithstanding, a non-statistical evaluation of the data does not seem to indicate that the concentrations of these contaminants are higher in plant workers than in laboratory or administration workers, for whom a lower exposure than that corresponding to plant workers could be expected.

Table 4 shows the current urinary levels (mean, median, standard deviation, and minimum and maximum values) of chlorophenols and 1-hydroxypyrene in composite samples belonging to the workers of the HWI. In turn, Table 5 summarizes a comparison of the current mean concentrations with those of the baseline survey and the monitoring studies performed between 2000 and 2004. The ratios corresponding to 1999/2005 and 2004/2005 are also given. There were important fluctuations in the concentrations of chlorophenols depending on the year of the survey, while 1-hydroxypyrene could be only detected in 2004.

The urinary levels of chlorophenols and 1-hydroxypyrene in the HWI workers classified according to the specific workplace are summarized in Table 6. Data show the baseline and current results, as well those concerning to the annual monitoring studies performed between both surveys. As for plasma samples, statistical comparison of the results according to the year of monitoring could be only carried out for plant workers, as only one composite sample was annually analyzed for the groups of laboratory and administration. Consequently, statistical comparison among the three groups of workers was unfeasible. For plant workers, 2,4- and 2,5-dichlorophenol levels were significantly increased with respect to the baseline survey, while those of the trichlorophenols decreased. In turn, the concentration of pentachlorophenol was the same than that found in the baseline survey. In relation to the 2004 results, no significant changes were noted for any compound. A non-statistical comparison of the current data shows that the concentrations of the dichlorophenols were higher in plant workers than those concerning the other 2 groups, while the levels of the remaining compounds, and those of 1-hydroxypyrene, were lower (or similar) in that group of workers. However, the significance of this comparison is not scientifically relevant.

Table 2. Concentrations (mean values) of organohalogenated compounds in plasma of workers at the HWI: Comparison of the current (2005) data with those from 1999 (baseline), 2000, 2001, 2002, 2003 and 2004.

	1999	2000	2001	2002	2003	2004	2005	Ratio 1999/2005	Ratio 2004/2005
HCB	152.0^{abcd}	115.4^{abc}	181.7^{ad}	225.5^{a}	49.8^{bcd}	61.3^{cd}	71.0^{d}	2.1	0.9
2,4,4'-Tri-PCB28	18.5^{a}	2.2^{bde}	3.4^{be}	2.1^{be}	0.3^{ce}	1.3^{d}	2.4^{e}	7.7	0.5
2,2',5,5'-Tetra-PCB52	10.4^{ae}	1.3^{be}	1.5^{be}	0.4^{ce}	<0.25	0.2^{de}	0.8^{e}	13.0	0.3
2,2',4,5,5'-Penta-PCB101	9.0^{a}	2.0^{be}	2.0^{bce}	0.9^{cde}	<0.25	0.6^{de}	1.5^{e}	6.0	0.4
2,2',3,4,4',5'-Hexa-PCB138	151^{a}	89.0^{ab}	74.0^{bd}	50.1^{bd}	22.1^{c}	76.3^{b}	48.0^{d}	3.1	1.6
2,2',4,4',5,5'-Hexa-PCB153	213^{a}	125.4^{ab}	103.8^{b}	103.9^{b}	52.6^{c}	40.0^{c}	110.8^{b}	1.9	0.4
2,2',3,4,4',5,5'-Hepta-PCB180	209^{abd}	121.7^{abd}	92.0^{acd}	198.5^{bd}	58.0^{c}	76.9^{cd}	114.8^{d}	1.8	0.7
PCDD/Fs	26.7^{a}	16.9^{ad}	10.0^{bd}	10.3^{bd}	6.0^{cd}	7.7^{bcd}	10.4^{d}	2.6	0.7

Results are given in µg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ /kg de lipid.

For each compound, different letters (a, b, c, d, e) indicate significant differences ($P < 0.01$) according to the non-parametric test U de Mann-Whitney.

Table 3. Concentrations (mean values) of organohalogenated compounds in plasma of workers at the HWI according to their specific workplaces

		Workers		
	Year	Plant	Laboratory	Administration
HCB	1999	134^{abc}	182	223
	2000	84^{abc}	179	179
	2001	143^{ac}	159	359
	2002	150^{a}	346	408
	2003	40^{bc}	65	75
	2004	59.0^{c}	87.3	44.2
	2005	50.5^{c}	74	150
	P	<0.05	-	-
2,4,4'-Tri-PCB28	1999	18.5^{ac}	22.4	13.2
	2000	2.5^{bc}	1.8	1.6
	2001	3.1^{bc}	3.2	4.7
	2002	2.0^{bc}	2.4	2.6
	2003	0.3^{bc}	0.4	0.3
	2004	1.3^{bc}	1.3	1.3
	2005	2.8^{c}	1.5	1.7
	P	<0.001	-	-
2,2',5,5'-Tetra-PCB52	1999	10.7^{a}	11.9	6.4
	2000	1.5^{bd}	1.1	0.6
	2001	1.3^{bd}	1.6	1.9
	2002	0.4^{cd}	0.5	0.5
	2003	ND	ND	ND
	2004	0.2^{cd}	0.4	0.3
	2005	1.1^{d}	ND	ND
	P	<0.001	-	-
2,2',4,5,5'-Penta-PCB101	1999	9.1^{a}	9.9	6.9
	2000	2.1^{bd}	1.8	1.5
	2001	1.9^{bcd}	2.1	2.6
	2002	0.9^{cd}	1.1	0.9
	2003	ND	ND	ND
	2004	0.5^{d}	1.3	0.5
	2005	1.8^{d}	0.8	0.8
	P	<0.01	-	-

2,2',3,4,4',5'-Hexa-PCB138	1999	150 ^{a}	164	134
	2000	79 ^{abe}	129	91
	2001	65 ^{bce}	94	89
	2002	41 ^{ce}	77	59
	2003	20 ^{de}	68	47
	2004	68 ^{bce}	127	60
	2005	41^{e}	55	71
	P	<0.01	-	-
2,2',4,4',5,5'-Hexa-PCB153	1999	213 ^{a}	228	188
	2000	114 ^{ab}	179	119
	2001	93 ^{b}	130	120
	2002	87 ^{b}	151	125
	2003	50^{b}	20	30
	2004	38 ^{b}	61	29
	2005	94^{b}	120	170
	P	<0.01	-	-
2,2',3,4,4',5,5'-Hepta-PCB180	1999	228 ^{abd}	203	91
	2000	113 ^{abd}	170	110
	2001	89 ^{acd}	110	86
	2002	176 ^{b}	278	209
	2003	59 ^{cd}	41	72
	2004	71 ^{cd}	119	61
	2005	97^{d}	130	170
	P	<0.05	-	-
PCDD/Fs	1999	26.4 ^{a}	31.1	30.5
	2000	16.8 ^{ad}	16.4	17.8
	2001	9.4 ^{bcd}	11.7	10.4
	2002	9.2 ^{bd}	13.5	11.6
	2003	6.0 ^{c}	6.4	5.2
	2004	8.2 ^{bcd}	9.2	4.4
	2005	11.5^{d}	6.8	9.5
	P	<0.05	-	-

ND: not detected. Results are given in μg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ/kg de lipid. For values corresponding to plant workers, different letters (a, b, c, d, e) indicate significant differences ($P < 0.05$) according to the non-parametric test U de Mann-Whitney.

Table 4. Concentrations (µg/g creatinine) of organic compounds in urines of workers of the HWI. Data concerning to the 2005 survey.

	Mean	Median	Standard Deviation	Minimum	Maximum
2,4-DCP	6.7	5.5	5.4	ND	13.1
2,5-DCP	93.4	92.1	59.4	12.7	165.5
2,4,5-TCP	0.2	0.2	0.2	ND	0.5
2,4,6- TCP	ND	ND	-	ND	1.0
PCP	0.4	0.2	0.63	ND	1.7
1-HP	ND	ND	-	ND	0.3

ND: not detected. DCP: Dichloropheno; TCP: Trichlorophenol; PCP: Pentachlorophenol: HP: Hydroxypyrene

Table 5. Concentrations (mean values) of organic compounds in urine of workers at the HWI: Comparison of the current (2005) data with those from 1999 (baseline), 2000, 2001, 2002, 2003 and 2004.

	Mean							Ratio 1999/05	Ratio 2004/05
	1999	2000	2001	2002	2003	2004	2005		
2,4-DCP	5.7^{a}	5.2^{bcd}	5.0^{abd}	2.4^{ab}	ND	7.5^{cd}	6.7^{ad}	0.9	1.1
2,5-DCP	66.1^{a}	121.3^{bc}	181.8^{bc}	96.8^{b}	ND	181.7^{cd}	93.4^{bd}	0.7	1.9
2,4,5-TCP	0.4^{a}	0.7^{a}	0.4^{ab}	0.1^{c}	ND	0.2^{bc}	0.2^{bc}	2	12
2,4,6-TCP	0.9^{a}	2.6^{bc}	1.0^{bd}	0.5^{ad}	ND	2.7^{bcd}	ND	-	-
PCP	0.5^{a}	1.9^{b}	1.1^{c}	0.9^{abc}	0.3^{a}	1.4^{bc}	0.5^{a}	1	2.8
1-HP	ND	ND	ND	ND	ND	0.2	ND	-	-

ND: not detected. For each compound, different letters (a, b, c, d) indicate significant differences ($P < 0.01$) according to the non-parametric test U de Mann-Whitney.

DCP: Dichloropheno; TCP: Trichlorophenol; PCP: Pentachlorophenol: HP: Hydroxypyrene

Table 6. Concentrations (mean values) of organic compounds in urine of workers at the HWI according to their specific workplaces

		Workers		
	Year	Plant	Laboratory	Administration
2,4-Dichlorophenol	1999	2.8^{a}	6.6	22.5
	2000	4.3^{bc}	3.9	9.8
	2001	3.4^{abc}	6.5	9.7
	2002	1.5^{ab}	2.6	5.7
	2003	ND	ND	ND
	2004	6.1^{cd}	3.7	17.0
	2005	8.4^{d}	3.6	3.1
2,5-Dichlorophenol	1999	19.2^{a}	108.7	321.5
	2000	80.7^{bc}	127.7	277.2
	2001	85.2^{bd}	177.9	571.8
	2002	48.4^{be}	101.6	285.8
	2003	1.92^{ae}	0.40	2.75
	2004	153.4^{cd}	115.6	360.8
	2005	104.7^{cb}	45.1	96.8
2,4,5-Trichlorophenol	1999	0.5^{ab}	0.2	0.3
	2000	0.6^{a}	1.2	0.4
	2001	0.3^{ac}	0.7	0.5
	2002	0.2^{c}	0.1	0.1
	2003	ND	ND	ND
	2004	0.2^{bc}	0.4	0.2
	2005	0.2^{ac}	0.3	0.3
2,4,6-Trichlorophenol	1999	1.1^{a}	0.15	0.3
	2000	3.5^{b}	1.0	0.6
	2001	0.9^{ab}	1.0	1.4
	2002	0.7^{a}	0.3	0.1
	2003	ND	ND	ND
	2004	3.4^{b}	0.3	0.3
	2005	ND	0.5	1.0

Pentachlorophenol	1999	0.5^{a}	0.1	0.5
	2000	1.9^{b}	1.9	1.7
	2001	1.1^{b}	1.0	1.4
	2002	0.6^{ab}	2.7	0.6
	2003	0.1^{ab}	0.1	0.4
	2004	1.7^{b}	1.1	0.6
	2005	0.5^{ab}	0.5	ND
1-Hydroxypyrene	1999	<0.04-1.1	<0.04-11.2	<0.04-0.2
	2000	<0.04-0.3	0.2	<0.04
	2001	<0.04-0.2	<0.04	<0.04
	2002	<0.04-0.1	<0.04	<0.04
	2003	<0.04-0.2	<0.04	<0.04
	2004	<0.04-0.3	<0.04	0.2
	2005	<0.04	<0.04	0.4

ND: not detected. For values corresponding to plant workers, different letters (a, b, c, d) indicate significant differences ($P < 0.05$) according to the non-parametric test U de Mann-Whitney.

