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Surface Water and Soil Chemistry Quality Assurance/Quality Control Audit Gill Creek Sediment Study January 23, 1989

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January 23, 1989
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E. I. du Pont de Nemours and Company
26th Street and Buffalo Avenue
Niagara Falls, New York 14302

Attention: Mr. Bev Adams

Olin Corporation
Lower River Road
Charleston, Tennessee 37310

Attention: Mr. Blaine Butaud

Re: Surface Water and Soil Chemistry
Quality Assurance/Quality Control Audit
Gill Creek Sediment Study

Gentlemen:

Woodward-Clyde Consultants (WCC) is pleased to present the results of the Quality Assurance/Quality Control (QA/QC) audit on the Gill Creek sampling program from June 9 through 16, 1988 at Niagara Falls, New York. Analytical results were audited by WCC personnel in accordance with the New York State Department of Environmental Conservation, State Contract Laboratory Protocol (NYSDEC-CLP) of November 1987.

If you have any questions, please contact us. We appreciate the opportunity to work with Du Pont and Olin on the Gill Creek project.

Sincerely,

WOODWARD-CLYDE CONSULTANTS

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SURFACE WATER AND SOIL CHEMISTRY
QUALITY ASSURANCE/QUALITY CONTROL AUDIT
GILL CREEK
NIAGARA FALLS, NEW YORK

Submitted to:

E. I. DUPONT DE NEMOURS AND COMPANY, INC.
and
OLIN CORPORATION

Prepared by:

WOODWARD-CLYDE CONSULTANTS

Plymouth Meeting, Pennsylvania

January 1989

EXECUTIVE SUMMARY

A Quality Assurance/Quality Control (QA/QC) DEC-CLP audit was performed on the analytical results of surface water and soil samples collected from Gill Creek, Niagara Falls, New York. Surface water and soil samples were collected from June 9 through 16, 1987, and were analyzed by General Testing Corporation (GTC) of Rochester, New York. Ten sediment samples and one duplicate sample were analyzed for the Hazardous Substance List (HSL) Compounds. Fifty-four sediment samples and nine duplicates, five surface water samples, five elutriate water samples, and seven field blanks were analyzed for site-specific compounds. Seven trip blanks were analyzed for volatile organics. Eight sediment samples were subcontracted to Midwest Research Institute in Kansas City, Missouri for dioxin and furan analysis. The analytical data were audited by Woodward-Clyde Consultants (WCC) audit personnel.

Holding times were exceeded for five volatile analyses and six base/neutral-acid extractions (BNA) in the HSL samples. Four BNA extracts were analyzed outside of holding times for the site-specific compounds.

One BNA surrogate and two pesticide/PCB surrogates exceeded spike recovery criteria for the HSL analyses. Phthalate interference and surrogate dilution were a problem in several of the HSL pesticide/PCB analyses. One volatile, twenty-one BNA and ninety-three pesticide/PCB surrogates exceeded the recommended spike recovery criteria for the site-specific compound analyses.

Eleven BNA and pesticide compounds exceeded the matrix spike criteria for the HSL analyses. Six metals also exceeded their matrix spike recovery criteria. One volatile and three BNA matrix spikes exceeded the matrix spike criteria for the site-specific compound analyses. Matrix spike compounds were diluted out in most pesticide/PCB analyses.

Bis-(2-ethylhexyl)phthalate was detected in one method blank associated with the HSL analyses.

This detailed QA/QC review of the Gill Creek data indicates several analytical violations. However, given the highly contaminated nature of the samples, these violations are

not considered to be serious ones. The samples do contain high concentrations of the chemicals analyzed. A QA/QC violation resulting in even an order-of-magnitude concentration difference would not change that conclusion. Consequently, WCC recommends that this set of analytical data be accepted with the appropriate data qualifiers and that QA/QC criteria be adhered to more strictly during the remediation phase of the program as contaminant concentrations are lowered.

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1.0 INTRODUCTION

This report presents Woodward-Clyde Consultants' (WCC) Quality Assurance/Quality Control (QA/QC) Audit of the analytical results for the Gill Creek water and sediment sampling program. The Gill Creek sampling program is a joint investigation commissioned by E.I. du Pont de Nemours and Company and the Olin Corporation both of Niagara Falls, New York. Samples were collected by WCC in June 1988 (Figure 1) and transported by General Testing Corporation (GTC) to their laboratory in Rochester, New York for analyses. The samples were analyzed using RCRA SW-846 Third Edition methods and holding times with the New York State Department of Environmental Conservation Contract Laboratory Protocol (NYSDEC-CLP) QA/QC deliverables package. Five samples were subcontracted to Empire Soils, Inc. in the Buffalo area for a grain size analyses. Eight samples were subcontracted to Midwest Research Institute (MRI) in Kansas City, Missouri for dioxin and furan analysis. Upon receipt, the analytical data were audited by WCC audit personnel using the NYSDEC-CLP document.

2.0 QA/QC AUDIT OF GENERAL TESTING DATA

Sixty-four sediment samples, ten surface water samples, seven field blanks, seven trip blanks, and nine duplicates were collected between June 9 through 16, 1988. The ten sediment samples listed in Table 1 were analyzed for the Hazardous Substance List (HSL) compounds. The remaining fifty-four sediment samples listed in Table 2 were analyzed for several site-specific compounds. Table 3 presents the site-specific compounds. The surface water samples were analyzed for the site-specific compounds using two different analytical procedures. Five surface water samples were analyzed using the NYSDEC-CLP and will be referred to as raw water samples. The remaining five surface water samples were collected with paired surface sediment samples for performance of the U.S. Army Corps of Engineers elutriate procedure. The sediments from the elutriate pairs were also analyzed for grain size. As part of the field sampling quality control, QA/QC field and trip blanks were collected and analyzed (Table 4).

In accordance with the NYSDEC-CLP, the following QA/QC items were reviewed.

- Holding times
- Surrogate spikes
- Matrix spikes and matrix spike duplicates
- Method blanks
- Instrument tuning and calibration
- Trip and Field Blanks
- Field Duplicates
- Chain-of-Custody Forms

Each of the QA/QC items presented above comprise a section of this report. Within each QA/QC section, the different data sets are discussed and QA/QC violations presented. In instances where data failed to meet QA/QC criteria, the sample results were checked to see that the correct qualifiers were applied by the laboratory in accordance with USEPA Laboratory Data Validation documents.

2.1 LABORATORY ANALYTICAL METHODS

All sediment and raw water samples were analyzed using methods cited in the SW-846 third edition (draft) (November 1986). The elutriate water samples were analyzed using the methods referenced in the EPA Technical Report EPA/CE-81-1, EPA/Corps of Engineers, Technical Committee on Criteria for Dredged and Fill Material, Procedures for Handling and Chemical Analysis of Sediment and Water Samples, May 1981 (Appendix A).

2.2 HOLDING TIME

The holding time is defined as the amount of time from sample receipt to extraction and/or analysis. Different holding times are specified for aqueous and sediment samples. For aqueous samples, the volatile organics analyses must be performed within fourteen days of sample receipt. Semi-volatile aqueous analyses, which include base/neutral extractables, acid extractables (BNA) and pesticides/PCBs require that the sample be extracted within seven days of receipt and analyzed within 40 days of extraction. The volatile analyses for sediment samples must be performed within fourteen days of sample receipt. Semi-volatile sediment analyses require that the sample be extracted within 14 days of receipt and analyzed within 40 days of extraction. Mercury preparation and analysis must occur

within 28 days of sample receipt into the laboratory. All other metals must be prepared and analyzed within 6 months of sample date.

