APPENDIX I

Monsanto

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

September 19, 1980

Mr. William A. Hueppauff
Rosalie Investment Company
1962 Clayton Road
Ballwin, Missouri 63011

Dear Mr. Hueppauff:

This will confirm our agreement to undertake analytical testing of six composite samples of chemical wastes which you will deliver to Monsanto. We will conduct our analysis using our ordinary procedures for the detection of polychlorinated biphenyls (PCBs) only. Our analysis will not undertake the identification of any other materials present in your samples. We will target to achieve a detection limit in the sample as analyzed (the composite) of five parts per million. This could vary depending on the nature and complexity of the sample matrix. If the sample contains interfering materials such as chlorinated pesticides or other chlorinated industrial wastes, the PCB analysis will be significantly more difficult and could result in achieving a higher detection limit.

Prior to conducting our analysis we shall extend an invitation to the Missouri Department of Natural Resources and the United States Environmental Protection Agency to have observers present during the procedure if they so desire.

Results of our analysis will be provided to you and will be made available to state and federal authorities as appropriate and may, in Monsanto's discretion, be made available publicly.

It is expressly agreed that Monsanto is not undertaking any obligation or liability except as expressly set forth herein and that Monsanto is providing this technical assistance in the public interest and at your specific request.

If this letter accurately sets forth our understanding and agreement, please sign one copy in the space indicated and return to me.

MONSANTO COMPANY

Accepted and agreed to:

Date 9-19-80

By Sept 19 80

By John H. Craddock
John H. Craddock, Manager
Product and Environmental Safety

MONS 022330

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

September 19, 1980

This letter documents transfer of six (6) composite samples of wastes removed by the Missouri Department of Natural Resources from the site near Caulk's Creek on property owned by Rosalie Investment Company.

A description of the samples is included on the attached receipt from Gary B. Snodgrass USEPA, Region VII, and Keith Schodien, Missouri Department of Natural Resources.

William A. Hueppauff hereby states that the samples are in the same condition as received from the Missouri Department of Natural Resources.

William A. Hueppauff 9-19-80

Orville Hicks hereby acknowledges receipt of the six (6) samples.

Orville Hicks 9/19/80

Witnessed by:

John H. Craddock 9-19-80

MONS 022331

Inventory of Samples Removed From Rosalie Investment Co. Property.

September 17, 1980 - Drum site in Drainageway

SK9908 - Composite Drum Sample
SK9909 - Composite Drum Sample
SK9910 - Composite Drum Sample

September 18, 1980 - Drum site along Caulk's Creek

SK9911 - Composite Drum Sample
SK9912 - Composite Drum Sample

September 18, 1980 - Dump site along Caulk's Creek containing Five (5) gallon cans and buckets.

SK9914 - Composite Soil Sample

Keith Schreiber

APPENDIX II

POLYCHLORINATED BIPHENYLS IN SAMPLES FROM CAULK'S CREEK SITE

INTRODUCTION

On September 19, 1980, five composited drum samples and one composited soil sample were received from a representative of Rosalie Investment Company. The samples were split samples which had been removed from sites near Caulk's Creek in West St. Louis County by representatives of the USEPA and the Missouri Department of Natural Resources (DNR). The sites were on land owned by Rosalie Investment Company. The samples were submitted for analysis for polychlorinated biphenyls, in response to an offer made by Monsanto Company to Rosalie Investment Company. The documents in Appendix I are records of the Monsanto offer and the transfer of the samples.

