ASSESSMENT OF THE IMPACT OF AN OLD MSWI. PART1 : LEVEL OF PCDD/Fs AND PCBs IN SURROUNDING SOILS AND EGGS

Catherine Pirard[1], Jean-François Focant[0], Anne-Cecile Massart[0], Edwin De Pauw[0]

[1]Mass Spectrometry Laboratory, University of Liege

Introduction

This paper reports dioxin and PCB concentrations in soils and chicken eggs collected near an old municipal solid waste incinerator (MSWI). The specimens were collected in 11 homes from Maincy (France), a rural area located 60km south of Paris and 5km from Melun, a 40000 inhabitants industrial city. Less than 2km away from Maincy stands the Vaux-le-Pénil MSWI. It began to operate in 1974 and was closed in June 2002 following a dioxin measures campaign of atmospheric emission. The facility with a capacity of 4 t/h, handled approximately 40000 tons of domestic waste per year, without any specific dioxin removal. Measured dioxin level was 226 ngTEQ/Nm³, more than 2000 fold higher than the actual European norm of 0.1ngTEQ/Nm³.

Methods and Materials

Sampling:

Selected sites were located between 1000 and 1500 m from the MSWI, under the prevailing wind stream (NE), except one situated about 2000 m south away from the incinerator. Characteristics of sites sampled are gathered in Table 1. For each site, soil was sampled 10 cm deep, at 2 distinct randomly selected spots, in private garden where chickens were foraging. After dried for one night at 100°C, they were kept into polyethylene (PE) sampling bags at room temperature. Between 4 and 6 eggs from each site were hard-boiled and separated yolks were pooled and placed at –20°C in PE vials.

Analytical method:

Chemicals, standard solutions and detailed procedures for analysis of dioxins and PCBs in eggs have already extensively been described previously[1, 2]. Briefly, extractions were performed by pressurized liquid extraction (ASE™ 200, Dionex, Sunnyvale, CA, USA). Hexane was used for hard-boiled yolk mixed to sodium sulfate, and toluene was used for dried and grinded soils, added to acidic silicagel. Further cleanup of all extracts was carried out using the automated Power-Prep™ (FMS Inc., Waltham, MA, USA) system using acidic silica, basic alumina and PX-21 carbon columns, and an additional high capacity disposable silica column for yolk extract. The PCB fraction, containing the 7 markers (A1260) and the mono-*ortho* PCBs, was analyzed by tandem in time mass spectrometry (GC-MS/MS) using a PolarisQ ion trap mass spectrometer (Austin, Tx, USA) coupled to a ThermoQuest Trace gas chromatograph. Final measurement of PCDD/Fs and c-PCBs was performed by GC-HRMS using an Autospec Ultima (Micromass, Manchester, UK) high resolution mass spectrometer and an Agilent (Palo Alto, CA, USA) 6890 Series GC equipped with a Rtx 5-MS (40m x 0.18mm ID x 0.20µm film thickness) capillary column (Restek, Evry, France).

Table 1 Characteristics of the selected sites.

Site #	Distance from MSWI	Direction	Type of housing	Space/hen (meters²)	Eggs/day	Age (years)	Commercial feed	Table scrap supplement	Household waste fire	Domestic heating	Chimney fire
1	1500 m	NE	lawn	150	1	1	yes	yes	no	natural gas	yes
2	1250 m	NE	agric. land	70	1	3	no	no	no	-	-
3	1250 m	NE	hens house	3	1/2	5	yes	yes	-	wood stove	yes
4	1500 m	NE	hens house	3	1/2	1-3	yes	yes	-	fuel oil	no
5	1000m	NE	lawn	125	1/2	1	yes	yes	yes	fuel oil	yes
6	1000m	NE	lawn	8	1/3	1-3	yes	no	no	natural gas	yes
7	1500m	N	lawn	40	1	1-3	yes	no	yes	electricity	yes
8	2250m	NE	lawn	33	1/2	1	yes	no	yes	wood stove	yes
9	1300m	NE	lawn	38	1	2	yes	no	yes	electricity	no
10	1250m	NE	lawn	333	1/2	0-7	yes	no	yes	fuel oil	no
11	2000m	S	hens house	20	1	1-2	yes	no	-	fuel oil	yes

