Making performance-based chemistry work: How we created comparable data among laboratories as part of a southern California marine regional assessment

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ABSTRACT- Quality assurance procedures to ensure consistency among chemistry laboratories typically involves the use of standard methods and state certification programs that require laboratories to demonstrate their ability to attain generic performance criteria. To assess whether these procedures are effective for ensuring comparability when processing local samples with potentially complex matrices, seven experienced, state-certified laboratories participated in an intercalibration exercise. Each laboratory was permitted to use their typical methodology for quantifying PAHs, PCBs, and DDT on shared samples collected from Santa Monica Bay and the Palos Verdes Shelf, two sites with a complex mix of constituents. In the initial intercalibration exercise, results from these laboratories differed by as much as an order of magnitude for all three chemical groups. Much, but not all, of the difference was attributable to differences in detection capability. A series of studies was conducted to identify the reasons for the observed differences, which varied among laboratories and included methodological differences, instrument sensitivity differences, and differing interpretations of chromatograms. Following these investigations and resulting modifications to laboratory procedures, the exercise was repeated. The average coefficient of variation among laboratories across all chemical parameters was reduced to less than 30%. Our results suggest that performance-based chemistry can produce comparable results, but the certification processes presently in place that focus on general laboratory procedures and simple matrices are insufficient to achieve comparability.

INTRODUCTION

Many environmental assessments require measurement and compilation of sediment chemistry data from multiple laboratories, either to extend temporal records for trends assessment or to extend geographic scale for spatial assessment. Such data compilations assume a degree of comparability among laboratories, even though analytical personnel, methods, and instrumentation may vary. Dissimilarity in sampling and sub-sampling techniques, sample preparation, clean-up procedures, detection capabilities, and instrumental techniques can all lead to differences in analytical results.

Data comparability is enhanced when the chemical analyses are conducted by State-certified laboratories that use standardized methods. The certification process requires laboratories to demonstrate their ability to attain generic performance criteria, but only partially satisfies the presumption of data comparability in real-world environmental assessments. Reliance on a *priori* performance demonstration with standardized methods may be unsatisfactory when new compounds are added to the analytical list, when detection goals are set below the demonstrated method capability, when sample matrix components confound the standardized methods, and when methods must be modified or replaced with non-standard procedures in order to meet project-specific goals.

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Standard reference materials (SRMs) are often used to help bridge such gaps and demonstrate performance capability among laboratories. However, SRMs fall short of the goal because certified values are typically present only for a subset of the target analytes and may be influenced by the limitations of the methods used to generate the certified results in the first place. Although SRMs are an important component in this process, additional steps may be necessary to insure high quality and comparable data.

To assess whether existing quality assurance criteria and analytical methods are effective for ensuring comparability when processing local samples with complex matrices, seven laboratories participated in an intercalibration exercise conducted as part of the Southern California Bight 1998 Regional Marine Monitoring Survey. All of the laboratories were certified by the State of California and had at least 10 years of experience. Here we present the results of that intercalibration exercise, identify reasons for observed differences, and discuss procedures important to increasing regional comparability with difficult samples and analytes.

METHODS

Sediment samples were collected from two locations in southern California. The first sample was collected from a station on the Palos Verdes Shelf (i.e., L.A. County Sanitation District Station 7C; Stull *et al.* 1986). This station was selected because it typically contains concentrations of DDT and PCB at the upper range as compared to other sediments in southern California. The second sample was collected from Santa Monica Bay (i.e., City of Los Angeles Station E-6; Bascom 1978). This station is known to have high concentrations of polynuclear aromatic hydrocarbons (PAHs). Both stations have complicated organic matrices as a result of decades of ocean disposal of municipal wastewater and various benthic processes. After collection, the sediment samples were thoroughly homogenized, divided, and placed into cleaned glass jars with Teflon® lids. They were then stored frozen at -20°C until distributed to the participating laboratories.

After receiving the frozen samples, each participating laboratory used their conventional sample preparation and analytical methods to measure PAHs, DDT, and PCBs. Extraction methods are presented in Table 1. Each laboratory was also allowed to use its own gas chromatographic (GC) detector providing they could obtain a specified Method Detection Limit (MDL). The GC Detectors used for this study included electron capture detectors, quadrupole mass spectrometers, and ion trap mass spectrometers.