SUMMARY

The six samples from the Caulk's Creek site were analyzed for polychlorinated biphenyls by our laboratory. Five of the samples (four composite drum samples and one soil sample) did not contain polychlorinated biphenyls above our experimental detection limit of five parts per million (ppm). These samples were subjected to standard cleanup techniques and the polychlorinated biphenyls were measured by gas chromatography/mass spectrometry (GC/MS). One composite drum sample was not amenable to GC/MS analysis because of the nature of the material in the sample. After the sample was cleaned up, the polychlorinated biphenyls were measured by electron capture gas chromatography (EC-GC). This sample contained 4 ppm polychlorinated biphenyls. (The lower detection limit for this technique resulted from reduced background contamination for this chromatographic detector for this sample.) Each of the samples was "spiked" with 5 ppm polychlorinated biphenyls to demonstrate our ability to measure the polychlorinated biphenyls at the stated detection limit. These spiked samples were analyzed identically to the unspiked samples. Our recovery of the polychlorinated biphenyls averaged 94% at the 5 ppm level.

DETAILS

Sampling

The six composite samples (five drum composites and one soil composite) were collected by USEPA and Missouri DNR personnel at the Caulk's Creek site. The samples were split at the site and one set was transmitted to our laboratory as documented in Appendix I. Upon receipt, the samples were entered into our sample log.

In our laboratory, the samples were aliquoted for analysis. The drum samples, which were not homogeneous, were stirred to mix as completely as possible. Ten gram aliquots were weighed into 100 mL volumetric flasks and diluted to volume with pesticide grade hexanes. The soil sample was handled in accordance with Standard Operating Procedure (SOP) EAN-80-SOP-006, SOP for Homogenizing, Subdividing and Preserving Sediment Samples. However, the sample was not sieved so that the integrity of the sample would not be affected by the sampling procedure.

Sample Cleanup (Drum Composites)

The diluted composite drum samples were cleaned up using standard procedures described in the ASTM Standard Method for Analysis of Environmental Materials for Polychlorinated Biphenyls, ASTM D3304-74. Five mL aliquots of the hexane solutions were subjected to alumina column cleanup, described in Section 9.2 of D3304. The cleaned up samples were concentrated to 5mL for subsequent determination of polychlorinated biphenyls. Two of the samples (SK 9910 and SK 9911) had excessive background interferences after column cleanup. These two samples were realiquoted and subjected to the sulfuric acid cleanup described in Section 9.1.9-9.1.2 of D3304. The acid washed fractions were then cleaned up with an alumina column as described above and concentrated for analysis.

The homogenized soil sample was extracted with isooctane in accordance with EAM-80-SOP-20 (Draft) Standard Operating Procedure for the Extraction of Semivolatile Organic Chemicals from Sediment. The composite soil sample contained less than 5% moisture, by weight.

Determination of Polychlorinated Biphenyls

The cleanup samples and extracts were analyzed for polychlorinated biphenyl by Selected Ion Monitoring gas chromatography/mass spectrometry (SIM GC/MS). The analysis conditions have been described previously in Environmental Sciences method ES-80-M-11, Determination of ... Polychlorinated Biphenyls ... In Low Boiling Organic Matrices, Sections 9 and 10.4. These are included in Appendix II. There were two deviations from the method as written. In Section 10.4.2, the column temperature was programmed from 120° to 280° at 16°/min. Secondly, the SIM groups and start times were changed to determine heptachlorobiphenyl instead of monochlorobiphenyl. The ions monitored for heptachlorobiphenyl were m/z 392 and 322. A revised Table II has been included in the Appendix to reflect this change.

One sample (SK 9910) was not amenable to determination of polychlorinated biphenyls by SIM GC/MS because of mass spectral interferences at the selected ions. The acid wash did not remove these interferences. This sample was analyzed by gas chromatography with an electron capture detector (EC-GC), which did not respond to the materials which interfered with SIM GC/MS. This procedure was similar to that described in Section 10, D3304. The specific conditions used are tabulated below.

Instrument: Varian 3700 Gas Chromatograph with Linear Electron Capture Detector

Column: 1 m by 2 mm i.d. glass column packed with 3% OV 101 on 100/120 mesh Gas Chrom Q

Column temperature: 220° C isothermal

Detector temperature: 350°C

Injection port temperature: 250°

MONS 022325

Carrier Gas: Nitrogen, 30 mL/min

Injection volume: 3 uL

The EC-GC was calibrated with duplicate reference standards over the operating concentration range, similar to the procedure used for SIM GC/MS.

