Tutors

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Grau de Química

Treball Final de Grau

Study, sampling and analysis of POPs in emissions and inmissions in environmental samples.

Estudi, captació i anàlisi de COPs en emissions i immissions de mostres ambientals.

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Si sabés que el món s'acaba demà, jo encara avui plantaria un arbre.

Martin Luther King Jr.

En primer lloc agrair a les dues persones que m'han guiat, aconsellat i ajudat desinteressadament en el transcurs d'aquest treball de fi de grau: Dra. Encarnación Moyano i l'aviat Dr. Joan Rivera-Austrui gràcies al qual molts dels coneixements que ara tinc en la matèria serien molt menors i les experiències viscudes durant aquest treball haurien sigut, com a mínim, menys divertides. Agrair a l'empresa Techno Spec la seva immillorable acollida i tracte per part de persones com Christiane Austrui i Margarita Blanco. A Jordi Sauló i Miguel Ángel Adrados, companys durant un temps al IDAEA-CSIC, per no dubtar en compartir els seus coneixements amb mi. Em resultaria imperdonable no agrair la immensa confiança que una persona tan distingida com el Dr. Josep Rivera Aranda va dipositar en mi des del dia que ens vam conèixer i es va assabentar de què estava estudiant. Als meus pares que m'han ensenyat tot el que no s'aprèn a una facultat i, en especial, a Annabel per TOT.

REPORT

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1. SUMMARY

The project is dedicated to environmental pollution assessment caused by dioxins and furans (PCDD/F) in the vicinity of industrial plants like cements and waste incinerators. It involves the active sampling of ambient air by means of two different sampling techniques: continuous monitoring at the plant's stack (emissions) and novel wind selective sampling (WindSelect®) on the vicinity of the facilities (inmissions). With a wind selective device we can sample (in a unique sampling place) the ambient air in two different cartridges depending on the precedence of the wind (2 sectors), and as the main objective, we can evaluate the influence of the facilities in the POP concentration on the ambient air of the nearby. Those samples have to be extracted and eluted following manual procedures or by automatic methods, and then analyzed with HRGC-HRMS, always proceeding with standard EN-1948 and EPA-1613 regulation. After the interpretation of the chromatograms, a results report has to be performed with the determination of the concentration in TEQ corresponding to each sector. Then some statistical studies are made to determine the influence of each pollutant in the final toxicity of the sample. Finally a Principal Component Analysis (PCA) is done in order to contrast the chemical footprint of the sample and determine the influence of the facilities in the contamination of the ambient air.

Keywords: PCDD/F, environmental, toxicity, monitoring, emission, inmission, HRGC, HRMS, POP, cement, waste, incinerator, PCA, TEQ

2. RESUM

El projecte està dedicat a l'avaluació de la contaminació ambiental causada per dioxines i furans (PCDD/F) a les proximitats de les plantes industrials com cimenteres i incineradores de residus. Aquest projecte també engloba la presa activa de mostres d'aire ambient a través de dues tècniques de mostreig diferents: el monitoratge en continu a les xemeneies de la planta (emissions) i el mostreig selectiu de vent (WindSelect®) en les proximitats de les instal·lacions (immissions). Amb un captador selector de vent (situat en un únic lloc), podem mostrejar en dos cartutxos diferents en funció de la procedència del vent (2 sectors), i així, com a principal objectiu, avaluar la influència de les instal·lacions de la planta en la concentració dels COP a les proximitats. Posteriorment a la captació, es procedeix a l'extracció i elució mitjançant operacions manuals o automàtiques, i, finalment, s'analitzen amb HRGC-HRMS, sempre seguint la normativa EN-1948 o EPA-1613. Després de la interpretació dels cromatogrames, es realitza un informe de resultats amb la determinació de la concentració en TEQ corresponent a cada sector. El projecte avança amb l'avaluació en termes estadístics per determinar la influència de cada contaminant en la toxicitat final de la mostra i, a través d'una anàlisi de components principals (PCA), poder contrastar la petjada química de la mostra i així determinar l'impacte de la indústria en la contaminació de l'aire ambient de les proximitats.

Paraules clau: PCDD/F, mediambiental, toxicitat, emissions, inmissions, HRGC, HRMS, COP, cimentera, residus, incineradora, PCA, TEQ.

3. INTRODUCTION

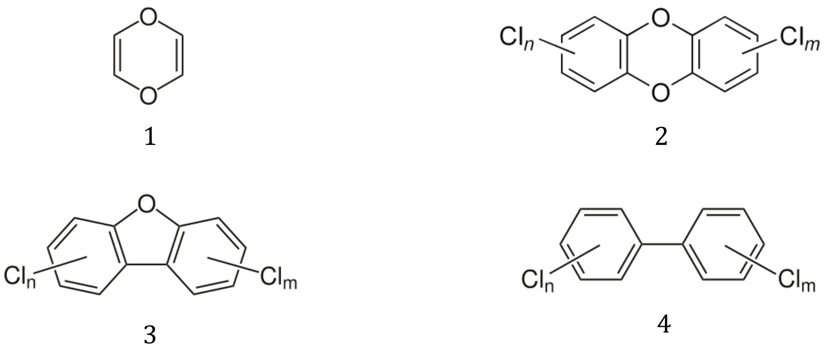
Nowadays societies produce huge amounts of Municipal Solid Waste (MSW) and Industrial Solid Waste (ISW), and commonly those wastes are disposed of by incineration. Also cement plants use to incinerate and co-incinerate several and different materials. These activities have so many advantages like reducing the amounts of waste while enabling energy recovery, but also some notable disadvantages. Maybe the most debated and important of them is the production and release of some well-known Persistent Organic Pollutants (POP) such as dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB).

3.1. DIOXINS AND FURANS

3.1.1 Structural and chemical aspects

Dioxins (1) and dioxin-like molecules are a group of chemicals that include the following compounds:

- Polychlorinated dibenzo-p-dioxins (PCDDs) (2), or simply dioxins. PCDDs are derivatives of dibenzo-p-dioxin. There are 75 PCDDs, and seven of them are specifically toxic.
- Polychlorinated dibenzofurans (PCDFs) (3), or furans. PCDFs are derivatives of dibenzofuran. There are 135 congeners (derivatives differing only in the number and location of chlorine atoms). Although strictly speaking, they are not dioxins, ten of them have "dioxin-like" properties.
- Polychlorinated biphenyls (PCBs) (4), which also are not dioxins, but twelve of them have "dioxin-like" properties. Under certain conditions PCBs may form dibenzofurans through partial oxidation.



1 2 3 4

Figure 1. Structures of: (1) 1,4-dioxin, (2) general polychlorinated dibenzo-p-dioxins (PCDDs), (3) general polychlorinated dibenzofuran (PCDF) and (4) general polychlorinated biphenyl (PCB).

The structure of dibenzo-p-dioxin (figure 2) is formed of two benzene rings joined by two oxygen bridges. This makes the compound an aromatic diether. The central dioxygenated ring is stabilized by the two flanking benzenes.

In PCDDs, chlorine atoms are bonded to this structure at any of the 8 different places on the molecule except the 5 and 10 positions (see figure 2).

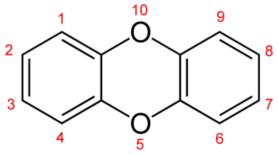


Figure 2. Substituent numbering scheme of dibenzo-1,4-dioxin

In table 1 can be found all the homologues and congeners of PCDD/Fs and PCBs depending on their chlorination number. As it can be seen, the most common dioxins, furans and polychlorinated biphenyls are those with an intermediate number of chlorines (tetra or pentachloro)

Homologue (abbreviation)	Number of congeners		
	PCDDs	PCDFs	PCBs
Monochloro (M)	2	4	3
Dichloro (D)	10	16	12
Trichloro (Tr)	14	28	24
Tetrachloro (T)	22	38	42
Pentachloro (P)	14	28	46
Hexachloro (Hx)	10	16	42
Heptachloro (Hp)	2	4	24
Octachloro (O)	1	1	12
Nonachloro			13
Decachloro			1
TOTAL	75	135	209

Table 1. Homologues and congeners of PCDDs, PCDFs and PCBs [1]

3.1.2. PCDD/F synthesis, generation and presence

Despite the large volume of research data related to the formation of PCDD/PCDF, the specific mechanism of PCDD/PCDF formation remains unclear, particularly for the formation of PCDD/PCDF on fly ash and air pollution control residues in the post-combustion zone of the waste incinerator and cement plant [2]. This is due in part to the very low concentrations of PCDD/PCDF involved and the consequent difficult and complex analytical systems and instrumentation required for their accurate analysis and quantification. PCDD/F are generated while burning hydrocarbons or organic matter in chlorine presence, this includes volcanic eruptions or even wildfires. Soils and sediments are the most important reservoirs of dioxins because of their high persistence in the environment. The most important exposure way for humans is the alimentation, which is responsible for almost 90% of our exposure, in fact, fish and meat represents the 80% of this exposure. It is good to be said that dioxins and furans in the human body are bioaccumulative during our whole life.

3.1.3 Toxicity

The most toxic PCDD, PCDF and PCB congeners are 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD [3]. While the mechanisms responsible of the toxicity have not been fully elucidated, their high affinity for the aryl hydrocarbon receptor (AhR) is believed to play a central role. The AhR is a transcription factor and its abnormal activation can disrupt cell function by altering gene transcription. The known toxic effects of 2,3,7,8-TeCDD exposure include, apart from death by direct high dose exposure, dermal effects, suppression of the immune system due to induction of cell death in immune cells, and cancer [4]. Not all PCDD, PCDF and PCB congeners activate the AhR; their binding is governed by their pattern of chlorine substitution and the planarity of their carbon skeletons. Toxic PCDD and PCDF congeners bear chlorine substituents in the β positions, i.e. the 2, 3, 7, and 8 positions for PCDD and PCDF. Toxic PCB congeners have at most one chlorine substituent in an ortho position, enabling them to adopt a planar configuration and fit into the AhR binding pocket. However, they may carry multiple chlorines in the meta (3, 3’, 5 and 5’) and para (4 and 4’) positions.