While laboratories were given considerable methodological freedom, there were several consensus-based restrictions that were placed to ensure consistent MDLs and reporting limits (RLs) among laboratories. First, a minimum sample size of 10 grams dry weight was specified because some techniques cannot handle larger sample sizes; but a minimum of 10 grams was required to reach the MDL required for the survey. Second, the GC column was restricted to the equivalent of a J&W DBXLB (Frame *et al.* 1996) for DDT/PCB analysis and to a DB-5 for the analysis of PAH. For electron capture detection, DB-5 was recommended, but not required, as the second column for verification purposes. Moreover, each laboratory was required to demonstrate that its chromatographic conditions, e.g. oven temperature ramping rate, separated 40 out of 41 congeners from our custom PCB Calibration standard.

This study included three phases. The first phase was an initial intercalibration exercise designed to determine how well the laboratories compared using their existing sample preparation and analytical methods. The second phase involved a series of informal studies to identify which laboratory procedures were contributing most to observed differences among laboratories. For example, these laboratory studies included the distribution of one laboratory's extract to other laboratories to determine if the observed differences were due to analysis of the extracts versus the extraction procedure itself. The third and final phase involved redistribution of the original intercalibration samples to assess whether the laboratory improvements identified in the laboratory studies were effective in improving comparability of the chemistry data.

RESULTS

For total detectable PAH, the differences among laboratories in the first intercalibration exercise were as high as an order of magnitude for both sediment samples (Tables 2 and 3). Most of these differences were attributable to differences in detection limits. For example, Laboratory 1 reported detectable values for less than 20% of the target compounds because most were below the detection limit used for the first intercalibration exercise; whereas Laboratory 7

Table 1. Extraction method and instrumentation used by each laboratory.

Laboratory Number	Extraction Method	DDT/PCB Gas Chromatograph Detector	PAH Gas Chromatograph Detector
1	Automated Solvent Extraction	Electron Capture Dector and Ion Trap Mass Spectrometer	Mass Spectrometer
2	Roller Table	Electron Capture Dector	Mass Spectrometer
3	Automated Solvent Extraction	Electron Capture Dector	Mass Spectrometer
4	Solvent Extraction	Electron Capture Dector	Mass Spectrometer
5	Roller Table	Electron Capture Dector	Mass Spectrometer
6	Microwave-Assisted Extraction	Mass Spectrometer (SIM Mode)	Mass Spectrometer
7	Automated Solvent Extraction	Electron Capture Dector	Mass Spectrometer

reported measurable concentrations for 100% of these compounds in both sediment samples because their MDL was much lower. However, detection limit differences did not explain all of the discrepancies, as exemplified by the order of magnitude difference for many of the compounds between Laboratories 3 and 4.

After the second intercalibration exercise, the laboratories only differed from the mean PAH value by about 30% in both sediment samples (Tables 4 and 5). The most notable changes were for Laboratories 1 and 4 that originally reported significantly lower values, and Laboratory 3 that reported higher values than the other laboratories after the first intercalibration exercise. The greater comparability among laboratories after the second intercalibration exercise was also apparent for individual compounds as indicated by the median coefficient of variation (CV) that was greater than 60% after the first exercise (Tables 2 and 3), but was less than 30% after the second exercise (Tables 4 and 5).

Similar patterns in the chemistry results for total detectable PCB and total detectable DDT (Tables 6–9) were found when comparing data from the first intercalibration exercise with those from the second intercalibration exercise. After the first exercise, there was about a factor of 3 difference among laboratories for both sediment samples. After the second intercalibration exercise, this difference was generally less than a factor of 2 between the highest

and lowest values reported. The largest change was in the 4,4'-DDE values because each laboratory experienced different problems with measuring these compounds at such high concentrations found in these sediments. For example, one laboratory found that they were not diluting the sample extract sufficiently to bring the peak size within the linear range of the detector. Another laboratory had to modify its extraction and clean-up procedures to adjust to the higher concentrations.

DISCUSSION

This study was a precursor to a regional survey of sediment chemical concentrations in southern California, similar to that of Schiff (2000). It was conducted to determine whether multiple laboratories using different methods could produce data of sufficient similarity, or if it was necessary instead to have a single laboratory conduct all analyses. While there were considerable differences prior to the intercalibration exercise, it was possible to at least partially resolve these differences and achieve more comparable results using a performance-based approach.

