ORGANIC POLLUTANTS IN AIR CLOSE TO CEMENT KILNS

Conesa JA[1], Gálvez A[1]

[1]Department of Chemical Engineering, University of Alicante, P.O. Box 99 E-03080 Alicante, SPAIN

Introduction

Chemicals emitted from a source into the environment could be directly transmitted to humans through air inhalation. However, these chemicals could also cross environmental media boundaries, transferring to soils, vegetation, water, biota, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs, and oral and skin absorption of chemicals from soils. Therefore, for accurate health risk estimation, the chemical concentrations in each of these environmental media must be determined. [1,2]

University and some villages of Alicante are near to two cement industries, one of them feds alternative fuels in the kiln. The pollutants emitted for both industries are cause for concern in the adjacent population and the university students and workers. For this reason an inmission study was carried out in air of the university, which is near to a divided highway too.

The pollutants considered in this work are polyciclic aromatic hydrocarbons (PAHs), dioxins and furans (PCDD/Fs). The analysis performed to samples respecting to these pollutants are shown.

Materials and Methods

The samples were collected in two sites located in the campus: UA-CIEN and UA-PTR. In both sites are placed a sampling station where some parameters of the air are monitored and a high volume sampler, model DIGITEL DL80 with a cyclone inlet, lets a determined volume of air goes through a quartz filter, collecting the particulate material. These filters contain the particles in suspension of the air and were analyzed to obtain the contents in PAHs and PCDD/DFs. The filters analyzed were selected of an amount of 500 filters sampled for one year and the 36 filters chosen were representative for all the year.

The volume of air sampled is different for all the samples, but it is near to 1000 m^3/filter. This quantity it is not enough to reach the detection limits of the dioxin analysis, because of that, groups of filters were analyzed together. Table 1 shows the code of filters used and the volume total analyzed in the samples for dioxins and PAHs. In case of PAHs, the concentrations expected were higher and only one filter was analyzed.

The analysis of dioxins and furans in the quartz filters were made following the U.S.EPA method 1613. The procedure comprises the extraction with toluene for 24 hours, change of solvent to hexane and cleanup using power-Prep System (FMS Inc., MA) with three different columns: silica, alumina, and activated carbon (FMS Inc. Boston, U.S.A.). 13C-labeled compounds included in the EPA 1613 method were used (Wellington Laboratories, Canada) .For HRGC, an Agilent HP5890 gas chromatograph equipped with a PTV inlet with a septumless head was used. For HRMS, a Micromass Autospec UltimaNT mass spectrometer (Micromass, Waters, U.K.) with a positive electron impact (EI+) source was employed

The semivolatile compounds were extracted with dichloromethane in a Soxhlet equipment for a total of 24 hours. PAHs analysis was carried out in a GC/MS, specifically in an Agilent 6890N gas chromatograph coupled with an Agilent 5973N mass spectrometer in SCAN mode. The column used was a DB-5 MS of length 30 m and an intern diameter of 0.25 mm. For identifying and quantifying the liquids, intern pattern of deuterated compounds were used (1,4-dichlorobenzene-D_4, naphthalene-D_8, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12} and perylene-D_{12}, Dr. Ehrenstorfer Laboratory, Germany).

SAMPLE	FILTERS	Σ VOLUME
PCDD/Fs ANALYSIS		
SAMPLE 1	FQR109, FQR110, FQR111	3837.9 Σvolume (m^3)
SAMPLE 2	FQR293, FQR294	3614.8 Σvolume (m^3)
SAMPLE 3	FQR339, FQR366, FQR367	3724.7 Σvolume (m^3)
SAMPLE 4	FQR96, FQR97, FQR98, FQR100	4574.3 Σvolume (m^3)
SAMPLE 5	FQR238, FQR239, FQR240, FQR241, FQR242	3973.3 Σvolume (m^3)
SAMPLE 6	FQR305, FQR315, FQR316	3692.6 Σvolume (m^3)
SAMPLE 7	FQR310, FQR311, FQR312, FQR313, FQR314	3704.6 Σvolume (m^3)
SAMPLE 8	FQR423, FQR424, FQR425, FQR427	4414.7 Σvolume (m^3)
SAMPLE 9	FQR475, FQR476, FQR477, FQR478	3767.3 Σvolume (m^3)
PAHs ANALYSIS		
SAMPLE 10	FQR 292	684.40 Σvolume (m^3)
SAMPLE 11	FQR304	766.74 Σvolume (m^3)
SAMPLE 12	FQR430	736.99 Σvolume (m^3)

Table 1: Samples analyzed

Results and Discussion

The results of the analysis of dioxins are in Table 2. The levels obtained are around 50 i-TEQ fg/m^3 which can be considered a value representative for a year. The samples 1, 4 and 9 have low concentrations owing to meteorological phenomena (saharan intrusion or thermal inversion) but the congener distribution is similar that the others samples (Figure 1).

