Assessment of Analytical Data
Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry Hazardous Waste Determination for K178

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October, 2001

U.S. Environmental Protection Agency
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1. Introduction

In response to our K178 hazardous waste listing proposal (65 FR 55684, September 14, 2000), E. I. Du Pont de Nemours and Company (DuPont) launched a significant sampling and analysis effort to characterize the waste streams that we proposed for listing. DuPont collected 61 solid samples from three chloride-ilmenite facilities to characterize those proposed to-be-listed nonwastewaters (i.e., Iron Rich^{TM} (1 stream) and wastewater treatment sludges (6 streams)). They also collected from those three facilities 44 wastewater samples to characterize wastewaters (11 streams) that produce the wastewater treatment sludges of interest. The solid samples were analyzed by the Severn Trent Lab (STL) located in West Sacramento, California and the wastewater samples were analyzed by the STL in Denver, Colorado. All samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (SW 6020- ICPMS) and/or Inductively Coupled Plasma-Atomic Emission Spectrometry (SW 6010- ICP) for total and Synthetic Precipitation Leaching Procedure (SPLP) metals that included 21 metals; 2 streams were also assessed via Toxicity Characteristic Leaching Procedure (TCLP). Appendix A includes DuPont's solid and wastewater sampling and analysis strategies for the three chloride-ilmenite facilities. STL's data packages were validated by Environmental Standards (ES) in Valley Forge, Philadelphia. DuPont's analytical data and quality assurance report (DuPont's report) is available in the docket for today's final rule.

We proposed to list K178 as hazardous because our data showed that the waste contained elevated levels of manganese and thallium that would be mobile in the subsurface and might pose risk via a groundwater ingestion scenario. DuPont submitted comments and data to support their position that thallium is not present in their wastes. DuPont also argued that their data show that the wastewater treatment sludges do not contribute to the overall risks in the modeled waste. Our assessment of DuPont's data focused on the reported total and TCLP/SPLP concentrations of four constituents of concern (i.e., antimony, arsenic, manganese, and thallium) in Iron Rich^{TM}, wastewater treatment sludges and wastewaters. The purpose of our assessment was to determine the validity of DuPont's waste analysis so we could then evaluate their comments suggesting that thallium is not present in their wastes. See *"Response to Comment Background Document"*, ICMP-00022, Comment 5a-3 for DuPont's relevant comments.

Section 2 discusses the procedures we followed for this assessment. Section 3 describes the products we generated upon completion of our review of DuPont's data. Section 4 assesses the validity of DuPont's waste analysis and evaluates their comments.

2. Review Procedures

We conducted a complete review of DuPont's report to determine the validity of their waste analysis. Various STL analytical operations were assessed, including waste sample shipments and handling; sample preparation; waste TCLP and SPLP leachate extractions; waste sample/leachate dilutions; laboratory ICP and ICPMS instrument output; laboratory raw data calculations; and reporting of final analytical data points.

DuPont's original report has 11 volumes. DuPont submitted, as requested, additional information and materials to facilitate our further review. DuPont's supplemental information package, which includes STL's original Contract Laboratory Program-like (CLP-like) electronic data package (in 9 CDs), is in the docket for today's final rule. Appendix B includes our electronic mail to DuPont requesting additional information and materials for our further assessment. DuPont's report and supplemental information package were reviewed by three chemists/senior data reviewers, Shen-yi Yang, Environmental Protection Specialist of EPA, Office of Solid Waste, Hazardous Waste Identification Division; Kelly Luck, Project QA Manager/Senior Data Validator of Dynamac Corporation; Ray Anderson, QA Manager and Laboratory Coordinator of Science Applications International Corporation.

3. Review Products

The EPA data reviewers prepared QA/QC review summary reports documenting their observations and assessment of the quality of each of the ten data sets. The data reviewers also updated DuPont's analytical data summary tables[1] to include (1) percent (%) moisture and pHs of the waste samples (if measured), and final pHs of TCLP/SPLP waste leachates; (2) the ICP results for 4 constituents of concern (i.e., antimony, arsenic, manganese, and thallium)[2]; (3) any revision to the ES-applied data qualifiers, including justifications for such revisions; and (4) the analytical results from EPA's sample, for easier comparison to DuPont's results.

Appendix C includes our review summary reports and updated analytical data summary tables for DuPont's ten data sets. The ten data sets are:

- Equalization Pond Sludge- Johnsonville Plant, New Johnsonville, TN
- Settling Pond Sludge- Johnsonville Plant, New Johnsonville, TN
- Hillside Pond Sludge- Johnsonville Plant, New Johnsonville, TN
- Equalization Pond Sludge- DeLisle Plant, Pass Christian, MS
- Disengagement Basin Sludge- DeLisle Plant, Pass Christian, MS
- Iron Rich^{TM} Filter Cake- Edge Moor Plant, Wilmington, DE
- Wastewater Treatment Sludge- Edge Moor Plant, Wilmington, DE
- Wastewater- Johnsonville Plant, New Johnsonville, TN
- Wastewater- DeLisle Plant, Pass Christian, MS
- Wastewater- Edge Moor Plant, Wilmington, DE

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[1] Originally submitted by DuPont in draft form in Attachment 5.1.3-B of their November 13, 2001 comments (ICMP-00022) and in final form in their December 22, 2000 comments (ICMP-L0003).

[2] While DuPont did not report ICP results for antimony, arsenic, and thallium as part of their formal comments, the analyses were automatically conducted when DuPont ran the ICP analyses for manganese and were submitted as part of DuPont's raw data package. We also assessed these results.

4. Assessment

Section 4.1 assesses the overall quality of DuPont's waste analysis. Section 4.2 responds to DuPont's comment pertaining to the presence of thallium in their wastes (ICMP-00022-5a-3).

4.1 The Validity of DuPont's Waste Analysis

STL performed waste analyses for a fast (two-week) turnaround time with a minimal (level I) QC check (by an analyst using a data review checklist) before delivery of the analytical data report to DuPont. ES performed a complete (100%) QA review following guidance from the "National Functional Guidelines for Inorganic Data Review" (US EPA, 2/94). The areas ES reviewed included: sample holding times, sample condition upon lab receipt, instrument (ICP and ICPMS) tuning and calibration, and field and laboratory QC sample results. ES made numerous hand-written additions (e.g., inorganic analyses support documentation, summaries for the laboratory's analysis for initial and continuing calibration verification standards, initial and continuing calibration blanks, interference check samples, serial dilutions, and PQLCRI standards) and changes (e.g., sample identification numbers, analysis date, method detection limits/reporting limits, dilution factors, and sample result calculations) throughout the entire report. The report was organized in a way that was difficult to follow and it has many data gaps that complicated our determination of whether those hand-written changes and corrections were justifiable. Most hand-written changes and corrections were not initialed nor dated by ES' data reviewers. Therefore, we requested STL's original CLP-like analytical data package to facilitate our further review.

In the course of our review, we found some major analytical problems with DuPont's waste analysis:

(1) STL's method detection limit (MDL) studies are outdated. STL's laboratory located in West Sacramento, California, which analyzed the Iron Rich™ and wastewater treatment sludge samples, conducted their ICP and ICPMS MDLs and reporting limits (RLs) studies for metals in early 1998[3]. This is unacceptable since the operating conditions, time in service, and maintenance affect the sensitivity of the instrument over time. A more appropriate time frame would have been on a quarterly basis[4]. In addition, the ICPMS Method 6020A used for these

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[3] STL's laboratory located in Denver, CO, which analyzed all the wastewater samples, conducted their ICP and ICPMS MDLs/RLs studies in early 2000.

[4] Contract Laboratory Program (CLP) labs according to the CLP Inorganics Statement of Work, ILMOS.OC, March 1999, require detection limit studies to be performed on a quarterly basis

analyses requires detection limit studies to be determined at least every three months and kept with the instrument log book[5]. We believe at a minimum the MDL studies should be performed on an annual basis. We were very surprised the STL-West Sacramento, California lab operated and responded to various external audits to establish applicable certifications without a more current MDL study because such audits generally request and review for documentation to support the establishment of proposed detection and reporting limits and verify if the frequency of MDL study updates is appropriate. STL's detection limits for ICPMS and ICP metals should have been adjusted routinely for all associated sample analyses and matrices to reflect changes in target analyte responses over time using the most current MDL data available. Since the MDL study data are outdated, the reported detection limits most likely do not reflect the current instrument operating conditions, sample preparations procedures, and potential sensitivity changes. Therefore, all low-level concentrations (at or near the reporting limit) and non-detect sample results associated with these outdated detection limits should be considered as estimated values and questionable validity.

(2) STL appears not to have used the actual sample weight in their calculations for total ICP and ICPMS metals results. Because a method-recommended sample weight (not the actual sample weight) was used in their calculations, the ICP and ICPMS results for total metals in all solid samples should only be considered to be accurate to no more than 2 significant figures.

(3) The accuracy of DuPont’s “non-detect” and low-level positive results of several analytes in many samples is questionable. Below are the problems we noticed in DuPont’s waste analysis.

- The way STL’s ICPMS instruments were calibrated

STL’s ICPMS instruments were calibrated using a single-point calibration, not a calibration curve[6]. The ICPMS instruments (M01 and M02) used to assess Iron Rich and pond sludge samples were calibrated using one standard (arsenic and manganese at 100 ug/l; antimony and

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(January, April, July, and October).

[5] The SW-846 Chapter One guidance does not set a frequency at which MDLs should be updated, however, Section 4.4.1 of Chapter One does state that the laboratory should have procedures in place for demonstrating method proficiency and determining the MDL. Therefore, the laboratory should establish a written policy that meets their certification requirements and allows the laboratory to update QC parameters at a reasonable interval.

[6] SW-846 allows the use of single-point calibration for both ICP (SW 6010) and ICPMS (SW 6020).

thallium at 50 ug/l) and optimized at the upper calibration level (manganese and arsenic at 80 ug/l; antimony and thallium at 40 ug/l). The ICPMS instrument (ICPMS1) used to assess wastewater sludge samples was calibrated and optimized using standards at the same level (arsenic, manganese, antimony and thallium at 200 ug/l). STL analyzed a practical quantitation limit standard (PQLCRI) for the ICP analysis, however, not for the ICPMS analysis. We could not determine the sensitivity and stability of their ICPMS machines below their calibration levels (manganese and arsenic at 80 ug/l; antimony and thallium at 40 ug/l for ICPMS M01 and M02; and arsenic, antimony and thallium at 200 ug/l for ICPMS1). With the various analytical problems described in this section that STL had, it seemed very unlikely that STL could have reliably measured arsenic, antimony, and thallium at levels in the vicinity of their MDLs (0.41, 0.16, and 0.1 ug/l, respectively for ICPMS M01 and M02; and 0.2, 0.2, and 0.02 ug/l, respectively for ICPMS1).

- Blank contamination

Numerous blank samples (e.g., method blanks, initial and continuing calibration blanks) with multiple analytes yielding concentrations above (two to fifteen times) their MDLs. As a result of this problem, positive results for arsenic, antimony, manganese, and thallium (as well as other analytes not discussed in this review) of many samples were qualified by ES as “U” (non-detect). See Appendix C for our review of Volumes 2, 4, 7, 8, 9 , 10, 11 of DuPont’s Analytical Data Report.

- Large negative instrument responses

Many samples had large negative instrument responses for antimony and thallium with absolute values greater than three to four times their MDLs. ES qualified the “non-detect” sample results with “UJ” indicating that their MDLs may have been higher than reported. See Appendix C for our review of Volumes 2, 3, 4, 5, 6, 7, 9, 11 of DuPont’s Analytical Data Reports.

- Possible carry-over problems

Many blank samples (method blanks, initial/continuing calibration blanks) exhibited contamination (four to six times the MDL for the thallium analysis associated with the Iron Rich and pond sludge samples; two to seventeen times the MDL for the antimony analysis associated with wastewater samples). Those blanks were analyzed immediately after an initial or a continuing calibration verification standard (ICV or CCV). There may have been carry-over problems. See Appendix C for our review of Volumes 2, 7, and 11 of DuPont’s Analytical Data Report.

(4) The ICPMS total and TCLP manganese results for the Iron Rich^{TM} and some pond sludge samples may have been biased low. In contrast, the corresponding ICP total and TCLP manganese results appear more reliable. The ICPMS instruments (ICPMS M01 and M02) used to assess Iron Rich and pond sludge samples were calibrated for manganese at 100 ug/l and their highest spikes for manganese at 200 ug/l had good recoveries. In DuPont's submissions, there was no information pertaining to the linear calibration range for its ICPMS manganese analysis. (In Volume 11 of DuPont's Analytical Data Report, STL-Denver, Colorado lab documented that its linear calibration range for manganese for the ICPMS instrument (ICPMS1) used to assess wastewater samples was 0-2000 ug/l.) Before multiplying the dilution factor to calculate the final results, the ICPMS responses for total manganese in Iron Rich and sludge samples were 5,523 ~ 17,127 ug/l and 180 ~ 4151 ug/l, respectively; and for TCLP manganese in Iron Rich and sludge samples were 6,778 ~ 16,976 ug/l and <100 ~ 7,211 ug/l, respectively. The ICPMS responses for total and TCLP manganese for Iron Rich and some sludge samples seemed very likely not have been diluted and analyzed properly within the linear calibration range for manganese. This may explain why the total and TCLP manganese results for the Iron Rich^{TM} and pond sludge samples analyzed by ICPMS were consistently lower (up to 23 percent) than those analyzed by ICP.

Based on these identified analytical problems, we believe that it is not appropriate to rely heavily on DuPont's ICPMS data. In their formal comments, DuPont reported two sets of results (ICP and ICPMS) for manganese, but only one set of results (i.e., ICPMS) for arsenic, antimony and thallium. While the calculated ICP results for arsenic, antimony, and thallium were not reported as part of their formal comments, the analyses were automatically conducted when the laboratory ran the ICP analyses for manganese and were submitted as part of DuPont's electronic raw data package. Because of the analytical problems we identified in DuPont's ICPMS analysis, we examined their raw data carefully to determine (1) whether or not DuPont's ICP results could be used to help evaluate the validity of their ICPMS results that were compromised by the previously identified analytical problems; and (2) whether or not we could use their ICP/ICPMS results to make any conclusions regarding the presence of thallium in DuPont's wastes. After a careful examination, we concluded the following:

(1) DuPont's ICP results were useful in assessing the validity of the ICPMS results for manganese and antimony, but were of less value in confirming ICPMS results for arsenic and thallium due to elevated detection limits.

Manganese:

The ICP manganese results were well within the linear calibration range and associated QC results met acceptance criteria. The linear calibration range for manganese (using ICPMS M01/02) is probably greater than 0-200 µg/L, however, we have no data in the laboratory package to verify that. Most ICPMS manganese results do agree quite well with the reported ICP manganese results (less than 10% difference). Some ICPMS total and TCLP manganese results are suspect or rejected because their results were lower than their ICP total manganese results by more than 10% or 20%, respectively. See Table 4.1-1 for the ICPMS results that are suspect or rejected.

Certain wastewater samples had positive ICPMS manganese results, but were qualified by ES as "U" (non-detect) due to blank contamination. Those ICPMS manganese results showed good replication, when compared to their corresponding ICP values. Therefore, we believe the ICPMS manganese results are acceptable and removed the qualifier. See our review of Volume 6 of DuPont's Analytical Data Report in Appendix C.

Antimony:

The ICP antimony results were well within the linear calibration range and QC results associated with samples met acceptance criteria. DuPont's ICP antimony results help substantiate the presence of total and leachable antimony in certain sludge samples. See our review of Volumes 3, 5, 6, and 7 of DuPont's Analytical Data Report in Appendix C.

Certain wastewater samples had positive ICPMS antimony results, but were qualified by ES as "U" (non-detect) or "J" (estimated) due to blank contamination. Those ICPMS antimony results showed good replication, when compared to their corresponding ICP values. Therefore, we believe the ICPMS antimony results are acceptable and removed the qualifiers. See our review of Volume 6 of DuPont's Analytical Data Report in Appendix C.

Arsenic:

The ICP arsenic results were well within the linear calibration range and QC results associated with samples met acceptance criteria. However, STL's ICP total and TCLP/SPLP arsenic results for Iron Rich and sludge samples were insensitive because they were reported as non-detect at higher MDLs (3.1 mg/kg for total; 0.22 mg/L for TCLP; and 0.043 mg/L for SPLP) than those by ICPMS (0.4 mg/kg for total; 0.002 mg/L for TCLP; and 0.00041 mg/L for SPLP). In other words, many ICP arsenic total and TCLP/SPLP results for Iron Rich and sludge samples could not be used to substantiate the corresponding ICPMS results that were compromised by the identified laboratory analytical problems. The ICP SPLP arsenic results were useful in our evaluation of the validity of ICPMS SPLP arsenic results for certain pond sludge samples, and ICPMS total arsenic results for wastewater samples. See our review of Volumes 5, 6, and 10 of DuPont's Analytical Data Report in Appendix C.

Thallium:

The ICP thallium results were well within the linear calibration range and QC results associated with samples met acceptance criteria. However, STL's ICP total and TCLP/SPLP thallium results for wastes (Iron Rich and pond sludges) and wastewater samples were insensitive because they were reported as non-detect at higher MDLs (MDLs for wastes:7.1 mg/kg for total; 0.27 mg/L for TCLP; and 0.053 mg/L for SPLP; MDL for wastewater: 0.0049 mg/L) than those by ICPMS (MDLs for wastes: 0.18 mg/kg for total; 0.0005 mg/L for TCLP; and 0.0001 mg/L for SPLP; for wastewaters: 0.00002 mg/L). In other words, DuPont's ICP thallium total and TCLP/SPLP results for Iron Rich, sludges, and wastewater samples could not be used to substantiate their corresponding ICPMS results that were compromised by the identified laboratory analytical problems.

Table 4.1-1 identifies the analytes/sample identification numbers for the ICPMS results that continue to be suspect or rejected after comparison to their corresponding ICP results and the places where we documented our reasons.

Table 4.1-1 Rejected or Suspect Data Points

Sample Type	**Analyte/Analysis**	**Samples Identification Numbers**	**Data Quality**	**Discussions in Appendix C**
Equalization Pond Sludge-Johnsonville	Mn-total (SW 6020-ICPMS)	JV-EP-M-4	Suspect	Volume 2
	As-SPLP (SW6020-ICPMS)	JV-EP-I-1, JV-EP-I-2, JV-EP-I-3, JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6	Suspect[1]	
	Tl-SPLP (SW 6020-ICPMS)	JV-EP-M-3, JV-EP-M-4, JV-EP-M-5	Suspect[1]	
		JV-EP-I-3, JV-EP-M-1, JV-EP-M-2	Suspect[2]	
Settling Pond Sludge-Johnsonville	As-total (SW6020-ICPMS)	JV-SP-M-2	Suspect	Volume 3
	Tl-SPLP (SW6020-ICPMS)	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5	Suspect[2]	
Hillside Pond Sludge-Johnsonville	As, Tl-TCLP/SPLP (SW6020-ICPMS)	JV-HP-1, JV-HP-2, JV-HP-3, JV-HP-4, JV-HP-5, JV-HP-6, JV-HP-7, JV-HP-8, JV-HP-9	Suspect	Volume 4
	Mn-total (SW6020-ICPMS)	JV-HP-2, JV-HP-8, JV-HP-9		

Table 4.1-1 Rejected or Suspect Data Points				
Sample Type	**Analyte/Analysis**	**Samples Identification Numbers**	**Data Quality**	**Discussions in Appendix C**
Equalization Basin Pond Sludge-DeLisle	As, Sb-total (SW6020-ICPMS)	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6	Suspect	Volume 5
	Tl-SPLP (SW6020-ICPMS)	DL-EQ-I-1, DL-EQI--2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6	Suspect[2]	
Disengagement Basin Pond Sludge-DeLisle	Sb-total (SW6020-ICPMS)	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6	Suspect	Volume 6
	Tl-SPLP (SW6020-ICPMS)	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6	Suspect[2]	
Iron Rich™	As, Sb-TCLP/SPLP (SW6020-ICPMS)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8	Suspect	Volume 7
	Tl-TCLP/ SPLP (SW6020-ICPMS)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8	Rejected	
	Mn-TCLP (SW6020-ICPMS)	EMI-1, MI-3, EMI-4, EMI-5, EMI-7, EMI-8	Suspect	
	As, Sb-total (SW6020-ICPMS)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8		
	Tl-total (SW6020-ICPMS)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8	Rejected	
	Mn-total (SW6020-ICPMS)	EMI-7	Suspect	
	Mn-total (SW6020-ICPMS)	EMI-1	Rejected	
Wastewater Treatment Sludge-Edge Moor	As-total (SW6020-ICPMS)	EMS-1, EMS-2, EMS-3, EMS-4, EMS-5, EMS-6, EMS-7, EMS-8	Suspect[1]	Volume 8
	Tl-total (SW6020-ICPMS)	EMS-3		
Wastewater-Johnsonville	Sb-total (SW6020-ICPMS)	JV-RC-1	Rejected	Volume 9
		JV-FW-1, JV-FW-2, JV-FW-3, JV-OS-1, JV-OS-2, JV-OS-3, JV-OS-4	Suspect[1]	
		JV-WTS-2, JV_WTS-4	Suspect[2]	
Wastewaters-Edge Moor	Sb-total (SW6020-ICPMS)	FWW-1, FWW-2, FWW-3, FWW-4, OWW-1	Rejected	Volume 11

Table 4.1-1 Rejected or Suspect Data Points

Sample Type	Analyte/Analysis	Samples Identification Numbers	Data Quality	Discussions in Appendix C
		OWW-1, OWW-2, OWW-3, OWW-4, FWW-4, KS-1, KS-2, KS-3, KS-4, OVS-1, OVS-2	Suspect[1]	
	Mn-total (SW6020-ICPMS	FWW-1, FWW-2, FWW-3, OVS-1, OVS-2 OVS-1, OVS-2	Suspect[1]	
	Tl-total (SW6020-ICPMS	OWW-2, OWW-3, OWW-4, KS-1, KS-2, KS-3, KS-4, OVS-2	Suspect[1]	
	Tl-total (SW6020-ICPMS	FWW-1, FWW-2, FWW-3, FWW-4, OWW-1	Suspect[2]	

As: arsenic; Mn: manganese; Sb, antimony; Tl, thallium.

1 The analyte was present in associated blanks. Positive results were qualified as “U” (non-detect).

2. The sample result had large negative instrument response with absolute value greater than twice the MDL. ES qualified the “non-detect” sample result with “UJ” indicating that the MDL may be higher than reported.

(2) We suspected the validity of DuPont’s ICPMS results for total and TCLP/SPLP thallium. DuPont’s ICP total, TCLP and SPLP thallium results conform to our ICP total, TCLP and SPLP thallium results. We do not agree with DuPont’s assertion that thallium is not present in the wastewater treatment solids. The detected thallium leachate values, however, are below the MDL and therefore, would not be used to support a regulatory determination. Section 4.2 discusses in detail our assessment of the validity of DuPont’s ICP/ICPMS thallium results.

4.2 Our Response to DuPont’s Comment (ICMP-00022-5a)

In its comment, DuPont stated that its sampling and analysis of process streams show that thallium is not present at the levels suggested by EPA. In response to the comment, we evaluated DuPont’s thallium data for Iron Rich^{TM}, wastewater treatment solids, and wastewaters.

4.2.1 Evaluation of DuPont’s Thallium Data for Iron Rich^{TM}

DuPont provided analytical data characterizing Iron Rich^{TM} for eight samples (plus 1 duplicate). These samples were comparable to our Iron Rich^{TM} sample (DPE-SO-01). All 8 samples and the duplicate were analyzed for total, TCLP and SPLP metals. A total of 21 metals including thallium were measured. Table 4.2-1 shows the ICPMS thallium levels in Iron Rich^{TM} as originally reported in Attachment 5.1.3-B of DuPont’s November 13, 2000 comment submission (ICMP-00022).

Table 4.2-1: Thallium in DuPont's Iron Rich™ (ICPMS- SW 6020)

Matrix	Total (mg/kg)	TCLP (mg/L)	SPLP (mg/L)
Iron Rich™	<0.18-0.33 U	<0.0005	<0.0005

U This analyte was present in associated blanks. Positive results were qualified as "U" (non-detect).

We believe that all of DuPont's results summarized in Table 4.2-1 should be rejected. We rejected total thallium results because of the first three analytical problems described previously in Section 4.1. We rejected the TCLP and SPLP data for the same reasons, and we believe these results were further compromised as a result of serious analytical problems (physical and/or memory interferences) that appeared in the ICPMS instrument output on the day that the TCLP and SPLP tests were conducted. Based on our assessment of these output, we believe for both total and TCLP/SPLP tests the lab should have terminated the analyses, corrected the problems, recalibrated the instrument, verified the new calibration, and re-analyzed the affected samples. See our review of Volume 7 of DuPont's Analytical Report in Appendix C for a detailed description of the specific analytical problems that we identified.

As stated previously in Section 4.1, because of the analytical problems we identified in DuPont's ICPMS analysis, we examined their raw data carefully to determine whether or not we could make any conclusions from their analyses regarding the presence of thallium in the Iron Rich™. We believe that DuPont's data, generated using ICP, for total and TCLP/SPLP concentrations of thallium may be valid and useable. See a detailed discussion in our review of Volume 7 of DuPont's Analytical Data Report. Table 4.2-2 compares the EPA and DuPont ICP thallium results.

Table 4.2-2: Thallium in DuPont's Iron Rich™, (ICP-SW 6010)

Analysis	EMI-1 through 8	EPA Sample (DPE-SO-01)
Total-6010 B (mg/kg)	<7.1	3.7 (18.4[1] EPA second analysis) (23.6 DuPont split)
TCLP-6010 B (mg/L)	<0.250	0.28 (0.27 EPA duplicate) (DuPont did not report their split result)
SPLP-6010 B (mg/L)	<0.050	0.012 (DuPont did not report their split result)

[1] Second analysis occurred on the same day with a 10X dilution

As Table 4.2-2 indicates, DuPont found no total or TCLP/SPLP thallium in their Iron Rich™ samples (EMI-1 to EMI-8 and EMI-6-Dup) above the laboratory reporting limits using ICP. We detected total thallium (3.7 mg/kg) in our sample (DPE-SO-01). We detected SPLP thallium in the sample at a level lower than DuPont's corresponding detection limits, and TCLP thallium at a level similar to DuPont's TCLP detection limit.

We believe that the validity of our total thallium value (3.7 kg/mg) is supported by even higher of thallium detected in a second run of our sample (DPE-SO-01) at 10 times dilution of 18.4 mg/kg, as well as by DuPont's split analysis of this sample at still higher level (23.6 mg/kg). (DuPont did not report TCLP and SPLP thallium results for the split sample.) Therefore, we conclude that our data are valid and representative of the waste in question.

4.2.2 Evaluation of DuPont's Thallium Data for Wastewater Treatment Solids and Wastewaters

DuPont collected 44 wastewater samples to characterize wastewaters (11 streams) and 53 pond sludge samples to characterize their wastewater treatment sludges (6 streams) resulting from the treatment of wastewaters. Their pond sludge samples were comparable to our sample (DPN-SO-01) of wastewater treatment sludge collected from Johnsonville's Hillside Pond. Tables 4.2-3 and 4.2-4 show the levels of thallium DuPont detected in their wastewater treatment solids and wastewaters as reported in Attachment 5.1.3-B of their November 13, 2000 comments.

Table 4.2-3: Thallium in DuPont's Wastewater Treatment Solids (ICPMS- SW 6020)

Matrix/Analysis	Total (mg/kg)	TCLP (mg/L)	SPLP (mg/L)
Edge Moor Wastewater Treatment Sludge	<0.9 - 0.22	NA	<0.0005 - <0.001
Johnsonville Hillside Pond	<0.018 - 0.43	<0.0005 - 0.0017	<0.0001 - 0.00098
Johnsonville Equalization	<0.018	NA	<0.0001 - 0.00045
Johnsonville Settling Pond	<0.18	NA	<0.0001
Delisle Equalization Basin	<0.18 - 0.84	NA	<0.0001
Delisle Disengagement Basin	<0.18 - 0.59	NA	<0.0001

Table 4.2-4: Thallium in DuPont's Wastewaters (ICPMS- SW 6020)

Matrix/Analysis	Total (mg/l)
Johnsonville Wastewaters	<0.0002 - <0.002
DeLisle Wastewaters	<0.0002 - <0.002
Edge Moor Wastewaters	<0.00002 - 0.00057

DuPont’s ICPMS analytical results for the wastewater treatments solids and wastewaters generated at all three facilities indicate that no wastewater treatment sludge samples contain leachable thallium at levels above the health-based limit HBL (0.001 mg/l) nor do any wastewater samples contain total thallium at levels above the HBL.

As described in Section 4.1, however, there were analytical problems (i.e., instrument calibration, blank contamination, large negative instrument responses, possible carry-over problems) commonly found in DuPont’s ICPMS thallium analysis. Therefore, we have no way to determine the accuracy of all DuPont’s non-detect and low thallium ICPMS results for the wastewater treatment solids and wastewaters. We believe, however, that DuPont’s ICP (SW6010) thallium data for wastewater treatment solids and wastewaters may be valid. Table 4.2-5 compares DuPont and EPA ICP thallium results for wastewater treatment solids. Table 4.2-6 provides the levels of total thallium in DuPont’s wastewaters, as measured by ICP analysis.

Table 4.2-5: Thallium in DuPont’s Wastewater Treatment Solids (ICP- SW 6010)

Matrix/Analysis	Total (mg/kg)	TCLP (mg/L)	SPLP (mg/L)
Edge Moor Wastewater Treatment Sludge	<35.5	NA	<0.053 (2 samples) 0.0019 - 0.033* (6 samples)
Johnsonville Hillside Pond	<7.1 - <14.2	<0.27 (2 samples) 0.01 - 0.16* (6 samples)	0.0015 - 0.041*
Johnsonville Equalization Pond	<7.1	NA	<0.053
Johnsonville Settling Pond, ICP	<7.1	NA	<0.053
Delisle Equalization Basin, ICP	<7.1	NA	<0.053
Delisle Disengagement Basin, ICP	<7.1	NA	<0.053
EPA sample (DPN-SO-01), ICP	7.2	<0.1	<0.0022/<0.01 (split)

Table 4.2-6: Thallium in DuPont’s Wastewaters (ICP- SW 6010)

Matrix/Analysis	Total (mg/L)
Johnsonville Wastewaters	<0.0049
DeLisle Wastewaters	<0.01 (7 samples) <0.1 (1 sample) 0.0047 - 0.0275J (9 samples)
Edge Moor Wastewaters	<0.0049

* The result is greater than instrument detection limit (IDL) but less than the reported method detection limit (MDL).
J This result is greater than the IDL and/or MDL but less than the laboratory reporting limit (RL).
NA Not analyzed.

Table 4.2-5 shows that no total thallium was detected in DuPont's wastewater treatment solids above the laboratory SW6010 MDLs. It also indicates that TCLP thallium was detected in DuPont's Johnsonville Hillside Pond sludge and SPLP thallium was detected in DuPont's Edge Moor wastewater treatment sludge and Johnsonville Hillside Pond sludge; each of these detections, however, were below the MDL of 0.053 mg/L. We detected total thallium in our sample (DPN-SO-01) at a level close to DuPont's corresponding detection limit; we did not detect TCLP thallium at a level lower than DuPont's TCLP detection limit.

Table 4.2-6 shows that low levels of total thallium were detected in DuPont's DeLisle wastewaters. These levels are unlikely to contribute significantly to the thallium concentrations of sludge.

In summary, we have significant concerns about DuPont's ICPMS thallium analysis. We suspect the validity of DuPont's ICPMS results for thallium. DuPont's ICP total, TCLP and SPLP thallium results conform to our ICP total, TCLP and SPLP thallium results. We do not agree with DuPont's assertion that thallium is not present in the wastewater treatment solids. The detected thallium leachate values, however, are below the MDL and therefore, would not be used to support a regulatory determination.

Appendix A

DuPont's Solids and Wastewaters Sampling and Analysis Strategies

Chloride-Ilmenite Facilities

ATTACHMENT 5.1.3-C

Solids Sampling Plan

Chloride-Ilmenite facilities

3. Sample Identification

Each sample will be identified with the following information on the label of the sample bottle and the corresponding information on the chain of custody form:

- Name of site
- Unique sample identifier
- Name of sampler
- Date and time of sampling

Additional information will be recorded in a field sampling logbook as described in Section III.D. of this plan.

4. Sample Collection

Each sample will be collected as a grab sample directly into the sample container.

A non-metallic plastic scoop will be used as necessary to collect samples of process solids. A stainless steel spatula will be used as necessary to collect the archive sample of process solids.