As part of the National Status and Trends Program, the National Institute of Standards and Technology (NIST) was funded by the National Oceanic and Atmospheric Adminstration (NOAA), and later by the U.S. EPA, to organize trace organic intercalibration exercises using marine matrix materi-

Table 2. PAH results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station 7C. ND = Not detected, * = Data not reported, Lab = Laboratory.**

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
Napthalene	ND	35	45	ND	31	58	42	42	10	25
2-Methylnaphthalene	NE	57	78	5	54	119	60	62	37	59
1-Methylnaphthalene	NE	23	32		28	66	26	38	18	51
Biphenyl	NE	44	54	17	25	57	21	36	17	48
2,6-Dimethylnaphthalene	28	30	62		39	64	38	44	16	36
Acenaphthylene	25	6	36	11	32	40	28	25	13	50
Acenaphthene	ND	ND	ND	ND	ND	ND	39	ND	***	***
2,3,5-Trimethylnaphthalene	ND	ND	ND	ND	ND	15	18	16	2	13
Fluorene	ND	7	9	ND	ND	20	6	10	6	63
Phenanthrene	ND	36	60	9	64	52	54	46	20	44
Anthracene	ND	ND	48	6	ND	49	34	34	20	58
1-Methylphenanthrene	ND	42	ND	ND	21	ND	15	26	14	55
Fluoranthene	ND	ND	53	12	57	64	63	50	22	43
Pyrene	43	255	374	20	109	108	151	151	124	82
Benz[a]anthracene	ND	ND	79	9	47	49	47	46	25	53
Chrysene	ND	ND	67	9	53	25	63	43	25	58
Benzo[b]fluoranthene	ND	ND	292	14	160	61	168	139	108	77
Benzo[k]fluoranthene	ND	ND	104	10	55	64	83	63	35	56
Benzo[e]pyrene	ND	233	241	19	191	77	198	160	91	57
Benzo[a]pyrene	ND	ND	236	16	186	64	174	135	91	68
Perylene	41	359	312	20	165	138	101	162	129	80
Indeno[1,2,3-c,d]pyrene	ND	ND	26	ND	ND	53	93	57	34	59
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	40	ND	***	***
Benzo[g,h,l]pyrene	ND	ND	91	ND	112	37	144	96	45	47
Total Detectable PAHs	137	1130	2300	177	1430	1280	1670	1160	781	67

Table 3. PAH results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station E6. ND = Not detected, * = Data not reported, Lab = Laboratory.**

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
Napthalene	54	171	279	27	139	259	211	163	97	59
2-Methylnaphthalene	129	485	721	59	405	615	653	438	258	59
1-Methylnaphthalene	61	172	272	23	181	222	226	165	91	55
Biphenyl	233	756	1140	97	606	770	650	607	350	58
2,6-Dimethylnaphthalene	131	217	401	37	228	203	356	225	124	55
Acenaphthylene	ND	4	ND	ND	ND	ND	10	7	4	59
Acenaphthene	ND	15	46	ND	ND	ND	7	23	20	89
2,3,5-Trimethylnaphthalene	ND	19	ND	4	15	ND	106	36	47	130
Fluorene	ND	38	75	2	24	69	26	39	28	72
Phenanthrene	ND	137	469	9	109	112	95	155	160	103
Anthracene	ND	ND	111	13	19	18	39	40	41	102
1-Methylphenanthrene	ND	154	ND	ND	51	ND	31	79	66	84
Fluoranthene	76	ND	495	26	87	108	173	161	171	106
Pyrene	91	ND	1120	28	79	111	165	266	421	158
Benz[a]anthracene	ND	ND	284	30	65	38	100	103	105	101
Chrysene	60	ND	320	31	83	46	136	113	108	96
Benzo[b]fluoranthene	ND	ND	672	19	205	38	178	222	264	119
Benzo[k]fluoranthene	ND	ND	205	18	77	41	68	82	73	89
Benzo[e]pyrene	ND	ND	367	11	171	63	195	161	138	85
Benzo[a]pyrene	ND	ND	409	13	162	ND	189	193	163	85
Perylene	ND	249	183	5	72	32	59	100	95	95
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	69	23	155	82	67	81
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	38	42	40	3	8
Benzo[g,h,l]pyrene	ND	ND	60	ND	109	30	163	90	58	64
Total Detectable PAHs	835	2420	7630	453	2960	2840	4030	3020	2380	79