Calculation of Results

The results for the SIM GC/MS determinations were calculated using an average response factor (RF) for each chlorobiphenyl homolog. Mixed standards containing equal weights of Aroclor® 1242 and Aroclor® 1254 were injected at least in duplicate on a daily basis to calibrate the instrumental response and determine the RF. The concentration of each homolog, Ci, was calculated using the following equation:

$$C_i = \frac{(RF_i)(A_i)(V_i)}{(W_i)}$$

where

C_i = concentration of the homolog (ppm)

RF_i = response factor (ppm/area count)

A_i = peak area for homolog (area counts)

V_i = volume of sample concentrate (mL)

W_i = sample weight (g) (0.5 g for drum composites
10 g for soil)

The total concentration of polychlorinated biphenyls in each sample was calculated by summing the C_i for all the homologs.

The results for the EC-GC measurements were calculated using a calibration curve of summed chlorobiphenyl peak area vs concentration, prepared by summing three Aroclor® 1254 standards in duplicate at each concentration. The concentration in the sample concentrate was read directly from the calibration curve. The concentration in the original sample was calculated using the equation:

$$C = \frac{(C_c)(V)}{(W)}$$

where C = concentration in original sample (ppm)

C_c = concentration from the calibration curve (ppm)

V = volume of the sample concentrate (mL)

W = sample weight (0.5 g)

(For both SIM GC/MS and EC-GC, equal injection volumes were used in all cases, so that the injection volume does not enter into the calculation; i.e., the methods were calibrated in concentration units, not mass units.)

QUALITY ASSURANCE

In order to assess the validity of the results for this study, each sample was spiked with 5 ppm of Aroclor® 1254. The recovery of the polychlorinated biphenyls at this level insured that if polychlorinated biphenyls were present in the samples at this level (our stated detection limit) we would have been able to measure them. The average recovery for all samples was 94%.

An attempt was made to measure the precision of the analyses by analyzing two samples (SK 9912 and SK 9914) in replicate. However, since no polychlorinated biphenyls were measured in those samples, the precision could not be calculated for the samples. However, based on replicate injections of the standards, the precision for the determinations can be estimated to be between 10% and 20% relative standard deviation for the SIM GC/MS measurements.

RESULTS

The results for this study are tabulated below.

DATA SUMMARY CAULK'S CREEK SITE SAMPLES

Sample #	Total Polychlorinated Biphenyls (ppm)	Cleanup Analysis	% Recovery 5 ppm Spike
SK 9908	ND < 5	Column, GC/MS	102%
SK 9909	ND < 5	Column, GC/MS	83%
SK 9910	4	Acid,Column, EC-GC	87%
SK 9911	ND < 5	Column, GC/MS	96%
SK 9912	ND < 5	Column, GC/MS	92%
SK 9914	ND < 5	Extract, GC/MS	111%

As can be seen, only sample SK 9910 contained measureable levels of polychlorinated biphenyls. This was the sample analyzed by EC-GC. (The lower detection limit for this technique resulted from the reduced background contamination from this sample for the EC detector.)

The results are indicative that polychlorinated biphenyl contamination at the Caulk's Creek site is not as widespread as feared. Even for the sample which did contain measureable levels, if we assume the composite represents seven drums, the most any one drum could contain is still less than 30 ppm. This level is below the 50 ppm US EPA action level.

Submitted by:

Monsanto Industrial Chemicals Company
Environmental Sciences Section - NIE
800 North Lindbergh Blvd.
St. Louis, Missouri 63166

Prepared by:

Robert G. Kaley, II
Research Group Leader

Approved by:

Richard L. Wasson
Director, Technology Support
Environmental Operations & Technology Planning