

Results from Laboratory Intercalibration Exercises in Southern California

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Southern California Intercalibration Exercises

- Bight 1998- Marine Sediment Intercalibration for DDTs, Congener PCBs, and PAHs using 2 locally derived materials
- Stormwater Monitoring Coalition- Intercalibration for Nutrients, TSS, and Metals using 2 locally derived simulated stormwater samples

Bight 1998

- Seven local public and commercial laboratories
- Performance-Based i.e. each lab used its existing methods
- All laboratories were ELAP certified
- Consensus-based RLs were chosen

Bight 98

- However reliance upon a priori performance demonstration with standardized methods may be unsatisfactory
 - 1) when new compounds are added,
 - 2) detection goals are set below the method capability,
 - 3) when sample matrix components confound the standardized methods,
 - 4) Or when standardized methods must be modified or replaced with non-standard methods in order to meet project specific goals

Bight 98

- Certified Reference Materials are often used to demonstrate performance capability but typically are not always certified for all compounds of interest in the range of concentration that may be obtained during a specific project
- Two local sediment samples were collected from Station 7C off Palos Verdes which is high in DDTs and PCBs, and Station E6 from Santa Monica Bay which is high in PAHs

Bight 98

- The process is the most critical component of achieving data comparability for the program
- Labs were given methodological freedom but some consensus-based restrictions were required:
 - 1) Minimum sample size needed to achieve project detection limit goals.
 - 2) GC column with a specific phase was required.
 - 3) Separation of 40 out of the 41 PCB congeners in our standard must be achieved.

Bight 98

- The Study included 3 phases
 1. Initial intercalibration to determine baseline comparability
 2. Informal studies to identify which lab procedures contributed the most to differences observed such as exchanging extracts
 3. Second round intercalibration exercise to assess improvements

PAHs

- For Total PAHs there were order of magnitude differences between the labs.
- Most of the difference was due to differences in detection limits. For example one lab reported detectable values in 20% of the compounds vs other labs reporting 100%.

PAHs (ng/dry g)

Round 1 Station E-6

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	%CV
Total PAHs	835	2420	7630	453	2960	2840	4030	3020 ± 2380	79

Round 2 Station E-6

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	% CV
Total PAHs	2573	3280	3650	3930	2610	3450	No Data	3390 ± 494	15

PAHs ng/dry g

Round 1 Station 7C

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	%CV
Total PAHs	137	1130	2300	177	1430	1280	1670	1160 ± 781	67

Round 2 Station 7C

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	% CV
Total PAHs	783	1570	1750	1420	1180	1300	No Data	1440 ± 224	15

DDTs and PCBs ng/dry g

Round 1 Station E6

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	%CV
Total DDTs	277	519	No Data	725	283	249	226	378 ± 182	48
Total PCBs	411	739	No Data	713	502	595	1030	657± 200	30

Round 2 Station E6

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	% CV
Total DDTs	No Data	579	521	541	297	299	No Data	447± 138	31
Total PCBs	No Data	678	732	688	513	562	No Data	635 ± 93	15

DDTs and PCBs ng/dry g

Round 1 Station 7C

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	%CV
Total DDTs	8460	16800	No Data	2190	19500	7350	6560	13400 ± 6760	50
Total PCBs	529	1950	No Data	1100	1920	785	1390	1280± 586	46

Round 2 Station 7C

Parameter	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Mean ± SD	% CV
Total DDTs	No Data	15500	19500	14400	8410	10900	No Data	13800± 4280	31
Total PCBs	No Data	1330	1500	1100	901	1080	No Data	1180 ± 232	20

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- Some of the method changes were related to extract dilutions and adjusting to high concentrations (DDTs), modification of extraction procedures to adjust to high concentrations, switching from older to newer instruments, interpretation of the chromatograms and identifying peaks, and consistent baselines between the labs

Bight 98

- The process itself is the key to success
- Two rounds of analyses
- Data was kept anonymous
- Meetings between the 2 exercises were conducted in a positive environment allowing open discussion of potential sources of the differences and information exchange
- Atmosphere of cooperation by the laboratories