Table 4. PAH results (ng/dry g or parts per billion [ppb]) for the second intercalibration exercise on sediments collected from Station 7C. ND = Not detected, * = Data not reported, Lab = Laboratory.**

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
Napthalene	***	32	28	34	27	11	***	27	9	35
2-Methylnaphthalene	45	54	63	56	51	54	***	54	6	11
1-Methylnaphthalene	***	19	29	20	29		***	24	5	22
Biphenyl	49	26	39	47	27	33	***	37	10	26
2,6-Dimethylnaphthalene	82	31	75	79	27	28	***	53	27	54
Acenaphthylene	***	15	42	87	43	12	***	40	30	76
Acenaphthene	***	ND	ND	7	ND	ND	***	ND	***	***
2,3,5-Trimethylnaphthalene	***	ND	ND	19	ND	14	***	17	4	22
Fluorene	***	3	21	13	ND	ND	***	13	9	72
Phenanthrene	***	71	53	58	69	66	***	63	8	12
Anthracene	***	20	39	44	24	21	***	29	11	38
1-Methylphenanthrene	***	25	ND	ND	ND	23	***	24	1	6
Fluoranthene	51	68	55	39	72	75	***	60	14	23
Pyrene	144	215	137	138	172	168	***	162	30	18
Benz[a]anthracene	48	46	61	56	30	60	***	50	12	24
Chrysene	36	58	63	78	74	63	***	62	15	24
Benzo[b]fluoranthene	***	163	267	103	53	95	***	136	83	61
Benzo[k]fluoranthene	***	49	80	63	50	95	***	67	20	29
Benzo[e]pyrene	97	124	193	131	62	113	***	120	43	36
Benzo[a]pyrene	76	141	203	109	67	52	***	108	57	52
Perylene	127	259	227	237	140	142	***	189	58	31
Indeno[1,2,3-c,d]pyrene	***	35	ND	ND	88	79	***	67	28	42
Dibenz[a,h]anthracene	***	18	ND	ND	ND	ND	***	ND	***	***
Benzo[g,h,I]pyrene	28	99	75	ND	75	91	***	74	28	38
Total Detectable PAHs	ND	1570	1750	1420	1180	1300	***	1440	224	15

Note: Laboratory No. 7 did not report any results for the second intercalibration exercise.

Table 5. PAH results (ng/dry g or parts per billion [ppb]) for the second intercalibration exercise on sediments collected from Station E6. ND = Not detected, * = Data not reported, Lab = Laboratory.**

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
Napthalene	173	162	170	191	139	193	***	171	20	12
2-Methylnaphthalene	388	435	480	532	336	525	***	449	78	17
1-Methylnaphthalene	***	145	185	166	153	144	***	159	17	11
Biphenyl	650	644	850	800	535	796	***	712	121	17
2,6-Dimethylnaphthalene	365	212	255	343	214	269	***	276	65	23
Acenaphthylene	***	8	ND	ND	ND	ND	***	ND	***	***
Acenaphthene	***	ND	25	15	ND	ND	***	20	7	35
2,3,5-Trimethylnaphthalene	***	22	ND	119	47	ND	***	62	50	81
Fluorene	ND	25	49	40	39	52	***	41	11	26
Phenanthrene	114	131	145	130	142	141	***	134	11	7
Anthracene	ND	33	34	58	41	29	***	39	11	29
1-Methylphenanthrene	ND	62	27	68	73	128	***	71	36	51
Fluoranthene	183	280	150	135	146	183	***	179	53	30
Pyrene	211	196	155	230	125	185	***	184	38	21
Benz[a]anthracene	93	126	145	118	37	114	***	105	38	36
Chrysene	115	88	120	152	127	145	***	124	23	18
Benzo[b]fluoranthene	***	164	330	179	60	92	***	165	105	63
Benzo[k]fluoranthene	***	63	103	167	60	90	***	97	43	45
Benzo[e]pyrene	117	115	155	183	51	115	***	123	44	36
Benzo[a]pyrene	94	109	195	191	52	65	***	118	62	52
Perylene	ND	91	78	110	70	26	***	75	31	42
Indeno[1,2,3-c,d]pyrene	***	44	ND	ND	88	66	***	66	22	33
Dibenz[a,h]anthracene	***	26	ND	ND	ND	ND	***	ND	***	***
Benzo[g,h,I]pyrene	34	100	ND	ND	80	97	***	78	30	39
Total Detectable PAHs	***	3280	3650	3930	2610	3450	***	3390	494	15

Note: Laboratory No. 7 did not report any results for the second intercalibration exercise.