Toxic Equivalent Factor (TEQ)

Toxic dioxin congeners and dioxin like compounds have the same mode of action and their toxic effects are additive and to enable comparisons between samples, a comparative scale of toxicity is used. This toxic equivalence (TEQ) value is calculated by giving the AhR activity of the most toxic congener (2,3,7,8-TeCDD) the toxic equivalence factor (TEF) one (TEF2,3,7,8-TeCDD = 1). The TEF2,3,7,8-TeCDD is then used as a benchmark to evaluate the toxicity of the other are activating congeners, i.e., a congener that shows half the AhR activating ability compared to 2,3,7,8-TeCDD receives the value TEF 0.5. To determine the TEQ value of a sample, the TEF values are multiplied by the congener concentration (equation 1). The resulting values are then summarized into a sample specific TEQ value.

$$TEQ = \sum [PCDDi \cdot TEFi] + [PCDFi \cdot TEFi] + [PCBi \cdot TEFi]$$

Equation 1. Sample TEQ value depends on the different toxicity of the congeners containing

The toxicity of samples with different congener distributions can be evaluated by comparing their TEQ values. The TEQ scales are re-evaluated periodically as more studies about their toxicity and effects on humans are done. In table 2 are shown the TEF values assigned to various POPs by the WHO2005-TEQ.

PCDD and PCDF	**TEF**	**PCB**	**TEF**
2,3,7,8-TeCDD	1	Planar PCB	
1,2,3,7,8-PeCDD	0.5	3,4,4',5-TeCB (81*)	0.0003
1,2,3,4,7,8-HxCDD	0.1	3,3',4,4'-TeCB (77*)	0.0001
1,2,3,6,7,8-HxCDD	0.1	3,3',4,4',5-PeCB (126*)	0.1
1,2,3,7,8,9-HxCDD	0.1	3,3',4,4',5,5'-HxCB (169*)	0.03
1,2,3,4,6,7,8-HpCDD	0.01		
OCDD	0.001	*Non- and mono- ortho PCB*	
		2,3,3',4,4'-PeCB (105*)	0.00003
2,3,7,8-TeCDF	0.1	2,3,4,4',5-PeCB (114*)	0.00003
1,2,3,7,8-PeCDF	0.05	2,3',4,4',5-PeCB (118*)	0.00003
2,3,4,7,8-PeCDF	0.5	2',3,4,4',5-PeCB (123*)	0.00003
1,2,3,4,7,8-HxCDF	0.1	2,3,3',4,4',5-HxCB (156*)	0.00003
1,2,3,6,7,8-HxCDF	0.1	2,3,3',4,4',5'-HxCB (157*)	0.00003
1,2,3,7,8,9-HxCDF	0.1	2,3',4,4',5,5'-HxCB (167*)	0.00003
2,3,4,6,7,8-HxCDF	0.1	2,3,3',4,4',5,5'-HpCB (189*)	0.00003
1,2,3,4,6,7,8-HpCDF	0.01		
1,2,3,4,7,8,9-HpCDF	0.01		
OCDF	0.001	** numbering according to IUPAC*	

Table 2. TEF of the toxic congeners of PCDD/F and PCBs. TEF are referred to World Health Organization (WHO_{2005})[5]

3.1.4 Regulation

When talking about regulation of the dioxins and furans we can distinguish two big fields of interest. One of them is the regulation of the *when* and the other one is the *how*. As so many other examples, we can find extremely different regulations between different countries of the European Union. This is still a controversial topic of discussion that will be talked properly in the *results and discussion* section. Answering the *when*, in Spain, and following a royal decree from 2003, dioxins and furans has to be measured in waste incinerators "…at least 4 times a year for heavy metals, dioxins and furans even though during the first 12 months of operation a measure has to be made at least every two months" [6]. These samplings have to be between 6 and 8 hours long for dioxins and furans [7].

On the other hand, we have the *how*, the methodology of the determination of the dioxins, furans and PCBs. UNE-EN-1948 is a European standard the title of which is "Emissions from stationary sources. Determination of the mass concentration of PCDD/F and dioxin-like PCBs". This norm is divided into 4 parts:

- UNE-EN-1948-1 (2007): Sampling of PCDD/PCDF
- UNE-EN-1948-2 (2007): Extraction and purification of PCDD/PCDF
- UNE-EN-1948-3 (2007): Identification and quantification of PCDD/PCDF
- UNE-EN-1948-4 (2011): Sampling and analysis of the dioxin-like PCBs

This regulation involves a concrete method in order to ensure that the recoveries of our different steps of the procedure are acceptable. The three main stages of the sampling and analysis of PCDD/F are the sampling, extraction and injection (GC-MS). So the method establishes that mass labeled standards of dioxins and furans must be spiked before each one of these operations. So we have sampling standards, extraction standards and injection standards, all of them of course different from each other. This spiking is going to tell us the quality of the recoveries of the process, so our final result can be accepted in statistical terms. All these standards were bought from *Wellington Laboratories.*

As can be seen, the whole process is highly regulated, and of course, during this entire project this standard was strictly followed.

3.2 SAMPLING

Depending on the sampling point, we can divide this field into emissions and inmisions. Emissions are those sample gatherings done in the stack, which means sampling directly in the smokestack of the plant. On the other hand, inmisions are those samplings done outside the facilities of the plant gathering ambient air on the vicinities. In both cases the methodology for the sampling of these compounds implies a very strict process but common parts like the cartridge used for sampling the dioxins and furans. This cartridge contains a Polyurethane Foam (PUF) with controlled specifications in order to optimize the gathering of the sample (see table 3).

Property	**Value**
Raw density	30 kg/m^3
Cell amount	18/cm^3
Tensile Strength DIN 53571	13 kPa/m^2
Elongation at Break DIN 53571	200%
Stuffer Hardness at 40ºC	3.5 kPa
Decomposition Temperature	>180ºC

Table 3. Properties and characteristics of the polyurethane foam (PUF)

Also, the way of preparing this PUF, is a common thing between inmissions and emissions. The cartridge has to be spiked with the sampling standards (*wellington laboratories*). These solutions contain the following concentrations of furans in order to know the recovery of this sampling process.

Sampling Standard	**1613LCS** [ng/mL]
2,3,7,8 [$^{37}Cl_4$]-Tetrachlorodibenzo-p-dioxin	40

Table 4. Sampling standards according to EPA-1613 of the Wellington® standard solutions

3.2.1 Emissions

Emissions are those samplings gathered directly in stack. The regulation is very specific in this field, and the material used for this purpose is strictly prepared. The device we use for emission sampling of dioxins and furans is from an Austrian company (Genius5-Instruments®), and in general terms disposed of a probe, a sucking unit, a gas meter and a cartridge where the sample was being accumulated. The most conflicting point in the sampling in emissions of PCDD/Fs is isokinetism. Isokinetism means that the gas speed at the nozzle entry of the probe has to be the same as the velocity at the sampling point (inside the stack) and it is a requirement for dioxin sampling in emissions and inmissions in order to ensure a representative sample of the air. If this were not done in this way, due to Venturi's effect, the amount of dioxins sucked by the probe and retained in the cartridge would not be correct.

3.2.2 Inmisions

Inmissions are those samplings gathered in the vicinities of the facilities of POP source. The purpose of this kind of sampling is the study and determination of the influence of these incinerators in the surroundings of the plant. In order to achieve this goal, we use a device (WindSelect©, Genius5-Instruments, Wien, Austria) that, depending on the direction of the wind flow, samples in one cartridge or in another, so, we can collect two independent samples and compare them.

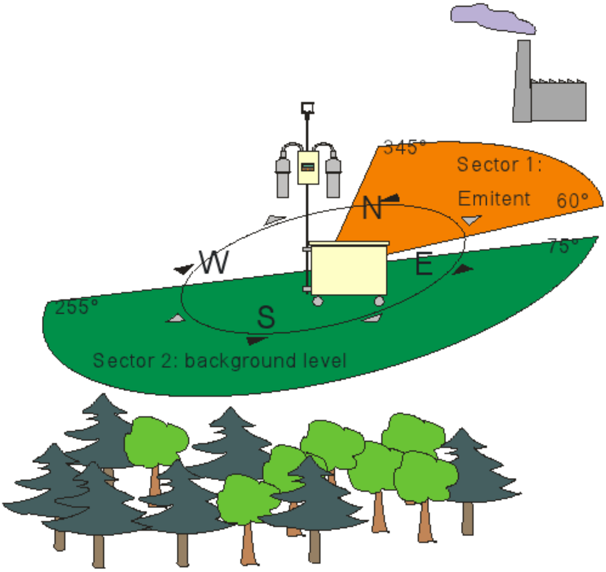


Figure 3. Diagram of how the ambient air is sampled in the WindSelect© device depending on the air flow direction of the wind

3.3 QUANTIFICATION

3.3.1 Extraction methods

There are several methods for extracting our PCDD/Fs from the PUF, but the EN-1948 standard indicates the proceedings for doing it. Soxhlet extraction is the one accepted in the regulation, although there are other methods and devices for the automation and time optimization of the process. Those devices also follow the same “column pattern” extraction, but using less solvents, time and personnel. Instead of manufacturing our own columns each time we need them, can be bought sealed and use them in a pressurized liquid extraction system (FMS, Fluid Management Systems, Boston, USA) in order to extract all the POP desired. Then the extraction is introduced into a PowerPrep© (FMS) device where the fractionation is carried using the appropriate solvents and collected in different containers that can be evaporated in a SuperVap© device.

