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Monitoring of ambient air PCDD/F levels in Portugal

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Abstract

As part of a monitoring program conducted by IDAD – Institute for Environment and Development and supported by regional municipal solid waste (MSW) management authorities, dioxin concentrations in ambient air were measured in three regions of Portugal: Porto, Lisbon and Madeira. These independent studies were performed with the intention of providing data as a basis for the evaluation of potential impacts of the operation of recently built MSW incinerators. Thus, 170 samples were collected in nine different sites from January 1999 till present. The measured levels revealed an extremely variable content of PCDDs/PCDFs depending both on the area and the season of the year. Samples taken in Porto and Lisbon reveal a similar homologue structure even if concentrations measured in the Porto region are significantly greater. Data from Madeira is characteristic of a remote site with some of the congeners concentrations below the detection limit.

Keywords: Dioxins; Furans; PCDDs/PCDFs; Ambient air concentrations; Background pollution

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) are ubiquitous in the environment. PCDDs and PCDFs are injected into the atmosphere by various combustion processes and dispersed throughout the environment by atmospheric transport. These compounds may be produced through the incineration of waste, released into the atmosphere, and transported at great distances before being transferred to other environmental matrices.

Between 1998 and 2000, state-of-the-art municipal solid waste (MSW) incinerators were constructed in Portugal, namely in the regions of Lisbon, Porto and Madeira. The construction of these MSW incinerators was accompanied by the development of comprehensive external environmental monitoring programs (Coutinho et al., 2001) with sampling of materials from different matrices such as ambient air, soil, locally produced vegetables, eggs and milk, as well as, breast milk and human blood (Calheiros et al., 2002). The data collected in these monitoring programs is being used to understand the environmental and public health impact of these units. The present paper focuses on the description and interpretation of PCDD/PCDF ambient air data obtained in Portugal between January 1999 and December 2004. A total of about 170 samples, collected from nine different sites, were available for this study.

2. Materials and methods

2.1. Sampling sites

Samples were collected from nine different sampling points located in the regions of Porto, Lisbon and Madeira. A location map of the sampling sites is provided in Fig. 1. A simple description of the main characteristics of the sampling sites is presented in Table 1.

These sites were selected with the intention of providing data as a basis for evaluation of potential impacts of the operation of recent built MSW incinerators.

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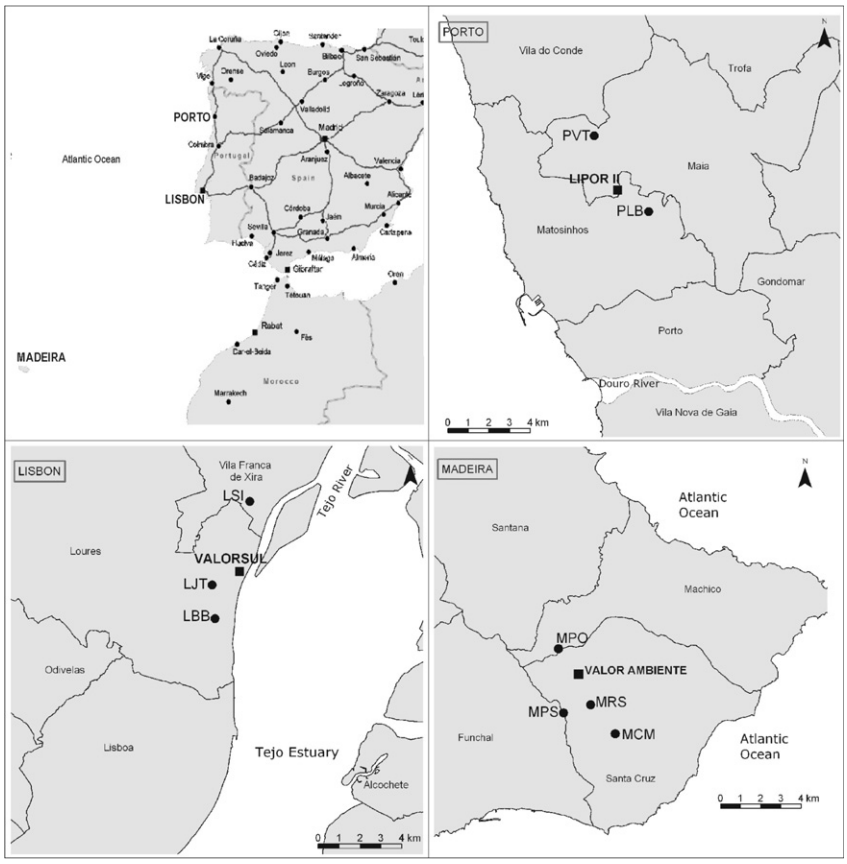

