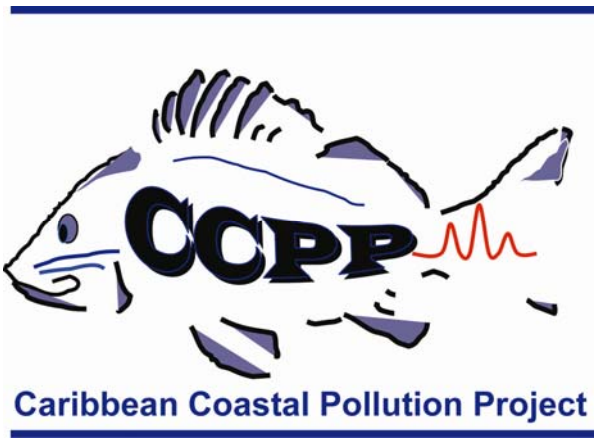
Caribbean Coastal Pollution Project (CCPP)

Inter-laboratory Comparison of the Analysis of Persistent organic Pollutants (POPs) in Certified Reference Material (CRM)



Final Report

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Introduction:
In order the assess the capacity of the regional laboratories at CINVESTAV and UWI Mona to analyse fish tissues for PCBs and organochlorine pesticides, an inter-laboratory comparison exercise was initiated involving analysis of IAEA-435 tuna homogenate by Trent University, the University of Windsor, UWI Mona in Jamaica and CINVESTAV in Mexico. Each laboratory conducted analysis of the CRM using independent analytical methods. The analytical results were compared between laboratories and relative to the certified concentrations provided with the material.

Methods:

All laboratories conducted analyses of the IAEA-435 certified reference material (CRM) of tuna homogenate. All laboratories extracted subsamples (n=7) of approximately 1 gram of the CRM material. Table 1 summarizes the preparation methods and analytical instrumentation used by the four laboratories for analysis of the CRM. The target compounds for the inter-laboratory comparisons are listed in Table 2:

Table 1: Methods used for sample preparation and analysis of the CRM at the four laboratories involved in the inter-laboratory comparison exercise.

	Windsor (GLIER)	**Trent**	**UWI Mona**	**CINVESTAV**
Extraction	Cold column	Cold column	Cold column	Solvent permeation
Lipid removal	GPC[1]	GPC	GPC	GPC (semi-automated)
Fractionation	Florisil	Silica	Florisil	Florisil
Analysis	GC-ECD (Agilent 7890)	GC-ECD (Varian Saturn)	GC-ECD (Agilent 7890)	GC-ECD (Hewlett Packard 5890)

1) GPC = Gel permeation chromatography

It should be noted that all laboratories except the CINVESTAV lab had access to analytical instruments that were purchased within the past 5 years, whereas the CINVESTAV lab used an older model Hewlett Packard 5890 Series II instrument for all analyses because of delays in the delivery of a new Agilent GC-ECD. The target compounds included in the inter-laboratory comparisons are listed in Table 2:

Table 2: List of target compounds included in the inter-laboratory comparison exercise for the analysis of the IAEA-435 tuna homogenate.

Organochlorine pesticides

- ∑ chlordanes: *cis*-chlordane, *trans*-chlordane, *oxy*-chlordane
- ∑ DDTs: o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT
- Aldrin
- Dieldrin
- Endrin
- Heptachlor
- *cis*-heptachlor epoxide
- *trans*-heptachlor epoxide
- Mirex

PCBs:

Congener numbers 17/18, 28/31, 33, 44, 49, 52, 70, 74, 82/151, 87, 66/95, 99, 101, 105/132, 110, 118, 128, 138,149,153, 156/171, 158, 170, 177, 180, 183, 187,191, 194,195/208,199/201,205, 206, 209

Results and Discussion:

The data illustrated in Figure 1 show the mean concentrations of PCB congeners determined in the analyses by the four laboratories relative to the certified mean values provided by the IAEA and the variance around those mean values (black squares with error bars). The data points where laboratories generated data that were outside of the acceptable range of the certified values are circled. The data indicate that the CINVESTAV lab generated values that were higher than the acceptable range for 11 of the PCB congeners with higher degrees of chlorination, whereas the GLIER lab generated values that were below the acceptable range for two of the less chlorinated PCB congeners. The UWI Mona lab was outside of the acceptable range for two of the congeners and the Trent lab was outside of the range for one congener. However, the relative concentrations of the PCB congeners were generally consistent across the four laboratories.