3.3.2 Quantification HRGC-HRMS

To follow the EPA-1613 guidelines, the methodology that has to be used is the isotope dilution analysis. Isotope dilution analysis is a method of determining the quantity of chemical substances. In its simplest conception, the method of isotope dilution comprises the addition of known amounts of isotopic labeled substances in the analyzed sample. Mixing of the isotopic standard with the sample effectively "dilutes" the isotopic enrichment of the standard and this forms the basis for the isotope dilution method. Isotope dilution is classified as a method of internal standardization, because the standard (isotopic-enriched form of analyst) is added directly to the sample. In addition, unlike traditional analytical methods which rely on signal intensity, isotope dilution employs signal ratios. Owing to both of these advantages, the method of isotope dilution is regarded among chemistry measurement methods of the highest metrological standing [8].

There are three main requirements for the results of the chromatography that must be strictly followed according to the procedure in order to ensure that our quantitative analysis of the sample is correct:

1) The isotopic ratio between the measured ions has to be the same as the theoretical value ± 20%
2) The retention time of a native 2,3,7,8-chlorosubstituted has to be in a window time of 0 to +3 seconds based on the retention time of the corresponding ^{13}C labeled isomer.
3) The signal-noise ratio of the raw data has to be at least 3:1 for the signal used for the quantification of the native.

Recovery factors:

The standards also determine which are the accepted recovery ratios of the ^{13}C labeled compounds depending on the congener. These values range from 17 to 197%.

If these requirements are not satisfied, then the results for the specific congener which is not following these recoveries cannot be accepted [10]. See appendix 2 for the detailed view of the recoveries accepted in each congener.

4. OBJECTIVES

The main objective of this work is to study the sampling and analysis of persistent organic pollutants in inmissions near a cement plant as well as their chemical aspects, toxicity and hazard, and, by statistical methods, the evaluation of the influence of the plant emissions to the ambient PCDD/F levels in the vicinities and near towns. To achieve this goal, a wind selective device makes possible to sample (in a unique sampling place) ambient air in to independent cartridges depending on the wind direction flow, thus differentiating between plant emissions contributions and background or other factors contributing to the concentration level. For the analysis of these samples, a sample treatment to extract, spike and separate these compounds and a determination by high resolution gas chromatography coupled to high resolution mass spectrometry using isotope dilution as quantification method, are performed following the European Union standard and EPA regulations. Then principal component analyses (PCA) are used to help in the interpretation of the results of the samples analyzed, and, finally, the knowledge of a report elaboration for the customer as well as the synthesis and writing aptitudes for this purpose.

5. EXPERIMENTAL SECTION

Note: because of confidentiality reasons, any specific information about town or industry where sampling was performed has not been included in this work.

5.1 SAMPLING

We installed our WindSelect© device (picture 1) in the vicinities of a cement plant. See appendix 1 for more information. This is the sampling data:

Picture 1: Windselect© device

- Start Up: 03/10/2014
- Finish: 15/11/2014
- Sampling time: 43 days
- Volume sampled:

(Cartridge 1, cartridge 2): 1271 m^3, 1052 m^3

Sampling standard	**S1** [pg]	**S1** [pg]
^{37}Cl-2,3,7,8 - TCDD	1002	985

Table 5. Standard added to the PUF as sampling standard from the EPA-1613CSS, Wellington laboratories©

As mentioned before, we can configure our device for sampling in two independent cartridges depending on the provenance of the wind, and two different sectors were defined (see figure 3). One covering the wind coming from the UWI wind (45º wide) and the other sector defined as the background wind (180º). This way, we can obtain two different samples, one with ambient air coming from the plant and the other one coming from the non-influenced sector.

5.2 SAMPLE EXTRACTION AND PURIFICATION

5.2.1 Materials and reagents

The materials used during the extraction and purification process are:

- Analytical balance.
- Soxhlet extractor of 200 mL, 50 mm internal diameter.
- Heating Mantle
- Rotary evaporator
- Glass column of 200 mm x 15 mm.
- Glass column of 200 mm x 10 mm.
- Round bottom flasks of 50, 100, 250 and 500 mL
- Erlenmeyer flasks of 25, 50, 125 and 250 mL
- Beakers of 50, 600 and 1000 mL
- Vials

To all this specific material we have to add some general material such as thermometer, tweezers, test tubes, spatula…

The reagents and solvents used during the extraction and purification process are:

- Toluene
- Dichloromethane
- Hexane
- Acetone
- H_2SO_4 concentrated
- NaOH, ACS grade, Baker
- Silica gel 60 particle size 0.063-0.2 mm, Merck
- Anhydride sodium sulfate, ACS grade, Merck
- Alumina (Al_2O_3), Supelco ©
- Dioxin and Furan standards, Wellington©.

The sample treatment includes all the procedures (extraction and clean-up) from the moment that the cartridge arrives to the laboratory to the point in which the sample is injected at the GC-MS. The standards we used to spike the sample in order to determine the recoveries of this step are detailed in table 6. The actual mass of those standards added in the sample are detailed in table 7.

Extraction Standard	**1613LCS** [ng/mL]
2,3,7,8-Tetrachloro [$^{13}C_{12}$] dibenzo-p-dioxin	100
1,2,3,7,8-Pentachloro [$^{13}C_{12}$] dibenzo-p-dioxin	100
1,2,3,4,7,8-Hexachloro [$^{13}C_{12}$] dibenzo-p-dioxin	100
1,2,3,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzo-p-dioxin	100
1,2,3,4,6,7,8-Heptachloro [$^{13}C_{12}$] dibenzo-p-dioxin	100
Octachloro [$^{13}C_{12}$] dibenzo-p-dioxin	200
2,3,7,8-Tetrachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,7,8-Pentachloro [$^{13}C_{12}$] dibenzofuran	100
2,3,4,7,8-Pentachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,4,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,7,8,9-Hexaachloro [$^{13}C_{12}$] dibenzofuran	100
2,3,4,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,4,6,7,8-Heptachloro [$^{13}C_{12}$] dibenzofuran	100
1,2,3,4,7,8,9-Heptachloro [$^{13}C_{12}$] dibenzofuran	100

Table 6. Extraction standards according to EPA-1613 of the Wellington® standard solutions

5.2.2 Soxhlet

The extraction we carried out in the laboratory was the one involving soxhlet. As we saw there are other automatic methods accepted in the standard that can be carried out. In the sampling methodology we also saw that we recollected our analytes in a foam called PUF (PolyUrethane Foam). Initially, and as a way to know the recovery of the extraction and purification stage and for the further determination of PCDD/Fs, we added the extraction standards detailed in table 7.

Extraction Standard actually added	**1613LCS** [pg]
2,3,7,8-Tetrachloro [$^{13}C_{12}$] dibenzo-p-dioxin	400
1,2,3,7,8-Pentachloro [$^{13}C_{12}$] dibenzo-p-dioxin	400
1,2,3,4,7,8-Hexachloro [$^{13}C_{12}$] dibenzo-p-dioxin	400
1,2,3,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzo-p-dioxin	400
1,2,3,4,6,7,8-Heptachloro [$^{13}C_{12}$] dibenzo-p-dioxin	400
Octachloro [$^{13}C_{12}$] dibenzo-p-dioxin	800
2,3,7,8-Tetrachloro [$^{13}C_{12}$] dibenzofuran	400
1,2,3,7,8-Pentachloro [$^{13}C_{12}$] dibenzofuran	400
2,3,4,7,8-Pentachloro [$^{13}C_{12}$] dibenzofuran	400
1,2,3,4,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	400
1,2,3,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	400

Extraction Standard actually added	**1613LCS** [pg]
1,2,3,7,8,9-Hexaachloro [$^{13}C_{12}$] dibenzofuran	400
2,3,4,6,7,8-Hexachloro [$^{13}C_{12}$] dibenzofuran	400
1,2,3,4,6,7,8-Heptachloro [$^{13}C_{12}$] dibenzofuran	400
1,2,3,4,7,8,9-Heptachloro [$^{13}C_{12}$] dibenzofuran	400

Table 7. Labeled standards added to the sample before extraction step from the EPA-1613 LCS (Wellington laboratories©)

Before placing the PUF into the Soxhlet, we initially cut the foam in some little pieces (3 cm long approximately) for helping the contact between the solvent and the PUF. Then we start the sample extraction inside the soxhlet with a heating mantle and refrigeration. The standards are added to a 50 mL beaker with 10 mL of toluene and the solution is allowed to stand during 2 hours. This solution will be used as a part of all the toluene used in the extraction (400 ml of toluene + 10 ml spiked toluene). The soxhlet makes 4 cycles an hour during 24 hours (96 cycles approximately). Then the solution is allowed to cool and then rotaevaporated under 40ºC without arriving to dryness, we stop the process when we have almost 2 mL. Then we add 100 mL of hexane and rotaevaporate again to 2 mL. Now the sample is extracted and ready for the purification process.

5.2.3 Purification

Before starting the purification process, we have to prepare the columns used for the fractioning of the POPs. The first column (**A**) is the silica column. We need three types of silica for our disposal: acid, basic and neutral. First of all we condition the neutral silica with three portions of DCM 5 minutes each and let it dry at ambient temperature. The acid one is prepared with 39.2 g of neutral silica in an Erlenmeyer, and then we add 61.6 g of concentrated sulfuric acid in 100 ml of water and stir until we have a homogeneous solution. The basic silica is prepared with 53 g of neutral silica in an Erlenmeyer, then we add 26.4 g of sodium hydroxide 1N in 100 ml of mili-Q water and stir until we have a homogeneous solution. Na_2SO_4 is used to remove the possible humidity in the sample.

