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Upper Great Lakes Connecting Channels Interlaboratory Performance Evaluation Study. QM-2: PAHs in Ampules

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UPPER GREAT LAKES CONNECTING CHANNELS INTERLABORATORY PERFORMANCE EVALUATION STUDY QM-2: PAHs IN AMPULES FINAL REPORT

by

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and

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MANAGEMENT PERSPECTIVE

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission. A Canada - U.S. binational study, involving the identification and assessment of the environmental impacts of toxic substances, in those areas, was initiated in 1984. In order to assist analytical laboratories contributing data to the UGLCC study, to generate reliable and accurate data, a Quality Management Work Group was formed and thirteen interlaboratory studies were implemented. This report describes the results from the second interlaboratory performance evaluation, QM-2, which consisted of the analysis of 16 PAHs, priority pollutants, in standard solutions. Results were received from seven out of 16 participating laboratories (four Canadian, three U.S.). Overall, most data received from the participants were satisfactory and comparable, except for some of the data from laboratory U079 and about half of the data from laboratory U063. All participating laboratories have been provided with appropriate feed-back.

PERSPECTIVE GESTION

La Commission mixte internationale a désigné les canaux reliant les Grands Lacs de la région supérieure "secteurs de préoccupation". En 1984, le Canada et les États-Unis ont entrepris une étude conjointe sur la détermination et l'évaluation des effets des substances toxiques sur l'environnement de ces régions. Afin d'aider les laboratoires qui participent à cette étude à fournir des données fiables et précises, on a créé le groupe de travail sur la gestion de la qualité et mis en oeuvre 13 études interlaboratoires. Le présent rapport décrit les résultats de la deuxième évaluation comparative de la performance des laboratoires, QM-2; dans le cadre de cette étude, on a analysé 16 HAP, polluants prioritaires, dans des solutions étalons. Sept laboratoires participants sur 16 ont fait parvenir leurs résultats (4 laboratoires canadiens et 3 américains). En général, presque toutes les données reçues étaient valables et compatibles, sauf certaines données du laboratoire U079 et environ la moitié des données du laboratoire U063. On a envoyé à tous les laboratoires participants les commentaires appropriés.

ABSTRACT

The Upper Great Lakes Connecting Channels (UGLCC) study recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, thirteen interlaboratory performance evaluation studies were designed and conducted by the Quality Management Work Group.

This report describes the results from the second interlaboratory performance evaluation study, QM-2, which consisted of the analysis of 16 PAHs in standard solutions. Results were received from seven out of 16 participating laboratories (4 Canadian, 3 U.S.).

The within-lab precision between duplicate samples for all laboratories was excellent and relative standard deviations were <10%, except for some data from laboratories U063 and U079. The interlaboratory comparability of PAH data was satisfactory with the exceptions noted above.

The agreement between the design values and the interlaboratory medians was good in most cases. Overall, most of the data received from the participants for QM-2 were satisfactory, except for some data from laboratory U079 and about half of the data from laboratory U063.

SOMMAIRE

L'assurance et le contrôle de la qualité (AC/CQ) sont des éléments essentiels à l'utilité générale des résultats de l'étude sur les canaux reliant les Grands Lacs de la région supérieure. Dans le cadre du programme AQ/CQ, le groupe de travail sur la gestion de la qualité a conçu et mené à bien 13 évaluations comparatives de la performance des laboratoires.

Le présent rapport décrit les résultats de la deuxième évaluation de performance, QM-2, soit l'analyse de 16 HAP en solutions étalons. Sept laboratoires participants sur 16 ont fait parvenir leurs résultats (4 laboratoires canadiens, 3 américains).

La précision des résultats pour des échantillons doubles dans un même laboratoire était excellente pour tous les laboratoires et les écarts-types relatifs étaient inférieurs à 10 p. 100, sauf pour certaines données provenant des laboratoires U063 et U079. La comparaison des données sur les HAP entre les laboratoires était donc satisfaisante, sauf en ce qui concerne les exceptions mentionnées plus haut.

Dans la plupart des cas, la compatibilité entre les valeurs théoriques et les médianes des laboratoires était bonne. En général, presque toutes les données envoyées par les participants à l'étude QM-2 étaient valables, à l'exception de quelques données du laboratoire U079 et environ la moitié des données du laboratoire U063.

INTRODUCTION

The Upper Great Lakes Connecting Channels (UGLCC) have been designated as "Areas of Concern" by the International Joint Commission (IJC). To identify and deal with the environmental problems, a three year binational study was started in 1984, involving Canadian and U.S. environmental and resource agencies, to study the St. Marys, St. Clair and Detroit Rivers, and Lake St. Clair. The study involves identifying, quantifying and determining the environmental impacts of conventional and toxic substances from various sources.

The UGLCCS recognizes Quality Assurance/Quality Control (QA/QC) aspects as crucial elements to the overall utility of study results. As part of the QA/QC program, thirteen interlaboratory performance evalution (QC) studies were designed and conducted by the Quality Management Work Group. The goal of these QC studies was to assist analytical laboratories, which are producing data for the UGLCC study, to generate reliable, accurate data and to assess their overall performance during the study. A total of some 100 parameters (organic, inorganic and physical properties) in three types of matrices (water, sediment and biota) will be assessed.

This second interlaboratory study, QM-2, was initiated on December 17, 1985. It involved the analysis of polyaromatic hydrocarbons (PAHs) in standard solutions. The original deadline for reporting results was set for March 20, 1986. However, several laboratories were late in reporting, so the study was closed on July 4, 1986.