2.2.1 HOLDING TIME - HAZARDOUS SUBSTANCE LIST

All pesticide/PCB extractions and analyses were within the specified holding times. However, five of eleven volatile samples exceeded the analysis holding time of fourteen days. Due to QA/QC problems, six of eleven base/neutral, acid extractable (BNA) samples required re-extraction outside the extraction holding time. These six samples were re-analyzed within the 40 day holding time of both the first and the second extraction date.

The following is a summary of HSL samples which exceeded holding time limits:

Parameter	Sample Number	No. of Days Exceeding Analytical Holding Time
Volatiles (Method 8020)	2-T6-SC, 2-T6-MC	3
	3-T8-MC, 1-T4-SC, 3-T8-SC	2

Parameter	Sample Number	No. of Days Exceeding Extraction Holding Time
BNA (Method 8270)	5-4G Dup, 5-4G	22
	4-T10-SC, 4-T10-MC	20
	5-5G, 1-T1C	18

2.2.2 HOLDING TIME - SITE-SPECIFIC COMPOUND LIST

ELUTRIATE SAMPLES: All volatile and semi-volatile extractions and analyses were within the recommended holding time for all samples.

SEDIMENT SAMPLES: All volatile analyses and semi-volatile extractions occurred within respective holding times. All pesticide/PCB extracts were analyzed within the specified holding time. However, four BNA samples were analyzed outside the forty day holding time. These exceedances are presented below:

Parameter	Sample Number	No. of Days Exceeding Analytical Holding Time
BNA (Method 8270)	1-T4-SC, 3-T7-2D, 3-T7-2D dup, 3-T8-2S	12

RAW WATER SAMPLES: All volatile and semi-volatile extractions and analyses occurred within their respective holding times for all samples.

2.3 SURROGATE SPIKES

Surrogate spikes are isotopically labeled compounds used to quantitate recoveries. Spikes were added to all volatile, semi-volatile and pesticide/PCB samples. Toluene-d8, bromofluorobenzene and bromochloropropane were used to spike the volatile samples analyzed for the HSL. Samples analyzed for site-specific volatile compounds were spiked with 2,3,5-trimethylbenzene. Nitrobenzene-d5, 2-fluorobiphenyl, terphenyl-d14, phenol-d6, 2-fluorophenol and 2,4,6,-tribromophenol were used to spike the base/neutral and acid extractable samples analyzed for the HSL. Only nitrobenzene-d5 and 2-fluorobiphenyl were used as surrogate spikes for the BNA samples analyzed for the site specific compounds. Dibutylchlorendate and tetrachloro-meta-xylene were used to spike the pesticide/PCB fraction in both HSL and site specific samples.

2.3.1 SURROGATE SPIKES - HAZARDOUS SUBSTANCE LIST

All volatile surrogate spike recoveries were within acceptable percent recovery ranges. One base/neutral sample exceeded the acceptable percent recovery range for nitrobenzene-d5. Four pesticide/PCB samples and one method blank exceeded the acceptable percent recovery range for dibutylchlorendate (DBC). Three pesticide/PCB samples exceeded the acceptable percent recovery range for tetrachloro-meta-xylene (TCMX). Both DBC and TCMX were diluted out of seven samples. Listed below are the samples with surrogate spike exceedances:

Sample	Percent Recovery	Surrogate Compound and Range
3-T8-SC	22	Nitrobenzene-d5 (23-120)
5-4G Dup	Phthalate Interference	Dibutylchlorendate (20-150)
5-4G	Phthalate Interference	Dibutylchlorendate (20-150)
	28	Tetrachloro-meta-xylene (40-152)
5-5G	Phthalate Interference	Dibutylchlorendate (20-150)
1-T1-C	Phthalate Interference	Dibutylchlorendate (20-150)
1-T1-CMS	Phthalate Interference	Tetrachloro-meta-xylene (40-152)
1-T1-CMSD	Phthalate Interference	Tetrachloro-meta-xylene (40-152)
Method Blank	Outside QC Limit	Dibutylchlorendate (20-150)
2-T6-SC	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
2-T6-MC	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
3-T8-MC	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
1-T4-SC	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
3-T8-SC	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
3-T8-SC(MS)	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)
3-T8-SC(MSD)	Diluted Out	Dibutylchlorendate (20-150)
	Diluted Out	Tetrachloro-meta-xylene (40-152)

According to NYSDEC-CLP methodology, the laboratory should have re-extracted and re-analyzed all samples associated with the method blank surrogate failure.

2.3.2 SURROGATE SPIKES - SITE-SPECIFIC COMPOUND LIST

ELUTRIATE SAMPLES: All surrogate recoveries for the volatile compounds were within the acceptable recovery criteria. Six BNA samples exceeded recovery criteria for the surrogate 2-fluorobiphenyl. Seven pesticide/PCB samples exceeded recovery criteria for both pesticide surrogates DBC and TCMX. The elutriate samples with surrogate exceedances are listed below.

Sample	Percent Recovery	Surrogate Compound and Range
Method Blank	36, 164	2-Fluorobiphenyl(43-116), Dibutylchlorendate (24-1
5-1E	34	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
1-2E	39	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
2-2E	35	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
3-2E	41	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
3-2EMS	42	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
3-2EMSD	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)
4-2E	40	2-Fluorobiphenyl (43-116)
	Diluted Out	Dibutylchlorendate (24-154)
	Diluted Out	Tetrachloro-meta-xylene (24-154)

According to NYSDEC-CLP methodology, the laboratory should have re-extracted and re-analyzed all samples associated with the method blank surrogate failure.

SEDIMENT SAMPLES: One volatile, thirteen BNA and seventy pesticide/PCB samples had surrogates exceeding spike recovery criteria. Surrogate exceedances are listed below.

Sample	Percent Recovery	Surrogate Compound and Range
5-1G	59	2,3,5-Trimethylbenzene (60-140)
	Diluted Out	Dibutylchlorendate (20-150)
2-T6-3S	122	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-3D	121	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-2D	124	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-2M	122	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-1S	124	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-3S	123	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
3-T8-1D	125	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
2-T6-1S	0	Nitrobenzene-d5 (23-120),
	0	2-Fluorobiphenyl (30-115)
	Diluted Out	Dibutylchlorendate (20-150)
1-T4-SC(MS)	16	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
1-T4-SC(MSD)	Diluted Out	Dibutylchlorendate (20-150)
1-T4-SC	Diluted Out	Dibutylchlorendate (20-150)
4-T9-3D Dup	121	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
4-T9-3S	122	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
4-T9-3D	139	Nitrobenzene-d5 (23-120)
	Diluted Out	Dibutylchlorendate (20-150)
Method Blank	263	Dibutylchlorendate (20-150)
4-T10-3S	Diluted Out	Dibutylchlorendate (20-150)
4-T10-3M	Diluted Out	Dibutylchlorendate (20-150)
5-2G	Diluted Out	Dibutylchlorendate (20-150)
4-T10-3D	Diluted Out	Dibutylchlorendate (20-150)
5-6G	Diluted Out	Dibutylchlorendate (20-150)
5-5G	Diluted Out	Dibutylchlorendate (20-150)
1-T1-C	Diluted Out	Dibutylchlorendate (20-150)
1-T3-C	Diluted Out	Dibutylchlorendate (20-150)
1-T2-C	Diluted Out	Dibutylchlorendate (20-150)
2-T5-1D	Diluted Out	Dibutylchlorendate (20-150)
2-T5-3S	Diluted Out	Dibutylchlorendate (20-150)
2-T5-2D Dup	Diluted Out	Dibutylchlorendate (20-150)

