RESULTS FROM THE 6TH ROUND OF THE ITALIAN INTERCALIBRATION STUDY FOR PCDD/F, PCB AND PAH IN FLY ASH AND SEDIMENT

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Abstract
In this paper we present the results of the 6th Italian intercalibration study concerning the determination of PCBs, PCDD/Fs and PAHs. In comparison with the previous edition, the number of participant showed a 17% increase. In fact, the study involved 50 laboratories and results were delivered by the scheduled deadline by 20 Italian laboratories and 14 foreign ones. Three sets of samples, two fly ash and one sediment, were sent for the analysis of PCDD/F, PCB and PAH. The performance of each participant result was estimated by means of the z score. Tables and graphs summarizing the results and comparing the performances of the laboratories were compiled in a specific report, which was sent to all the participants. The possibility that the extraction methods and the resolution of the MS instruments could be a source of bias was investigated using statistical tests.

Introduction
In the year 2000, the Interuniversity National Consortium "Chemistry for the Environment" (INCA), prompted the 1st 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. In fact, in the year 2000 only three laboratories took part in international intercalibration studies[1,2]. Given the small number of Italian laboratories which could participate, foreign laboratories were also invited to join the study, which was repeated in the following years. PCBs dioxin-like were included in the list of the analytes in 2001 and PAHs were added in 2004, since, according to some recent literature, PAHs toxicity may, in some instances, be of the same order of magnitude of PCDD/Fs.[3] 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 34 in 2006. In this paper we present the results of the sixth CIND edition, which took place in 2006.

Methods and materials
In 2006, three sets of samples were delivered to 50 laboratories for the analysis of PCDD/F, PCB and PAH. A first set was taken from a real environmental matrix, namely sediment, collected in the Lagoon of Venice. The other two came from two incinerator fly ash affected by two contamination levels. These will be named High and Low sets in the following.
Sediment was collected and large debris, >1cm, were separated 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. Fly ash samples were grinded and sieved, through a 100µm sieve. The material thus obtained, 20kg per set, was then homogenized again and divided into five parts, which were analyzed twice, in order to ascertain their homogeneity. After passing this test, the samples were stored in amber glass containers and sent to the participants.

Results
Of the total of 50 registered participants, 34 laboratories, of which 20 were Italian ones, reported results by the set deadline. Results reported as non detected values were excluded from the evaluation: the data set thus obtained was named “raw data”. The results presented in this paper were obtained after a statistical treatment of the original data. After calculating the mean and standard deviation values for each congener and for each matrix, namely HIGH, LOW and SEDIMENT sets, outliers were removed according with the following criterion:

$$x_i < \bar{x}_i - 2s \qquad \text{or} \qquad x_i > \bar{x}_i + 2s$$

where $\bar{x}_i$ and *s* are, respectively, the sample mean and the sample standard deviation.

The application of this criterion led to the removal of 160 data, i.e. the 6.0% of the whole set of original data. On the remaining data set, named "treated data", the following statistical indexes were computed: mean, median, standard deviation, Interquartile Range, and coefficient of variation, for each matrix and class of compounds. The performance of each participant result was estimated by means of the z-scores coefficients, z_i:

$$z_i = \frac{x_i - \bar{x}}{s}$$

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.

The results are shown in the Tables 1-3, in which are reported, for each congener and for each matrix, the sample mean, $\bar{x}_i$, the sample standard deviation, *s*, 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.