Fig. 1. Map of the three monitoring regions and detailed location of the sampling sites.

Table 1
Characteristics of the sampling sites

Location	Site ID	Land use	Altitude (m ASL)	Comments
Porto				
Leça do Balio	PLB	Suburban	57	
V.N. Telha	PVT	Suburban	88	
Lisbon				
S.J. Talha	LJT	Suburban	70	Winter only
Bobadela	LBB	Suburban	43	
P.S. Iria	LSI	Suburban	67	Summer only
Madeira				
Ribeiro Serrão	MRS	Rural	850	
Pico da Silva	MPS	Forest	1115	
Poiso	MPO	Forest	1390	Exposed to synoptic winds
Camacha	MCM	Rural	700	

2.1.1. Porto

In accordance with the MSW management plan adopted for Porto, Portugal, a MSW incinerator with the capacity of 400 000 tons per year (commonly referred as LIPOR II) was constructed. An ambient air-monitoring program for the MSW incinerator in the region of Porto was designed with the main objective of evaluating the effects of the operation of this facility on the surrounding area. Since 1998, sampling of ambient air for PCDD/F analysis was performed at six different sites. Regular monitoring was restricted to two sites, Leça do Balio and V.N. Telha, with samples taken every three months through December 2004.

2.1.2. Lisbon

The MSW processing plant of Valorsul is a waste-to-energy facility located in Loures, a municipality just north of the city of Lisbon. This incinerator was designed to process a total of approximately 650 000 tons per year of MSW.

The Valorsul unit includes a flue gases removal system that is similar to LIPOR II in Porto and includes the following processes:

- injection of an aqueous ammonia solution at the boilers combustion chamber for the removal of nitrogen oxide;
- semi-dry removal of acid gases by injection of wet limestone;
- injection of activated carbon for the removal of PCDD/F and heavy metals;
- high efficiency fabric filters for removal of particulate matter.

The ambient air monitoring program has been running continuously since February 1999 with sampling three

times a year in three sites: Bobadela, S.Iria da Azóia (only summer) and S. João da Talha (only winter).

2.1.3. Madeira

The Solid Waste Treatment Plant of Valor Ambiente is located on the East side of Madeira Island, NE of Funchal, the regional capital city. The MSW incineration facility includes two independent incineration lines, with a total processing capacity of about 120 000 tons a year. A contiguous unit for hospital and slaughterhouse waste incineration was installed in the same location but it is not yet in operation. This later unit has a capacity of circa 7000 tons a year.

An ambient air monitoring program has been conducted since March 2002, at four sampling sites in the vicinity of the Madeira MSW plant. All sampling points can be considered as being located in rural or even background areas. One of the specificities of this monitoring program is the high altitude of the sampling locations with two of the sites located above 1000 m. Site MPO has a very special location because it is located on the ridge of the island at an altitude 1390 m. Consequently, this site is strongly affected by synoptic winds that are mainly from the northern sector.

2.2. Sample collection and analysis

The sampling apparatus for PCDDs/PCDFs in ambient air was constructed according to German guideline VDI 3498 Part 2, 2002. The sampling apparatus consisted basically of a filter system, a mast, a suction pump, a gas volumeter and timer. Particulate matter (PM) in the air was collected on a glass fiber filter. Filter-passing matter was collected on a polyurethane foam. To monitor the effectiveness of sampling, a second polyurethane (PU) foam was connected downstream. The volume of air drawn through the sampling device at a rate of $4\ m^3\ h^{-1}$ and measured with a gas volumeter during the sampling period (72 h) was approximately $290\ m^3$.