Sample	Percent Recovery	Surrogate Compound and Range
2-T5-2D	Diluted Out	Dibutylchlorendate (20-150)
2-T5-2DMS	Diluted Out	Dibutylchlorendate (20-150)
2-T5-2DMSD	Diluted Out	Dibutylchlorendate (20-150)
2-T5-1S	Diluted Out	Dibutylchlorendate (20-150)
2-T5-1D Dup	Diluted Out	Dibutylchlorendate (20-150)
2-T5-2S	Diluted Out	Dibutylchlorendate (20-150)
2-T6-2D	Diluted Out	Dibutylchlorendate (20-150)
2-T6-2DMS	Diluted Out	Dibutylchlorendate (20-150)
2-T6-2DMSD	Diluted Out	Dibutylchlorendate (20-150)
2-T6-1D	Diluted Out	Dibutylchlorendate (20-150)
2-T6-3D	Diluted Out	Dibutylchlorendate (20-150)
2-T5-3D	Diluted Out	Dibutylchlorendate (20-150)
2-T6-2S	Diluted Out	Dibutylchlorendate (20-150)
3-T7-2S	Diluted Out	Dibutylchlorendate (20-150)
3-T7-1S	Diluted Out	Dibutylchlorendate (20-150)
4-T11-2D	Diluted Out	Dibutylchlorendate (20-150)
4-T11-2DMS	Diluted Out	Dibutylchlorendate (20-150)
4-T11-2DMSD	Diluted Out	Dibutylchlorendate (20-150)
4-T11-2S	Diluted Out	Dibutylchlorendate (20-150)
4-T9-2D	Diluted Out	Dibutylchlorendate (20-150)
4-T9-1S	Diluted Out	Dibutylchlorendate (20-150)
4-T9-1D	Diluted Out	Dibutylchlorendate (20-150)
4-T11-1D	Diluted Out	Dibutylchlorendate (20-150)
4-T11-1S	Diluted Out	Dibutylchlorendate (20-150)
4-T11-3D	Diluted Out	Dibutylchlorendate (20-150)
4-T10-1S	Diluted Out	Dibutylchlorendate (20-150)
4-T11-3D dup	Diluted Out	Dibutylchlorendate (20-150)
4-T11-3S	Diluted Out	Dibutylchlorendate (20-150)
4-T9-1M	Diluted Out	Dibutylchlorendate (20-150)
5-3G	Diluted Out	Dibutylchlorendate (20-150)
4-T9-2D	Diluted Out	Dibutylchlorendate (20-150)
4-T9-2S	Diluted Out	Dibutylchlorendate (20-150)
4-T11-1M	Diluted Out	Dibutylchlorendate (20-150)
5-4G	Diluted Out	Dibutylchlorendate (20-150)
3-T7-1D Dup	Diluted Out	Dibutylchlorendate (20-150)
3-T8-1D Dup	Diluted Out	Dibutylchlorendate (20-150)
3-T7-1D	Diluted Out	Dibutylchlorendate (20-150)
Method Blank	156	Dibutylchlorendate (20-150)
3-T7-2D	Diluted Out	Dibutylchlorendate (20-150)
3-T7-2D Dup	Diluted Out	Dibutylchlorendate (20-150)
3-T8-2S	Diluted Out	Dibutylchlorendate (20-150)
4-T10-2S	Diluted Out	Dibutylchlorendate (20-150)
4-T10-2D	Diluted Out	Dibutylchlorendate (20-150)
4-T10-1D	Diluted Out	Dibutylchlorendate (20-150)

According to NYSDEC-CLP methodology, the laboratory should have re-extracted and re-analyzed all samples associated with the method blank surrogate failures. Also, sample 2-T6-1S should have been re-extracted and re-analyzed for the base/neutral compounds due to two surrogates exceeding recovery criteria. Positive results for 2-T6-1S should be considered qualitative (J qualifier) and non-detects are invalid (R qualifier).

RAW WATER SAMPLES: All volatile surrogate recovery results were within the recommended limits. Two BNA and nine pesticide/PCB surrogate analyses exceeded spike recovery criteria. Surrogate exceedances are listed below:

Sample	Percent Recovery	Surrogate Compound and Range
5-1E	203	Dibutylchlorendate (24-154)
5-1EMS	274	Dibutylchlorendate (24-154)
	924	Tetrachloro-meta-xylene (24-154)
5-1EMSD	202	Dibutylchlorendate (24-154)
1-2E	213	Dibutylchlorendate (24-154)
	40	2-Fluorobiphenyl (43-116)
2-2E	166	Dibutylchlorendate (24-154)
3-2E	155	Dibutylchlorendate (24-154)
	37	2-Fluorobiphenyl (43-116)
4-2E	168	Dibutylchlorendate (24-154)
Method Blank	215	Dibutylchlorendate (24-154)

According to NYSDEC-CLP methodology, the laboratory should have re-extracted and re-analyzed all samples associated with the method blank surrogate failure.

2.4 MATRIX SPIKES/MATRIX SPIKE DUPLICATES

Matrix spikes are used to evaluate the ability of a given compound to be extracted and detected for a given sample matrix. Matrix spike duplicates indicate the relative precision per matrix. The spiked recovery is the percentage of the spiking compound detected from the sample matrix. Matrix spikes are used on volatile, semi-volatile, pesticide/PCB, and metals analyses. The percent recovery of metal matrix spike and metal matrix spike duplicate analyses are used to validate the metal data associated with that spike.

Matrix spike percent recovery failures for volatile, semi-volatile and pesticide/PCB compounds are used in conjunction with other QA/QC information to validate data.

2.4.1 MATRIX SPIKES/MATRIX SPIKE DUPLICATES HAZARDOUS SUBSTANCE LIST

A matrix spike (MS) and a matrix spike duplicate (MSD) were analyzed with each batch of HSL samples for each sample matrix. The ranges of acceptable recoveries were exceeded by 11 organic compounds and 6 inorganic analytes in the two MS and MSD samples. MS and MSD samples with spiked recoveries failures are listed below.

Sample	Matrix Spike	Percent Recovery Value	Percent Recovery Limit
1-T1-C(MS)	Pyrene	208	35-142
	Heptachlor	32	35-130
	Endrin	20	42-139
	Barium	64.9	75-125
	Manganese	52.5	75-125
	Thallium	56.7	75-125
1-T1-C(MSD)	gamma-BHC	135	46-127
	Heptachlor	0	35-130
	Aldrin	6.8	34-132
	Endrin	31	42-139
2-T6-MC(MS)	1,2,4-Trichlorobenzene	0	38-107
	4-Chloro-3-methylphenol	0	36-103
	Acenaphthene	30	31-137
	2,4-Dinitrotoluene	12.4	28-89
	Pyrene	34	35-142
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
	Antimony	133.3	75-125
	Barium	0	75-125
	Silver	3.3	75-125
	Sodium	63.8	75-125

Sample	Matrix Spike	Percent Recovery Value	Percent Recovery Limit
2-T6-MC(MSD)	Trichloroethene	56	62-137
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134

The results of the MS and MSD analyses were used to calculate relative percent difference (RPD) values for each analyte. The following is a list of RPD values which exceeded the RPD limit values:

Sample	Matrix Spike	RPD Value	RPD Limit
1-T1-C(MS) & (MSD)	1,1-Dichloroethene	37	22
	Acenaphthene	34	19
	Pyrene	103	36
	Heptachlor	NC*	31
	Aldrin	135	43
	Endrin	46	45
	Barium	25.7	20
	Cadmium	43.8	20
	Calcium	22.7	20
2-T6-MC(MS & (MSD)	Phenol	40	35
	1,4-Dichlorobenzene	50	27
	N-Nitroso-di-n-propylamine	92	38
	1,2,4-Trichlorobenzene	200	23
	4-Chloro-3-methylphenol	200	33
	Acenaphthene	72	19
	4-Nitrophenol	51	50
	2,4-Dinitrotoluene	102	47
	Pyrene	70	36
	gamma-BHC	NC	50
	Heptachlor	NC	31
	Aldrin	NC	43
	Dieldrin	NC	38
	Endrin	NC	45
	4,4'-DDT	NC	50
	Barium	29.0	20
	Copper	84.1	20
	Lead	125	20
	Silver	132.4	20

*NC = Not Calculated

Several RPD values were unable to be calculated due to dilution of the spiking compounds being diluted out of the sample. Inorganic sample results that were affected by matrix spike exceedances were correctly qualified by the laboratory.

