RESULTS FROM THE 5TH ROUND OF THE INTERCALIBRATION STUDY FOR PCDD/F, PCB AND PAH IN SEDIMENT

S. Raccanelli[1], A. Petrizzo[2], M. Favotto[1] and R. Pastres[2]

[1]Interuniversity National Consortium "Chemistry for the Environment" (Consorzio I.N.C.A.), Via delle Industrie 21/8, I-30175, Marghera (VE) – Italy; [2]Department of physical chemistry, University of Venice "Ca' Foscari", Dorsoduro 2137, I-30123, Venezia - Italy.

Introduction

Before 1999, when contaminated foodstuff was found in Belgium, in Italy PCB e PCDD/F could be determined with a sensibility as adequate as it is needed in food analysis only by five laboratories. As a follow up of this contamination event, some Italian laboratories began to update their analytical equipment in order to meet the increasing demand for routinary food controls, but in the year 2000 only three laboratories took part in international intercalibration studies[1,2].

In the year 2000, the Interuniversity National Consortium "Chemistry for the Environment" (INCA), prompted the CIND, i.e. the first Italian Intercalibration study for PCDD/F, in order to give to all Italian laboratories the possibility of intercomparing their analytical perfomances. Given the small number of Italian laboratories which could participate, foreign laboratories were also invited to join the study. The study was repeated in the following years and in this paper we present the results of the fifth CIND edition, which took place in 2005.

The success of these studies is demonstrated by the steady increase in the number of participating Italian laboratories which grew from 7 in 2000 to 21 in 2005. The peak in the participation was reached in 2004 with 51 laboratories, of which 33 were foreign ones.

It was decided to carry out the studies using real environmental matrices, namely sediment and fly ash. Since 2004, PAH were included, since, according to some recent literature, their toxicity may, in some instances, be of the same order of magnitude of the PCDD/F one.[3]

Methods and materials

In the 2005 edition of the study, two sets of sediment samples, both collected in the Lagoon of Venice, were sent to 55 laboratories for the analysis of PCDD/F, PCB and PAH. The first sediments were collected in the canals surrounding the Industrial area, which have been contaminated by the industrial residuals of chemical plants. On average, their contamination level is much higher than in the rest of the lagoon and, therefore, they were termed the HIGH set of samples. The set of samples termed LOW, was instead collected in the southern part of the Lagoon, which is affected by contamination sources other than the industrial ones.

After collection, large debris, >1cm, were separated from the sediment by hand. Subsequently, the sediment, about 50 Kg per set, was homogeneized "in situ" and then dried at low temperature, about 40°C, grinded and sieved, through a 100µm sieve. The material thus obtained, 20kg per set, were then homogeneized again and divided into five parts, which were analyzed twice, in order to ascertain the their homogeneity. After passing this test, the samples were stored in amber glass containers and sent to the participants.

Results

Of the total of 55 registered participants, 29 laboratories were able to report results before the set deadline. Among these, 21 laboratories were Italian ones. The results presented in this paper were obtained after a statistical treatment of the original data. The data were pretreated by setting the ND values as NA values. In this way, it was not necessary to assign arbitrary values, which could alter the results of the subsequent statistical treatments. The remaining data formed the data set named "raw data".

After calculating the mean and standard deviation values for each congener and for each sediment set, namely HIGH and LOW sediment sets, a second screening was performed, in order to remove the outliers.

A datum x_i was considered outlier and removed if:

$x_i < \mu - 2$ STD or $x_i > \mu + 2$ STD

were μ and STD indicated respectively the sample Standard Deviation.
The statistical treatment led to the elimination of 104 data, i.e. the 5.5% of the whole set of original data. On the remaining data, named "treated data", the following statistical indexes were computed: mean, median, standard deviation, Interquartile Range, and coefficient of variation. for each sediment type and class of compounds. We computed the z-scores coefficients, z_i, obtained by normalizing the data x_i:

$$z_i = \frac{x_i - \mu}{STD}$$

In order to estimate the overall toxicity of the samples, the TEQ of PAH were computed according to [3]. Then, the TEQ(PCDD/F + PCB) and TEQ(PCDD/F + PCB + PAH) values were calculated by summing the corresponding TEQ(PCDD/F), TEQ(PCB) and TEQ(PAH) values, only when simultaneously available.
Moreover, we tried to highlight the different resolutions, "high" and "low", and extraction techniques, "ASE", "SOXHLET" and "SHAKING", used by the laboratories.
The results are shown in the Tables 1 and 2, in which are reported, for each congener and for each matrix, the mean, μ, the standard deviation, STD, and the variation coefficient, CV, obtained by the laboratories which gave at least one valid determination, and in Fig. 1, in which are reported the values of TEQ(PCDD/F + PCB + PAH) and the corresponding z-scores for the high set.

Tab.1 PAH - Results from the two sediment sets "HIGH" and "LOW". All levels in ng/g.

PAH	HIGH			LOW		
	MEAN	ST.DEV.	CV%	MEAN	ST.DEV.	CV%
Benzo[a]anthracene	527	147	27.90%	42	12	29.70%
Chrysene	653	215	32.90%	45	12	27.39%
Benzo[b+j+k]fluoranthene	1935	647	33.43%	87	26	30.55%
Benzo[a]pyrene	723	223	30.83%	41	12	28.76%
Indeno[1,2,3cd]pyrene	764	225	29.52%	34	14	39.70%
Dibenzo[a,h]anthracene	260	112	43.10%	9	5	56.52%
Benzo[ghi]perylene	938	276	29.40%	38	16	42.30%
Total	5880	1532	26.05%	296	84	28.40%
TEQ(PAH)	1.1581	0.3411	29.45%	0.0619	0.0168	27.15%
TEQ(PCDD/F + PCB + PAH)	1.4867	0.3102	20.86%	0.0705	0.0180	25.53%

Tab.2 PCDD/F and PCB - Results from the two sediment sets "HIGH" and "LOW". All levels in ng/g.

PCDD/F	HIGH			LOW		
	MEAN	ST.DEV.	CV%	MEAN	ST.DEV.	CV%
2,3,7,8-TeCDD	0.0044	0.0011	24.95%	0.0001	0.0001	62.30%
1,2,3,7,8-PeCDD	0.0141	0.0043	30.66%	0.0006	0.0006	95.86%
1,2,3,4,7,8-HxCDD	0.0237	0.0058	24.27%	0.0007	0.0006	95.41%
1,2,3,6,7,8-HxCDD	0.0260	0.0057	21.70%	0.0008	0.0005	66.56%
1,2,3,7,8,9-HxCDD	0.0216	0.0055	25.49%	0.0006	0.0004	64.65%
1,2,3,4,6,7,8-HpCDD	0.3618	0.0771	21.30%	0.0064	0.0022	33.84%
OCDD	1.6298	0.3523	21.62%	0.0281	0.0157	55.98%
2,3,7,8-TeCDF	0.1190	0.0191	16.09%	0.0022	0.0011	50.15%
1,2,3,7,8-PeCDF	0.1606	0.0267	16.61%	0.0022	0.0007	30.91%
2,3,4,7,8-PeCDF	0.1471	0.0349	23.70%	0.0022	0.0007	32.79%
1,2,3,4,7,8-HxCDF	0.8103	0.1871	23.10%	0.0061	0.0020	32.06%
1,2,3,6,7,8-HxCDF	0.3769	0.0853	22.64%	0.0035	0.0010	27.90%
1,2,3,7,8,9-HxCDF	0.1234	0.0992	80.34%	0.0013	0.0011	84.60%
2,3,4,6,7,8-HxCDF	0.2192	0.0388	17.69%	0.0027	0.0008	29.39%
1,2,3,4,6,7,8-HpCDF	3.4483	0.8620	25.00%	0.0262	0.0052	19.66%
1,2,3,4,7,8,9-HpCDF	0.6282	0.1446	23.02%	0.0040	0.0024	59.51%
OCDF	10.0664	2.5433	25.26%	0.0406	0.0083	20.48%
TEQ	0.3212	0.0468	14.57%	0.0038	0.0012	33.21%
PCB	**HIGH**			**LOW**		
	MEAN	**ST.DEV.**	**CV%**	**MEAN**	**ST.DEV.**	**CV%**
PCB #77	2.0999	0.6564	31.26%	0.0431	0.0433	100.36%
PCB #126	0.1307	0.0345	26.37%	0.0027	0.0012	43.87%
PCB #169	0.0417	0.0134	32.05%	0.0008	0.0004	58.66%
PCB #81	0.0875	0.1394	159.35%	0.0028	0.0039	140.82%
PCB #105	6.7295	1.8961	28.18%	0.2153	0.0743	34.53%
PCB #114	0.3971	0.2951	74.32%	0.0132	0.0110	83.02%
PCB #118	18.8527	5.9910	31.78%	0.7025	0.2583	36.77%
PCB #123	0.8520	0.8561	100.49%	0.0409	0.0577	140.94%
PCB #156	2.1252	0.4679	22.02%	0.0809	0.0356	44.01%
PCB #157	0.5633	0.2903	51.54%	0.0197	0.0094	47.44%
PCB #167	1.3078	0.6733	51.48%	0.0483	0.0264	54.75%
PCB #189	0.4457	0.1067	23.93%	0.0112	0.0056	50.14%
TEQ (PCB)	0.0154	0.0060	38.71%	0.0004	0.0002	46.90%
TEQ(PCDD/F + PCB)	0.3475	0.0609	17.52%	0.0042	0.0013	31.18%

