Bypass Dust

NORTHUMBRIAN WATER
Scientific Services

DIOXIN/FURAN

ANALYSIS REPORT

NUMBER D7109

UKAS TESTING
1181

This analysis is based on Northumbrian Water Scientific Services Organics Laboratory method O-36 which is accredited under the **UKAS** accreditation scheme.

DIOXIN/FURAN

ANALYSIS REPORT

NUMBER D7109

Laboratory Address:

Northumbrian Water Scientific Services
Northumberland Dock Road
Howdon
Wallsend
Tyne & Wear
NE28 0QD

Report Ref: D7109

Client Address:

D Quick
Hanson Cement
Padeswood Works
Padeswood
Mold
Flintshire
CH7 4HB

Prepared by: B Shields **Signed:** **Date:** 15/11/13

Issued under the authority of Steve Wilson – Laboratory Manager (Howdon Organics)

CONTENTS

SECTION 1

SUMMARY

One sample taken on behalf of Hanson Cement was analysed for dioxin and furan contamination. Analysis of the sample gave the following TEQ values on an air dried basis (to 2 significant figures).-

	Toxic Equivalent Results ng/kg				
Sample	**NATO/CCMS ITEQ**	**WHO (1998) HUMANS TEQ**	**WHO (2005) HUMANS TEQ**	**WHO (1998) FISH TEQ**	**WHO (1998) BIRDS TEQ**
BYPASS DUST PADESWOOD RUN 1	17	17	14	16	34

The total (tetra to octa chlorinated) dioxin/furan content of the sample is indicated below on an air dried basis (to 2 significant figures):-

Sample	**Total Results ng/kg**
BYPASS DUST PADESWOOD RUN 1	920

Full results for individual congeners and homologue group totals together with information on any deviations from methodology/quality systems is shown in section 2.

INTRODUCTION

One sample was submitted to Northumbrian Water Scientific Services by Hanson Cement for analysis to determine the levels of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) present.

The analysis covered the 17 PCDD and PCDF congeners containing chlorine substitution at the 2,3,7 and 8 positions so that Toxicity Equivalents could be calculated based on the NATO/CCMS and WHO systems.

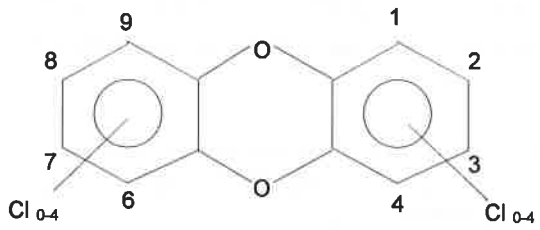
The sample was received on 04/11/13. Details of the sample are shown below.

CONTRACT - HANSONCEM_00244

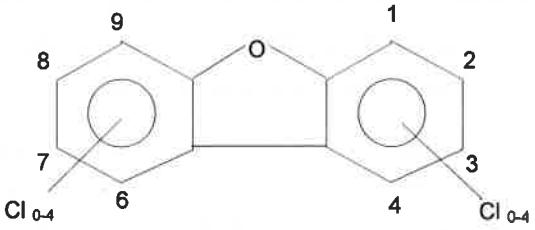
DATE REC'D	SAMPLE	LAB N°	REF
04/11/13	BYPASS DUST	659035	D7109

DIOXINS AND FURANS

PCDDs and PCDFs form a group of 210 closely related substances. The structural formulae are shown below. A dioxin or furan molecule can have as few as one or as many as eight chlorine atoms attached to the molecule at any of eight locations. The combination of number and position of the chlorine atoms gives rise to 75 possible dioxins and 135 furans.