2.4.2 MATRIX SPIKES/MATRIX SPIKE DUPLICATES SITE-SPECIFIC COMPOUND LIST

Due to the reduced number and type of compounds being analyzed, different BNA Matrix Spike (MS) compounds and their respective SW-846 limits were used. The BNA semi-volatile compounds and limits were 1,3-dichlorobenzene (D-172), 1,4-dichlorobenzene (20-124), 1,2-dichlorobenzene (32-129), hexachloroethane (40-113), 1,2,4-trichlorobenzene (44-142), hexachlorobutadiene (24-116) and hexachlorobenzene (D-152). The MS compounds selected were appropriate for the compounds being analyzed and acceptable percent recoveries were reported.

EI TRIATE SAMPLES: All volatile and BNA matrix spikes had recoveries within the specified recovery criteria. Six pesticide/PCB spikes were diluted out of the spiked samples presented below.

Sample	Matrix Spike	Percent Recovery Value	Percent Recovery Limit
3-2E(MS)	gamma-BHC	Diluted Out	56-123
	Heptachlor	Diluted Out	40-131
	Aldrin	Diluted Out	40-120
	Dieldrin	Diluted Out	50-126
	Endrin	Diluted Out	56-121
	4,4'-DDT	Diluted Out	38-127
3-2E(MSD)	gamma-BHC	Diluted Out	56-123
	Heptachlor	Diluted Out	40-131
	Aldrin	Diluted Out	40-120
	Dieldrin	Diluted Out	50-126
	Endrin	Diluted Out	56-121
	4,4'-DDT	Diluted Out	38-127

All inorganic matrix spikes had recoveries within control limits.

SEDIMENT SAMPLES: The ranges of acceptable recoveries were exceeded by one volatile and three BNA compounds in 8 spiked samples. The pesticide/PCB spikes were diluted out in all MS and MSD samples. Consequently, RPD values could not be calculated for these compounds. All inorganic matrix spike recoveries were within the specified control limits. Presented below are the percent recovery failures:

Sample	Matrix Spike	Percent Recovery Value	Percent Recovery Limit
4-T11-2D(MS)	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
4-T11-2D(MSD)	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
2-T5-2D(MS)	Hexachlorobutadiene	Spiked Too Low	24-116
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
2-T5-2D(MSD)	Hexachlorobutadiene	Spiked Too Low	24-116
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
	Chlorobenzene	125	65-120

Sample	Matrix Spike	Percent Recovery Value	Percent Recovery Limit
2-T5-2D(MS)	Hexachlorobutadiene	Spiked Too Low	24-116
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
2-T6-2D(MSD)	Hexachlorobutadiene	Spiked Too Low	24-116
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
1-T4-SC(MS)	1,2-Dichlorobenzene	29	32-129
	Hexachloroethane	37	40-113
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134
1-T4-SC(MSD)	Hexachlorobutadiene	136	24-116
	gamma-BHC	Diluted Out	46-127
	Heptachlor	Diluted Out	35-130
	Aldrin	Diluted Out	34-132
	Dieldrin	Diluted Out	31-134
	Endrin	Diluted Out	42-139
	4,4'-DDT	Diluted Out	23-134

RPD values exceeded the RPD limits in one volatile and nine BNA analyses. The RPD exceedances are presented below:

Sample	Matrix Spike	RPD Value	RPD Limit
4-T11-2D(MS) & (MSD)	gamma-BHC	NC*	50
	Heptachlor	NC	31
	Aldrin	NC	43
	Dieldrin	NC	38
	Endrin	NC	45
	4,4'-DDT	NC	50
2-T5-2D(MS) & (MSD)	gamma-BHC	NC	50
	Hexachlorobenzene	67	40
	Heptachlor	NC	31
	Aldrin	NC	43
	Dieldrin	NC	38
	Endrin	NC	45
	4,4'-DDT	NC	50
	Chlorobenzene	75.9	30
2-T6-2D(MS) & (MSD)	Hexachlorobutadiene	NC	40
	Hexachlorobenzene	63	40
	gamma-BHC	NC	50
	Heptachlor	NC	31
	Aldrin	NC	43
	Dieldrin	NC	38
	Endrin	NC	45
	4,4'DDT	NC	50
1-T4-SC(MS) & (MSD)	1,3-Dichlorobenzene	89	40
	1,4-Dichlorobenzene	84	40
	1,2-Dichlorobenzene	80	40
	Hexachloroethane	86	40
	1,2,4-Trichlorobenzene	86	40
	Hexachlorobutadiene	79	40
	Hexachlorobenzene	65	40
	gamma-BHC	NC	50
	Heptachlor	NC	31
	Aldrin	NC	43
	Dieldrin	NC	38
	Endrin	NC	45
	4,4'-DDT	NC	50

* = Not Calculated due to dilution problems.

RAW WATER SAMPLES: All volatile and BNA matrix spikes had recoveries within acceptable limits. In the pesticide/PCB fraction, the compound Aldrin

exceeded the percent recovery criteria of 40-120 percent with recoveries of 30 percent in the matrix spike and 32 percent in the matrix spike duplicate. All RPD values were within the recommended limits for the value BNA and pesticide/PCB fractions.

2.5 METHOD BLANKS

Method blanks are samples of distilled, deionized, contaminant-free water prepared in the laboratory and used to check for laboratory contamination during processing. All method blanks were checked for contaminants. In situations where method blank contamination was reported, the sample data was checked to see that the appropriate data qualifiers were used.

2.5.1 METHOD BLANKS - HAZARDOUS SUBSTANCE LIST

Three method blanks were run during the volatile analyses. All values were below detection limits. Two method blanks were analyzed during the semi-volatile analyses. Bis(2-ethylhexyl)phthalate (2380 ppb) was the only compound present. Bis(2-ethylhexyl)phthalate was below detection in all associated samples. All pesticide/PCB blanks had no reportable concentrations detected.

2.5.2 METHOD BLANKS - SITE-SPECIFIC COMPOUND LIST

Method blanks were analyzed with the BNA, volatile, and pesticide/PCB analyses.

ELUTRIATE SAMPLES: No reportable compounds were detected in the method blanks.

SEDIMENT SAMPLES: No reportable compounds were detected in the method blanks.

RAW WATER SAMPLES: No reportable compounds were detected in the method blanks.

2.6 INSTRUMENT TUNING AND CALIBRATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning, and continuing calibration checks document satisfactory maintenance and adjustment of the instrument on a routine basis throughout the day.

2.6.1 INSTRUMENT TUNING AND CALIBRATION - HAZARDOUS SUBSTANCE LIST

Prior to sample analyses, the instruments were tuned and calibrated. The compounds Decafluorotriphenylphosphine (DFTPP) and Bromofluorobenzene (BFB) were used for instrument tuning. All ion abundance criteria and calibration frequencies were achieved for the organic analyses.