STUDY PROFILE

From the returned questionnaires, the following 16 laboratories affirmed that they would participate in this study: U001, U005, U009, U063, U072, U079, U085, U013, U014, U028, U057, U075, U077, U078, U086, U090. By the time the study was closed, the last nine laboratories had not sent back any results. See the list of participants at the end of this report. Laboratory U014 found PAHs in toluene unsuitable for analysis by either GC/MS or HPLC. Laboratory U075 did not submit any results, since the method which they used to analyze the samples submitted under the UGLCC program specified using dichloromethane and isooctane. Toluene created some chromatography problems for this laboratory. Laboratory U086 stated that they would submit their results later, but to date no results have been received.

Since erratic in-house standard solutions had been shown to be the single major source of error in previous interlaboratory studies for organic parameters, the present study was designed to evaluate the accuracy of the participants' calibration standards for PAHs.

Each laboratory was provided with four ampules as described in Table 1. All standard solutions and the above test samples were prepared by the Quality Assurance and Methods Section (QAMS) of the National Water Research Institute (NWRI). Stock solutions for the PAHs were prepared from in-house analytical standards of purity greater than 98%. The design values and interlaboratory medians for

each parameter are given in Table 2. The design values were verified against NBS SRM 1647 by two analysts on different dates. The same PAH samples were also used in IJC Interlaboratory Study 52 involving 15 laboratories. The design values of these samples were confirmed by the interlaboratory medians of the IJC study.

Participants were asked to analyze samples 201-204 for 16 PAHs (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)-fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3,-cd)pyrene, naphthalene, phenanthrene and pyrene). In order to provide a rough indication of the precision of such analyses, these samples were sent out in blind duplicate pairs, as shown in Table 1.

RESULTS AND DISCUSSION

Analytical Methodology

All standard solutions could be quantified by direct injection into a gas chromatograph using either a flame ionization detector or a mass spectrometer and a suitable capillary column. If HPLC analysis was used some dilution of samples was needed. Two out of the seven reporting laboratories used GC/FID with capillary columns. Three laboratories used GC/MS, and U079 used GC/MS for only four parameters (naphthalene, acenaphthylene, acenaphthene and fluorene). Two laboratories used HPLC. See Table 3 for details of the methodology.

Data Evaluation

All raw data submitted by the participants are listed by parameter in the data summary (Appendix II). Since the number of samples analyzed was limited (4) and the number of reporting laboratories was small ($\leq$7) and varied for each parameter, neither the Youden ranking technique nor the computerized flagging procedure were used to evaluate the data. To evaluate the precision and accuracy of the PAH results in this study, the percent recoveries (reported results vs design values or interlaboratory medians) were calculated for each laboratory and tabulated in Table 4. (See Appendix I for a glossary of terms used in Table 4.) In some cases, because of the small number of reported results and the presence of outliers, the median did not coincide with the design value.

To provide a semi-quantitative evaluation of the results, the results were designated as very low, low, high and very high, based on the reported results as a % of the design value as shown below:

$\geq$ 150%	very high
149%-125%	high
124%-76%	satisfactory
75%-51%	low
$\leq$ 50%	very low

See Table 5 for a summary of each laboratory's results.

General Comments

Only one of the seven reporting laboratories reported their data by the originally set deadline (U079). Computer printouts with the raw data were sent to all reporting laboratories for verification in April, 1986. All laboratories except U063 returned their results verified. A final data summary was sent to the participating laboratories, the Quality Management Work Group, the Work Group Chairmen, and the M.C. and A.I.C. chairmen on July 11, 1986.

After reviewing the data summary, containing all of the laboratories' data, laboratory U063 discovered some anomalies in their previously reported data and submitted some updated results for PAHs on August 6, 1986. These late changes were not incorporated into this report, but can be found in Appendix III.

The overall comparability of interlaboratory PAH data was satisfactory. After rejection of outliers, the interlaboratory relative standard deviation for all PAHs in most samples was between 20 and 30%. All of the laboratories except U063, analyzed all 16 US EPA PAH priority pollutants (U063 did not analyze benzo(k)fluoranthene). Laboratories U005 and U072 could not separate some isomeric pairs. See lab-specific comments for details. In most cases the difference between the interlaboratory mean and median was less than 10%. Due to the presence of outlying data from laboratory U063 and in the case of acenaphthylene from U072, there was a >20% difference

between the mean and median for acenaphthylene, anthracene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene and benzo(k)fluoranthene for some samples (see Appendix II). Agreement between design values and interlaboratory medians for most PAHs was good for samples 201 and 202, although the medians were more than 15% lower than the design values in the cases of acenaphthene, chrysene, fluorene, phenanthrene and pyrene. For samples 203 and 204, the medians were more than 20% lower than the design values in the cases of acenaphthene, acenaphthylene, benzo(a)anthracene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene. The poorer agreement is probably due to the lower concentration range of samples 203 and 204, as some laboratories could not detect some parameters. Except for results from laboratory U063 on samples 203 and 204 for all parameters, and U079 for some parameters, the precision of within lab analysis was very good for the rest of the participants since the difference between duplicate analysis was usually <10%. The reported detection limits ranged from 0.02 ng/µℓ to 1.0 ng/µℓ. Laboratories U001 and U009 did not report any detection limits.

Lab-Specific Comments

See explanation of low, very low, high and very high on page 4.

U001

Results for samples 201 and 202 were accurate with 77-120% recovery, except naphthalene which was very high (152% of the design value). However, all PAH results for samples 203 and 204 were low (15-64% recovery). These data suggest that detector linearity was probably a problem for U001. For naphthalene, anthracene and dibenz(a,h)anthracene, samples 201 and 202 had "estimated" results reported, while samples 203 and 204 had "not detected" results. Precision between duplicate results was excellent since identical results were reported in all cases. No detection limits were reported.