5. Sample Preservation

Samples will be packed with ice or artificial ice in sample coolers to ensure that the samples are maintained at 4 ± 2 C until arrival at the lab.

Samples being archived on-site should be stored on-site at 4 ± 2 C.

C. ANALYSIS

1. Analytical Parameters

Process solids samples should be analyzed for the following parameters:

- Target metal analytes in the sample (total composition),
- Target metal analytes in TCLP extract (for Iron Rich Filter Press Cake only),
- Target metal analytes in SPLP (synthetic precipitation leaching procedure) extract,
- Total suspended solids or % solids.

Target metal analytes are listed in section C.3 below.

2. Preparation Methods

For total composition analysis, digestion prior to analysis will be via Method 3050 or 3051.

3. Target Metal Analytes

For process solids samples, target metal analytes and associated EPA Health-Based Limits are presented in Table 1. Planned quantitation limits and planned analytical methods are included in Table 1 where available.

In this test program, the quantitation limit for each metal in the SPLP extracts are requested to be than the EPA health-based limit in Table 1 for the corresponding metal. For example, the requested quantitation limit for thallium in the SPLP extract is less than 1.3 ug/L. Additionally, the quantitation limit for each metal in the TCLP extract must be the lowest achievable by the best equipment available to the laboratory for analysis of TCLP extracts.

4. Analytical Methods

SPLP will be performed via SW-846 Method 1312.

TCLP will be performed via SW-846 Method 1311

For total composition analysis, ICP-AES via SW-846 Method 6010B or Method 6010B-trace (as noted in Table 1) is requested.

For analysis of TCLP and SPLP extracts, ICP-AES analysis via SW-846 Method 6010B is requested for several metal analytes.

However, for certain analytes (e.g., Thallium), analysis of SPLP extract via SW-846 Method 6020 (ICP-MS) or via an SW-846 7000 series atomic absorption (AA) method is required to ensure that the quantitation limit is less than the health-based limit in Table 1. The SW-846 AA method for Thallium is Method 7841. Also see section C.3 above.

The field duplicate samples will also be analyzed for all analytical parameters.

Analysis will be performed by the laboratory via SW-846 procedures. In accordance with Method 6010B and Method 6020, matrix spike and matrix spike duplicate laboratory samples, method blanks, and as other laboratory QC samples required by these methods will be analyzed.

5. Laboratory

Process solids samples will be sent to the following laboratory:

Severn Trent Laboratory-Sacramento
880 Riverside Parkway
West Sacramento, CA 95605
(916) 374-4408

The laboratory project coordinator for this project is as follows:

Robert Weidenfeld
(916) 374-4333

II. POND SLUDGE

A. STREAMS

The following streams are being sampled and analyzed:

DeLisle

- Equalization Basin Sludge (RIN 108)
- Disengagement Basin Sludge (RIN 108)

Johnsonville

- Hillside Pond Sludge (RIN 108)
- Johnsonville Equalization Pond Sludge (RIN 107)
- Johnsonville Settling Pond Sludge (RIN 107)

Based on ore assay, significant temporal variability in these streams is not expected for the metals of interest as they are not the constituents that vary appreciably ore to ore.

B. SAMPLING

1. Containers

Samples for metals analysis will be collected in laboratory-supplied precleaned wide-mouth 1 liter plastic sample bottles. Accompanying archive samples will be collected in other laboratory-supplied precleaned wide-mouth 500-ml ICHEM glass sample bottles. Equipment blank samples will be collected in laboratory-supplied precleaned sample bottles and will be preserved with nitric acid prior to analysis.

2. Number of Samples

For pond sludge samples (except the Johnsonville Hillside Pond), to account for any spatial variability, grab samples are being collected by stratified random sampling across a grid over each pond. Nine grab samples from each pond will be collected.

The number of pond samples was determined using the methodology contained in SW-846 Chapter 9. For the Johnsonville Hillside Pond, due to limited free liquid in the unit and inability to access regions of the unit by other methods, the samples will be collected from the edge of the unit at approximately equally-spaced points around the perimeter and extending as far as the sampling equipment is capable out into the unit.

Each grab sample will be accompanied by collection of an archive sample (for a total of 9 archive samples per pond). One field duplicate sample will be collected for each pond.

Additionally, following decontamination of pond sludge sampling equipment, a sample of DI water rinsate of sampling equipment will be collected at least once for each pond as an equipment blank.

The selection of pond sample locations was done using random-number generated points applied to a grid. The grid was laid out as 10 foot by 10 foot squares in the case of all ponds except the Johnsonville Settling Pond. The irregular shape of the Johnsonville

Settling Pond does not lend itself to a grid design; hence, random number generation was used to determine length and width coordinates for sampling as described in Example 2 of Chapter 9 in SW-846 (page 41). To ensure stratified random sampling for all the ponds except the Johnsonville Hillside Pond, 1/3 of the pond samples will be collected from the area influenced by the feed plume to the pond, and 2/3 of the pond samples will be collected from the remaining area of the pond. Since the Johnsonville Hillside Pond does not have a feed plume, the Hillside Pond has been divided into 3 thirds for sampling.

Random number selection for all units was done using the random number tables in CRC Standard Mathematical Tables, 20th Edition and truncating the number to the last three digits for grid selection. Non-repeating numbers were selected from these random number tables to designate the grid squares to be sampled. For ponds undergoing stratified random sampling, random numbers were selected in two rounds with one round for the area influenced by the feed plume to the pond and the other round for the remaining area of the pond.

Planned sampling locations for DeLisle Equalization Basin are presented in Figure 1.

Planned sampling locations for DeLisle Disengagement Basin are presented in Figure 2.

Planned sampling locations for Johnsonville Hillside Pond are presented in Figure 3.

Planned sampling locations for Johnsonville Equalization Pond are presented in Figure 4.

Planned sampling locations for Johnsonville Settling Pond are presented in Figure 5.

3. Sample Identification

Each sample will be identified with the following information on the label of the sample bottle and the corresponding information on the chain of custody form:

- Name of site
- Unique sample identifier
- Name of sampler
- Date and time of sampling

Additional information should be recorded in a field sampling logbook as described in Section III.D. of this plan.

4. Sample Collection

Non-metallic collection equipment will be used for this sampling. Except for the Hillside Pond, pond sludge sampling will be accomplished using a dipper apparatus such as the one pictured in Figure 9-11 of SW-846 Chapter 9.

For the Hillside Pond, a non-metallic trier (sample corer) is planned for use in sample collection.

5. Sample Preservation

Samples will be packed with ice or artificial ice in sample coolers to ensure that the samples are maintained at 4 ± 2 C until arrival at the lab.

Samples being archived on-site should be stored on-site at 4 ± 2 C.

C. ANALYSIS

1. Analytical Parameters

Pond sludge samples should be analyzed for the following parameters:

- Target metal analytes in the sample (total composition),
- Target metal analytes in SPLP (synthetic precipitation leaching procedure) extract, and
- Total suspended solids or % solids.

Hillside Pond sludge samples should also be analyzed for the following additional parameter:

- Target metal analytes in TCLP extract,

Target metal analytes are listed in section C.3 below

2. Preparation Methods

For total composition analysis, digestion prior to analysis will be via Method 3050 or 3051.

3. Target Metal Analytes

For pond sludge samples, target metal analytes and associated EPA Health-Based Limits are presented in Table 1. Planned quantitation limits and planned analytical methods are included in Table 1 where available.

In this test program, the quantitation limit for each metal in the SPLP extracts are requested to be than the EPA health-based limit in Table 1 for the corresponding metal. For example, the requested quantitation limit for thallium in the SPLP extract is less than 1.3 ug/L.

4. Analytical Methods

SPLP will be performed via SW-846 Method 1312.

TCLP will be performed via SW-846 Method 1311.

For total composition analysis, ICP-AES via SW-846 Method 6010B or Method 6010B-trace (as noted in Table 1) is requested.

For analysis of SPLP extracts, ICP-AES analysis via SW-846 Method 6010B is requested for several metal analytes.

However, for certain analytes (e.g., Thallium), analysis of SPLP extract via SW-846 Method 6020 (ICP-MS) or via an SW-846 7000 series atomic absorption (AA) method is <u>required</u> to ensure that the quantitation limit is less than the health-based limit in Table 1. The SW-846 AA method for Thallium is Method 7841. Also see section C.3 above.

The field duplicate samples will also be analyzed for all analytical parameters.

Analysis will be performed by the laboratory via SW-846 procedures. In accordance with Method 6010B and Method 6020, matrix spike and matrix spike duplicate samples, method blanks, and other laboratory QC samples required by these methods will be analyzed.

5. Laboratory

Pond sludge samples will be sent to the following laboratory:

Severn Trent Laboratory-Sacramento
880 Riverside Parkway
West Sacramento, CA 95605
(916) 374-4408

The laboratory project coordinator for this project is as follows:

Robert Weidenfeld
phone (916) 374-4333
fax (916) 372-7768

III. QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) is the process for ensuring that all data and the decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

A. PROJECT ORGANIZATION

The overall Project Manager for this sampling and analysis program is:

Brian R. Coleman
DuPont White Pigments
Chestnut Run Plaza 709
Centre Blvd.
Wilmington, DE 19805
phone (302) 999-2122
fax (302) 999-4396

The Quality Assurance Officer for this sampling and analysis program is:

Dave Timmons
DuPont Engineering

Brandywine 9304
1007 Market Street
Wilmington, DE 19898
phone (302) 774-8056
fax (302) 774-8110

The Field Sampling Coordinators for the sites involved in this program are listed below.

DeLisle Plant:

Linda Bernard
DuPont DeLisle Plant
7685 Kiln-DeLisle Road
Pass Christian, MS 39571
phone (228) 255-2479

Edge Moor Plant:

Leonard Fasullo
DuPont Edge Moor Plant
104 Hay Road
Edge Moor, DE 19809
phone (302) 761-2298

Johnsonville Plant:

Scott Goodman
DuPont Johnsonville Plant
1 DuPont Road
New Johnsonville, TN 37134
phone (931) 535-1467

B. Quality Control Measures

Analysis of field duplicate samples, field equipment blanks (where appropriate), laboratory method blanks, laboratory matrix spike samples and spike duplicates, routine laboratory control samples (LCS), and routine laboratory control sample duplicates (LCSD) provides information necessary to verify the quality of the data collected in this program. Collection of field duplicates and analysis of field duplicates and laboratory matrix spikes and spike duplicates are described in Sections I and II.

To minimize potential for contamination and to ensure use of the same custody procedures across all sites involved in this program, the laboratory will send the following to the sites being sampled:

- sample bottles,

- coolers for sample bottles,
- chain of custody forms,
- custody seals, and
- DI water for use in collecting equipment blank samples.

C. Sample Custody

An essential part of a sampling and analysis project is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples will be traced from the time of collection through analysis and final disposition through use of chain of custody forms.

Required components of the chain of custody for this program are:

- sample seals,
- chain-of-custody record, and
- sample analysis request.

The form for chain of custody and sample analysis request to be employed for this sampling is being provided by the analytical laboratory.

1. Sample Seals

Sample seals will be used on each sample shuttle (cooler) from the laboratory to detect unauthorized tampering of samples following sample collection up to the time of analysis. Sample seals will be supplied by the laboratory with the sample shuttles.

The seals will include the following information:

- Sample numbers enclosed in the shuttle. (These numbers must be identical with the numbers on the sample labels.)
- Name of collector.
- Date and time of sampling.
- Place of collection.

The seal must be attached in such a way that it is necessary to break it in order to open the sample shuttle. Seals are to be affixed to shuttles before the samples leave the custody of sampling personnel.

2. Chain of Custody Record

To establish the documentation necessary to trace sample possession from the time of collection, a chain of custody record will be filled out and will accompany each shipment of samples. This record will contain the following information:

- Sample number.
- Sample description.

- Signature of collector.
- Date and time of collection.
- Place and address of collection.
- Signature of persons involved in the chain of possession.
- Inclusive dates of possession.

The sample analysis request portion of the chain of custody form will note the analyses to be performed.

D. FIELD SAMPLING LOGBOOK

All information pertinent to field sampling are to be recorded in a logbook. This should be a bound volume with consecutively numbered pages (a laboratory or other suitable notebook).

Entries in the logbook are to include the following:

- Location of sampling point.
- Name of field contact.
- Location of sample point.
- Brief description of the source of the sample.
- Type of material (e.g., sludge, wastewater).
- Numbers and volumes of samples taken.
- Description of sampling point and sampling methodology.
- Date and time of collection.
- Collector's sample identification number(s).
- Sample distribution (e.g., name of laboratory) and how transported.
- References, such as maps or photographs of the sampling site.
- Field observations.
- Any field measurements made.
- Signatures of personnel responsible for observations.

The function of the logbook is to record sufficient information so that the sampling event can be reconstructed without reliance on the sample collector's memory. The logbook is to be forwarded to the Quality Control Officer when completed for all sampling.

Table 1. Target Metal Analytes for Process Solids and Pond Sludge

Metal*	EPA Health-Based Limit (HBL) **	Total Composition Quantitation Limit		SPLP Quantitation Limit***	
	(mg/L)	(mg/kg)	Method	(mg/L)	Method
Aluminum	16	20	6010B	less than HBL	6010B
Antimony	0.0063	1	6010B Trace	less than HBL	6020
Arsenic	0.00074	1	6010B Trace	lowest achievable	6020
Barium	1.1	20	6010B	less than HBL	6010B
Beryllium	0.031	0.5	6010B Trace	less than HBL	6010B
Boron	1.4	20	6010B	less than HBL	6010B
Cadmium	0.0078	0.5	6010B Trace	less than HBL	6020
Chromium	23	1	6010B Trace	less than HBL	6010B
Cobalt	0.94	1	6010B	less than HBL	6010B
Copper	1.3	5	6010B	less than HBL	6010B
Iron	5	2.5	6010B	less than HBL	6010B
Lead	0.015	0.5	6010B Trace	less than HBL	6020
Manganese	0.73	1	6010B Trace	less than HBL	6010B + 6020
Molybdenum	0.078	4	6010B	less than HBL	6010B
Nickel	0.31	4	6010B	less than HBL	6010B
Selenium	0.078	1	6010B Trace	less than HBL	6020
Silver	0.078	0.5	6010B Trace	less than HBL	6010B
Thallium	0.0013	1	6010B Trace	less than HBL	6020
Tin	9.4	10	6010B	less than HBL	6010B
Vanadium	0.14	5	6010B Trace	less than HBL	6010B
Zinc	4.7	2	6010B	less than HBL	6010B

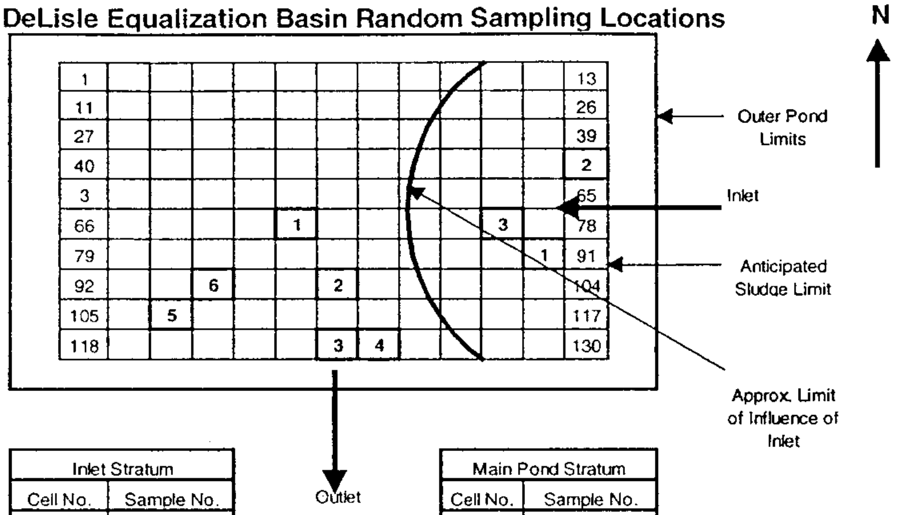
* Target metal analytes are based on the metal constituents with health-based limits in Table 3.27 of the Titanium Dioxide Listing Background Document (EPA, 2000)

** EPA Health-Based Limits from Table 3.27 of the Titanium Dioxide Listing Background Document (EPA, 2000)

*** If an analyte cannot be quantitated to a level below the HBL in the SPLP extract, then it should be quanitated to the lowest achievable level by the best equipment available to the laboratory for analysis of this sample matrix.

Figure 1

DeLisle Equalization Basin Random Sampling Locations



Inlet Stratum	
Cell No.	Sample No.
90	DL-EQ-I-1
52	DL-EQ-I-2
76	DL-EQ-I-3

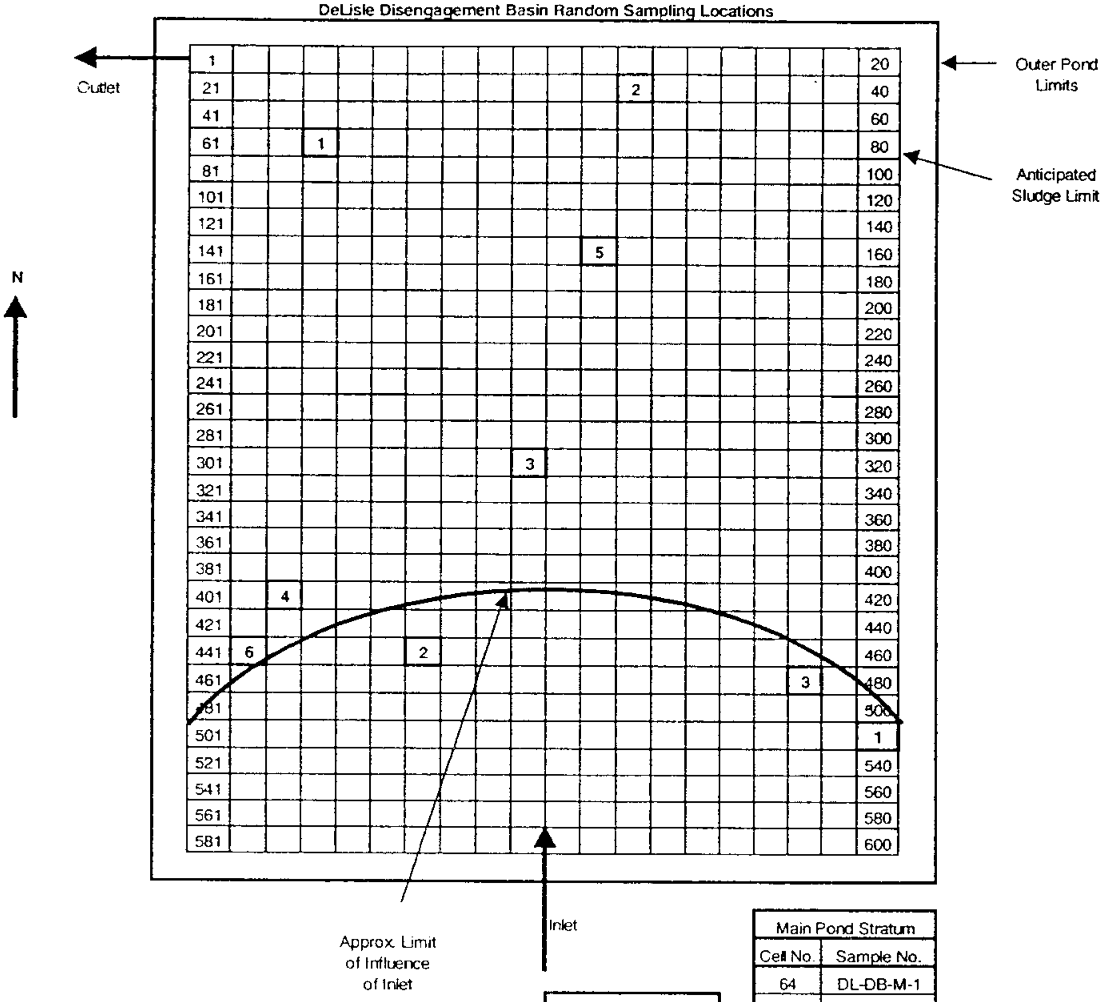
Main Pond Stratum	
Cell No.	Sample No.
71	DL-EQ-M-1
98	DL-EQ-M-2
124	DL-EQ-M-3
125	DL-EQ-M-4
107	DL-EQ-M-5
95	DL-EQ-M-6

CRC Standard Mathematical Tables
20th Edition. Page 601
Random Number Table
start - col. 9, row 92
stop - col. 11, row 87

Pond is divided into 10'x10' cells numbered from 1 to 130 starting at northwest corner.
The Main Pond Area Stratum Locations were selected first.
Any cell that falls within the limit of influence of the inlet is skipped.
The last three digits of the random number are used.
The Inlet sampling locations were determined by selecting three random numbers that correspond to grid numbers within the area of influence.
All measurements are +/- 5 feet or +/- 5°.

Figure 2

DeLisle Disengagement Basin Random Sampling Locations



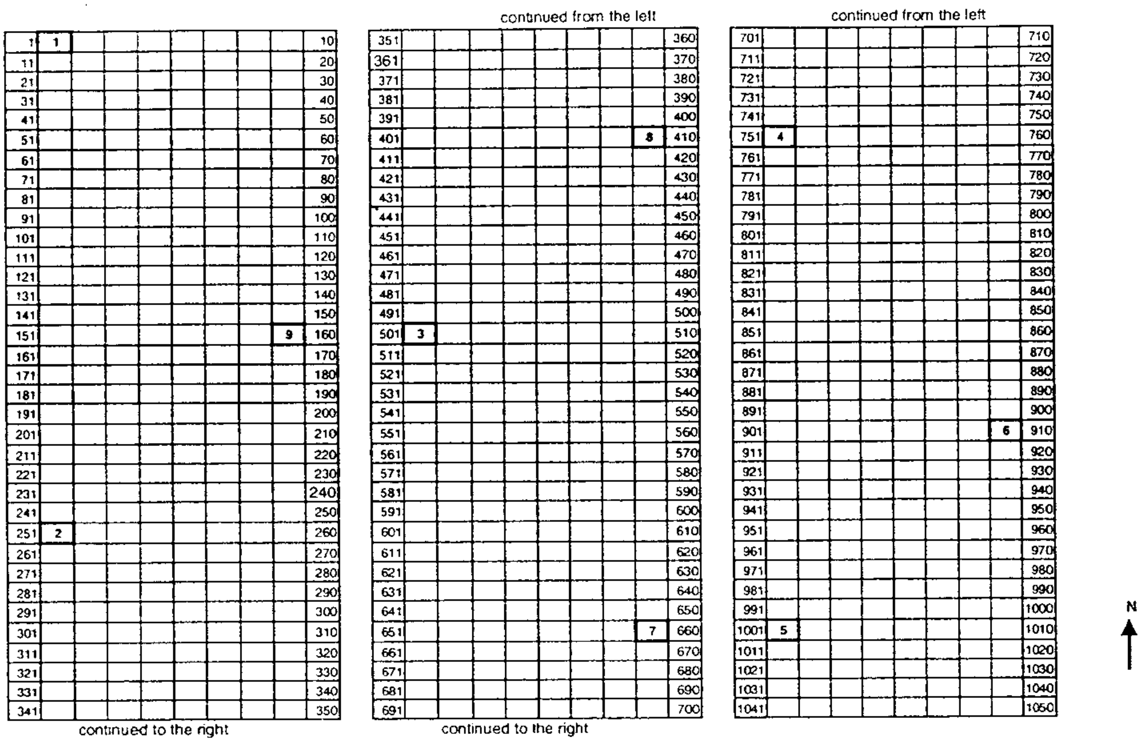
Inlet Stratum	
Cell No.	Sample No.
520	DL-DB-I-1
447	DL-DB-I-2
478	DL-DB-I-3

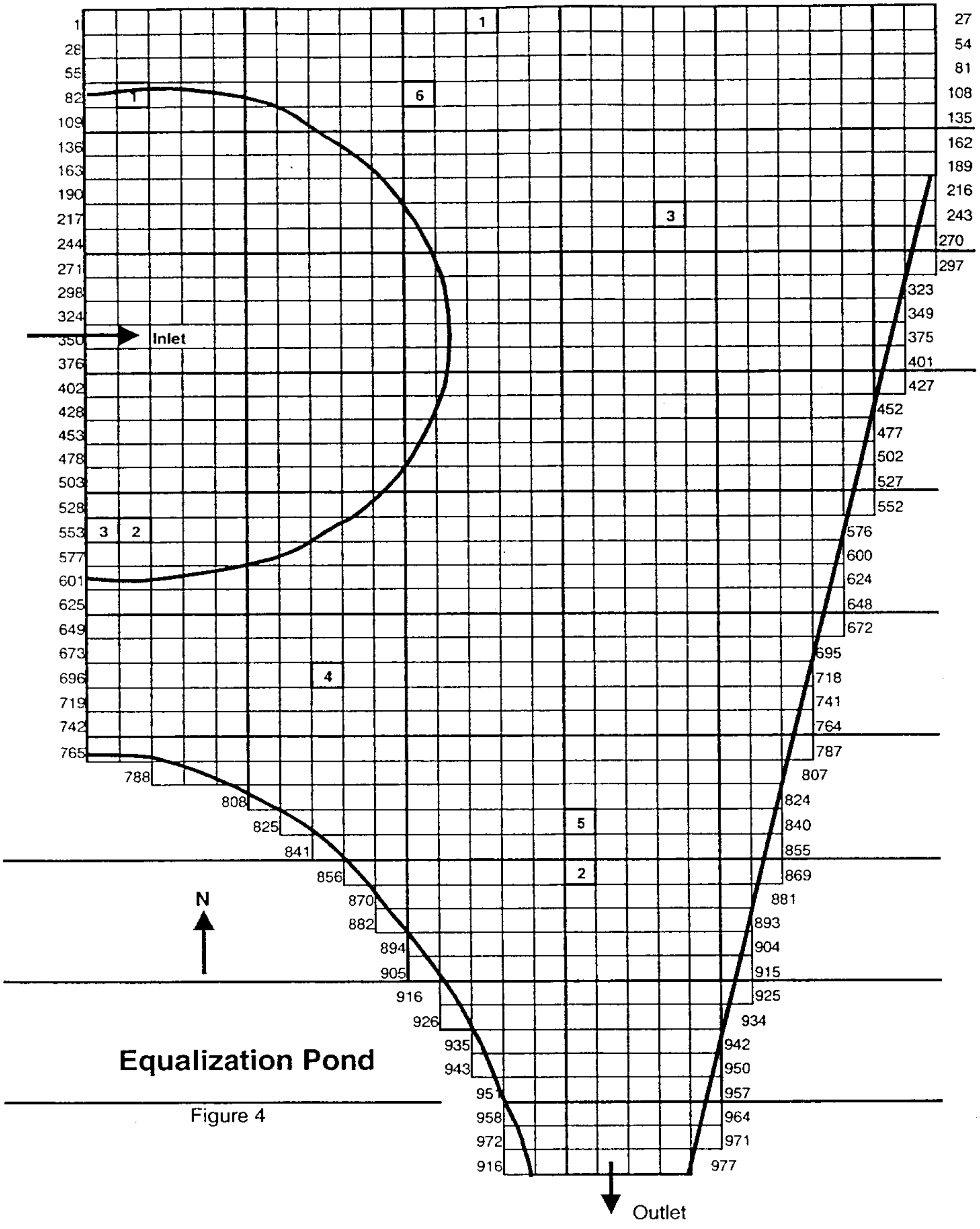
Main Pond Stratum	
Cell No.	Sample No.
64	DL-DB-M-1
33	DL-DB-M-2
310	DL-DB-M-3
403	DL-DB-M-4
152	DL-DB-M-5
442	DL-DB-M-6

Pond is divided into 10'x10' cells numbered from 1 to 600 starting at northwest corner.

Figure 3

JVHillside Pond Sample Locations



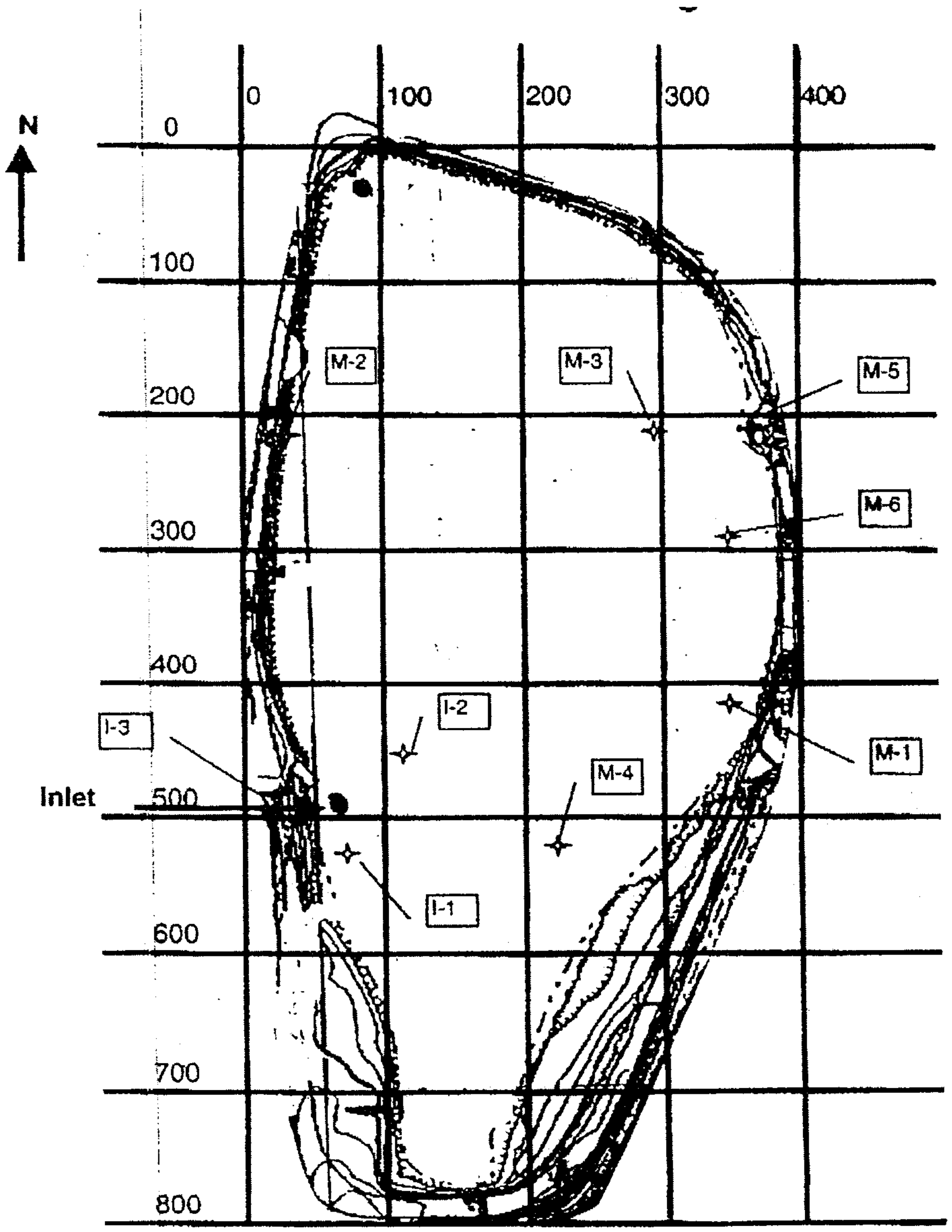


Equalization Pond

Figure 4

Figure 5

Johnsonville SettlingPond



ATTACHMENT 5.1.3-D

Wastewater Sampling Plan

Chloride-Ilmenite facilities

EPA TIO2 LISTING PROPOSAL
DUPONT METALS SAMPLING AND ANALYSIS PROGRAM
WASTEWATER STREAMS

EPA has proposed to list wastewater treatment solids from the TiO2 manufacturing process as hazardous waste. Suspended solids in wastewater influent streams generally affect the nature of the sludge produced during wastewater treatment. EPA has delineated several wastewater streams as containing non-Bevill exempt solids. Data is needed to indicate the potential impact of metals and solids in these wastewater streams on the metals levels in wastewater treatment solids generated from treatment of these wastewater streams. Wastewaters are being directly analyzed for metals down to the lowest achievable quantitation limits in order to provide data indicative of metals levels in the solids suspended in these wastewaters without first filtering very large quantities of wastewater.

Section I describes sampling and analysis for wastewater streams. Section II describes quality assurance and quality control plans for this program.