The entire silica column is filled with:

- 2 g of Na_2SO_4
- 0.5 neutral silica
- 10 g of acid silica
- 0.5 g of neutral silica
- 5 g of basic silica
- 0.5 g of neutral silica
- Spun glass

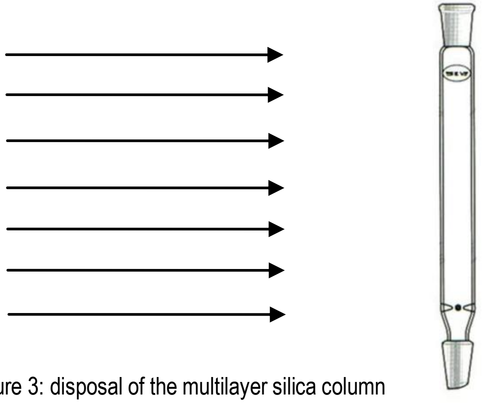


Figure 3: disposal of the multilayer silica column

Both basic and acid silica is prepared in the laboratory, but can also be bought. The upper part of the column is in charge of carbonizing the possible interferences and the basic part is just for neutralizing the acidity before passing to the alumina column.

The second column (**B**) is prepared with 6g of alumina and 3 g of Na_2SO_4 ended with a layer of spun glass, and is coupled to the column A.

We first collect with the toluene all the compounds that are not carbonized with the acid part of the multilayer silica column and are not interacting with the alumina. PCBs, furans and dioxins are retained in the alumina column, so we start the elution of our pollutants.

The elution of the PCBs is made using hexane:DCM (9:1) as solvent and this fraction is collected in a round bottom flask. Then dioxins and furans are eluted with hexane:DCM (1:1). This last eluting step of the PCDD/Fs is more critical because the solvent used can interact with many other compounds so one next purification step is needed in this fraction: active carbon column. After eluting the PCBs, a third active carbon column (**C**) is coupled to the alumina one so dioxins and furans can be purified and cleaned up from other interferences and be collected into the flask.

These fractions are then rotaevaporated and using hexane are transferred to a 2 ml vial. This vial is introduced into the PasVial® and brought to dryness with N_2 flow. Once both vials are dry, one with PCBs and the other one with the dioxins and furans, they are ready for being spiked with the injection standards.

Injection standards	**S1** [pg]	**S2** [pg]
^{37}Cl-1,2,3,4 - TCDD	400	401
^{37}Cl-1,2,3,7,8,9 - HeCDD	400	401

Table 8. Injection standards added on each of the samples from the EPA-1613ISS (Wellington laboratories©)

5.3 QUANTIFICATION HRGC-HRMS

Instrumental analysis: The analyses of the cleaned-up extracts were done on a high resolution gas chromatograph coupled to a high resolution mass spectrometer (HRGC-HRMS). All analyses were performed on an Agilent gas chromatograph fitted with a high resolution 40 m x 0.18 mm i.d. x 0.18 µm film thickness DB-5ms fused silica column (J&W Scientific, CA, USA) connected through a heated transfer line kept at 280ºC to a Autospec Ultima NT (Waters, Manchester, UK) high resolution mass spectrometer (EBE geometry) controlled by a Masslynx data system.

Isotope dilution method:

This method allows us to quantify the 17 toxic dioxins and furans in our sample. Chromatograms for each m/z window are extracted, and as can be seen in Figure 4 the first chromatogram corresponds to 2,3,7,8-TCDF with an exact mass of 303.9016 m/z. In this chromatogram we can see all the signals corresponding to this m/z value distributed along their retention time. It must be point out that there are 38 different dibenzofuran congeners with 4 chlorine substituents (see table 1) and all of these isomers appear within the same exact mass window because all of them have the same molecular mass. We use the labeled ^{13}C-2,3,7,8 TCDF congener as internal standard, and as can be seen in figure 4 only one chromatographic peak is observed for the corresponding m/z value (315.9419 m/z), and its retention time is the same as the native compound. Because we know the quantity spiked on the sample, the area ratio allows us to determine the quantity of the native congener in the sample.

A second extracted chromatogram is also considered taking into account the intensity of the m/z= M + 2, (305.899 m/z). This is usually the most abundant isotope of the congener in terms of relative natural abundance, and, as in the first chromatogram, we find all the signals corresponding to all the congeners having this mass. We use this M + 2 chromatogram to verify the natural abundance ratio compliance (M/M+2), that confirms the correct selection of the quantified analyte.

Quantify Sample Report **MassLynx 4.0 SCN503** Page 1 of 23

Dataset:

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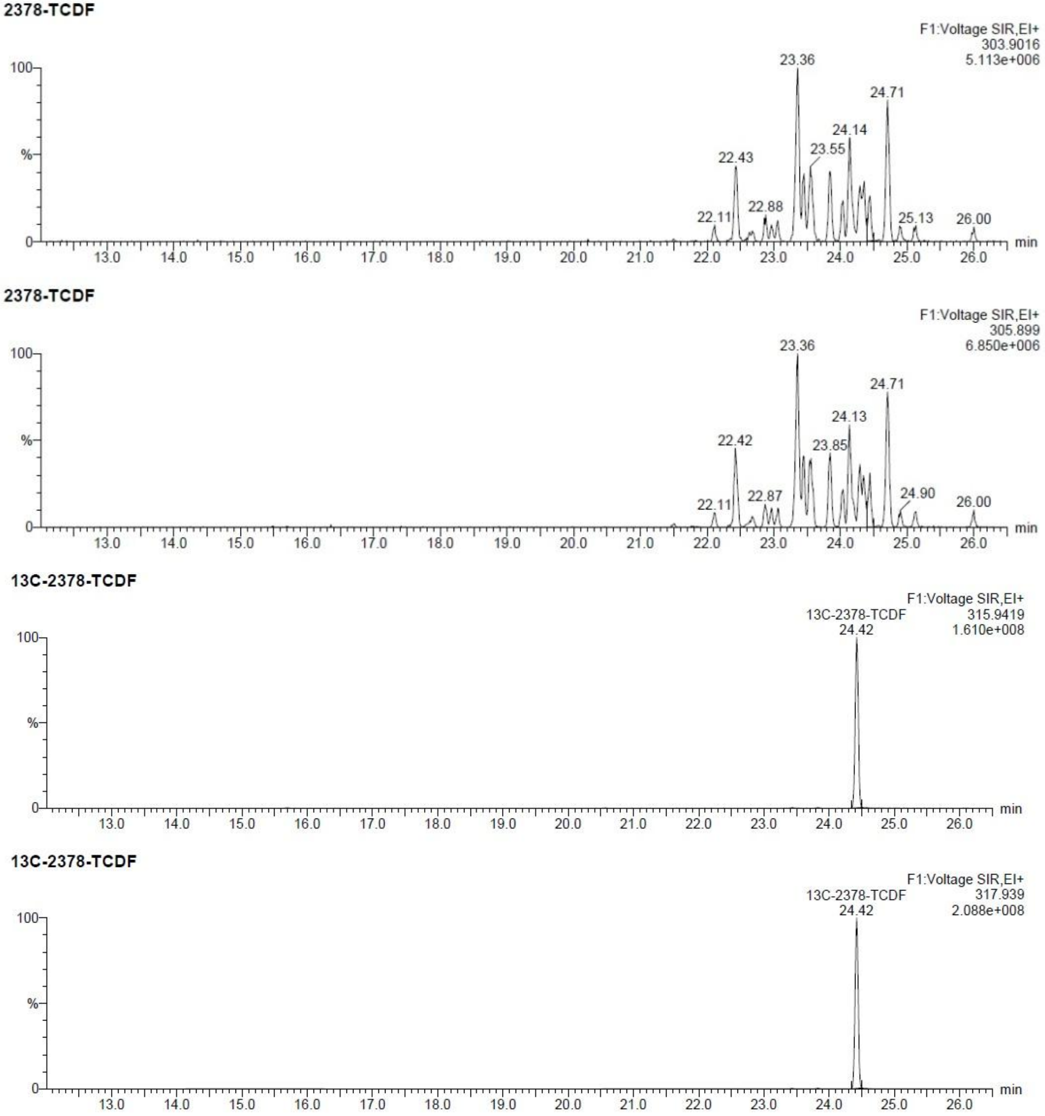