Results and Discussion

Sums of the 7 dioxins, the 10 furans, the 4 non-*ortho* (77, 81, 126, 169), the 8 mono-*ortho* (105, 114, 118, 123, 156, 157, 167, 189) PCBs and congeners of the Aroclor 1260 (28, 52, 101, 138, 153, 180) are given in Table 2. Aroclor 1260 did not include PCB-28 and -52 for soil samples, and PCB-52 for eggs, because of them high LOQ value by the time of the measurement. PCB levels in soils were low, as those usually observed in Europe[3-6]. Dioxin and furan concentrations in most soils sampled were higher than the range of 1 to 10 pg-TEQ/g d.m. regularly found in rural, forest or pasture soils in Belgium, Germany, Luxembourg, Spain and U.K.[7]. Only two areas (#7 and #11) showed levels comparable to European background. Referring to German recommended limit values of PCDD/Fs in soils[8], site #7 was the only one showing dioxin level below the target value of 5 pgTEQ/g d.m. Site #5 was above the limitation for agricultural land uses (40 pgTEQ/g). All other soils were in the range of 5-40 pgTEQ/g, defined as acceptable range for unrestricted cultivation of foodstuff but for which of critical land use such as grazing management should be avoided. Following these recommendations, one should not encourage residents of Maincy to raise free-ranging chickens for egg production and consumption. Soils sampled around MSWI older than 20 years have been proven to be more contaminated than others, with characteristic OCDD and HpCDD of combustion pattern [9-11]. Values up to 55 pgTEQ/g d.m. were found in Spain, in Italy or in USA, in the vicinity of facilities dating from 1973 to 1983. Levels in soils from Maincy, as well as patterns, fully converge to those data. Both of particularly low contaminated areas (soils #7 and #11 were the ones not located in the North-East from the MSWI, the prevailing wind direction.

Principal component analysis (PCA) was performed to compare pattern of the ten soils from Maincy and some European data gathered from recent literature[9, 11-15]. The 17 variables were concentration of individual 2,3,7,8-substituted congeners in term of percentage of the sum of all 2,3,7,8-substitued compounds. The three first components would explain 80.9% of the variance of the data set. The distribution of soils on the three first PC showed different patterns for soils. Soil #2 and #6 clearly stand out from other soil samples, and were quite similar to UK's soils affected by MSWI ash spillage. They were characterised by high content of HpCDD, HxCDF2, HxCDF4, and low chlorinated dioxin congeners (tetra- to hexa-CDD), and low content of OCDD and OCDF. Surprisingly, no backyard fire was reported around area #2 and #6. Nevertheless, Jimenez et al.[10] have observed this kind of fingerprint on non-urban soils and soils polluted by incineration of cars and illegal car scraps. Sites #1, #7 and #8 form another cluster which is highly positively correlated with HpCDD, weakly positively correlated with hexaCDDs, PeCDD and TCDD. This pattern is close to traffic emissions as described by Jimenez et al.