I. SAMPLING & ANALYSIS

A. STREAMS

The streams below (to the extent that they are available during this sampling and analysis program) are being sampled and analyzed. Since wastewater from batch caustic scrubbing of chlorine gas is not expected to contain metals of interest and since such wastewater is expected to require significant dilution prior to analysis (resulting in elevated detection limits), wastewaters from such scrubbers are not included in this program.

The wastewater streams, their Residual Identification Numbers (RINs), expected estimated TDS (total dissolved solids), and expected estimated TSS (total suspended solids) are as follows:

Edge Moor

Wastewater Stream	**RIN**	**TDS (est.)**	**TSS (est.)**
Oxidation vent scrubber wastewater	RIN 9	2%	up to 1%
Oxidation wastewater (intermittent)	RIN 11	low	~1%
Finishing wastewater (to wastewater treatment)	RIN 10	low	200 mg/L
Dryer (Scrub Solids Kiln) scrubber wastewater	RIN 13	low	1-2%

Johnsonville

Wastewater Stream	**RIN**	**TDS (est.)**	**TSS (est.)**
Finishing wastewater	RIN 6	1-2%	1%
Oxidation scrubber wastewater	RIN 104	3%	0.1%
Wet treatment scrubber wastewater	RIN 111	0.1%	nil
Railcar trailer product wash out	RIN 112	low	20%

Wastewater Stream	RIN	TDS	TSS (est.)
Oxidation scrubber wastewater	RIN 6	2%	600 mg/L
Oxidation wastewater (intermittent)	RIN 103	low	10 mg/L
Finishing wastewater	RIN 8	low	700 mg/L
HCl storage scrubber water	RIN 9	low	10 mg/L

B. SAMPLING

1. Containers

Samples for metals analysis will be collected in laboratory-supplied precleaned 500 mL plastic sample bottles preconditioned with a small amount of nitric acid added prior to sending to the site. Samples for TSS and TDS analysis will be collected in laboratory-supplied precleaned 250 mL plastic sample bottles that do not contain nitric acid.

2. Number of Samples

One grab sample per day will be collected for each stream over 4 days for a total of 4 samples per wastewater stream. One field duplicate sample will be collected for each wastewater stream over the course of this sampling program as the 5th sample per wastewater stream.

At the same time that each metals grab sample is collected, a second grab sample of each stream will be collected each day for TSS and TDS analysis.

To the extent that wastewater sampling equipment is used, a sample of DI water rinsate of such sampling equipment will be collected prior to collecting the initial sample and following collection of the final sample after equipment decontamination to provide two equipment blanks per such wastewater stream.

Archive samples are not planned.

3. Sample Identification

Each sample should be identified with the following information on the label of the sample bottle and the corresponding information on the chain of custody form:

- Name of site
- Unique sample identifier
- Name of sampler
- Date and time of sampling

Additional information should be recorded in a field sampling logbook as described in Section II.D. of this plan.

4. Sample Collection

Each sample will be collected as a grab sample directly into the sample container.

If sampling equipment is used, equipment blanks will be collected as described in section B.2 above.

5. Sample Preservation

Samples will be packed with ice or artificial ice in sample coolers to ensure that the samples are maintained at 4 ± 2 C until arrival at the lab. Additionally, as noted in section B.1, bottles for collecting wastewater samples for metals analysis have been preconditioned with nitric acid.

Samples being archived on-site should be stored in an appropriate laboratory refrigerator on-site at 4 ± 2 C.

C. ANALYSIS

A key goal of the wastewater metals analyses and the corresponding wastewater TSS analyses is to provide data to estimate the concentration of each metal in the total suspended solids (TSS) in the corresponding wastewater stream and in turn to estimate the SPLP concentration for each metal. Therefore:

- Given the low TSS levels expected in most of the wastewater streams, it is necessary to pursue the lowest achievable quantitation limits for these samples, especially for those metals for which EPA has proposed low health-based limits for SPLP-extractable metals in the solids.

- If the TSS level in a sample is high enough to provide sufficient solid sample for metals analysis, the resulting solid sample should be analyzed for total composition in lieu of the wastewater sample.

- Reporting down to the method detection limit (MDL) is requested.

1. Analytical Parameters

Wastewater samples will be analyzed for the following parameters:

- Target metal analytes in the sample (total composition),
- Total suspended solids (TSS), and
- Total dissolved solids (TDS).

Target metal analytes are discussed in section C.3 below.

2. Preparation Methods

Prior to metals analysis, the pH of the sample will be determined in the laboratory as appropriate to provide information to the analyst to minimize the need for pre-digestion dilution in order to assist in attaining the lowest achievable quantitation limits.

Where the TSS level in a sample is high enough to provide sufficient solid sample for metals analysis, the resulting solid sample should be analyzed for total composition in lieu of the wastewater sample. For total compositional analysis of such a solids sample, digestion prior to analysis will be via Method 3050 or 3051. Method 3052 digestion is not required.

For total composition analyses of wastewater samples, digestion prior to analysis will be via Method 3005A or 3010A.

Sample dilutions will be minimized to the extent practicable to ensure the lowest achievable quantitation limits.

3. Target Metal Analytes

For wastewater samples, target metal analytes, planned analytical methods, and planned quantitation limits are presented in Table 1.

Note that sodium may be present in one or more wastewater streams as a major component of TDS.

4. Analytical Methods

Total composition analysis of undiluted digestates (or minimally diluted where dilution is essential) is requested for the metal analytes in Table 1 via the methods designated in Table 1.

The field duplicate samples will also be analyzed for all analytical parameters.

ICP-AES analysis will be performed via SW-846 Method 6010B.

ICP-MS analysis will be performed via SW-846 Method 6020.

In accordance with Method 6010B and Method 6020, matrix spike and matrix spike duplicate samples, method blanks, and other laboratory QC samples required by these methods will be analyzed.

5. Laboratory

Process solids samples will be sent to the following laboratory:

STL Denver
4955 Yarrow St.
Arvada, CO 800002
(303) 736-0100

The laboratory project coordinator for this project is as follows:

Gail DeRuzzo
(303) 736-0100

II. QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) is the process for ensuring that all data and the decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

A. PROJECT ORGANIZATION

The overall Project Manager for this sampling and analysis program is:

Brian R. Coleman
DuPont White Pigments
Chestnut Run Plaza 709
Centre Blvd.
Wilmington, DE 19805
phone (302) 999-2122
fax (302) 999-4396

The Quality Assurance Officer for this sampling and analysis program is:

Dave Timmons
DuPont Engineering
Brandywine 9304
1007 Market Street
Wilmington, DE 19898
phone (302) 774-8056
fax (302) 774-8110

The Field Sampling Coordinators for the sites involved in this program are listed below.

DeLisle Plant:

Linda Bernard
DuPont DeLisle Plant
7685 Kiln-DeLisle Road
Pass Christian, MS 39571
phone (228) 255-2479

Edge Moor Plant:

Leonard Fasullo
DuPont Edge Moor Plant
104 Hay Road
Edge Moor, DE 19809
phone (302) 761-2298

Johnsonville Plant:

Scott Goodman
DuPont Johnsonville Plant
1 DuPont Road
New Johnsonville, TN 37134
phone (931) 535-1467

B. Quality Control Measures

Analysis of field duplicate samples, field equipment blanks (where appropriate), laboratory method blanks, laboratory matrix spike samples and spike duplicates, routine laboratory control samples (LCS), and routine laboratory control sample duplicates (LCSD) provides information necessary to verify the quality of the data collected in this program. Collection of field duplicates and analysis of field duplicates and laboratory matrix spikes and spike duplicates are described in Sections I.

To minimize potential for contamination and to ensure use of the same custody procedures across all sites involved in this program, the laboratory will send the following to the sites being sampled:

- sample bottles,
- coolers for sample bottles,
- chain of custody forms,
- custody seals, and
- DI water for use in collecting equipment blank samples.

C. Sample Custody

An essential part of a sampling and analysis project is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples will be traced from the time of collection through analysis and final disposition through use of chain of custody forms.

Required components of the chain of custody for this program are:

- sample seals,
- chain-of-custody record, and
- sample analysis request.

The form for chain of custody and sample analysis request to be employed for this sampling is being provided by the analytical laboratory.

1. Sample Seals

Sample seals will be used on each sample shuttle (cooler) from the laboratory to detect unauthorized tampering of samples following sample collection up to the time of analysis. Sample seals will be supplied by the laboratory with the sample shuttles.

The seals will include the following information:

- Sample numbers enclosed in the shuttle. (These numbers must be identical with the numbers on the sample labels.)
- Name of collector.
- Date and time of sampling.
- Place of collection.

The seal must be attached in such a way that it is necessary to break it in order to open the sample shuttle. Seals are to be affixed to shuttles before the samples leave the custody of sampling personnel.

2. Chain of Custody Record

To establish the documentation necessary to trace sample possession from the time of collection, a chain of custody record will be filled out and will accompany each shipment of samples. This record will contain the following information:

- Sample number.
- Sample description.
- Signature of collector.
- Date and time of collection.
- Place and address of collection.
- Signature of persons involved in the chain of possession.
- Inclusive dates of possession.

The sample analysis request portion of the chain of custody form will note the analyses to be performed.

D. FIELD SAMPLING LOGBOOK

All information pertinent to field sampling are to be recorded in a logbook. This should be a bound volume with consecutively numbered pages (a laboratory or other suitable notebook).

Entries in the logbook are to include the following:

- Location of sampling point.
- Name of field contact.
- Location of sample point.
- Brief description of the source of the sample.

- Type of material (e.g., sludge, wastewater).
- Numbers and volumes of samples taken.
- Description of sampling point and sampling methodology.
- Date and time of collection.
- Collector's sample identification number(s).
- Sample distribution (e.g., name of laboratory) and how transported.
- References, such as maps or photographs of the sampling site.
- Field observations.
- Any field measurements made.
- Signatures of personnel responsible for observations.

The function of the logbook is to record sufficient information so that the sampling event can be reconstructed without reliance on the sample collector's memory. The logbook is to be forwarded to the Quality Control Officer when completed for all sampling.

Table 1. Target Metal Analytes for Wastewater Streams

Metal*	Total Composition Quantitation Limit**	
	(ug/L)	Method
Aluminum		6010B
Antimony	2.0	6020
Arsenic	5.0	6020
Barium		6010B
Beryllium	1.0	6020
Boron		6010B
Cadmium	1.0	6020
Chromium	2.0	6010B
Cobalt		6010B
Copper		6010B
Iron	100	6010B
Lead	1.0	6020
Manganese	1.0	6020
Molybdenum		6010B
Nickel	40	6010B
Selenium	5.0	6020
Silver	5.0	6020
Thallium	1.0	6020
Tin		6010B
Titanium	10	6010B
Vanadium	5.0	6020
Zinc		6010B

* Target metal analytes are the metal constituents with health-based limits in Table 3.27 of the Titanium Dioxide Listing Background Document (EPA, 2000) plus titanium.

** Numerical quantitation limits for some target metal analytes were not available from the laboratory when this document was prepared.

Appendix B

Correspondence

Shen-yi Yang
02/09/2001 01:39 PM

To: gregg.w.martin@usa.dopont.com
robert.j.giraud@usa.dopont.com

cc: Lillian Bagus/DC/USEPA@EPA
Gwen DiPietro/DC/USEPA/US@EPA
Sue Burnell/DC/USEPA/US@EPA

Subject: Request for Additional Information on Analytical Package

Dear Mr. Martin:

The Waste Identification Branch has been reviewing the quality assurance summary report and data for the process waste and pond sludge samples collected from three DuPont facilities for the titanium dioxide listing determination. During our preliminary review, we found information and data gaps in the report. To facilitate our further review, we need you to provide us by next Friday (February 19, 2001) with the following:

A. General Information

1. The CLP data package Severn Trent delivered to Environmental Standards.
2. Severn Trent's lab method detection limits (MDLs) studies for both the ICP (SW 846 6010) and ICP/MS (SW 846 6020 analyses.
   Please explain how these studies were used to support the laboratory's reporting limits. In Volume 7, there is a handwritten un-paginated sheet after page 160, titled "Analysis MDLs, converted to instrument levels" that confuses processes used for the detection limit determinations. That page provides a list of the current MDLs, but it is nor clear how they relate to the instrument detection limits (IDLs) and the laboratory reporting limits (RLs).

3. Please identify the digestion methods used for both solids and aqueous samples.
4. Please specify the components and their concentration levels in lab standards (i.e., ICV, CCV, ICSA, ICSAB).
5. Please describe how Severn Trent prepared standards to calibrate both ICP and ICP/MS, and their calibration curves for all metals, especially for thallium.

B. Information Needed for Volumes 3, 4, and 7:

New Johnsonville Settling Pond (Volume 3):

1. Please provide all SPLP ICP/MS lab outputs.

New Johnsonville Hillside Pond (Volume 4):

1. Please provide all TCLP ICP/MS lab outputs.
2. Please provide all SPLP ICP and ICP/MS lab outputs.
3. Please provide ICP and ICP/MS lab outputs for the equipment blank.
4. Please provide ICP and ICP/MS raw data for the LCS, MS, and MSD analyses.

EdgeMoor (Volume 7):

1. Please clarify the dilution factors for samples analyzed for total concentrations of metals using 6020 and verify that the MDLs, Rls, and sample results are corrected appropriately to reflect sample dilutions.

   There are three places in this report noting dilutions of samples and TCLP/SPLP leachates: (1) data validator's narrative (Section 1, page 3, bullet 6); (2) lab case narrative (Section 4, page 3); and (3) lab's correspondence to data validator dated November 10, 2000 (Section 5). These three sources do not consistency describe the same dilutions for various runs. After examining the lab's sample preparation worksheets and the analytical run logs, we are still not clear how the samples were diluted for the analysis.

2. Please provide lab outputs for total and ICP-SPLP analyses (Section 3, pages 276-277 and 279-284, and pages 237-244).
3. Please provide lab outputs for ICP/MS-SPLP analysis (Section 3, pages 434-442).
4. Please provide lab outputs for ICP/MS-MN analysis (Section 3, pages 466-485).
5. Please provide lab outputs for ICP/MS for total analysis (Section 3, pages 523-526, 535-544, 552-556, 558-560, 562, 564, 583-596).
6. Please provide ICP and ICP/MS raw data for the LCS, MS, and MSD analyses.

If you have questions concerning this request, please contact me at (703) 308-0437.

Shen-yi Yang, Chemist
EPA Office of Solid Waste
Hazardous Waste Identification Division
Waste Identification Branch

cc: Robert J. Girand, Dupont

Appendix C

Review Products

Volume 2

Equalization Pond Sludge-Johnsonville Plant, New Johnsonville, TN

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

Review Summary for Dupont's Analytical Data Report (Volume 2)
Johnsonville Plant Equalization Pond Sludge Samples
Johnsonville Plant, New Johnsonville, Tennessee

Shen-yi Yang
February 20, 2001

Introduction:

The purpose of this review is to evaluate the validity of Dupont's waste analysis submitted in response to our K178 listing proposal. DuPont collected samples on October 20, 2000 at its Johnsonville Plant Equalization Pond in New Johnsonville, Tennessee. All samples were analyzed by Seven Trent Lab (STL) in West Sacramento, CA for total and SPLP leachate concentrations of 21 metals using two EPA SW-846 Methods (SW 6010, ICP and SW 6020, ICPMS). STL's data package was validated by Environmental Standards (ES) in Valley Forge, PA. DuPont submitted for our review STL's analytical results and ES' review summary in a document entitled "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000 at the Johnsonville Plant Equalization Pond in New Johnsonville, Tennessee for the DuPont Engineering TiO2 Listing Project", December 13, 2000".

This data package includes 9 pond sludge samples, 1 field duplicate, and 1 equipment blank. The sample identification numbers are: JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6, JV-EP-I-1, JV-EP-I-1DUP, JV-EP-I-2, JV-EP-I-3, and JV-SP-EQB. My review focused on the validity of total and SPLP results of four constituents of concern (i.e., antimony, arsenic, manganese, and thallium). DuPont reported two sets (ICP and ICPMS) of results for manganese and one set (i.e., ICPMS) of results for antimony, arsenic, and thallium. While they did not report ICP results for antimony, arsenic, and thallium, these analyses were automatically conducted when DuPont ran the ICP analyses for manganese. We obtained STL's original CLP-like data package on 2/16/01 and also assessed these results.

Conclusions:

The overall quality of the total/SPLP Sb results and SPLP manganese results analyzed by ICPMS and the total and SPLP results for manganese analyzed by ICP is acceptable. Data users need to consider the followings.

7. The results for antimony, arsenic, manganese, and thallium (as well as the other metals not examined in this review) in all samples should only be considered to be accurate to 2 significant figures. The laboratory appears not to have used the actual sample weight in their calculations but simply used a method recommended sample weight.

8. ICPMS total results for manganese may be estimated low. Based on the information in DuPont's submissions, I cannot determine the linear calibration range for the ICPMS manganese analysis. The instrument was calibrated from 0-100 ug/l and the highest spike was 200 ug/l. The ICPMS responses for Mn in sludge samples were from 180 to 4151 ug/l for total analysis. I could not determine if all samples were diluted and analyzed properly within the linear calibration range for Mn. Their ICPMS total Mn results are consistently lower (up to 11 percent) than their ICP total Mn results.

9. Data users may also consider ICP total and SPLP Mn results. The ICP Mn results were well within the linear range of the instrument and associated QC results met acceptance criteria.

10. ICPMS total and SPLP thallium results of sludge samples are questionable.

11. STL's MDL studies for ICPMS was conducted in 1998. The detection limits for Tl analysis may be higher than reported.

I reviewed ICP total and SPLP leachate results for As, Sb, Tl and found those results are acceptable (all QC sample results met acceptance criteria). ICP total and SPLP As, Sb, Tl results of all sludge samples are, therefore, included in the Analytical Data Summary Table 3.

Detailed Discussions:

- STL performed waste analyses for a fast turnaround time with minimal (level I) QC check (by an analyst using a data review checklist) before delivery of analytical data report. ES performed a complete QA review following guidance from the "National Functional Guidelines for Inorganic Data Review" (US EPA, 2/94). ES reviewed the following areas: sample holding times, sample condition upon lab receipt, instrument tuning and calibration, and field and laboratory QC sample results. ES made hand-written additions (e.g., blank analyses results summary, percent recoveries and relative percent differences of QC samples) and changes (e.g., sample identification numbers, method detection limits/reporting limits) throughout the entire report. STL's entire analytical data package was reviewed to determine if ES' hand-written additions and changes are justifiable.

- STL's sample preparation sheets and run logs show that sample size used and dilutions made for various analyses were appropriate. The method detection limits (MDLs), reporting limits (RLs), and positive sample results appeared in the analytical data table properly reflect sample dilutions.

- The six analytical batches in this data package are:

1. ICP total analysis (analytical batch number: 301091; instrument JAII, P1):

All QC sample results met acceptance criteria. The total results for As, Mn, Sb, and Tl of all sludge samples are acceptable. The laboratory appears not to have used the actual sample weight in their calculations but simply used a method recommended sample weight of 5 grams. This resulted in some differences in the results calculated from the raw data versus those reported in Table 3. Because not to have used the actual sample weight in their calculations, the results for antimony, arsenic, manganese, and thallium (as well as the other metals not examined in this review) in all samples should only be considered to be accurate to 2 significant figures.

DuPont reported no detection of As or Tl in SPLP leachates of all sludge samples at MDLs that were higher our MDLs for As and Tl.

2. The ICP SPLP analysis (analytical batch number: 299408; instrument JAII, P1):

All QC sample results met acceptance criteria. The SPLP results for As, Mn, Sb, and Tl of all sludge samples are acceptable. DuPont's sample results are consistent with EPA sample results (DPN-SO-01). DuPont reported no detection of Sb, As, and Tl in SPLP leachates of all sludge samples at MDLs that were higher than our MDLs for As, Sb, and Tl for DPN-SO-01.

3. ICP analysis for equipment blank (analytical batch number: 0298423; instrument JAII, P1)

Presence of Mn in the method blank and high recovery (120%) of POLCRI standard indicate that the positive Mn result of the equipment blank (JV-SP-EQB) is estimated and flagged "J" on the analytical data table.

4. ICPMS total analysis (analytical batch number: 301264; Perkin Elmer ICPMS, M2):

The quality of total results of Sb is acceptable. Most QC sample results met acceptance criteria, except the followings.

- As was found in the method blank at level (0.0012 ppm) that is three times of MDL. All positive SPLP As results were qualified with"U". Relative percent difference (R%D) of field duplicates for total concentration of As was quite high (73%). ICPMS total As results of all sludge samples were qualified with "J".

- Matrix spike results for As and Sb were outside acceptance range (65% and 56%, respectively). As and Sb are within control limits in the associated duplicate laboratory control samples indicating a matrix effect rather than a method performance issue. Matrix spike result was not calculated for Mn because its concentration in the sample was lot higher high than that of the spike.

- Tl was present in associated blank samples. Tl was present in initial calibration blank (ICB > 2X MDL); in method blank (MB > 4X MDL); and in continuing calibration blank (CCB > 3X MDL)).

- Although Mn was present in the associated method blank (0.41 mg/kg), total Mn results of all sludge samples were relatively high compared to the level of contaminations that could be possibly introduced during the analysis. It is unnecessary to qualify the total Mn results for the samples.

- Based on the information DuPont has provided, we cannot determine the linear calibration range for Mn. The instrument was calibrated from 0-100 ug/l and the highest spike was 200 ug/l. The ICPMS responses for Mn in sludge samples were from 180 to 4151 ug/l. I could not determine if all samples were diluted and analyzed properly within the linear calibration range for Mn. Since the ICP Mn results were well within the linear range of the instrument and associated QC results met acceptance criteria. Data users may also consider ICP total Mn results. I suspect the ICPMS total Mn result of one sample (JV-EP-M-4) because it is lower than its ICP total Mn result by 11 percent.

5. ICPMS SPLP analysis (analytical batch number: 299437; Perkin Elmer ICPMS, M01)

- High percent difference (16%) was observed for Mn in the associated serial dilution analysis, the SPLP Mn results of all sludge sample are considered estimated and have been flagged "J" in the analytical summary data table.

- (as discussed in the ICPMS total Mn analysis.) The ICPMS responses for Mn in SPLP leachates were from 435 to 2830 ug/l. We could not determine if all samples were diluted and analyzed properly within the linear calibration range for Mn. Since the ICPMS SPLP Mn results were comparable to the ICP SPLP Mn results. I believe that the ICPMS SPLP results are acceptable.

- SPLP Tl results of sludge samples are questionable.

STL's ICPMS Tl analysis is suspect at low calibration range. The ICPMS instrument was calibrated using one standard (0.050 ppm) and optimized at upper calibration level (0.040 ppm). Tl was present in associated blanks (Tl was present in ICB, 6X MDL; CCB2 and CCB3, 5X MDL; CCB6 at 2X MDL). Those blanks were analyzed right after initial and continuing calibration verification standards (ICV, CCV, 0.040 ppm). There may be a carry-over problem with this analysis. STL's ICPMS trace level Tl analysis is suspect. ES qualified three samples (JV-EP-M-3, JV-EP-M-4, JV-EP-M-5) with "U".

Three samples (JV-EP-M-1, JV-EP-M-2, JV-EP-M-3) had large negative instrument responses with absolute value greater than three or four times MDL that indicated that the MDL for Tl might be higher than reported. ES qualified those samples with "UJ".
STL conducted its MDL studies for ICPMS in early 1998. The MDL for ICPMS Tl is out dated.

6. ICPMS analysis for equipment blank (analytical batch number: 0298452; Perkin Elmer ICPMS, M01):

- Although Mn was present in the associated method blank and the equipment blank (JV-SP-EQB), total ICPMS Mn results of all sludge samples were relatively high compared to the level of contaminations that could be possibly introduced during the analysis. It is unnecessary to qualify the total ICPMS Mn results for the samples.

Summary of ES-Applied Data Qualifiers:

Qualifier	Reason	Analyte	Samples
U	This analyte was present in an associated method blank.	As - SPLP (SW6020)	JV-EP-I-1, JV-EP-I-2, JV-EP-3, JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6
	This analyte was present in associated blanks.	Tl-SPLP (SW6020)	JV-EP-M-3, JV-EP-M-4, JV-EP-M-5
J	Low matrix spike recovery indicates that this results should be considered to be estimated.	As and Sb-total (SW6020)	JV-EP-I-1, JV-EP-I-2, JV-EP-3, JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6
J	A high percent difference (14%) was observed in the associated serial dilution analysis indicates that these results should be considered to be estimated.	Mn-SPLP (SW6020)	JV-EP-I-1, JV-EP-I-2, JV-EP-3, JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6
J	Poor duplication in the analysis of field duplicate samples indicates that these results should be considered to be estimated	Mn-total (SW6010 and SW6020)	JV-EP-I-1, JV-EP-I-2, JV-EP-3, JV-EP-M-1, JV-EP-M-2, JV-EP-M-3, JV-EP-M-4, JV-EP-M-5, JV-EP-M-6
UJ	Negative results with an absolute value greater than twice the MDL indicates that the MDLs may be higher than reported.	Tl - SPLP (SW6020)	JV-EP-M-1, JV-EP-M-2, JV-EP-I-3
S	The sample may not have been diluted and analyzed properly within its linear calibration range	Mn-Total (SW6020)	JV-EP-M-4

Constituent of concern	Analysis	Table 3: Equalization Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/Split
		JV-EP-I-1	JV-EP-I-2	JV-EP-I-3	JV-EP-M-1	JV-EP-M-2	JV-EP-M-3	JV-EP-M-4	JV-EP-M-5	JV-EP-M-6	Average	
% Moisture		81.8	80.7	87.0	82.8	81.1	86.8	74.0	84.5	79.1	81.9	69.6
Antimony	Total-6010B	3.2	<2.2	<2.2	2.6	<2.2	2.5	<2.2	<2.2	<2.2	<2.2	0.7
	Total-6020	0.64 J	0.35 J	0.27 J	0.54 J	0.39 J	0.43 J	0.31 J	0.64 J	0.30 J	0.43	
	SPLP-6010B	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	0.021/<0.01
	SPLP-6020	<0.00016	<0.00016	0.00024 J	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016		
Arsenic	Total-6010B	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	2.8
	Total-6020	1.9 J	1.9 J	1.9 J	2.9 J	0.85 J	4.2 J	0.66 J	1.0 J	3.5 J	3.09	
	SPLP-6010B	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.0035/<0.01
	SPLP-6020	0.0023 U	0.0026 U	0.0035 U	0.0027 U	0.0014 U	0.0025 U	0.0015 U	0.0018 U	0.0020 U	0.0023 U	
Barium	Total	24.0	37.4	21.8	38.4	56.0	42.1	77.8	32.4	51.6	42.4	49.6
	SPLP	0.92 J	0.075 J	0.089 J	0.080 J	0.094 J	0.075 J	0.11 J	0.081 J	0.084 J	0.182	0.12/0.0118
Boron	Total	1.8 U	1.3 U	ND	ND	ND	1.4 U	ND	0.44 U	ND		24.5

Constituent of concern	Analysis	Table 3: Equalization Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/Split
		JV-EP-I-1	JV-EP-I-2	JV-EP-I-3	JV-EP-M-1	JV-EP-M-2	JV-EP-M-3	JV-EP-M-4	JV-EP-M-5	JV-EP-M-6	Average	
	SPLP	0.15 J	0.10 J	0.13 J	0.10 J	0.085 J	0.11 J	0.080 J	0.098 J	0.11 J	0.11	0.45/0.379
Chromium	Total	330 J	434	207	413	478	610	683	220	884	473	499
Chromium	SPLP	ND	ND	ND	ND	ND	ND	ND	ND	ND		<0.005/<0.003
Cobalt	Total	2.4 J	3.9	1.6	3.6	8.0	4.0	10.7	3.2	5.7	4.8	7.0
	SPLP	<0.0074	<0.0074	<0.0074	0.0085 U	0.012 U	<0.0074	0.012 U	0.011 U	<0.0074		<0.005
Iron	Total	12,200 J	18,200	8,230	16,000	40,600	19,700	57,400	17,000	26,900	24,025	63,200
	SPLP	1.9	1.7	0.63	1.4	5.7	2.6	9.0	4.2	2.1	3.2	2.2/3.37
Lead	Total	27.9 J	33.1	15.2	31.6	79.7	52.5	103	33.8	62.7	48.8	42.4
	SPLP	ND	ND	ND	0.00017 U	ND	ND	0.00018 U	0.00022 U	0.0020 U		0.002 (1)/ 0.0054
Manganese	Total-6010B	580 J	1,220	484	997	2,150	831	3,070	742	1,520	1,288	2,890
	Total-6020	548 J	1,160	443	953	2,080	769	2,770 S	732	1,410	1207	
	SPLP-6010B	0.5	1.3	0.48	1.3	2.3	0.48	2.2	2.6	0.90	1.33	1.5/3.1

Constituent of concern	Analysis	Table 3: Equalization Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/Split
		JV-EP-I-1	JV-EP-I-2	JV-EP-I-3	JV-EP-M-1	JV-EP-M-2	JV-EP-M-3	JV-EP-M-4	JV-EP-M-5	JV-EP-M-6	Average	
	SLPL-6020	0.5 J	1.3 J	0.44 J	1.3 J	2.4 J	0.46 J	2.1 J	2.5 J	0.89 J		
Nickel	Total	9.5 J	20.6	8.2 J	14.9	38.5	16.8	52.2	16.7	25.2	22.5	59.8
Nickel	SPLP	<0.016	<0.016	<0.016	<0.016	0.050 J	<0.016	0.060 J	0.026 J	<0.016		0.007
Thallium	Total-6010B	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	7.2
	Total-6020	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18		
	SPLP-6010B	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.0022/<0.01
	SPLP-6020	<0.0001	<0.0001	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	0.00018 U	0.00011 U	0.00045 U	<0.0001		
Vanadium	Total	189 J	354	172	289	751	508	1,000	398	671	481	1,060
	SPLP	ND	ND	0.017 J	ND	ND	ND	ND	ND	ND		<0.005/<0.002

Volume 3

Settling Pond Sludge-Johnsonville Plant, New Johnsonville, TN

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

Subject: **Revised QA/QC Review of "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the Johnsonville Plant Settling Pond in Johnsonville, Tennessee for the DuPont Engineering TiO2 Listing Project"**

By: **Kelly Luck, Senior Data Validator, Dynamac Corporation**

Date: **March 9, 2001**

The analytical results for pond sludge samples collected by DuPont at the Johnsonville Settling Pond and analyzed by Severn Trent Laboratories (West Sacramento, CA) were subjected to a quality assurance review by Environmental Standards, Inc. (Valley Forge, PA). The results of their review were submitted in a document entitled "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the Johnsonville Plant Settling Pond in Johnsonville, Tennessee for the DuPont Engineering TiO2 Listing Project", December 13, 2000. The Environmental Standards QA review has been examined to verify the correctness of their conclusions and to make overall conclusions regarding the quality of the analytical data for the pond sludge samples. This report was revised on March 9, 2001 following receipt and evaluation of the entire laboratory data package from DuPont. The sections pertaining to "Verification of results," "Sample size and dilutions," and "Application of data qualifiers by ES: Negative responses" under "Detailed Considerations" were revised. In addition, three new sections, "Internal standard recoveries," "Manganese linear range," and "Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium" were added. Table 4 was revised to add qualifiers to certain total arsenic results and to add the results for 6010 antimony, arsenic, and thallium.

<u>Notes</u>:

1. The analytical results for the samples, with the applied data qualifiers, and listed in Table 4 below.

2. Analytical results for only the following metals (both total and SPLP) were examined in this review: antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium.

3. Results for the following samples were examined and considered in this review: JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, and JV-SP-M-6. One field duplicate sample was collected (JV-SP-M-6-DUP) and the results for this sample was examined to evaluate the field duplicate precision. However, the results for this sample was not reported in Table 4.

4. The QA review stated that there was an equipment blank, JV-EP-EQB, associated with these

samples that was analyzed with a different sample set. However, based on the sample number assigned to the equipment blank, it appears that it should be associated with the Johnsonville Equalization Pond samples and not the Johnsonville Settling Pond samples. There was not enough information in the review to determine whether the equipment blank was supposed to be associated with the settling pond samples and no results for this sample were included in the review; therefore, I did not consider the equipment blank results in my evaluation of the data quality.

Conclusions:

The QA review conducted by Environmental Standards (ES) was very thorough, involving examination of all QC requirements for the methods (initial and continuing calibration, laboratory blanks, interference check samples, matrix spike recoveries, field duplicates, laboratory control samples, serial dilutions, and sample quantitation). Based on the raw data included in the submission, ES verified the reported results for all QC results, and used the raw data to evaluate QC data for which summary tables were not provided (such as for initial and continuing calibration verification recoveries). The data qualifiers applied by ES are appropriate and have been verified by this data reviewer, except as discussed below under "Detailed Considerations."