The PCDDs/PCDFs, which were deposited on the glass fibre filter and absorbed in the PU foam, were extracted and separated from interfering components in a multistage separation process. They were quantified by gas chromatography/mass spectrometry, according to DIN ISO 12884. For control of laboratory blanks firstly the solvents (nanograde) were tested lot wise before usage. Secondly the PU-foams used for sampling were tested after the cleaning procedure based on VDI 3498 to determine the blank situation. With every batch of samples a laboratory blank was done in parallel.

3. Results and discussion

This paper presents data on concentrations of PCDDs and PCDFs obtained from the sampling sites and available by December 2004. It is important to mention, that in the computation of the $\sum$TEQ values of the 17 congeners of PCDD/Fs calculated using I-TEF (International Toxicity Equivalency Factor) that for those congeners below the detection limit the actual concentration was assumed to be half the detection limit. Detection limits are variable depending of the congeners and amount of air sampled. The detection limit was determined according to VDI 2449 Part 1.

Ambient air sampling of PCDDs/PCDFs in Porto region began in summer 1998, with atmospheric PCDD/PCDF characterization of about 90 samples completed by December 2004. A recent study (Coutinho et al., 2004) showed that the shutdown of two medical waste incinerators in Porto in January 2001 caused a sharp decrease in concentrations of PCDD/F of about 50% in both the winter and the summer months. This effect was noticed not only in the total concentration of these compounds, but also on the homologue and congener pattern of the samples. As a consequence of this pattern change, only data collected after the winter of 2001 is used in the current paper.

3.1. Dioxins and furan levels

Table 2 summarizes PCDD/F data in ambient air for the nine monitoring sites used for this study. Measured

Table 2
PCDD/F levels measured in the monitoring sites and information on other variables

Site	*N*	$\sum P_{4-8}$CDD/F (pg m^{-3})	OCDD (% of $\sum$)	D/F ratio	$\sum$TEQ (fg m^{-3})	Min (fg m^{-3})	Max (fg m^{-3})	2,3,4,7,8 PCDF (%$\sum$TEQ)
Porto	42	13	23.4	1.6	149			24.5
PLB	24	14	23.6	1.5	151	9.8	816.8	24.5
PVT	18	13	23.0	1.7	147	13.0	456.8	24.6
Lisbon	50	3.7	18.5	1.3	34			24.4
LJT (winter)	13	4.0	22.2	1.5	39	7.2	152.5	24.8
LBB	25	4.2	19.3	1.3	38	2.0	138.9	23.7
LSI (summer)	12	1.9	13.9	1.2	19	6.3	74.7	26.0
Madeira	25	1.0	8.0	0.64	15			25.9
MRS	7	1.8	6.0	0.60	25	7.8	59.6	31.1
MPS	7	1.3	7.1	0.89	17	2.2	28.9	25.7
MPO	7	0.2	9.0	0.65	4.0	1.7	6.7	18.4
MCM	4	0.8	11.1	0.58	11	7.0	15.8	29.9

concentrations of the sum of the tetra- to octa-CDD/Fs homologues in ambient air vary between 0.2 and 15 pg m^{-3}. According to Lohmann and Jones (1998), PCDD/F concentrations for the sum of the tetra- through octa-PCDD/F homologues (and the $\sum$TEQ) are typically as follows: remote, <0.5 pg m^{-3} ($\sum$TEQ < 10 fg m^{-3}); rural, ~0.5–4 pg m^{-3} ($\sum$TEQ ~ 20–50 fg m^{-3}); and urban/industrial, ~10–100 pg m^{-3} ($\sum$TEQ ~ 100–400 fg m^{-3}).

Application of these criteria to the data for each station in Table 2 indicates that the only sites that can be classified as urban/industrial (as far as ambient air PCDD/F concentrations are concerned) are the two stations for Porto: PLB and PVT. In Porto, maximum concentrations above 400 fg I-TEQ m^{-3} were measured. The other seven sites, with the exception of site MPO on Madeira, should be classified as rural based on the data in Table 2.