Figure 4. Chromatogram of the native and ^{13}C labeled 2,3,7,8 TCDF

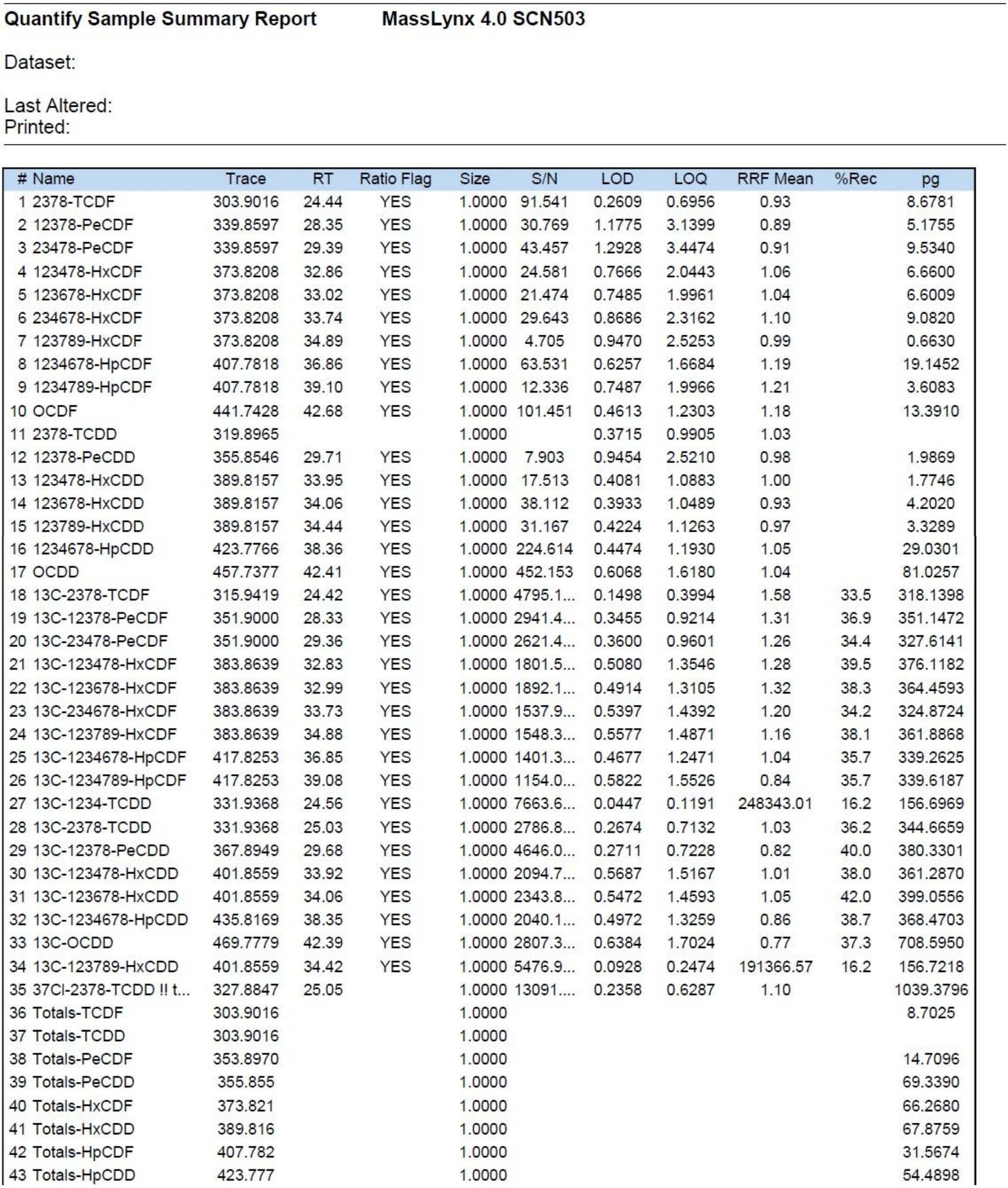
6. RESULTS AND DISCUSSION

The method described in the experimental section has been used to analyze different samples and table 9 summarizes the results obtained for two of these samples (cartridges). Cartridge number one belongs to sector 1 (ambient air coming from the industrial state), and cartridge number two belongs to sector 2 (ambient air coming from the town).

Congener	Sector 1 [total pg]	Sector 2 [total pg]
2,3,7,8-TCDF	8.42	5.96
1,2,3,7,8-PeCDF	4.23	5.11
2,3,4,7,8-PeCDF	9.31	6.10
1,2,3,4,7,8-HxCDF	7.46	5.99
1,2,3,6,7,8-HxCDF	5.91	6.12
2,3,4,6,7,8-HxCDF	9.79	7.83
1,2,3,7,8,9-HxCDF	1.00	1.00
1,2,3,4,6,7,8-HpCDF	18.49	17.91
1,2,3,4,7,8,9-HpCDF	6.00	6.00
OCDF	30.00	30.00
2,3,7,8-TCDD	1.00	1.00
1,2,3,7,8-PeCDD	2.89	1.81
1,2,3,4,7,8-HxCDD	1.19	1.82
1,2,3,6,7,8-HxCDD	5.12	3.67
1,2,3,7,8,9-HxCDD	4.82	2.55
1,2,3,4,6,7,8-HpCDD	28.61	28.94
OCDD	86.41	73.16
Sampling period	**43 days**	
Sample volume (m^3)	**1271.11**	**1052.49**
I-TEQ pg/sample	**12.83 ± 1.67**	**10.08 ± 1.31**
TOTAL I-TEQ (fg/m^3)	**9.1 ± 1.2**	**8.3 ± 1.1**

Table 9: summary of the analyses of PCDD and PCDF in the two cartridges (sector 1 and sector 2).

On figure 5 we can observe the detailed information about the HRGC/HRMS quantification of sector 1 sample with information like retention time (RT), the verification of the ratio flag, LOD, LOQ, standard recoveries, signal/noise ratio and mass determination. See appendix 3 for seeing the sector 2 results.



Quantify Sample Summary Report **MassLynx 4.0 SCN503**

Dataset:

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#	Name	Trace	RT	Ratio Flag	Size	S/N	LOD	LOQ	RRF Mean	%Rec	pg
1	2378-TCDF	303.9016	24.44	YES	1.0000	91.541	0.2609	0.6956	0.93		8.6781
2	12378-PeCDF	339.8597	28.35	YES	1.0000	30.769	1.1775	3.1399	0.89		5.1755
3	23478-PeCDF	339.8597	29.39	YES	1.0000	43.457	1.2928	3.4474	0.91		9.5340
4	123478-HxCDF	373.8208	32.86	YES	1.0000	24.581	0.7666	2.0443	1.06		6.6600
5	123678-HxCDF	373.8208	33.02	YES	1.0000	21.474	0.7485	1.9961	1.04		6.6009
6	234678-HxCDF	373.8208	33.74	YES	1.0000	29.643	0.8686	2.3162	1.10		9.0820
7	123789-HxCDF	373.8208	34.89	YES	1.0000	4.705	0.9470	2.5253	0.99		0.6630
8	1234678-HpCDF	407.7818	36.86	YES	1.0000	63.531	0.6257	1.6684	1.19		19.1452
9	1234789-HpCDF	407.7818	39.10	YES	1.0000	12.336	0.7487	1.9966	1.21		3.6083
10	OCDF	441.7428	42.68	YES	1.0000	101.451	0.4613	1.2303	1.18		13.3910
11	2378-TCDD	319.8965			1.0000		0.3715	0.9905	1.03		
12	12378-PeCDD	355.8546	29.71	YES	1.0000	7.903	0.9454	2.5210	0.98		1.9869
13	123478-HxCDD	389.8157	33.95	YES	1.0000	17.513	0.4081	1.0883	1.00		1.7746
14	123678-HxCDD	389.8157	34.06	YES	1.0000	38.112	0.3933	1.0489	0.93		4.2020
15	123789-HxCDD	389.8157	34.44	YES	1.0000	31.167	0.4224	1.1263	0.97		3.3289
16	1234678-HpCDD	423.7766	38.36	YES	1.0000	224.614	0.4474	1.1930	1.05		29.0301
17	OCDD	457.7377	42.41	YES	1.0000	452.153	0.6068	1.6180	1.04		81.0257
18	13C-2378-TCDF	315.9419	24.42	YES	1.0000	4795.1...	0.1498	0.3994	1.58	33.5	318.1398
19	13C-12378-PeCDF	351.9000	28.33	YES	1.0000	2941.4...	0.3455	0.9214	1.31	36.9	351.1472
20	13C-23478-PeCDF	351.9000	29.36	YES	1.0000	2621.4...	0.3600	0.9601	1.26	34.4	327.6141
21	13C-123478-HxCDF	383.8639	32.83	YES	1.0000	1801.5...	0.5080	1.3546	1.28	39.5	376.1182
22	13C-123678-HxCDF	383.8639	32.99	YES	1.0000	1892.1...	0.4914	1.3105	1.32	38.3	364.4593
23	13C-234678-HxCDF	383.8639	33.73	YES	1.0000	1537.9...	0.5397	1.4392	1.20	34.2	324.8724
24	13C-123789-HxCDF	383.8639	34.88	YES	1.0000	1548.3...	0.5577	1.4871	1.16	38.1	361.8868
25	13C-1234678-HpCDF	417.8253	36.85	YES	1.0000	1401.3...	0.4677	1.2471	1.04	35.7	339.2625
26	13C-1234789-HpCDF	417.8253	39.08	YES	1.0000	1154.0...	0.5822	1.5526	0.84	35.7	339.6187
27	13C-1234-TCDD	331.9368	24.56	YES	1.0000	7663.6...	0.0447	0.1191	248343.01	16.2	156.6969
28	13C-2378-TCDD	331.9368	25.03	YES	1.0000	2786.8...	0.2674	0.7132	1.03	36.2	344.6659
29	13C-12378-PeCDD	367.8949	29.68	YES	1.0000	4646.0...	0.2711	0.7228	0.82	40.0	380.3301
30	13C-123478-HxCDD	401.8559	33.92	YES	1.0000	2094.7...	0.5687	1.5167	1.01	38.0	361.2870
31	13C-123678-HxCDD	401.8559	34.06	YES	1.0000	2343.8...	0.5472	1.4593	1.05	42.0	399.0556
32	13C-1234678-HpCDD	435.8169	38.35	YES	1.0000	2040.1...	0.4972	1.3259	0.86	38.7	368.4703
33	13C-OCDD	469.7779	42.39	YES	1.0000	2807.3...	0.6384	1.7024	0.77	37.3	708.5950
34	13C-123789-HxCDD	401.8559	34.42	YES	1.0000	5476.9...	0.0928	0.2474	191366.57	16.2	156.7218
35	37Cl-2378-TCDD !! t...	327.8847	25.05		1.0000	13091....	0.2358	0.6287	1.10		1039.3796
36	Totals-TCDF	303.9016			1.0000						8.7025
37	Totals-TCDD	303.9016			1.0000						
38	Totals-PeCDF	353.8970			1.0000						14.7096
39	Totals-PeCDD	355.855			1.0000						69.3390
40	Totals-HxCDF	373.821			1.0000						66.2680
41	Totals-HxCDD	389.816			1.0000						67.8759
42	Totals-HpCDF	407.782			1.0000						31.5674
43	Totals-HpCDD	423.777			1.0000						54.4898

Figure 5: Quantification via HRGC-HRMS of the sector 1 sample.