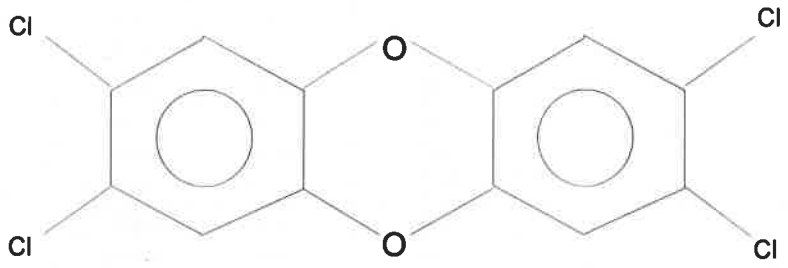


A Dioxin Molecule



A Furan Molecule

It is both the number of chlorine atoms and position in the molecule that determines the physical and chemical properties, as well as the toxicity of a given dioxin or furan. The most hazardous dioxin has chlorine substitution at the 2,3,7 and 8 positions and is therefore called 2,3,7,8-tetrachlorodibenzo-p-dioxin.



2,3,7,8-Tetrachlorodibenzo-p-dioxin

TOXIC EQUIVALENTS

In order to assess the toxicity of complex mixtures of PCDDs, PCDFs and PCBs the concept of toxic equivalents was devised. Toxic Equivalent Factors (TEF) are assigned to individual dioxins, furans and PCBs on the basis of how toxic they are in comparison with 2,3,7,8-TCDD, the most potent dioxin which has been assigned a value of 1.0. By comparison, animal and cell tests show that 2,3,7,8-TCDF is approximately one-tenth as toxic as 2,3,7,8-TCDD. Consequently its toxic equivalent factor is 0.1.

Of the 210 dioxins and furans, 17 contribute most to the toxicity of a complex mixture and are of most concern. Of the 209 PCBs 12 contribute most to the toxicity of a complex mixture and are of most concern. `Therefore it is these 29 compounds that have TEFs assigned shown in the table below for various schemes.

TEF tables	**NATO/CCMS**	**WHO (1998)**	**WHO (2005)**	**WHO (1998)**	**WHO (1998)**
Congener		**Humans/ mammals**	**Humans/ mammals**	**Fish**	**Birds**
2,3,7,8-TCDF	0.1	0.1	0.1	0.05	1
2,3,7,8-TCDD	1.0	1	1	1	1
1,2,3,7,8-PeCDF	0.05	0.05	0.03	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	0.3	0.5	1
1,2,3,7,8-PeCDD	0.5	1	1	1	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.1	0.1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.001	<0.001*
OCDF	0.001	0.0001	0.0003	0.0001	0.0001
OCDD	0.001	0.0001	0.0003	<0.0001*	0.0001
PCB BZ 81	-	0.0001	0.0003	0.0005	0.1
PCB BZ 77	-	0.0001	0.0001	0.0001	0.05
PCB BZ 123	-	0.0001	0.00003	<0.000005*	0.00001
PCB BZ 118	-	0.0001	0.00003	<0.000005*	0.00001
PCB BZ 114	-	0.0005	0.00003	<0.000005*	0.0001
PCB BZ 105	-	0.0001	0.00003	<0.000005*	0.0001
PCB BZ 126	-	0.1	0.1	0.005	0.1
PCB BZ 167	-	0.00001	0.00003	<0.000005*	0.00001
PCB BZ 156	-	0.0005	0.00003	<0.000005*	0.0001
PCB BZ 157	-	0.0005	0.00003	<0.000005*	0.0001
PCB BZ 169	-	0.01	0.03	0.00005	0.001
PCB BZ 189	-	0.0001	0.00003	<0.000005*	0.00001

* **NB** Where < figure is quoted for TEF the actual figure is used in all calculations in this report giving a worst case scenario.

METHOD

The analytical method used for the analysis is based on the American EPA Method 1613.

SPIKING AND EXTRACTION

Air dried soil samples are ground, spiked with a mixture of 16 stable isotopically labelled standards, (see following page for spiking scheme), mixed and allowed to equilibrate. The samples are then soxhlet extracted for a minimum of 16 hours with toluene. Ash samples are pre-treated with hydrochloric acid before being spiked and extracted as above.