Table 6. DDT and PCB results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station 7C. ND = Not detected, * = Data not reported, Lab = Laboratory.**

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
4,4'-DDE	6570	12900	***	17100	16300	5930	4830	10600	5500	52
4,4'-DDD	410	886	***	1090	8	384	285	510	401	79
4,4'-DDT	547	683	***	1490	480	185	483	645	447	69
2,4'-DDE	820	1870	***	2060	769	769	801	1180	610	52
2,4'-DDD	113	413	***	363	328	73	143	239	146	51
2,4'-DDT	7	26	***	ND	352	12	23	84	150	179
Total Detectable DDTs	8460	16800	***	21900	19500	7350	6560	13400	6760	50
PCB 18	ND	18	***	23	12	10	13	15	5	34
PCB 28	25	49	***	45	33	12	42	35	14	41
PCB 52	46	91	***	98	61	55	88	73	22	30
PCB 49	30	65	***	64	39	17	60	46	20	44
PCB 44	56	80	***	70	46	31	60	57	17	30
PCB 37	ND	230	***	ND	163	10	3	102	113	111
PCB 74	29	57	***	54	34	35	58	44	13	30
PCB 70	78	150	***	104	71	52	137	99	39	39
PCB 66	61	129	***	73	79	25	90	76	34	45
PCB 101	12	95	***	73	302	50	73	101	102	102
PCB 99	24	58	***	49	22	31	52	39	15	39
PCB 119	ND	ND	***	ND	ND	ND	2	ND	ND	ND
PCB 87	18	ND	***	28	440	24	44	111	184	166
PCB 110	24	335	***	ND	90	46	85	116	125	108
PCB 81	ND	ND	***	ND	ND	10	38	24	20	83
PCB 151	ND	ND	***	30	20	12	14	19	8	43
PCB 77	ND	ND	***	8	24	8	2	10	10	91
PCB 149	24	54	***	50	12	28	40	35	16	47
PCB 123	ND	ND	***	9	3	11	ND	8	4	58
PCB 118	60	102	***	94	10	48	87	67	35	52
PCB 114	ND	ND	***	ND	ND	9	***	ND	***	***
PCB 168/153	23	97	***	83	37	34	99	62	35	55
PCB 105	ND	85	***	62	21	32	49	50	25	50
PCB 138	ND	117	***	ND	314	26	975	358	429	120
PCB 158	ND	ND	***	ND	7	21	6	11	8	74
PCB 187	9	22	***	17	9	14	22	15	6	38
PCB 183	ND	10	***	8	6	8	11	8	2	21
PCB 126	ND	ND	***	ND	ND	8	ND	ND	***	138
PCB 128	ND	20	***	14	7	12	16	14	5	34
PCB 167	ND	ND	***	5	ND	6	3	5	1	29
PCB 177	ND	12	***	ND	4	9	10	9	3	37
PCB 200	ND	3	***	18	ND	5	***	8	8	94
PCB 156	ND	ND	***	7	ND	13	15	12	4	36
PCB 157	ND	ND	***	ND	ND	7	1	4	4	97
PCB 180	11	40	***	1	18	19	48	23	18	78
PCB 170	ND	19	***	ND	13	14	21	17	4	24
PCB 169	ND	ND	***	ND	13	9	ND	7	6	88
PCB 189	ND	5	***	3	ND	6	2	4	2	50
PCB 194	ND	9	***	4	6	12	2	7	4	57
PCB 206	ND	ND	***	6	4	6	21	9	8	81
Total Detectable PCBs	529	1950	***	1100	1920	785	1390	1280	586	46

Note: Laboratory No. 3 did not report any results for PCB or DDT inthe first intercalibration exercise.

Table 7. DDT and PCB results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station E6. ND = Not detected, *** = Data not reported, Lab = Laboratory.