4. Discussion

Since the eighties of the twentieth century, and focused mainly on emissions of PCDD/Fs, in most developed countries waste incinerators have became "a symbol" of environmental contamination and human health risks. In recent years, and due to the stringent changes in legislation (Davy, 2004), as well as a better knowledge of the risks related with these facilities (Domingo, 2002a,b), in certain ambits of the public opinion of some countries, that perception has been slightly modified. However, a strong opposition and concern regarding waste incineration is still notably present. Consequently, it is essential that information concerning these facilities are quite clear and transparent, which implies that monitoring studies are periodically performed and the results widely spread. These were the main reasons to measure baseline levels and to design a surveillance program related with the HWI here studied. This program also includes the biological monitoring of a number of organic substances in the HWI workers. In the baseline survey, the levels of these compounds were individually measured in blood and urine samples. However, it was expected that after some years a number of workers could desist from participating in the program, while other became retired, or simply could leave the work in the HWI. Therefore, although also due to economical reasons, after the baseline survey all studies have been carried out by measuring the levels of the chemicals in composite samples.

Information concerning health risks of workers in waste incinerators are rather scarce. In addition, most health studies (respiratory function, oxidative DNA damage, hepatic function, gene expression, etc.) are more focused on workers in MSW incinerators (MSWI) (Hu et al., 2003, 2006; Charbotel et al., 2005; Yoshida et al., 2006) than in those working at HWI (Bakoglu et al., 2004). With respect to biological monitoring studies of organic substances, most of them have been also performed in subjects employed in MSWI and are mainly focused on blood PCDD/F levels. A summary of recent studies (2003-2005) is next reviewed.

Leem et al. (2003) reported that the average TEQ concentration of PCDD/Fs in workers and residents near MSW incinerators in Korea was 12.2 ng I-TEQ/kg lipid, while that in residents from an area around an industrial waste incinerator was 53.4 ng I-TEQ/kg lipid. It was found that the oxidative stress of residents near the industrial waste incinerator was higher than that in workers and residents from the area around the MSWI. No data about workers in the industrial incinerator were reported. Kumagai et al. (2004) determined the levels of PCDD/Fs in blood of subjects working in 13 Japanese MSWIs. The mean serum concentration was 28 ng TEQ/kg lipid. It was noted that the concentrations of HxCDFs and HpCDFs in serum of the workers were significantly higher than that of the general population. Hu et al. (2004) monitored ambient air concentrations of PCDD/Fs in three MSWIs in Taiwan. Blood PCDD/F levels of 133 workers randomly selected from these facilities were also measured. The median PCDD/F concentration in blood of all workers was 15.3 ng WHO-TEQ/kg lipid (range: 5.5-59.0). Kim et al. (2005a) determined PCDD/F and co-PCB levels in blood samples of 13 workers from two MSWI from Seoul, Korea. Mean PCDD/F and co-PCB levels were 10.4 and 7.3 ng I-TEQ/kg lipid, respectively. In turn, Moon et al. (2005) reported geometric mean PCDD/F concentrations of 3.14 and 6.60 ng TEQ/kg lipid for workers and residents near MSWIs in Korea, respectively. Recently, Chen et al. (2006) determined the levels of PCDD/Fs in serum of 25 temporary MSWI maintenance workers in Taiwan before and after annual maintenance. Mean concentrations were 20.35 and 23.87 ng WHO-TEQ/kg lipid, before and after periodic maintenance respectively, being the difference statistically significant. On the other hand, Kumagai and Koda (2005) determined the levels of PCDD/Fs in serum samples of 5 workers at a infectious waste incinerator in Japan, at 1 month and 16 months after the end of occupational PCCD/F exposure. The results were compared with PCDD/F levels corresponding to controls. One month after the end of occupational exposure mean TEQ for the workers was 49 ng/kg lipid (2.7 times higher than that of controls), while at 16 months the mean decreased to 29.4 ng TEQ/kg lipid (1.6 times higher than that of controls).

With respect to biological monitoring of PCDD/Fs and related compounds in workers at industrial waste incinerators, Kim et al. (2005b) measured PCDD/F concentrations in 2 office workers and 3 plant workers of a Korean industrial incinerator. Mean values were 9.6 and 70.1 ng I-TEQ/kg lipid for office and plant workers, respectively. In addition, there were differences between PCDD/F levels in the blood of short-term and long-term workers. It was concluded that exposure to PCDD/Fs occurred as a result of the operation of the incinerator. In the current study, the mean PCDD/F concentration for all workers was 10.4 ng I-TEQ/kg lipid, while that corresponding to plant workers only was

11.5 ng I-TEQ/kg lipid, which is notably lower than that found by Kim et al. (2005b): 70.1 ng I-TEQ/kg lipid. The current mean PCDD/F concentration is also lower than those found in most of the above studies concerning blood of workers in MSW/infection incinerators (Kumagai and Koda, 2005; Hu et al., 2004; Kim et al., 2005b; Chen et al. 2006), while are similar to those reported by Leem et al. (2003).

On the other hand, it is interesting to note that the current plasma PCDD/F concentrations in workers of the HWI are also lower than those found in recent studies in which PCDD/F levels were determined in blood samples of non-exposed populations. Thus, Chen et al. (2005) reported mean PCDD/F levels of 15.2 and 17.0 ng WHO-TEQ/kg lipid in serum samples of general men and women from Taiwan, while Masuda et al. (2005) found a mean PCDD/F concentration of 15.8 ng WHO-TEQ/kg lipid in blood samples of general Japanese individuals. Moreover, the mean PCDD/F levels found in the present survey are also lower or similar to those reported for subjects living in the vicinity of MSWIs or industrial incinerators In relation to it, Park et al. (2004) found mean PCDD/F concentrations of 12.2 and 11.0 ng I-TEQ/kg lipid in blood samples of individuals living within 5 km and 12 km, respectively, from an industrial waste incinerator of Korea. A slightly high mean value (14.1 ng I-TEQ/kg lipid) was recently reported by Lee et al. (2005) in serum samples of 95 volunteers living near a Taiwanese MSWI, while mean PCDD/F levels of 12.3 and 11.8 ng I-TEQ/kg lipid were found in blood samples of subjects living in the vicinity of MSWIs from Korea. In contrast, a comparatively high median value, 45.7 ng WHO-TEQ/kg lipid, was reported by Pirard et al. (2005) in blood samples of 10 non-occupationally exposed volunteers who had lived within a 2 km radius of an old MSWI of France for at least 25 years.

With respect to the remaining organic compounds here analyzed, the most remarkable finding is the lack of important differences in the plant workers among the current values and those obtained in the previous annual surveys (2000-2004), while their levels are generally lower than those of the baseline survey. Moreover, although a statistical comparison could not be performed, it seems, at least apparently, that there were not important differences between the three groups of workers, differences that would be based on the levels of exposure. A comparison of the current data concerning these compounds with results from other studies is difficult taking into account the scarce data on the levels of these compounds that have been reported in blood/urine of incinerators workers.

In summary, the results of the 2005 (current) survey together with those obtained in the 2000-2004 studies, show that after 6 years of regular operation in the HWI, the workers are not significantly exposed to PCDD/Fs in their workplaces. PCDD/F levels in blood were similar or even lower than those corresponding to various non-exposed populations. A similar conclusion can be also obtained for the remaining organic substances internally biomonitored.

Acknowledgement

This study was financially supported by GRECAT, SA, Spain.

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Discussió de l'article del Capítol IV

Nivells de compostos organoclorats en plasma i orina

Es va observar un descens en les concentracions d'HCB en plasma respecte a l'estudi control (ratio 1999/2005: 2.1). En quant als PCBs, les concentracions dels congèneres 28, 101, 138 i 153 també van ser significativament inferiors a les de l'estudi control, mentre que pels congèneres 52 i 180 només aparentment inferiors (no significatiu). La tendència a la baixa en els nivells de PCBs en plasma sembla evident.

La concentració de PCDD/Fs en plasma, de 10.4 ng I-TEQ/kg lípid, va ser estadísticament inferior a la trobada a l'estudi control, 26.7 ng I-TEQ/kg lípid.

Encara que no es van poder realitzar tests estadístics degut al reduït nombre de mostres en els grups d'administració i laboratori, els resultats obtinguts no van semblar indicar que les concentracions del grup de planta (on es podria esperar que els treballadors estiguessin més exposats) fossin superiors als dels dos primers grups.

Els nivells de 2,4- i 2,5- diclorofenol en orina van ser significativament superiors als trobats a l'estudi control, mentre que els dels triclorofenols van ser inferiors. Respecte a la concentració del pentaclorofenol, va ser la mateixa a la determinada en l'estudi control.

La comparació no estadística mostra que les concentracions actuals de diclorofenols van ser superiors pels treballadors de planta respecte als altres dos grups, mentre que pels altres clorofenols i l'hidroxipirè van ser similars (o inferiors) per aquell grup.

Els resultats van indicar que els treballadors no estaven significativament exposats en els seus llocs de treball a PCDD/Fs o a les altres substàncies organoclorades monitoritzades.

Capítol V

Anàlisi de la incertesa en l'avalució de riscos

Article 6 :

Kumar V, Mari M, Schuhmacher M, Domingo JL

Partitioning total variance in risk assessment: Application to a municipal solid waste incinerator

Environmental Modelling & Software (En premsa)

Article 6: "Partitioning total variance in risk assessment: Application to a municipal solid waste incinerator"

Abstract

Comprehensive health risk assessment based on aggregate exposure and cumulative risk calculations requires a better understanding of exposure variables and uncertainty associated with them. Although there are many sources of uncertainty in system models, two basic kinds of parametric uncertainty are fundamentally different from each other: natural/stochastic and epistemic uncertainty. However, conventional methods such as standard Monte Carlo sampling (MCS), which assumes vagueness as random property, may not be suitable for this type of uncertainty analysis. An improved systematic uncertainty and variability analysis can provide insight into the level of confidence in model estimates, and it can aid in assessing how various possible model estimates should be weighed. The main goal of the present study was to introduce, Fuzzy Latin Hypercube Sampling (FLHS), a hybrid approach for incorporating epistemic and stochastic uncertainties separately. An important property of this technique is its ability to merge inexact generated data of the LHS approach to increase the quality of information. The FLHS technique ensures that the entire range of each variable is sampled with proper incorporation of uncertainty and variability. A fuzzified statistical summary of the model results produces a detailed sensitivity analysis, which relates the effects of variability and uncertainty of input variables to model predictions. The feasibility of the method has been tested with a case study, analyzing total variance in the calculation of incremental lifetime risks due to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) for the residents living in the surroundings of a municipal solid waste incinerator (MSWI) in the Basque Country, Spain.

***Keywords**: Uncertainty; Variability; Fuzzy set; Latin Hypercube sampling; Municipal solid waste incinerator; Health risks

1. Introduction

Recent health risk assessment studies often consider aggregate exposure and cumulative risk calculation. Accumulated uncertainty in the final result can produce a misleading assessment if it is not incorporated adequately. Studies in risk analysis have shown that consideration of different sources of uncertainty may be crucial for reliable results. Uncertainty and ignorance associated with assessments and predictions on which to base policies make the communication even more difficult (van der Sluijs, 2007). The characterization and quantification of uncertainty and variability in health risk assessment are important to prevent erroneous inferences in multimedia modeling and exposure assessment, which may lead to major environmental policy implications (Frey i Zhao, 2004).