CLEANUP AND ANALYSIS

The extracts are washed with concentrated sulphuric acid and aqueous potassium hydroxide if particularly dirty before being dried and concentrated. Impurities are removed from the extracts by column chromatography using silica and alumina columns.

The resulting extracts are concentrated and solvent exchanged to give a final volume of 10 µl in nonane.

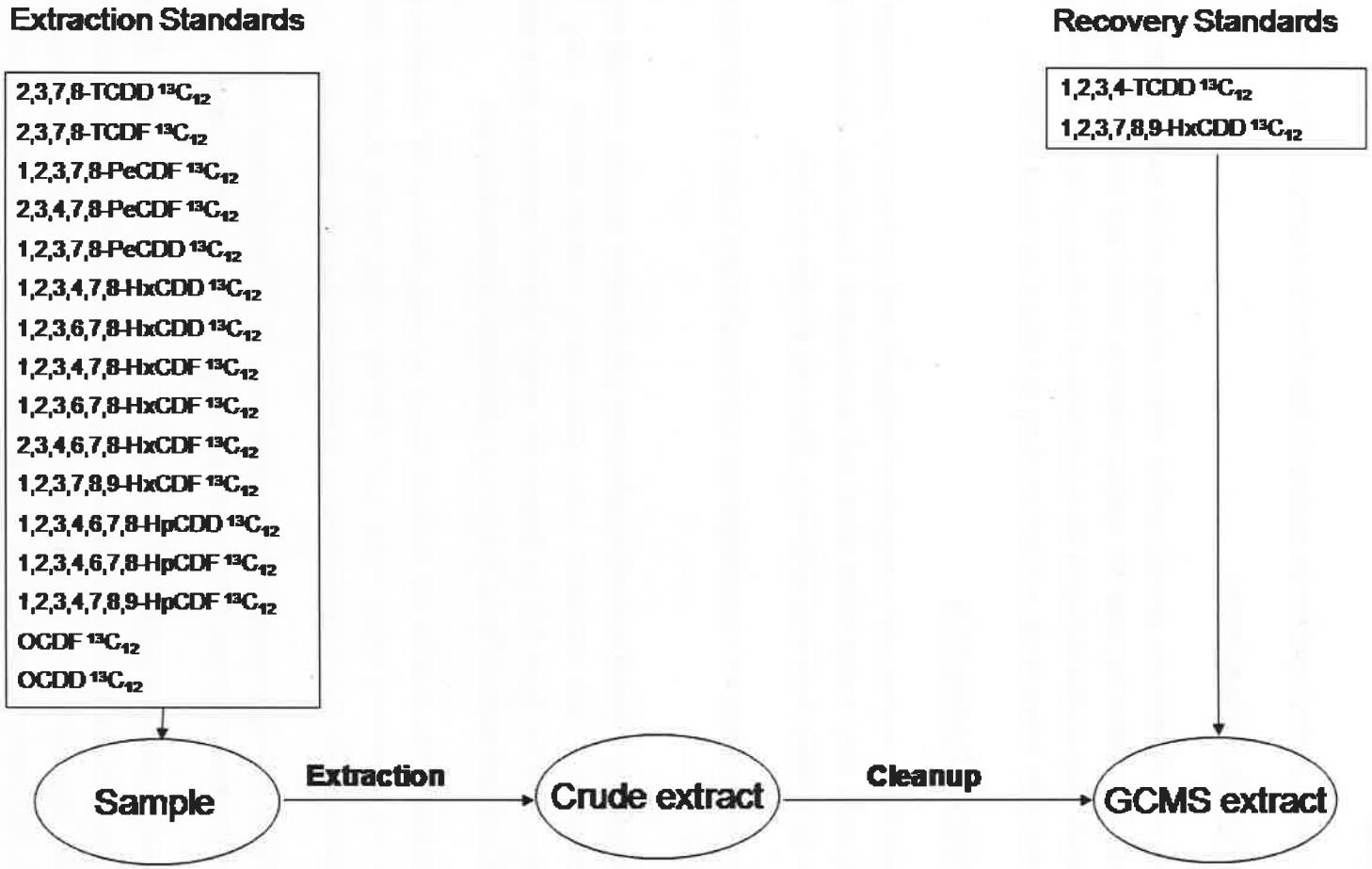
Two isotopically labelled internal standards are added before analysis by high resolution gas chromatography- high resolution mass spectrometry (HRGC-HRMS) using an isotope dilution method for those 2,3,7,8 isomers for which labelled analogues are available and an internal standard method for the non 2,3,7,8 substituted isomers and totals.