Instrument calibration was performed using initial and continuing calibration check compounds. For the initial instrument calibration, the average response factor (RF) for the system performance check compounds (SPCC) and the percent relative standard deviation (RSD) for the calibration check compounds (CCC), were all within acceptable limits. For continuing calibrations, two standards (Individual A) exceeded the percent deviation (%D) criteria once for Endrin and three times for 4,4'-DDT. Since there were no reportable concentrations, these exceedances did not affect the associated analytical results.

As part of instrument tuning, linearity checks were also performed. Linearity exceedances in the pesticide/PCB fraction were reported twice for aldrin and three time for 4,4'-DDT. Since these compounds had no reportable concentration in the associated samples, the analytical results were not affected.

A retention shift was reported for dibutylchlorendate during the analysis of eight samples which exceeded the %D criteria. These shifts varied a few percentage points in the eight samples. Due to high contaminant concentrations and the complex sample matrix, interpretation of these shifts has been left to the discretion of the analytical chemist.

The inorganic instrument performance criteria were all within acceptable limits.

2.6.2 INSTRUMENT TUNING AND CALIBRATION - SITE-SPECIFIC COMPOUND LIST

ELUTRIATE SAMPLES: Ion abundance criteria for DFTPP and BFB and frequency of initial and continuing calibrations were achieved for all of the organic analyses. All initial qualification checks for linearity were acceptable with the exception of Aldrin which exceeded the %RSD criteria. This exceedance does not affect the samples analyzed since there were no reportable Aldrin concentrations. All continuing calibration %D were acceptable except for 4,4'-DDT in 4 samples. These exceedances do not affect the samples analyzed since there were no reportable 4,4-DDT concentrations.

The inorganic instrument performance criteria were all within acceptable limits.

SEDIMENT SAMPLES: Ion abundance criteria for DFTPP and BFB and frequency of initial and continuing calibrations were achieved for all organic analyses. For the initial and continuing calibrations of retention times, all criteria were found to be within control limits except the fifteen %D exceedances which are presented below.

Compound	Frequency
4,4'-DDT	(5 times)
Hexachlorobenzene	(2 times)
1,3,5-Trichlorobenzene	(3 times)
1,2,4-Trichlorobenzene	(1 times)
Hexachlorobutadiene	(3 times)
Endrin	(1 times)

In some instances the correct data qualifiers were not used. The laboratory was notified and corrected data sheets are being issued. Retention time shifts were unable to be evaluated in several samples due to DBC elution in the 15 + 10 percent Florisil cleanup fraction. In addition, DBC was not included in 10 pesticide standard mixes. According to the EPA validation document, the retention time shift can not be evaluated in the absence of DBC. Therefore, no sample qualifiers were used.

Four linearity exceedances occurred for the DDT/Endrin percent breakdown criteria. Aldrin and 4,4'-DDT each exceeded criteria twice.

The inorganic instrument performance criteria were all within acceptable limits.

RAW WATER SAMPLES: Ion abundance criteria for DFTPP and BFB and frequency of initial and continuing calibrations were achieved for all of the organic analyses. For the initial and continuing calibrations, all criteria were found to be within control limits. Dibutylchlorendate had a percent difference exceedance for a retention time for sample 4-2E. However, due to the highly contaminated nature of the samples, this exceedance was not considered to be a problem.

The inorganic instrument performance criteria were all within acceptable limits.

2.7 TRIP/FIELD BLANKS

All trip blanks were collected and analyzed for volatiles at the required frequency of 1 per day. Seven field (rinseate) blanks were collected and analyzed for the site-specific compounds.

The table below lists all field and trip blanks exceeding holding times.

Sample	Fraction	Days Exceeding Holding Time
FB (6/14)	BNA, Pest/PCB	3, 2
FB (6/15)	BNA, Pest/PCB	2, 1
FB (6/16)	BNA, Pest/PCB	1, 1

Field and trip blank samples were reviewed for surrogate spike recovery exceedances. All volatile, base/neutral and acid extractable surrogate recoveries were within the recommended limits. However, pesticide/PCB surrogate interference was reported in several samples. Reason for the interference was not included with the analytical data. The following is a list of these exceedances:

Sample	% R	Surrogate Compound and Range
FB (6/9)	Interference	Dibutylchlorendate (24-154)
FB (6/11)	Interference	Dibutylchlorendate (24-154)
FB (6/14)	Interference	Dibutylchlorendate (24-154)
FB (6/15)	Interference	Dibutylchlorendate (24-154)
FB (6/16)	Interference	Dibutylchlorendate (24-154)

All field and trip blanks did not have any compounds detected in the associated laboratory method blanks.

2.8 FIELD DUPLICATES

Field duplicates were collected and analyzed at the required frequency. One field duplicate was collected and analyzed for the HSL compounds. Eight sediment duplicates were collected and analyzed for the site-specific compounds. Duplicates were analyzed with the other samples and their QA/QC was incorporated in the previous discussions.

2.9 CHAIN-OF-CUSTODY FORMS

Chain-of-custody forms were included with the analytical report. The date, time and sample locations were recorded. The use of preservatives and the amount of each was also noted on the forms.

3.0 QA/QC REVIEW OF MIDWEST RESEARCH INSTITUTE DATA

As part of the Gill Creek analytical program, eight sediment samples were analyzed for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofuran (PCDF) using RCRA Method 8280 (draft): 4-T10-SC, 4-T10-MC, 2-T6-SC, 2-T6-MC, 3-T8-MC, 3-T8-SC, 1-T4-SC, and 3-T8-MC dup. The analyses were subcontracted by WCC to Midwest Research Institute (MRI) of Kansas City, Missouri. In general, all QA/QC requirements were met. Spiking solutions utilized native dibenzo-dioxin and dibenzofuran analytes and isotopically labeled (^{13}C) standards for initial calibration. Continuing calibration QA/QC requirements were accomplished using native and isotopically labelled compounds as required. Retention time performance checks were done and were within the method specific requirements.

Tables 5, 6, and 7 present duplicate, percent recovery, and spike check results. Lab duplicate analyses generally are in agreement with four points being quite high (between 72 to 101 percent). The field duplicate result indicated good agreement in general.

Recoveries of chlorinated dioxins and furans from spikes samples were acceptable but on the high side. For example, OCDD an OCDF recoveries were 255 and 288 percent, respectively. PeCDD and PeCDF (1,2,3,7,8 isomers) spikes were not recovered. The reason for this discrepancy is not known.

Table 7 is the analysis of the spiking solution. There is very good agreement between the spike level (theoretical) and the amount found (actual). The recoveries ranged from 83 to 186 percent with the majority (13 of 17) points ranging between 90 to 135 percent.

Although discrepancies in duplicate analysis, recoveries, and spike check analysis are evident, it must be recalled that the analyses were conducted at the parts per billion to parts per trillion level. Thus variations in terms of percentages may be large, but the variations in terms of amount are small.

The actual analytical data for each sample are contained in the attachment titled "Analysis Report Forms." TCDF and TCDD were found in every sample. However, the TCDF concentrations did not exceed 8.79 ppb in any of the samples. Given the fact that TCDF is considered to be 0.1 times as toxic as TCDD, therefore, the actual maximum "TCDD equivalents" for TCDF is 0.879 ppb. The maximum measured value for TCDD was 0.283 ppb with the majority of samples exhibiting concentrations of less than 0.150 ppb and in a number of samples concentrations were less than 0.025 ppb.

Other dioxins and furans were found at concentrations up to 36 ppb; however, these compounds are much less toxic (0.5 to 0.001 times) than TCDD. Therefore, on a "TCDD equivalents" basis, none of the compounds was found to be above the 1 ppb level. OCDD is considered non-toxic with respect to TCDD. Therefore, it is not included when calculating "toxic equivalents."