The monitoring station located in Poiso, Madeira (MPO) is an example of a remote site. Measurements were performed at 1390 m above sea level in the middle of the Atlantic Ocean. Moreover, it important to mention that the prevalent wind direction at this site is from N-NW. This is the direction of the less inhabited coast of the island. In most circumstances ambient air sampled in this location (MPO) is not affected by local emissions and might be representative of background concentrations at remote sites of the northern hemisphere at mid-latitudes.

Fig. 2 shows the difference that occurs between the three regions. In Porto, approximately 75% of the ambient air samples show dioxin and furan levels above 60 fg I-TEQ m^{-3}. In Lisbon, three quarters of the samples present dioxin concentrations below 40 fg I-TEQ m^{-3}. The difference between the statistical distributions calculated for both sets of data is very significant bearing in mind that there is not an immediate explanation for it, and it cannot be explained by any natural characteristic of any of these regions. Both monitoring programs include territory with suburban characteristics belonging to the Porto and Lisbon metropolitan areas. Porto and Lisbon have similar population sizes and densities, similar industrial occupation and moreover, the monitoring stations are located in the suburbs and consequently, with similar type of land-use. Concentrations measured in Lisbon are comparable to those found in rural and non-contaminated urban areas (WHO, 1995): 41.3% of PCDD/PCDF concentrations in this region range from 30 to 50 fg I-TEQ m^{-3}. On the other hand, in Porto, 41.5% of samples collected are in the 80–200 fg I-TEQ m^{-3} range, approximately four times higher than the Lisbon levels. Levels measured in Porto are consistent with data published for Barcelona, on the NE coast of the Iberian Peninsula, where the reported maximum concentrations were in the range of 600–800 fg I-TEQ m^{-3} (Abad et al., 2002).

The same statistical analysis performed on the Madeira data-set indicates that only one fourth of the samples show levels above 16 fg I-TEQ m^{-3}. This fact is consistent with the remote location of the island and the relatively high altitude of the monitoring sites.

3.2. PCDD/PCDF seasonal variation

In determining the seasonal behaviour of PCDDs/PCDFs, two periods were considered, Spring/Summer (April–September) and Autumn/Winter (October–March), referred to as Summer (S) and Winter (W) in all figures presented in this paper. Fig. 3 shows the temporal evolution of the average PCDD/F concentrations, expressed in I-TEQ, for the Spring/Summer and Autumn/Winter periods.

The presence of a seasonal pattern is very clear in the data obtained in Porto and Lisbon. The mean

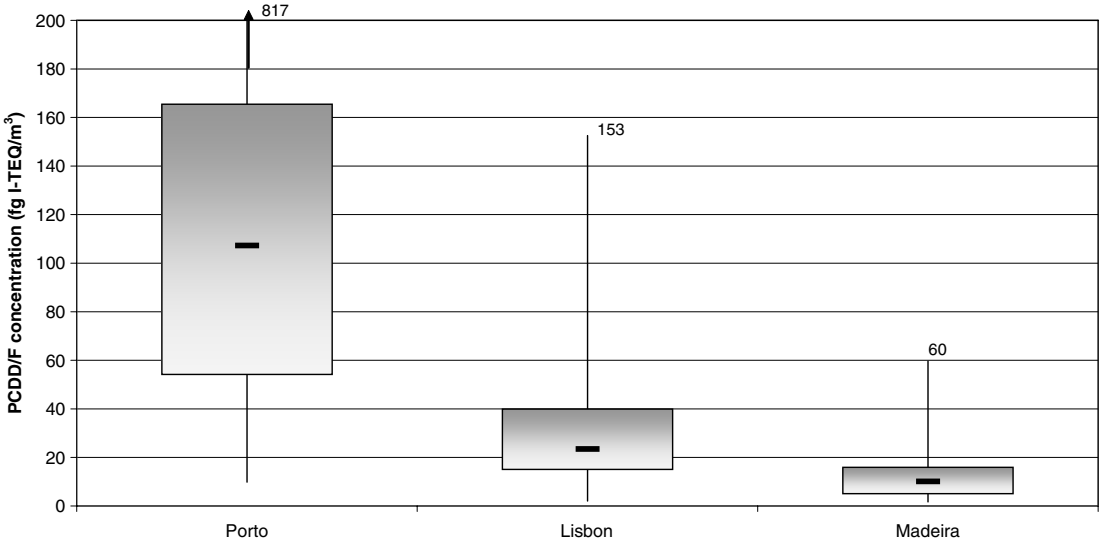

Fig. 2. PCDD/PCDF statistical parameters: mean, minimum, percentile 25, percentile 75 and maximum determined for ambient air samples collected in the Porto, Lisbon and Madeira, Portugal.

