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PRECISION OF CHLORINATED HYDROCARBON MEASUREMENTS

It is often important in environmental studies to determine whether or not average levels of potential toxicants vary with space, time, health, species, sex, size, or some other parameter. Such determinations require some knowledge of the variability of the results being compared. Therefore, in our trace organics program for the past year, we have investigated the degree of variability of our measurements of chlorinated hydrocarbons in sediments, fish tissues, wastewaters, storm runoff, and aerial fallout. The param-eter we have selected for this purpose is the coefficient of variation (CV: expressed as a percentage), which is defined as 100 times the standard deviation of a set of values divided by its mean.

These studies have shown that, when aliquots of a homogenized sample are considered, the majority of the CV's for all but the lowest concentrations of a given compound fall within the 10- to 20-percent range. Of course, in a study involving a set of replicate samples from the sea, analytic variability is only a part of overall variability, which includes variations in details of sampling, handling, and dissection as well as natural variability.

To investigate the variability of our results for sediment samples, we performed analyses for DDT and PCB residues in grab samples of ocean bottom sediments collected during 1976 from four stations within the Bight known to contain different levels of these synthetic organic contaminants. Two procedures were used in preparing and analyzing the samples. In the first, all sediment samples from a particular station were homogenized; six aliquots of the homogenate were then analyzed individually, and a mean value for each set of aliquots was obtained: The CV's for these means thus represent analytic variability rather than field sampling variability. The second procedure involved analyses of three nonhomogenized grab samples from each of two of the stations for which homogenized samples had been analyzed.

The results are given in Table 1. The CV's for total DDT, total PCB, and total measurable chlorinated hydrocarbons in sediments collected off Palos Verdes Peninsula and in Santa Monica Bay ranged from 4 to 13 percent. In contrast, CV's for the results from the San Diego control station, where the PCB and DDT levels are, respectively, three and four orders of magnitude below those found off Palos Verdes Station A (near the Joint Water Pollution Control Plant (JWPCP) municipal wastewater outfall diffusers there), ranged between 13 and 28 percent.

The CV's for the total DDT and total PCB results from the three nonhomogenized grab samples from Palos Verdes Stations A and B ranged from 10 to 33 percent, considerably higher than the CV's for the values obtained after homogenization. For example, the respective CV's from the Station B homogenized and nonhomogenized samples for total DDT were 4 and 19 percent; for total PCB, 9 and 33 percent; for total chlorinated hydrocarbons, 4 and 20 percent. This comparison suggests that compositing several samples per station prior to analysis could efficiently reduce overall variability.

Table 2 presents results of a corresponding study on flesh of Dover sole collected in 1976 off Palos Verdes at a station 4 km northwest of the JWPCP outfall diffusers. The first set of data was obtained from a homogenate of muscle tissue from six of these flatfish; the second set was obtained from individual analyses of another six fish randomly selected from the same collection. The CV's for total DDT and total PCB in the homogenized samples were 14 and 18 percent, respectively; those for the nonhomogenized set were 81 and 80 percent, respectively. Again, these results demonstrate that compositing of samples prior to analysis could significantly reduce the variability observed in such surveys in this region. It also should be noted that, although the average level of hexachlorobenzene (HCB) measured in the flesh composites was four orders of magnitude below that for total DDT, the coefficient of variation for both values was 14 percent.

Three aliquots of Hyperion 7-mile outfall "sludge" effluent collected in 1976 were analyzed for ortho- and para-dichlorobenzene (o-DCB and p-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), and HCB; the results were as follows:

Component	Mean (µg/liter)	CV
p-DCB	52	9
0-DCB	21	11
1,2,4-TCB	61	3
HCB	1.4	12

The CV's are similar to those usually obtained for DDT and PCB compounds.

Since 1973, with the support of the U.S. Environmental Protection Agency, we have analyzed 1-week composites of final effluent collected twice yearly from the five major dischargers of municipal wastewater to the Bight. To better evaluate this large data base for individual chlorinated hydrocarbons, we have calculated CV values for each avail-able replicate pair and then averaged the mean concentrations and their corresponding CV's. The results for 1973-75, listed in Table 3, show that our values for total DDT and total PCB in these effluents typically have CV's of 10 to 25 percent. However,

higher CV's occur when the concentration of a given chlorinated hydrocarbon approaches or falls below 0.1 ppb.