U005

This laboratory's results were on the low side. Nine parameters had low results (<75% recovery) and only benzo(a)pyrene in sample 201 was high (126% recovery). For samples 203 and 204, anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene were not detected. There was no resolution of benzo(a)anthracene and chrysene or benzo(b)fluoranthene and benzo(k)fluoranthene. The precision between duplicate results was in most cases within ±10%.

U009

This laboratory's results were precise (within ±10%) and fairly accurate (60-119% recovery). Eight parameters had low results, mainly for samples 203 and 204. No detection limits were reported.

U063

Several of this laboratory's results were erratic. The accuracy was in most cases poor (67-479% recovery of the design value). Fourteen of the parameters analyzed had some high or very high results while three parameters had some low results.

Anthracene in sample 204 was not detected. The precision between duplicates for samples 201 and 202 was within ±10% in most cases, but for samples 203 and 204 the RSD in most cases was >40%. No results were reported for benzo(k)fluoranthene. No raw data verification was returned. When contacted by telephone, the laboratory requested to have the results remain as reported. See Appendix III for changes to data reported on August 6, 1986. These changes are not incorporated into this report. The precision for these new results did not change and the accuracy was still poor although it improved somewhat (24-144% recovery). Thirteen of the parameters had some low or very low results and anthracene results for samples 201 and 202 were still slightly high.

U072

Overall, for the parameters reported, the performance of this laboratory was good. Most parameters were quite accurate (90-121% recovery). Acenaphthylene results for samples 201 and 202 were very high (420% recovery) but it was not detected in samples 203 and 204. Benzo(k)fluoranthene was somewhat high in sample 203 (131% recovery). The precision was within ±10% in all cases. There was no resolution of acenaphthene and fluorene, benzo(a)anthracene and chrysene and indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. Naphthalene was not analyzed.

U079

Overall the accuracy of this laboratory was less satisfactory. Ten parameters had some low or very low results. Five parameters had some high or very high results. The accuracy was poor, ranging from 32-301% recovery. For all parameters except benzo(a)pyrene, benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene, there was at least one outlying high or low result. Fluorene was not detected in samples 203 and 204. The precision between duplicate results in some cases was poor, with the RSD as high as 88% for pyrene in samples 201 and 202.

U085

The accuracy for samples 201 and 202 was in most cases good. Five parameters had low results and one parameter had a high result. The precision was in most cases within ±10%. For samples 203 and 204 all of the parameters had low or very low results. For samples 203 and 204, six parameters had results reported as "trace" (below their detection limit) and two parameters had "not detected" results. The precision between samples 203 and 204 was poor. Most of the results had a RSD over 30%.

COMMENTS

The design of this interlaboratory performance evaluation study (QM-2) is necessarily simple due to limited resources and time available. It involved only four standard PAH solutions at concentrations which are easy to analyze. There are no interferences and minimal or no manipulation required to analyze these standard solutions. Therefore both precision and accuracy should be very easy to achieve by a competent laboratory. One should expect precision and accuracy better than ±25% for these types of samples at these concentrations. If the data are not satisfactory for these standard solutions, it is inconceivable what the data would look like from analysis of real samples, which require multi-steps (such as extraction, clean-up and evaporation).

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LIST OF PARTICIPANTS

Detroit Wastewater Treatment Plant, Detroit, Michigan

Michigan Department of Public Heath, Lansing, Michigan

National Water Research Institute, ECD, Burlington, Ontario

Ontario Ministry of the Environment, Rexdale, Ontario

US EPA, GLNPO, The Bionetics Corp., Chicago, Illinois

Water Quality National Laboratory, Burlington, Ontario

Zenon Environmental Inc., Burlington, Ontario

The following laboratories were given samples, but did not submit any results:

Barringer Magenta, Rexdale, Ontario

Great Lakes Environmental Research Laboratory,NOAA, Ann Arbor, Michigan

Michigan Department of Natural Resources, Lansing, Michigan

NWRI, ECD, Burlington, Ontario

US Army Corps of Engineers, Detroit, Michigan

US EPA/Raytheon Service Corp., Grosse Ile, Michigan

US Geological Survey, Arvada, Colorado

EPS, Wastewater Technology Centre, Burlington, Ontario

Mann Testing Laboratory, Mississauga, Ontario - Volunteer laboratory

Table 1. Samples distributed for analysis in QM-2.

Sample	Description
201	Mixture of 16 PAHs in toluene
202	Same as 201
203	Mixture of 16 PAHs in toluene
204	Same as 203

Table 2. Design values and interlaboratory medians for PAHs. All values are in pg/ul.

Parameter	Sample Number 201 and 202			Sample Number 203 and 204		
	Design Value	Median		Design Value	Median	
		201	202		203	204
acenaphthene	10.9	8.86	8.62	1.09	.820	.775
acenaphthylene	9.53	9.00	9.20	0.953	.620	.601
anthracene	8.34	7.50	7.47	0.334	.305	.330
benzo(a)anthracene	10.4	9.74	9.98	2.08	1.40	1.47
benzo(a)pyrene	9.54	9.11	10.3	0.954	1.06	.977
benzo(b)fluoranthene	9.29	9.08	9.49	0.929	.921	.730
benzo(g,h,i)perylene	9.47	9.06	9.19	0.947	1.01	.935
benzo(k)fluoranthene	10.7	10.0	8.80	0.535	.545	.520
chrysene	9.45	8.21	6.96	1.89	1.18	1.20
dibenz(a,h)anthracene	10.0	9.20	8.83	1.00	1.00	.835
fluoranthene	12.0	10.1	9.70	4.80	3.27	3.70
fluorene	11.7	9.22	8.84	1.17	.800	.800
indeno(1,2,3-cd)pyrene	8.89	8.47	8.09	0.889	.711	.691
naphthalene	6.59	7.62	5.57	0.659	.532	.600
phenanthrene	12.7	9.40	9.60	2.54	1.44	1.47
pyrene	12.0	10.9	10.0	4.80	3.60	3.76

Table 3. Analytical Methodology for PAHs.