On figure 6 and 7 we can observe the pattern of the amount of dioxins present in our samples.

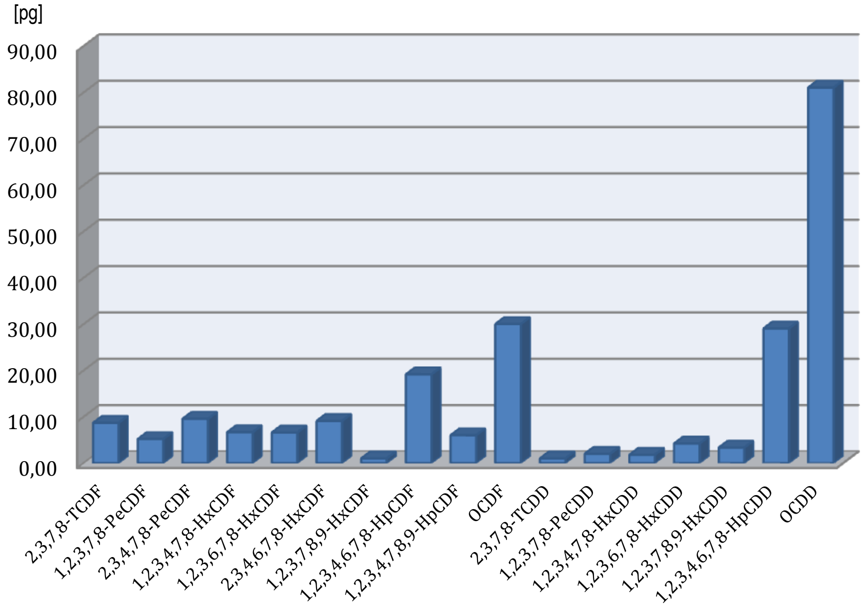

Figure 6: PCDD/F profile from **sector 1** (air coming from the industrial state)

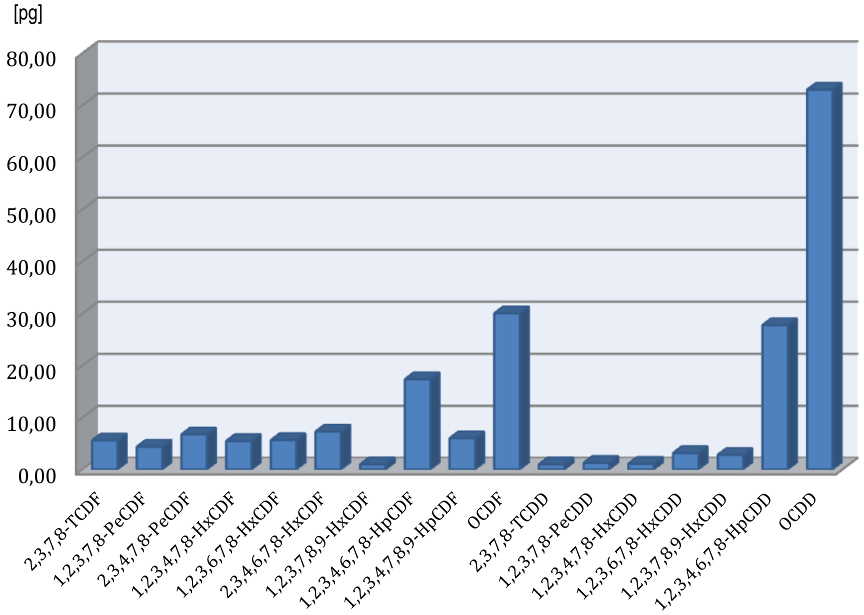

Figure 7: PCDD/F profile from **sector 2** (air coming from the town)

When considering the TEF of every individual congener we obtain the charts shown in Figures 8 and 9 obtained by the following way: for example the 2,3,7,8-TeCDF has a concentration of 8.68 pg in the sample, and multiplied for its TEF value (0.1), the I-TEQ resultant is 0.87 pg/sample.

PCDD and PCDF	**TEF**	**I-TEQ** [pg/sample]
2,3,7,8-TeCDF	0.1	0.84
1,2,3,7,8-PeCDF	0.05	0.26
2,3,4,7,8-PeCDF	0.5	4.77
1,2,3,4,7,8-HxCDF	0.1	0.74
1,2,3,6,7,8-HxCDF	0.1	0.51
1,2,3,7,8,9-HxCDF	0.1	0.91
2,3,4,6,7,8-HxCDF	0.1	0.10
1,2,3,4,6,7,8-HpCDF	0.01	0.18
1,2,3,4,7,8,9-HpCDF	0.01	0.06
OCDF	0.001	0.003
2,3,7,8-TeCDD	1	1.00
1,2,3,7,8-PeCDD	0.5	0.99
1,2,3,4,7,8-HxCDD	0.1	0.12
1,2,3,6,7,8-HxCDD	0.1	0.51
1,2,3,7,8,9-HxCDD	0.1	0.48
1,2,3,4,6,7,8-HpCDD	0.01	0.28
OCDD	0.001	0.08

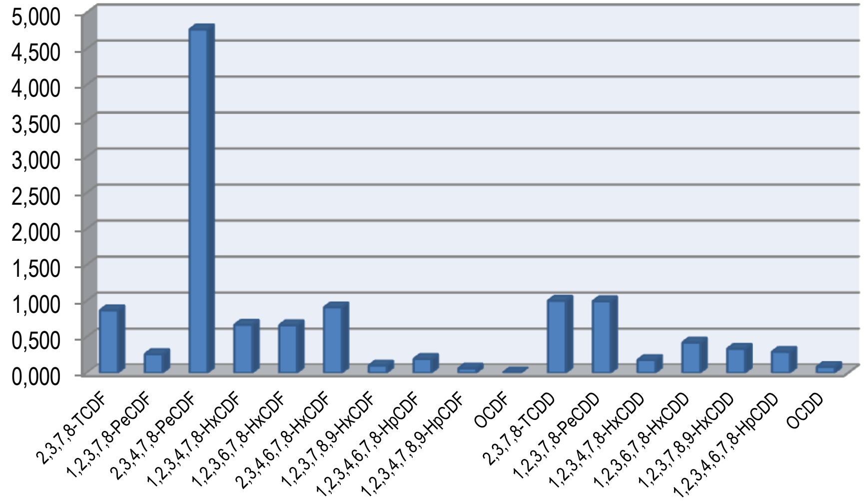

Figure 8: PCDD/F I-TEQ profile from **sector 1** considering each TEF value

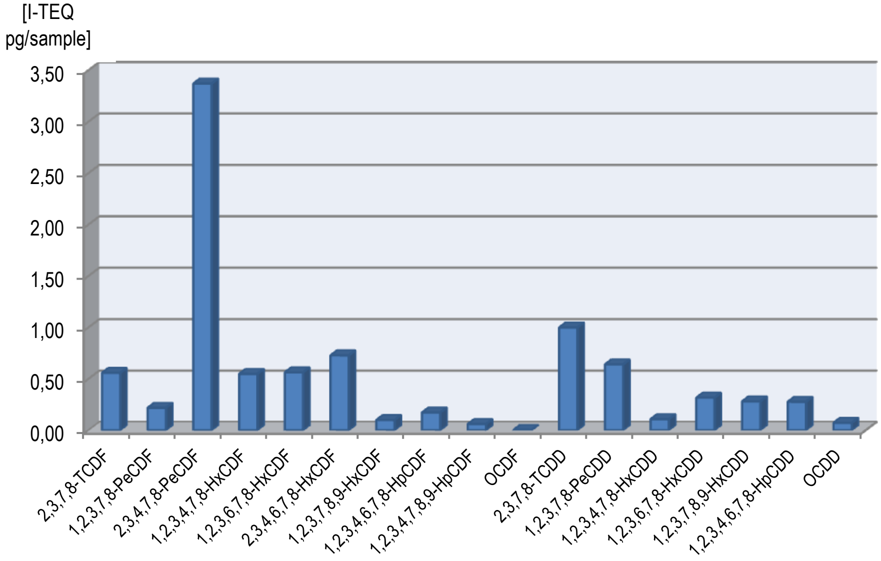

Figure 9: PCDD/F I-TEQ profile from **sector 2** considering each TEF value

The specific distribution of the different congeners in a determination of dioxins and furans is characteristic of the process that originates them. This property called "chemical footprint" is used in some studies of ambient air in order to identify the sources of emission contributing to the presence of these pollutants. With the objective of comparing the profiles obtained in the samples associated to sector 1 and sector 2 with the typical profiles of a cement (with or without coincineration) and of an emission of vehicles with diesel fuel, a PCA (principal component analysis) was done. This statistical tool allows us to compare qualitatively the similitude between different sets of data. Figure 10 represents the double projection graphic obtained that superposes the graphics of punctuations and charges. In the figure, the different samples (red spots: S1, S2 and the profile patterns conventional clinker, clinker with coincineration and diesel traffic) are heterogeneously distributed without showing any obvious similitude between them (proximity in the graphic).