Except for total and SPLP boron, the analytical results for these samples are acceptable. Although there were some QC results outside the specified QC limits, resulting in the application of data qualifiers to certain results, none of the QC results indicate that any of the results in Table 4 should be rejected.

Detailed Considerations:

1. **Verification of results:** The reported results in Table 4 for antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium (total and SPLP) in each sample were verified from raw data in the laboratory data package. For total metals results (both 6010 and 6020), the laboratory did not use the actual sample weight (which varied from 5.00 g to 5.05 g) in their calculations but simply used a value of 5. This resulted in some differences in the results calculated from the raw data versus those reported in Table 4. Because the laboratory did not use the actual sample weight in their calculations, the results for total metals (both 6010 and 6020) in all samples should only be considered to be accurate to 2 significant figures.

   Because the laboratory did not account for dilutions in their reporting of MDLs and RLs, ES re-calculated the MDLs and RLs to account for dilutions, and reported these recalculated values. It appears that ES re-calculated the MDL for 6020 total arsenic incorrectly: based on a laboratory-reported MDL of 0.08 mg/kg and a dilution factor of 5 for 6020 total metal analyses (25x dilution divided by 5 g sample weight for all samples), the correct MDL should be 0.4 mg/kg, not 0.25

mg/kg as reported by ES. This correction of the MDL does not affect any sample results in Table 4, as all results for total arsenic were greater than 0.4 mg/kg.

2. **pH results:** The reported pH of the final SPLP leachate was added to Table 4 for all samples. The report did not include any data pertaining to sample pH.

3. **Sample size and dilutions:** The laboratory used the standard sample size (100 g) for SPLP extractions. The volume of sample/leachate used for analysis was 50 mL, which is less than the recommended amount of 100 mL. For total metals analysis, the laboratory digested 5 g of each sample, which is more than the recommended sample size of 1 g. Based on information on the run logs (no other source of sample dilution information could be found), 6010 analyses for total metals were conducted at a 5x dilution for all samples, and 6020 analyses for total metals were conducted at a 25x dilution for all samples. The sample sizes and dilutions seem appropriate.

4. **Reasonableness of total and SPLP results**: One issue that ES did not address in their review was the reasonableness of total and SPLP results, in consideration of the fact that SPLP results reflect a 20x dilution of the sample (and therefore SPLP results should be at least 20x less than total results). A comparison of these results indicates that SPLP results are much higher than expected, based on total results, for boron (all samples except JV-SP-M-2). An examination of the associated QC and laboratory blank data does not reveal any obvious explanation for these discrepancies. Because the unreasonable results appear in all or almost all samples for boron, the results for total and SPLP boron must be considered to be suspect in these samples.

5. **Application of data qualifiers by ES:**

5.1 *Blank contamination:* Based on the trace-level presence of certain target analytes in laboratory blanks, ES applied U qualifiers to some of the analytical results. The application of these qualifiers was verified in all cases. However, I disagreed with the application of the qualifiers in one case.

ES applied a U qualifier to the results for SPLP iron in JV-SP-I-1. I could find no justification for this qualifier and have removed it from the result in Table 4.

The ES report stated that the equipment blank associated with this sample set was JV-EP-EQP. As stated above, because this submission did not include the results for that equipment blank and because I could not verify that it was associated with this sample set, I did not examine the potential for blank contamination in the equipment blank.

5.2 *Field duplication:* One field duplicate sample was collected with this sample set (JV-SP-M-6-DUP). Field duplicate precision was evaluated by ES and these results were verified as correct. The precision for SPLP iron fell outside the QC limits. Based on this, ES qualified the results for SPLP iron in samples JV-SP-M-6 and JV-SP-M-6-DUP as estimated (J qualifier). Typically, the results of field duplicate analyses are applied to all samples of the same matrix as that of the field duplicate pair. Because all samples in this sample set are of the same matrix (pond sludge), then the J qualifier should be applied to the results for SPLP iron in all samples. (Note that the U qualifier takes precedence over the J qualifier in some of the samples.)

5.3 *Negative responses:* ES appeared to evaluate the raw data, and apply UJ qualifiers to any non-detect results if a negative response with an absolute value greater than 2x the method detection limit (MDL) was observed for that element in the sample, based on data qualifiers that were applied in the other data packages. However, for this package, that evaluation appears to not have been done for thallium. Evaluation of the raw data for ICP-MS analyses by this reviewer indicates that a negative response greater than 2x the MDL was observed for SPLP thallium in all samples except JV-SP-I-2. I have added UJ qualifiers to the results for SPLP thallium in these samples; the negative responses indicate that the MDL may be higher than reported.

5.4 *Matrix spike recovery:* A sample within this sample set was used for matrix spike analyses for SPLP metals and a sample from the Johnsonville Equalization Basin sample set was used for matrix spike analyses for total metals. The results for SPLP metals were within QC limits (75-125%) for all analytes. For total metals, the results were outside the QC limits for antimony and arsenic (recoveries of 56% and 65%, respectively). Because of these low recoveries, ES correctly qualified all results for total antimony and arsenic as estimated (J qualifier).

5.5 *Results below the reporting limit:* ES applied J qualifiers to all results (that had not been previously qualified) which were reported as greater than the MDL but less than the reporting limit. All applications of this qualifier have been verified as correct.

6. **Serial dilution:** A sample from within this sample set was evaluated for serial dilution for SPLP analyses (both 6010 and 6020). In both cases, only manganese had sufficiently high results for serial dilution to be evaluated ($50xMDL) and in both cases the percent difference was within QC limits (0-10%) for manganese. Serial dilution precision for total metals was evaluated using a sample outside this sample set.

7. **Negative responses for thallium:** As stated previously, negative responses for thallium with an absolute value greater than 2xMDL were observed for some samples in the SPLP analyses. Because of this, the raw data were examined to determine whether any trends could be observed. For the total thallium analyses, a positive response (>MDL) was observed in the method blank and in the first continuing calibration blank (CCB). A positive response (<MDL) was observed in the initial calibration blank (ICB), the ICSA standard, and one of the CCBs. A negative response

with an absolute value less than the MDL was observed in the remaining CCBs and in all the samples. Based on these data, there does not seem to be a problem with thallium in the total metals analysis.

For SPLP thallium analyses, a positive response >MDL was observed in the ICB, a positive response <MDL was observed in the ICSA standard and in one CCB, and a negative response with an absolute value less than the MDL was observed in the CCBs. No raw data for the method blank were provided. However, as stated previously, large negative responses were observed in the sample results (those for which raw data were included). Based on this, there does not appear to be a problem with the thallium analysis at the instrument but there may be a problem with the matrix of the samples interfering with SPLP thallium analysis.

8. **Additional issues:** A sample outside this sample set (but within the DuPont sample sets) was used for the matrix spike for total metals; this sample was from the sample set containing the Johnsonville Equalization Basin samples. Because the matrix for the Settling Pond samples can be considered to be similar to that for the Equalization Basin sample, the results from the total metals matrix spike were applied to samples within this sample set. A sample within the sample set was used for a matrix spike for SPLP metals.

   The laboratory did not analyze any laboratory duplicates or matrix spike duplicates. Although this means that the laboratory did not fulfill all QC requirements of the methods, this is not considered to affect the quality of the data, in consideration of the fact that field duplicate precision was generally quite good.

9. **Internal standard recoveries:** Internal standard recoveries for 6020 analyses (both total and SPLP) were well within the QC limits of 30-120% for all samples (recoveries were 90-110%). No trend in recovery values was observed..

10. **Manganese linear range:** For 6020 analyses, the calibration verification standard for manganese was at 100 µg/L and the laboratory control standard was at 200 µg/L. All raw data results for total and SPLP manganese from 6020 analyses were >200 µg/L, at 201-7211 µg/L. The laboratory did not provide any information pertaining to the linear range of the ICP-MS instrument for any analytes. The instrument was not calibrated using a calibration curve, but rather a single-point calibration was performed (SW-846 allows the use of single-point calibration for both 6010 and 6020). Because the calibration verification standard is supposed to be near the mid-point of the calibration range and because it seems unlikely that the laboratory would spike the control standard at the top of the linear range, the ICP-MS linear range for manganese is probably greater than 0-200 µg/L. However, there are no data in the laboratory package to verify this conclusion.

Although it cannot be verified that the ICP-MS results for manganese were within the linear range of the instrument, the results do agree quite well with the reported ICP-AES results (average RPD of 6.1% for total manganese and 10% for SPLP manganese). The ICP-AES results were well within the linear range of the instrument. Therefore, I believe the ICP-MS results for manganese are acceptable.

11. **Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium:** Although the laboratory did not report 6010 results for antimony, arsenic, and thallium, results for these analytes were included in the raw data. The raw data results for 6010 antimony, arsenic, and thallium were compared to the reported results for 6020 antimony, arsenic, and thallium; see Table 4. However, the 6010 results for were not useful for comparison as all responses were less than the reported MDLs (2.2, 3.1, and 7.1 mg/kg for total antimony, arsenic, and thallium, respectively, and 0.031, 0.043, and 0.053 mg/L for SPLP antimony, arsenic, and thallium, respectively) except for SPLP arsenic in one sample, JV-SP-M-2 at 0.057 mg/L. Because the 6010 SPLP arsenic result does not agree with the 6020 SPLP arsenic result (<MDL), with the 6010 total arsenic result (<MDL) or with the 6020 total arsenic result (0.58 mg/kg) for that sample, it must be considered to be suspect.

Summary of Applied Data Qualifiers:

Qualifier	Reason	Analyte	Samples
U	This analyte was present in an associated blank.	B - total	JV-SP-I-1, JV-SP-I-2, JV-SP-M-1, JV-SP-M-3
		Fe - SPLP	JV-SP-M-3. JV-SP-M-5
		V - SPLP	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-3, JV-SP-M-5
J	Poor matrix spike recovery indicates that these results should be considered to be estimated.	Sb - total	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, JV-SP-M-6
		As - total	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, JV-SP-M-6
J	Poor field duplicate precision indicates that these results should be considered to be estimated.	Fe - SPLP	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-4, JV-SP-M-6
UJ	Negative results with an absolute value greater than twice the MDL indicates that the MDLs may be higher than reported.	Tl - SPLP	JV-SP-I-1, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, JV-SP-M-6
J	Because results are greater than the MDL but less than the reporting limit, results should be considered to be estimated.	As - SPLP	JV-SP-I-2, JV-SP-I-3, JV-SP-M-4
		Ba - SPLP	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-2, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, JV-SP-M-6
		B - total	JV-SP-M-2
		B - SPLP	JV-SP-I-1, JV-SP-I-2, JV-SP-I-3, JV-SP-M-1, JV-SP-M-3, JV-SP-M-4, JV-SP-M-5, JV-SP-M-6

Constituent of concern	Analysis	Table 4: Settling Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/ Split
		JV-SP-I-1	JV-SP-I-2	JV-SP-I-3	JV-SP-M-1	JV-SP-M-2	JV-SP-M-3	JV-SP-M-4	JV-SP-M-5	JV-SP-M-6	Average	
% Moisture		79.1	78.0	85.7	81.9	81.5	79.7	84.0	82.7	81.7	81.6	69.6
Antimony	Total-6010B	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	0.7
	Total-6020	0.10 J	0.23 J	0.078 J	0.24 J	0.32 J	0.16 J	0.23 J	0.31 J	0.13 J	0.2	
	SPLP-6010B	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	0.021/<0.01
	SPLP-6020	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016	<0.00016		
Arsenic	Total-6010	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	2.8[1]
	Total-6020	0.71 J	0.79 J	<0.4 J	0.74 J	0.58 J	0.53 J	0.59 J	0.41 J	0.76 J	0.6	
	SPLP-6010B	<0.043	<0.043	<0.043	<0.043	0.057	<0.043	<0.043	<0.043	<0.043	<0.043	<0.0035/<0.01
	SPLP-6020	<0.00041	0.00052 J	0.00048 J	<0.00041	<0.00041	<0.00041	0.00065 J	<0.00041	<0.00041		
Barium	Total	36.6	29.6	21.4	26.1	37.4	35.4	21.5	28.9	28.3	29.5	49.6
	SPLP	0.076 J	0.076 J	0.074 J	0.083 J	0.079 J	0.071 J	0.078 J	0.085 J	0.082 J	0.078	0.12/0.0118
Boron	Total	0.54 U	2.5 U	ND	2.3 U	8.2 J	1.2 U	ND	ND	ND		24.5
	SPLP	0.16 J	0.13 J	0.086 J	0.19 J	0.35	0.12 J	0.071 J	0.10 J	0.089 J	0.144	0.45/0.379
Chromium	Total	600	349	306	289	340	414	259	401	359	368	499

Constituent of concern	Analysis	Table 4: Settling Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/ Split
		JV-SP-I-1	JV-SP-I-2	JV-SP-I-3	JV-SP-M-1	JV-SP-M-2	JV-SP-M-3	JV-SP-M-4	JV-SP-M-5	JV-SP-M-6	Average	
Chromium	SPLP	ND	ND	ND	ND	ND	ND	ND	ND	ND		<0.005/<0.003
Cobalt	Total	5.4	2.4	1.2	2.2	4.0	2.9	2.1	2.2	1.8	2.7	7
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		<0.005
Iron	Total	43,900	28,300	18,000	26,200	37,600	32,600	26,800	26,900	24,300	27,600	63,200
	SPLP	0.063 U	0.18	0.46	1.6	0.96	0.15 U	1.0	0.020 U	1.3 J	0.637	2.2/3.39
Lead	Total	20.8	21.2	6.4	15.9	30.6	23.7	14.0	14.0	18.9	18.4	42.4
	SPLP	<0.00015	<0.00015	<0.00015	<0.00015	<0.00015	<0.00015	<0.00015	<0.00015	<0.00015		0.002[2] / 0.0054
Manganese	Total-6010B	3,980	2,570	1,370	1,430	2,310	2,680	1,300	2,530	1,790	2,218	2,890
	Total-6020	3,610	2,370	1,260	1,310	2,220	2,540	1,270	2,420	1,720		
	SPLP-6010B	0.20	0.44	2.2	2.8	0.89	0.37	1.0	0.37	1.6	1.1	1.5/3.1
	SPLP-6020	0.20	0.39	1.9	2.5	0.81	0.32	0.90	0.32	1.5		
Nickel	Total	37.9	34.5	18.9	22.7	34.3	29.6	24.9	26.6	22.1	27.9	59.8
	SPLP	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016		0.007
Thallium	Total-6010B	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	7.2

Constituent of concern	Analysis	Table 4: Settling Pond Sludge, RIN 107, Johnsonville										Comparable EPA Sample (DPN-SO-01)/ Split
		JV-SP-I-1	JV-SP-I-2	JV-SP-I-3	JV-SP-M-1	JV-SP-M-2	JV-SP-M-3	JV-SP-M-4	JV-SP-M-5	JV-SP-M-6	Average	
Thallium	Total-6020	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18		
	SPLP-6010B	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.0022/<0.01
	SPLP-6020	<0.0001 UJ	<0.0001	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ		
Vanadium	Total	1,240	656	510	579	724	840	559	808	664	731	1,060
	SPLP	0.010 U	0.011 U	0.015 U	0.0034 U	<0.0032	0.0067 U	<0.0032	0.015 U	<0.0032	0.0073	<0.005/<0.002
pH of SPLP leachate	SPLP	7.85	7.74	7.56	7.37	7.20	7.25	7.43	7.52	7.47		

1 In the Analytical Data Report, this result was qualified “E” due to low matrix spike recovery.

2 In the Analytical Data Report, it stated that this result is less than the typical laboratory reporting limit, but greater than the calculated instrument detection limit.

Volume 4

Hillside Pond Sludge-Johnsonville Plant, New Johnsonville, TN

MEMORANDUM

To: Shen-yi Yang, EPA OSW
From: Ray Anderson, SAIC
Subject: Data Review of Dupont New Johnsonville, Volume 4
Date: February 23, 2001

Data review and validation were performed on the laboratory analytical results for 9 solid, 2 equipment blanks, and 1 field duplicate samples collected from the Dupont New Johnsonville facility on October 21, 2000. The samples were submitted on October 23, 2000 by Dupont to Severn Trent Laboratories, STL in West Sacramento, CA. STL received all samples noted on chain-of-custody (COC) documentation on October 24, 2000. The analytical report from STL and validated by Environmental Standards, contained the sample results for total, TCLP, SPLP metals, and percent moisture. All analyses were performed using SW-846 methodology which included ICP Method 6010 for Al, Ba, Be, B, Cr, Co, Cu, Fe, Mn, Mo, Ni, Ag, Sn, V, and Zn; and ICP-MS Method 6020 for Sb, As, Cd, Pb, Mn, Se, and Tl. The analytical data package designated as “Volume 4 Hillside Pond New Johnsonville Plant” included the data validation report dated December 13, 2000 from Environmental Standards. Due to missing information in the STL analytical report as initially provided, additional laboratory data were submitted by Dupont to EPA on February 15, 2001. For the combined laboratory data along with validation report the following observations are noted:

Observations:

! The dates on the chain-of-custody (COC) documentation are misleading. The first occurrence of the “relinquished by” date and signature along with the “received by” date and signature were dated prior to the actual sample date on October 21, 2000. This is technically impossible since you cannot relinquish or receive samples unless something has been collected. Accurate COC information is important in order to track the sample handling and transport prior to receipt by the laboratory.

! The STL data report delivered to Environmental Standards was dated November 6, 2000. This represents a less than two week sample turnaround time based on the laboratory receipt date on October 24, 2000. Within this two week period the laboratory was able to complete the total and leachate analyses, do a comprehensive data review, and submit a full data package in order to support a complete independent data validation effort. Although this accomplishment is not impossible, the typical laboratory analysis turnaround is 3 to 4 weeks for a complete analytical data package. Frequently, when the laboratory is required to accelerate the turnaround time the number of reanalyses are limited, quality control analyses are not always project-specific, and the amount of time allotted for internal data review and report preparation is limited. As a result the overall data quality and usability is sometimes questionable.

! For some reason Environmental Standards selectively choose to include those sections of the laboratory data package in order to support their overall data assessment. In many instances the original laboratory raw data were corrected and revised by Environmental Standards. These handwritten revisions that include changes to the sample ID, dilution factor, method detection limit, reported result, and laboratory assigned qualification were usually accompanied by a logical explanation, however, in most cases the revisions were not dated or initialed by the responsible party. Good Laboratory Practices (GLP) dictate that all raw data corrections using a single line through the error should be initialed and dated by the responsible individual. It is therefore assumed that the majority of the uninitialed corrections were performed by Environmental Standards with hopefully, the laboratory's agreement. It is noted in the validation report that the laboratory was asked to provide additional revised data to respond to the initial validation findings. However, aside from the leachate preparation logs, all the remaining laboratory data appear to be the original version with handwritten marked-up corrections.

! The detection limit data provided in the February 15, 2001 response to EPA contains the ICP and ICP/MS MDL and RL data for STL-Sacramento that were determined in early 1998. This is unacceptable since the instrument operating conditions, time in service, and maintenance affect the sensitivity over time. A more realistic time frame would have been on a quarterly basis. I'm very surprised the lab has been able to operate and respond to various external audits without a more current MDL study. In addition, the numerous CCBs with multiple analytes yielding concentrations above the MDLs were the norm. This further reinforces that the existing 1998 MDL study is outdated. The reporting limits should also be adjusted based on the most current MDL data.

! The ICP aqueous MDLs reported for Ba (0.0010), Be (0.0010), and Mn (0.0010) are different than those reported in the 1998 MDL study.

! Nearly all continuing calibration blanks (CCBs) associated with the ICP total analyses contained trace level contaminants greater than the MDLs. In addition the practical quantitation standard (PQLCRI) recovery was greater than 115% for Ba, Co, Fe, Mo, Sn, and Zn. This was also followed with high positive results for Ba and Zn, and large negative results for B and Mn in the interference check sample (ISCA). The CCB results together with the high PQLCRI recoveries are an indication of possible laboratory induced contamination and should be considered when using any sample concentration near the reporting limit. The ISCA results suggest that the high levels of Fe detected in all samples probably affected the ability to detect B, Ba, Mn, and Zn at concentrations below the respective levels spiked into the ISCAB. The exact concentrations are unknown, since this information was not provided by the laboratory.

! There is no reference to the preparation methods used to digest the total and leachate samples. In addition, the TCLP and SPLP logs sheets do not specifically state SW-846 methods were used and this information was submitted electronically by STL to Environmental Standards after the original report was delivered.

- The data report is very disorganized and difficult to follow in the format prepared by Environmental Standards. This together with a less than accurate laboratory case narrative and the numerous data validation corrections due to method detection limit discrepancies are an indication the laboratory hastily performed the required analyses at the expense of meeting all the data quality objectives.

- The average TCLP and SPLP final leachate pHs compared favorably to the final pH values for EPA sample DPN-SO-01. Therefore, the differences in leachate concentrations between the Dupont samples compared to the EPA sample should only be attributed to the difference in the total concentration.

- All the summarized total results, except samples JV-HP-6, and JV-HP-3 dup, for both ICP and ICP-MS were either calculated and reported incorrectly by the laboratory or Environmental Standards. The actual sample weight used to digest and prepare the samples for analysis was not used to calculate the final sample concentrations. Instead, a default weight of 1.00 grams was used and this results in an erroneously reported higher concentration. This reporting error affects all total metals results and it becomes more prominent with larger concentrations. The results are biased by the following percentages: HP-1 (2%), HP-2 (1%), HP-3 (3%), HP-4 (1%), HP-5 (2%), HP-7 (1%), HP-8 (2%), and HP-9 (1%).

- All ICP total samples were initially analyzed undiluted and then diluted due to high levels of titanium and iron. All reported target analytes were then calculated from the diluted sample analyses. However, the undiluted results are probably more representative of the actual sample concentrations. In most cases, these values are slightly lower than the diluted concentration.

- The TCLP and SPLP analyses were performed at the same time the Iron Rich^{TM} leachate samples were analyzed. During this time, the responses for Tl, Se, and As exhibited decreased instrument sensitivity based on an unusual number of negative responses. For this reason, the reported results for Tl, Se, and As can only be viewed as estimated concentrations and should be used for comparison purposes only.

- In many cases the ICP and ICP/MS CCB needed to be run consecutively due to the number of analytes that were detected above the MDLs. In fact for the most part, all CCBs contained at least one detected target analyte concentration that exceeded the reported MDL. Also, the initial ICP TCLP and SPLP analyses were all rejected due to poor CCB results. This provides further confirmation that MDL studies are not current. In addition, all low-level sample results should be questioned since the potential exists for laboratory induced contamination.

- Although the total Pb concentrations were reported from the ICP/MS analyses, it is interesting the values detected from the ICP analyses are on the average of 3 times greater than the ICP/MS results.

Conclusions:

I believe the Hillside Pond ICP and ICP/MS totals data are valid and representative, however, they are biased high due to calculation errors and possibly using diluted as opposed to undiluted sample responses. Conversely, all ICP/MS leachate data due to a number quality control issues (poor CCB responses and instrument instability as a result of the high degree of negative responses) are of questionable value.

Constituent of concern	Analysis	Table 5, Hillside Pond Sludge, RIN 108, Johnsonville												EPA Sample (DPN-SO-01)/ Split
		JV-HP-1	JV-HP-2	JV-HP-3	JV-HP-4	JV-HP-5	JV-HP-6	JV-HP-7	JV-HP-8	JV-HP-9	Average	MDL	RL	
% Moisture		68.6	67.2	63.1	67.8	56.1	66.8	63.1	64.1	63.2	64.4			69.6
Antimony	Total-6020	0.29 J	0.25 J	0.58 J	0.93 J	0.41 J	0.59 J	0.26 J	0.40 J	0.24 J	0.439	0.05	1.0	0.7
	Total-6010	6.0	3.1	5.7	4.4	9.3	6.7	2.2	3.9	5.5	5.2	2.2	6.0	
	TCLP-6020	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008		0.008	0.01	<0.5/<0.01
	TCLP-6010	< 0.16	< 0.16	0.04 B	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16		0.16	0.3	
	SPLP-6020	<0.00016	<0.00016	<0.00016	0.00012 B	0.00095 J	<0.00016	<0.00016	<0.00016	<0.00016		0.00016	0.002	0.021/<0.001
	SPLP-6010	0.011 B	0.0029 B	< 0.031	< 0.031	0.0013 B	0.0074 B	0.0045 B	0.0030 B	0.010 B	0.0113	0.031	0.06	
Arsenic	Total-6020	1.5 J	1.4 J	1.4 J	1.7 J	1.8 J	2.4 J	0.89 J	2.1 J	3.6 J	1.87	0.40	1.0	2.8
	Total-6010	< 3.1	< 3.1	< 3.1	< 3.1	< 6.2	< 3.1	< 3.1	< 3.1	< 3.1		3.1	30	
	TCLP-6020	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021		0.0021	0.01	<0.5/<0.01
	TCLP-6010	0.05 B	0.08 B	0.09 B	0.08 B	0.07 B	0.30 L	0.08 B	0.22 L	< 0.22		0.22	1.5	
	SPLP-6020	<0.00041	<0.00041	<0.00041	<0.00041	0.0030	<0.00041	<0.00041	<0.00041	<0.00041		0.00041	0.002	<0.0035/<0.01
	SPLP-6010	< 0.043	0.0087 B	< 0.043	0.0041 B	0.0089 B	0.0031 B	0.0080 B	< 0.043	0.0091B		0.043	0.3	
Barium	Total	46.4	53.1	57.5	52.8	68.0	54.3	49.5	60.9	54.4	55.2	0.2	100	49.6
	TCLP	0.23	0.22	0.24	0.17	0.19	0.18	0.22	0.23	0.28	0.22	0.0022	1.0	<2/0.306
	SPLP	0.053 J	0.058 J	0.064 J	0.055 J	0.055 J	0.057 J	0.058 J	0.059 J	0.052 J	0.057	0.0004	0.2	0.12/0.0118
Boron	Total	0.81 L	2.3 L	< 0.40	< 0.40	< 0.80	< 0.40	< 0.40	2.1 L	< 0.40		0.40	20	24.5
	TCLP	0.23 L	0.93 J	0.10 L	< 0.055	< 0.055	< 0.055	0.059 J	< 0.055	0.057 J		0.055	1.0	/0.532
	SPLP	0.066 J	0.082 J	0.12 J	0.035 J	0.044 J	0.025 J	0.051 J	0.081 J	0.043 J	0.061	0.011	0.2	0.45/0.379

Constituent of concern	Analysis	Table 5, Hillside Pond Sludge, RIN 108, Johnsonville												EPA Sample (DPN-SO-01)/ Split
		JV-HP-1	JV-HP-2	JV-HP-3	JV-HP-4	JV-HP-5	JV-HP-6	JV-HP-7	JV-HP-8	JV-HP-9	Average	MDL	RL	
Chromium	Total	717	796	815	758	1,020	822	728	799	858	813	1.35	5.0	499
	TCLP	0.015 U	< 0.014	0.014 L	0.008 B	< 0.014	0.009 B	0.020 U	0.011 B	0.007 B		0.014	0.05	0.06/0.278
	SPLP	< 0.0028	< 0.0028	< 0.0028	< 0.0028	< 0.0028	< 0.0028	< 0.0028	< 0.0028	< 0.0028		0.0028	0.01	<0.005/<0.003
Cobalt	Total	3.0	3.1	4.5	4.1	4.9	4.2	3.5	5.1	4.0	4.0	0.05	0.5	7.0
	TCLP	0.042 J	<0.037	0.041 J	0.050 J	<0.037	<0.037	0.057 J	<0.037	0.069 J		0.037	0.25	0.13
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		0.0074	0.05	<0.005
Iron	Total	43,400	47,800	58,700	51,600	63,000	53,900	48,500	66,100	56,900	54,433	0.45	50	63,200
	TCLP	161	134	260	147	169	174	199	219	306	197	0.0195	0.5	567/493
	SPLP	0.039 U	< 0.0039	0.44 J	0.016 U	0.034 U	0.020 U	0.030 U	0.54	0.039 U		0.0039	0.1	2.2/3.39
Lead	Total-6020	26.6 J	29.7 J	27.2 J	24.7 J	32.5 J	21.5 J	21.7 J	32.8 J	22.0 J	26.5	0.05	0.5	42.4
	Total-6010	84.5	74.4	83.2	99.9	100	92.6	54.4	83.1	97.8	85.5	2.2	10	
	TCLP-6020	< 0.00075	< 0.00075	< 0.00075	< 0.00075	< 0.00075	< 0.00075	< 0.00075	< 0.00075	<0.00075		0.00075	0.005	<0.5/.015
	TCLP-6010	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16		0.16	0.5	
	SPLP-6020	< 0.00015	< 0.00015	< 0.00015	< 0.00015	0.0036 U	< 0.00015	< 0.00015	< 0.00015	<0.00015		0.00015	0.001	0.002 (1)/ 0.0054
	SPLP-6010	< 0.031	0.0043 B	< 0.031	0.0033 B	< 0.031	< 0.031	< 0.031	< 0.031	< 0.031		0.031	0.1000	
Manganese	Total-6010B	3,810	4,370	5,790	5,120	5,600	5,220	4,500	5,220	5,990	4828	1.5	7.5	2,890
	Total-6020	3,600	3,690	5,300 S	4,740	5,090	4,850	4,150	4,560 S	5,310 S		0.05	0.5	
	TCLP-6010B	92.2	81.6	77.9	80.9	81.8	72.5	93.3	82.6	70.8	78.6	0.0035	0.075	47.4/53.9

Constituent of concern	Analysis	Table 5, Hillside Pond Sludge, RIN 108, Johnsonville												EPA Sample (DPN-SO-01)/ Split
		JV-HP-1	JV-HP-2	JV-HP-3	JV-HP-4	JV-HP-5	JV-HP-6	JV-HP-7	JV-HP-8	JV-HP-9	Average	MDL	RL	
Manganese	TCLP-6020	83.5	79.2	72.1	77.6	75.1	67.8	86.1	76	64.6		0.0007	0.005	
	SPLP-6010B	1.5	1.2	2.2	0.36	0.56	0.38	0.56	1.3	0.67	0.97	0.0007	0.015	1.5/3.1
	SPLP-6020	1.3	1.1	2.0	0.35	0.52	0.32	0.49	1.1	0.56		0.00014	0.001	
Nickel	Total	36.8	44.1	53.0	51.1	59.6	52.6	41.9	62.0	53.4	50.5	9.0	20	59.8
	TCLP	0.52 J	0.53 J	0.73	0.65	0.62	0.61	0.57 J	0.64	0.88	0.64	0.08	0.2	1.2
	SPLP	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016		0.016	0.04	0.007
Thallium	Total-6020	<0.18	<0.18	0.23 U	0.23 U	0.43 U	<0.18	<0.18	<0.18	<0.18		0.18	0.5	7.2
	Total-6010	< 7.1	< 7.1	< 7.1	< 7.1	< 14.2	< 7.1	< 7.1	< 7.1	< 7.1		7.1	200	
	TCLP-6020	<0.0005	<0.0005	<0.0005	0.00055 U	0.0017 U	0.0013 U	<0.0005	<0.0005	<0.0005		0.0005	0.005	<2/<0.1
	TCLP-6010	0.02 B	0.04 B	0.01 B	0.12 B	0.13 B	0.11 B	< 0.27	< 0.27	0.16 B		0.27	10	
	SPLP-6020	<0.0001	<0.0001	<0.0001	<0.0001	0.00098 U	<0.0001	<0.0001	<0.0001	<0.0001		0.0001	0.001	<0.0022<0.01
	SPLP-6010	0.041 B	0.0096 B	0.010 B	0.0058 B	0.0080 B	0.0114 B	0.0133 B	0.0015 B	0.023 B	0.0137	0.053	2.0	
Vanadium	Total	1,560	1,600	1,780	1,710	2,120	1,880	1,570	1,660	1,840	1747	1.25	25	1,060
	TCLP	0.0095 B	< 0.016	0.009 B	0.007 B	0.011 B	< 0.016	0.009 B	< 0.016	< 0.016		0.016	0.25	<0.05/0.0628
	SPLP	0.017 U	0.041 J	0.0039 U	0.031 J	0.017	0.016 U	0.035 J	0.0025 B	0.017 U	0.022	0.0032	0.05	<0.005/<0.002
Initial pH	TCLP	6.87	6.81	6.84	6.89	6.67	7.03	6.71	6.88	6.54				
Initial pH	SPLP													
Final pH	TCLP	5.39	5.41	5.51	5.65	5.63	5.68	5.59	5.52	5.54				

Constituent of concern	Analysis	Table 5, Hillside Pond Sludge, RIN 108, Johnsonville												EPA Sample (DPN-SO-01)/ Split
		JV-HP-1	JV-HP-2	JV-HP-3	JV-HP-4	JV-HP-5	JV-HP-6	JV-HP-7	JV-HP-8	JV-HP-9	Average	MDL	RL	
Final pH	SPLP	7.04	7.01	7.01	6.93	6.74	7.26	7.18	7.16	7.02				

L Result is greater than the method detection limit but less than the laboratory reporting limit.
B Result is greater than the suspected instrument detection limit but less than the method detection limit.
Note: The 6020 TCLP and SPLP arsenic and thallium results should be considered as estimated values due to poor instrument sensitivity exhibited during the leachate analyses.
S The samples may not have been iluted and analyzed properly within the linear calibration range for Mn. The ICPMS total Mn result of three samples (JV-HP-M-2, JV-HP-8, and JV-HP-8) are suspect because their results are lower than their ICP total Mn results by 18%, 14%, and 13%, respectively.