Table 4 lists the results obtained from triplicate samples of storm runoff collected in 1973 from the Los Angeles River. Each of three samples was a composite of approximately six depth-integrated collections—equal portions of each collection were transferred to the three collection bottles to minimize sampling variability. The data include CV's for total DDT, dieldrin, and 1254 PCB of 11, 12, and 38 percent, respectively.

Table 5 shows the results of analyses of aerial fallout samples collected at Redondo Beach in the spring of 1974. Eight triplicate sets of 1-day samples, four triplicate sets of 2-day samples, two quadruplicate sets of 4-day samples, and one quadruplicate set of 8-day samples were analyzed. The mean quantity of each chlorinated hydrocarbon, and the coefficients of variation for each set of samples, was first computed. Averages of these values (except those for the 8-day set) were then taken. These results show that, in general, the longer the sampling period, the better the precision of the aerial fallout data, probably because of the increased sample size. The CV's for total DDT and 1254 PCB in the 8-day collections (similar to our usual 1-week sampling interval) are 8 and 20 percent, respectively.

In conclusion, our present techniques for analyzing DDT, dieldrin, PCB, and chlorinated benzene residues in samples of sediments, organisms, municipal wastewater, surface runoff, and dry aerial fallout appear to yield results that usually have a coefficient of variation of about 20 percent or less. Of course, such values will vary and should be determined for each study as part of the search for statistically significant differences. But results such as those described above are useful as rough estimates of limits of resolution and as indications of whether apparent differences are likely to be real or merely the result of analytic and/or field variability.

Table 1. Means (mg/dry kg) and coefficients of variation (in parentheses) of chlorinated hydrocarbon concentrations in sediments collected from four different areas of the Southern California Bight in 1976.

| | Homogenized Samples (6 aliquots/station) | | | | Nonhomogenized Samples (3 grabs/station) | |
| | Palos Verdes* | | Santa | San Diego | Palos Verdes | |
Component	Station A	Station B	Monica Bay	Control Station	Station A*	Station B*
o,p'-DDE	9.7 (15%)	4.5 (16%)	0.014 (23%)	0.0001 (60%)	7.5 (21%)	6.2 (12%)
p,p'-DDE	72 (10%)	27 (5%)	0.086 (5%)	0.0016 (20%)	56 (10%)	45 (22%)
o,p'-DDD	1.8 (18%)	0.5 (15%)	—	—	1.2 (36%)	0.9 (28%)
p,p'-DDD	9.1 (11%)	1.8 (20%)	—	—	8.7 (14%)	3.3 (6%)
o,p'-DDT	0.2 (67%)	0.1 (45%)	0.002 (22%)	0.0004 (29%)	0.1 (45%)	0.1 (44%)
p,p'-DDT	1.6 (32%)	0.3 (15%)	0.006 (25%)	0.0013 (58%)	0.8 (70%)	0.3 (5%)
Total DDT	94 (10%)	34 (4%)	0.11 (5%)	0.0034 (28%)	75 (10%)	56 (19%)
1242 PCB	4.3 (10%)	0.6 (8%)	0.031 (2%)	0.0014 (30%)	2.3 (38%)	1.2 (30%)
1254 PCB	6.6 (16%)	1.6 (11%)	0.18 (5%)	0.014 (16%)	5.7 (13%)	3.0 (34%)
Total PCB	11 (13%)	2.2 (9%)	0.208 (4%)	0.015 (16%)	7.9 (20%)	4.2 (33%)
Total**	105 (8%)	36 (4%)	0.32 (4%)	0.019 (13%)	83 (11%)	60 (20%)

*Stations A and B are 2 and 12 km northwest of the municipal wastewater outfall system, respectively.
**Total measurable chlorinated hydrocarbons.

Table 2. Means (mg/wet kg) and coefficients of variation (in parentheses) of chlorinated hydrocarbon concentrations in the flesh of Dover sole collected from the Palos Verdes shelf on 5 November 1976.