Several different classifications of uncertainty have been suggested (Alefeld, 1983; Haimes, 1998; van Asselt i Rotmans, 2002; Van den Berg i col·ls., 2006). However, for the objectives of the current study, only parametric uncertainty has been considered. The parametric uncertainty has been classified on the basis of its source and nature. Sources of parameter uncertainty are measurement errors, sampling errors, variability, and the use of surrogate data (Moschandreas i Karuchit, 2005). Measurement errors refer to random (imprecision) or systematic errors (bias), while sampling errors are errors from small sample size and/or misrepresentative samples. Heterogeneity in environmental and exposure-related data includes seasonal variation, spatial variation, and variation of human activity patterns by age, gender, and geographic location, leading to variability errors. Surrogate data refer to errors from the use of substitute data. Van Asselt and Rotmans, (2002) and (Van den Berg i col·ls., 2006) classified uncertainty based on its nature. They called it *Epistemic uncertainty/imprecision*, and *Stochastic uncertainty/natural variability*. Epistemic uncertainty which results from incomplete knowledge about the system under study, is reducible by additional studies (e.g. further research and data collection). Stochastic uncertainty which stems from variability of the underlying stochastic process is non-reducible for a given system and under specific management scenario. Natural variability has also been termed (basic) variability, randomly uncertainty, objective uncertainty, inherent variability, (basic) randomness, and type-I uncertainty. Terms for epistemic uncertainty are systematic uncertainty, subjective uncertainty, lack-of-knowledge or limited-knowledge uncertainty, ignorance, specification error, prediction error, and type-II uncertainty (Haimes, 1998; Rotmans i van Asselt, 2001; van Asselt i Rotmans, 2002; Merz i Thieken, 2005; Moschandreas i Karuchit, 2005; Refsgaard i col·ls., 2007). In this paper, the term uncertainty is used to denote epistemic, variability to denote stochastic uncertainty, and total variance or simply variance to denote total uncertainty and variability in the outcome.

In spite of this obvious distinction, uncertainty and variability have been used as synonym. Some of the reasons are the blurred knowledge about uncertainty and variability and the lack of commonly agreed guidelines on uncertainty characterization and appropriate methodology. Consequently, in uncertainty estimation both type of uncertainty are clubbed together and treated as random variables, though epistemic uncertainty is not random in nature. The purpose of uncertainty analysis is to provide decision makers with a complete spectrum of information concerning the assessment and its quality. It also gives some scope to improve predictive results (Rotmans i Asselt, 2005). When the uncertainty in the risk estimate is unacceptable for decision-making, additional data are acquired for the major uncertainty contributing model components. This process is repeated until the level of residual uncertainty is acceptable. For this we need to identify uncertainty components which are reducible. Further, separate measurements can provide us relevant information to the risk management decision (Spencer i col·ls., 2001).

From a practical viewpoint, it is rare to encounter only one type of uncertainty. Pure variability would mean that all relations and their parameters which describe the random process are exactly known. Pure epistemic uncertainty would mean that a deterministic process is considered, but the relevant information cannot be obtained (e.g. due to the inability to measure the relevant parameters) (Merz i Thieken, 2005). For example, given a parameter X with total variance V_x, it can sometimes be straightforward to partition the variance into uncertainty and variability components, where α is the uncertainty component and (1- α) attributable to variability (Fig. 1). Notwithstanding, there also can be an intermediate vague region in which uncertainty and variability commingle. So sometime it is difficult to separate and in that case it needs special handling to measure both uncertainty and variability together.

Several approaches to uncertainty analysis in environmental risk analysis have been developed (Isukapalli, 1999; Schulz i Huwe, 1999). Among them, probabilistic approaches (e.g. Monte Carlo Simulation) are quite common and have been commonly used in the treatment and processing of uncertainty for solution of system modeling (Schuhmacher i col·ls., 2001). Another prominent approach based on fuzzy set theory (e.g. fuzzy alpha-cut analysis) has been recently applied in various fields including environmental modeling for uncertainty quantification (Isukapalli, 1999; Mauris i col·ls., 2001; Cho i col·ls., 2002; Hanss, 2002; Kentel i Aral, 2004; Josephs i col·ls., 2005). However this model has been branded as too conservative and basically applied in pure epistemic condition (Mauris i col·ls., 2001). However, all these methods have been developed to handle either variability or uncertainty of the process parameters or they club

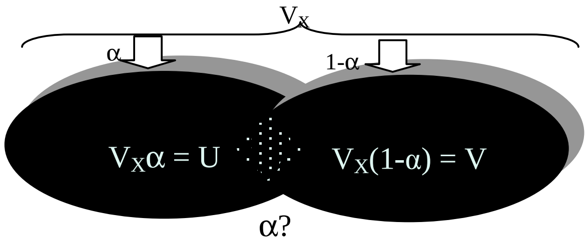


Fig. 1. Separating uncertainty and variability.

them together without valid distinction in analysis. Few recent efforts have been made to treat them separately. One common approach used in this field is 2D Monte Carlo Analysis, which classifies epistemic uncertainty as second order uncertainty (Simon, 1999). This technique requires knowledge of parameter values and their statistical distribution from which a formal mathematical description of uncertainty must be developed. However, site investigation is generally not detailed enough to determine values for some of the parameters and their distribution pattern, and sufficient data may not be collected for calibrating a model (Kentel and Aral, 2005). These approaches suffer from an obvious lack of precision and specific site-characterization, making difficult to determine how much error is introduced into the result due to assumptions and prediction. Recently, a number of authors have suggested adopting other approaches in the data limited situation. (Refsgaard i col·ls., 2007) reported: 'The test theory of classical statistics permits the testing of a sample for randomness. If the sample does not exhibit the property of randomness, other uncertainty models such as, e.g. fuzzy randomness must be adopted'. Previously, (Möller i col·ls., 2002) presented the idea of Fuzzy Randomness and formalized the concept of random variable and uncertain variable. (Kentel i Aral, 2005) introduced 2D Fuzzy Monte

Carlo and applied it in the area of health risk assessment. 2D Fuzzy Monte Carlo and Fuzzy Randomness have been classified as hybrid approach mixing the concept of probability and fuzzy set theory. The present study aims to continue this area of research and introduces a new hybrid approach, Fuzzy Latin Hypercube Sampling (FLHS), for uncertainty and variability analysis. It needs lesser computational effort and allows incorporating parameters correlation. Further we present a way to apply sensitivity analysis in fuzzy-stochastic modeling paradigm. The feasibility of the method has been validated analyzing total variance in the calculation of incremental lifetime risks due to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) for the residents living in the surroundings of a municipal solid waste incinerator (MSWI) in the Basque Country, Spain.

2. Background

2.1. Fuzzy sets and numbers

Fuzzy set theory replaces the two-valued set-membership function with a real-valued function; that is to say, membership is treated as a possibility or as a degree of truthfulness. Likewise, one assigns a real value to assertions as an indication of their degree of truthfulness. Membership functions define the degree of participation of an observable element in the set. Fuzzy numbers are the fuzzy set defined on the set of real numbers and have special significance. They represent the intuitive concept of *approximate numbers,* such as *"around, close to, approximately etc".* The fuzzy set that contains all fuzzy numbers with a membership of $\alpha \in [0,1]$ and above is called the *a-cut* of the membership function (Abebe i col·ls., 2000) (fig. 2). So the *α-cut* represents the degree of sensitivity of the system to the behavior under observation. Fuzzy α-cut technique is based on the extension principle (Zadeh, 1965), which implies that functional relationships can be extended to involve fuzzy arguments. It can be used to map the dependent variable as a fuzzy set. In simple arithmetic operations, this principle can be analytically used. However, in most practical modeling applications involving complex structural relationships (e.g. partial differential equations), analytical applications of the extension principle are difficult. Therefore, interval arithmetic can be used to carry out the analysis (Abebe i col·ls., 2000). Arithmetic on fuzzy numbers can be defined in terms of arithmetic operations on their α-cuts (on closed intervals).

This principle is generalized as: a membership level $\mu_A(x) \in [0, 1]$ is assigned to all elements x (i.e. the elements belong to the set to a certain degree) (Klir i Yuan, 1995; Hanss, 2002). The core of the set is defined as the subset for which $\mu_A = 1$. The support is the subset for which $\mu_A > 0$ (also known as the input vertex). The α-cut is a generalized support: the subset for which $\mu_A \geq \alpha$, with $0 < \alpha \leq 1$. The α-sublevel technique (Hanss, 2002) consists of subdividing the membership range of a fuzzy number into α-sublevels at membership levels $\mu_j = j/m$, for $j = 0, 1, ...m$ (Fig. 2). This allows numerically representing the fuzzy number by a set of $m + 1$ interval $[a_j, b_j]$. A triangular fuzzy number, subdivided into intervals using $m = 5$, is depicted in Fig. 2.

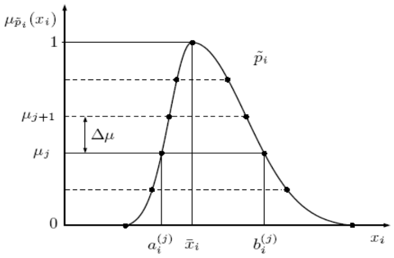


Fig. 2. Implementation of the i^{th} uncertain parameter as a fuzzy number $\tilde{p}_i$ decomposed into intervals (α-cuts).

In fuzzy simulation, for each α-level of the parameter, the model is run to determine the minimum and maximum possible values of the output. This information is then directly used to construct the corresponding membership function of the output which is used as a measure of uncertainty.

2.2. Latin Hypercube Sampling (LHS)

The LHS technique proposed by (McKay i col·ls., 1979) is a type of stratified Monte Carlo sampling, where the range of each of the *K* variables included in the uncertainty analysis $X_1, X_2, ...X_k$ is divided into N intervals in such a way that the probability of the variable falling in any of the intervals is $1/N$. One value is selected at random from each interval. The N values obtained for the first variable X_1 are randomly paired with the N values of the second variable X_2. These pairs are furthermore randomly combined with the sampled values of the third variable, and so on. It finally results in N combinations of k variables. This set of *k*-tuples is the Latin hypercube sample that is used for successive execution of model runs. When using LHS, the variable space is sampled with relatively few samples and the number of samples recommended in the literature span from 4*K/3 ((Iman i Helton, 1985), to 2*K ((McKay, 1992), to much larger ((Pebesma i Heuvelink, 1999).

3. Method

3.1. Concept: Fuzzy Latin Hypercube Sampling technique

In this study, the Fuzzy Latin Hypercube Sampling (FLHS) technique is proposed. This technique uses a combination of probability and possibility theory to include imprecise probabilistic information in risk analysis model. It allows the characterization of both uncertainty and variability in one or more input variables. Parameters can be uncertain, variable, or uncertain-variable. The variability in the random variables of the model is treated using probability density functions (PDFs), while the uncertainty associated with them is treated using fuzzy membership functions for the parameters of these random variables. Thus, means and standard deviations of these PDFs are modeled as fuzzy numbers. This modeling structure gives a generalized framework for uncertainty analysis. All three uncertainty cases can be represented by a single definition. In the case of only uncertain parameters, standard deviation can be zero, whereas in the case of only variable parameters membership function (MF) can represent the highest degree of certainty (i.e. $\mu(\mathrm{x}) = 1$). Generally, membership functions used are triangular and trapezoidal. One important difference between triangular membership function and triangular PDF is that the area below the PDF is equal to the unity. The support of the membership function provides all possible values for the variable, and any number outside the support is not possible according to fuzzy set definition. The base of the probability density function covers all the values, which have positive probabilities. Our purpose was not to provide an alternative approach to 2D MCA, which treated imprecise probability or second order uncertainty, but to use FLHS for the same purpose although with a different concept. FLHS is treating uncertainty and variability in the parameters separately using hybrid fuzzy probability set theory. For a detailed discussion on Fuzzy probability, the readers can refer to the seminal paper of (Zadeh, 1984). This framework of uncertainty analysis encourages the modelers for detailed uncertainty characterization, and at the same time gives enough space to carry out modeling task in case of insufficient information on parameters distribution. If the available information is sufficient for detailed characterization of uncertainty and variability, the method can provide a detailed analysis of uncertainty and variability contribution in the final result. However, in all cases the method can give insight into uncertainty and variability contribution of different parameters in the final result, which would help modeler/decision maker to collect more data or to improve observation of major parameters in order to improve results. The readers may also refer to (Guyonnet i col·ls., 2003) for a brief discussion of the same topic.