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
4,4'-DDE	207	316	***	474	123	188	151	254	123	48
4,4'-DDD	17	26	***	35	21	10	26	24	8	36
4,4'-DDT	2	67	***	79	42	17	10	34	30	89
2,4'-DDE	25	54	***	30	23	13	21	27	14	51
2,4'-DDD	26	56	***	107	67	5	14	46	38	84
2,4'-DDT	1	ND	***	ND	6	16	4	7	6	97
Total Detectable DDTs	277	519	***	725	283	249	226	378	182	48
PCB 18	ND	7	***	12	6	11	8	9	2	26
PCB 28	18	17	***	22	20	ND	27	21	4	18
PCB 52	26	24	***	39	29	31	40	30	7	22
PCB 49	15	18	***	25	17	3	24	17	7	42
PCB 44	45	26	***	27	19	14	34	26	11	42
PCB 37	ND	29	***	21	15	22		22	5	25
PCB 74	ND	16	***	17	12	13	25	17	5	27
PCB 70	24	29	***	37	30	15	52	31	12	37
PCB 66	35	42	***	40	32	9	39	33	12	37
PCB 101	50	52	***	44	84	29	64	53	17	33
PCB 99	19	16	***	15	14	13	35	20	8	41
PCB 119	ND	ND	***	ND	ND	ND	2	ND	***	***
PCB 87	16	26	***	26	22	23	33	24	5	22
PCB 110	18	63	***	7	35	33	66	38	22	58
PCB 81	ND	ND	***	ND	ND	14	23	19	7	35
PCB 151	ND	ND	***	17	15	9	13	13	3	25
PCB 77	ND	ND	***	8	ND	7	2	6	4	64
PCB 149	25	31	***	40	14	25	37	29	9	30
PCB 123	ND	ND	***	6	4	12	ND	7	4	61
PCB 118	48	50	***	56	8	32	74	45	21	46
PCB 114	ND	ND	***	ND	ND	11	***	ND	***	***
PCB 168/153	27	62	***	61	21	32	100	50	27	55
PCB 105	ND	36	***	35	15	21	29	27	8	30
PCB 138	36	50	***	49	8	33	80	45	23	51
PCB 158	ND	6	***	ND	5	11	67	22	30	135
PCB 187	ND	16	***	15	5	15	22	15	6	37
PCB 183	ND	9	***	7	4	9	11	8	2	29
PCB 126	ND	ND	***	ND	ND	19	1	10	13	134
PCB 128	ND	17	***	15	7	12	16	13	4	29
PCB 167	ND	ND	***	3	ND	8	3	4	3	61
PCB 177	ND	9	***	8	5	8	12	8	2	25
PCB 200	ND	4	***	21	ND	6	***	10	9	90
PCB 156	ND	ND	***	5	ND	14	12	9	4	44
PCB 157	ND	ND	***	ND	ND	10	1	4	5	121
PCB 180	10	32	***	1	43	18	43	25	16	65
PCB 170	ND	22	***	24	5	17	22	17	7	41
PCB 169	ND	ND	***	ND	ND	11	ND	ND	***	***
PCB 189	ND	4	***	1	ND	8	2	3	3	86
PCB 194	ND	13	***	7	7	11	3	8	3	42
PCB 206	ND	14	***	4	ND	6	9	8	4	53
Total Detectable PCBs	411	739	***	713	502	595	1030	657	200	30

Note: Laboratory No. 3 did not report any results for PCB or DDT in the first intercalibration exercise.

Table 8. DDT and PCB results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station 7C. ND = Not detected, *** = Data not reported, Lab = Laboratory.