Volume 5

Equalization Pond Sludge- DeLisle Plant, Pass Christian, MS

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

Subject: **Revised QA/QC Review of "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the DeLisle Plant Equalization Basin in Pass Christian, Mississippi for the DuPont Engineering TiO2 Listing Project"**

By: **Kelly Luck, Senior Data Validator, Dynamac Corporation**

Date: **March 9, 2001**

The analytical results for pond sludge samples collected by DuPont at the DeLisle Plant Equalization Basin and analyzed by Severn Trent Laboratories (West Sacramento, CA) were subjected to a quality assurance review by Environmental Standards, Inc. (Valley Forge, PA). The results of their review were submitted in a document entitled "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the DeLisle Plant Equalization Basin in Pass Christian, Mississippi for the DuPont Engineering TiO2 Listing Project", December 13, 2000. The Environmental Standards QA review has been examined to verify the correctness of their conclusions and to make overall conclusions regarding the quality of the analytical data for the pond sludge samples. This report was revised on March 9, 2001 following receipt and evaluation of the entire laboratory data package from DuPont. The sections pertaining to "Verification of results," "Sample size and dilutions," and "Reasonableness of total and SPLP results" under "Detailed Considerations" were revised. In addition, three new sections, "Internal standard recoveries," "Manganese linear range," and "Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium" were added. Table 6 was revised to add qualifiers to certain total arsenic results and to add the results for 6010 antimony, arsenic, and thallium.

Notes:

1. The analytical results for the samples, with the applied data qualifiers, are listed in Table 6 below.

2. Analytical results for only the following metals (both total and SPLP) were examined in this review: antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium.

3. Results for the following samples were examined and considered in this review: DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, and DL-EQ-M-6. One equipment blank (DL-EQ-EQBLK) and one field duplicate sample were collected (DL-EQ-M-4-DUP) and the results for these samples were examined to evaluate the potential for blank contamination and the field duplicate precision, respectively. However, the results for these field QC samples are not reported in Table 6.

Conclusions:

The QA review conducted by Environmental Standards (ES) was very thorough, involving examination of all QC requirements for the methods (initial and continuing calibration, laboratory and equipment blanks, interference check samples, matrix spike recoveries, field duplicates, laboratory control samples, serial dilutions, and sample quantitation). Based on the raw data included in the submission, ES verified the reported results for all samples and QC results, and used the raw data to evaluate QC data for which summary tables were not provided (such as for initial and continuing calibration verification recoveries). The data qualifiers applied by ES are appropriate and have been verified by this data reviewer, except as discussed below under "Detailed Considerations."

Except for total antimony, total arsenic, and total and SPLP boron, the analytical results for these samples are acceptable. Although there were some QC results outside the specified QC limits, none of the QC data indicate that any of the results in Table 6 should be rejected.

<u>Detailed Considerations</u>:

1. **Verification of results:** The reported results in Table 6 for antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium (total and SPLP) in each sample were verified from raw data in the laboratory data package. For total metals results (both 6010 and 6020), the laboratory did not use the actual sample weight (which varied from 5.00 g to 5.05 g) in their calculations but simply used a value of 5. This resulted in some differences in the results calculated from the raw data versus those reported in Table 6. Because the laboratory did not use the actual sample weight in their calculations, the results for total metals (both 6010 and 6020) in all samples should only be considered to be accurate to 2 significant figures.

   Because the laboratory did not account for dilutions in their reporting of MDLs and RLs, ES re-calculated the MDLs and RLs to account for dilutions, and reported these recalculated values. It appears that ES re-calculated the MDL for 6020 total arsenic incorrectly: based on a laboratory-reported MDL of 0.08 mg/kg and a dilution factor of 5 for 6020 total metal analyses (25x dilution divided by 5 g sample weight for all samples), the correct MDL should be 0.4 mg/kg, not 0.25 mg/kg as reported by ES. Using the correct MDL, all results for 6020 total arsenic reported in Table 6 should be considered to be non-detectable. I have applied a "U" qualifier to 6020 total arsenic results reported as detectable in Table 6.

2. **pH results:** The reported pH of the final SPLP leachate was added to Table 6 for all samples. The report did not include any data pertaining to sample pH.

3. **Sample size and dilutions:** The laboratory used the standard sample size (100 g) for SPLP extractions. The volume of sample/leachate used for analysis was 50 mL, which is less than the recommended amount of 100 mL. For total metals analysis, the laboratory digested 5 g of each sample, which is more than the recommended sample size of 1 g. Based on information on the run logs (no other source of sample dilution information could be found), 6010 analyses for total metals were conducted at a 5x dilution for all samples, and 6020 analyses for total metals were conducted at a 25x dilution for all samples. The sample sizes and dilutions seem

appropriate.

4. **Reasonableness of total and SPLP results**: One issue that ES did not address in their review was the reasonableness of total and SPLP results, in consideration of the fact that SPLP results reflect a 20x dilution of the sample (and therefore SPLP results should be at least 20x less than total results). A comparison of these results indicates that SPLP results are much higher than expected, based on total results, for antimony and arsenic (all samples), and boron (all samples except DL-EQ-M-4 and DL-EQ-M-6). Because there appears to be no explanation for these discrepancies, based on an examination of the associated QC and laboratory blank data, the results for total and SPLP boron must be considered to be suspect in these samples. Based on comparison of 6010 and 6020 results for total and SPLP antimony and arsenic (see 11 below), the results for total antimony and arsenic must be considered suspect in these samples; the results for SPLP antimony and arsenic are acceptable.

5. **Application of data qualifiers by ES:**

5.1 *Blank contamination:* Based on the trace-level presence of certain target analytes in laboratory and equipment blanks, ES applied U qualifiers to some of the analytical results. The application of these qualifiers was verified in all cases, using the raw data for the blanks. However, I disagreed with the application of the qualifiers in two cases.

ES applied U qualifiers to the results for total thallium in two samples (DL-EQ-M-2 and DL-EQ-M-3) based on detection of thallium in one of the continuing calibration blanks (CCBs) in the associated analytical run. I have removed these qualifiers because the CCB in which thallium was detected was at the beginning of the analytical run and the two samples were near the end of the run. Thallium was not detected in any of the CCBs which bracketed the analysis of these samples.

ES applied U qualifiers to the results for SPLP 6010 manganese in all samples, based on detection of manganese in all associated CCBs. Although application of the qualifier is technically correct, the results of the SPLP 6020 manganese analyses indicate that the levels of manganese detected in the 6010 SPLP analyses are real (i.e., the 6010 and 6020 SPLP manganese results agree very favorably). Therefore, I do not believe that the 6010 SPLP manganese results should be qualified due to blank contamination.

5.2 *Field duplication:* One field duplicate sample was collected with this sample set (DL-EQ-M-4-DUP). Field duplicate precision was evaluated by ES and their calculations were verified as correct. The precision for total cobalt fell outside the QC limits. Based on this, ES qualified the results for total cobalt in samples DL-EQ-M-4 and DL-EQ-M-4-DUP as estimated (J qualifier). Typically, the results of field duplicate analyses are applied to all samples of the same matrix as that of the field duplicate pair. Because all samples in this sample set are of the same matrix (pond sludge), the J qualifier should be applied to the results for total cobalt in all samples.

5.3 *PQLCRI standard:* ES applied J qualifiers to certain results because of high recoveries observed in the PQLCRI standard, which is a standard that contains target analytes at low levels (the practical quantitation limit for each analyte; the practical quantitation limits for each analyte were not defined in the submission). When recoveries outside the QC limits are observed in this standard, results which are less than 3x the level in the standard are qualified as estimated. The qualifiers that ES applied because of this QC exceedance were verified as correct.

5.4 *Negative responses:* ES applied UJ qualifiers to the non-detect results for SPLP thallium in all samples (except DL-EQ-I-2) because a negative response with an absolute value greater than 2x the method detection limit was observed for thallium in the samples. All instances of use of this qualifier have been verified as correct (see below for additional discussion of negative responses for thallium).

5.5 *Results below the reporting limit:* ES applied J qualifiers to all results (that had not been previously qualified) which were reported as greater than the MDL but less than the reporting limit. All applications of this qualifier have been verified as correct. In addition, J qualifiers were applied to certain results for 6010 SPLP manganese from which I had removed the ES-applied U qualifier.

6. **Serial dilution:** A sample from within this sample set was evaluated for serial dilution for SPLP analyses (both 6010 and 6020). In both cases, the percent difference was within QC limits (0-10%) for detected analytes. Serial dilution precision for total metals was evaluated using a sample outside this sample set.

7. **Negative responses for thallium:** As stated previously, negative responses for thallium with an absolute value greater than 2xMDL were observed for most samples in the SPLP analyses. Because of this, the raw data were examined to determine whether any trends could be observed. For the total thallium analyses, a positive response (>MDL) was observed in the first CCB in the analytical run (see above discussion of blank contamination). A positive response (<MDL) was observed in the initial calibration blank (ICB), the ICSA standard, and four of the CCBs. A negative response with an absolute value less than the MDL was observed in the remaining CCBs. No raw data for the method blank were provided. All samples, with the exception of DL-EQ-M-2 and DL-EQ-M-3 which had positive results for thallium greater than the MDL, had slight positive or negative responses for thallium, each with an absolute value less than the MDL. Based on these data, there does not seem to be a problem with thallium in the total metals analysis.

For SPLP thallium analyses, a positive response greater than 2xMDL was observed in the ICSA solution; however, because none of the samples had high levels of the interferents in the ICSA solution, no qualification of data was necessary. A positive response greater than 2xMDL was also observed in the ICB and the first CCB. The remaining CCBs all had slight positive or negative responses for thallium, each with an absolute value less than the MDL. As stated previously, large negative responses were observed in almost all sample results; the absolute values of these responses were of the order of 4-6 times the MDL. Based on the calibration data and the sample results, there does not appear to be a problem with the thallium analysis at the instrument but there may be a problem with the matrix of the samples interfering with SPLP thallium analysis.

8. **Additional issues:** A sample outside this sample set (but within the DuPont sample sets) was used for the matrix spike for total metals; a sample within the sample set was used for a matrix spike for SPLP metals. No qualifiers due to matrix spike recoveries were applied to the data in Table 6; therefore the use of a sample outside the sample set is not an issue.

   The laboratory did not analyze any laboratory duplicates or matrix spike duplicates for ICP-MS. Although this means that the laboratory did not fulfill all QC requirements of the method, this is not considered to affect the quality of the data, in consideration of the fact that field duplicate precision was generally quite good.

9. **Internal standard recoveries:** Internal standard recoveries for 6020 analyses (both total and SPLP) were well within the QC limits of 30-120% for all samples (recoveries were 89-112%). No trend in recovery values was observed.

10. **Manganese linear range:** For 6020 analyses, the calibration verification standard for manganese was at 100 µg/L and the laboratory control standard was at 200 µg/L. Because all raw data results for manganese from 6020 analyses were << 100 µg/L, and because the calibration verification standard is supposed to near the midpoint of the linear range, it can be concluded that no 6020 manganese results were outside the linear range of the instrument.

11. **Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium:** Although the laboratory did not report 6010 results for antimony, arsenic, and thallium, results for these analytes were included in the raw data. The raw data results for 6010 antimony, arsenic, and thallium were compared to the reported results for 6020 antimony, arsenic, and thallium; see Table 6. These results have been added to Table 6. The 6010 results for thallium were not useful for comparison as all responses were less than the MDL of 7.1 mg/kg (total) or 0.053 mg/L (SPLP) or were negative (absolute value <2xMDL). For total arsenic, 6010 results were all less than the MDL of 3.1 mg/kg or were negative (absolute value <3xMDL). Results for 6010 SPLP arsenic generally agreed with the 6020 SPLP arsenic results. We note that the MDL for 6010 total arsenic was more than 20x the MDL for 6010 SPLP arsenic; therefore, it would be possible for samples to contain detectable levels of 6010 SPLP arsenic that would be non-detectable in the total 6010 analyses.

    For total antimony, the 6010 results were of an order of magnitude higher than those for 6020 total antimony. The results for 6010 SPLP antimony generally agreed with the 6020 SPLP antimony results, although all were less than the MDL of 0.031 mg/L. As stated previously, the results for 6020 total antimony and 6020 SPLP antimony, as well as for 6020 total arsenic and

6020 SPLP arsenic, did not agree (when the 20x “dilution” is taken into consideration). Based on the 6010/6020 comparisons, it appears that the 6020 SPLP antimony and arsenic results are correct and that the 6020 total antimony and arsenic results are suspect.

<u>Summary of Applied Data Qualifiers</u>:

Qualifier	Reason	Analyte	Samples
U	This analyte was present in an associated blank.	B - total	DL-EQ-I-2, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
		Cr - SPLP	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-3
		Fe - SPLP	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
U	ES reported an incorrect (too low) MDL for this analyte.	As - total	DL-EQ-M-1
J	Poor field duplicate precision indicates that these results should be considered to be estimated.	Co - total	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
J	High recovery of a quantitation limit standard indicates that these results should be considered to be estimated.	Ni - total	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
UJ	Negative results with an absolute value greater than twice the MDL indicates that the MDLs may be higher than reported.	Tl - SPLP	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
J	Because results are greater than the MDL but less than the reporting limit, results should be considered to be estimated.	Sb - total	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
		Ba - total	DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-2
		B - SPLP	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
		Pb - total	DL-EQ-M-1
		Pb - SPLP	DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5
		Mn - SPLP (6010B)	DL-EQ-I-1, DL-EQ-I-2, DL-EQ-I-3, DL-EQ-M-1, DL-EQ-M-2, DL-EQ-M-3, DL-EQ-M-4, DL-EQ-M-5, DL-EQ-M-6
		Ni - SPLP	DL-EQ-M-3
		Tl - total	DL-EQ-M-3

Constituent of concern	Analysis	Table 6: Equalization Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-EQ-I-1	DL-EQ-I-2	DL-EQ-I-3	DL-EQ-M-1	DL-EQ-M-2	DL-EQ-M-3	DL-EQ-M-4	DL-EQ-M-5	DL-EQ-M-6	Average	
% Moisture		82.8	85.1	82.1	83.1	81.8	77.2	85.3	78.7	78.4	81.6	69.6
Antimony	Total-6010B	<2.2	2.3	<2.2	4.2	3.0	<2.2	5.7	5.0	4.7		0.7
	Total-6020	0.18 J	0.11 J	0.11 J	0.33 J	0.11 J	0.091 J	0.095 J	0.068 J	0.12 J	0.13	
	SPLP-6010B	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031	0.021
	SPLP-6020	0.012	0.024	0.013	0.014	0.0064	0.021	0.0080	0.0088	0.010	0.013	
Arsenic	Total-6010B	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	2.8
	Total-6020	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4		
	SPLP-6010B	0.11	0.13	0.12	0.096	0.078	0.11	0.12	0.10	0.054	0.10	<0.0035
	SPLP-6020	0.14	0.15	0.11	0.090	0.089	0.12	0.13	0.10	0.077	0.11	
Barium	Total	28.6	15.5 J	19.2 J	25.0	17.0 J	24.4	22.7	21.3	23.5	21.9	49.6
	SPLP	0.20	0.46	0.48	0.58	0.57	0.27	0.33	0.27	0.41	0.40	0.12
Boron	Total	<0.4	0.52 U	<0.4	0.62 U	0.62 U	0.44 U	4.8 U	0.68 U	1.7 U	1.1	24.5
	SPLP	0.071 J	0.094 J	0.092 J	0.11 J	0.10 J	0.066 J	0.094 J	0.062 J	0.083 J	0.086	0.45
Chromium	Total	6.9	5.1	5.1	3.1	3.1	9.5	4.6	5.8	3.8	5.2	499

Constituent of concern	Analysis	Table 6: Equalization Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-EQ-I-1	DL-EQ-I-2	DL-EQ-I-3	DL-EQ-M-1	DL-EQ-M-2	DL-EQ-M-3	DL-EQ-M-4	DL-EQ-M-5	DL-EQ-M-6	Average	
Chromium	SPLP	0.0085 J	0.011 U	0.0089 U	ND	ND	0.011 U	ND	ND	ND		<0.005
Cobalt	Total	0.7	0.35 J	0.52	0.36 J	0.97	0.22 J	2.2 J	0.4 J	0.92	0.74	7
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		<0.005
Iron	Total	338	184	213	157	220	267	434	272	307	266	63,200
	SPLP	0.090 U	0.099 U	0.11 U	0.069 U	0.12 U	0.063 U	0.20 U	0.054 U	0.13 U	0.103	2.2
Lead	Total	0.92	0.58	0.63	0.39 J	0.53	0.87	1.1	0.87	0.72	0.73	42.4
	SPLP	0.0017	0.0012	0.0020	0.00079 J	0.00054 J	0.00070 J	0.00077 J	0.00058 J	0.0016	0.0011	0.002 (1)
Manganese	Total-6010B	17.2	9.9	11.0	8.4	11.2	15.4	19.5	13.2	12.5	13.0	2,890
	Total-6020	17.3	10.4	11.3	8.9	11.4	15.3	17.9	11.9	11.3		
	SPLP-6010B	0.0023 J	0.0036 J	0.0038 J	0.0033 J	0.0033 J	0.0028 J	0.0026 J	0.0020 J	0.0046 J	0.003	1.5
	SPLP-6020	0.0028	0.0037	0.0047	0.0034	0.0036	0.0021	0.0026	0.0014	0.0053		
Nickel	Total	9.6 J	5.2 J	6.9 J	3.6 J	4.5 J	17.1	8.9 J	9.2 J	6.6 J	7.9	59.8
	SPLP	<0.016	<0.016	<0.016	<0.016	<0.016	0.018 J	<0.016	<0.016	<0.016		0.007
Thallium	Total-6010B	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	7.2

Constituent of concern	Analysis	Table 6: Equalization Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-EQ-I-1	DL-EQ-I-2	DL-EQ-I-3	DL-EQ-M-1	DL-EQ-M-2	DL-EQ-M-3	DL-EQ-M-4	DL-EQ-M-5	DL-EQ-M-6	Average	
Thallium	Total-6020	<0.18	<0.18	<0.18	<0.18	0.84	0.25 J	<0.18	<0.18	<0.18		
	SPLP-6010B	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.0022
	SPLP-6020	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ		
Vanadium[7]	Total	29.4	31.0	31.6	36.1	25.3	22.9	31.6	20.3	35.8	29.3	1,060
	SPLP	0.94	0.63	0.81	0.91	0.67	0.4	1.0	0.41	0.66	0.71	<0.005
pH of SPLP leachate	SPLP	9.01	9.24	9.35	8.82	9.30	9.37	9.51	9.37	8.87		7.489

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[7] Note that all vanadium SPLP values exceed the HBL of 0.14.

Volume 6

Disengagement Basin Sludge- DeLisle Plant, Pass Christian, MS

Subject: Revised QA/QC Review of "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the DeLisle Plant Disengagement Basin in Pass Christian, Mississippi for the DuPont Engineering TiO2 Listing Project"

By: Kelly Luck, Senior Data Validator, Dynamac Corporation

Date: March 9, 2001

The analytical results for pond sludge samples collected by DuPont at the DeLisle Plant Disengagement Basin and analyzed by Severn Trent Laboratories (West Sacramento, CA) were subjected to a quality assurance review by Environmental Standards, Inc. (Valley Forge, PA). The results of their review were submitted in a document entitled "Quality Assurance Review of the Pond Sludge Samples Collected on October 20, 2000, at the DeLisle Plant Equalization Basin in Pass Christian, Mississippi for the DuPont Engineering TiO2 Listing Project", December 13, 2000. The Environmental Standards QA review has been examined to verify the correctness of their conclusions and to make overall conclusions regarding the quality of the analytical data for the pond sludge samples. This report was revised on March 9, 2001 following receipt and evaluation of the entire laboratory data package from DuPont. The sections pertaining to "Verification of results," "Sample size and dilutions," and "Reasonableness of total and SPLP results" under "Detailed Considerations" were revised. In addition, three new sections, "Internal standard recoveries," "Manganese linear range," and "Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium" were added. Table 7 was revised to add qualifiers to certain total arsenic results and to add the results for 6010 antimony, arsenic, and thallium.

Notes:

1. The analytical results for the samples, with the applied data qualifiers, are listed in Table 7 below.

2. Analytical results for only the following metals (both total and SPLP) were examined in this review: antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium.

3. Results for the following samples were examined and considered in this review: DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, and DL-DB-M-6. One equipment blank (DL-DB-EQBLK) and one field duplicate sample were collected (DL-DB-I-1-DUP) and the results for these samples were examined to evaluate the potential for blank contamination and the field duplicate precision, respectively. However, the results for these field QC samples are not reported in Table 7.

Conclusions:

The QA review conducted by Environmental Standards (ES) was very thorough, involving examination of all QC requirements for the methods (initial and continuing calibration, laboratory and equipment blanks, interference check samples, matrix spike recoveries, field duplicates, laboratory control samples, serial dilutions, and sample quantitation). Based on the raw data included in the submission, ES verified the reported results for all samples and QC results, and used the raw data to evaluate QC data for which summary tables were not provided (such as for initial and continuing calibration verification recoveries). The data qualifiers applied by ES are appropriate and have been verified by this data reviewer, except as discussed below under "Detailed Considerations."

Except for total antimony and total and SPLP boron, the analytical results for these samples are acceptable. Although there were some QC results outside the specified QC limits, none of the QC results indicate that any of the results in Table 7 should be rejected.

Detailed Considerations:

1. **Verification of results:** The reported results in Table 7 for antimony, arsenic, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, thallium, and vanadium (total and SPLP) in each sample were verified from raw data in the laboratory data package. For total metals results (both 6010 and 6020), the laboratory did not use the actual sample weight (which varied from 5.00 g to 5.03 g) in their calculations but simply used a value of 5. This resulted in some differences in the results calculated from the raw data versus those reported in Table 7. Because the laboratory did not use the actual sample weight in their calculations, the results for total metals (both 6010 and 6020) in all samples should only be considered to be accurate to 2 significant figures.

   Because the laboratory did not account for dilutions in their reporting of MDLs and RLs, ES re-calculated the MDLs and RLs to account for dilutions, and reported these recalculated values. It appears that ES re-calculated the MDL for 6020 total arsenic incorrectly: based on a laboratory-reported MDL of 0.08 mg/kg and a dilution factor of 5 for 6020 total metal analyses (25x dilution divided by 5 g sample weight for all samples), the correct MDL should be 0.4 mg/kg, not 0.25 mg/kg as reported by ES. Using the correct MDL, some results for 6020 total arsenic reported in Table 7 should be considered to be non-detectable. I have applied a "U" qualifier to these results in Table 7.

2. **pH results:** The reported pH of the final SPLP leachate was added to Table 7 for all samples except DL-DB-I-2; the result for this sample was illegible in the data submission. The report did not include any data pertaining to sample pH.

3. **Sample size and dilutions:** The laboratory used the standard sample size (100 g) for SPLP extractions except that less than 100 g was used for samples DL-DB-M-1 (54 g), DL-DB-M-2 (46 g), DL-DB-M-4 (63 g), and DL-DB-M-5 (79 g); the extraction fluid volume

was adjusted accordingly. The volume of sample/leachate used for analysis was 50 mL, which is less than the recommended amount of 100 mL. For total metals analysis, the laboratory digested 5 g of each sample, which is more than the recommended sample size of 1 g. Based on information on the run logs (no other source of sample dilution information could be found), 6010 analyses for total metals were conducted at a 5x dilution for all samples, and 6020 analyses for total metals were conducted at a 25x dilution for all samples. The sample sizes and dilutions seem appropriate.

4. **Reasonableness of total and SPLP results:** One issue that ES did not address in their review was the reasonableness of total and SPLP results, in consideration of the fact that SPLP results reflect a 20x dilution of the sample (and therefore SPLP results should be at least 20x less than total results). A comparison of these results indicates that SPLP results are much higher than expected, based on total results, for antimony (for samples DL-DB-I-1, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, and DL-DB-M-3), and boron (samples DL-DB-M-1, DL-DB-M-2, and DL-DB-M4). Because there appears to be no explanation for these discrepancies, based on an examination of the associated QC and laboratory blank data, the results for total and SPLP boron must be considered to be suspect in these samples. Based on comparison of 6010 and 6020 results for total and SPLP antimony (see 11 below), the results for total antimony must be considered suspect in these samples; the results for SPLP antimony are acceptable.

5. **Application of data qualifiers by ES:**

5.1 *Blank contamination:* Based on the trace-level presence of certain target analytes in laboratory and equipment blanks, ES applied U qualifiers to some of the analytical results. The application of these qualifiers was verified in all cases. However, I disagreed with the application of the qualifiers in two analyses.

The ES-applied U qualifiers to the results for total barium in one sample (DL-DB-M-3), total chromium in three samples (DL-DB-I-2, DL-DB-M-1, and DL-DB-M-2), and total thallium in two samples (DL-DB-I-1, and DL-DB-M-6) are not appropriate. ES applied these qualifiers based on the levels of these analytes detected in the continuing calibration blanks (CCBs) in the analytical run. I have removed these qualifiers because the CCBs which were used in applying these qualifiers were not CCBs that bracketed the analysis of samples in the analytical run. Only CCBs which bracketed the analysis of the samples in this sample set should be used in determining when to apply qualifiers for blank contamination.

ES applied U qualifiers to the results for total 6020 manganese in some samples and to the results for SPLP 6010 manganese in all samples, based on detection of manganese in associated blanks. Although application of these qualifiers is technically correct, the results of the total 6010 manganese analyses indicate that the levels of manganese detected in the 6020 total analyses are real. Similarly, the SPLP 6020 manganese analyses indicate that the levels of manganese detected in the 6010 SPLP analyses are real. Therefore, I do not believe that the

6020 total manganese or 6010 SPLP manganese results should be qualified due to blank contamination and I have removed these qualifiers.

5.2 *Field duplication:* One field duplicate sample was collected with this sample set (DL-DB-I-1-DUP). Field duplicate precision was evaluated by ES and these results were verified as correct. All results fell within QC limits.

5.3 *PQLCRI standard:* ES applied J qualifiers to certain results because of high recoveries observed in the PQLCRI standard, which is a standard that contains target analytes at low levels (the practical quantitation limit for each analyte; the practical quantitation limits for each analyte were not defined in the submission). When recoveries outside the QC limits are observed in this standard, results which are less than 3x the level in the standard are qualified as estimated. The qualifiers that ES applied because of this QC exceedance were verified. In addition, this qualifier was applied to the results for total chromium in samples DL-DB-I-2, DL-DB-M-1, DL-DB-M-2, DL-DB-M-4, and DL-DB-M-6 and to the results for 6010 total manganese in samples DL-DB-I-2, DL-DB-M-2, DL-DB-M-4, and DL-DB-M-5. ES had qualified these results with a U which I had removed.

5.4 *Negative responses:* ES applied UJ qualifiers to the non-detect results for SPLP thallium in all samples because a negative response with an absolute value greater than 2x the method detection limit was observed for thallium in the samples. All instances of use of this qualifier have been verified as correct (see below for additional discussion of negative responses for thallium).

5.5 *Results below the reporting limit:* ES applied J qualifiers to all results (that had not been previously qualified) which were reported as greater than the MDL but less than the reporting limit. All applications of this qualifier have been verified. In addition, J qualifiers were applied to certain results for 6020 total manganese and all results for 6010 SPLP manganese because all results were greater than the MDL but less than the reporting limit; ES had qualified these results with a U which I had removed.

6. **Serial dilution:** A sample from within this sample set was evaluated for serial dilution for total metals analyses (both 6010 and 6020); for SPLP, a sample outside the set was used for serial dilution analyses. For SPLP, the percent difference was within QC limits (0-10%) for detected analytes. For total metals, the percent difference was outside the QC limits for 6020 manganese (at 11.6%). Because of this, the results for 6020 total manganese were correctly qualified with a J by ES.

7. **Negative responses for thallium:** As stated previously, negative responses for thallium with an absolute value greater than 2xMDL were observed for most samples in the SPLP analyses. Because of this, the raw data were examined to determine whether any trends could be observed. For the total thallium analyses, a positive response (>MDL) was observed in the ICSA; however, because none of the samples had high levels of the interferents in the ICSA

solution, no qualification of data was necessary. The associated CCBs all had slight positive or negative responses for thallium, each with an absolute value less than the MDL. All samples, with the exception of DL-DB-I-1 and DL-DB-M-6, which had positive results for thallium greater than the MDL, had slight positive or negative responses for thallium, each with an absolute value less than the MDL. Based on these data, there does not seem to be a problem with thallium in the total metals analysis.

For SPLP thallium analyses, a positive response greater than 2xMDL was observed in the ICSA solution; however, because none of the samples had high levels of the interferents in the ICSA solution, no qualification of data was necessary. A positive response greater than 2xMDL was also observed in the ICB. The associated CCBs all had slight positive or negative responses for thallium, each with an absolute value less than the MDL. As stated previously, large negative responses were observed in the sample results; the absolute values of these responses were of the order of 6-7 times the MDL. Based on the calibration data and the sample results, there does not appear to be a problem with the thallium analysis at the instrument but there may be a problem with the matrix of the samples interfering with SPLP thallium analysis.

8. **Additional issues:** A sample outside this sample set (but within the DuPont sample sets) was used for the matrix spike for SPLP metals; a sample within the sample set was used for a matrix spike for total metals. No qualifiers due to matrix spike recoveries were applied to the data in Table 7; therefore the use of a sample outside the sample set is not an issue.

   The laboratory did not analyze any laboratory duplicates or matrix spike duplicates for ICP-MS. Although this means that the laboratory did not fulfill all QC requirements of the method, this is not considered to affect the quality of the data, in consideration of the fact that field duplicate precision was generally quite good.

9. **Internal standard recoveries:** Internal standard recoveries for 6020 analyses (both total and SPLP) were well within the QC limits of 30-120% for all samples (recoveries were 72-120%). No trend in recovery values was observed..

10. **Manganese linear range:** For 6020 analyses, the calibration verification standard for manganese was at 100 µg/L and the laboratory control standard was at 200 µg/L. Because all raw data results for manganese from 6020 analyses were << 100 µg/L, and because the calibration verification standard is supposed to near the midpoint of the linear range, it can be concluded that no 6020 manganese results were outside the linear range of the instrument.

11. **Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, and thallium:** Although the laboratory did not report 6010 results for antimony, arsenic, and thallium, results for these analytes were included in the raw data. The raw data results for 6010 antimony, arsenic, and thallium were compared to the reported results for 6020 antimony, arsenic, and thallium; see Table 7. The 6010 results for thallium were not useful for comparison

as all responses were less than the MDL of 7.1 mg/kg (total) or 0.053 mg/L (SPLP) or were negative (absolute value <2xMDL). For total arsenic, 6010 results were all less than the MDL of 3.1 mg/kg or were negative (absolute value <MDL). Results for 6010 SPLP arsenic generally agreed with the 6020 SPLP arsenic results, although the MDL (0.043 mg/L) was much higher for 6010 analyses.

For total antimony, the 6010 results were of an order of magnitude higher than those for 6020 total antimony. The results for 6010 SPLP antimony generally agreed with the 6020 SPLP antimony results, although the MDL (0.031 mg/L) was much higher for 6010 analyses. As stated previously, the results for 6020 total antimony and 6020 SPLP antimony did not agree (when the 20x "dilution" is taken into consideration). Based on the 6010/6020 comparisons, it appears that the 6020 SPLP antimony results are correct and that the 6020 total antimony results are suspect.