Since our main goal was neither to convert probability density functions into membership functions, nor to utilize one in place of another, no direct numerical comparisons for the calculated risk estimates are provided. Some researchers have attempted to compare fuzzy and stochastic simulation results but they have adopted different measures for their comparison. Guyonnet et al. (2003) have proposed possibility and necessity measures at different α-cut levels to be compared with percentile value at corresponding probability level. However (Abebe i col·ls., 2000) have used the ratio of the 0.1-level support to the value α for which the membership function is equal to 1 from fuzzy α-cut simulation, as a basis for comparision with the ratio of the standard deviation to the mean value from Monte Carlo simulation. Kentel and Aral, (2004) have used overlapped membership function and the bar chart of the normalized frequency distribution to compare the results. Clearly these differences are due to inherent differences in the definition, meaning and treatment of the uncertainty as utilized in each method. Further research is needed to properly define adequate criteria for the comparison of FLHS methodology with other approaches. Our primary aim in this paper is however to propose a computational framework for FLHS and providing an interpretation of the results generated by FLHS.

3.2. Modeling procedure

There is no clearly agreed upon definition of Fuzzy probabilistic modeling. However, three components are nearly always at the heart of all risk modeling: 1) variability/uncertainty characterization (use of probability distributions or fuzzy distribution/membership functions to describe and represent uncertainty), 2) propagation of uncertainty through sampling (statistical, fuzzy etc) of the input parameter distributions and multiple model runs, and 3) presentation of model outputs (again as probability distributions or fuzzy distributions) (Crowe, 2002). The FLHS implementation has been also restricted to this basic framework of risk modeling providing as additional feature the two tiered propagation of variability and uncertainty in the model simulation. Nevertheless, a comparison should not be drawn with other classical methods.

3.2.1. Characterization of uncertain variables

Given an arithmetic function f that depends on n uncertain parameters $X_1, X_2, ..., X_n$, represented as fuzzy numbers, the function output $q = f(X_1, X_2, ..., X_n)$ is also a fuzzy number. Using the α-level technique, each input parameter is decomposed into a set P_i of $k+1$ intervals $X_i^{(j)}$, $j = 0, 1,..., k$ where

$$P_i = \{ X_i^{(0)}, X_i^{(1)}, ..., X_i^{(k)} \} \tag{1}$$

with $X_i^{(j)} = [a_i^{(j)}, b_i^{(j)}]$, $a_i^{(j)} \leq b_i^{(j)}$, $i = 1,2,...,n,$ $j = 1,2,...,k.$ (2)

where $a_i^{(j)}$ and $b_i^{(j)}$ denote the lower and upper bound of the interval at the membership level μ_j for the i^{th} uncertain parameter. Instead of applying interval arithmetic like fuzzy *α* -cut (FAC) method (Abebe i col·ls., 2000), now all parameters are transformed into an array using combinatorial combination taking each end of the interval one at a time for each parameters and at each membership level separately. A similar transformation has been used by Hanss, (2002). Purpose of this transformation is to evaluate the target function for each possible combinations arising from discretisation of uncertain parameters. These transformed arrays $\hat{X}_i^{(j)}$ takes the following form:

$$\hat{X}_i^{(j)} = \left(\underbrace{\overbrace{\underbrace{\left(a_i^{(j)},\ldots,a_i^{(j)}\right)}_{2^{n-1} elements},\underbrace{\left(b_i^{(j)},\ldots,b_i^{(j)}\right)}_{2^{n-1} elements}}^{1},\ldots,\overbrace{\underbrace{\left(a_i^{(j)},\ldots,a_i^{(j)}\right)}_{2^{n-1} elements},\underbrace{\left(b_i^{(j)},\ldots,b_i^{(j)}\right)}_{2^{n-1} elements}}^{2^{i-1}th\ pair}}_{2^{i-1}\ pairs} \right) \qquad (3)$$

The evaluation of function *f* is now carried out by evaluating the expression separately at each of the positions of the arrays using the conventional arithmetic. The obtained result is a deterministic multi-valued decomposed interval, which can be retransformed to get a fuzzy valued result using recursive approximation (Zimmermann 1991).

3.2.2 Characterization of random variables

Characterization of random variables has been done using Latin hypercube sampling (LHS). LHS selects *N* different values from each of *n* variables $X_1, X_2, \ldots, X_n$ in the following manner. The range of each variable is divided into *N* non-overlapping intervals on the basis of equal probability. One value from each interval is randomly selected with respect to the probability density in the interval. The *N* values thus obtained for X_1 are paired in a random manner (equally likely combinations) with the *N* values of X_2. These *N* pairs are combined in a random manner with the *N* values of X_3 to form *N* triplets, and so on until *N n*-tuplets are formed. These *N n*-tuplets are the same as the *N n* -dimensional input vectors described in the previous paragraph. It is convenient to think on this sample (or any random sample of size*N*) as forming an (*N n*) matrix of input where the *i*th row contains specific values of each of the *n input* variables to be used on the *i*th run of the computer model.

3.2.3 Fuzzy-stochastic measures

Taking the clue from fuzzy probability function proposed by Kato et al. (1999) when the mean and standard deviation are fuzzy numbers, we here propose a fuzzy version of stochastic measures. Using the heuristic of this method together with Fuzzy Transformation method, the fuzzy cumulative distribution function (FCDF) and fuzzy linear correlation coefficient (FLCC) for fuzzy random variables can be calculated. This procedure, for a fuzzy-stochastic variable $\tilde{X}$ that has a normal distribution with fuzzy mean $\tilde{m}$, and fuzzy standard deviation $\tilde{\sigma}$, is next illustrated:

3.2.3.1 Fuzzy CDF

For standardized normal variables, the Cumulative Distribution Function (CDF) $F(x;m,\sigma^2)$ can be defined as:

$$F(x;m,\sigma^2)=\Phi(\frac{x-m}{\sigma}) \tag{4}$$

Here F is an arithmetic function with three uncertain parameters. Suppose $\tilde{x}$ is a realization of fuzzy-stochastic variable $\tilde{X}$ *(*which in this case are derived from output of FLHS simulation run of target model*) and* $\tilde{m}$, $\tilde{\sigma}$ are the fuzzy mean and fuzzy standard deviation of the fuzzy stochastic variable $\tilde{X}$. *So* all three parameters are fuzzy-random variables which can be decomposed (as in equation 2) using the α-level technique, into a set of $k+1$ intervals $\tilde{m}^{(j)}$, $\tilde{\sigma}^{(j)}$, $\tilde{x}^{(j)}$ *j = 0,1,..., k*

$$\tilde{m}=\{\tilde{m}^{(0)},\tilde{m}^{(1)},...,\tilde{m}^{(k)}\} \tag{5}$$

$$\tilde{\sigma} = \{ \tilde{\sigma}^{(0)}, \tilde{\sigma}^{(1)}, \ldots \tilde{\sigma}^{(k)} \} \qquad (6)$$

$$\tilde{x} = \{ \tilde{x}^{(0)}, \tilde{x}^{(1)}, \ldots \tilde{x}^{(k)} \}$$

where

$$\tilde{m}^{(j)} = \left[\tilde{m}_l^{(j)}, \tilde{m}_u^{(j)} \right], \ \tilde{\sigma}^{(j)} = \left[\tilde{\sigma}_l^{(j)}, \tilde{\sigma}_u^{(j)} \right] \text{ and } \tilde{x}^{(j)} = \left[\tilde{x}_l^{(j)}, \tilde{x}_u^{(j)} \right] \qquad (7)$$

where l and u denote the lower and upper bound of the interval at the membership level μ_j.

Now all three parameters are transformed into an array using similar combinatorial combination as used in equation 3. The resultant array will have 8 combinations at each membership level. So for α-cut level j, the vertex of $\Phi(x)$ can be calculated as:

$$\begin{gathered} F_1 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_l^{(j)}}{\tilde{s}_l^{(j)}} \right), F_2 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_l^{(j)}}{\tilde{s}_u^{(j)}} \right), F_3 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_u^{(j)}}{\tilde{s}_l^{(j)}} \right), F_4 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_u^{(j)}}{\tilde{s}_u^{(j)}} \right), \\ F_5 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_l^{(j)}}{\tilde{s}_l^{(j)}} \right), F_6 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_l^{(j)}}{\tilde{s}_u^{(j)}} \right), F_7 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_u^{(j)}}{\tilde{s}_l^{(j)}} \right), F_8 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_u^{(j)}}{\tilde{s}_u^{(j)}} \right) \\ j = 0,1,\ldots,k \qquad (8) \end{gathered}$$

The fuzzy-valued result $\tilde{F}(\tilde{x})$ of the CDF can be achieved in its decomposed form:

$$\tilde{F}(\tilde{x}) = \left[\tilde{F}(\tilde{x})_l^{(j)}, \tilde{F}(\tilde{x})_u^{(j)} \right], \qquad j = 0,1,\ldots,k \qquad (9)$$

by retransforming the arrays $\tilde{F}(\tilde{x})$ using recursive formulae (Zimmermann 1991)

$$\tilde{F}(\tilde{x})_l^{(j)} = min(F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8), \qquad j = 0,1,...,k \tag{10}$$

$$\tilde{F}(\tilde{x})_u^{(j)} = max(F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8), \qquad j = 0,1,...,k \tag{11}$$

3.2.3.2 Sensitivity analysis measures

The sensitivity contribution of the model parameters to the model output can be quantified by various measures (Janssen i col·ls., 1992). Many of these measures are based on regression and correlation analyses and commonly used for stochastic model analysis. They are applied to the original parameter and output values or to their rank-transformed values in case of a monotonic nonlinear relation. Given that some of these measures lead to similar results in identifying the sensitive parameters (Manache, 2001), only the linear correlation coefficient (LCC) is considered in this study. However other similar measures like the standardized regression coefficient (SRC), the semipartial correlation coefficient (SPC) can be derived in similar fashion.

Fuzzy Linear Correlation Coefficient (FLCC)

Given a sample of n-independent pairs of observations (x_1, y_1); (x_2, y_2);… ;(x_n; y_n), the sample correlation coefficient r_{xy} between x and y is calculated as

$$r_{xy} = cov(x,y) \big/ \sigma_x \times \sigma_y \tag{12}$$

Clearly r_{xy} is an arithmetic function with three parameters. Here all three parameters may not be fuzzy-random variables. Let us assume that X_i represents input parameters which may be fuzzy, fuzzy-stochastic or stochastic variable and y denotes the output of the target model, so in this case it will be output of FLHS simulation which will be fuzzy-stochastic variable provided any of input parameter is fuzzily combined with other stochastic variables or fuzzy-stochastic variables. Similar to Fuzzy CDF derivation, parameters are decomposed using the α-level technique, into a set of $k+1$ intervals and then transformed as in equation 3. Depending on type of X_i it can have 4 to 8 functional combination of r_{xy} from which $\tilde{r}_{xy}$ can be derived using recursive formulae.

Similarly the fuzzy standardized regression coefficient (FSRC), the fuzzy semipartial correlation coefficient (FSPC), and other sensitivity measure for fuzzy-stochastic variables can also be calculated. Selection of estimators depends on the problem and objective of the study. For example regression based estimators can yield results that may be statistically insignificant or counter intuitive (Neter *et al.*, 1996).

4 Case Study

Recently, a new MSWI which treats around 250,000 tones per year of domestic wastes started its regular operations in the Basque Country (North of Spain). The facility is placed at 3 km from a metropolitan area with population around a million of inhabitants. In order to estimate the impact of the new MSWI on the environment and the population living in the neighborhood, fate and transport models were applied to estimate PCDD/F concentrations in different compartments. In turn, these concentrations were used to estimate the exposure of the local population and to assess human health risks. The methodology is summarized in four main steps:

1) Definition of the area of study. Receptor sites were the nearest villages, in some of which agricultural activities are important.
2) Fate and transport model. PCDD/F concentrations were estimated in different compartments (soil, plants, meat and milk) using a multi-compartmental model.
3) Human exposure model. Inhalation of air and resuspended dust, dermal absorption, and ingestion of soil and local foods (vegetables, meat and milk) were the exposure pathways considered.
4) Risk characterization. Together with exposure results, safety PCDD/F benchmarks were used to evaluate the carcinogenic and non-carcinogenic risks (Katsumata and Kastenberg, 1997; Van Leeuwen et al., 2000).