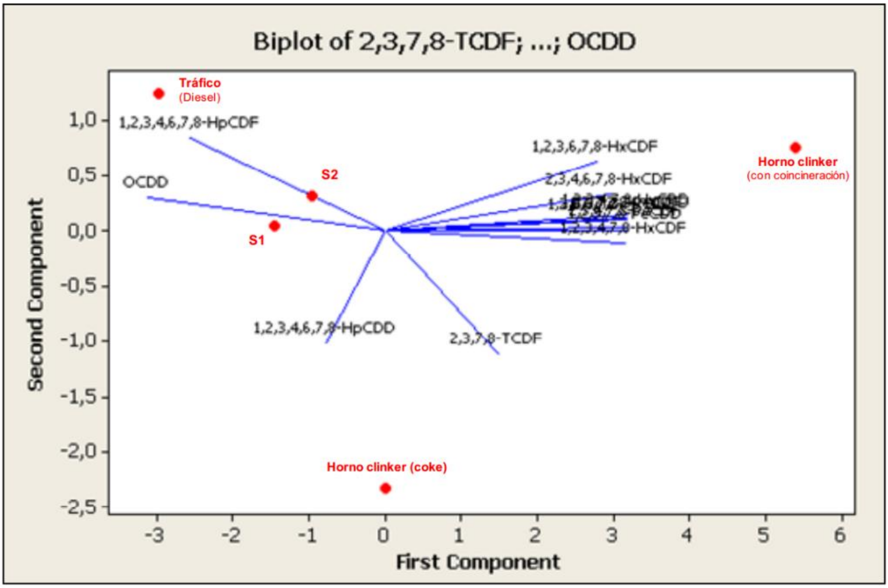

Figure 10: Plot of the principal component analysis about S1, S2, diesel fuel and clinker production with and without coincineration profiles. These profiles (except S1 and S2) are based on different characteristic sources found in literature [9].

7. CONCLUSIONS

Samples S1 and S2 are very close to diesel profile plot in PCA. Therefore an influence of diesel diffuse emissions shows up concerning both S1 and S2, proving a contribution of diesel fuel based traffic in this ambient air samples.

In general aspects, the levels of dioxins and furans found in the samples are acceptable for a rural zone comparing with studies found in the literature [9]: 9.1 and 8.3 I-TEQ fg/m^3 and we can conclude that no influence of this urban cement plant is observed in the dioxin and furan levels in the ambient air of the nearby towns. Some typical values of rural zones are between 5 and 45 I-TEQ fg/m3 with an average value in Catalunya (Spain) of 28 I-TEQ fg/m3, 47 I-TEQ fg/m3 in Turkey or 25 I-TEQ fg/m3 in Madeira (Portugal). In suburban zones we can find values as 34 and 149 I-TEQ fg/m3 for Lisbon and Porto (Portugal) respectively. In urban zones typical values are from 8 to 618 I-TEQ fg/m3 with an average of 112 I-TEQ fg/m3 in Catalunya (Spain). In urban zones typical values are from 8 to 618 I-TEQ fg/m3 with an average of 112 I-TEQ fg/m3 in Catalunya (Spain).

The use of a wind selective device, along with statistical evaluation of the results, has proven to be an appropriate way to determine if potential polluters as Urban Waste Incinerators, Industrial Waste Incinerators or cement manufacturers have a real influence in the dioxin and furan contamination of the nearby. Moreover, facilities can use this approach for the assessment on ambient air levels, in a way that integrates in the sample all sources present in the area, including punctual emissions (fires, non-steady operations…) as there are integrated on a long term sampling period.

HRGC and HRMS are the appropriate tools to quantify such a low concentration of analytes in the samples (4 – 10 pg/sample). Minimum resolution needed is 10.000 in order to properly differentiate all the native and labeled congeners of PCDDs and PCDFs.

Principal Component analysis (PCA) is a very useful tool to visually show the typical emission profiles of the different studied sources, and for the further comparison with the analyzed samples.

8. REFERENCES AND NOTES

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9. ACRONYMS

PCDD: PolyChlorinated Dibenzo-p-Dioxins.

PCDF: PolyChlorinated DibenzoFurans.

TeCDD/F: TetraChloro Dibenzo Dioxin/Furan.

PeCDD/F: PentaChloro Dibenzo Dioxin/Furan.

HxCDD/F: HexaChloro Dibenzo Dioxin/Furan.

HeCDD/F: HeptaChloro Dibenzo Dioxin/Furan.

OCDD/F: OctaChloro Dibenzo Dioxin/Furan.

PCB: PolyChlorinated Biphenyls.

DCM: Dichloromethane.

COP: *Contaminants Orgànics Persistents*

POP: Persistent Organic Pollutants.

HRMS: High Resolution Mass Spectrometry.

HRGC: High Resolution Gas Chromatography.

PCA: Principal Component Analysis.

TEQ: Toxic Equivalence.

TEF: Toxic Equivalence Factor.

EPA: Environmental Protection Agency.

PUF: PolyUrethane Foam.

Pg: Picogram.

Fg: Femptogram.