Summary of Applied Data Qualifiers:

Qualifier	Reason	Analyte	Samples
U	This analyte was present in an associated blank.	Ba - total	DL-DB-M-1
		B - total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
		Cr - total	DL-DB-M-4
		Fe - SPLP	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-6
		Pb - total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
		V - SPLP	DL-DB-M-5
U	ES reported an incorrect (too low) MDL for this analyte.	As - total	DL-DB-M-1, DL-DB-M-5
J	Poor precision in serial dilution analyses indicates that these results should be considered to be estimated.	Mn - 6020 total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
J	High recovery in a quantitation limit standard indicates that these results should be considered to be estimated.	Cr - total	DL-DB-I-2, DL-DB-M-1, DL-DB-M-2, DL-DB-M-5, DL-DB-M-6
		Mn - 6010 total	DL-DB-I-2, DL-DB-M-2, DL-DB-M-4, DL-DB-M-5
		Ni - total	DL-DB-I-1, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
UJ	Negative results with an absolute value greater than twice the MDL indicates that the MDLs may be higher than reported.	Tl - SPLP	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
J	Because results are greater than the MDL but less than the reporting limit, results should be considered to be estimated.	Sb - total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5
		As - total	DL-DB-M-2
		Ba - total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
		Ba - SPLP	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
		B - SPLP	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-3, DL-DB-M-4, DL-DB-M-5, DL-DB-M-6
		Co - total	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-5, DL-DB-M-6
		Pb - SPLP	DL-DB-I-3, DL-DB-M-1, DL-DB-M-2, DL-DB-M-4, DL-DB-M-5
		Mn - 6010	DL-DB-I-1, DL-DB-I-2, DL-DB-I-3, DL-DB-M-1,

Qualifier	Reason	Analyte	Samples
		Tl - total	DL-DB-I-1
		V - SPLP	DL-DB-I-2

Constituent of concern	Analysis	Table 7, Disengagement Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-DB-I-1	DL-DB-I-2	DL-DB-I-3	DL-DB-M-1	DL-DB-M-2	DL-DB-M-3	DL-DB-M-4	DL-DB-M-5	DL-DB-M-6	Average	
% Moisture		92.4	91.2	92.5	96.9	96.8	90.3	94.5	93.6	93.2	93.5	69.6
Antimony	Total-6010B	7.4	3.0	4.6	2.9	3.0	3.8	4.2	<2.2	6.6		0.7
	Total-6020	0.77 J	0.49 J	0.41 J	0.16 J	0.24 J	0.059 J	0.73 J	0.11 J	1.1	0.452	
	SPLP-6010B	0.068	<0.031	0.052	<0.031	<0.031	<0.031	<0.031	<0.031	<0.031		0.021
	SPLP-6020	0.076	0.014	0.057	0.014	0.021	0.012	0.015	0.0045	0.021	0.026	
Arsenic	Total-6010B	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	2.8
	Total-6020	3.7	1.6	2.3	<0.4 J	0.45 J	<0.4	2.1	<0.4 J	2.7	1.5	
	SPLP-6010B	0.16	<0.043	0.090	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043		<0.0035
	SPLP-6020	0.14	0.0077	0.078	0.0066	0.012	0.011	0.010	0.0047	0.012	0.031	
Barium	Total	11.9 J	11.1 J	10.4 J	1.8 U	2.2 U	4.8 J	5.8 J	8.9 J	13.1 J	7.8	49.6
	SPLP	0.11 J	0.072 J	0.088 J	0.10 J	0.096 J	0.084 J	0.10 J	0.095 J	0.089 J	0.093	0.12
Boron	Total	2.1 U	1.0 U	1.5 U	1.8 U	1.7 U	2.3 U	0.94 U	5.1 U	1.8 U	2.0	24.5

Constituent of concern	Analysis	Table 7, Disengagement Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-DB-I-1	DL-DB-I-2	DL-DB-I-3	DL-DB-M-1	DL-DB-M-2	DL-DB-M-3	DL-DB-M-4	DL-DB-M-5	DL-DB-M-6	Average	
	SPLP	0.065 J	0.043 J	0.061 J	0.12 J	0.15 J	0.063 J	0.090 J	0.096 J	0.067 J	0.084	0.45
Chromium	Total	7.6	2.3 U	10.1	2.5 U	2.1 U	3.8	1.4 U	2.1 U	2.6 U	3.8	499
Chromium	SPLP	ND	ND	ND	ND	ND	ND	ND	ND	ND		<0.005
Cobalt	Total	0.19 J	0.068 J	0.20 J	0.078 J	0.081 J	0.52	<0.05	0.2 J	0.088 J	0.16	7
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		<0.005
Iron	Total	312	100	375	175	118	311	63.1	170	127	194	63,200
	SPLP	0.0093 U	0.0058 U	0.0064 U	0.034 U	0.037 U	0.0058	0.062 U	ND	0.0098 U	0.021	2.2
Lead	Total	0.44 U	0.25 U	0.47 U	0.20 U	0.11 U	0.57 U	0.16 U	0.26 U	0.25	0.3	42.4
	SPLP	<0.00015	<0.00015	0.00046 J	0.00022 J	0.00085 J	<0.00015	0.00017 J	0.00018 J	<0.00015	0.00046	0.002 (1)

Constituent of concern	Analysis	Table 7, Disengagement Basin, Delisle										Comparable EPA Sample (DPN-SO-01)
		DL-DB-I-1	DL-DB-I-2	DL-DB-I-3	DL-DB-M-1	DL-DB-M-2	DL-DB-M-3	DL-DB-M-4	DL-DB-M-5	DL-DB-M-6	Average	
Manganese	Total-6010B	8.3	3.7 J	9.7	4.5	3.3 J	8.9	3.2 J	3.4 J	5.5	5.46	2,890
	Total-6020	8.1 J	3.7 J	8.6 J	4.1 J	2.9 J	8.2 J	3.4 J	3.6 J	5.1 J		
	SPLP-6010B	0.0010 J	0.0025 J	0.0014 J	0.0084 J	0.0098 J	0.0018 J	0.011 J	0.0063 J	0.0040 J	0.0053	1.5
	SPLP-6020	0.0012	0.0025	0.0020	0.0091	0.011	0.0014	0.011	0.0067	0.0036		
Nickel	Total	12.0 J	<1.8	16.6	<1.8	<1.8	9.5 J	2.5 J	3.5 J	2.1 J	5.4	59.8
	SPLP	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016		0.007
Thallium	Total-6010B	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1		7.2
	Total-6020	0.24 J	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	0.59		
	SPLP-6010B	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053	<0.0022
	SPLP-6020	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ	<0.0001 UJ		
Vanadium	Total	114	36.8	76.0	17.7	20.7	44.4	27.4	22.4	60.9	46.7	1,060
	SPLP	0.48	0.038 J	0.34	0.060	0.083	0.052	0.080	0.0066 U	0.11	0.14	<0.005
pH of SPLP leachate	SPLP	8.24	0	7.93	7.75	7.64	7.61	7.67	7.45	7.73		7.489

* This value was illegible in the data package as received.

Volume 7

Iron Rich^{TM} Filter Cake- Edge Moor Plant, Wilmington, DE

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

MEMORANDUM

To: Shen-yi Yang, EPA OSW
From: Ray Anderson, SAIC
Subject: Data Review of Dupont Edgemoor, Volume 7
Date: February 12, 2001

Data review and validation were performed on the laboratory analytical results for 8 solid, 1 equipment blank, and 1 field duplicate samples collected from the Dupont Edgemoor facility over a 4-day period from October 18, 2000 to October, 22, 2000. The samples were submitted on October 23, 2000 by Dupont to Severn Trent Laboratories, STL in West Sacramento, CA. STL received all samples noted on chain-of-custody (COC) documentation on October 24, 2000. In addition, STL also received the field duplicate sample (EMI-6 dup) which was not designated on the COC. The analytical report from STL and validated by Environmental Standards, contained the sample results for total, TCLP, SPLP metals, and percent moisture. All analyses were performed using SW-846 methodology which included ICP Method 6010 for Al, Ba, Be, B, Cr, Co, Cu, Fe, Mn, Mo, Ni, Ag, Sn, V, and Zn; and ICP-MS Method 6020 for Sb, As, Cd, Pb, Mn, Se, and Tl. The analytical data package designated as “Volume 7 Iron Rich^{TM} Edge Moor Plant” included the data validation report dated December 13, 2000 from Environmental Standards. Due to missing information in the STL analytical report as provided, it is impossible to completely verify and validate the summarized sample and quality assurance data results. Given the available laboratory data along with validation report the following observations are noted:

Observations

! It is unclear when the original analytical report from STL was delivered to either Dupont or Environmental Standards. Based on the correspondence letter from STL to Environmental Standards dated November 10, 2000, one can assume the original laboratory report was probably dated the first week of November 2000. The actual date is not important, however, given the laboratory received the samples on October 24, 2000 they were able to complete the total and leachate analyses, do a comprehensive data review, and submit a full data package in order to support a complete independent data validation effort in approximately 2 weeks. Although this accomplishment is not impossible, the typical laboratory analysis turnaround is 3 to 4 weeks for a complete analytical data package. Frequently, when the laboratory is required to accelerate the turnaround time the number of reanalyses are limited, quality control analyses are not always project-specific, and the amount of time allotted for internal data review and report preparation is limited. As a result the overall data quality and usability is sometimes questionable.

! The Volume 7 report appears to have been prepared by Environmental Standards and does not include the full laboratory analytical data package. There are numerous gaps in the laboratory data pagination that confirm the report is less than complete. For example, all ICP total analyses, except the 10X dilution for EMI-1, and all ICP and ICP-MS SPLP analyses are missing the instrument raw data output. In addition, all matrix spike/matrix spike duplicate (MS/MSD) and laboratory control standards (LCS) raw data were not present. Without these laboratory data it is impossible to completely verify the validation report findings and the summarized analytical data.

! For some reason Environmental Standards selectively choose to include those sections of the laboratory data package in order to support their overall data assessment. In many instances the original laboratory raw data were corrected and revised by Environmental Standards. These handwritten revisions that include changes to the sample ID, dilution factor, method detection limit, reported result, and laboratory assigned qualification were usually accompanied by a logical explanation, however, in most cases the revisions were not dated or initialed by the responsible party. Good Laboratory Practices (GLP) dictate that all raw data corrections using a single line through the error should be initialed and dated by the responsible individual. It is therefore assumed that the majority of the uninitialed corrections were performed by Environmental Standards with hopefully, the laboratory's agreement. It is noted in the validation report that the laboratory was asked to provide additional revised data to respond to the initial validation findings. However, aside from the leachate preparation logs, all the remaining laboratory data appear to be the original version with handwritten marked-up corrections.

! There were no detection limit study data provided to substantiate the reported method detection limits (MDLs) and the sample data reporting limits (Rls). Typically, these studies are done on a quarterly basis or more frequently if major instrument maintenance is required.

! Nearly all continuing calibration blanks (CCBs) associated with the ICP total analyses contained trace level contaminants greater than the MDLs. In addition the practical quantitation standard (PQLCRI) recovery was greater than 115% for Ba, Co, Fe, Mo, Sn, and Zn. This was also followed with high positive results for Ba and Zn, and large negative results for B and Mn in the interference check sample (ISCA). The CCB results together with the high PQLCRI recoveries are an indication of possible laboratory induced contamination and should be considered when using any sample concentration near the reporting limit. The ISCA results suggest that the high levels of Fe detected in all samples probably affected the ability to detect B, Ba, Mn, and Zn at concentrations below the respective levels spiked into the ISCAB. The exact concentrations are unknown, since this information was not provided by the laboratory.

! The ICP-MS total and leachate analyses for Tl were very erratic and unstable below the initial and continuing calibration (ICV and CCV) concentration of 40 ppb. The TCLP and SPLP analyses were performed on October 30, 2000 while the total analyses were performed on October 31, 2000. On each day the initial calibration blank (ICB) concentration for Tl exceeded the reported MDLs. In addition, 6 of the 8 continuing calibration blanks (CCBs) associated with the total analyses contained Tl contamination above the MDL. Conversely, the CCBs associated with the leachate analyses initially yielded positive responses for Tl, however, after the first TCLP analysis all the subsequent CCBs and TCLP samples exhibited negative responses for Tl. The SPLP responses for Tl could not be verified since the raw data were not provided. These erratic Tl responses are either an indication the instrumentation is unstable at concentrations below 40 ppb or the leachate matrices adversely affected the ability to reliably detect a low-level Tl concentration.

! The validation report indicated that the laboratory choose to dilute all ICP-MS SPLP samples by a factor of five prior to analyses due to high levels of chloride present. It is unclear how this decision was made since chloride was not a target analyte and the ICP SPLP analyses were performed without dilution. Furthermore, assuming chloride is a potential ICP-MS interference it is not clear if the laboratory spiked the ICSA and ICSAB with chloride to measure what if any affect it’s presence may have hindered the target analyte detection.

! There is no reference to the preparation methods used to digest the total and leachate samples. In addition, the TCLP and SPLP logs sheets do not specifically state SW-846 methods were used and this information was submitted by STL to Environmental Standards after the original report was delivered. Furthermore, the start and end times for the TCLP and SPLP samples are exactly the same. This is somewhat unusual since there were a total 20 samples to leach and the leaching fluids are different between the TCLP and SPLP.

! Even after acknowledging the missing laboratory data, the report is very disorganized and difficult to follow in the format prepared by Environmental Standards. This together with a less than accurate laboratory case narrative and the numerous data validation corrections are an indication the laboratory hastily performed the required analyses at the expense of meeting all the data quality objectives.

! The average TCLP leachate final pH is slightly more basic while the average SPLP leachate final pH is slightly more acidic than the respective final leachate ph for EPA sample DPE-SO-01. These pH differences are probably not substantial enough to explain any differences in the Dupont as compared to the EPA leachate data. However, the high total Fe concentrations detected in the Dupont samples may have inhibited the leaching of other more toxic metals.

Conclusions:

Given the incomplete laboratory data package provided to supplement Environmental Standard’s data validation report, a comprehensive data review and verification is not possible. At a minimum all laboratory raw data used to support the sample and quality assurance summary results are necessary in order to adequately assess the data validity, adherence to the required data quality objectives, and the overall data usability. In the absence of any additional laboratory data, the STL reported sample results that were further qualified by Environmental Standards should be used with caution since the overall validity is questionable at this time.

Review Summary for Dupont's Analytical Data Report (Volume 7)
Edge Moor Plant, Wilmington, Delaware
Iron Rich^{TM} Filter Cake Samples Collected from Titanium Dioxide Manufacturing Process
for the DuPont Engineering Titanium Dioxide Listing Project

Shen-yi Yang
February 26, 2001

Introduction:

The purpose of this review is to evaluate the validity of Dupont's waste analysis submitted in response to our K178 listing proposal. DuPont collected Iron Rich^{TM} filter cake samples on October 18, 19, 20, 21, and 22, 2000 at its Edge Moor Plant, Wilmington, Delaware. All samples were received by Seven Trent Lab (STL) located in West Sacramento, California on October 24, 2000 and analyzed for total concentrations of 16 metals (aluminum, barium, beryllium, boron, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, tin, vanadium, silver, and zinc) by EPA SW-846 Method 6010B (ICP); for total concentrations of 9 metals (antimony, arsenic, beryllium, cadmium, cobalt, lead, manganese, selenium, and thallium) by EPA SW-846 Method 6020 (ICPMS). Samples were also analyzed for SPLP and TCLP concentrations of 15 metals (aluminum, barium, beryllium, boron, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, tin, vanadium, silver, and zinc) by EPA SW-846 Method 6010B (ICP); and for SPLP and TCLP concentrations of 7 metals (antimony, arsenic, cadmium, lead, manganese, selenium, and thallium) by EPA SW-846 Method 6020 (ICPMS). STL's data package was sent to Environmental Standards (ES) in Valley Forge, PA on November 6, 2000 for validation. DuPont submitted for our review STL's analytical results and ES' review summary in a document entitled "Quality Assurance Review of the Iron Rich^{TM} Filter Cake Process Solid Samples Collected on October 18, 19, 20, 21, and 22, 2000 at the Edge Moor Plant in Wilmington, Delaware for the DuPont Engineering TiO2 Listing Project", December 13, 2000".

This data package includes 8 solid samples, 1 field duplicate, and 1 equipment blank. The sample identification numbers are: EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-6DUP, EMI-7, EMI-8, Equipment Blank. My review focused on the validity of total and TCLP/SPLP concentrations of four constituents of concern (i.e., antimony, arsenic, manganese, and thallium). STL presented data in a CLP-like package. DuPont reported two sets (ICP and ICPMS) of results for manganese and one set (i.e., ICPMS) of results for antimony, arsenic, and thallium. While they did not report ICP results for antimony, arsenic, and thallium, these analyses were automatically conducted when STL ran the ICP analyses for other metals. We obtained STL's CLP-like data package on 2/16/01 and also assessed these results.

Conclusions:

The quality of the ICPMS analytical results for antimony, arsenic, manganese, and thallium is questionable and the quality of the ICP analytical results for antimony, arsenic, manganese, and thallium is acceptable. The following Table shows my assessment of the quality of the ICPMS total and TCLP/SPLP results of all samples for antimony, arsenic, manganese and thallium. See "Detailed Discussions" for reasons why these data points were rejected or suspect.

Analyte	ICPMS-Total	ICPMS-TCLP	ICPMS-SPLP
Antimony (Sb)	suspect	suspect	suspect
Arsenic (As)	suspect	suspect	suspect
Manganese (Mn)	suspect (one sample), rejected (one sample)	suspect (6 samples)	acceptable
Thallium (Tl)	rejected	rejected	rejected

All QC sample results for the ICP analysis for As, Sb, Mn, and Tl met acceptance criteria. ICP total results for As, Sb, Mn, and Tl were, therefore, added to the analytical summary table.

Observations:

- Sample EMI-6DUP was shipped with other samples to STL, but not included on the Chain of Custody sheets.

- STL performed waste analyses for a fast (two-week) turnaround time with minimal QC check before delivery of analytical data report. ES performed a complete (100%) QA review following guidance from the "National Functional Guidelines for Inorganic Data Review" (US EPA, 2/94). The areas ES reviewed include: sample holding times, sample condition upon lab receipt, instrument (ICP and ICPMS) tuning and calibration, field and laboratory QC sample results, and quantitation of results.

- ES made numerous hand-written additions (i.e., inorganic analyses support documentation, summaries for laboratory's analysis for initial and continuing calibration verification standards, initial and continuing blanks, interference check samples, serial dilutions, and PQLCRI standards) and corrections (i.e., sample identification numbers, analysis date, method detection limits/reporting limits, dilution factors, and sample results calculations) throughout the entire report. The report was organized in a way that was difficult to follow and it has many data gaps that complicated our determination of whether those hand-written changes and corrections were justifiable. All hand-written changes and corrections were not initialed nor dated by ES' data reviewer(s).

- Inconsistencies appeared in places where note sample dilutions. There are three places in this report noting dilutions of samples and TCLP/SPLP leachates: (1) data validator's narrative (Section 1, page 3, bullet 6); (2) laboratory case narrative (Section 4, page 3); and (3) laboratory's correspondence to ES data validator dated November 10, 2000 (Section 5). These three places do not consistently describe the same dilutions for various analytical runs, which raises the question of whether the dilutions were correctly included in the reported results. Omission of a dilution factor would result in under-reported results. STL's sample preparation worksheets, analytical run logs, and analytical data summary tables were examined to verify if method detection limits (MDLs), reporting limits (RLs), and sample results were corrected appropriately to reflect sample dilutions.

- The report contains only the ICP/ICPMS outputs for laboratory QC samples, not the ICP/ICPMS outputs for the Iron Rich^{TM} samples. On February 7, 2001, we requested additional information from DuPont for our further review. Appendix B includes an electronic mail listing the additional information and materials we requested for our assessment of Dupont's data usability for listing determination.

Detailed Discussions:

- There are three analytical batches in this report.

  (1) ICP total, and ICP TCLP/SPLP analyses (analytical batch number: 001030EA; instrument JAII)

  All QC sample results met acceptance criteria for As, Sb, Mn, and Tl. QC results reviewed include method blanks, high standard, initial calibration verification, initial calibration blank, reporting limit verification, interference check sample, continuing calibration blanks and continuing calibration verification standards, serial dilution, duplicates, and matrix spike/matrix spike duplicate. ICP total and ICP TCLP/SPLP results for As, Sb, Mn, and Tl were added to the analytical summary table.

  (2) ICPMS TCLP and SPLP analyses (analytical batch number: 0302129 and 0302153; Perkin Elmer Elan 6000 ICPMS M01):

  <u>ICPMS TCLP/SPLP results for As and Sb were suspect because they may be biased low.</u>

  - The ICPMS was calibrated and optimized in the high calibration range but was not stable at the low calibration range. STL's instrument calibration was examined to determine if its

ICPMS was calibrated properly to detect contaminants at low concentration levels. STL's ICPMS was calibrated, as required by SW-846 Method 6020, by one standard (Mn and As at 100 ug/l; Sb and Tl at 50 ug/l) and optimized by initial and continuing calibration verification standards (ICV and CCVs for Mn and As, 80 ug/l; for Sb and Tl, 40 ug/l). The PQLCRI standard was not analyzed to verify the reporting limits for all analytes. Therefore, there was no way to determine the stability and sensitivity of STL's ICPMS below the optimum levels for As, Sb, and Tl (80 ug/l, 40 ug/l, and 40 ug/l, respectively).

- STL experienced serious analytical problems (i.e., blank contaminations, carry-over problem). Physical and memory interferences seemed to be present. The nebulizer of the ICPMS might have been clogged by samples (physical interference). The intensities of internal standards for As, Sb, and Tl dropped considerably to 30%, 45%, and 59% off their original levels. This problem might have affected the aerosol flow rate and caused instrument drift. Sensitivity was therefore lost and negative values resulted from the way they calibrated (one-point calibration). Numerous (or nearly all) blank samples that were analyzed immediately after a calibration verification standard were contaminated (memory interference). A longer run time or rinse period between samples could have helped eliminate this problem. The lab analyst should have terminated the analysis, corrected the problems, re-calibrated the instrument, verified the new calibration, and re-analyzed the affected samples.

ICPMS TCLP/SPLP results for Tl were rejected because they were biased low.

In addition to the analytical problems listed above for the ICPMS TCLP/SPLP analysis for As and Sb, there are problems exist for the ICPMS TCLP and SPLP analyses for thallium.

- Large negative responses were seen in associated blanks (ICB, MB, and CCBs) and samples for the ICPMS TCLP and SPLP analyses for thallium. The MDL for ICPMS thallium may be higher than reported.

- The SPLP leachates of all samples analyzed in between blanks (CCB9, CCB10, and CCB11) had large negative thallium results, the SPLP Tl leachate results are questionable.

ICPMS TCLP results for Mn were suspect because they may be biased low.

In addition to the analytical problems listed above for the ICPMS TCLP/SPLP analysis for As and Sb, there is one problem for the ICPMS TCLP analysis for Mn.

- The ICPMS was calibrated for Mn from 0 to 100 ug/l. The highest spike was 200 ug/l. In DuPont's submissions, there were no discussion about STL-West Sacramento, CA lab's

ICPMS linear calibration range for Mn. (In Volume 11 of DuPont analytical data report, STL-Denver, CO lab stated that its ICPMS linear calibration range for Mn is 0-2000 ug/l.) Before multiplying the dilution factor to calculate the final results, the ICPMS responses for TCLP Mn were from 6778 to 16,976 ug/l. The sample responses for Mn were very likely outside the calibration range. This may explain why the TCLP Mn results of all Iron Rich^{TM} samples analyzed by ICPMS were consistently lower than those analyzed by ICP. Since the ICP Mn results were well within the linear range of the instrument and associated QC results met acceptance criteria. Data users may also consider ICP total Mn results. I suspect the ICPMS TCLP Mn result of six samples (EMI-1, EMI-3, EMI-4, EMI-5, EMI-7, EMI-8) because their results were lower than their ICP total Mn results greater than 10 percent.

(3) ICPMS total analysis (analytical batch number: 0304465; Perkin Elmer Elan 6000 ICPMS M01):

<u>ICPMS total results for As and Sb were suspect because they may be biased low.</u>
- As stated earlier, the ICPMS was calibrated and optimized in the high calibration range but was not stable at the low calibration range. STL's ICPMS was calibrated, as required by SW-846 Method 6020, by one standard (Mn and As at 100 ug/l; Sb and Tl at 50 ug/l) and optimized by initial and continuing calibration verification standards (ICV and CCVs for Mn and As, 80 ug/l; for Sb and Tl, 40 ug/l. There was no way to determine the stability and sensitivity of STL's ICPMS below the optimum levels for As, Sb, and Tl (80 ug/l, 40 ug/l, and 40 ug/l, respectively)

- Low MS/MSD recoveries (30%#%R#75%) were reported for Sb indicating sample matrix interference may exist.

- The MDL for As may be higher than reported. The "non-detected" results are questionable and may be under-reported. Low MS/MSD recoveries (30%#%R#75%) were also reported for As indicating sample matrix interference may exist.

<u>ICPMS total results for Tl were rejected because they were biased low.</u>

In addition to the analytical problem listed above for the ICPMS total analysis for As and Sb, there are problems for the ICPMS total analyses for thallium.

- The analysis of the continuing calibration blanks (CCBs) displayed high results (> the reporting limit) for thallium. Those blanks might have been contaminated by Tl via carry-over problem. Instead of correcting the problem and re-analyzing the affected samples as required by SW 846 Method 6020, STL re-sloped the ICPMS by re-analysis of the CCBs.

- All samples were diluted 5-fold (5X) for the ICPMS analysis. Tl levels in all samples were low, and might have been diluted out.

<u>One total ICPMS Mn result was suspect and one total Mn result was rejected because they may be biased low</u>

- Two samples (EMI-1 and EMI-7) were diluted 5X and six samples plus one duplicate (EMI-2, EMI-3, EMI--4, EMI--5, EMI--6, EMI--8, EMI--6 Dup) were diluted 25 X. Before multiplying the dilution factors to calculate final Mn results, the Mn responses for EMI-1 and EMI-7 were 17,085 ug/l and 17,127 ug/l, respectively; and the Mn responses for EMI-2, EMI-3, EMI--4, EMI--5, EMI--6, EMI--8, EMI--6 Dup were from 5523 ug/l to 6973 ug/l. As stated earlier, in DuPont's submissions, there were no discussion about STL-West Sacramento, CA lab's ICPMS linear calibration range for Mn. The sample responses for Mn were very likely outside of the calibration range. This may explain why the total Mn results of all Iron Rich^{TM} samples analyzed by ICPMS were consistently lower than those analyzed by ICP. Since the ICP Mn results were well within the linear range of the instrument and associated QC results met acceptance criteria. Data users may also consider the ICP total Mn results. The ICPMS TCLP Mn result of one sample (EMI-7) was suspect because it was lower than its ICP total Mn result by 12 percent. The ICPMS total Mn result of one sample (EMI-1) was rejected because it was lower than its ICP total Mn result by 23%.

C For the reasons discussed above, I disagree with the data qualifiers ES applied to sample results for Mn, As, Sb, and Tl. Listed below is a summary of the data qualifiers now appeared in Table 8.

<u>Summary of Data Qualifiers</u>:

Qualifier	**Reason**	**Analyte**	**Samples**
S	See reasons listed in pages 3	As, Sb-TCLP/SPLP (SW6020)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8
R	See reasons listed in 4	Tl-TCLP/ SPLP (SW6020)	EMI-1, EMI-3, EMI-4, EMI-5, EMI-7, EMI-8
S	See reasons listed in 4	Mn-TCLP (SW6020)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8
S	See reasons listed in 5	As, Sb-total (SW6020)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8
R	See reasons listed in page 5	Tl-total (SW6020)	EMI-1, EMI-2, EMI-3, EMI-4, EMI-5, EMI-6, EMI-7, EMI-8
S	See reasons listed in page 5	Mn-total (SW6020)	EMI-7

Qualifier	Reason	Analyte	Samples
R	See reasons listed in pages 6.	Mn-total (SW6020)	EMI-1

Constituent of concern	Analysis	Table 8, Iron Rich, Edge Moor									Comparable EPA Sample (DPE-SO-01)
		EMI-1	EMI-2	EMI-3	EMI-4	EMI-5	EMI-6	EMI-7	EMI-8	Average	
% Moisture		54.9	53.0	53.2	54.6	57.4	54	52.3	55.8	54.4	58.1
Antimony	Total-6020B	0.67 S	0.35 S	0.33 S	0.54 S	0.34 S	0.22 S	0.47 S	0.27 S	0.4 S	
	Total-6010	3.5	3.66	3.55	<2.2	<2.2	3.96	3.11	3.17	2.89	0.9
	TCLP-6020B	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S		
	TCLP-6010	0.17	<0.155	<0.155	<0.155	<0.155	<0.155	<0.155	<0.155		0.021
	SPLP-6020B	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S	<0.0008 S		
	SPLP-6010	0.0571	<0.031	0.044	0.041	0.056	0.048	<0.031	0.0248	0.038	0.02
Arsenic	Total-6020B	<0.40 S	<0.40 S	<0.40 S	<0.40 S	<0.40 S	<0.40 S	<0.40 S	<0.40 S		
	Total-6010	<3.1	4.33	<3.1	<3.1	<3.1	<3.1	4.96	<3.1		2.2
	TCLP-6020B	<0.002 R	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S		
	TCLP-6010	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	0.26	<0.22		<0.0035

Constituent of concern	Analysis	Table 8, Iron Rich, Edge Moor									Comparable EPA Sample (DPE-SO-01)
		EMI-1	EMI-2	EMI-3	EMI-4	EMI-5	EMI-6	EMI-7	EMI-8	Average	
	SPLP-6020B	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S	<0.002 S		
Arsenic	SPLP-6010	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043	<0.043		0.001 (1)
Barium	Total	114	160	157	136	125	132	75.3	79.2	122	178
	TCLP	0.76	2.0	1.8	1.4	1.5	2.3	0.43	1.1	1.4	2.4 (1)
	SPLP	0.15 J	0.56	0.56	0.33	0.44	1.1	0.10 J	0.35	0.45	0.92
Boron	Total	8.8 J	15.9 J	19.1 J	13.0 J	14.3 J	21.9 J	<0.8 UJ	10.3 J	13.0	30.0
	TCLP	0.30 J	0.95	0.97	0.56	0.83	0.83	0.17 J	0.48 J	0.64	1.7
	SPLP	0.14 J	0.49	0.51	0.26	0.51	0.45	0.096 J	0.31	0.35	0.61
Chromium	Total	743	1,230	1,180	970	1,020	1,070	674	991	984	777
	TCLP	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014	<0.014		<0.05
	SPLP	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028	<0.0028		0.002 (1)
Cobalt	Total	33.3 J	57 J	56.7 J	45.3 J	46.6 J	50.3 J	24.2 J	37.2 J	43.8	44.5
	TCLP	0.14	0.41	0.30	0.30	0.40	0.22 U	0.14 U	0.22 U	0.27	0.43
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		<0.005
Iron	Total	142,000 J	117,000 J	116,000 J	130,000 J	125,000 J	129,000 J	140,000 J	134,000 J	129,000	91,600
	TCLP	251	404	362	398	541	341	351	515	395	348
	SPLP	0.014 U	0.23 U	0.090 U	0.46	1.6	0.56	0.040 U	0.58	0.447	0.18

Constituent of concern	Analysis	Table 8, Iron Rich, Edge Moor									Comparable EPA Sample (DPE-SO-01)
		EMI-1	EMI-2	EMI-3	EMI-4	EMI-5	EMI-6	EMI-7	EMI-8	Average	
Lead	Total	181 J	322 J	296 J	230 J	213 J	244 J	137 J	181 J	226	309
	TCLP	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075		0.03 (1)
Lead	SPLP	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075		0.003 (1)
Manganese	Total-6010B	10,500	18,900	18,600	15,000	15,500	15,800	9,550	15,300	14,893	10,600
	Total-6020	8,540 R	17,400 S	17,200 S	13,800 S	14,400 S	14,700 S	8,560 R	14,600 S	13,650 S	
	TCLP-6010B	192	304	320	263	262	452	187	287	283	252
	TCLP-6020	164 S	287 S	290 S	239 S	235 S	424 S	169 S	258 S	258 S	
	SPLP-6010B	1.7	10.4	10.2	9.7	19.6	20.8	2.0	13.4	10.9	16.3
	SPLP-6020	1.7	10.6	10.3	10.1	19.7	20.7	1.9	12.7	11.0	
Nickel	Total	88.4 J	169	156	113	116	140	69.1	116	121	91.8
	TCLP	<0.08	0.25	0.14	0.21	0.28	<0.08	0.14 J	0.15 J	0.16	0.5
	SPLP	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016		<0.005

Constituent of concern	Analysis	Table 8, Iron Rich, Edge Moor									Comparable EPA Sample (DPE-SO-01)
		EMI-1	EMI-2	EMI-3	EMI-4	EMI-5	EMI-6	EMI-7	EMI-8	Average	
Thallium	Total-6020B	0.24 R	<0.18 R	0.33 R	0.25 R	<0.18 R	<0.18 R	<0.18 R	<0.18 R		
	Total-6010	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1	<7.1		3.7 23.6 split (18.4 dup)
	TCLP-6020B	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R		
	TCLP-6010	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250	<0.250		0.28 (0.27 dup)
	SPLP-6020B	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R	<0.0005 R		
	SPLP-6010	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050		0.012
Vanadium	Total	526	198	160	313	180	127	451	165	265	240
	TCLP	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016		0.0003 (1)
	SPLP	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032		<0.005
Initial pH	TCLP	5.33	5.47	5.53	5.58	5.69	5.64	5.67	5.75		6.999
Initial pH	SPLP										
Final pH	TCLP	5.73	5.92	6.02	5.92	5.96	6.05	5.79	6.01		5.63
Final pH	SPLP	4.78	4.93	6.20	6.32	6.13	6.29	6.41	6.46		6.97

Volume 8

Wastewater Treatment Sludge- Edge Moor Plant, Wilmington, DE

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

MEMORANDUM

To: Shen-yi Yang, EPA OSW
From: Ray Anderson, SAIC
Subject: Data Review of Dupont Edgemoor Wastewater Treatment Sludge, Volume 8
Date: February 23, 2001

Data review and validation were performed on the laboratory analytical results for 8 sludge, 1 equipment blank, and 1 field duplicate samples collected from the Dupont Edgemoor facility over a 5-day period from October 18, 2000 to October, 22, 2000. The samples were submitted on October 23, 2000 by Dupont to Severn Trent Laboratories, STL in West Sacramento, CA. STL received all samples noted on chain-of-custody (COC) documentation on October 24, 2000. In addition, STL also received the field duplicate sample (EMS-4 dup) which was not designated on the COC. The analytical report from STL and validated by Environmental Standards, contained the sample results for total, SPLP metals, and percent moisture. All analyses were performed using SW-846 methodology which included ICP Method 6010 for Al, Ba, Be, B, Cr, Co, Cu, Fe, Mn, Mo, Ni, Ag, Sn, V, and Zn; and ICP-MS Method 6020 for Sb, As, Cd, Pb, Mn, Se, and Tl. The analytical data package designated as “Volume 8 Wastewater Sludge Edge Moor Plant” included the data validation report dated December 13, 2000 from Environmental Standards. Due to missing information in the STL analytical report as initially provided, additional laboratory data were submitted by Dupont to EPA on February 15, 2001. For the combined laboratory data along with validation report the following observations are noted:

Observations:

! The STL data report delivered to Environmental Standards was dated November 6, 2000. This represents a less than two week sample turnaround time based on the laboratory receipt date on October 24, 2000. Within this two week period the laboratory was able to complete the total and leachate analyses, do a comprehensive data review, and submit a full data package in order to support a complete independent data validation effort. Although this accomplishment is not impossible, the typical laboratory analysis turnaround is 3 to 4 weeks for a complete analytical data package. Frequently, when the laboratory is required to accelerate the turnaround time the number of reanalyses are limited, quality control analyses are not always project-specific, and the amount of time allotted for internal data review and report preparation is limited. As a result the overall data quality and usability is sometimes questionable.