Identification of the dioxins and furans is based on comparison of GC retention time ranges and the ion abundance ratios of the m/z's with the corresponding retention time ranges of authentic standards and the theoretical ion abundance ratios of the exact m/z's.

If results for individual targeted dioxins/furans (i.e. 2,3,7,8 substituted) exceed the calibration range of the instrument then these results are flagged in the analytical report.

The mass spectrometer is operated at a resolution of >=10000 to minimize the potential for interference. Selected ions characteristic of the PCDDs and PCDFs are monitored together with ions characteristic of polychlorinated diphenyl ethers which may interfere with the PCDFs. The mass spectrometer is continuously calibrated during acquisition to correct for any mass drift by allowing a reference compound FC43 to bleed into the system.

EPA 1613 LABELLED STANDARD ADDITIONS (AES 036)



SECTION 2

RESULTS

The following pages contain the detailed analytical results for the isomer specific analysis for each sample and blank along with homologue group totals and recovery information for the labelled standards.

A matrix blank is analysed alongside the samples to show any possible contamination. This is normally a sample of dioxin-free quartz sand for solid samples.

The following points should be noted.

- All results are on a dry weight basis.
- Results have not been blank corrected. Results have not been rounded. This is to permit further processing if necessary and does not imply the level of accuracy. Summary results on page 5 have been rounded to two significant figures.
- n.d. - not detected – Detection limits for the analysis are calculated on a sample specific basis by the GCMS software, and are based on a signal to noise value of 2.5 to 1
- Results marked * are over the normal calibration limit of the method.
- The total results for TCDD and TCDF homologue groups do not include the 1,2,8,9 isomers due to the fact that these components elute prior to the first of the PeCDFs on the DB5-MS column used. Acquisition windows have been set up to acquire the first eluting PeCDF in preference to the two tetrachlorinated isomers identified above.
- All quality criteria in the method O36 have been met with any deviations outlined below.

Deviations from methodology/quality criteria/comments: -none.

DIOXIN-FURAN RESULTS

CLIENT HANSON CEMENT **CONTRACT** HANSONCEM_00244

SAMPLE LABORATORY BLANK

LAB NO N/A **REF** D7109

		NATO	WHO TEQ			
CONGENER	**ng/kg**	**I-TEQ**	**Humans[a]**	**Humans[b]**	**Fish[a]**	**Birds[a]**
2,3,7,8-TCDF	<0.049	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,7,8-TCDD	<0.068	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-PeCDF	<0.086	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,7,8-PeCDF	<0.076	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-PeCDD	<0.1	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8-HxCDF	<0.08	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,6,7,8-HxCDF	<0.083	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,6,7,8-HxCDF	<0.083	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8,9-HxCDF	<0.133	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8-HxCDD	<0.16	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,6,7,8-HxCDD	<0.175	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8,9-HxCDD	<0.163	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,6,7,8-HpCDF	1.3955	0.0140	0.0140	0.0140	0.0140	0.0140
1,2,3,4,7,8,9-HpCDF	<0.073	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,6,7,8-HpCDD	<0.186	n.d.	n.d.	n.d.	n.d.	n.d.
OCDF	<0.064	n.d.	n.d.	n.d.	n.d.	n.d.
OCDD	<0.182	n.d.	n.d.	n.d.	n.d.	n.d.
	TOTAL	**0.0140**	**0.0140**	**0.0140**	**0.0140**	**0.0140**