As mentioned before, the present study is focused on parametric uncertainties; however model for this case study may have other form of uncertainties like numerical uncertainties (discretisation or programming errors), topographies, climatic variability, etc. Information about the equations used in the multi-compartmental model, the exposure model, and the characterization of the health risk model for this case study can be found in the Annex I.

4.1. Estimation of parameters uncertainty

The first step of uncertainty and variability analysis is the uncertainty characterization. Once all available information has been collected and evaluated, appropriate probability density functions and membership functions can be specified for variable and uncertain parameters, respectively. Estimations are based on site specific data, previously reported values, as well as some basic assumptions (Schuhmacher i col·ls., 2001). Parameters are characterized as crisp, random/variable, uncertain/fuzzy, and uncertain-variable/fuzzy-random. Crisp variables do not contain any uncertainty. Thus, they are represented by a single value. Variability associated with random variables is represented by probability density functions. Uncertainty associated with fuzzy variables is represented by membership functions, whereas uncertainty-variability of fuzzy-random variables is represented by fuzzy-probability density functions. As example, a sample data set is provided in Table 1. A detailed list of characterized input parameters used in the multi-compartmental model is given in Annex II.

Table 1

A Sample of parameters with their uncertainty characterization

Parameters	**Definition**	**Units**	**Uncertainty Type**	**Distribution /Value**[*]	**Note**
TD	Total time period of deposition	year	Uncertain	Tri(30, 40, 60)	1
May	Average annual moisture (rainfall, snowfall)	cm/yr	variable	Min: 100.04; Mean: 111.74; Max: 128.93 Std: 11.06	2
Vd	Dry deposition velocity[a]	cm/sec	Uncertain &Variable	UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])	3
BD	Bulk density	g/cm^3	Variable	Uni(0.93-1.84)	4

[1]. Expected life time of MSWI could be 30-60 years. [2]Extracted from 10 years data of the area (1994-2004).

[3]Depends on the size of the air particles. [4]From Hoffman and Baes (1979)

[*] Tri = Triangular, Uni = Uniform, UniTri = Uniform Triangular (represent variability and uncertainty respectively).

[a] Detailed calculation is provided in Annex II (Table 2).

4.2. Simulation and propagation of uncertainty

After characterizing the uncertainty and/or variability associated with each input parameters, the FLHS technique is used to propagate these uncertainty. The total variance in the result can then be estimated. This propagation results in a fuzzy probability distribution functions for the estimated risk. Even though the Latin Hypercube Sampling needs lesser sample size compared to normal Monte-Carlo, a higher sample size (1000) has been used to validate the results from previous work of (Schuhmacher i col·ls., 2001). Further 11 levels (0-0.1-1 α-cuts) of fuzzy discretisation have been used which have further been discretised into lower and upper bounds. Under consideration of the fuzzy randomness of the uncertain input values, the obtained result values were also fuzzy random variables.

FLHS simulation produces two PDFs/CDFs (i.e., one for upper and one for lower bound) for each α-cut level. For the triangular membership function used in this case study, the lower and the upper bound at α-cut 1.0 are the same. Thus, a total of 21 risk PDFs/CDFs were generated with 11 levels of fuzzy discretisation. These discrete distributions were used to generate fuzzy risks values corresponding to each percentile. To represent the results, box plots were used. The simplicity of the box plot makes it ideal as a means of comparing many samples simultaneously. It was used to compare distributions at different possibilities level. Box plots of the individual α-cut levels were lined up side by side on a common scale, and the various attributes of the results compared at a glance. Obvious differences were immediately apparent. Data which will not lend itself to standard analysis can be identified. In the current case study, the box plots have been used to show the 5th, 25th, 50th, 75th, and 95th, percentiles of model outcome, in this case PCDD/F concentrations or risk due to exposure to PCDD/Fs. It has been drawn separately for lower and upper membership functions.

The box length gives an indication of the sample variability, while the line across the box shows where the sample is centered. The length of the notch (along the box, not its depth into the box) is a "robust estimate of uncertainty about the median". The notches should be interpreted as a rough indication of the magnitude of a significant difference. The position of the box in its whiskers and the position of the line in the box also indicate whether the sample is symmetric or skewed, either to the right or left. For a symmetric distribution, long whiskers, relative to the box length, can betray a heavy tailed population and short whiskers, a short tailed population. The commonly accepted method among statisticians for drawing the whiskers is 1.5 times the interquartile range (IQR). Any data value larger than that should be marked as an outlier.

The membership function of mean and standard deviation of different results has also been plotted to represent uncertainty associated with the result. Further sensitivity analysis to calculate relative contribution of different uncertain parameters to the total uncertainty has been also done. This is useful to handle reducible source of uncertainty in parameters.

5. Results and discussion

The output of FLHS simulation is fuzzy probabilistic distributions, which can be represented in various forms (multi-plot of PDF/CDFs over different α-cuts). Several forms of information can be extracted from the results. In the present case study, results have been shown according to the conventional way used by risk modeler community. The frequency distribution has been plotted at three levels of uncertainty, lower α-0, α-1 and upper α-0, which basically represent min-mode-max pattern in triangular membership function (MF). The box plots have been plotted for all 11 α-cut levels at lower and upper uncertainty levels. Further minimum, mode and maximum values for respective triangular MFs have been shown for mean and standard deviation to represent possibilistic uncertainty distribution of fuzzy variability. Sensitivity analysis is presented in Tables and pie-charts. Analysis has been broken down at each step of modeling exercise involving compartmental sub-models from air deposition models and exposure models.

5.1. Results from multi-compartmental model

A fuzzified statistical summary of PCDD/F concentrations in different media obtained from the multi-compartmental model is shown in Table 2. Large uncertainty in the output has been observed on the current characterization of input parameters. The distribution of PCDD/F concentrations in soil due to air deposition of the MSWI emission is depicted in Fig. 3. The distributions at different α-cut levels show a different

Table 2
Mean and standard deviation of PCDD/Fs concentration in different media obtained from air deposition model with three levels of uncertainty (lower α-cut 0, α-cut 1, and upper α-cut 0).

Media	**Mean concentration [min mode max]**	**Uncertainty (Triangular Std) [min mode max]**
Soil	[1.01, 1.98, 54.7]* E-12	[0.28, 0.48, 23.6] * E-12
Meat	[0.2, 0.9, 109.2] * E-8	[0.12, 0.53, 33.72] * E-8
Milk	[0.3, 1.2, 90.85] * E-8	[0.2, 0.6, 25.9] * E-8
Fruits	[0.3, 0.9, 20.1] * E-10	[0.12, 0.23, 37.18] * E-10
Vegetables	[0.2, 0.4, 10.0] * E-10	[0.01, 0.12, 1.86] * E-10

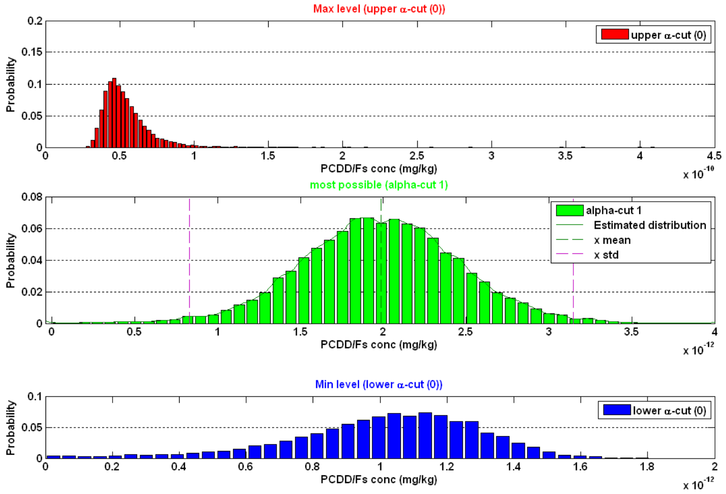


Fig. 3. Distribution of PCDD/F concentrations in soil at three uncertainty levels (upper α-cut 0, α-cut 1, and lower α-cut 0).

behavior. The most possible value (α-cut 1) shows a normal distribution, whereas the minimum value (lower α-cut 0) is displaying a negative skewness, and the maximum value (upper α-cut 0) is displaying a positive skewness. In turn, the box plotsat 11 α-cut levels (Fig. 4) show a high variability across different possibility levels (α-cut levels). Since the notches in the box plot do not overlap, it can be concluded with 95% confidence that the true medians differ. Sensitivity analysis shows how much each uncertain parameter contributes to the overall uncertainty of the prediction. Major contributors to uncertainty in soil deposition are soil loss constant (ks) (55%), dry deposition velocity (Vd) (30%), and volumetric washout ratio for particulates (Wp) (14%) (Fig. 5). Surprisingly, the concentration of PCDD/Fs in air (Cair) is not a major source of uncertainty, which emphasizes the need to collect more site specific data. The approximated membership function of the fuzzy expected value of PCDD/F in soil concentrations is also depicted in Fig. 5.

Similar analysis of PCDD/F concentrating in milk exhibits distributions at different α-levels (Fig. 6). In this case, all three uncertainty levels exhibited a positive skweness. However, the most possible value (α-cut 1) has shown a similar distribution pattern to lower

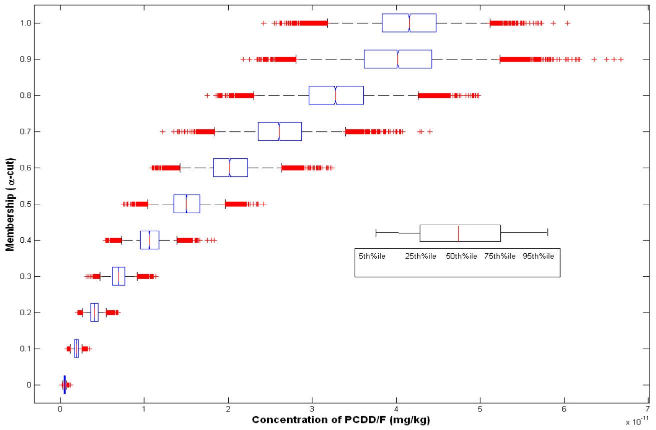


Fig. 4. Box plot of PCDD/F concentrations in soil at lower level of membership (lower α-cut levels).

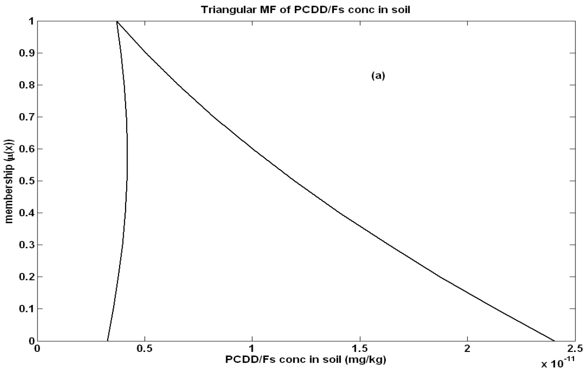
α-cut 0 (minimum value), which can further be confirmed from box plots (Fig. 7). It can be interpreted as the PCDD/F concentrations in milk would likely be at a lower side of estimation than to the max-value. There are a large number of outliers across all the possibility levels. However, those are mostly mild outliers as they hardly go beyond three times the Interquartile ranges (3IQRs). At the upper lowest possibility level (upper α-cut 0) of the PCDD/F concentrations in milk, there are some extreme outliers which explain the high uncertainty toward max-value side of the α result. Sensitivity analysis shows fraction of wet deposition (Fw) (33%), plant surface loss coefficient (kp) (23%), particle deposition velocity

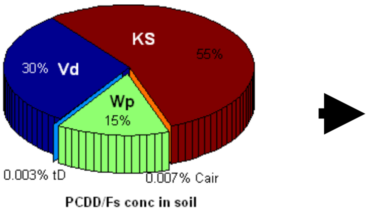
(Vd) (22%), and volumetric washout ratio for particulates (Wp) (11%) as major contributors towards uncertainty (Table 3). However PCDD/F concentrations in air (Cair), the total time period of deposition (TD) are not a major source of uncertainty (Table 3). The approximated membership function of the fuzzy expected value of PCDD/F concentrations in milk is shown in Fig. 8. The most expected value of PCDD/F concentrations in milk denotes closeness to minimum possibility level, which can be interpreted as 'expected value of PCDD/F concentrations in milk would be low to moderate, or it has low possibility of getting maximum value'.

