Results of the Northern Contaminants Program Phase 9 Interlaboratory Study

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Introduction

- The Northern Contaminants Program (NCP) Quality Assurance/Quality Control (QA/QC) Program assesses the performance of laboratories providing data to NCP and the Arctic Monitoring and Assessment Programme (AMAP).
- The interlaboratory study involves analysis of biological tissue certified reference materials and injection-ready analytical standards for trace metals and persistent organic pollutants.
- The number of participating laboratories increased to 47 from 46 in the previous study and has doubled since Phase 1 (19 laboratories in 2005/2006).
- This ongoing international study provides a valuable data set for evaluating data comparability between laboratories reporting concentrations of emerging contaminants in natural matrices.

Interlaboratory Study Design

- Total number of participating laboratories was 47.
- Each laboratory selected target contaminant groups for which analysis would be performed (Table 1).
- Analysis of natural matrix samples and/or injection-ready analytical standards (Table 2) was performed for selected target contaminants.

Table 1. *Target contaminant groups and number of laboratories providing results*

Contaminant Group	Acronym	# of Labs	# of NCP Labs	# of AMAP Labs
Polybrominated Diphenyl Ethers	PBDEs	18	8	10
Brominated and Chlorinated Flame Retardants	BFRs/CFRs	11	6	8
Dioxins/Furans/Dioxin-Like Polychlorinated Biphenyls	PCDD/PCDF /DLPCBs	12	2	5
Organochlorine Pesticides	OCs	20	5	10
Polychlorinated Biphenyls	PCBs	22	6	12
Perfluoroalkyl Acids	PFAAs	14	5	7
Polychlorinated Naphthalenes	PCNs	6	3	4
Chlorinated Paraffins	CPs	2	1	1
Organophosphorous Flame Retardants	OPFRs	4	2	2
Trace Metals	TMs	17	3	8
Mercury	Hg	26	9	12
Methyl Mercury	MeHg	11	4	6

Table 2. *Natural-matrix samples and standards with corresponding sample sizes*

Matrix	NCP III-9 Sample ID	Description	Sample Size
Natural-Matrix Samples	S1	Lake Huron Carp tissue[1]	10 g
	S2	Lake Ontario Chinook Salmon tissue[2]	10 g
	S3	Lake Ontario Lake Trout tissue[3]	10 g
	S4	Mediterranean mussel tissue[4]	10 g
	S5	Lake Trout extract in hexane[5]	5 mL
	S6	Blank nonane[5]	5 mL
	S7	Blank methanol[5]	5 mL
Injection Ready Analytical Standards (IRSs)	PBDE-5	20-120 ng/mL, toluene[6]	1.2 mL
	BFRs/CFRs-2	200-2400 ng/mL, toluene[6]	1.2 mL
	DFDLP-4	20-120 ng/mL, nonane[6]	1.2 mL
	PCBs-5	40-290 ng/mL, nonane[6]	1.2 mL
	OCs-3	0.2-2.0 µg/mL, isooctane[6]	1.2 mL
	PFC-4	160-410 ng/mL, methanol[6]	1.2 mL
	PCN-4	100-300 ng/mL, nonane[6]	1.2 mL
	OPFRs-2	500-1000 ng/mL, toluene[6]	1.2 mL
	CP-1	C10-C13, 63% Cl, 8000 ng/mL, isooctane[5]	2 mL
	CP-2	C10-C13, 51.5% Cl, 500 ng/mL, isooctane[5]	2 mL
	TM-1	50-500 µg/mL, water (2% nitric acid)[7]	2.5 mL
	TM-2	75-150 µg/mL, water (2% nitric acid)[7]	2.5 mL
	Hg	5 ng/mL, water, 0.2% hydrochloric acid[8]	1.5 mL
	MeHg	1 ng/mL, water, 0.2% hydrochloric acid[9]	1.5 mL

Data Evaluation

- Results were evaluated using the statistical method "Robust Statistics: A Method of Coping with Outliers."[10]
- Analysis offers characterization of small sample size data sets without removal of outliers by assigning these values a lesser weight.
- Analysis was performed for analytes with a number of data points ≥ 3.

  Robust Study Average = Median ($\hat{\mu}$)

  Robust Standard Deviation ($\hat{\sigma}$) = 1.5 × Median Absolute Deviation

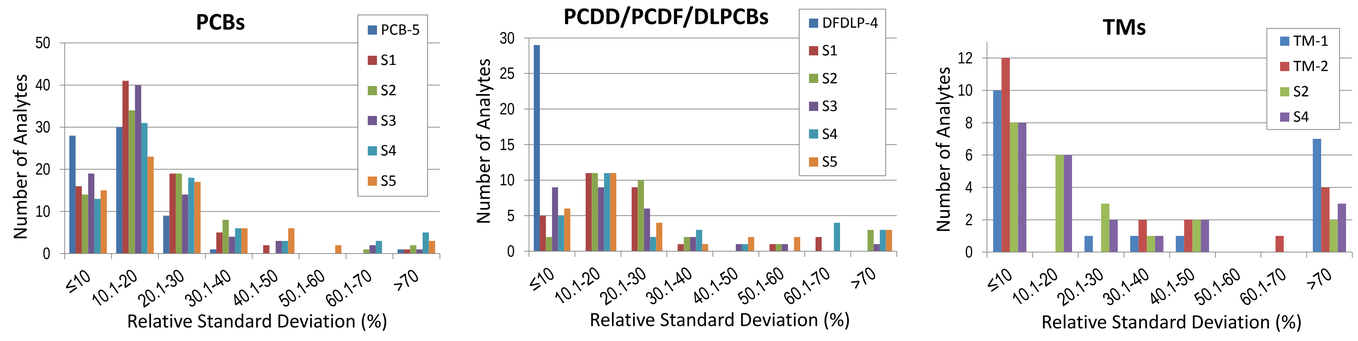
- Z-scores[11] were calculated as an alternative measure of proficiency as follows:

  $Z = (\text{data point} - \hat{\mu}) / \hat{\sigma}$

Results and Discussion

Interlaboratory Variability

- Laboratories showed higher variability for analysis of biological tissue samples relative to analytical standards.
- Low variability was observed for PCBs, PCDD/PCDF/DLPCBs, and TMs as demonstrated in the figures below.