[10] (high content of hexa-, hepta- and octa-CDDs) although soils collected near an important Belgian interchange freeway were characterised by low value of OCDD, and high value of low chlorinated furans (TCDF, PeCDF1, PeCDF2, HxCDF1 and HxCDF3). The other soils from Maincy were in the same cluster than the ones located in the vicinity of MSWI, but also than Belgian agricultural area and UK's urban or rural background. These soils were mainly characterised by high value of OCDD. PCA did not allowed to bring out connection between dioxin levels or pattern and specific location, type of soil sampled (lawn, agricultural land or upper manure layer from hen house), type of domestic heating (oil-fired, natural gas, stove or electricity), occasional or frequent backyard household waste incineration, or chimney fire. Available literature about congener specific PCB level in eggs is scarce, and very few describe situation for free-ranging chickens, while it is now well accepted that these latter are particularly exposed to environmental pollutants by mean of soil and insect ingestion. Two samples from area # 9 and #11 were well above the European norm of 200 ng/g of fat for the 7 marker PCBs. Other egg samples were less contaminated and could be legally commercialised but remain nevertheless between 6 and 25 fold higher than levels usually observed in Spain (2-5 ng/g fat) for commercial eggs[16, 17]. Amounts of dioxin-like PCBs in most European countries (0.1 to 0.6 pgTEQ/g fat)[16-18] are considerably below the values of 0.35 to 46.4 pgTEQ/g fat found in eggs from our study. It is noteworthy that all samples (except site #8) were above the maximum level of 3 pgTEQ/g fat authorized in Europe, only in taking account of coplanar and mono-*ortho* PCBs, whereas until now this limit is fixed for dioxins without counting dioxin-like compounds. They were also above concentrations observed by Traag et al.[19] in eggs laid by free-ranging chicken (6 pgTEQ/g fat). Dioxin levels in commercial eggs are around 1 pgTEQ/g fat, up to 2-4 pgTEQ when they are from free-range rearing, with values sometimes up to 36 pgTEQ/g of fat as observed in a German survey[20]. In the present work, 5 from the 11 egg pools (#6, #7, #8, #10 and #11) showed comparable levels than discussed just above, two of them (#3 and #9) were at 25 pgTEQ/g fat, the usual upper range, and 4 (from area #1, #2, #4 and #5) exhibited very high levels, above 70 pgTEQ/g fat. They were some of the most contaminated eggs dedicated for personal consumption. Levels are comparable to eggs from Oroville (Northern California, US) where a pentachlorophenol wood treatment facility had been devastated by large fires[21]. According to these authors, soil concentrations and foraging behaviour would be significantly associated with egg concentrations. In this study, PCDD/F levels in eggs were also rather correlated with levels in soils, but eggs from site#1, #2 and #4 showed high dioxin amounts compared to those found in associated soils. One (Site#2) of these 3 outliers might be explained by the absence of commercial feed available for hens. Animals get most of their feed from the environment (maize from farming, vegetation, soil organisms, etc). Hence, the intake from potentially contaminated soil would be bigger than for chickens for which commercial food was provided at libitum. For both other sites where very high dioxin contents were found in eggs, no evidence appears to us as potential explanation. On the other hand, we have not observed any influence of foraging behaviour or area size where chicken used to forage on dioxin concentration and pattern in eggs. Although it was suggest by Harnly et al.[21] and Schuler et al.[22].