4.0 RECOMMENDATIONS

This detailed QA/QC review of the Gill Creek data indicates several analytical violations. However, given the highly contaminated nature of the samples these violations are not considered to be serious ones. The samples do contain high percentages of the chemicals analyzed at fairly high concentrations. A QA/QC violation resulting in even an order-of-magnitude concentration difference would not change that conclusion. Consequently, WCC recommends that this set of analytical data be accepted with the appropriate data qualifiers and that QA/QC criteria be adhered to more strictly during the remediation phase of the program as contaminant concentrations are lowered.

/WM-39D

TABLE 1

HAZARDOUS SUBSTANCE LIST SAMPLES

5-4G Dup
5-4G
4-T10-SC (+ Dioxin)
4-T10-MC (+ Dioxin)
5-5G
1-T1-C
2-T6-SC (+ Dioxin)
2-T6-MC (+ Dioxin)
3-T8-MC (+ Dioxin)
1-T4-SC (+ Dioxin)
3-T8-SC (+ Dioxin)

TABLE 2

SITE-SPECIFIC COMPOUND SAMPLES

4-T11-2D	1-T2-C
4-T11-2S	2-T5-1D
4-T9-2D Dup	2-T5-3S
4-T9-1S	2-T5-2D Dup
4-T9-1D	2-T5-2D
4-T11-1D	2-T5-1S
4-T11-1S	2-T5-1D Dup
4-T9-1M	2-T5-2S
5-2G	2-T6-3S
4-T9-3D	2-T6-1S
4-T9-3S	2-T6-1S
4-T11-1M	2-T6-2D
5-4G [illegible]	2-T6-1D
4-T10-3S	2-T5-3D
4-T10-3D	2-T6-3D
4-T10-1D	2-T6-2S
4-T10-1S	3-T7-2S
4-T10-3D Dup	3-T7-1S
4-T12-3D	3-T7-1D Dup
4-T12-3S	3-T8-1D Dup
4-T9-3D Dup	3-T8-3D
4-T10-3S	3-T8-2D
4-T9-3S	3-T8-2M
4-T9-3D	3-T8-1S
4-T10-3M	3-T8-1D
5-3G	3-T7-1D
5-3G	1-T4-SC
4-T10-3D	3-T7-2D
5-3G	3-T7-2D Dup
1-T1-C	3-T8-2S
1-T3-C	3-T8-3S
5-1G	

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TABLE 3

SITE-SPECIFIC COMPOUNDS

Semi-volatiles

1,3 - Dichlorobenzene
1,4 - Dichlorobenzene
1,2 - Dichlorobenzene
Hexachloroethane
1,3,5 - Trichlorobenzene
1,2,4 - Trichlorobenzene
1,2,3, - Trichlorobenzene
Hexachlorobutadiene
1,2,3,5 - Tetrachlorobenzene + 1,2,4,5 - Tetrachlorobenzene
1,2,3,4, - Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene

Volatiles

Chlorobenzene
Total Volatile Solids

Pesticide/PCB

alpha - BHC
beta - BHC
delta - BHC
Lindane
Heptachlor
Aldrin
Heptachlorepoxide
Endosulfan I
Dieldrin
4,4'-DDE
Endrin
Endosulfan II
4,4'-DDD
Endosulfan Sulfate
4,4'-DDT
Methoxychor
Endrin Ketone
alpha - chlordane
gamma - chlordane
Toxaphene
Arochlor - 1016
Arochlor - 1221
Arochlor - 1232
Arochlor - 1242
Arochlor - 1248
Arochlor - 1260

Inorganics

Mercury

TABLE 4

FIELD BLANK/TRIP BLANK SAMPLES

Equipment Blank (6/9)
Equipment Blank (6/10)
Equipment Blank (6/11)
Equipment Blank (6/13)
Trip Blank (6/9)
Trip Blank (6/10)
Trip Blank (6/11)
Trip Blank (6/13)
Equipment Blank (6/14)
Equipment Blank (6/15)
Equipment Blank (6/16)
Trip Blank (6/14)
Trip Blank (6/15)
Trip Blank (6/16)

TABLE 5

MRI
DUPLICATE SAMPLE ANALYSIS RESULTS

Compound	Lab Duplicate (4-T10-SC(HSL)) Lab ID 8301 (pg/g)	Lab ID 5975[a] (pg/g)	Range %	Field Duplicate (3-T8-MC(HSL)) Lab ID 8305 (pg/g)	Lab ID 8306[b] (pg/g)	Range %
2,3,7,8-TCDD	ND[c]	ND	--	ND	ND	--
1,2,3,7,8-PeCDD	ND	ND	--	ND	ND	--
1,2,3,4,7,8-HxCDD	ND	ND	--	ND	ND	--
1,2,3,6,7,8-HxCDD	948	1,240	27	103	167	47
1,2,3,7,8,9-HxCDD	241	252	4	46	70	43
1,2,3,4,6,7,8-HpCDD	1,850	2,480	29	665	841	23
OCDD	2,160	5,610	89	2,750	2,760	0.4
2,3,7,8-TCDF	1,030	1,230	18	304	407	29
1,2,3,7,8-PeCDF	73.2	ND	--	7.5	13	55
2,3,4,7,8-PeCDF	367	176	72	89.2	131	38
1,2,3,4,7,8-HxCDF	908	950	5	239	355	39
1,2,3,6,7,8-HxCDF	137	170	21	ND	23	--
2,3,4,6,7,8-HxCDF	64.5	ND	--	ND	42	--
1,2,3,7,8,9-HxCDF	107	ND	--	34	63	60
1,2,3,4,6,7,8-HpCDF	567	948	50	337	352	4
1,2,3,4,7,8,9-HpCDF	105	238	78	81	92	13
OCDF	4,090	12,500	101	2,140	2,965	32

a = This sample labeled as "Matrix spike duplicate" on mass spec ion plots, 9208G15X3 and 9208G18X9. It is the unspiked duplicate portion of sample 4-T10-SC(HSL).
b = Average of replicate injections.
c = Not detected.

/WM-39D

TABLE 6

MRI
SPIKED SAMPLE ANALYSIS RESULTS (4-T10-SC(HSL))

Compound	Spike Level (pg/g)	Average form Unspiked Samples (pg/g) MRI ID 5975/8301	Spiked Samples (pg/g) MRI ID 5974	Recovery (%)
2,3,7,8-TCDD	246	ND[a]	245	100
1,2,3,7,8-PeCDD	252	ND	ND	NR[b,c]
1,2,3,4,7,8-HxCDD	604	ND	652	108
1,2,3,6,7,8-HxCDD	627	1,094	1,620	84
1,2,3,7,8,9-HxCDD	627	247	991	119
1,2,3,4,6,7,8-HpCDD	615	2,165	3,310	186[c]
OCDD	1,208	3,885	6,960	255[c]
2,3,7,8-TCDF	249	1,130	1,390	104
1,2,3,7,8-PeCDF	248	37	ND	NR[c]
2,3,4,7,8-PeCDF	248	276	295	8[c]
1,2,3,4,7,8-HxCDF	612	929	1,770	137
1,2,3,6,7,8-HxCDF	617	154	692	87
2,3,4,6,7,8-HxCDF	628	32	697	106
1,2,3,7,8,9-HxCDF	608	54	638	96
1,2,3,4,6,7,8-HpCDF	615	758	1,550	129
1,2,3,4,7,8,9-HpCDF	624	172	797	100
OCDF	1,217	8,295	11,700	280[c]

a = Not detected.
b = Not recovered.
c = Data are outside the data quality objective of 60-140 percent.