! With the exception of EMS-1 and EMS-7 all ICP and ICP/MS total results are biased high since the exact sample weight was not used to calculate the reported concentration. The results are biased by the following percentages: EMS-2 (0.6%), EMS-3 (0.8%), EMS-4 (1%), EMS-5 (0.4%), EMS-6 (0.6%), and EMS-8 (0.4%).

- The detection limit data provided in the February 15, 2001 response to EPA contains the ICP and ICP/MS MDL and RL data for STL-Sacramento that were determined in early 1998. This is unacceptable since the instrument operating conditions, time in service, and maintenance affect the sensitivity over time. A more realistic time frame would have been on a quarterly basis. I'm very surprised the lab has been able to operate and respond to various external audits without a more current MDL studies. In addition, the numerous CCBs with multiple analytes yielding concentrations above the MDLs were the norm. This further reinforces that the existing 1998 MDL study is outdated. The reporting limits should also be adjusted based on the most current MDL data.

- The ICP/MS As MDL reported as 0.25 mg/kg should be 0.40 mg/kg to account for the 25X dilution and 5g sample weight.

- The ICP/MS SPLP samples were all diluted by either 5X or 10X due to high levels of Ca detected in the totals analyses. Even with these dilutions, the As, Se, Tl, and Pb responses were negative for the majority of the samples. This is a similar situation to that experienced with the Hillside Pond leachate samples.

- Overall most CCBs were contaminated with at least one analyte above the reported MDL.

Conclusions:

I believe the Edgemoor Wastewater Treatment sludge ICP and ICP/MS totals data are valid and representative, however, they are biased high due to calculation errors and possibly using diluted as opposed to undiluted sample responses. Conversely, all ICP/MS leachate data due to a number quality control issues (poor CCB responses and instrument instability as a result of the high degree of negative responses) are of questionable value.

Constituent of concern	Analysis	Table 9, Wastewater treatment sludge, Edge Moor											EPA Sample (DPN-SO-01)	EPA Sample (DPE-SO-01)
		EMS-1	EMS-2	EMS-3	EMS-4	EMS-5	EMS-6	EMS-7	EMS-8	Average	MDL	RL		
% Moisture		94.2	93.2	94.0	95.0	95.8	93.9	95.3	94.6	94.5			69.6	58.1
Antimony	Total-6020	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25		0.25	5	0.7	0.9
	Total-6010	3.8 B	1.9 B	2.7 B	2.6 B	1.5 B	3.3 B	2.8 B	2.6 B		11	30		
	SPLP-6020	<0.0016	<0.0016	<0.0016	<0.0016	<0.0016	<0.0008	<0.0008	<0.0008		0.0016	0.02	0.021	0.02
	SPLP-6010	0.047 L	0.069	0.051 L	0.045 L	0.056 L	0.041 L	0.047 L	0.035 L	0.0489	0.031	0.06		
Arsenic	Total-6020	0.78 U	0.61 U	0.38 U	0.62 U	0.65 U	0.37 L	0.44 U	0.58 U	0.55	2.0	5.0	2.8	2.2
	Total-6010	< 15.5	< 15.5	5.2 B	5.3 B	3.0 B	< 15.5	< 15.5	2.6 B		15.5	150		
	SPLP-6020	<0.0041	<0.0041	<0.0041	<0.0041	<0.0041	<0.002	<0.002	<0.002		0.0041	0.02	<0.0035	0.001 (1)
	SPLP-6010	0.0048 B	0.032 B	0.0164 B	< 0.043	0.0387 B	< 0.043	< 0.043	< 0.043	0.0330	0.043	1.5		
Barium	Total	12.0 J	12.1 J	4.3 J	9.7 J	6.5 J	6.5 J	3.1 J	4.6 J	7.4	0.2	100.0	49.6	178
	SPLP	0.20 J	0.21 J	0.20 J	0.23 J	0.19 J	0.17 J	0.22	0.17 J	0.20	0.0004	0.2	0.12	0.92
Boron	Total	4.2 U	3.1 U	1.9 U	3.1 U	2.8 U	3.0 U	2.3 U	3.0 U	2.9	2.0	100	24.5	30.0
	SPLP	0.19 J	0.14 J	0.17 J	0.33 J	0.15 J	0.084 J	0.084 J	0.079 J	0.15	0.011	0.2	0.45	0.61
Chromium	Total	3.3	2.6	0.72 U	1.1 U	1.0 U	1.4 U	0.57 U	2.8	1.7	1.35	5.0	499	777
	SPLP	0.0015 B	<0.0028	<0.0028	<0.0028	<0.0028	0.0016 B	0.0017 B	<0.0028		0.0028	0.01	<0.005	0.002 (1)
Cobalt	Total	0.30 J	0.26 J	0.09 J	0.15 J	0.14 J	0.20 J	0.10 J	0.22 J	0.18	0.25	2.5	7	44.5
	SPLP	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074	<0.0074		0.0074	0.05	<0.005	<0.005

Constituent of concern	Analysis	Table 9, Wastewater treatment sludge, Edge Moor											EPA Sample (DPN-SO-01)	EPA Sample (DPE-SO-01)
		EMS-1	EMS-2	EMS-3	EMS-4	EMS-5	EMS-6	EMS-7	EMS-8	Average	MDL	RL		
Iron	Total	1,470	879	290	405	364	555	299	1,320	698	0.45	50	63,200	91,600
Iron	SPLP	0.0054 L	0.0047 L	0.0041 L	0.0056 L	<0.0039	<0.0039	<0.0039	<0.0039		0.0039	0.1	2.2	0.18
Lead	Total-6020	1.2 L	0.84 L	0.28 J	0.66 L	0.40 J	0.50 L	0.23 J	0.81 L	0.62	0.25	2.50	42.4	309
	Total-6010	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11		11	50		
	SPLP-6020	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.00075	<0.00075	<0.00075		0.0015	0.01	0.002 (1)	0.003 (1)
	SPLP-6010	< 0.031	< 0.031	< 0.031	< 0.031	< 0.031	< 0.031	< 0.031	< 0.031		0.031	0.1		
Manganese	Total-6010	62.9	47.3	14.2	28.1	19.3	21.8	10.5	23.5	28.6	1.5	7.5	2,890	10,600
	Total-6020	57.8 J	46.7 J	15.2 J	29.6 J	20.8 J	23.9 J	11.4 J	25.0 J		0.25	2.5		
	SPLP-6010	0.23	0.042 U	0.081 U	0.21	0.12	0.011 U	0.0059 U	0.0028 U	0.091	0.0007	0.015	1.5	16.3
	SPLP-6020	0.24	0.048	0.090	0.22	0.14	0.011	0.0060 L	0.0033 L		0.0014	0.01		
Nickel	Total	<9	1.0 B	<9	<9	<9	<9	<9	<9		9	20	59.8	91.8
	SPLP	0.013 B	<0.016	<0.016	0.021 L	<0.016	<0.016	<0.016	<0.016		0.016	0.04	0.007	<0.005
Thallium	Total-6020	<0.9	<0.9	0.22 U	<0.9	<0.9	<0.9	<0.9	<0.9		0.9	2.5	7.2	3.7
	Total-6010	< 35.5	< 35.5	< 35.5	< 35.5	< 35.5	< 35.5	< 35.5	< 35.5		35.5	1000		
	SPLP-6020	<0.001	<0.001	<0.001	<0.001	<0.001	<0.0005	<0.0005	<0.0005		0.001	0.01	<0.0022	0.012
	SPLP-6010	0.033 B	< 0.053	0.0108 B	0.012 B	< 0.053	0.0152 B	< 0.053	0.0019 L	0.0290	0.053	2.0		
Vanadium	Total	25.1	27.3	10.7 L	20.3 L	16.3 L	26.2	17.8 L	28.3	21.5	1.3	25.0	1,060	240

Constituent of concern	Analysis	Table 9, Wastewater treatment sludge, Edge Moor											EPA Sample (DPN-SO-01)	EPA Sample (DPE-SO-01)
		EMS-1	EMS-2	EMS-3	EMS-4	EMS-5	EMS-6	EMS-7	EMS-8	Average	MDL	RL		
	SPLP	0.0056 L	0.024 U	0.022 U	0.015 U	0.017 U	0.025 J	0.024 J	0.015 U	0.018	0.0032	0.05	<0.005	<0.005
Initial pH	SPLP													
Final pH	SPLP	6.59	6.73	6.94	7.03	7.07	6.55	6.84	6.89					

L	Result is greater than the method detection limit but less than the laboratory reporting limit.
B	Result is greater than the suspected instrument detection limit but less than the method detection limit.

Volume 9

Wastewater- Johnsonville Plant, New Johnsonville, TN

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

Subject: **QA/QC Review of "Quality Assurance Review of the Wastewater Samples Collected on October 20, 21, 221, and 23, 2000, at the Johnsonville Plant in New Johnsonville, Tennessee for the DuPont Engineering TiO2 Listing Project"**

By: **Kelly Luck, Senior Data Validator, Dynamac Corporation**

Date: **March 19, 2001**

The analytical results for wastewater samples collected by DuPont at the Johnsonville Plant and analyzed by Severn Trent Services (Denver, CO) were subjected to a quality assurance review by Environmental Standards, Inc. (Valley Forge, PA). The results of their review were submitted in a document entitled "Quality Assurance Review of the Wastewater Samples Collected on October 20, 21, 221, and 23, 2000, at the Johnsonville Plant in New Johnsonville, Tennessee for the DuPont Engineering TiO2 Listing Project", December 13, 2000. The Environmental Standards QA review has been examined to verify the correctness of their conclusions and to make overall conclusions regarding the quality of the analytical data for the wastewater samples.

Notes:

1. The analytical results for the samples, with the applied data qualifiers, are listed in Tables 1, 2, and 3 below.

2. Analytical results for only antimony, arsenic, manganese, and thallium, as well as total suspended solids (TSS) and total dissolved solids (TDS), were examined in this review.

3. Results for the following samples were examined and considered in this review: JV-FW-1, JV-FW-2, JV-FW-3, JV-FW-4, JV-OS-1, JV-OS-2, JV-OS-3, JV-OS4, JV-WTS-1, JV-WTS-2, JV-WTS-3, JV-WTS-4, and JV-RC-1. Four field duplicate samples were collected (JV-FW-3DUP, JV-OS-3DUP, JV-WTS-3DUP, and JV-RC-1DUP) and the results for these samples were examined to evaluate field duplicate precision. However, the results for these field QC samples are not reported in Tables 1, 2, or 3.

Conclusions:

The QA review conducted by Environmental Standards (ES) was very thorough, involving examination of all QC requirements for the methods (initial and continuing calibration, laboratory and equipment blanks, interference check samples, matrix spike recoveries, field duplicates, laboratory control samples, serial dilutions, and sample quantitation). Based on the raw data included in the submission, ES verified the reported results for all QC results, and used the raw data to evaluate QC data for which summary tables were not provided (such as for initial and continuing calibration verification recoveries). The data qualifiers applied by ES are appropriate and have been verified by this data reviewer, except as discussed below under "Detailed Considerations."

Detailed Considerations:

1. **Verification of results:** The reported results in Tables 1, 2, and 3 for antimony, arsenic, manganese, thallium, TDS, and TSS in each sample were verified from the raw data included in the laboratory data package (received in CD format). For the total metals results for the solid sample (JV-RC-1), it appears that the laboratory did not use the actual sample weight (of 1.03 g) in their calculations but simply used a value of 1 (because the laboratory apparently accounted for the sample weight at the instrument level, it is not completely clear that the 1.03 value was not used). This resulted in some differences in the results calculated from the raw data versus those reported in Table 3. Because the laboratory appears not to have used the actual sample weight in their calculations, the results for antimony, arsenic, manganese, and thallium (as well as the other metals not examined in this review) in sample JV-RC-1 should only be considered to be accurate to 2 significant figures.

   It appears that the instrumentation used by the laboratory was able to take dilution factors and sample weights into account when reporting results; e.g., all samples analyzed by 6020 (ICP-MS) were diluted 10x prior to analysis, and this dilution was accounted for in the raw data outputs. However, not all dilutions were taken into account. For example, samples JV-OS-1, JV-OS-2, JV-OS-3, and JV-OS-4 were all diluted 10 fold prior to digestion because of poor pH preservation (see below), and this dilution was not taken into account in the ICP-MS raw data outputs, requiring that the raw data results be multiplied by 10 to get actual sample results. This 10x multiplication appears not to have been done for sample JV-OS-4; therefore, the study reviewer has modified the results for antimony, arsenic, manganese, and thallium in sample JV-OS-4 in Table 2 by multiplying them by 10. [Note that this 10x multiplication factor should be applied to all other ICP-MS results for JV-OS-4.] Application of this 10x dilution factor gives results which agree more readily with the results for samples JV-OS-1, JV-OS-2, and JV-OS-3.

   Sample JV-OS-3 required additional dilution for manganese because the associated internal standard recovery was outside QC limits in the initial analysis. The overall dilution factor (stated in the laboratory's reported results for manganese) was 1000x, which would reflect the 10x dilution this sample received prior to digestion (because of poor pH preservation), the 10x dilution that all samples received for ICP-MS analysis, and a 10x dilution to bring the internal standard recovery to within QC limits. Because one of those 10x dilutions was already accounted for in the raw data outputs, the raw data results for this sample should have been multiplied by 100 to get actual sample results. However, the laboratory appeared to have multiplied the results by 1000 to get the reported result for manganese. I believe that the raw data should have been multiplied by 100 and not 1000, I modified the result for manganese in sample JV-OS-3 in Table 2 from 90.2 to 9.02 µg/L. [Note that the revised result agrees more readily with the manganese results in the other JV-OS samples as well as with the manganese result of 13.3 µg/L in the field duplicate of this sample.]

Because some dilution factors were taken into account in the ICP-MS instrumentation and were already accounted for in the raw data outputs, it was sometimes difficult for the study reviewer to verify sample results; it could not always be determined which dilution factors were already accounted for in the raw data. In addition, the case narrative in the laboratory data package provided an explanation for the 10x dilution that was used for the JV-OS samples but did not provided any explanation for any other dilutions. The only source of information on dilution factors in the raw data was from hand-written notes on the ICP-MS raw data outputs.

2. **pH results:** Aqueous samples must be preserved to pH <2 for proper metals analysis. Samples JV-OS-1, JV-OS-2, JV-OS-3, and JV-OS-4 were received at the laboratory at pH >14; the inability to properly preserve these samples was apparently related to the nature of the samples (oxidation scrubber wastewater). The high pH required the samples to be diluted 10 fold prior to digestion (to avoid reaction with the strong acids used for digestion). The pH of all other aqueous samples in this set was <2.

3. **Sample size and dilutions:** The laboratory used the standard sample size (1 g) for the solid sample. For all samples except the JV-OS samples, the volume of sample used for analysis was 50 mL, which is less than the recommended amount of 100 mL. For the JV-OS samples, 5 mL was used for sample analysis, which is how the 10x dilution for these samples was accomplished. Based on information on the laboratory sample results sheets, 6020 analyses were conducted at a 10x dilution for all samples (resulting in a 100x dilution factor for the JV-OS samples). The sample sizes and dilutions seem appropriate.

4. **Application of data qualifiers by ES:**

4.1 *Blank contamination:* Based on the trace-level presence of certain target analytes in laboratory and equipment blanks, ES applied U qualifiers to some of the analytical results. The application of these qualifiers was verified in all cases. However, I disagreed with the application of the qualifiers to two results.

The ES-applied U qualifiers to the results for arsenic and manganese in the solid sample (JV-RC-1) are not appropriate. ES applied these qualifiers based on the levels of these analytes detected in the continuing calibration blanks (CCBs) in the analytical run. I have removed these qualifiers because the CCBs which were used in applying these qualifiers were not CCBs that bracketed the analysis of this sample in the analytical run. Only CCBs which bracketed the analysis of the sample should be used in determining when to apply qualifiers for blank contamination.

4.2 *Field duplication:* Four field duplicate samples were collected with this sample set (JV-FW-3DUP, JV-OS-3DUP, JV-WTS-3DUP, and JV-RC-1DUP). The precision for TSS fell outside the QC limits for the FW, OS, and RC field duplicate pairs. Based on this, ES qualified the results for TSS in samples JV-FW-3, JV-OS-3, and JV-RC-1 as estimated (J qualifier). Typically, the results of field duplicate analyses are applied to all samples of the same matrix as that of the field duplicate pair. Therefore, a J qualifier should be applied to positive TSS results in all JV-FW and JV-OS samples.

4.3 *Negative responses:* ES apparently evaluated the raw data and applied UJ qualifiers to the non-detect results for certain analytes when a negative response with an absolute value greater than 2x the method detection limit was observed. However, two additional instances where this qualifier should have been applied were observed in the raw data: the response for antimony in samples JV-WTS-2 and JV-WTS-4 was negative with an absolute value greater than two times the MDL. A "UJ" qualifier was applied to these results in Table 3.

4.4 *Matrix spike/matrix spike duplicate analyses:* The solid sample (JV-RC-1) and one aqueous sample (JV-FW-1) were subjected to matrix spike and matrix spike duplicate analyses. For the solid sample, extremely low recoveries (<5%) were observed for antimony and arsenic. As a results, ES applied an "R" qualifier to the non-detect result for antimony and a "J" qualifier to the positive result for arsenic in sample JV-RC-1; these applications of data qualifiers are correct.

For the aqueous sample, high recovery (>125%) was observed for antimony, and the precision of the duplicate analyses was outside the QC limits. No application of data qualifiers was necessary as all positive antimony results in aqueous samples had previously been qualified due to blank contamination.

4.5 *Results below the reporting limit:* ES applied J qualifiers to all results (that had not been previously qualified) which were reported as greater than the MDL but less than the reporting limit. All applications of this qualifier have been verified. [Note that the laboratory applied "B" qualifiers to these results (which is the standard qualifier that laboratories apply to inorganic data which is greater than the MDL/IDL but less than the RL), and ES correctly changed these to "J" qualifiers.]

5. **Serial dilution:** Two samples from within this sample set were evaluated for serial dilution for total metals analyses; the percent difference was within QC limits (0-10%) for detected analytes.

6. **Negative responses for thallium:** Although negative responses for thallium were observed in some samples, all responses had an absolute value less than 2xMDL.

7. **Internal standard recoveries:** Internal standard recoveries for 6020 analyses were within the QC limits of 30-120% for all samples, except one standard in JV-OS-3 (discussed above). This sample was diluted and reanalyzed and the internal standard recovery in the diluted sample was within QC limits.

8. **Manganese linear range:** For 6020 analyses, the laboratory provided the linear range for all analytes. For manganese, the linear range was to 2000 µg/L at the instrument. All manganese results for samples in this set were <<2000 µg/L.

9. **Comparison of ICP-MS (6020) and ICP-AES (6010) results for antimony, arsenic, manganese, and thallium:** Results for antimony, arsenic, manganese, and thallium from ICP-AES analyses were not reported by the laboratory and were not available in the raw data for 6010 analyses.

Summary of Applied Data Qualifiers:

Qualifier	Reason	Analyte	Samples
R	Extremely poor matrix spike recovery indicates that this result should be considered to be unusable.	Sb - total	JV-RC-1
U	This analyte was present in an associated blank.	Sb - total	JV-FW-1, JV-FW-2, JV-FW-3, JV-OS-1, JV-OS-2, JV-OS-3, JV-OS-4
J	Extremely poor matrix spike recovery indicates that this results should be considered to be estimated.	As - total	JV-RC-1
J	Poor duplication in the analysis of field duplicate samples indicates that these results should be considered to be estimated.	TSS	JV-FW-1, JV-FW-2, JV-FW-3, JV-FW-4, JV-OS-1, JV-OS-2, JV-OS-3, JV-OS-4, JV-RC-1
UJ	Negative results with an absolute value greater than twice the MDL indicates that the MDLs may be higher than reported.	Sb - total	JV-WTS-2, JV-WTS-4
J	Because results are greater than the MDL but less than the reporting limit, results should be considered to be estimated.	As - total	JV-FW-2, JV-FW-3, JV-FW-4, JV-WTS-3
		Mn - total	JV-FW-1, JV-FW-2, JV-FW-3, JV-OS-1, JV-OS-2, JV-OS-3, JV-OS-4, JV-WTS-1, JV-WTS-2, JV-WTS-3, WTS-JV-4
		TSS	JV-WTS-4

Constituent of Concern	Analysis	Table 1: Finishing Wastewater – RIN 6 – Johnsonville *Annual Waste Stream Generation Rate: 6,566,998 Mtons/yr*				
		JV-FW-1	JV-FW-2	JV-FW-3	JV-FW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		17800	22400	20100	232	15133
Total Suspended Solids – 160.2 (mg/L)		23.0 (J)	199 (J)	30.0 (J)	6.0 (J)	64.5
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010B	9.3J	14.9	20.1	<3.4	
	6020	3.8 (U)	10.7 (U)	20.2 (U)	<2	11.6
Arsenic	6010B	<3.6	<3.6	14.1	<3.6	
	6020	<2	3.5 (J)	11.1 (J)	2.7 (J)	5.8
Barium	6010B	<2.2	3.3 (J)^{B}	<2.2	18.5	–
Boron	6010B	55.2 (J)^{B}	51.0 (J)^{B}	46.4 (J)^{B}	28.6 (J)^{B}	45.3
Chromium	6020	6.3 (U)^{B}	7.8 (U)^{B}	<2.1 (UJ)	<2.1 (UJ)	–
Cobalt	6010B	<1	<1	<1	<1	–
Iron	6010B	<12	<12	<12	<12	–
Lead	6020	<2.3	<2.3	<2.3	<2.3	–
Manganese	6010B	<0.5	<0.5	<0.5	<0.5	<0.5
	6020	0.80 (J)	1.4 (J)	0.94 (J)	<0.76	1.0

Constituent of Concern	Analysis	Table 1: Finishing Wastewater – RIN 6 – Johnsonville *Annual Waste Stream Generation Rate: 6,566,998 Mtons/yr*				
		JV-FW-1	JV-FW-2	JV-FW-3	JV-FW-4	Average
Nickel	6010B	5.5 (J)[B]	<2	<2	<2	–
Thallium	6010B	6.3 (U)	<4.9	<4.9	<4.9	
	6020	<0.2	<0.2	<0.2	<0.2	–
Vanadium	6020	11.1 (J)[B]	29.8 (J)[B]	23.6 (J)[B]	<2	21.5

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

UJ = This analyte was not detected, but the detection limit is probably higher due to a low bias identified during the quality assurance review.

[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.

Constituent of Concern	Analysis	Table 2: Oxidation Scrubber Wastewater – RIN 104 – Johnsonville *Annual Waste Stream Generation Rate: 6 Mtons/yr*				
		JV-OS-1	JV-OS-2	JV-OS-3	JV-OS-4	Average
Total Dissolved Solids – 160.1 (mg/L)		368000	359000	359000	361000	361750
Total Suspended Solids – 160.2 (mg/L)		492 (J)	3140 (J)	1170 (J)	9560 (J)	3590
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010B	105	114	132	116	
	6020	53.7 (U)	34.5 (U)	26.5 (U)	**27.2 (U)**	**35.3**
Arsenic	6010B	13400	12100	13400	13200	
	6020	10500	10800	9880	**10000**	**10295**
Barium	6010B	118	88.6 (J)^{B}	219	136	140
Boron	6010B	1260	1250	1200	1180	1222
Chromium	6020	58.5 (U)^{B}	46.5 (U)^{B}	<212 (UJ)	<2.1 (UJ)	–
Cobalt	6010B	<10	13.4 (J)^{B}	<10	<10	–
Iron	6010B	974 (J)^{B}	846 (J)^{B}	1170	1080	1017
Lead	6020	<22.8	<22.8	<22.8	<2.3	–
Manganese	6010B	<5	<5	8.32 (J)	9.5 (J)	
	6020	16.1 (J)	13.1 (J)	**9.02 (J)**	**8.4 (J)**	**11.7**

Constituent of Concern	Analysis	Table 2: Oxidation Scrubber Wastewater – RIN 104 – Johnsonville *Annual Waste Stream Generation Rate: 6 Mtons/yr*				
		JV-OS-1	JV-OS-2	JV-OS-3	JV-OS-4	Average
Nickel	6010B	338 (J)^B	300 (J)^B	346 (J)^B	316 (J)^B	325
Thallium	6010B	<49	<49	<49	<49	<49
	6020	<2	<2	<2	**<2**	–
Vanadium	6020	352 (J)^B	361 (J)^B	3210 (J)^B	32.0 (J)^B	989

U = This analyte should be considered “ not-detected” because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

Bolded values were changed based on a review of the raw data.

Constituent of Concern	Analysis	Table 3: Wet Treatment Scrubber Wastewater – RIN 111 – Johnsonville				
		JV-WTS-1	JV-WTS-2	JV-WTS-3	JV-WTS-4	Average
Total Dissolved Solids – 160.1 (mg/L)		174	197	182	176	182
Total Suspended Solids – 160.2 (mg/L)		<1.2	5.0	<1.2	2.0 (J)	–
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010B	<3.4	<3.4	<3.4	<3.4	<3.4
	6020	<2	<2 (UJ)	<2	<2 (UJ)	–
Arsenic	6010B	<3.6	<3.6	<3.6	<3.6	<3.6
	6020	<2	<2	13.5 (J)	<2	–
Barium	6010B	21.8	27.8	21.6	19.3	22.6
Boron	6010B	28.5 (J)^{B}	28.1 (J)^{B}	23.7 (J)^{B}	25.7 (J)^{B}	26.5
Chromium	6020	<2.1 (UJ)	<2.1 (UJ)	<10.6 (UJ)	<2.1 (UJ)	–
Cobalt	6010B	<1	<1	<1	<1	–
Iron	6010B	54.5 (J)^{B}	66.4 (J)^{B}	60.3 (J)^{B}	38.0 (J)^{B}	54.8
Lead	6020	<2.3	<2.3	<2.3	<2.3	–
Manganese	6010B	2.1 (J)	3.0 (J)	1.6 (J)	0.95 (J)	
	6020	1.9 (J)	3.7 (J)	17.8 (J)	1.1 (J)	6.1

Constituent of Concern	Analysis	Table 3: Wet Treatment Scrubber Wastewater – RIN 111 – Johnsonville				
		JV-WTS-1	JV-WTS-2	JV-WTS-3	JV-WTS-4	Average
Nickel	6010B	<2	<2	<2	<2	–
Thallium	6010B	5.8 (U)	<4.9	<4.9	<4.9	
	6020	<0.2	<0.2	<0.2	<0.2	–
Vanadium	6020	<2	2.2 (J)[B]	17.1 (J)[B]	<2	–

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

UJ = This analyte was not detected, but the detection limit is probably higher due to a low bias identified during the quality assurance review.

R = Unusable result.

[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.

Table 3: Railcar Trailer Product Wash Out – RIN 112 – Johnsonville

***These samples are solids from wastewaters.** **Metal results are reported on a dry-weight basis.**

Constituent of Concern	Analysis	JV-RC-1
		Sample Number 002
Total Dissolved Solids – 160.1 (mg/L)		34200 ^{Q}
Total Suspended Solids – 160.2 (mg/L)		534 (J)^{Q}
		Sample Number 001
% Moisture	160.3	51.3
	Total	mg/kg (Validation Qualifier)
Antimony	6010B	1.01 (J)
	6020	<0.041 (R)
Arsenic	6010B	<0.92
	6020	0.033 (J)
Barium	6010B	0.77 (U)^{B}
Boron	6010B	<1
Chromium	6020	0.95 (U)
Cobalt	6010B	<0.31
Iron	6010B	17.7 (J)^{B}

Table 3: Railcar Trailer Product Wash Out – RIN 112 – Johnsonville

***These samples are solids from wastewaters. Metal results are reported on a dry-weight basis.**

Constituent of Concern	Analysis	JV-RC-1
Lead	6020	0.22 (U)
Manganese	6010B	0.39 (J)
	6020	0.74
Nickel	6010B	4.7 (J)[B]
Thallium	6010B	<0.82
	6020	<0.0041
Vanadium	6020	1.8

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

R = Unusable result – analyte may or may not be present in this sample.

[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.

[Q] = LAB FOOTNOTE: Severn Trent Lab and Environmental Standards did not define this qualifier.

Volume 10

Wastewater- DeLisle Plant, Pass Christian, MS

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

MEMORANDUM

To: Shen-yi Yang, EPA OSW
From: Ray Anderson, SAIC
Subject: Data Review of Dupont DeLisle, Volume 10
Date: March 20, 2001

Data review and validation were performed on the laboratory analytical results for 16 wastewater and 4 field duplicate samples collected from the Dupont DeLisle facility on October 20 to 23, 2000. The samples were submitted on October 23, 2000 by Dupont to Severn Trent Laboratories, STL in Denver, CO. STL received all samples noted on chain-of-custody (COC) documentation on October 24, 2000. The analytical report from STL and validated by Environmental Standards, contained the sample results for total metals, total dissolved solids, and total suspended solids. All metals analyses were performed using SW-846 methodology which included ICP Method 6010 for Al, Ba, B, Co, Cu, Fe, Mo, Ni, Sn, Ti, and Zn; and ICP-MS Method 6020 for Sb, As, Be, Cd, Cr, Pb, Mn, Se, Ag, Tl, and V. The analytical data package designated as "DeLisle Pant EPA TiO2 Wastewater Sampling" dated November 9, 2000, along with the data validation report dated December 13, 2000 from Environmental Standards titled "Volume 10 Wastewater Stream Samples DeLisle" were evaluated for this review. Based on the reports as noted, the following additional observations are noted:

Observations

- Of the Dupont data I have reviewed thus far, the DeLisle data package is the most complete from a data quality standpoint. The wastewater analytical results table dated January 29, 2001, has been updated to include the ICP results for Sb, As, Cr, Pb, Mn, Tl, and Zn. Overall, when there is a positive ICP/MS value that compares to the corresponding ICP value, the precision in most cases is excellent. The exceptions are Tl detected in the FINWW and OXSCWW ICP samples and not detected in the ICP/MS samples. However, only two of the ICP Tl results were above the reported MDL, so most Tl values at best can only be considered as estimated.