Lab. No.	LC or GC Column Type	Detector
U001	GC — 30 m x .32 mm ID SPB-5 capillary column	MS (quantitation by peak height)
U005	GC — 30 m x .25 mm ID DB-5 capillary column	MS
U009	GLC — simultaneous dual capillary column DB-1701, SE-54	FID
U063	GC — details not supplied	MS
U072	HPLC — 25 cm x 4.6 mm ID Supelco LC-18	UV (quantitation by peak height)
U079	naphthalene, acenaphthylene, acenaphthene, fluorene — GC - Ultra #2 H.P. capillary column	MS (quantitation by peak area)
	remaining compounds — HPLC - Supelco PAH column	UV (quantitation by peak area)
U085	GC — 25 m SE-54 capillary column	FID

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U001

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	78.9	78.9	58.7	58.7	97.1	99.8	78.0	82.6
acenaphthylene	96.5	96.5	48.3	48.3	102	100	74.2	76.5
anthracene	120(E)	120(E)	ND	ND	133(E)	134(E)	ND	ND
benzo(a)anthracene	118	118	25.5	25.5	126	123	37.9	36.1
benzo(a)pyrene	78.6	78.6	18.9	18.9	82.3	72.8	17.0	18.4
benzo(b)fluoranthene	95.8	95.8	15.1	15.1	98.0	93.8	15.2	19.2
benzo(g,h,i)perylene	111	111	64.4	64.4	116	114	60.4	65.2
benzo(k)fluoranthene	82.2	82.2	35.5	35.5	88.0	100	34.9	36.5
chrysene	87.8	87.8	16.9	16.9	101	119	27.1	26.7
dibenz(a,h)anthracene	100(E)	100(E)	ND	ND	109(E)	113(E)	ND	ND
fluoranthene	80.0	80.0	52.1	52.1	95.0	99.0	76.5	67.6
fluorene	76.9	76.9	47.0	47.0	97.6	102	68.8	68.8
indeno(1,2,3-cd)pyrene	116	116	40.5	40.5	122	127	50.6	52.1
naphthalene	152(E)	152(E)	ND	ND	131(E)	180(E)	ND	ND
phenanthrene	78.0	78.0	43.3	43.3	105	103	76.4	74.8
pyrene	79.2	79.2	57.3	57.3	87.2	95.0	76.4	73.1

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U005

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	66.1	67.9	73.4	64.2	81.3	85.8	97.6	90.3
acenaphthylene	64.0	77.6	83.9	63.0	67.8	80.4	129	99.8
anthracene	69.5	69.5	ND	ND	77.3	77.6	ND	ND
benzo(a)anthracene	NS	NS	NS	NS	NS	NS	NS	NS
benzo(a)pyrene	126	122	ND	ND	132	113	ND	ND
benzo(b)fluoranthene	NS	NS	NS	NS	NS	NS	NS	NS
benzo(g,h,i)perylene	81.3	102	ND	ND	85.0	106	ND	ND
benzo(k)fluoranthene	NS	NS	NS	NS	NS	NS	NS	NS
chrysene	NS	NS	NS	NS	NS	NS	NS	NS
dibenz(a,h)anthracene	71.0	88.0	ND	ND	77.2	99.7	ND	ND
fluoranthene	84.2	80.8	83.3	77.1	100	100	122	100
fluorene	63.2	64.1	68.4	68.4	80.3	84.8	100	100
indeno(1,2,3-cd)pyrene	82.1	84.4	ND	ND	86.2	92.7	ND	ND
naphthalene	78.9	81.9	91.0	91.0	68.2	96.9	113	100
phenanthrene	74.0	73.2	74.8	74.8	100	96.9	132	129
pyrene	90.8	87.5	93.8	87.5	100	105	125	112

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U009

Parameter	% Recovery from Design Value Sample				% Recovery from Median Sample			
	201	202	203	204	201	202	203	204
acenaphthene	83.6	79.2	77.1	78.0	103	100	102	110
acenaphthylene	81.2	78.2	67.2	70.3	86.0	81.0	103	111
anthracene	94.6	89.6	92.8	98.8	105	100	102	100
benzo(a)anthracene	93.7	96.0	87.0	91.3	100	100	129	129
benzo(a)pyrene	95.5	108	115	119	100	99.7	104	117
benzo(b)fluoranthene	99.6	107	74.3	78.6	102	105	74.9	100
benzo(g,h,i)perylene	79.7	91.6	77.1	81.3	83.3	94.3	72.3	82.4
benzo(k)fluoranthene	81.9	87.6	72.9	72.9	87.6	106	71.6	75.0
chrysene	64.8	68.1	62.4	63.5	74.5	92.5	100	100
dibenz(a,h)anthracene	72.5	75.8	67.0	67.0	78.8	85.8	67.0	80.2
fluoranthene	95.4	92.2	90.8	94.2	113	114	133	122
fluorene	80.6	75.4	70.1	71.8	102	99.8	103	105
indeno(1,2,3-cd)pyrene	76.9	74.7	58.5	59.6	80.8	82.1	73.1	76.7
naphthalene	89.5	85.6	80.4	78.9	77.4	101	99.6	86.7
phenanthrene	63.6	60.1	56.7	57.9	86.0	79.5	100	100
pyrene	83.8	82.7	80.6	78.3	92.2	99.2	108	100