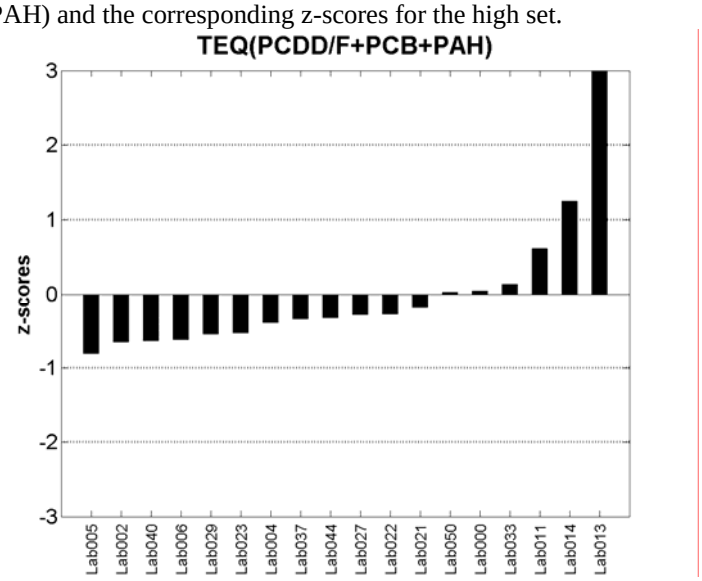

Fig.1. TEQ(PCDD/F + PCB + PAH) and the corresponding z-scores for

Tab.1 PAH - Fly ash, "HIGH" and "LOW" and sediment results. Concentrations are in ng/g.

PAH	HIGH			LOW			SEDIMENT		
	MEAN	ST.DEV.	CV%	MEAN	ST.DEV.	CV%	MEAN	ST.DEV.	CV%
Benzo[a]anthracene	263.1306	79.2338	30.11%	2.4218	2.3422	96.71%	43.6637	17.6002	40.31%
Chrysene	672.0418	281.8789	41.94%	3.1392	2.7382	87.23%	44.0663	14.5968	33.12%
Benzo[b+j+k]fluoranthene	989.3323	548.2431	55.42%	3.9291	6.8581	174.55%	94.1528	60.7245	64.50%
Benzo[a]pyrene	125.1771	76.9083	61.44%	1.4003	2.2933	163.77%	45.0426	25.1822	55.91%
Indeno[1,2,3cd]pyrene	355.0369	198.1956	55.82%	2.5841	6.1796	239.13%	35.3114	16.0124	45.35%
Dibenzo[a,h]anthracene	61.0208	38.2158	62.63%	1.0843	2.5287	233.22%	9.6554	6.0142	62.29%
Benzo[ghi]perylene	463.4341	245.9841	53.08%	2.0219	4.6030	227.65%	34.7965	17.2024	49.44%
Total	2939.302	1328.498	45.20%	15.6854	20.5470	130.99%	291.8541	124.7441	42.74%
TEQ(PAH)	0.5099	0.2509	49.20%	0.0028	0.0033	116.13%	0.0657	0.0353	53.69%

Tab.2 PCDD/F - Fly ash, "HIGH" and "LOW" and sediment results. Concentrations are in ng/g.