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
4,4'-DDE	***	11800	14800	11800	6680	8610	***	10700	3150	29
4,4'-DDD	***	791	994	693	382	398	***	652	262	40
4,4'-DDT	***	879	562	334	326	434	***	507	229	45
2,4'-DDE	***	1720	2780	1210	908	1230	***	1570	736	47
2,4'-DDD	***	300	383	317	102	264	***	273	105	38
2,4'-DDT	***	13			6	11	***	10	4	35
Total Detectable DDTs	***	15500	19500	14400	8410	10900	***	13800	4280	31
PCB 18	***	13	18	17	10	12	***	14	3	24
PCB 28	***	35	54	34	24	29	***	35	11	32
PCB 52	***	72	91	73	47	71	***	71	16	22
PCB 49	***	49	53	46	33	43	***	45	8	17
PCB 44	***	54	66	53	37	47	***	51	11	21
PCB 37	***	156	36	9	11	14	***	45	63	139
PCB 74	***	47	73	38	40	47	***	49	14	28
PCB 70	***	93	83	74	65	82	***	79	11	13
PCB 66	***	95	98	72	57	60	***	76	19	25
PCB 101	***	101	77	63	51	78	***	74	19	25
PCB 99	***	54	68	49	33	34	***	48	15	31
PCB 119	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 87	***	29	63	35	32	34	***	39	14	36
PCB 110	***	40	269	220	61	64	***	131	106	81
PCB 81	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 151	***	ND	22	23	8	16	***	17	7	41
PCB 77	***	ND	ND	ND	5	6	***	6	1	24
PCB 149	***	45	49	34	31	39	***	40	8	19
PCB 123	***	ND	9	6	8	7	***	7	1	19
PCB 118	***	94	85	67	60	77	***	77	14	18
PCB 114	***	ND	ND	ND	19	ND	***	19	***	***
PCB 168/153	***	71	71	59	56	54	***	62	8	13
PCB 105	***	53	44	46	51	50	***	49	4	8
PCB 138	***	126	22	ND	62	66	***	69	43	62
PCB 158	***	10	ND	ND	6	4	***	6	3	49
PCB 187	***	15	21	12	15	18	***	16	3	21
PCB 183	***	8	10	5	7	9	***	8	2	23
PCB 126	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 128	***	18	19	12	9	20	***	15	5	31
PCB 167	***	ND	ND	2	8	8	***	6	3	58
PCB 177	***	ND	11	9	8	8	***	9	1	16
PCB 200	***	ND	ND	4	ND	4	***	4	0.4	10
PCB 156	***	ND	11	10	ND	21	***	14	6	44
PCB 157	***	ND	ND	1	ND	ND	***	ND	***	***
PCB 180	***	28	35	16	31	33	***	28	8	27
PCB 170	***	15	21	10	11	15	***	14	4	29
PCB 169	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 189	***	2	ND	ND	ND	ND	***	ND	***	***
PCB 194	***	4	18	ND	7	10	***	10	6	62
PCB 206	***	ND	ND	ND	4	5	***	5	0.4	9
Total Detectable PCBs	***	1330	1500	1100	901	1080	***	1180	232	20

Note: Laboratory No. 1 and 7 did not report any results for PCB or DDT inthe first intercalibration exercise.

Table 9. DDT and PCB results (ng/dry g or parts per billion [ppb]) for the first intercalibration exercise on sediments collected from Station E6. ND = Not detected, *** = Data not reported, Lab = Laboratory.

Compound	Lab-1	Lab-2	Lab-3	Lab-4	Lab-5	Lab-6	Lab-7	Mean	SD	%CV
4,4'-DDE	***	390	332	345	164	219	***	290	94	33
4,4'-DDD	***	24	24	28	3	18	***	19	10	51
4,4'-DDT	***	49	69	70	45	25	***	52	19	36
2,4'-DDE	***	57	32	20	17	17	***	29	17	60
2,4'-DDD	***	55	64	78	49	14	***	52	24	46
2,4'-DDT	***	3	ND	ND	19	6	***	9	9	92
Total Detectable DDTs	***	579	521	541	297	299	***	447	138	31
PCB 18	***	12	11	8	9	9	***	10	2	15
PCB 28	***	17	24	19	19	18	***	19	3	13
PCB 52	***	29	46	33	28	31	***	34	7	21
PCB 49	***	18	20	20	15	16	***	18	2	13
PCB 44	***	23	26	23	18	18	***	22	4	17
PCB 37	***	35	16	6	20	20	***	19	11	55
PCB 74	***	15	15	18	12	16	***	15	2	14
PCB 70	***	32	30	34	27	28	***	30	3	10
PCB 66	***	33	33	35	28	23	***	30	5	16
PCB 101	***	59	88	40	87	46	***	64	22	35
PCB 99	***	31	69	23	15	15	***	31	22	73
PCB 119	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 87	***	19	26	24	24	19	***	22	3	14
PCB 110	***	15	56	64	23	38	***	39	21	53
PCB 81	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 151	***	16		16	4	10	***	11	5	48
PCB 77	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 149	***	29	34	32	7	23	***	25	11	44
PCB 123	***	ND	5	5	4	8	***	5	2	28
PCB 118	***	46	46	51	10	40	***	39	17	43
PCB 114	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 168/153	***	47	50	53	39	29	***	44	10	22
PCB 105	***	27	24	33	28	22	***	27	4	16
PCB 138	***	41	14	47	33	40	***	35	13	36
PCB 158	***	6	ND	ND	8	8	***	8	1	16
PCB 187	***	14	16	14	11	15	***	14	2	12
PCB 183	***	11	7	7	7	12	***	9	3	30
PCB 126	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 128	***	23	17	14	6	9	***	14	7	50
PCB 167	***	ND	ND	3	ND	4	***	4	1	38
PCB 177	***	7	7	7	4	8	***	7	2	23
PCB 200	***	ND	ND	6	ND	ND	***	6	***	***
PCB 156	***	ND	6	7	ND	3	***	5	2	39
PCB 157	***	ND	ND	1	ND	ND	***	ND	***	***
PCB 180	***	24	22	ND	16	17	***	20	4	20
PCB 170	***	15	14	15	6	18	***	14	4	32
PCB 169	***	ND	ND	ND	***	ND	***	ND	***	***
PCB 189	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 194	***	10	9	8	4	7	***	8	2	29
PCB 206	***	7	ND	11	ND	5	***	8	3	33
Total Detectable PCBs	***	678	732	688	513	562	***	635	93	15