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U063

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	135	133	107	179	166	168	143	252
acenaphthylene	144	149	118	236	152	154	181	374
anthracene	285	305	186	ND	317	340	203	ND
benzo(a)anthracene	89.7	100	67.3	129	95.8	104	100	182
benzo(a)pyrene	220	229	142	319	231	212	127	311
benzo(b)fluoranthene	394	479	262	466	403	469	264	593
benzo(g,h,i)perylene	190	205	147	307	199	211	138	311
benzo(k)fluoranthene	NA	NA	NA	NA	NA	NA	NA	NA
chrysene	98.4	98.4	69.3	133	113	134	111	210
dibenz(a,h)anthracene	151	152	90.0	170	164	172	90.0	204
fluoranthene	103	127	68.1	156	123	157	100	202
fluorene	124	126	81.2	150	157	166	119	220
indeno(1,2,3-cd)pyrene	218	214	127	240	229	235	159	308
naphthalene	178	170	118	178	154	201	147	195
phenanthrene	120	124	96.5	119	162	165	170	205
pyrene	97.5	109	64.6	136	107	131	86.1	174

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U072

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	NS	NS	NS	NS	NS	NS	NS	NS
acenaphthylene	420	420	ND	ND	444	435	ND	ND
anthracene	90.0	92.3	90.0	90.0	100	103	98.4	90.9
benzo(a)anthracene	NS	NS	NS	NS	NS	NS	NS	NS
benzo(a)pyrene	106	111	105	94.3	111	103	94.3	92.1
benzo(b)fluoranthene	105	109	108	108	108	106	109	137
benzo(g,h,i)perylene	NS	NS	NS	NS	NS	NS	NS	NS
benzo(k)fluoranthene	98.1	102	131	121	105	124	128	125
chrysene	NS	NS	NS	NS	NS	NS	NS	NS
dibenz(a,h)anthracene	103	103	110	100	112	117	110	120
fluoranthene	90.0	90.0	100	91.7	107	111	147	119
fluorene	NS	NS	NS	NS	NS	NS	NS	NS
indeno(1,2,3-cd)pyrene	NS	NS	NS	NS	NS	NS	NS	NS
naphthalene	-	-	-	-	-	-	-	-
phenanthrene	89.8	92.9	90.6	86.6	121	123	160	150
pyrene	90.0	90.0	100	95.8	99.1	108	133	122

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U079

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	59.5	32.1	36.7	91.2	73.3	40.6	48.8	128
acenaphthylene	66.9	34.9	49.5	63.1	70.9	36.2	76.1	100
anthracene	83.3	68.1	64.4	119	92.7	76.0	70.5	120
benzo(a)anthracene	76.4	70.3	80.8	70.7	81.6	73.2	120	100
benzo(a)pyrene	95.2	81.4	111	102	99.7	75.4	100	100
benzo(b)fluoranthene	88.3	80.6	99.1	78.6	90.3	78.9	100	100
benzo(g,h,i)perylene	93.1	85.6	135	116	97.4	88.1	127	118
benzo(k)fluoranthene	105	78.7	290	301	112	95.7	284	310
chrysene	86.9	73.7	106	74.1	100	100	169	117
dibenz(a,h)anthracene	88.1	88.3	117	60.3	95.8	100	117	72.2
fluoranthene	79.3	42.1	57.5	56.7	94.2	52.1	84.4	73.5
fluorene	145	75.6	ND	ND	184	100	ND	ND
indeno(1,2,3-cd)pyrene	98.2	86.3	101	95.8	103	94.8	127	123
naphthalene	142	75.0	80.7	162	122	88.7	100	178
phenanthrene	61.7	59.6	47.6	47.6	83.4	78.9	84.0	82.3
pyrene	149	34.8	61.9	56.9	164	41.7	82.5	72.6

*See Appendix I for explanation of codes.

Table 4. Percent recovery calculated from the design values and the interlaboratory medians for PAHs.

Lab Number: U085

Parameter	% Recovery from Design Value				% Recovery from Median			
	Sample				Sample			
	201	202	203	204	201	202	203	204
acenaphthene	119	128	110	64.2	147	162	146	90.3
acenaphthylene	94.4	96.5	63.0	52.5	100	100	96.8	83.2
anthracene	87.5	85.1	Tra	Tra	97.3	95.0	Tra	Tra
benzo(a)anthracene	95.2	68.3	48.1	28.8	102	71.1	71.4	40.8
benzo(a)pyrene	83.9	74.4	Tra	Tra	87.8	68.9	Tra	Tra
benzo(b)fluoranthene	91.5	96.9	Tra	Tra	93.6	94.8	Tra	Tra
benzo(g,h,i)perylene	98.2	86.6	Tra	Tra	103	89.2	Tra	Tra
benzo(k)fluoranthene	93.5	78.5	Tra	Tra	100	95.5	Tra	Tra
chrysene	70.9	59.3	42.3	37.0	81.6	80.5	67.8	58.3
dibenz(a,h)anthracene	92.0	80.0	ND	ND	100	90.6	ND	ND
fluoranthene	79.2	77.5	62.5	41.7	94.1	95.9	91.7	54.1
fluorene	49.6	48.7	25.6	25.6	62.9	64.5	37.5	37.5
indeno(1,2,3-cd)pyrene	92.2	95.6	Tra	ND	96.8	105	Tra	ND
naphthalene	80.4	83.5	75.9	45.5	69.6	98.7	94.0	50.0
phenanthrene	74.0	75.6	51.2	35.4	100	100	90.3	61.2
pyrene	100	83.3	75.0	47.9	110	100	100	61.2

*See Appendix I for explanation of codes.