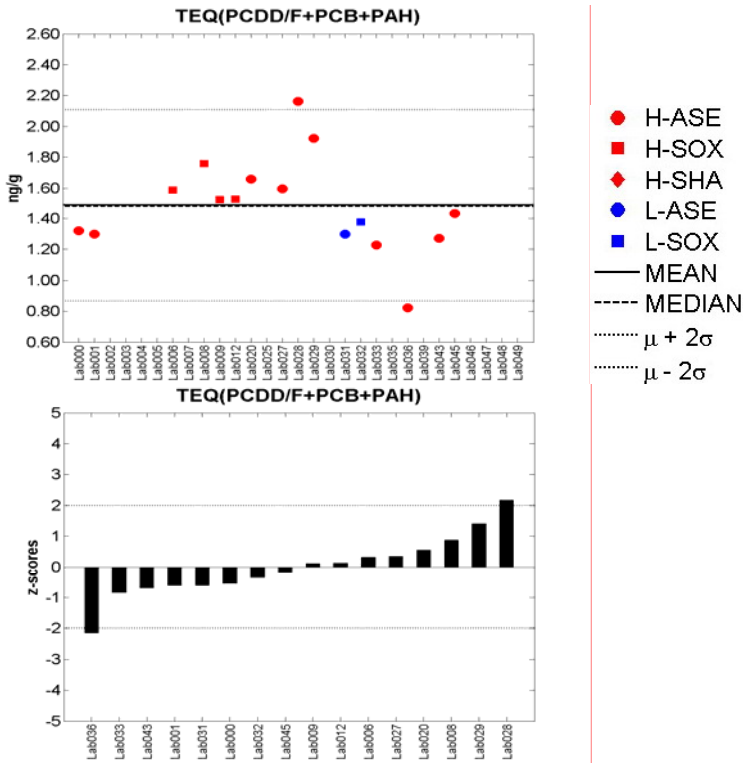

Fig.1 TEQ(PCDD/F + PCB + PAH) and the corresponding z-scores for the high set.

Conclusion

Of the participating laboratories to the 5th CIND edition, 53% were able to report the results for PCDD/f, PCB and PAH. Remarkably, 21 laboratories were Italian ones, compared with the 7 Italian laboratories which participated to the first edition, held in 2000. This increase demonstrates the usefulness of these intercalibration studies in improving the analytical standards in Italy. Furthermore, the five CIND editions has provided an archive of test samples, which are freely available upon request and could be used by laboratories for further testing their performances.

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