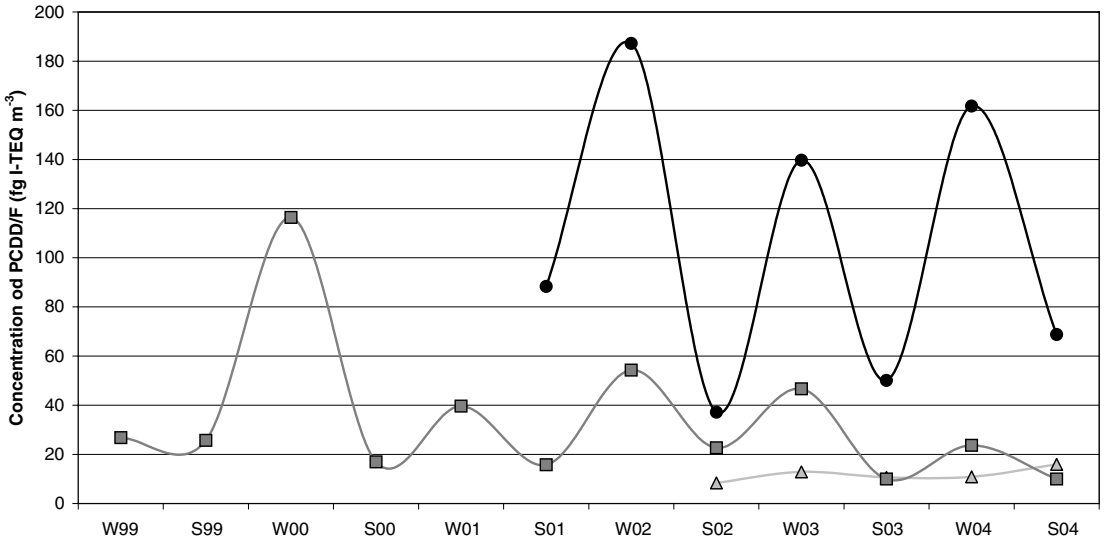

Fig. 3. Average seasonal concentrations of PCDD/PCDF from winter 1999 (W99) to summer 2004 (S04) for Porto (black circles), Lisbon (grey squares) and Madeira (light grey triangles).

value (67 fg I-TEQ m^{-3}) and the concentration range (10–171 fg I-TEQ m^{-3}) measured in Porto during Summer are significantly lower than during winter (mean: 224 fg I-TEQ m^{-3}, range: 69–817 fg I-TEQ m^{-3}). Note that the ratio of summer to winter values is approximately 1:3 for the mean but it reaches a ratio of about 1:6 at the extreme values.

This seasonal variation of PCDD/PCDF concentrations in ambient air is noteworthy and consistent with previous findings in other air sheds (Hiester et al., 1997; Environmental Protection Department, 2000). One factor that explains this seasonal pattern is the seasonal variation of the atmospheric boundary layer, generally referred to as the mixing layer. The height of the mixing layer displays a strong seasonal cycle, with the height of the well-mixed atmosphere at ~1000–2000 m during strongly sunny afternoons in summer, but decreasing to a few hundred meters or less in a cloudy day in winter. This situation is explained by the fact that during summer at mid latitudes, there is often more heating during the day than cooling during the short night. The convective mixed layer starts shallow in the morning, but rapidly grows to its full extent in the beginning of the afternoon. On the contrary, during winter at mid latitudes, there is often more cooling at night than heating during the short day, and consequently stable boundary layers dominate (Stull, 1995). Hence, local emissions to the atmosphere will be less well dispersed during winter. This process is particularly effective for emissions that occur near ground level because a reduced height of the well-mixed atmosphere favours an accumulation of pollutants and result in increasing ambient concentrations (Lohmann et al., 2003).