Table 3

Sensitivity analysis for diet intake

Parameters	Fraction contribution of total uncertainty
Vd	0.224
Cair	1.6E-11
Wp,	0.1078
TD	2.8E-13
ks	0.0627
Fw	0.3311
kp	0.2364
SIR	0.0379





Parameters	Fraction contribution of total uncertainty
ks	0.55
Vd	0.3035
Wp	0.1464
Cair	0.00007
TD	0.00003

Fig. 5. (a) Membership Function of PCDD/F concentrations in soil and (b) sensitivity chart of uncertain parameters used in calculating PCDD/Fs concentration in soils.

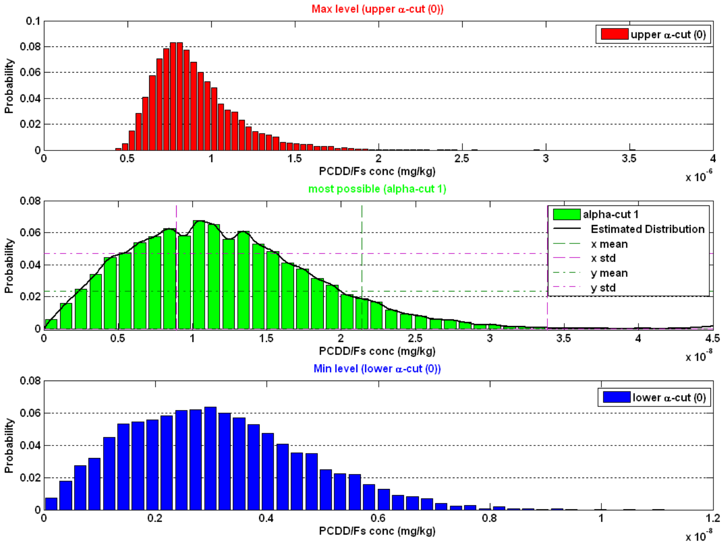


Fig. 6. Distribution of PCDD/F concentrations in milk with at three uncertainty levels (Upper α-cut 0, α-cut 1, and Lower α-cut 0).

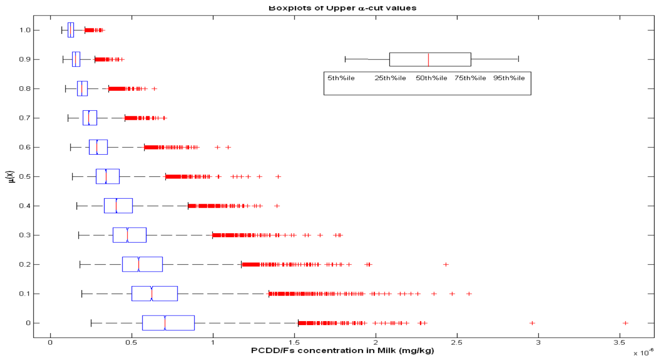


Fig. 7. Box plot of PCDD/F concentrations in milk at upper level of membership (upper α-cut level).

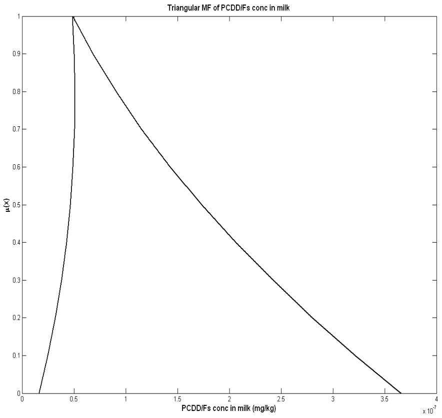


Fig. 8. Membership Function of PCDD/F concentrations in milk.

5.2. Results from exposure models

A fuzzified statistical summary of exposure to PCDD/Fs by the population living in the vicinity of the MSWI is presented in Table 4. The distribution of exposure due to air inhalation with three level of uncertainty band is depicted in Fig. 9. It is a positively skewed distribution with higher variability toward max-value. The distribution of total exposure to PCDD/Fs to the population through different media is shown in Fig. 10, which are positively skewed at all three levels of uncertainty. Estimated mean and standard deviation has been also shown for most possible distribution (i.e. for α-cut 1). Detailed possibilistic-probabilistic analysis can be done from box plots of lower and upper α-cut levels. Since most of the notches in the boxes do not overlap, we can conclude with 95% confidence that the true medians differ across different possibility levels. Further analysis of whiskers show how distribution has been skewed at different possibility levels. It also shows the mild and extreme outliers present across the possibility levels. For example, outliers present at lower α-cut 0.8 or upper α-cut 0 are quite notable. From these data, it can be interpreted that there is less likelihood of getting these maximum risk value and result decision should not be based on these values. Outliers can be the result of conceptualization or modeling error so at least a detail validity analysis should be performed before considering it for risk decision. This information is particularly important comparing with classical worst case risk analysis method which doesn't give information on likelihood of decision variable.

Table 4

Mean and standard deviation of PCDD/Fs intake through different exposure media with three levels of uncertainty (lower α-cut 0, α-cut 1, and upper α-cut 0).

Exposure Media	**Mean exposure**	**Uncertainty (Triangular Std)**
	[min, mode , max]	**[min mode max]**
Food ingestion	[0.3, 0.8, 130.5] *E-12	[0.3, 0.9, 129.2] *E-12
Air inhalation	[0.22, 0.29, 0.34] *E-13	[0.07, 0.09, 0.1]* E-13
Dermal absorption	[0.0, 0.2, 10.77]* E-16	[0.0, 0.07, 4.79]* E-16
Soil ingestion	[2.0, 3.6, 205.2]* E-20	[0.9, 1.6, 111.7] * E-20
Resuspended particles inhalation	[0.4, 0.66, 24.17] *E-32	[0.17, 0.25, 12.46] *E-32

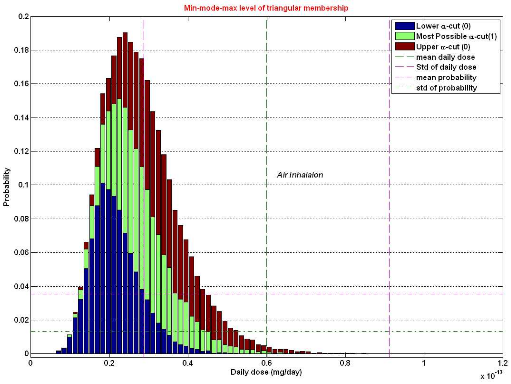


Fig. 9. Distribution of air inhalation with uncertainty band.

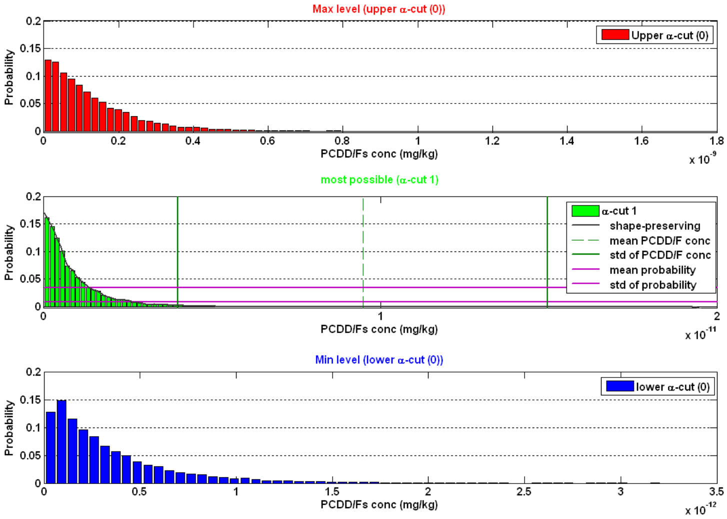


Fig. 10. Distribution of total doses at three uncertainty levels (upper α-cut 0, α-cut 1; and lower α-cut 0).

Sensitivity analysis (Fig. 11 b) shows that 99% risk is from exposure to PCDD/F contaminated diets source. Less that 1% of the total PCDD/F exposure is due to the direct MSWI emissions, which can also be validated from previous results in this area (Schuhmacher i col·ls., 2001). The tolerable average intake levels of PCDD/Fs established by the WHO are between 1 and 4 pg WHO-TEQ/kg/day for lifetime exposure (Schuhmacher i col·ls., 2001). Closer examination of box plots (Fig. 12) reveals that excluding the extreme outliers, most values lie within 1 pg WHO-TEQ/kg/day limit. Also, the total exposure value at 50th percentile (below 0.1 pg WHO-TEQ/kg//day) and 90th percentile (below 0.2 pg WHO-TEQ/kg//day) are far below to the tolerable limit. Consequently, it can be concluded that in the current case study the MSWI would not mean a substantial risk to the population living in the area under potential influence of the emissions of the facility.

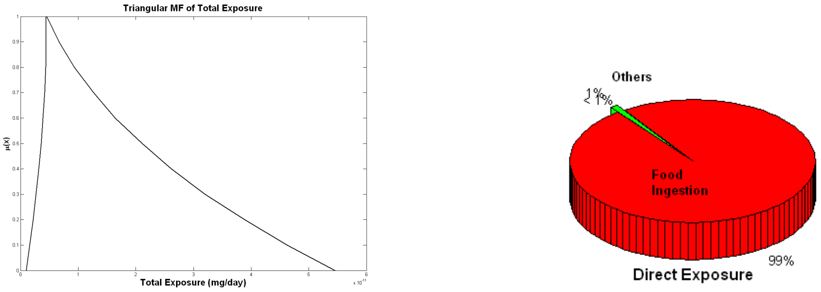


Fig. 11. (a) Membership Function of total exposure to PCDD/Fs and (b) sensitivity analysis for total exposure.

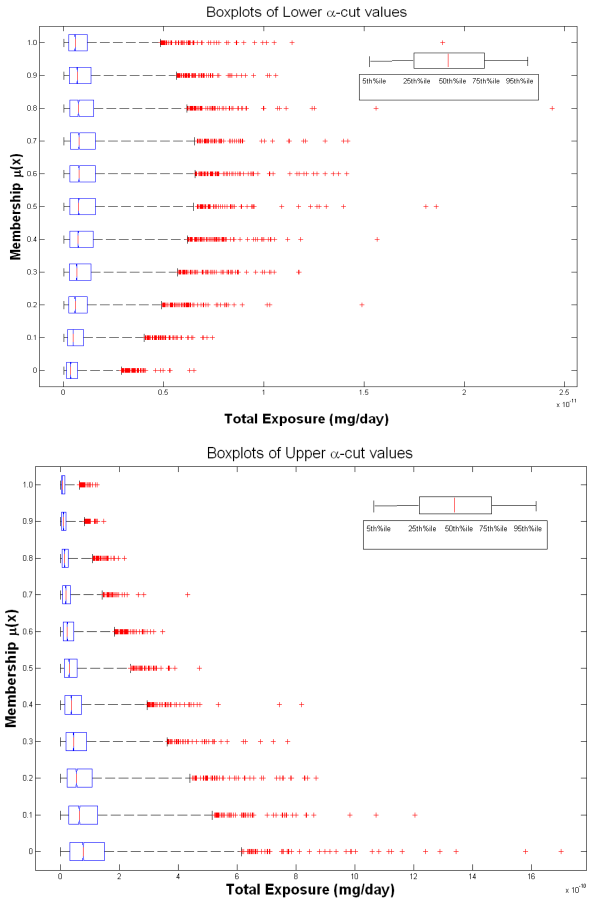


Fig. 12. Box plot of total exposure for lower (a) and upper (b) level of membership (lower and upper α-cut levels)

5.3 Risk evaluation

The non-carcinogenic and carcinogenic risks from direct, indirect (food source), and total exposure are shown in Tables 5 and 6, respectively. The results show the mean, standard deviation, 10th percentile, the central tendency of risk (50th percentile), and the reasonable maximum exposure (RME) (90th percentiles). All this statistical measures have been calculated at three levels of uncertainty: minimum value (lower α-cut 0), most possible value (α-cut 1), and maximum value (upper α-cut 0). It can be seen that the median (50th percentile) of non-carcinogenic risk due to PCDD/Fs for the population living in the surroundings of the MSWI is in the range of 0.0001 – 0.004 and most likely risk would be 0.002 (Table 5). The results also reveal that the uncertainty of the risk estimated, as defined by the ratio of the 90th to 10th percentile (Schuhmacher i col·ls., 2001) is in the range of 0.06 – 1383, and the most likely value would be 18.4 (Table 5).