SMC

- 14 laboratories
- Analytes and Reporting Levels were agreed upon prior to the exercise
- Reporting levels were based on one-half the lowest water quality threshold
- A calibration standard must include a point at or below the required RL

SMC

• Analyte	Units	Target RL
• TSS	mg/L	5
• NO3+NO2 as N	mg/L	0.2
• Ammonia as N	mg/L	0.1
• Total Phosphorus	mg/L	0.1
• TKN	mg/L	0.2
• TOC	mg/L	1

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• Analyte	Units	Target RL
• Arsenic	µg/L	2
• Cadmium	µg/L	1
• Chromium	µg/L	5
• Nickel	µg/L	4
• Lead	µg/L	1
• Selenium	µg/L	2
• Silver	µg/L	1
• Zinc	µg/L	10

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- Accuracy Goal of 80-120% except TKN and Total P was 70-130%
- Precision Goal of $\pm 20\%$
- One sample was simulated urban runoff from a parking lot
- Second sample was simulated rural runoff from a clean rural site
- Third sample was a certified solution purchased from ERA near expected sample concentration

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Warning Limit $\pm 2SD$; Control Limit $\pm 3SD$

Analyte	Units	ERA Mean	ERA Warning Limit	ERA Control Limit	LU Mean	LU Warning Limit	LU Control Limit	LR Mean	LR Warning Limit	LR Control Limit
TSS	mg/L	NA	NA	NA	122	11	16	337	83	124
NH3	mg/L	0.551	0.51	0.76	1.33	0.45	0.66	0.341	0.166	0.249
TKN	mg/L	0.796	0.554	0.834	2.95	0.89	1.33	3.64	2.13	3.19
Total P	mg/L	0.746	0.171	0.258	0.288	0.220	0.330	0.388	0.338	0.507
TOC	mg/L	NA	NA	NA	26.5	6.4	9.5	6.63	3.77	5.64
As	µg/L	7.05	1.59	2.38	3.13	0.81	1.22	2.58	1.14	1.70
Cd	µg/L	2.96	0.33	0.49	0.306	0.074	0.111	0.466	0.112	0.168
Cr	µg/L	30.2	3.4	5.2	5.51	2.08	3.12	13.2	4.2	6.4
Cu	µg/L	12.7	2.3	3.5	116	25	37	19.3	8.8	13.2
Pb	µg/L	7.10	0.71	1.06	8.74	1.30	1.96	8.87	2.53	3.77
Ni	µg/L	32.1	4.0	6.03	13.1	2.0	2.94	5.08	1.15	1.72
Se	µg/L	17.7	4.3	6.6	1.88	0.89	1.33	1.44	0.81	1.21
Ag	µg/L	6.74	1.18	1.77	0.106	0.041	0.063	0.069	0.060	0.09
Zn	µg/L	79.1	21.7	32.6	153	28	42	468	106	159

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Analyte	Units	ERA	LU	LR
TSS	mg/L	NA	5	12
NH3	mg/L	46	17	24
NO3+NO2	mg/L	5	8	10
TKN	mg/L	35	15	29
Total P	mg/L	11	38	43
TOC	mg/L	NA	12	28
As	µg/L	11	13	22
Cd	µg/L	6	12	12
Cr	µg/L	6	19	16
Cu	µg/L	9	11	23
Pb	µg/L	5	7	14
Ni	µg/L	6	7	11
Se	µg/L	12	24	28
Ag	µg/L	9	20	44
Zn	µg/L	14	9	11

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- Labs were given a letter grade based on accuracy and precision using a mean value with the outliers eliminated.
- Out of 14 Labs, 10 labs received an A, 2 Labs received a B, one Lab received a C , and one Lab received an F

SMC

- The same open/anonymous process was used
- It was concluded that several items needed to be specified within the methods to insure data comparability including sample homogenization and sub-sampling, TKN length time and temperature for the digestion, Total Phosphorus digestion standardization, and Trace Metals digestion time and temperature, and final sample volume

Conclusions

- Exercises must include a process for new labs to participate
- The intercalibration exercise for organics requires 2 rounds and information exchange to achieve comparability
- Being ELAP certified does not guarantee comparability
- These exercises require a large financial/time commitment by the labs
- Some QAQC parameters must be chosen such as the RL so that project goals are met