An additional contribution to the seasonal variation might be household wood burning for heating in winter. Several authors documented that burning wood at low temperature with low burning efficiency may increase PCDD/PCDF emissions (Dyke et al., 1997; Lavric et al., 2004; Vikelsoe and Andersen, 2004).

No seasonal fluctuations are observed in the data collected in Madeira. Madeira has a very mountainous orography, with 65% of its surface having slopes above 25%. In this region during summer, temperature inversions with altitude are fairly common (Coutinho et al., in press). Monitoring stations are in most occasions above this inversion layer. The existence of thermal inversions in summer and in winter, added to the very low concentrations that are measured in this region, due to relatively few local dioxin sources prevent the occurrence of any potential seasonal phenomena.

3.3. Homologue profiles

Homologue profiles were analysed in order to derive some further indications of the possible dioxin sources and to investigate differences between the three regions (see Fig. 4). Additionally these results are compared with "averaged" ambient air pattern obtained by Lohmann and Jones (1998) through a thorough literature review on ambient air measurement from Europe, the USA, Japan and Australia. Fig. 3 includes error bars representing single standard deviations.

Observation of Fig. 4 shows a significant contrast between data measured in Porto and Lisbon with ambient air data monitored in Madeira. The homolog pattern of Porto and Lisbon coincides with the "average" worldwide homologue structure presented by Lohmann and Jones (1998). Generally, a reduction in the PCDF concentration was observed as the chlorination level increased. The opposite was found for PCDD compounds where concentration increases with the degree of chlorination. In these samples,

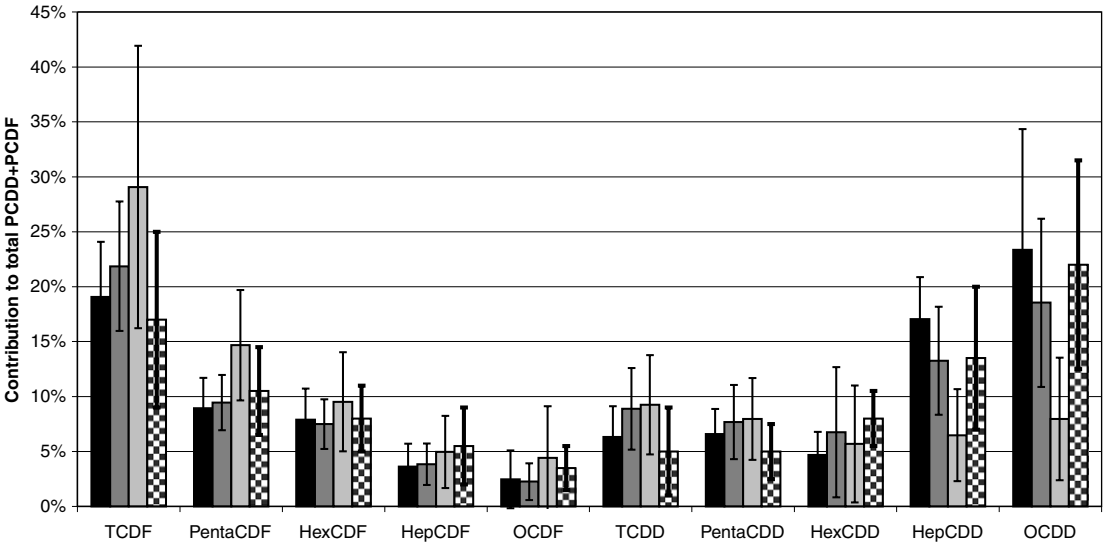

Fig. 4. Average homologue profiles of ambient air samples collected at Porto (black), Lisbon (dark grey), Madeira (light grey) and worldwide averaged ambient air (squared) adapted from Lohmann and Jones (1998). Error bars represent a single standard deviation.

the total amount of tetra-furans, and hepta- and octo-dioxins represent approximately 55% of the total burden of PCDD/F. The relative contribution of OCDD (see Table 2), which is usually the most abundant homologue, varies from 23% in the 2 sites in Porto to 14–22% in the Lisbon sites. Note that apparently a seasonality factor occurs for OCDD because the lower contribution included in Table 2 corresponds to site LSI where monitoring was restricted to the summer season. A similar effect is noticeable in the ratio PCDD/PCDF (D/F): in the case of Porto there is a relative homogeneity between the two sites with D/F values of ~1.6, but in Lisbon a variability between 1.2 and 1.5 is observable. Once more the lowest value is found at the LSI site.