WHO: World Health Organization

UWI: Urban Waste Incinerator

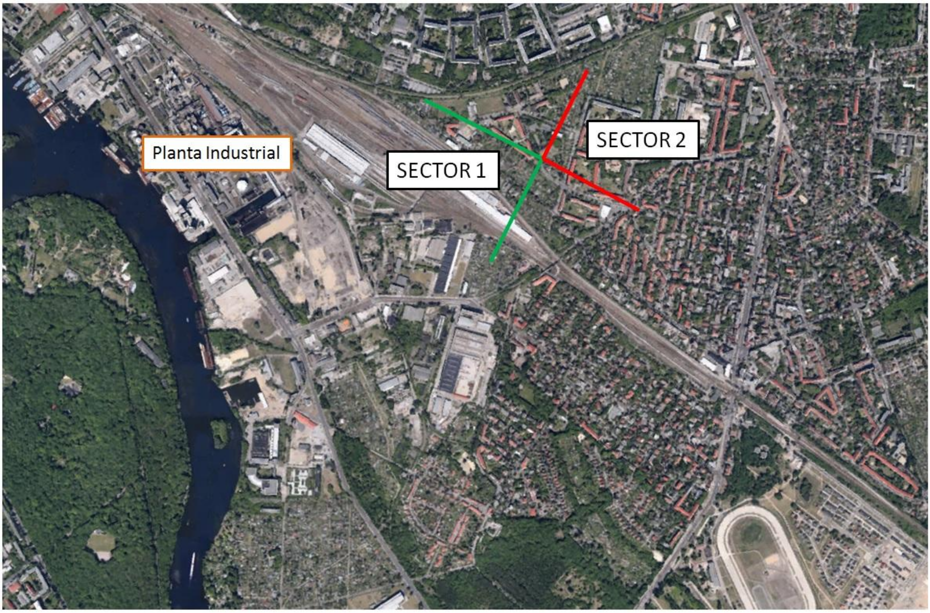
EBE: Emitter-Base-Emitter

LOD: Limit Of Detection

LOQ: Limit Of Quantification

APPENDICES

APPENDIX 1: SAMPLING POINT LOCATION



APPENDIX 2: RECOVERY FACTORS ALLOWED IN EPA-1613

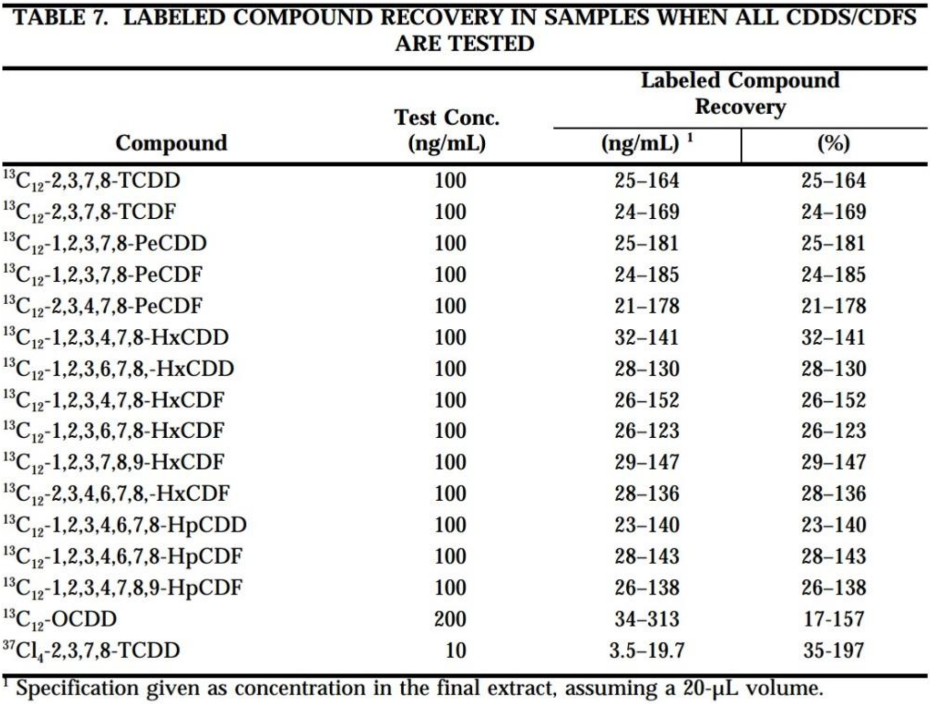
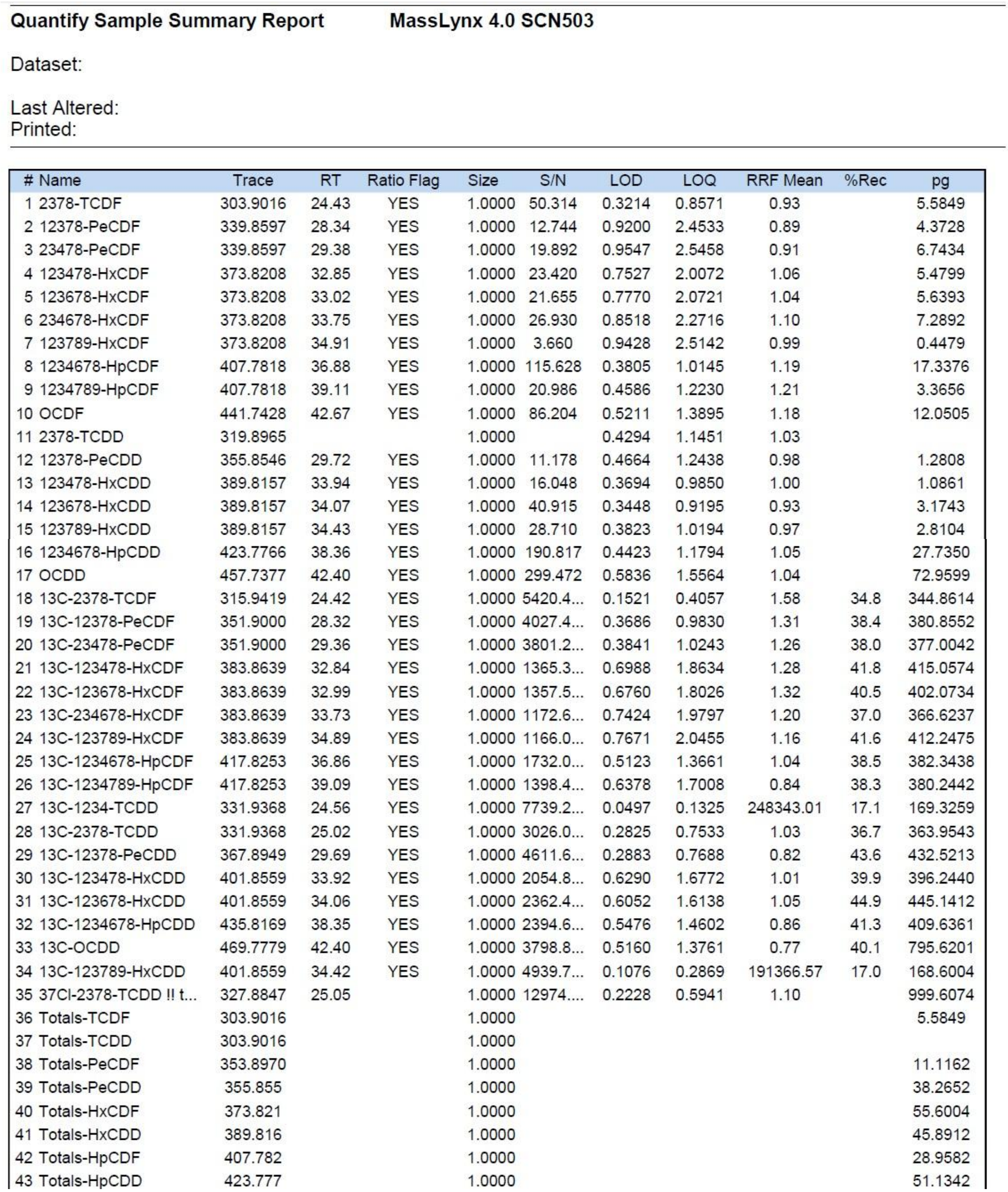


TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25–164	25–164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24–169	24–169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25–181	25–181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24–185	24–185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21–178	21–178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32–141	32–141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28–130	28–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26–152	26–152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26–123	26–123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29–147	29–147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28–136	28–136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23–140	23–140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28–143	28–143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26–138	26–138
$^{13}C_{12}$-OCDD	200	34–313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5–19.7	35-197

[1] Specification given as concentration in the final extract, assuming a 20-μL volume.

APPENDIX 3: QUANTIFICATION REPORT OF S2



Quantify Sample Summary Report **MassLynx 4.0 SCN503**

Dataset:

Last Altered:
Printed:

#	Name	Trace	RT	Ratio Flag	Size	S/N	LOD	LOQ	RRF Mean	%Rec	pg
1	2378-TCDF	303.9016	24.43	YES	1.0000	50.314	0.3214	0.8571	0.93		5.5849
2	12378-PeCDF	339.8597	28.34	YES	1.0000	12.744	0.9200	2.4533	0.89		4.3728
3	23478-PeCDF	339.8597	29.38	YES	1.0000	19.892	0.9547	2.5458	0.91		6.7434
4	123478-HxCDF	373.8208	32.85	YES	1.0000	23.420	0.7527	2.0072	1.06		5.4799
5	123678-HxCDF	373.8208	33.02	YES	1.0000	21.655	0.7770	2.0721	1.04		5.6393
6	234678-HxCDF	373.8208	33.75	YES	1.0000	26.930	0.8518	2.2716	1.10		7.2892
7	123789-HxCDF	373.8208	34.91	YES	1.0000	3.660	0.9428	2.5142	0.99		0.4479
8	1234678-HpCDF	407.7818	36.88	YES	1.0000	115.628	0.3805	1.0145	1.19		17.3376
9	1234789-HpCDF	407.7818	39.11	YES	1.0000	20.986	0.4586	1.2230	1.21		3.3656
10	OCDF	441.7428	42.67	YES	1.0000	86.204	0.5211	1.3895	1.18		12.0505
11	2378-TCDD	319.8965			1.0000		0.4294	1.1451	1.03		
12	12378-PeCDD	355.8546	29.72	YES	1.0000	11.178	0.4664	1.2438	0.98		1.2808
13	123478-HxCDD	389.8157	33.94	YES	1.0000	16.048	0.3694	0.9850	1.00		1.0861
14	123678-HxCDD	389.8157	34.07	YES	1.0000	40.915	0.3448	0.9195	0.93		3.1743
15	123789-HxCDD	389.8157	34.43	YES	1.0000	28.710	0.3823	1.0194	0.97		2.8104
16	1234678-HpCDD	423.7766	38.36	YES	1.0000	190.817	0.4423	1.1794	1.05		27.7350
17	OCDD	457.7377	42.40	YES	1.0000	299.472	0.5836	1.5564	1.04		72.9599
18	13C-2378-TCDF	315.9419	24.42	YES	1.0000	5420.4...	0.1521	0.4057	1.58	34.8	344.8614
19	13C-12378-PeCDF	351.9000	28.32	YES	1.0000	4027.4...	0.3686	0.9830	1.31	38.4	380.8552
20	13C-23478-PeCDF	351.9000	29.36	YES	1.0000	3801.2...	0.3841	1.0243	1.26	38.0	377.0042
21	13C-123478-HxCDF	383.8639	32.84	YES	1.0000	1365.3...	0.6988	1.8634	1.28	41.8	415.0574
22	13C-123678-HxCDF	383.8639	32.99	YES	1.0000	1357.5...	0.6760	1.8026	1.32	40.5	402.0734
23	13C-234678-HxCDF	383.8639	33.73	YES	1.0000	1172.6...	0.7424	1.9797	1.20	37.0	366.6237
24	13C-123789-HxCDF	383.8639	34.89	YES	1.0000	1166.0...	0.7671	2.0455	1.16	41.6	412.2475
25	13C-1234678-HpCDF	417.8253	36.86	YES	1.0000	1732.0...	0.5123	1.3661	1.04	38.5	382.3438
26	13C-1234789-HpCDF	417.8253	39.09	YES	1.0000	1398.4...	0.6378	1.7008	0.84	38.3	380.2442
27	13C-1234-TCDD	331.9368	24.56	YES	1.0000	7739.2...	0.0497	0.1325	248343.01	17.1	169.3259
28	13C-2378-TCDD	331.9368	25.02	YES	1.0000	3026.0...	0.2825	0.7533	1.03	36.7	363.9543
29	13C-12378-PeCDD	367.8949	29.69	YES	1.0000	4611.6...	0.2883	0.7688	0.82	43.6	432.5213
30	13C-123478-HxCDD	401.8559	33.92	YES	1.0000	2054.8...	0.6290	1.6772	1.01	39.9	396.2440
31	13C-123678-HxCDD	401.8559	34.06	YES	1.0000	2362.4...	0.6052	1.6138	1.05	44.9	445.1412
32	13C-1234678-HpCDD	435.8169	38.35	YES	1.0000	2394.6...	0.5476	1.4602	0.86	41.3	409.6361
33	13C-OCDD	469.7779	42.40	YES	1.0000	3798.8...	0.5160	1.3761	0.77	40.1	795.6201
34	13C-123789-HxCDD	401.8559	34.42	YES	1.0000	4939.7...	0.1076	0.2869	191366.57	17.0	168.6004
35	37Cl-2378-TCDD !! t...	327.8847	25.05		1.0000	12974....	0.2228	0.5941	1.10		999.6074
36	Totals-TCDF	303.9016			1.0000						5.5849
37	Totals-TCDD	303.9016			1.0000						
38	Totals-PeCDF	353.8970			1.0000						11.1162
39	Totals-PeCDD	355.855			1.0000						38.2652
40	Totals-HxCDF	373.821			1.0000						55.6004
41	Totals-HxCDD	389.816			1.0000						45.8912
42	Totals-HpCDF	407.782			1.0000						28.9582
43	Totals-HpCDD	423.777			1.0000						51.1342