Sample	PCDD/Fs (I-TEQ fg/m^3)
1	5.36
2	40.7
3	59.4
4	6.43
5	85.56
6	61.80
7	45.32
8	32.18
9	6.69

Table 2: PCDD/Fs analysis

In the European Union (EU) several similar samples were analysed. The EU affirms that the maximum level of exposition found is 14800 fg/m^3 [3] and in the same report, the UK autorities estimates that the average level to what population is someted is 200 fg/m^3. In a study performed in Rome the level are maintained between 5 and 250 fg/m^3 also througouh one year.[4]

Regard to the congener distribution, Figure 1 shows the profile for the 17 toxic congeners, and this can give an idea of the origin of such pollutants.

PAH	*10*	*11*	*12*
Naphthalene	1.56	1.77	0.35
Acenaphtylene	0.14	0.00	0.00
Acenaphtene	0.00	0.00	0.00
Fluorene	0.17	0.00	0.00
Phenanthrene	0.11	0.19	0.06
Anthracene	0.00	0.00	0.00
Fluoranthene	0.51	0.59	0.14
Pyrene	0.55	0.67	0.14
Benzo(a)anthracene	1.34	1.03	0.50
Chrysene	1.51	1.74	0.38
Benzo(b)fluoranthene	0.00	0.22	0.07
Benzo(k)fluoranthene	0.00	0.66	0.17
Benzo(a)pyrene	0.31	0.37	0.73
Indeno(1,2,3-cd)pyrene	0.34	0.55	0.18
Dibenz(a,h)anthracene	0.05	0.06	0.02
Benzo(g,h,i)perylene	0.36	0.61	0.21
TOTAL (mg/m^3)	6.95	8.46	2.95

Table 3: PAHs analysis

It could be observed that the congeners that most contribute to the air toxicity in all samples are the 1,2,3,4,6,7,8-HpCDF, OCDF, 1,2,3,4,6,7,8-HpCDD and OCDD. The congener distribution in samples 1, 4 and 9 are similar but with lower concentrations. Various authors found similar distributions that have been considered typical of urban environment, i.e., the cement factory (sited at 3 km of the sampling point) seems not to influence the dioxin content in air. [5]