In the case of Madeira, the furans fraction is larger than that of the dioxins, and the D/F ratio varies between 0.58 and 0.89. The most important homologue by far is represented by the tetra-furans, with a contribution close to 30% to the sum PCDD/F. The most remarkable feature of the homologue pattern for the Madeira samples is that there is certain homogeneity in the contribution of each dioxin homologue groups with partial contribution between 6% and 9%. In these samples the relative contribution of OCDD is between 6% and 11% for all sites. This fact does not match with the conclusion of Lohmann and Jones (1998) that states that the contribution of OCDD appears to be higher (>50%) in rural areas.

3.4. Congener profiles

Additional information about the type of PCCD/F and about the origin of the ambient air can be obtained by the study of the congener profile. The contributions, in percentage, of the individual 2,3,7,8-substituted congeners in relation to the total I-TEQ concentrations of the three sampling regions are shown in Fig. 5. In the same figure, data obtained from Lohmann and Jones (1998) was included.

It turns out that the average congener profiles for Porto, Lisbon and Madeira are relatively similar to each other. The striking reduction in the D/F ratio that was observable in the homologues is not noticeable in the congeners. 2,3,4,7,8-penta furan makes the single most important contribution to the $\sum$TEQ, accounting for about 25% of the toxicity. If site-specific data is analysed (see Table 2), we can conclude that there is a strong homogeneity in the contribution of this congener between the Porto and Lisbon sites. This is an indication that no seasonality effect occurs for this congener. The average 2,3,4,7,8-penta furan contribution in the Madeira region is very close to the same value (25.9%), but the observation from site to site shows that it varies between 18.4% and 31.1%. The lowest contribution was measured in MPO, where the lowest overall I-TEQ levels were monitored.

Congener profiles obtained in these three regions are coincident with average global data, with the exception of the uncommon contribution of 2,3,7,8-tetra dioxin in Madeira that reaches a value above 15, about double the usual value. This characteristic should be studied with care for the relative contribution of each congener in samples with overall low I-TEQ levels strongly depends on the strategy applied in the treatment of concentrations below the detection limit. In the particular case of the Madeira sites, 60% of the samples reported 2,3,7,8-tetra dioxin concentration less than the detection limit. The detection limit depends on the total amount of air sampled and ranges between 1 and ~5 fg I-TEQ m^{-3}. Additionally, a significant fraction of samples reported levels below the detection limit for the congeners 1,2,3,7,8,9-hexa furan (88%) and 1,2,3,4,7,8-hexa dioxin (52%). The assumption used in this paper that, in these circumstances, the actual concentration