Table 5. Summary of laboratory results based on the % recovery of the design value. (See page 4.)

Lab. No.	Parameter	Comments
U001	acenaphthene	samples 203 & 204 - low
	acenaphthylene	samples 203 & 204 - v. low
	anthracene	samples 203 & 204 - ND
	benzo(a)anthracene benzo(a)pyrene benzo(b)fluoranthene	samples 203 & 204 - v. low
	benzo(g,h,i)perylene	samples 203 & 204 - low
	benzo(k)fluoranthene crysene	samples 203 & 204 - v. low
	dibenz(a,h)anthracene	samples 203 & 204 - ND
	fluoranthene	samples 203 & 204 - low
	fluorene indeno(1,2,3-cd)pyrene	samples 203 & 204 - v. low
	naphthalene	samples 201 & 202 - v. high; 203 & 204 - ND
	phenanthrene	samples 203 & 204 - v. low
	pyrene	samples 203 & 204 - low
U005	acenaphthene	all 4 samples - low
	acenaphthylene	samples 201 & 204 - low
	anthracene	samples 201 & 202 - low; 203 & 204 - ND
	benzo(a)pyrene	sample 201 - high; 203 & 204 - ND
	benzo(g,h,i)perylene indeno(1,2,3-cd)pyrene	samples 203 & 204 - ND
	dibenz(a,h)anthracene	sample 201 - low; 203 & 204 - ND
	fluorene, phenanthrene	all 4 samples - low
U009	acenaphthylene	samples 203 & 204 - low
	benzo(b)fluoranthene	sample 203 - low
	benzo(k)fluoranthene	samples 203 & 204 - low
	chrysene	all 4 samples - low
	dibenz(a,h)anthracene	samples 201,203 & 204 - low
	fluorene	samples 203 & 204 - low
	indeno(1,2,3-cd)pyrene	samples 202,203 & 204 - low
	phenanthrene	all 4 samples - low

Table 5. Summary of laboratory results based on the % recovery of the design value. continued

Lab. No.	Parameter	Comments
U063	acenaphthene acenaphthylene	samples 201 & 202 - high sample 204 - v. high
	anthracene	samples 201,202 & 203 - v. high sample 204 - ND
	benzo(a)anthracene	sample 203 - low; 204 - high
	benzo(a)pyrene benzo(g,h,i)perylene	samples 201,202 & 204- v. high; 203 - high
	benzo(b)fluoranthene	all 4 samples - v. high
	chrysene	sample 203 - low; 204 - high
	dibenz(a,h)anthracene	samples 201,202 & 204 - v. high
	fluoranthene	sample 202 - high; 203 - low; 204 - v. high
	fluorene	sample 202 - high; 204 - v. high
	indeno(1,2,3-cd)pyrene	samples 201,202 & 204 - v. high; 203 - high
	naphthalene	samples 201,202 & 204 - v. high
	pyrene	sample 203 - low; 204 - high
U072	acenaphthylene	samples 201 & 202 - v.high; 203 & 204 - ND
	benzo(k)fluoranthene	sample 203 - high
U079	acenaphthene	sample 201 - low; 202 & 203 - v. low
	acenaphthylene	samples 201 & 204 - low; 202 & 203 - v. low
	anthracene	samples 202 & 203 - low
	benzo(a)anthracene	samples 202 & 204 - low
	benzo(g,h,i)perylene	samples 203 - high
	benzo(k)fluoranthene	samples 203 & 204 - v. high
	chrysene	samples 202 & 204 - low
	dibenz(a,h)anthracene	sample 204 - low
	fluoranthene	sample 202 - v. low 203 & 204 - low
	fluorene	sample 201 - high; 203 & 204 - ND
	naphthalene	sample 201 - high; 204 - v. high
	phenanthrene	sample 201 & 202 - low; 203 & 204 - v. low
	pyrene	sample 201 - high; 202 - v. low, 203 & 204 - low

Table 5. Summary of laboratory results based on the % recovery of the design value. continued

Lab. No.	Parameter	Comments
U085	acenaphthene	sample 202 - high; 204 - low
	acenaphthylene	samples 203 & 204 - low
	anthracene benzo(a)pyrene benzo(b)fluoranthene benzo(g,h,i)perylene benzo(k)fluoranthene	samples 203 & 204 - trace amounts (below detection limit)
	indeno(1,2,3-cd)pyrene	sample 203 - trace; 204 - ND
	benzo(a)anthracene,chrysene	sample 202 - low; 203 & 204 - v. low
	dibenz(a,h)anthracene	samples 203 & 204 - ND
	fluoranthene	sample 203 - low; 204 - v. low
	fluorene	all four v. low
	naphthalene, pyrene	sample 204 - v. low
	phenanthrene	samples 201 & 203 - low; 204 - v. low

APPENDIX I

GLOSSARY OF TERMS

NA: not analyzed

NRA: not routinely analyzed

N or ND: not detected

NAPP: not applicable

Tra: trace, below detection limit

NS: not separated, two parameters co-eluted together

E: estimate value

W: A "W" code is used with a reported result when no measurement was possible due to no response of the instrument to the sample. The "W" is preceded by the smallest determinative division that can be used in the units used in reporting.