Note: Laboratory No. 1 and 7 did not report any results for PCB or DDT inthe first intercalibration exercise.

als. To determine whether all of our laboratories had achieved comparability, we established performance criteria based on the NIST intercalibration exercises. To indicate acceptable performance according to the NIST criteria, results from each laboratory needed to be within 40% of the mean value for 80% of the sentinel compounds. We were able to achieve this goal, even with samples that were selected to be more challenging than average. Still, it is important to recognize that we did observe larger differences for some compounds. We concluded that it is unrealistic to expect that that all compounds will be measured within 40% of the mean values, even within the most rigorous performance-based exercise.

Resolving pre-existing differences among laboratories resulted from many factors, including adjustments to sample extraction methods such as adding additional drying agents, improvement of clean-up procedures such as changing or increasing adsorbents, changing sample sizes, adjusting GC oven parameters for improved separation, and switching from older instrumentation to newer instrumentation with greater sensitivity. Another major factor affecting the results was interpretation of the chromatograms themselves. For example, in some cases a laboratory ignored a peak that other laboratories were identifying as a target analyte. In other cases, peaks were switched, or the procedure for drawing baselines used for integrating the peaks needed to be refined to provide consistency between laboratories.

A detailed description of the specific analytical factors identified that contributed to the variability has not been provided here since they are numerous and varied for each laboratory. Some of the larger factors controlling the variation were described earlier. The specific changes each laboratory made are not critical because another set of laboratories would probably encounter different issues and the critical factor for improving comparability among laboratories is the process itself. Equally important was providing the laboratories with experience handling extremely difficult matrices and a communication process that started with consensus on sample size, maximum MDL, and chromatographic separation, but extended to nearly every decision about sample processing alternatives. A good performance-based approach fosters communication among laboratories that would not normally occur in its absence. Another important factor in reducing inter-laboratory variability was the recognition among participants that a performance-based approach conducted on samples collected locally was worth the commitment. For many of the laboratories, the studies associated with achieving comparability consumed more effort than processing the actual samples from the regional survey that this exercise was intended to support. We believe that the increased knowledge and staff education gained through participation offset the extra cost of the time invested.

Our results suggest that performance based chemistry can produce comparable results, even given a wide range of approaches and instrumentation. However, we also found that the certification process presently in place, which focuses only on general laboratory procedures and simple matrices, is insufficient to achieve comparability for all samples encountered in the field. While project-specific intercalibration exercises will probably always be necessary to achieve the level of comparability that we achieved here, there are several changes to the certification process that would improve performance- based chemistry on an ongoing basis. First, additional methods flexibility is needed since certified methods presently lag behind current technology. For instance, California's certified methods for PCB are still based on Aroclors, which presents a challenge when projects such as this one are based on congeners. Additionally, there needs to be a wider array of reference materials. All of the laboratories that participated in this study had previously passed NIST's SRM exercise and were State-certified in California. However, the available SRM material does not contain certified values for DDT and the matrix was limited to dried samples that did not test the laboratories' ability to handle wet samples.

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