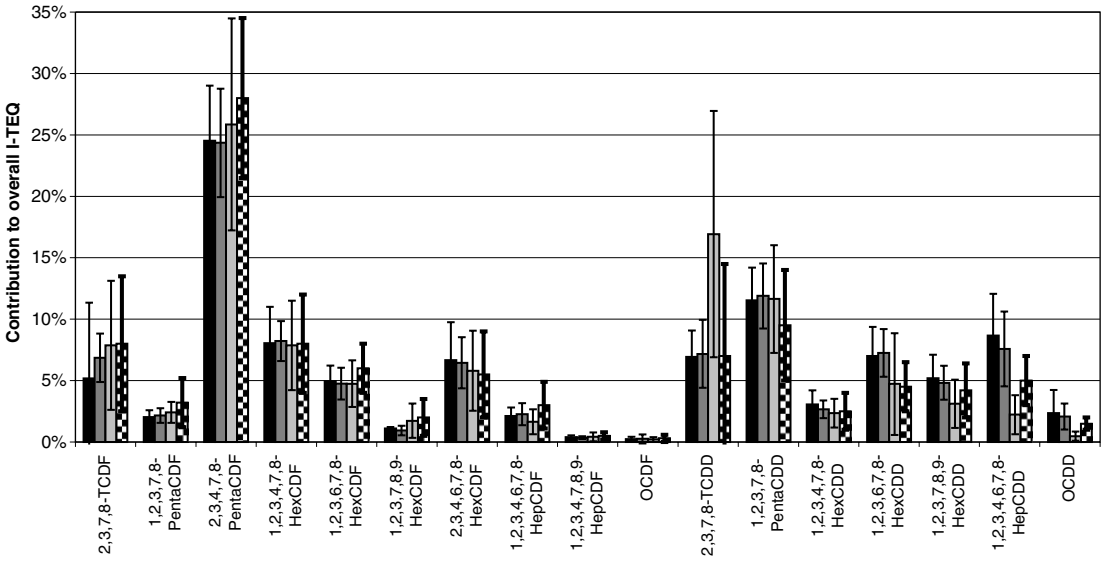

Fig. 5. Average congener profiles of ambient air samples collected at Porto (black), Lisbon (dark grey), Madeira (light grey) and worldwide averaged ambient air (squared) adapted from Lohmann and Jones (1998). Error bars represent a single standard deviation.

is half the detection limit may produce an overestimation of the real contribution of these congeners.

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References

Abad, A., Caixach, J., Rivera, J., Gustems, L., Massagué, G., Puig, O., 2002. Surveillance programme on dioxin levels in ambient air sites in Catalonia (Spain). Chemosphere 49 (7), 697–702.

Calheiros, J., Coutinho, M., Borrego, C., Santos, R., Papke, O., 2002. PCDD/PCDF levels in human blood and breast milk in the region of Oporto. Organohalogen Compounds 55, 279–282.

Coutinho, M., Ferreira, J., Gomes, P., Mata, P., Borrego, C., 2001. Atmospheric baseline levels of PCDD and PCDF in the region of Oporto. Chemosphere 43, 497–500.

Coutinho, M., Pereira, M., Borrego, C., 2004. Air quality impact of the shut-down of an hospital waste incinerator in the Oporto region. Organohalogen Compounds 66, 2181–2186.

Coutinho, M., Ribeiro, C., Pereira, M., Borrego, C., in press. Simulation of the plume emitted by a municipal waste incinerator in the Madeira Island. International Journal of Environment and Pollution.

Dyke, P., Coleman, P., James, R., 1997. Dioxins in ambient air, bonfire night 1994. Chemosphere 34, 1191–1201.

Environmental Protection Department, Government of Hong Kong Special Administrative Region, 2000. An Assessment of Dioxin Emissions in Hong Kong: Final Report. <http://www.info.gov.hk>.

Hiester, E., Bruckmann, P., Böhm, R., Eynck, P., Gerlach, A., Mülder, W., Ristow, H., 1997. Pronounced decrease of PCDD/PCDF burden in ambient air. Chemosphere 34, 1231–1243.

Lavric, E., Konnov, A., De Ruyck, J., 2004. Dioxin levels in wood combustion – a review. Biomass and Bioenergy 26 (2), 115–145.

Lohmann, R., Jones, K., 1998. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. The Science of the Total Environment 219 (1), 53–81.

Lohmann, R., Brunciak, P., Dachs, J., Gigliotti, C., Nelson, E., Van Ry, D., et al., 2003. Processes controlling diurnal variations of PCDD/Fs in the New Jersey coastal atmosphere. Atmospheric Environment 37, 959–969.

Stull, R., 1995. Meteorology Today for Scientists and Engineers. West Publishing Company, St. Paul Minnesota.

Vikelsoe, J., Andersen, H.V., 2004. Dioxin in Danish air. Organohalogen Compounds 66, 2203–2208.

WHO, 1995. Updating and revision of the air quality guidelines for Europe. Report on the WHO Working Group on PCBs, PCDDs and PCDFs. Denmark.