T: The "T" code is used with values between the Criterion of Detection and the "W" value. The Criterion of Detection is commonly thought of by many as the limit of detection.

APPENDIX II

UGLCC INTERLABORATORY PERFORMANCE EVALUATION STUDY

QM-2 PAHs IN AMPULES

FINAL DATA SUMMARY

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: ACENAPHTHENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	8.6	8.6	.64	.64
U005	7.2	7.4	.8	.7
U009	9.11	8.63	.84	.85
U063	14.7	14.5	1.17	1.95
U079	6.49	3.50	.400	.994
U085	13.	14.	1.2	.7
TOTAL LABS REPORTING	6	6	6	6
TOTAL LABS USED	6	6	6	6
MEAN	9.85000	9.43833	.84167	.97233
STD DEV	3.28229	4.17622	.30779	.49599
MEDIAN	8.85500	8.61500	.82000	.77500

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/03/15.

PARAMETER: ACENAPHTHYLENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	9.2	9.2	.46	.46
U005	6.1	7.4	.8	.6
U009	7.74	7.45	.64	.67
U063	13.7	14.2	1.12	2.25
U072	40.	40.		
U079	6.38	3.33	.472	.601
U085	9.0	9.2	.6	.5
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	6	6
MEAN	13.16000	12.96857	.68200	.84683
STD DEV	12.10270	12.34898	.24605	.69158
MEDIAN	9.00000	9.20000	.62000	.60050

ANALYSIS OF PAH$_B$

PRINTOUT PREPARED: 86/09/15.

PARAMETER: ANTHRACENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	10.	10.	N	N
U005	5.8	5.8	N	N
U009	7.89	7.47	.31	.33
U063	23.8	25.4	.62	N
U072	7.5	7.7	.3	.3
U079	6.95	5.68	.215	.396
U085	7.3	7.1	N	N
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	4	3
MEAN	9.89143	9.87857	.36125	.34200
STD DEV	6.26222	6.99357	.17769	.04911
MEDIAN	7.50000	7.47000	.30500	.33000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: BENZO(A)ANTHRACENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	12.3	12.3	.53	.53
U009	9.74	9.98	1.81	1.90
U063	9.33	10.4	1.40	2.68
U079	7.95	7.31	1.68	1.47
U085	9.9	7.1	1.0	.6
TOTAL LABS REPORTING	5	5	5	5
TOTAL LABS USED	5	5	5	5
MEAN	9.84400	9.41800	1.28400	1.43600
STD DEV	1.57300	2.20244	.52348	.90605
MEDIAN	9.74000	9.98000	1.40000	1.47000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: BENZO(A)PYRENE NG/UL

SAMPLE RESULTS

LAB	201		202		203		204
U001	7.5		7.5		.18		.18
U005	12.0		11.5	N		N	
U009	9.11		10.27		1.10		1.14
U063	21.0		21.8		1.35		3.04
U072	10.1		10.6		1.0		.3
U079	9.08		7.77		1.06		.977
U085	8.0		7.1	N		N	
TOTAL LABS REPORTING	7		7		7		7
TOTAL LABS USED	7		7		5		5
MEAN	10.97000		10.94857		.93800		1.24740
STD DEV	4.66033		5.09194		.44421		1.06748
MEDIAN	9.11000		10.27000		1.06000		.97700

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: BENZO(B)FLUORANTHENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	8.9	8.9	.14	.14
U009	9.25	9.97	.59	.73
U063	36.6	44.5	2.43	4.33
U072	9.8	10.1	1.0	1.0
U079	8.20	7.49	.921	.730
U085	8.5	9.0 N	N	
TOTAL LABS REPORTING	6	6	6	6
TOTAL LABS USED	6	6	5	5
MEAN	13.54167	14.99333	1.03620	1.38600
STD DEV	11.31019	14.48565	.84957	1.67551
MEDIAN	9.07500	9.48500	.92100	.73000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: BENZO(G,H,I)PERYLENE NG/UL

SAMPLE RESULTS

LAB	201		202		203		204	
U001	10.5		10.5		.61		.61	
U005	7.7		9.7	N		N		
U009	7.55		8.67		.73		.77	
U063	18.0		19.4		1.39		2.91	
U079	8.82		8.10		1.26		1.10	
U085	9.3		8.2	N		N		
TOTAL LABS REPORTING		6		6		6		6
TOTAL LABS USED		6		6		4		4
MEAN		10.31167		10.76167		1.00250		1.34750
STD DEV		3.92026		4.33216		.38965		1.06146
MEDIAN		9.06000		9.18500		1.00500		.93500

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/03/15.

PARAMETER: BENZO(K)FLUORANTHENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	8.8	8.3	.19	.19
U009	8.76	9.37	.39	.39
U072	10.5	10.9	.7	.55
U079	11.2	8.42	1.55	1.61
U085	10.	8.4 N	N	
TOTAL LABS REPORTING	5	5	5	5
TOTAL LABS USED	5	5	4	4
MEAN	9.85200	9.17800	.70750	.71000
STD DEV	1.06748	1.03982	.59958	.62826
MEDIAN	10.00000	8.80000	.54500	.52000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: CHRYSENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	8.3	8.3	.32	.32
U009	6.12	6.44	1.18	1.20
U063	9.30	9.3	1.31	2.52
U079	8.21	6.96	2.00	1.40
U085	6.7	5.6	.8	.7
TOTAL LABS REPORTING	5	5	5	5
TOTAL LABS USED	5	5	5	5
MEAN	7.72600	7.32000	1.12200	1.22800
STD DEV	1.29162	1.47845	.62379	.83709
MEDIAN	8.21000	6.96000	1.18000	1.20000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: DIBENZ(A,H)ANTHRACENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	10.	10.	N	N
U005	7.1	8.8	N	N
U009	7.25	7.58	.67	.67
U063	15.1	15.2	.90	1.70
U072	10.3	10.3	1.1	1.0
U079	8.81	8.83	1.17	.603
U085	9.2	8.0	N	N
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	4	4
MEAN	9.68000	9.91571	.96000	.99325
STD DEV	2.68985	2.56767	.22465	.50210
MEDIAN	9.20000	8.83000	1.00000	.83500