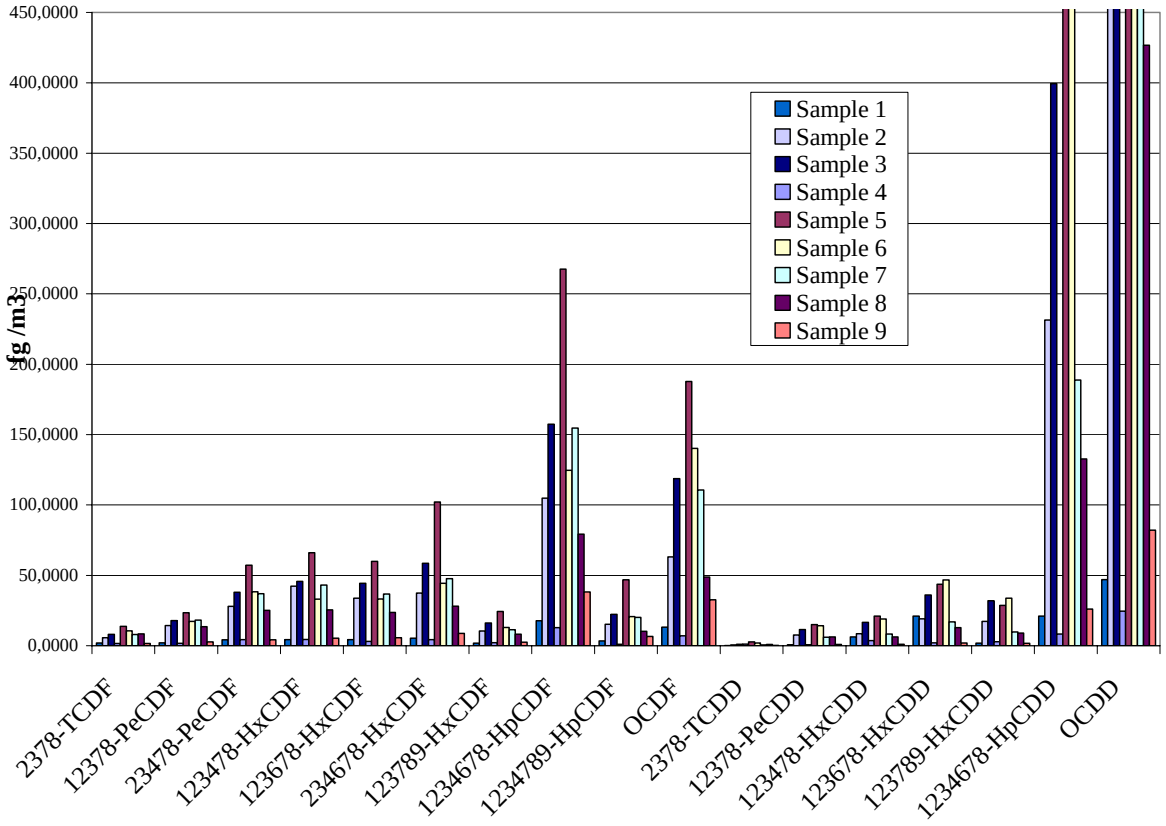

Figure 1: PCDD/Fs congener profile

The concentrations obtained for the aromatic hydrocarbons are in Table 3. Results show that, altough there are some differences between the samples, all of them present levels around 1-10 ng/m3. PAHs profiles (Figure 2) are also similars, with a major presence of species as naphtalene, fluorantene, crisene, pyrene and benzo(a)antrazene.

Literature on this subject is scarce. Mainly is focused in the pollutants found with poliuretane spume (PUFs) trapping molecules with lower molecular weights. In a recent paper we can found some data about the levels of PAHs in air from rural and urban areas in China. Levels are much higher than those found in the present work, maybe due to the differences in the sampling system, without differences in the profiles of both areas. [6]

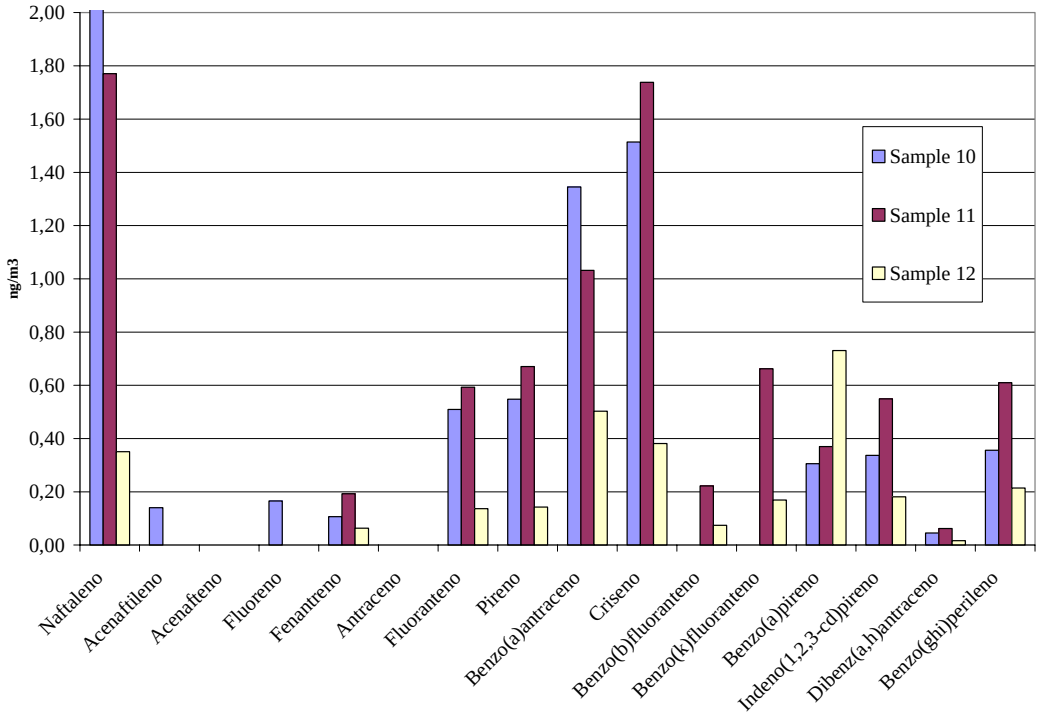

Figure 2: PAHs profile

Acknowledgements

Support for this work was provided by "Vicerrectorado de Infraestructura y Ampliación del campus", University of Alicante.

The authors acknowledge the Laboratory of Dioxins of the IIQAB-CSIC and Dr. Rivera their collaboration in this investigation.

References

1. Nessel SC, Butler JP, Post GB, Held JL, Gochfeld M, Gallo MA. J. *Exp. Anal. Environ. Epidemiol.* 1991; 1: 283.
2. Zemba SG, Green LC, Crouch AC, Lester RR. *J. Hazard. Mater.* 1996; 47 : 229.
3. "Compilation of EU Dioxin Exposure and Health Data. Summary Report" *Report produced for European Commission DG Environment UK Department of the Environment Transport and the Regions (DETR)*, October 1999. http://europa.eu.net
4. Turrio-Baldassarri L, Abate V, Iacovella N, Monfredini F, Menichini E. *Chemosphere*. 2005; 59 : 1517.
5. Abad E, Rivera J . "Dioxinas y furanos", Ministerio de Medio Ambiente, 2001. ISBN 84-498-1989-X
6. Duan X Bi, Tan J, Sheng G, Fu J. *Atmospheric Research.* 2005; 78 : 190.