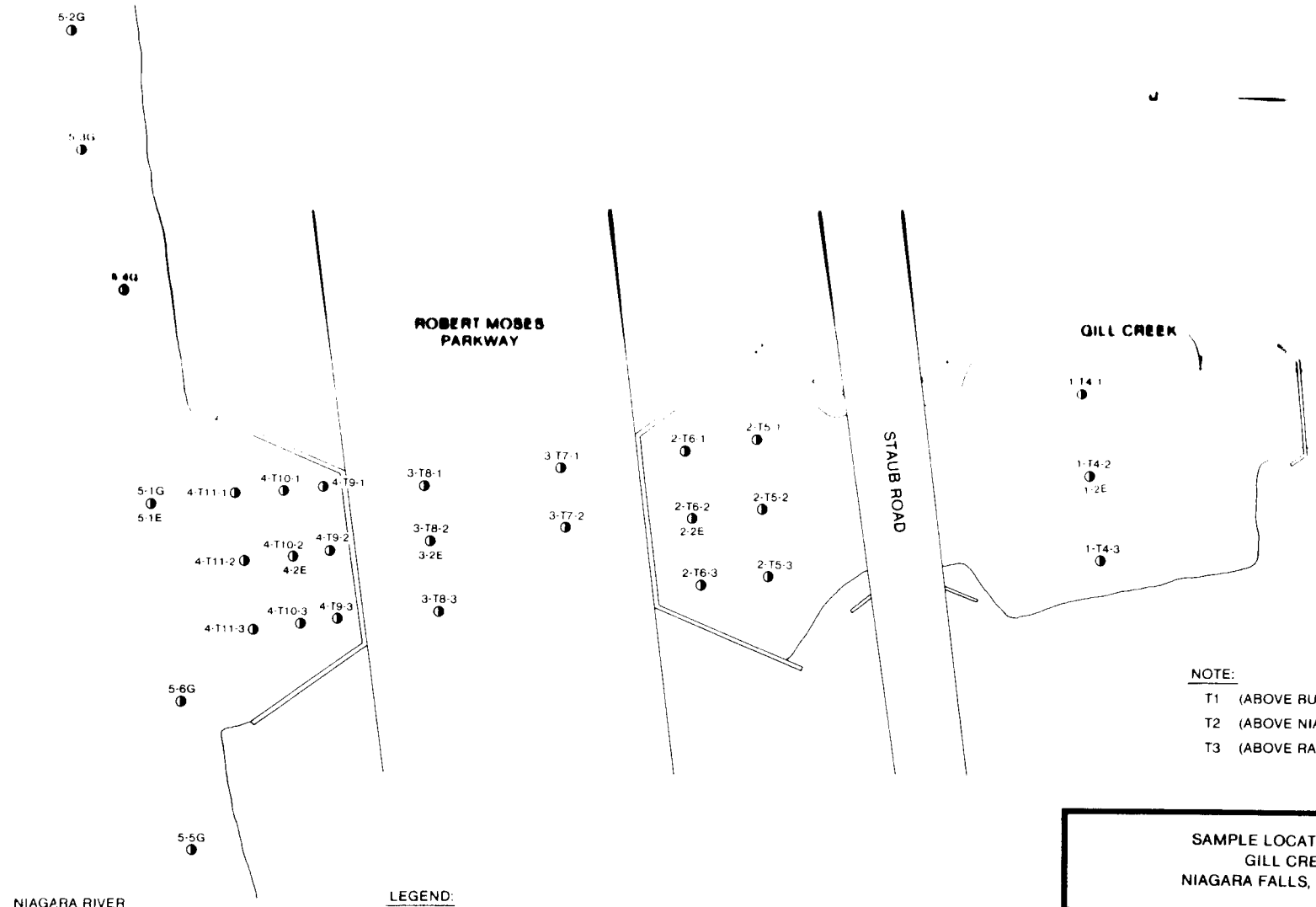
/WM-39D

TABLE 7

MRI
SPIKE CHECK RESULTS

Compound	Spike Level (pg/g)	Amount Found (pg/g)	Percent Recovery
2,3,7,8-TCDD	97	92	95
1,2,3,7,8-PeCDD	99	107	108
1,2,3,4,7,8-HxCDD	239	373	156
1,2,3,6,7,8-HxCDD	245	221	90
1,2,3,7,8,9-HxCDD	245	455	186
1,2,3,4,6,7,8-HpCDD	244	385	158
OCDD	479	518	108
2,3,7,8-TCDF	98	101	103
1,2,3,7,8-PeCDF	98	107	109
2,3,4,7,8-PeCDF	98	132	135
1,2,3,4,7,8-HxCDF	242	229	95
1,2,3,6,7,8-HxCDF	244	249	102
2,3,4,6,7,8-HxCDF	249	206	83
1,2,3,7,8,9-HxCDF	241	251	104
1,2,3,4,6,7,8-HpCDF	244	254	104
1,2,3,4,7,8,9-HpCDF	247	246	100
OCDF	482	514	107

/WM-39D

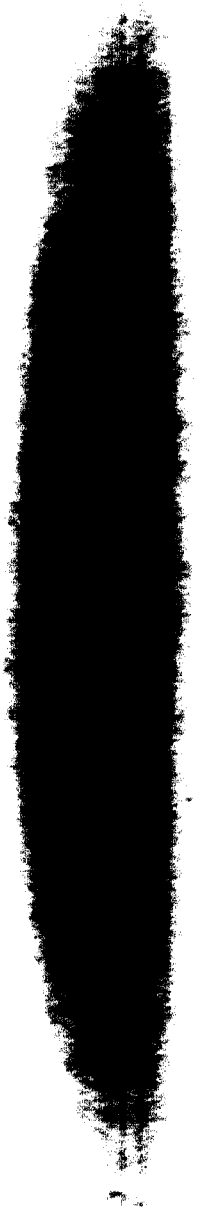


SAMPLE LOCATION PLAN
GILL CREEK
NIAGARA FALLS, NEW YORK

WOODWARD-CLYDE CONSULTANTS
CONSULTING ENGINEERS, GEOLOGISTS, AND ENVIRONMENTAL SCIENTISTS

Drawn by J.C	SCALE IN FEET 0 40	Date 10/11/88
Checked R.G		# 88C2056.2A

FIGURE 1



Appendix A

Elutriate [illegible] from relationships between total sediment concentration and biological uptake or changes in water quality. Also, a review of the technical literature indicated no correlations between total composition and sedimentary effects on water quality.[24]

Elutriate test

The elutriate test is a simplified simulation of the dredging and disposal process wherein predetermined amounts of dredging site water and sediment are mixed together to approximate a dredged material slurry.[2,20] The elutriate in the supernatant resulting from the vigorous 30-min shaking of one part sediment from the dredging site with four parts water (vol/vol) collected from the dredging site followed by a 1-hr settling time and appropriate centrifugation and 0.45 μ filtration. Thus, it will be necessary to collect both water and sediment samples to perform the elutriate test. When evaluating a dredging operation, the sediment should be collected at the dredging site and the water should be collected at the dredging and the disposal site. To evaluate a fill material activity, samples should be collected from the source of the fill material and the water should be collected from the disposal site.

Water sample collection. Collection should be made with an appropriate noncontaminating water sampling device. Either discrete samplers such as Kemmerer or Van Dorn samplers or continuous collectors such as submersible pumps may be used. The volume of water required will depend on the number of analyses to be performed. For each sample to be subjected to elutriate testing, it is suggested that a minimum of 4 ℓ be collected at the disposal site and 8 ℓ be collected at the dredging site to evaluate a dredging operation and/or 12 ℓ be collected at the disposal site to evaluate a fill material disposal operation. This will provide 4 ℓ of water for analyses and sufficient water to prepare triplicate elutriates. (Each elutriate should yield 2.0 to 2.2 ℓ of standard elutriate for analysis.) If the samples are to be analyzed for trace organics or a large number of constituents, a proportionately larger initial sample should be collected.