Median Values vs. Design Values

- On average, median values were within 25% of corresponding design values for injection-ready standards (Figures 1-2) and natural matrix samples (Figures 3-5).

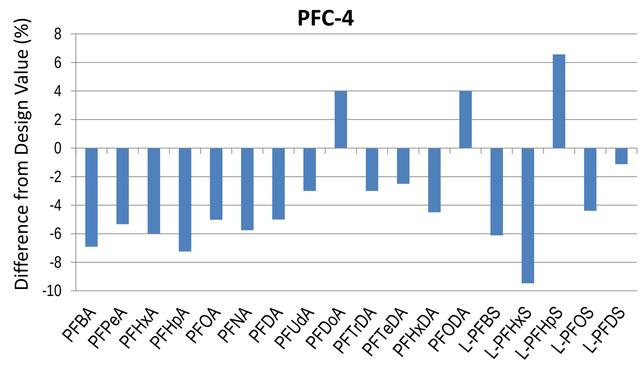


Figure 1. *Difference between study medians and design values for injection-ready PFC-4 analytical standard.*

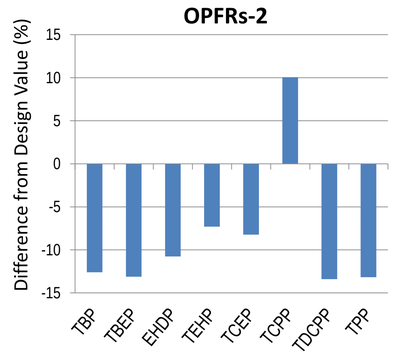
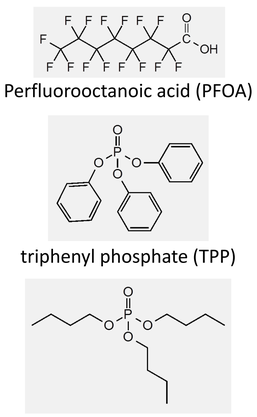


Figure 2. *Difference between medians and design values for OPFRs-2 standard.*



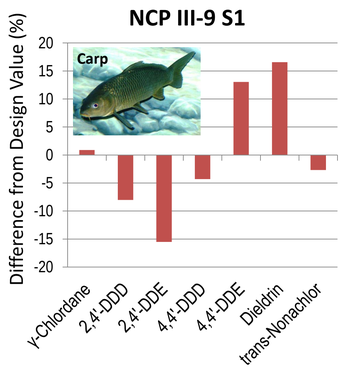


Figure 3. *Difference between medians and design values for OCs in NCP III-9 S1.*

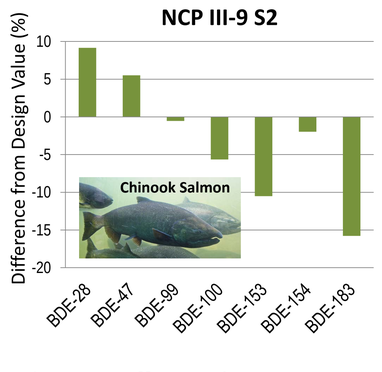


Figure 4. *Difference between medians and design values for PBDEs in NCP III-9 S2.*

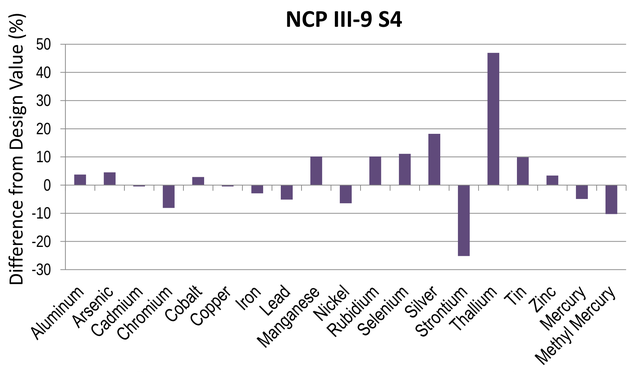


Figure 5. *Difference between study medians and design values for TMs, Hg, and MeHg in NCP III-9 S4.*

Z-Scores

- For PBDEs, PCDD/PCDF/DLPCBs, PCBs, OPFRs, TMs, and Hg, ≥80% of sample results had z-scores ranging between 2 and -2, indicating the percentage of acceptable data as defined by ISO 13528.[11]
- For all injection-ready standards, >80% of z-scores ranged between 2 and -2, with the exception of CPs, for which z-scores could not be calculated due to insufficient data.

Conclusions

- Increased participation helps expand the NCP QA/QC program database and improve data comparability of results.
- Assessing performance of emerging contaminants is an asset of the program due to the limited availability of natural matrix reference materials.
- The NCP III Phase 9 interlaboratory study final report will be completed in early 2016.
- The NCP III Phase 10 interlaboratory study will begin in January 2016 and is open to all interested laboratories.

References

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Acknowledgements

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