PCDD/F	HIGH			LOW			SEDIMENT		
	MEAN	**ST.DEV.**	**CV%**	**MEAN**	**ST.DEV.**	**CV%**	**MEAN**	**ST.DEV.**	**CV%**
2,3,7,8-TeCDD	0.0527	0.0125	23.75%	0.0007	0.0006	91.44%	0.0003	0.0004	119.26%
1,2,3,7,8-PeCDD	0.3976	0.0861	21.65%	0.0010	0.0008	73.94%	0.0008	0.0009	109.82%
1,2,3,4,7,8-HxCDD	0.4091	0.0725	17.73%	0.0014	0.0014	98.38%	0.0009	0.0011	133.38%
1,2,3,6,7,8-HxCDD	1.0904	0.2834	25.99%	0.0020	0.0022	111.66%	0.0014	0.0020	150.68%
1,2,3,7,8,9-HxCDD	0.8465	0.2652	31.33%	0.0027	0.0028	103.39%	0.0012	0.0016	124.96%
1,2,3,4,6,7,8-HpCDD	5.4721	1.0264	18.76%	0.0030	0.0035	114.65%	0.0128	0.0180	141.12%
OCDD	4.7720	2.8309	59.32%	0.0195	0.0303	154.99%	0.0304	0.0123	40.63%
2,3,7,8-TeCDF	0.7477	0.2124	28.40%	0.0009	0.0007	81.89%	0.0025	0.0017	68.56%
1,2,3,7,8-PeCDF	1.4750	0.2133	14.46%	0.0015	0.0013	84.69%	0.0042	0.0092	219.49%
2,3,4,7,8-PeCDF	1.8262	0.4671	25.58%	0.0015	0.0017	114.68%	0.0044	0.0093	208.42%
1,2,3,4,7,8-HxCDF	2.0897	0.4324	20.69%	0.0027	0.0044	161.76%	0.0070	0.0031	44.49%
1,2,3,6,7,8-HxCDF	2.1470	0.5615	26.15%	0.0031	0.0041	132.51%	0.0044	0.0037	82.45%
1,2,3,7,8,9-HxCDF	0.6537	0.5804	88.77%	0.0036	0.0041	114.58%	0.0021	0.0023	109.10%
2,3,4,6,7,8-HxCDF	1.9779	0.7385	37.34%	0.0053	0.0088	167.39%	0.0039	0.0046	120.43%
1,2,3,4,6,7,8-HpCDF	5.8170	0.9178	15.78%	0.0088	0.0161	182.63%	0.0314	0.0131	41.66%
1,2,3,4,7,8,9-HpCDF	1.4403	0.3208	22.27%	0.0082	0.0099	120.70%	0.0047	0.0026	55.48%
OCDF	5.0769	1.4296	28.16%	0.0154	0.0267	173.29%	0.0443	0.0134	30.38%
TEQ	2.5666	0.4581	17.85%	0.0034	0.0045	131.45%	0.0057	0.0066	117.02%

Tab.3 PCB - Fly ash, "HIGH" and "LOW" and sediment results. Concentrations are in ng/g.

	HIGH			LOW			SEDIMENT		
	MEAN	**ST.DEV.**	**CV%**	**MEAN**	**ST.DEV.**	**CV%**	**MEAN**	**ST.DEV.**	**CV%**
PCB #77	1.0987	0.3341	30.41%	0.0097	0.0093	95.91%	0.0347	0.0101	29.03%
PCB #126	0.6884	0.1820	26.43%	0.0012	0.0011	90.23%	0.0043	0.0016	37.03%
PCB #169	0.2443	0.0710	29.05%	0.0007	0.0009	130.27%	0.0011	0.0007	64.50%
PCB #81	0.2450	0.1130	46.11%	0.0026	0.0049	188.65%	0.0032	0.0064	199.97%
PCB #105	3.6399	0.8797	24.17%	0.0184	0.0184	100.29%	0.2202	0.0421	19.10%
PCB #114	0.2960	0.1400	47.30%	0.0012	0.0012	98.31%	0.0082	0.0023	28.25%
PCB #118	7.6959	2.3044	29.94%	0.0500	0.0608	121.80%	0.7145	0.1519	21.26%
PCB #123	0.3456	0.3271	94.66%	0.0024	0.0019	79.02%	0.0211	0.0195	92.63%
PCB #156	1.6594	0.4659	28.08%	0.0059	0.0072	120.50%	0.0780	0.0125	16.02%
PCB #157	0.5302	0.3383	63.80%	0.0016	0.0020	125.66%	0.0186	0.0032	17.15%
PCB #167	0.6540	0.2455	37.54%	0.0032	0.0034	104.53%	0.0485	0.0356	73.46%
PCB #189	0.4640	0.0776	16.73%	0.0009	0.0008	91.58%	0.0100	0.0030	29.48%
TEQ (PCB)	0.0710	0.0236	33.21%	0.0002	0.0002	153.65%	0.0005	0.0003	61.44%
TEQ(PCDD/F + PCB)	2.6848	0.4647	17.31%	0.0039	0.0061	154.13%	0.0246	0.0906	368.67%

Discussion

We tried to assess whether the differences in the extraction techniques or in the resolution of the MS could be a source of bias. A non-parametric statistical test, U-test, was used for comparing the median values obtained using different extraction techniques, "ASE", "SOXHLET", "MICROWAVE" or "ULTRASONIC". The results of the test did not evidence any statistical difference, at a p-level of 0.05, for 94% of the PCDD/Fs, 98% of PCBs and almost the 100% of PAHs. Instead, differences between medians were found to be significant in 48% of the PCDD/F congeners and in the 16% of the PCB congeners, when the test was applied to the comparison of the median values obtained by using HRMS vs those obtained using LRMS or LRMS/MS.