Component	Homogenate of Flesh from Six Fish		Individual Analyses of Flesh from Six Fish	
o,p'-DDE	0.75	(14%)	0.71	(74%)
p,p'-DDE	7.9	(15%)	8.6	(81%)
o,p'-DDD	—	—	0.05	(82%)
p,p'-DDD	0.26	(14%)	0.27	(91%)
o,p'-DDT	0.02	(59%)	0.01	(78%)
p,p'-DDT	0.02	(17%)	0.01	(58%)
Total DDT	8.9	(14%)	9.6	(81%)
1242 PCB	0.17	(20%)	0.18	(79%)
1254 PCB	0.50	(19%)	0.50	(81%)
Total PCB	0.67	(18%)	0.68	(80%)
Total	9.6	(14%)	10.3	(81%)
HCB	0.0020	(14%)	—	—

Table 3. Average means (µg/liter) and average coefficients of variation (in parentheses of chlorinated hydrocarbon concentrations in municipal wastewaters discharged to the Southern California Bight, 1973-75.

Component	Los Angeles County	Hyperion 5-mile	Hyperion 7-mile	Orange County	Point Loma	Oxnard
o,p'-DDE	0.58 (13%)	ND	ND	ND	ND	ND
p,p'-DDE	1.6 (8.0%)	0.014 (16%)	1.6 (8.5%)	0.03 (71%)	0.02 (20%)	0.08 (14%)
o,p'-DDD	0.38 (17%)	ND	0.29 (42%)	ND	0.03 (23%)	0.005 (28%)
p,p'-DDD	1.9 (10%)	0.045 (20%)	1.8 (2.4%)	0.18 (61%)	0.07 (19%)	0.10 (66%)
o,p'-DDT	0.10 (28%)	0.028 (26%)	0.59 (48%)	0.002 (24%)	0.04 (53%)	0.15 (19%)
p,p'-DDT	0.21 (34%)	0.048 (17%)	0.60 (57%)	0.007 (50%)	0.04 (14%)	0.08 (14%)
Total DDT	4.3 (10%)	0.12 (16%)	2.3 (27%)	0.15 (46%)	0.11 (18%)	0.25 (27%)
Dieldrin	0.11 (62%)	0.057 (62%)	0.83 (22%)	0.17 (23%)	0.05 (74%)	0.009 (11%)
1242 PCB	1.7 (8.1%)	0.15 (15%)	40 (7.6%)	7.1 (3.9%)	3.8 (7.4%)	0.14 (66%)
1254 PCB	0.99 (8.9%)	0.29 (13%)	29 (9.0%)	1.1 (6.9%)	0.65 (14%)	0.29 (16%)
Total PCB*	2.6 (9.7%)	0.36 (12%)	63 (5.4%)	5.8 (5.8%)	3.6 (11%)	0.39 (13%)

* The average value for total PCB is different from the sum of values for 1242 and 1254 PCB because the two components were not quantified in all samples.

Table 4. Means and coefficients of variation of chlorinated hydrocarbon concentrations in Los Angeles River storm runoff, 8 March 1973.

Component	Mean (µg/liter)	CV
p,p'-DDE	0.12	18%
p,p'-DDD	0.10	33%
o,p'-DDT	0.37	10%
p,p'-DDT	0.41	17%
Total DDT	0.99	11%
Dieldrin	0.17	12%
1242 PCB	<1.1	—
1254 PCB	0.77	38%
Total PCB	<1.9	—

Table 5. Average means (ng) and average coefficients of variation for chlorinated hydrocarbon concentrations in aerial fallout samples collected at Redondo Beach, 1974.

	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	Total DDT	1254 PCB
1-day samples						
Mean	16	22	15	66	126	42
CV	15%	24%	22%	24%	17%	34%
2-day samples						
Mean	23	39	43	126	231	80
CV	15%	12%	13%	16%	11%	29%
4-day samples						
Mean	37	81	83	226	425	155
CV	14%	17%	13%	6%	6%	15%
8-day samples						
Mean	39	103	109	311	561	187
CV	31%	13%	24%	4%	8%	20%