TOTALS	**ng/kg**
TCDFs	0.1922
TCDDs	0.1159
PeCDFs	1.2893
PeCDDs	0.1797
HxCDFs	0.5082
HxCDDs	n.d.
HpCDFs	1.5812
HpCDDs	n.d.
OCDF	n.d.
OCDD	n.d.
TOTAL	**3.8665**

[a] WHO 1998 TEQ values, [b] WHO 2005 TEQ values

LABELLED STANDARD RECOVERIES

CLIENT HANSON CEMENT **CONTRACT** HANSONCEM_00244

SAMPLE LABORATORY BLANK

LAB NO N/A **REF** D7109

EXTRACTION STANDARDS	RECOVERY %
$^{13}C_{12}$ 2378 TCDF	73
$^{13}C_{12}$ 2378 TCDD	65
$^{13}C_{12}$ 12378 PeCDF	78
$^{13}C_{12}$ 23478 PeCDF	77
$^{13}C_{12}$ 12378 PeCDD	74
$^{13}C_{12}$ 123478 HxCDF	91
$^{13}C_{12}$ 123678 HxCDF	94
$^{13}C_{12}$ 234678 HxCDF	86
$^{13}C_{12}$ 123789 HxCDF	70
$^{13}C_{12}$ 123478 HxCDD	87
$^{13}C_{12}$ 123678 HxCDD	89
$^{13}C_{12}$ 1234678 HpCDF	84
$^{13}C_{12}$ 1234789 HpCDF	66
$^{13}C_{12}$ 1234678 HpCDD	73
$^{13}C_{12}$ OCDF	65
$^{13}C_{12}$ OCDD	69

All of the recoveries quoted above are within the acceptance limits of method O36.

DIOXIN-FURAN RESULTS

CLIENT HANSON CEMENT **CONTRACT** HANSONCEM_00244

SAMPLE BYPASS DUST

LAB NO 659035 **REF** D7109

		NATO	WHO TEQ			
CONGENER	**ng/kg**	**I-TEQ**	**Humans[a]**	**Humans[b]**	**Fish[a]**	**Birds[a]**
2,3,7,8-TCDF	11.0667	1.1067	1.1067	1.1067	0.5533	11.0667
2,3,7,8-TCDD	<0.17	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-PeCDF	<0.312	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,7,8-PeCDF	15.8378	7.9189	7.9189	4.7513	7.9189	15.8378
1,2,3,7,8-PeCDD	<0.206	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8-HxCDF	15.1588	1.5159	1.5159	1.5159	1.5159	1.5159
1,2,3,6,7,8-HxCDF	11.1622	1.1162	1.1162	1.1162	1.1162	1.1162
2,3,4,6,7,8-HxCDF	14.2518	1.4252	1.4252	1.4252	1.4252	1.4252
1,2,3,7,8,9-HxCDF	5.7084	0.5708	0.5708	0.5708	0.5708	0.5708
1,2,3,4,7,8-HxCDD	3.4667	0.3467	0.3467	0.3467	1.7334	0.1733
1,2,3,6,7,8-HxCDD	7.7655	0.7766	0.7766	0.7766	0.0777	0.0777
1,2,3,7,8,9-HxCDD	4.9996	0.5000	0.5000	0.5000	0.0500	0.5000
1,2,3,4,6,7,8-HpCDF	109.5561	1.0956	1.0956	1.0956	1.0956	1.0956
1,2,3,4,7,8,9-HpCDF	8.3426	0.0834	0.0834	0.0834	0.0834	0.0834
1,2,3,4,6,7,8-HpCDD	52.3410	0.5234	0.5234	0.5234	0.0523	0.0523
OCDF	110.5404	0.1105	0.0111	0.0332	0.0111	0.0111
OCDD	132.8591	0.1329	0.0133	0.0399	0.0133	0.0133
	TOTAL	**17.2227**	**17.0036**	**13.8847**	**16.2170**	**33.5392**