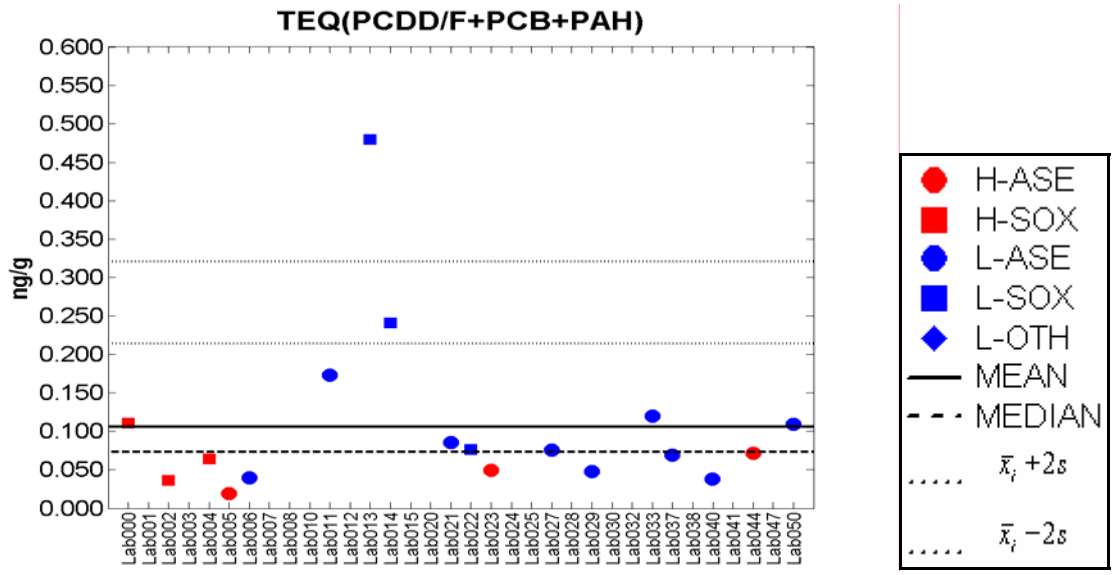

Fig. 2. Comparison among the estimates of the Total Equivalent Toxicity, in relation to the extraction methods(ASE: ASE; SOX: SOXHLET; OTH: MICROWAVE and ULTRASONIC) and the MS resolution (H: HRMS; L: LRMS and LRMS/MS).

Conclusion

The increase in the quality of the laboratories participating to the intercalibration study is proved by the fact that 53% of the laboratories were able to report the results for PCDD/f, PCB and PAH. Remarkably, 20 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 six 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.

Acknowledgement

The authors wish to thank Dr. Ivano Battaglia and Dr. Simona Manganelli, without whom these studies could not have been held with yearly frequency, and the Mass Spectrometry Division of the Italian Chemical Society, which has given its patronage to all CIND editions.

References

1. van Bavel B., Fifth Round of the International Intercalibration Study, Umea University, 2000.
2. Lindström G., Småsuen Haug L., Nicolaysen T., Intercalibration on Dioxin in Food, Folkehelsa, 2000.
3. Klimm C., Hofmaier A.M., Schramm K.W., Kettrup A. (1999), Using TEF concept for assessing toxic potency of polycyclic aromatic hydrocarbons in industrial samples. *Organohalogen Compouds*, 40, 39-42.