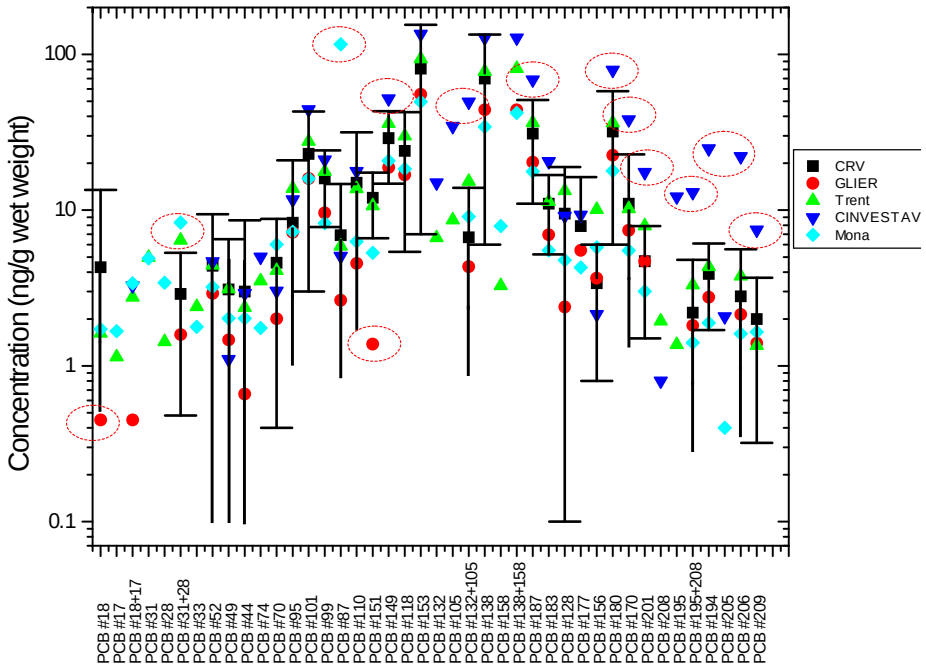

Figure 1: Mean concentrations (ng/g wet weight) of PCB congeners analyzed in the IAEA-435 tuna homogenate by the four participating laboratories relative to the mean and accepted range of values provided for the CRM.

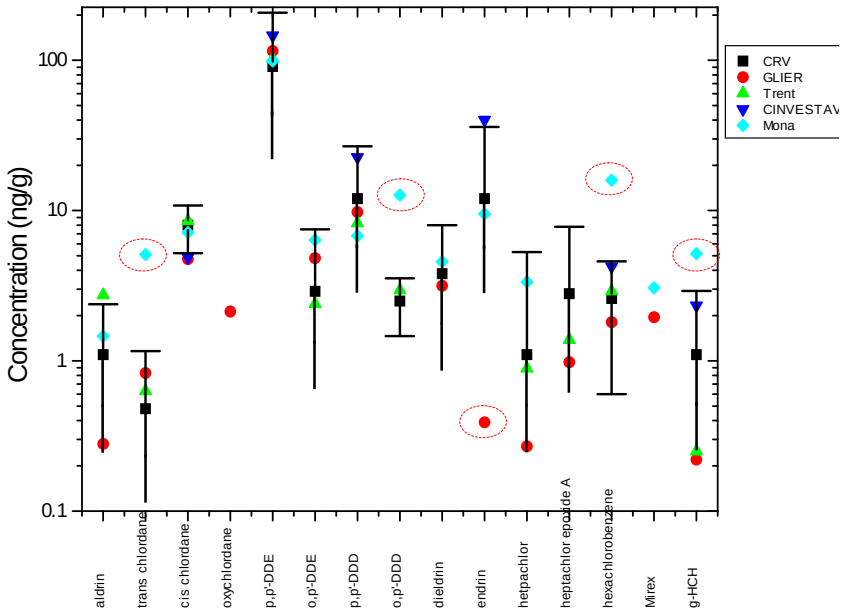

Figure 2: Mean concentrations (ng/g wet weight) of organochlorine pesticides analyzed in the IAEA-435 tuna homogenate by the four participating laboratories relative to the mean and accepted range of values provided for the CRM.

The results for the analysis of organochlorine pesticides illustrated in Figure 2 show that the UWI Mona lab had mean concentrations that fell outside of the acceptable range of concentrations for four of the pesticides, and the GLIER lab had one value that fell outside of the acceptable range. Once again, however, the pattern for the relative concentrations of the target analytes were generally consistent among the laboratories.

Overall, these results indicate that the regional laboratories have the capacity to generate analytical data for PCBs and organochlorine pesticides that are within acceptable limits of variability, or exceed or fall short of the acceptable limits by less than an order of magnitude. In the opinion of the analytical experts at the University of Windsor (GLIER) and Trent University who were participating in the inter-laboratory comparison exercise, the performances of the regional laboratories at UWI Mona and CINVESTAV were sufficiently satisfactory to proceed to analysis of samples of white grunt for the monitoring study of POPs contamination within the wider Caribbean region. However, it must be recognized that the IAEA-435 tuna homogenate CRMs were not an ideal surrogate for the analysis of white grunt tissues as the levels of PCBs were relatively high and the levels of organochlorine pesticides were relatively low in these samples, compared to the low PCBs and higher organochlorine pesticides expected in fish samples from the Caribbean.

Conclusions:

The two regional laboratories at UWI Mona and CINVESTAV are qualified to analyze fish samples for the target PCBs and organochlorine pesticides, provided that there is external oversight of the analytical data (i.e. by Windsor and Trent). However, these two laboratories should immediately implement a Quality Control/Quality Assurance program to monitor and validate their performance, including:

1) Documentation of method validation procedures
2) Determination of method detection limits
3) Monitoring of recoveries of internal standards
4) Formalized assessment of the analysis of standard reference materials (SRMs), such as the NIST 1974 SRM (Lake Michigan fish)
5) External laboratory audits of QA Procedures
6) Participation in other programs for round-robin comparisons.