Table 5

Non-carcinogenic risk: Mean, standard deviation, and 10th, 50th, 90th percentiles with three levels of uncertainty (lower α-cut 0, α-cut 1, and upper α-cut 0)

		Direct Risk	**Diet Risk**	**Total Risk**
		[min, mode , max]	**[min, mode , max]**	**[min, mode , max]**
Mean		[1.1 1.5 1.8]*E-5	[0.2 3.4 69]*E-3	[0.21 3.41 69.02]*E-3
SD[a]		[4.1 5.5 6.4]*E-6	[1.2 1.7 31]*E-4	[1.2 1.72 31.2]*E-4
Percentiles	**10th**	[0.5 0.6 0.8]*E-5	[0.0 0.3 6.5]*E-3	[0.01 0.36 6.58]*E-3
	50th	[0.8 1.1 1.3]*E-5	[0.1 1.9 3.9]*E-3	[0.11 1.91 3.91]*E-3
	90th	[1.7 2.2 2.6]*E-5	[0.4 6.6 13.8]*E-3	[0.42 6.62 13.83]*E-3

[a] *SD = standard deviation*

Table 6

Carcinogenic risk: Mean, standard deviation, and 10th, 50th, 90th percentiles with three levels of uncertainty (lower α-cut 0, α-cut 1, and upper α-cut 0)

		Direct Risk **[min, mode , max]**	**Diet Risk** **[min, mode , max]**	**Total Risk** **[min, mode , max]**
Mean		[1.9 2.5 3.0]*E-10	[0.3 5.5 114.8]*E-8	[0.32 5.53 114.81]*E-8
SD[a]		[1.5 2.1 2.4]*E-10	[0.4 7.8 16.9]*E-9	[0.50 7.82 17.01]*E-9
Percentiles	**10th**	[0.3 0.4 0.4]*E-10	[0.03 0.3 5.1]*E-8	[0.03 0.31 5.11]*E-8
	50th	[1.5 2.1 2.4]*E-10	[0.1 2.7 56.5]*E-8	[0.12 2.82 56.52]8E-8
	90th	[4.0 5.3 6.2]*E-10	[0.7 13.8 289.1]*E-8	[0.80 13.90 289.26]*E-8

[a] *SD = standard deviation*

With respect to the total carcinogenic risk, the median increment in individual lifetime is in the range of (3.2 – 1148)$\times 10^{-7}$, and the most likely value would be 5.53 $\times$ 10^{-7} (Table 6). Similarly, the uncertainty of the risk estimated is in the range of 0.16 – 9642, being the most probable value 44.84 (Table 6). From the obtained results, it can be concluded that according to the WHO recommendations neither the emissions from the MSWI (direct exposure), nor the indirect exposure (diet) to PCDD/Fs would mean any additional risk for the health of the general population living in the vicinity of the MSWI during its life time.

5. Conclusions

In the current case study, only parametric uncertainty consisting of natural variability and epistemic uncertainty has been analyzed. However, the proposed methodology (FLHS) can be used to evaluate other uncertainty components (e.g. model uncertainty and scenario uncertainty). FLHS technique can encompass uncertainty in the inventory, in fate and transport processes, and in exposure pathways to potential receptors. The outputs of these models are also fuzzy probability distributions that, if correctly constructed, represent an expected or "all possible estimates" of the risk and the uncertainty associated with that estimate, conditioned on the model assumptions. As other probabilistic models which generally include probabilistically based sensitivity and uncertainty analyses, FLHS can also give sensitivity measures that can be used in uncertainty reduction and measurement of the value of uncertainty reduction. However, in contrast to classical probabilistic sensitivity measures which failed to separate uncertainty and variability, FLHS can do it effectively. In summary, FLHS clearly separates controllable and uncontrollable uncertainty associated with models, which helps the models /and decision makers to identify the priority area in order to improve the results.

Further validation is needed to test the degree of satisfaction of compliance guideline. For example different risk compliance guidelines have been developed to compare results from stochastic simulation; similar guidelines should be developed to give general uncertainty estimates in accordance with U-V (Uncertainty-Variability) classification. Guyonnet et al. (2003) has proposed possibility and necessity measures to test the degree of satisfaction of the compliance guideline. However it still needs to be tested and adopted by different regulatory bodies before it is used more broadly in the modeller's community.

It also offers new research direction to modeler community to further improve the uncertainty analysis approach. In environmental risk analysis, an immediate need is to develop more uniform guidelines to characterize uncertainty and variability associated with different environmental models. In this study, no attempt has been made to compare FLHS with other evolving techniques in this area considering fundamental differences in assumption of defining uncertainty and variability. Comparison of the FLHS results is not straight forward. Some researchers have attempted to compare first order fuzzy and stochastic simulation results but they have adopted different measures for their comparison ((Guyonnet i col·ls., 2003). However, FLHS is a hybrid second order uncertainty analysis method and comparison with other similar modeling paradigm like 2D Monte-Carlo, or even second order fuzzy simulation need different set of comparison criteria. Notwithstanding, as all these are emerging modeling techniques, it needs further research, and then an adequate comparison can be performed. Also further research to develop decision analysis models, which directly use U-V outcomes in risk assessment and decision making process, will enhance the framework.

Software Availability

A toolbox for Matlab has been developed for use in health risk assessment. It is still in beta version and very specialized for health risk assessment. However, in due time a generalized version will be released. It can be made available upon specific request.

ACKNOWLEDGEMENTS

Vikas Kumar was supported by URV scholarship grant and later Marie Curie early stage training grant at Catchment Science Centre, University of Sheffield. Authors are grateful for the comments of two anonymous reviewers.

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Annex I

Risk Characterization model.

Table 7

Compartmental concentrations.

COMPARTMENTAL CONCENTRATIONS	
Environmental concentrations Soil $Cs = \frac{100(Dp + Dv + L_{DIF})}{ks \cdot BD \cdot Zs}\left(1 - \exp(-ks \cdot TD)\right)$ where: $Dp = 0.31536 \cdot Vd \cdot Cpa$ $Dv = C_{air} \cdot May \cdot Wp \cdot 10^{-8}$ $L_{DIF} = 0.31536 \cdot Kt \cdot Cva$ $Kt = \left(\frac{Da}{Zs}\right) \cdot \left(1 - \left(\frac{BD}{\rho_S}\right) - \theta_{SW}\right)$	Cs: concentration of contaminant in soil (µg/g); Dp: yearly dry deposition rate (g/m^2 year); Dv: yearly wet deposition rate (g/m^2 year); L_{DIF}: atmospheric diffusion flux (g/m^2 year); ks: soil loss constant (yr^{-1}); TD: time period over which deposition occurs (yr); Zs: soil mixing depth (cm); BD: bulk density (g/cm^3); Vd: dry deposition velocity (cm/sec); Cpa: particle bound concentration of contaminant (µg /m^3); Cair: concentration of contaminant in air (µg /m^3); May: average annual moisture (cm/yr); Kt: gas phase mass transfer coefficient (cm/s); Cva: vapor phase air concentration of contaminant (µg/m^3); Da: diffusion coefficient of contaminant in air (cm^2/s); ρs: solids particle density (g/cm^3); θsw: volumetric soil water content (ml/cm^3); Cpd: concentration in plant due to particle deposition (µg/g); Fw: fraction of wet deposition that adheres to plant surfaces (unitless); Kp: plant surface loss coefficient (yr $^{-1}$); Tp: time of plant's exposure to deposition (yr); Yp: yield or standing crop biomass (kg/m^2); Cpr: concentration plant due to root uptake (µg/g); Br: soil to plant bioconcentration factor (g soil/g plant); C_{beef}: concentration in beef (mg/kg); Fi: fraction of plant grown on contaminated soil and eaten by the animal (unitless); Qp: quantity of plant eaten by the animal (kg plant/d); Cp= Cpd + Cpr (µg/g); Qs: quantity of soil eaten by the animal (kg soil/d); Ba_{beef}: biotransfer factor for beef (d/kg); C_{milk}: concentration in milk (mg/kg); Ba_{milk}: biotransfer factor for milk (d/kg). s: quantity of soil eaten by the animal (kg soil/d); Ba_{beef}: biotransfer factor for beef (d/kg); C_{milk}: concentration in milk (mg/kg); Ba_{milk}: concentration in milk (mg/kg); Ba_{milk}: biotransfer factor for milk (d/kg)
Plants Deposition $Cpd = \frac{1000 \cdot (Dp + Fw \cdot Dv)}{kp \cdot Yp} \cdot \left(1 - \exp(-kp \cdot Tp\ )\right)$ Root uptake $Cpr = Cs \cdot Br$	
Food chain concentrations Beef $C_{beef} = (\Sigma\, FiQp \cdot Cp + Qs \cdot Cs) \cdot Ba_{beef}$ Milk $C_{milk} = (\Sigma\, FiQp \cdot Cp + Qs \cdot Cs) \cdot Ba_{milk}$	

Table 8

Exposure model.

EXPOSURE MODEL	
Air inhalation $ADD_{inh} = \frac{C_{air} \cdot IR \cdot AFI_i \cdot EF}{1000 \cdot BW \cdot 365}$ Inhalation of resuspended dust $ADD_{res} = \frac{Cres \cdot IR \cdot RET \cdot AFI_i \cdot EF}{1000 \cdot BW \cdot 365}$ where: $C_{res} = 10^{-6} \cdot Cs \cdot Cpa \cdot Fres$	ADD_{inh}: inhalation of air average daily dose (mg/kg day); Cair: PCDD/F air concentrations g I-TEQ/m^3; IR: inhalation rate (m^3/day); AFI_i: adsorption factor for inhalation; EF: exposure frequency (day/year); BW: body weight (kg); ADD_{res}: inhalation of resuspended dust average daily dose (mg/kg day); Cres: concentration in resuspended dust (µg/m^3); RET: fraction retained in the lung (unitless); Cpa: particle concentration in air (µg/m^3); Fres: fraction of resuspended soil in particle concentration (unitless); Cs: soil concentration (µg/g); ADD_d: dermal absorption daily dose (mg/kg day); AF: adherence factor (mg/cm^2); SA: exposed skin surface (m^2/day); ABS_d: dermal absorption factor (unitless); ADDs ingestion average daily dose (mg/kg day); CRs: soil consumption rate (mg/day); AFI_g: gastrointestinasl absorption factor (unitless); ADD_f: food ingestion average daily dose (mg/kg day); CF_i: concentration in "i" food (µg/g): CRF: consumption rate of each "i" food type (g/day); Fi; fraction of food each "i" food type produced in the contaminated area (unitless).
Dermal absorption $ADD_d = \frac{Cs \cdot AF \cdot SA \cdot ABS_d \cdot EF}{10^2 \cdot BW \cdot 365}$	
Ingestion of soil $ADD_s = \frac{Cs \cdot CRs \cdot AFI_g \cdot EF_s}{10^6 \cdot BW \cdot 365}$	
Ingestion of contaminated food $ADD_f = \frac{CFi \cdot CRF_i \cdot Fi \cdot AFI_g \cdot EF_f}{1000 \cdot BW \cdot 365}$	

Table 9

Health risk characterization model.