From this survey and similarly to literature data, dioxin and furan congeners contribute to 80 to 90% of the total WHO-TEQ in most case. Although a value of 4.4 pgTEQ/g fat is measured for PCDD/Fs, this raised up to 57 pgTEQ when dioxin-like PCBs are included. This shows the importance of including PCBs in TEQ calculations

Conclusion

Although PCB levels in Maincy's soils were comparable to what observed in Europe, PCDD/F concentrations in most soils were markedly higher than usual background. PCA highlighted 3 distinct patterns including one typical pattern to soils located in the vicinity of MSWI. No difference in level or pattern has been observed between soils sampled in "the open air" or inside henhouse. Levels of PCDD/Fs in eggs were high and one should not encourage their consumption.
Concentrations in eggs and in soils were partly correlated.

Acknowledgements

This research was supported by the University of Liège and the "C.A.R.T.". Authors would also like to thank the mayor of Maincy, Mrs Coffinet as well as the participating population, for providing samples.

References

1. Focant J.-F. , Eppe G., Pirard C. and De Pauw E. (2001) J. Chromatogr. A 925, 207.
2. Pirard C., Focant J.-F. and De Pauw E. (2002) Anal. Bioanal. Chem. 372, 373.
3. Alcock R.E., Johnston A.E., McGrath S.P., Berrow M., Jones K.C. (1993) Environ. Sci. Technol. 27, 1918.
4. Backe C., Cousins I.T. and Larsson P. (2004) Environmental Pollut 128, 59.
5. Covaci A., Manirakiza P. and Schepens P. (2002) Bull. Environ. Contam. Toxicol. 68, 97.
6. Manz M., Wenzel K.-D., Dietze U. and Schüürmann G. (2001) Sci. Tot. Environ. 277, 187.
7. Compilation of EU Dioxin exposure and health data- task 2-page 6/13-table 2-Octobre 1999
8. Basler A. (1995) Environ. Sci. Pollut. Res. 2, 117.
9. Schuhmacher M, Granero S, Rivera J, Müller L., Llobet J.M. and Domingo J.L. (2000) Chemosphere 40, 593.
10. Jimenez B., Eljarrat E., Hernandez L.M., Rivera J. and Gonzalez M.J. (1996) Chemosphere 32, 1327.
11. Lorber M, Pinsky P, Gehring P, Braverman C,Winters D. and Sovocool W. (1998) Chemosphere 37, 2173.
12. Final report of the “Convention Région Wallonne n°981/3901”, December 2001.
13. Duatre-Davidson R, Sewart A, Alcock R.E, Cousins I.T. and Jones K.C. (1997) Environ. Sci. Technol. 31, 1.
14. Schuhmacher M, Granero S, Xifró A, Domingo J.L, Rivera J. and Eljarrat E. (1998) Chemosphere 37, 2127.
15. Rotard W., Christmann W. and Knoth W. (1994) Chemosphere 29, 2193.
16. Eljarrat E., Monjonell J. and Rivera J. (2002) J. Agric. Food Chem. 50, 1161.
17. Llobet J.M., Bocio A., Domingo, J.L., Teixido, A., Casas C., and Müller L. (2003) J. Food Protect. 3, 479.
18. Rose M., White S., Harrison N. and Gleadle A. (2001) Oragnohalogen Compds 52, 143.
19. Traag W., Portier L., Bovee T., van der weg G., Onstenk C., Elghouch N., Coors R., v;d; Kraats C. and Hoogenboom R. (2002) Organohalogen Compds 57, 245.
20. Malish R. (1998) Chemosphere 37, 1678.

21. Harnly M.E., Petreas M.X., Flattery J. and Goldman R. (2000) Environ. Sci. technol. 34, 1143.
22. Schuler F., Schmid P.and Schlatter Ch. (1997) Chemosphere 34, 711.

Table 2 Concentrations of PCBs and PCDD/Fs in soils and eggs from Maincy.

	Site # 1	Site # 2	Site # 3	Site # 4	Site # 5	Site # 6	Site # 7	Site # 8	Site # 9	Site # 10	Site # 11
SOILS (pgTEQ/g d.m.)											
PCBs											
A1260 [a]	< LOQs	17.16	-	41.23	21.89	< LOQs	8.73	15.78	24.40	-	14.79
mono-ortho	0.19	0.16	-	0.43	0.64	0.16	0.19	0.17	0.71	-	0.27
non-ortho	1.14	0.83	1.54	1.54	2.16	0.71	0.61	0.61	1.38	-	1.68
PCDD/Fs											
Dioxins	7.59	5.15	6.26	12.39	43.53	7.34	1.95	6.78	30.51	-	3.52
Furans	5.86	5.98	6.56	7.48	15.51	4.28	1.31	5.45	6.65	-	3.07
Total TEQ	**14.58**	**11.95**	**24.25**	**21.41**	**60.75**	**12.34**	**3.79**	**12.77**	**38.54**	**-**	**8.27**
EGGS (pgTEQ/g lipid)											
	Site # 1	Site # 2	Site # 3	Site # 4	Site # 5	Site # 6	Site # 7	Site # 8	Site # 9	Site # 10	Site # 11
PCBs											
A1260 [b]	28.10	50.82	43.41	120.36	37.84	49.80	140.74	27.01	298.97	111.27	310.46
mono-ortho	0.67	1.43	1.13	3.83	0.97	0.98	5.56	0.50	10.50	3.01	6.08
non-ortho	11.72	23.55	8.75	19.58	9.88	4.59	13.39	0.35	16.21	6.14	46.40
PCDD/Fs											
Dioxins	45.85	45.84	13.35	67.39	54.71	3.64	6.19	2.99	16.55	8.83	2.81
Furans	25.57	75.71	10.92	28.03	31.44	2.62	4.49	2.11	9.20	5.70	3.26
Total TEQ	**83.81**	**146.53**	**34.15**	**118.83**	**97.00**	**11.83**	**29.64**	**5.94**	**52.46**	**23.68**	**58.55**

[a] ng/g d.m.

[b] ng/g lipid