TOTALS	**ng/kg**
TCDFs	144.1268
TCDDs	10.0986
PeCDFs	80.9213
PeCDDs	25.9545
HxCDFs	74.4076
HxCDDs	45.9478
HpCDFs	192.9229
HpCDDs	100.3226
OCDF	110.5404
OCDD	132.8591
TOTAL	**918.1016**

[a] WHO 1998 TEQ values, [b] WHO 2005 TEQ values

LABELLED STANDARD RECOVERIES

CLIENT HANSON CEMENT **CONTRACT** HANSONCEM_00244

SAMPLE BYPASS DUST

LAB NO 659035 **REF** D7109

EXTRACTION STANDARDS	RECOVERY %
$^{13}C_{12}$ 2378 TCDF	79
$^{13}C_{12}$ 2378 TCDD	77
$^{13}C_{12}$ 12378 PeCDF	85
$^{13}C_{12}$ 23478 PeCDF	79
$^{13}C_{12}$ 12378 PeCDD	79
$^{13}C_{12}$ 123478 HxCDF	87
$^{13}C_{12}$ 123678 HxCDF	92
$^{13}C_{12}$ 234678 HxCDF	89
$^{13}C_{12}$ 123789 HxCDF	81
$^{13}C_{12}$ 123478 HxCDD	93
$^{13}C_{12}$ 123678 HxCDD	96
$^{13}C_{12}$ 1234678 HpCDF	39
$^{13}C_{12}$ 1234789 HpCDF	74
$^{13}C_{12}$ 1234678 HpCDD	82
$^{13}C_{12}$ OCDF	71
$^{13}C_{12}$ OCDD	79

All of the recoveries quoted above are within the acceptance limits of method O36.

SECTION 3

EXPLANATION OF APPENDICES

APPENDIX 1 CHAIN OF CUSTODY FORMS/EXTRACTION/AUTOSAMPLER LISTS

These pages show copies of forms that document the progress of the sample from the sampling stage through all analysis stages.

The chain of custody form documents the date that the sample was taken and contains sample identification information together with records of the transfer of the sample prior to analysis.

The extraction log shows the dates of all extraction and cleanup processes, including details of the spiking standards used for analysis. The final extract volume after addition of internal standards is also shown.

The autosampler list shows the run order of the samples GCMS analysis together with the datafile names under which data is stored.

APPENDIX 2 GLOSSARY

This is a list of abbreviations used in this report.

APPENDIX 1

Page No.

NWSS / COMMERCIAL SAMPLE SUBMISSION SHEET

CLIENT	Hanson Cement	NWSS CONTRACT REF	HANSONCEM-00244
CLIENT PROJECT MANAGER	D. Quick	NWSS PROJECT MANAGER	J McBride
TEL		AGREED TURNAROUND	

NORTHUMBRIAN WATER
Scientific Services
Tel: 0191 296 8366
email nwss.customer@nwl.co.uk

MATRIX: CL water	Effluent	Gas	Sludge	Soil	Water	Sample Name / Sample Point	Consent	Sampler	Sample Comments	On-Site Results	Analysis / Test Schedule Required	DATE SAMPLED	TIME SAMPLED	NWSS LAB No.
				/		BYPASS		MD	BYPASS DUST		WLSA 00109	30/10/13	1530	659035
				/		"		"	"		"	"	41°C	

ADDITIONAL INFORMATION / HAZARD DATA

Detail any health or reactive hazards associated with your samples. Enclose Material Safety Data Sheets where appropriate.

KEY TO SAMPLE SOURCE / CONSENT

PWS – Private Water Supply	TS – Tank Supplied / Tank
SP – Swimming Pool waters	

ENTERED BY: P Cobb (DATE) 4/11/13

NO. OF SAMPLES CORRECT? ✓ (DATE)

IF NO THEN REPORTED TO:

CHAIN OF CUSTODY

Relinquished By: MH	Date: 04/11/13	Received By: P Cobb
Relinquished By:	Date:	Received By:
Relinquished By:	Date:	Received By:

Invoicing Information

Samples without a valid PO no & invoice address will not be analysed until this information is provided. This may delay reporting of your results. Name & signature of person submitting samples must also be provided.