HEALTH RISK CHARACTERIZATION	
No carcinogenic risk	ADD: average daily dose (mg/kg day); HQ: Hazard quotient (unitless); RfD: reference dose (mg/kg day); ER: excess cancer risk (unitless); ED: exposure duration (yr); SF: slope factor (mg/kg day)$^{-1}$; AT: average lifetime (yr).
$HQ = ADD / RfD$	
Carcinogenic risk	
$ER = ADD \cdot ED \cdot SF / AT$	

Annex II

Table 10

General parameters of multi-compartmental model.

Parameter	Symbol	Units	Uncertainty Type	Distribution /Value	Comments/References
Total time of deposition	TD	yr	Uncertain	Tri(30, 40, 60)	Expected life time of MSWI was assumed to be 30-60 years
Soil mixing depth	Zs	cm	Variable	Uni(10-20)	(US EPA, 1998)
Average annual moisture (rainfall, snowfall)	May	cm/yr	Variable	Min: 100.04; Mean: 111.74; Max: 128.93 Std: 11.06	Extracted from 10 years data of the area (1994-2004) (Ministerio de Medio Ambiente)
Bulk density	BD	g/cm^3	Variable	Uni(0.93-1.84)	(Hoffman and Baes, 1979)
Volumetric soil water content	θsw	ml/cm^3	Variable	Uni(0.03-0.40)	(Hoffman and Baes, 1979)
Solids particle density	ρs	g/cm^3	Variable	Uniform(2.6-2.7)	(Hillel, 1980; Blake and Hartge, 1996)
Yield crop biomass of plant group (vegetables/fruits)	Yp	kg/m^2	Variable	Uni(0.24-0.31)	(Belcher and Travis, 1989; Shor et al., 1982)
Quantity of plant eaten by the animal	Qpi	kg/day	Variable	Dairy Cattle: Uni(2.6-11); Beef cattle: Uni(0.47-8.8)	Derived from data of seven types of grains, two types of forage and two types of silage for beef and dairy cattle (US EPA , 1997)
Soil consumption rate (animal)	Qs	kg/day	Variable	Dairy Cattle: Uni(0.1367-2.64); Beef cattle: Uni(0.13-1.17)	(US EPA, 1997) (1-18% of dry matter intake)
Time of plant's exposure to deposition per harvest	Tp	yr	Variable	Uni(0.0822- 0.1644)	(Belcher and Travis, 1989)
Dry deposition velocity*	Vd	cm/sec	Uncertain &Variable	UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])	Depends on the size of the air particles. Estimation is shown in Table 2

* Separate calculation has been provided in table 2

Calculation of deposition velocity

The emissions were modeled in three size classes of particles. Velocity of particle is a function of dry deposition mass flux in particle size interval and airborne particle concentration in particle size interval. Estimated velocity in particle size interval has considered percentage composition.

Table 11

Particle size distribution and velocity estimation

Particles Size	**AbsoluteVelocity (cm/sec)**	**Particle Percentage (%)**	**Estimated Velocity (cm/sec)**
< 2 µm	7.11E-03	70.0- 87.5	4.98E-03-6.22E-03
< 2-1000 µm	2.87E-01	9.5- 25.0	2.73E-02-7.18E-02
>1000 µm	2.47	3.0-5.0	7.41E-02-1.235E-01
[2 500 1000]	[7.11E-03 2.87E-01 2.47]		UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])

Table 12

Contaminant Specific parameters (in this case PCDD/Fs)

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Comments
Contaminant air concentration	C_{air}	mg/m^3	Uncertain & Variable	Tri([2.10E-10, 9.27E-11, 3.50E-10], [1.05e-13, 1.05e-12, 1.05e-10])	Derived from routine sampling in the area (10 samples)
Water partition coefficient	K_{ow}		Variable	(4.62E+06, 0.73)	Caltox database
Fraction of food produced in the contaminated area	Fi	unitless	Variable	Uni(0.01 0.1)	The consumption of food produced in contaminated area was assumed to be 1-10%.
Diffusion coefficient of contaminant in air	Da	cm^2/s	Variable	Normal(4.2E-1, 0.08)	Caltox database
Fraction of wet deposition that adheres to plant surfaces	Fw	unitless	Uncertain	[0.5 0.6 0.7]	(US (EPA, 1998))
Soil loss constant	Ks	yr^{-1}	Uncertain &Variable	Uni([0.76 0.81 0.90], [0.03 0.07 0.11])	Calculated using formula in (EPA, 1998)
Volumetric washout ratio for particulates	Wp	unitless	Uncertain	[1.00E+2 1.05E+2 1.1E+2]	(US (EPA, 1998))
Plant surface loss coefficient	K_p	unitless	Uncertain	[14.0 18.0 21.0]	(US (EPA, 1998))

Table 13

Input Parameters for exposure model

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Observation
Body weight	BW	Kg	Uncertain &Variable	Lognormal(67.52 ± 12.22)	(Arija et al., 1996)
				Lognormal(77.1 ± 13.5)	(Smith, 1994)
Inhalation Rate	IR	m^3/day	Uncertain &Variable	Lognormal(20 ± 2)	(Shin et al., 1998)
				Uniform(5.05-17.76)	(Finley, 1994a)
Fraction retained in the lung	RET	unitless	Uncertain	Tri(45 60 70**)**	(Nessel et al., 1991)
Absorption factor for inhalation	AFIi	unitless	Uncertain	100	(Nessel et al., 1991)
Soil ingestion rate (human)	CRs	mg/day	Uncertain &Variable	Lognormal(3.44 ± 0.8)	(LaGrega et al., 1994)
				Tri 25 (0.1- 50**)**	(Lagoy, 1987)
Consumption rate of vegetables	CRF_{veg}	g/day	Variable	Lognormal (99 ± 80)	(Arija et al., 1996)
Consumption rate of fruit	CRF_{fruit}	g/day	Variable	Lognormal (236 ± 174)	(Arija et al., 1996)
Consumption rate of milk	CRF_{milf}	g/day	Variable	Lognormal (226 ± 177)	(Arija et al., 1996)
Consumption rate of beef	CRF_{beef}	g/day	Variable	Lognormal (180 ± 84)	(Arija et al., 1996)
Gastrointestinal absorption factor	AFI_g	unitless	Uncertain	Tri(40 60 100)	(Nessel et al., 1991)
Exposed skin surface area (Adult: head, hands, forearms, lower legs)	SA	m^2/day	Uncertain	Tri(0.20 0.53 0.58)	(US EPA, 1992)
Adherence Factor	AF	mg/cm^2	Uncertain	Tri (0.52 71 0.9)	(Finley, 1994b)
Dermal absorption factor	ABSd	unitless	Uncertain	Tri (0.001 0.003 0.03)	(Katsumata and Kastenberg, 1997)
Exposure Frequency	EF	day/yr	Variable	Tri 345 (180-365)	(Smith, 1994)

Table 14

Specific chemical parameters (PCDD/Fs) for risk evaluation

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Observation
Average Lifetime	AT	yr	Variable	Lognormal (75 ± 5)	(Frey, 1993)
Exposure duration (adult resident)	ED	yr	Variable	Lognormal (11.4 ± 13.7)	(Israeli, 1992)
Tolerable Daily Intake	TDI	mg/kg day	Variable	Uniform (1E-9 - 4E-9)	(van Leeuwen et al., 2000)
Slope Factor	SF	$(mg/kg\ day)^{-1}$	Variable	Uniform (34000-56000)	(Katsumata and Kastenberg, 1997)

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Discussió de l'article del Capítol V

Respecte al model multicompartimental, l'anàlisi de sensibilitat va mostrar que en la deposició en sòls, la constant de perdua del sòl (ks) (55%), la velocitat de deposició seca (vd) 30%), i la proporció volumètrica de neteja de partícules (Wp) (14%) eren les variables que contribuïen majoriatariament a la incertesa.

Per altra banda, el valor més esperat de concentració de PCDD/Fs en llet va denotar la seva proximitat al nivell minim de possibilitat, el que es podria interpretar com a que el valor esperat de PCDD/Fs en llet seria baix o moderat, amb poca possibilitat de tenir un valor alt.

Pel que fa al model d'exposició l'anàlisi de sensibilitat, va mostrar que el 99% del risc era derivat de la dieta, mentre que menys de l'1% provindria de les emissions directes de la incineradora.

Els resultats d'aquest d'estudi van indicar que la incineradora no suposa un risc considerable per la població que viu en l'àrea sota la seva influència.

Capítol VI

Conclusions generals

1. En el present estudi s'ha avaluat l'impacte ambiental i els riscos per la salut derivats de diferents incineradores de residus. Amb aquesta finalitat s'han monitoritzat els nivells de diversos compostos orgànics persistents i metalls pesants en diferents matrius ambientals i biològiques.

2. Les herbes i els sòls han demostrat ser bons monitors de contaminació ambiental a curt i llarg termini, respectivament. Per altra banda, l'aire s'ha utilitzat com a monitor d'emissions actuals. A través dels nivells en aquests monitors s'han estudiat les variacions temporals/espacials a les rodalies d'incineradores. En cap cas s'han observat variacions importants atribuïbles a les incineradores. Els nivells trobats han estat generalment en el rang més baix en comparació amb d'altres zones industrials d'arreu del món. Els resultats obtinguts impliquen que les incineradores estudiades no són una font significativa de PCDD/Fs i metalls pesants.

3. S'han avaluat els riscos per exposició a metalls pesants a les rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona. La relació entre les concentracions de metalls en sòls i els PRG ha estat menor a 100% en tots els casos. Així mateix, per tots els metalls el HQ ha estat inferior a 1, indicant que els nivells són segurs per la població. Només la ingestió d'As ha superat el màxim risc carcinogènic acceptable de 10^{-6}. Per altra banda, cal destacar que aquest límit ha estat superat per sòls de diferents països.

4. S'han avaluat els riscos per exposició a PCDD/Fs a les rodalies de la Incineradora de Residus Industrials de Tarragona. Per adults i nens de l'àrea més propera a la planta incineradora, l'exposició ambiental només ha representat un 0.1% de l'exposició total (ambiental més dieta). En l'àrea urbana, aquest percentatge augmenta fins a un 3.8 i 1.4% per adults i nens, respectivament.

5. Els discs PUF són una bona alternativa barata i simple de monitoritzar els nivells en aire de COPs durant períodes llargs de temps. S'han calculat els fluxes d'aire a través dels discs PUF per diferents COPs. Els resultats han estat 2, 3.8 i 3.3 m^3/dia per PCDD/Fs, PCBs i PCNs, respectivament.

6. La tècnica estadística d'Anàlisi de Components Principals ha mostrat ser efectiva per:

    a. establir diferències/similituds entre les emissions anteriors i les actuals
    b. establir diferències/similituds entre mostres properes i llunyanes a la font de contaminació
    c. trobar correlacions entre diferents contaminants
    d. identificar les principals fonts que afecten a les concentracions ambientals de cada contaminant

7. S'han determinat les concentracions de diferents compostos organoclorats en sangs i orines de treballadors d'una incineradora de residus industrials amb l'objectiu de determinar si aquests estan exposats a aquestes substàncies. La monitorització biològica no ha indicat impregnació dels treballadors de la incineradora. Per altra banda, els resultats de PCDD/Fs en plasma han mostrat un descens que estaria correlacionat amb la disminució de la concentració de PCCD/Fs observada en els últims anys en totes les matrius ambientals i en aliments.

8. La tècnica del Latin Hypercube Sampling ha permès conèixer quins eren els paràmetres que introdueixen més incertesa dintre del model multicompartimental i d'avaluació de riscos i conèixer com aquesta es propaga en dels models.

9. Els resultats obtinguts no han indicat en cap cas que les incineradores estudiades fossin una font rellevant de compostos organoclorats i de metalls pesants i, per tant, un risc addicional per la gent que viu a les rodalies. A més, l'anàlisi dels resultats ha indicat que els nivells actuals de PCDD/Fs estan més relacionats amb altres tipus de fonts (pex., el trànsit) que en les pròpies emissions de les incineradores.

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