Samples must be stored in glass containers if trace organic analyses are to be performed. Generally, either plastic or

glass containers may be used for other parameters. The samples should be maintained at 4°C until analyzed but never frozen. The storage period should be as short as possible to minimize changes in the characteristics of the water. Disposal site water should be analyzed or split and preserved immediately. The remainder of the water should be used in the elutriate test, which should be processed within 1 week of collection.

Sediment sample collection. Samples should be taken from the fill or the dredging site with a grab or a corer. Approximately 3 ℓ of sediment or fill material would provide sufficient sample to prepare triplicate 3-ℓ elutriates. Again, if the resultant standard elutriates are to be analyzed for trace organics or a large number of constituents, a proportionately larger initial sample should be collected.

Samples may be stored in plastic bags, jars, or glass containers. However, if trace organic analyses are to be performed, glass containers with teflon-lined lids are required. A special precaution that must be taken with sediment samples is to ensure that the containers are completely filled with sample and that air bubbles are not trapped in the container. This step is necessary to minimize sample oxidation that could influence elutriate test results.[2,22]

The samples should be stored immediately at 4°C. They must not be frozen or dried prior to use. The storage period should be as short as possible to minimize changes in the characteristics of the sediment. It is recommended that samples be processed within 1 week of collection.

Apparatus. The following apparatus are required to perform the elutriate test. Prior to use, all glassware, filtration equipment, and filters should be washed with 5 to 10 percent (or stronger) hydrochloric acid (HCl) and then rinsed thoroughly with deionized water. The necessary apparatus include:

a. Acid-rinsed plastic bottles for collection of water samples.

b. Plastic jars or bags ("Whirl-Pak," plastic freezer containers, etc. for collecting dredged or fill material samples.

c. Laboratory shaker capable of shaking 2-ℓ flasks at approximately [illegible] excursions/minute. Box type or wrist-action shakers are acceptable.

d. Several 1-ℓ graduated cylinders.

e. Large [illegible] cm powder funnels.

f. Several 2-ℓ, large-mouth graduated Erlenmeyer flasks.

g. Vacuum or pressure filtration equipment, including vacuum pump or compressed air source, and an appropriate filter holder capable of accomodating 47-, 105-, or 155-m-diameter filters.

h. Membrane filters with a 0.45-μ pore-size diameter. The filters should be soaked in 5 M HCl for at least 2 hr prior to use.

i. Centrifuge capable of handling six 1- or 0.5-ℓ centrifuge bottles at 3000 to 5000 rpm. International Model K or Sorval Super Speed are acceptable models.

j. Wide-mouth, 1-gal capacity glass jars with teflon-lined screw-top lids for use as sample containers when samples are to be analyzed for trace organics. (It may be necessary to purchase jars and teflon sheets separately; in this case, the teflon lid liners may be prepared by the laboratory personnel.)

Test procedure. The stepwise test procedure is given below:

a. Subsample a minimum volume of 1 ℓ each of dredging site and disposal site water. If it is known in advance that a large number of measurements are to be performed, the size of each subsample should be increased to meet the anticipated needs.

b. Filter an appropriate portion of the disposal site water through an acid-soaked 0.45-μ pore-size membrane filter that has been prerinsed with approximately 100 ml of disposal site water. The filtrate from the rinsing procedure should be discarded.

c. Analyze the filtered disposal site sample as soon as possible. If necessary, the samples may be stored at 4°C after splitting and the appropriate preservatives have been added (Table 2-4). Filtered water samples may also be frozen with no apparent destruction of sample integrity.

d. Repeat steps a, b, and c with dredging site water. This step is omitted with a fill material sample.

e. Subsample approximately 1 ℓ of sediment from the well-mixed original sample. Mix the sediments and unfiltered dredging site water in a volumetric sediment-to-water ratio of 1:4 at room temperature (22 ± 2°C). This is best done by the method of

volumetric displacement.[23] One hundred milliliters of unfiltered dredging site water is placed into a graduated Erlenmeyer flask. The sediment subsample is then carefully added via a powder funnel to obtain a total volume of 300 ml. (A 200-ml volume of sediment will now be in the flask.) The flask is then filled to the 1000-ml mark with unfiltered dredging site water, which produces a slurry with a final ratio of one volume sediment to four volumes water.

This method should provide 700 to 800 ml of water for analysis. If the analyses to be run require a larger volume of water, the initial volumes used to prepare the elutriate slurry may be proportionately increased as long as the solid-to-liquid ratio remains constant (e.g. mix 400 ml sediment and 1600 ml unfiltered dredging site water). Alternately, several 1-ℓ sediment/dredging site water slurries may be prepared as outlined above and the filtrates combined to provide sufficient water for analysis. The procedure continues as follows:

f. (1) Cap the flask tightly with a noncontaminating stopper and shake vigorously on an automatic shaker at about 100 excursions per minute for 30 min. A polyfilm-covered rubber stopper is acceptable for minimum contamination.

(2) During the mixing step given above, the oxygen demand of the dredged material may cause the dissolved oxygen concentration in the elutriate to be reduced to zero. This change can alter the release of chemical contaminants from dredged material to the disposal site water and reduce the reproducibility of the elutriate test.[21] If it is known that anoxic conditions (zero dissolved oxygen) will not occur at the disposal site or if reproducibility of the elutriate test is a potential problem, the mixing may be accomplished by using a compressed air-mixing* procedure instead of the mechanical mixing described in Step f (1). After preparation of the elutriate slurry, an air-diffuser tube is inserted just set to the bottom of the flask. Compressed air should be passed through a deionized water trap and then through the diffuser tube and the slurry. The flow rate should be adjusted to agitate the mixture

* This procedure can cause the loss of highly volatile chemical constituents. If volatile materials are of concern, compressed air mixing should not be used.

vigorously for 30 min. In addition, the flasks should be stirred manually at 10-min intervals to ensure complete mixing.

g. After 30 min of shaking or mixing with air, allow the suspension to settle for 1 hr.

h. After settling, carefully decant the supernatant into appropriate centrifuge bottles and then centrifuge. The time and revolutions per minute during centrifugation should be selected to reduce the suspended solids concentration substantially and, therefore, shorten the final filtration process. After centrifugation, vacuum or pressure filter approximately 100 ml of sample through a 0.45-μ membrane filter and discard the filtrate. Filter the remainder of the sample to give a clear final solution (the standard elutriate) and store at 4°C in a clean, noncontaminating container in the dark. The filtration process is intended for use when the standard elutriate is to be analyzed for conventional chemical contaminants. When the elutriate is to be analyzed for organic contaminants and PCB's, filtration should not be used since organic concentrations can be reduced by sorption. Centrifugation should be used to remove particulate matter when the standard elutriate is to be analyzed for specific organics.

i. Analyze the standard elutriate as soon as possible. If necessary, the samples may be stored at 4°C after splitting and the appropriate preservatives have been added.

j. Prepare and analyze the elutriate in triplicate. The average of the three replicates should be reported as the concentration of the standard elutriate.

Sediment fractionation

Chemical constituents associated with sediments may be distributed in many chemical forms. The purpose of a fractionation procedure is to better define this distribution. This objective is achieved by leaching a sample with a series of successively harsher extraction agents. Reagents used in the procedure to be described below consist of interstitial water, ammonium acetate, hydroxylamine, hydrogen peroxide, citrate-dithionate, and hydrofluoric acid-nitric acid.

The premise of the fractionation procedure is that a specific geochemical phase is defined by a specific chemical