Purchase Order Number/WRN

Invoice Address (where NWSS/NWL should send invoice)

Name: _____ Signature: _____

SAMPLE EXTRACTION LOG

LAB NO	N/A	654144	659035	N/A			
PCBs REQD ?	Y	Y	Y	Y			
SAMPLE ID	LAB BLANK	UNIV_EDIN 40280 COMBINED 3 350°C	HANSONCEM BYPASS DUST PADESWOOD RUN 1	DX3			
WT/VOL/TRAP	1.085	1.012	1.070	1.023			
SIGN	JLR / [illegible]						

$^{13}C_{12}$ STD ADDITIONS

DATE/TIME	4/11/13	/1530					
STD	LS2 300913 / PCBES1 250112						
VOL	20µL/20µL						
SIGN	JLR / [illegible]						

EXTRACTION

EXT DATES & TIMES	4/11/13 1600	5.11.13 → 17.00	→	→			
GLASSWARE N°	1	2	3	6			

ALUMINA CLEANUP

DATE	7/11/13	→	→	→			
SIGN	JLR / [illegible]						
PCB KEEP?	Y	Y	Y	Y			

MIXED SILICA CLEANUP

DATE	6/11/13	→	→	→			
SIGN	JLR / [illegible]						

OTHER CLEANUPS 1

TYPE							
DATE	N/A	→	→	→			
SIGN							

OTHER CLEANUPS 2

TYPE							
DATE	N/A	→	→	→			
SIGN							

CONCENTRATION INTO NONANE

DATE	7/11/13						
VOL	10µL		→	→			
SIGN	JLR / [illegible]						

RECOVERY STD ADDITION

DATE/TIME	7/11/13 /1345						
STD	LS2 101013						
VOL	10µL		→	→			
Final VOL	20µL						
SIGN	JLR / [illegible]						

AUTOSAMPLER RUN LIST

Date of Run 14/11/13

A/S POSITION	DATA FILE NAME	LAB NUMBER	SAMPLE DETAILS	NOTES
1	gvb001	—	BORIC2 COLUMN CHECK	
2	02		CS1	
3	03		CS2	
4	04		CS3	
5	05		CS4	
6	06		CS5	
7	07		N	
8	08		N	
9	09		N	
10	10		N	
11	11		LAB BLANK 4.11.13	
12	12	654444	COMBINED 3 550°C	
13	13	—	N	
14	14	654035	PAGESWOOD RUN 1	
15	15	—	N	
16	16		DX3 4.11.13	
17	17		N	
4	18		CS3	

COMMENTS N - None wash.

APPENDIX 2

GLOSSARY

The following terms and abbreviations are used throughout this report.

PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
PeCDD	Pentachlorodibenzo-p-dioxin
PeCDF	Pentachlorodibenzofuran
HxCDD	Hexachlorodibenzo-p-dioxin
HxCDF	Hexachlorodibenzofuran
HpCDD	Heptachlorodibenzo-p-dioxin
HpCDF	Heptachlorodibenzofuran
OCDD	Octachlorodibenzo-p-dioxin
OCDF	Octachlorodibenzofuran
HxCDPE	Hexachlorodiphenyl ether
HpCDPE	Heptachlorodiphenyl ether
OCDPE	Octachlorodiphenyl ether
NCDPE	Nonachlorodiphenyl ether
DCDPE	Decachlorodiphenyl ether
TEF	Toxic Equivalent Factor
TEQ	Toxic Equivalent
I-TEF	International Toxic Equivalent Factor (NATO/CCMS)
I-TEQ	International Toxic Equivalent (NATO/CCMS)