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: FLUORANTHENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	9.6	9.6	2.5	2.5
U005	10.1	9.7	[illegible].0	3.7
U009	11.45	11.06	4.36	4.52
U063	12.4	15.2	3.27	7.49
U072	10.8	10.8	[illegible].8	4.4
U079	9.51	5.05	2.76	2.72
U085	9.5	9.3	3.0	2.0
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	7	7
MEAN	10.48000	10.10143	3.52714	3.90429
STD DEV	1.12174	2.99928	.86642	1.84954
MEDIAN	10.10000	9.70000	3.27000	3.70000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: FLUCRENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	9.0	9.0	.55	.55
U005	7.4	7.5	.8	.8
U009	9.43	8.82	.82	.84
U063	14.5	14.7	.95	1.76
U079	17.0	8.85 N	N	
U085	5.8	5.7	.3	.3
TOTAL LABS REPORTING	6	6	6	6
TOTAL LABS USED	6	6	5	5
MEAN	10.52167	9.09500	.68400	.85000
STD DEV	4.32070	3.02095	.25590	.55299
MEDIAN	9.21500	8.83500	.80000	.80000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: INDENO(1,2,3CD)PYRENE NG/UL

SAMPLE RESULTS

LAB	201		202		203		204	
U001	10.3		10.3		.36		.36	
U005	7.3		7.5	N		N		
U009	6.84		6.64		.52		.53	
U063	19.4		19.0		1.13		2.13	
U079	8.73		7.67		.902		.552	
U085	8.2		8.5	N		N		
TOTAL LABS REPORTING	6		6		6		6	
TOTAL LABS USED	6		6		4		4	
MEAN	10.12833		9.93500		.72800		.96800	
STD DEV	4.70063		4.61049		.35146		.80108	
MEDIAN	8.46500		8.08500		.71100		.69100	

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: NAPHTHALENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	10.	10. N	N	
U005	5.2	5.4	.6	.6
U009	5.90	5.64	.53	.52
U063	11.7	11.2	.78	1.17
U079	9.33	4.94	.532	1.07
U085	5.3	5.5	.5	.3
TOTAL LABS REPORTING	6	6	6	6
TOTAL LABS USED	6	6	5	5
MEAN	7.90500	7.11333	.58840	.73200
STD DEV	2.79087	2.73735	.11319	.37252
MEDIAN	7.61500	5.57000	.53200	.60000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/03/15.

PARAMETER: PHENANTHRENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	9.9	9.9	1.1	1.1
U005	9.4	9.3	1.9	1.9
U009	8.08	7.63	1.44	1.47
U063	15.2	15.8	2.45	3.01
U072	11.4	11.6	2.3	2.2
U079	7.84	7.57	1.21	1.21
U085	9.4	9.6	1.3	.9
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	7	7
MEAN	10.17429	10.22857	1.67143	1.68429
STD DEV	2.51228	2.84886	.54536	.74132
MEDIAN	9.40000	9.60000	1.44000	1.47000

ANALYSIS OF PAHs

PRINTOUT PREPARED: 86/09/15.

PARAMETER: PYRENE NG/UL

SAMPLE RESULTS

LAB	201	202	203	204
U001	9.5	9.5	2.75	2.75
U005	10.9	10.5	4.5	4.2
U009	10.05	9.92	3.87	3.76
U063	11.7	13.1	3.10	6.53
U072	10.8	10.8	4.8	4.6
U079	17.9	4.17	2.97	2.73
U085	12.	10.	3.6	2.3
TOTAL LABS REPORTING	7	7	7	7
TOTAL LABS USED	7	7	7	7
MEAN	11.83571	9.71266	3.65571	3.83857
STD DEV	2.81110	2.71316	.76215	1.45725
MEDIAN	10.90000	10.00000	3.60000	3.76000

APPENDIX III

Changes submitted on August 6, 1986 by laboratory U063

UGLCC INTERLABORATORY STUDY

QM-2 PAH RESULTS (ng/uL)

	201	202	203	204
naphthalene	5.1	5.28	0.60	0.24
acenaphthylene	6.0	6.84	0.91	0.45
acenaphthene	6.0	6.7	0.87	0.46
anthracene	10.4	12.0	0.48	ND
benzo(a)anthracene	4.1	4.9	1.08	0.54
benzo(a)pyrene	9.2	10.3	1.04	0.62
benzo(b)fluoranthene & benzo(k)fluoranthene	16.0	21.0	1.88	0.88
benzo(g,h,i)perylene	7.9	9.15	1.08	0.59
chrysene	4.1	4.3	1.01	0.51
dibenz(a,h)anthracene	6.6	7.2	0.7	0.34
fluoranthene	5.4	7.2	2.53	1.52
fluorene	6.34	6.93	0.74	0.35
indeno(1,2,3-cd)pyrene	8.48	8.96	0.87	0.43
phenanthrene	6.64	7.45	1.90	0.61
pyrene	5.11	6.18	2.40	1.32