- All ICP matrix spike/matrix spike duplicate (MS/MSD) recoveries were within the laboratory established control limits and well within the generally accepted 80-120% recovery limits. For the ICP/MS MS/MSD analyses, Mn at (155%) in the MS and Ag at (21 and 22%) in the MS/MSD analyses were the only matrix spike outliers. Since the MSD recovery for Mn was an acceptable 117%, data qualification could be applied to the reported sample concentration, however, in my opinion it is not necessary. Conversely, Ag was not detected in the sample analysis and the reported detection limits should be qualified as estimated due to the poor MS/MSD recoveries.

- Three of the four field duplicate samples yielded at least one precision outlier as measured by percent reproducibility (%RPD). In particular, HCLW-02, Ti (183%); OXOWW-04, Al (118%), Ti (131%), Sn (103%), and Mn (48%); and OXSCWW-03 Mn (69%), Al (39%), Fe (95%), and Ti (70%). Although these precision outliers seem unreasonable, they are more indicative of the sample concentration variability rather than poor analytical precision. A review of the chain-of-custody documentation indicated that all field duplicates were collected the same times as their corresponding field samples. This was probably accomplished by collecting double the sample volume in order to fill two sets of sample containers. However, a review of the TSS data indicates that for samples OXOWW-04 (ND), OXOWW-04 Dup (9 mg/L), and OXSCWW-03 (32 mg/L) and OXSCWW-03 Dup (48 mg/L), some settling occurred during the sample collection procedures. The problem is there is no way to definitively say that the results from either sample is more representative. Rather than qualify the data based on poor duplicate precision, I would suggest averaging the values above the reporting limits and using an average concentration.

! An equipment blank was not collected for this sampling effort, but it is unclear what if any field equipment was used during sample collection. An equipment blank analysis would not be appropriate assuming all wastewater samples were collected directly in the sample containers.

! Method detection limit study data were provided to EPA on February 15, 2001, as an additional response to EPA's comments on the Environmental Standards Data Validation Report. For the STL Denver lab, ICP MDL data were reported for three separate instruments with each study performed on a separate day (2/16/00, 2/17/00, and 8/29/00). The MDLs reported in the DeLisle data package were an assortment of the values from the three MDL studies. This is unacceptable simply because it is not possible. Although this discrepancy has very little impact on the reported results, the correct MDLs are useful in evaluating whether to use concentrations detected above the MDL but below the reporting limit. The instrument used to perform the DeLisle analyses needs to be confirmed in order to assign the correct MDL values.

! The samples were digested using 50 mL, and for six samples 5 mL diluted to 50 mL, rather than the customary 100 mL. This was probably due to limited volume (250 mL) for several samples. However, for trace-level analyses it is important to use the full method-recommended sample volume since 100 mL will always be more representative of the sample composition than 50 mL.

! As noted previously, six samples were digested using 5 mL diluted to a final volume of 50 mL which represent a pre-analysis dilution of 10X. These same samples were diluted for ICP/MS analysis at the instrument by a factor 10 for a total dilution factor of 100X. Although the dilution factor was not displayed in the ICP/MS raw data header information, it was handwritten on each of the applicable pages. It appears the data results were correctly multiplied by the 100X dilution factor, however, this should be further confirmed by Dupont via STL.

Conclusions:

Based on the favorable data agreement between the ICP and ICP/MS data, the DeLisle wastewater results are considered valid and representative, however, the poor field precision data should be considered when using the results for HCLW-02, OXOWW-04, and OXSCWW-03. In addition, the overall favorable quality assurance data indicates the sample matrix was generally free from inferences and the analytical systems were operating efficiently.

Constituent of Concern	Analysis	Table 4: Finishing Wastewater – RIN 8 – DeLisle *Annual Waste Stream Generation Rate:2,859,842 Mtons/yr*				
		DL-FINWW-1	DL-FINWW-2	DL-FINWW-3	DL-FINWW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		6030	7630	6320	8930	7227
Total Suspended Solids – 160.2 (mg/L)		23.0	21.0	33.0	26.0	25.7
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6020	32.5	9.1	6.6	29.8	19.5
	6010	28.5	9.9 L	8.6 L	32.1	19.8
Arsenic	6020	3.6	18.5	24.3	4.7	12.8
	6010	6.2 L	22.2	28.5	6.4 L	15.8
Barium	6010B	20.4	31.9	18.6	12.6	20.9
Boron	6010B	195	265	194	144	199
Chromium	6020	<10.6	12.4 (U)^{B}	2.6 (U)^{B}	4.1 (U)^{B}	6.4
Chromium	6010	3.6 L	12.4	4.2 L	4.4 L	6.2
Cobalt	6010B	<1	<1	<1	<1	–
Iron	6010B	162	829	37.0 (J)^{B}	215	311
Lead	6020	<2.3	<2.3	<2.3	<2.3	–
Lead	6010	<3.0	<3.0	<3.0	<3.0	–

Constituent of Concern	Analysis	Table 4: Finishing Wastewater – RIN 8 – DeLisle *Annual Waste Stream Generation Rate:2,859,842 Mtons/yr*				
		DL-FINWW-1	DL-FINWW-2	DL-FINWW-3	DL-FINWW-4	Average
Manganese	6020	13.6	35.9	10.4	10.5	17.6
Manganese	6010	12.9	28.7	10.7	9.5	15.5
Nickel	6010B	2.1 (J)[B]	6.9 (J)[B]	3.6 (J)[B]	2.3 (J)[B]	3.7
Thallium	6020	<0.2	<0.2	<0.2	<0.2	–
	6010	5.2 L	8.1 L	4.8 L	2.6 L	5.2
Vanadium	6020	<10	<10	4.3 (J)[B]	4.7 (J)[B]	–
Zinc	6010	44.4	253	7.3 L	50.1	88.7

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).
[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.
L = Result is greater than the instrument detection and/or method detection limits but less than the laboratory reporting limit.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) results for DLFINWW-1, DLFINWW-2, DLFINWW-3, DLFINWW-4, for antimony as "U" (non-detect), and for arsenic as "J" (estimated). These ICPMS antimony and arsenic results showed good precision in almost all cases, when compared to their corresponding ICP values. Therefore, we removed the qualifiers.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) manganese results for DLFINWW-1 and DLFINWW-2 as "U" (non-detect). These ICPMS manganese results showed good precision, when compared to their corresponding ICP values. Therefore, we removed the qualifier.

Constituent of Concern	Analysis	Table 5: HCL Storage Scrubber Water – RIN 9 – DeLisle				
		DL-HCLW-1	DL-HCLW-2	DL-HCLW-3	DL-HCLW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		485	497	494	1050	631
Total Suspended Solids – 160.2 (mg/L)		<1.2	<1.2	<1.2	4.0	–
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6020	<2	<2	<2	66.3	–
	6010	1.0 L	<10	<10	71.9	–
Arsenic	6020	<2	<2	<2	46.5	–
	6010	<10	<10	1.6 L	49.1	–
Barium	6010B	33.2	36.0	37.0	152	64.5
Boron	6010B	196	201	195	279 (J)^{B}	218
Chromium	6020	<2.1	<2.1	<2.1	1570	–
Chromium	6010	<10	<10	<10	1570	–
Cobalt	6010B	<1	<1	<1	17.5 (J)^{B}	–
Iron	6010B	53.4 (J)^{B}	29.6 (J)^{B}	64.2 (J)^{B}	126000	31537
Lead	6020	<2.3	<2.3	<2.3	272	–
Lead	6010	<3.0	<3.0	<3.0	189	–

Constituent of Concern	Analysis	Table 5: HCL Storage Scrubber Water – RIN 9 – DeLisle				
		DL-HCLW-1	DL-HCLW-2	DL-HCLW-3	DL-HCLW-4	Average
Manganese	6020	31.0	33.0	33.6	919	254
	6010	30.4	31.6	33.2	927	256
Nickel	6010B	<2	21.4 (J)[B]	3.0 (J)[B]	899	308
Thallium	6020	<0.2	<0.2	<0.2	<0.2	–
Thallium	6010	<10	<10	<10	<10	–
Vanadium	6020	<2	<2	<2	1770	–
Zinc	6010	1.6 L	<20	2.5 L	291	–

U = This analyte should be considered “ not-detected” because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).
[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.
L = Result is greater than the instrument detection and/or method detection limits but less than the laboratory reporting limit.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) result for DLHCLW-4, for antimony as “U” (non-detect), and for arsenic as “J” (estimated). These ICPMS antimony and arsenic results showed good precision, when compared to their corresponding ICP values. Therefore, we removed the qualifiers.

Constituent of Concern	Analysis	Table 6: Oxidation Wastewater (Intermittent) – RIN 103 – DeLisle				
		DL-OXOWW-1	DL-OXOWW-2	DL-OXOWW-3	DL-OXOWW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		430	479	458	461	457
Total Suspended Solids – 160.2 (mg/L)		2.0 (J)^{B}	<1.2	16.0	<1.2	–
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6020	<2	<2	<2	<20	–
	6010	3.0 L	1.3 L	<10	8.1 L	–
Arsenic	6020	52.7	27.6	31.1	<20	37.1
	6010	61.0	20.3	25.4	6.5 L	28.3
Barium	6010B	586	206	480	<22	424
Boron	6010B	231	209	225	190 (J)^{B}	214
Chromium	6020	6.7 (U)^{B}	<2.1	<2.1	<21.2	–
Chromium	6010	8.9 L	1.7 L	2.2 L	6.1 L	4.7
Cobalt	6010B	<1	<1	<1	<10	–
Iron	6010B	970	88.0 (J)^{B}	134	<120	397
Lead	6020	4.3 (J)^{B}	<2.3	<2.3	<22.8	–
Lead	6010	<3.0	<3.0	<3.0	<3.0	–

Constituent of Concern	Analysis	Table 6: Oxidation Wastewater (Intermittent) – RIN 103 – DeLisle				
		DL-OXOWW-1	DL-OXOWW-2	DL-OXOWW-3	DL-OXOWW-4	Average
Manganese	6020	153	53.3	83.5	35.9	81.4
	6010	128	45.8	68.4	34.2 L	69.1
Nickel	6010B	7.6 (J)[B]	2.9 (J)[B]	2.7 (J)[B]	<20	4.4
Thallium	6020	<0.2	<0.2	<0.2	<2	–
Thallium	6010	<10	<10	<10	4.7 L	–
Vanadium	6020	7.5 (J)[B]	<2	2.7 (J)[B]	<20	–
Zinc	6010	28.8	5.6 L	4.5 L	3.1 L	10.5

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).
[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.
L = Result is greater than the instrument detection and/or method detection limits but less than the laboratory reporting limit.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) arsenic results for DL-OXOWW-2, DL-OXOWW-3 as "J" (estimated). These ICPMS arsenic results showed good precision, when compared to their corresponding ICP values. Therefore, we removed the qualifier.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) manganese results for DL-OXOWW-4 as "U" (non-detect). This ICPMS manganese result showed good precision, when compared to its corresponding ICP value. Therefore, we removed the qualifier.

Constituent of Concern	Analysis	Table 7: Oxidation Scrubber Wastewater – RIN 6 – DeLisle *Annual Waste Stream Generation Rate: 9,259 Mtons/yr*				
		DL-OXSCWW-1	DL-OXSCWW-2	DL-OXSCWW-3	DL-OXSCWW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		115000^{Q}	119000^{Q}	86400	71300^{Q}	97925
Total Suspended Solids – 160.2 (mg/L)		38.0	66.0	32.0 (J)	21.0	39.2
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6020	<20	<20	<20	<20	–
	6010	<100	<100	<100	<100	–
Arsenic	6020	<20	<20	<20	<20	–
	6010	12.2 L	<100	<100	<100	–
Barium	6010B	497	395	301	227	355
Boron	6010B	438 (J)^{B}	363 (J)^{B}	331 (J)^{B}	274 (J)^{B}	351
Chromium	6020	<21.2	<21.2	<21.2	<106	–
Chromium	6010	18.0 L	9.5 L	16.7 L	10.5 L	13.7
Cobalt	6010B	<10	<10	<10	<10	–
Iron	6010B	1260	1230	793 (J)^{B}	670 (J)^{B}	988
Lead	6020	<22.8	<22.8	<22.8	<22.8	–
Lead	6010	<30.0	<30.0	<30.0	<30.0	–
Manganese	6020	41.6	39.0	29.3	<38	36.6

Constituent of Concern	Analysis	Table 7: Oxidation Scrubber Wastewater – RIN 6 – DeLisle *Annual Waste Stream Generation Rate: 9,259 Mtons/yr*				
		DL-OXSCWW-1	DL-OXSCWW-2	DL-OXSCWW-3	DL-OXSCWW-4	Average
	6010	41.7 L	33.9 L	29.3 L	28.0 L	33.2
Nickel	6010B	110 (J)[B]	118 (J)[B]	59.1 (J)[B]	38.6 (J)[B]	81.4
Thallium	6020	<2	<2	<2	<2	–
	6010	27.5 L	<100	5.8 L	25.6 L	–
Vanadium	6020	<20	<20	<20	<100	–
Zinc	6010	34.3 L	15.7 L	35.2 L	40.6 L	31.5

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).
[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.
[Q] = LAB FOOTNOTE:
L = Result is greater than the instrument detection and/or method detection limits but less than the laboratory reporting limit.

Associated blanks exhibited contamination, ES qualified positive ICPMS (SW 6020) manganese results for DL-OXSCWW-1, DL-OXSCWW-2, DL-OXSCWW-3, as "U" (non-detect). These ICPMS manganese result showed good precision, when compared to its corresponding ICP value. Therefore, we removed the qualifier.

Volume 11

Wastewater- Edge Moor Plant, Wilmington, DE

Assessment of Analytical Data Submitted by DuPont
In Response to Proposed Inorganic Chemical Industry
Hazardous Waste Determination for K178

October 26, 2001

Review Summary for Dupont's Analytical Data Report (Volume 11)
Edge Moor Plant Wastewater Stream Samples
Edge Moor Plant, Wilmington, Delaware

Shen-yi Yang
March 15, 2001

Introduction:

The purpose of this review is to evaluate the validity of Dupont's waste analysis submitted in response to our K178 listing proposal. DuPont collected wastewater stream samples on October 19, 20, 21, and 22, 2000 at its Edge Moor Plant, Wilmington, Delaware. All samples were analyzed by Seven Trent Lab (STL) Denver, located in Arvada, Colorado for total concentrations of 11 metals (aluminum, barium, boron, cobalt, copper, iron, molybdenum, nickel, tin, titanium, and zinc) by EPA SW-846 Method 6010B (ICP) and 11 metals (antimony, arsenic, beryllium, cadmium, chromium, lead, manganese, selenium, silver, thallium, and vanadium) by EPA SW-846 Method 6020 (ICPMS), total dissolved solids (TDS) by MCAWW Method 160.1, and total suspended solids (TSS) by MCAWW Method 160.2. STL's data package was validated by Environmental Standards (ES) in Valley Forge, PA. DuPont submitted for our review STL's analytical results and ES' review summary in a document entitled "Quality Assurance Review of the Wastewater Samples Collected on October 19, 20, 21, and 22, 2000 at the Edge Moor Plant, Wilmington, Delaware for the DuPont Engineering TiO2 Listing Project", December 18, 2000".

This data package includes 16 wastewater samples, 4 field duplicates, and 2 equipment blanks. The sample identification numbers are: FWW-1, FWW-2, FWW-3, FWW-3 DUP, FWW-4, KS-1, KS-2, KS-3, KS-3 DUP, KS-4, EQB-1, EQB-2, OWW-1, OWW-2, OWW-3, OWW-3 DUP, OWW-4, OVS-1, OVS-2, OVS-3, OVS-3 DUP, OVS-4. My review focused on the validity of total concentrations of four constituents of concern (i.e., antimony, arsenic, manganese, and thallium). DuPont reported one sets (ICPMS) of results for antimony, arsenic, manganese, and thallium. While they did not report ICP results for antimony, arsenic, manganese, and thallium, these analyses were automatically conducted when STL ran the ICP analyses for other metals. We obtained STL's original CLP-like data package on 2/16/01 and also assessed these results.

Conclusions:

The quality of the ICPMS results is questionable. Data users need to consider the following for data that required qualification. See page 5 for a summary of ES-applied data qualifiers. The ICP total results for As, Sb, Mn, and Tl appear more reliable, therefore, were added to the analytical summary table.

1. The positive results for several metals in several samples were qualified due to <u>blank contamination</u>.

2. Antimony was detected in initial calibration blanks (ICBs) and continuing calibration blanks (CCBs) at levels greater than laboratory reporting limit (RL). According to SW-846 Method 6020, ICB and CCB must be < RL to be accepted. In the ICPMS analysis for D0J250181 and D0K290239, the lab consistently analyzed two consecutive initial calibration blanks (ICBs) and continuing calibration blanks (CCBs) throughout the analytical sequences. In all cases, Sb was observed at a concentration greater than the reporting limit (RL) in the initial CCB analyses. STL re-analyzed the CCBs to reshape the calibration slope as opposed to correcting the analytical condition and re-analyzing the affected samples.

2. The levels of contaminations (antimony in ICBs/CCBs and thallium in CCBs) were greater than 2X MDL. The negative bias (with an absolute value of the response > 2X MDL) observed in ICBs for thallium normally indicates that the method detection limit for thallium may be higher than reported. Therefore, it was difficult to determine how accurate the antimony and thallium results of all DuPont Edge Moor wastewater samples are.

3. STL used two or three blank samples (CCBs) to clean the ICPMS system (re-slope). There may be physical and/or memory interference.

4 Sample matrix effect interfered the detection of Sb and As in the samples collected from DuPont's three wastewater streams (FWW, OVS; and OWW). The "non-detected" results for Sb and As in several samples were qualified as unusable with "R" due to extremely low matrix spike/matrix spike duplicate recoveries. The positive results were qualified as estimated with "J".

5. The "non-detected" results for Tl in many samples were qualified due to observed negative bias in the associated blank analysis; The detection limits for Tl analysis may be higher than reported.

6. The results for all metals in one sample (FWW-3DUP) were qualified due to preservation of the sample prior to filtering the solids. Field duplicate results were reviewed but were not included in the analytical data summary table.

7. All QC sample results met acceptance criteria for As, Sb, Mn, and Tl. ICP total results for As, Sb, Mn, and Tl were, therefore, added to the analytical summary table.

Observations:

C One cooler received at 13.9EC, therefore samples (FWW-3Dup, OWW-3Dup, OVS-3Dup, KS-3Dup) were analyzed for metals only, not TDS/TSS. This temperature is outside the 4±2EC criterion for sample preservation.

C STL performed waste analyses for a fast turnaround time with minimal (level I) QC check (by an analyst using a data review checklist) before delivery of analytical data report. ES performed a complete QA review following guidance from the "National Functional Guidelines for Inorganic Data Review" (US EPA, 2/94). The areas ES reviewed include: sample holding times, sample condition upon lab receipt, instrument tuning and calibration, field and laboratory QC sample results, and quantitation of results.

C ES made hand-written additions (i.e., summaries for laboratory's analysis for initial and continuing calibration verification standards, initial and continuing blanks, interference check samples) and corrections (i.e., sample identification numbers, method detection limits/reporting limits, dilution factors, and sample results calculations) throughout the entire report. ES properly documented their corrections.

C Samples of one wastewater stream (FWW-1, FWW-2, FWW-3 and FWW-4) were treated as solids; samples were centrifuged. Solid portions were used to determine percent (%) moisture and digested for metal analysis. Water portion was used to determine total dissolved solids (TDS) and total suspended solids (TSS). All metals were reported on a dry-weight basis.

C STL's ICPMS linear calibration ranges for Mn, As, Sb, and Tl are from 1 to 2000 ug/l. ICPMS was continuing calibrated at 200 ug/l.

Detailed Discussions:

C ICP total analysis (analytical batch number: 0299536; instrument number 016)

All QC sample results met acceptance criteria for As, Sb, Mn, and Tl. QC results reviewed include method blanks, high standard, initial calibration verification, initial calibration blank, reporting limit verification, interference check sample, continuing calibration blanks and continuing calibration verification standards, serial dilution, duplicates, and matrix spike/matrix spike duplicate. ICP total results for As, Sb, Mn, and Tl were added to the analytical summary table.

C ICP total analysis (analytical batch number: 0299521; instrument number 016)

All QC sample results met acceptance criteria for As, Sb, Mn, and Tl. QC results reviewed include method blanks, high standard, initial calibration verification, initial calibration blank, reporting limit verification, interference check sample, continuing calibration blanks and continuing calibration verification standards, serial dilution, duplicates, and matrix spike/matrix spike duplicate. ICP total results for As, Sb, Mn, and Tl were added to the analytical summary table.

C ICPMS total analysis (analytical batch number: 0302165; Elan 6000, ICPMS1):

- Mn was present in the associated method blank (0.17 ug/l).
Total Mn results of all samples were relatively high compared to the level of contaminations that could be possibly introduced during the analysis. It is unnecessary to qualify the total Mn results for the samples.

- Antimony was present in ICBs and CCBs.
The antimony levels in blanks were ICB1 > 14XMDL; ICB2 >3X MDL; and CCBs are between 2X MDL and 15X MDL. According to SOP for SW 6020, ICB and CCB must be < RL to be accepted. The lab did not find out reasons why ICB/CCB were out of control to correct the problems, and did not re-analyze the affected samples. The lab only re-analyzed the CCB to re-slope the calibration curve.

- Negative bias (absolute value of the response > 2X MDL) was observed in ICBs for thallium. The method detection limit for thallium may be higher than reported. The reported detection limits for total thallium in OWW-1 may be higher than reported.

- Thallium was present in CCBs. The thallium level in one CCB was >5X MDL.

- Sample matrix effect interfered the detection of antimony and arsenic.

Antimony: Extremely low matrix spike and matrix spike duplicate recoveries (% rec. MS/MSD) (19% and 19%, spiked at 200 ug/l). The associated laboratory control standard (LCS) and the method blank were within control limits, these anomalies are considered to be due to sample matrix interference. Positive results of Sb in samples OWW-1, OWW-2, OWW-3, and OWW-4 are considered "estimated".

Arsenic: Extremely low % recoveries of MS/MSD (22% and 25%, when spiked at 200ug/l). The associated laboratory control standard (LCS) and the method blank (MB) were within control limits, these anomalies are considered to be due to sample matrix interference. The result for arsenic in samples KS-1, KS-2, KS-3 and KS-4 were estimated.

C ICPMS total analysis (analytical batch number: 0302164; Elan 6000, ICPMS1):

- Antimony was present in ICBs and CCBs.
Their levels in blanks were ICB1 > 3XMDL; ICB2 >14X MDL; and CCBs are between 2X MDL and 15X MDL. ES stated in the report that "antimony was detected in initial calibration blank (ICB) and continuing calibration blanks (CCBs) at levels greater than laboratory reporting limit (RL). According to SOP for SW 6020, ICB and CCB must be < RL to be accepted. The lab did not find out reasons why ICB/CCB were out of control to correct the problems, and did not re-analyze the affected samples. The lab only re-analyzed the CCB to re-slope the calibration curve.

- Mn was present in the associated blanks (method blank and equipment blank). The Mn results of samples FWW-1, FWW-2, FWW-3 were qualified with “U”.

. - Sample matrix effect interfered the detection of antimony and arsenic

Antimony: Extremely low recoveries sample matrix spike and sample matrix spike duplicate recoveries (MS=5.7 % and MSD= 2.6 % when spiked at 59 mg/kg) and high percent relative difference of the MS/MSD (%RPD = 76) . The associated laboratory control standard (LCS) and the method blank were within control limits, these anomalies are considered to be due to sample matrix interference. The “non-detected” results in samples FWW-1, FWW-2, FWW-3 are “unuseable”; The positive result for antimony in FWW-4 was estimated.

Arsenic: Extremely low % recoveries of MS/MSD (MS= 1.3% and MSD=1.9% when spiked at 59 mg/kg) and high percent relative difference of the MS/MSD (%RPD = 32). The associated laboratory control standard (LCS) and the method blank (MB) were within control limits, these anomalies are considered to be due to sample matrix interference. The “positive” results in samples FWW-1, FWW-2, FWW-3, and FWW-4 was estimated.

Summary of ES-Applied Data Qualifiers:

Qualifier	**Reason**	**Analyte**	**Samples**
U	This analyte was present in an associated initial and continuing calibration blanks.	Sb - total (SW6020)	OWW-1, OWW-2, OWW-3, OWW-4, FWW-4, KS-1, KS-2, KS-3, KS-4, OVS-1, OVS-2
	This analyte was present in an associated blanks.	Mn-total (SW6020)	FWW-1, FWW-2, FWW-3, OVS-1, OVS-2, OVS-3, OVS-4
	This analyte was present in associated blanks.	Tl-total (SW6020)	OWW-2, OWW-3, OWW-4, KS-1, KS-2, KS-3, KS-4, OVS-2
R	The non-detected results were qualified due to extremely low recoveries of sample matrix spike and sample matrix spike duplicates.	Sb - total (SW6020)	FWW-1, FWW-2, FWW-3
J	Low recoveries of sample matrix spike and sample matrix spike duplicates indicates that this results should be considered to be estimated.	As-total (SW6020)	FWW-1, FWW-2, FWW-3, FWW-4, KS-1, KS-2, KS-3, KS-4, OVS-1, OVS-2, OVS-3, OVS-4, OWW-1, OWW-2, OWW-3, OWW-4
UJ	Negative bias (with an absolute value greater than twice the MDL) was observed in ICBs indicates that the MDLs may be higher than reported.	Tl - total (SW6020)	FWW-1, FWW-2, FWW-3, FWW-4, OWW-1

Constituent of Concern	Analysis	Table 8: Finishing Wastewater – RIN 10 – Edge Moor *Annual Waste Stream Generation Rate: 4.53 Mtons/yr* **These samples were treated as solids. All metal analyses are reported on dry-weight basis.**				
		FWW-1	FWW-2	FWW-3	FWW-4	Average
		Sample 012	Sample 014	Sample 016	Sample 019	
Total Dissolved Solids – 160.1 (mg/L)		116000^{Q}	11100^{Q}	56500	115000^{G}	74650
Total Suspended Solids – 160.2 (mg/L)		484^{Q}	260^{Q}	506^{Q}	516^{Q}	441
% Moisture **(see footnote)**		76.2	79.3	52.2	49.5	
		Sample 011	Sample 013	Sample 015	Sample 018	
	Total	mg/kg (Validation Qualifier)	mg/kg (Validation Qualifier)	mg/kg (Validation Qualifier)	mg/kg (Validation Qualifier)	mg/kg
Antimony	6020	<0.084 (R)	0.097 (R)	<0.042 (R)	0.078 (U)	–
Arsenic	6020	0.046 (J)	0.051 (J)	0.029 (J)	0.044 (J)	0.042
Barium	6010B	0.91 (U)^{B}	1.1 (U)^{B}	0.52 (U)^{B}	0.38 (U)^{B}	0.73
Boron	6010B	<2.1	<2.5	<1.1	<1	–
Chromium	6020	1.4 (U)	1.6 (U)	1.1 (U)	1.4 (U)	1.4
Cobalt	6010B	<0.63	<0.73	<0.31	<0.3	–
Iron	6010B	19.5 (J)^{B}	26.7 (J)^{B}	12.2 (J)^{B}	25.4	20.9
Lead	6020	0.21 (J)^{B}	0.18 (J)^{B}	0.12 (J)^{B}	0.20	0.18
Manganese	6020	0.63 (U)	0.79 (U)	0.77 (U)	0.94	0.78
Nickel	6010B	1.4 (J)^{B}	1.4 (J)	1.0 (J)^{B}	1.3 (J)^{B}	1.3

Constituent of Concern	Analysis	Table 8: Finishing Wastewater – RIN 10 – Edge Moor *Annual Waste Stream Generation Rate: 4.53 Mtons/yr* **These samples were treated as solids. All metal analyses are reported on dry-weight basis.**				
		FWW-1	FWW-2	FWW-3	FWW-4	Average
Thallium	6020	<0.0084 (UJ)	<0.0097 (UJ)	<0.0042 (UJ)	<0.004 (UJ)	–
Vanadium	6020	1.4 (J)^{B}	0.80 (J)^{B}	0.91 (J)^{B}	1.3	1.1

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

UJ = This analyte was not detected, but the detection limit is probably higher due to a low bias identified during the quality assurance review.

R = Unusable result.

Constituent of Concern	Analysis	Table 9: Dryer (scrub solids kiln) Scrubber Wastewater – RIN 13 – Edge Moor				
		KS-1	KS-2	KS-3	KS-4	Average
Total Dissolved Solids – 160.1 (mg/L)		1160	868^{G}	1360	1400	1197
Total Suspended Solids – 160.2 (mg/L)		216	2060^{Q}	344	144	691
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010	4.7	< 3.4	5.1	3.6	
	6020	0.23 (U)	0.63 (U)	0.95 (U)	0.63 (U)	0.61
Arsenic	6010	<3.6	45.7	5.6	9.2	
	6020	5.8 (J)	47.2 (J)	5.4 (J)	12.4 (J)	17.7
Barium	6010B	49.5	301	49.7	87.4	122
Boron	6010B	188	202	234	229	213
Chromium	6020	14.2	183	12.7	24.7	58.6
Cobalt	6010B	2.7 (J)^{B}	40.3	3.1 (J)^{B}	9.5 (J)^{B}	13.9
Iron	6010B	6830	101000	6470	11800	31525
Lead	6020	11.1	148	9.7	21.1	47.5
Manganese	6010	331	4341	395	1982	
	6020	279	3780	337	1780	1544
Nickel	6010B	8.2 (J)^{B}	95.5	9.6 (J)^{B}	31.7 (J)^{B}	36.2

Constituent of Concern	Analysis	Table 9: Dryer (scrub solids kiln) Scrubber Wastewater – RIN 13 – Edge Moor				
		KS-1	KS-2	KS-3	KS-4	Average
Thallium	6010	<4.9	<4.9	<4.9	<4.9	<4.9
Thallium	6020	0.052	0.57	0.053	0.085	0.19
Vanadium	6020	17.5	191	15.3	27.7	62.9

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

[B] = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.

[G] = LAB FOOTNOTE: STL and ES did not define this qualifier.

[Q] = LAB FOOTNOTE: STL and ES did not define this qualitier.

Constituent of Concern	Analysis	Table 10: Oxidation Vent Scrubber Wastewater – RIN 9 – Edge Moor *Annual Waste Stream Generation Rate: 59,589 Mtons/yr*				
		OVS-1	OVS-2	OVS-3	OVS-4	Average
Total Dissolved Solids – 160.1 (mg/L)		5070[Q]	6460	2890	3140	4390
Total Suspended Solids – 160.2 (mg/L)		70.0	68.0	90.0	101	82.2
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010	<3.4	<3.4	<3.4	4.5	
	6020 (analyzed on 11/2/00)	<1 (R)	<1 (R)	<1 (R)	<1 (R)	–
	6020 (reanalyzed on 12/4/00)	0.70 (U)	0.30 (U)	<0.2	<0.2	–
Arsenic	6010	<3.6	<3.6	<3.6	<3.6	<3.6
	6020 (analyzed on 11/2/00)	<1 (R)	<1 (R)	<1 (R)	<1 (R)	–
	6020 (reanalyzed on 12/4/00)	0.46 (J)[B]	0.46 (J)[B]	0.31 (J)[B]	0.42 (J)[B]	0.41
Barium	6010B	30.0	31.3	32.2	30.8	31.1
Boron	6010B	35.9 (J)[B]	52.0 (J)[B]	30.8 (J)[B]	28.5 (J)[B]	36.8
Chromium	6020	3.3 (U)[B]	4.2 (U)[B]	1.2 (U)[B]	1.7 (U)[B]	2.6
	6020	2.4 (U)	2.5 (U)	1.7 (U)[B]	1.8 (U)[B]	2.1

Constituent of Concern	Analysis	Table 10: Oxidation Vent Scrubber Wastewater – RIN 9 – Edge Moor *Annual Waste Stream Generation Rate: 59,589 Mtons/yr*				
		OVS-1	OVS-2	OVS-3	OVS-4	Average
Cobalt	6010B	<1	<1	<1	<1	–
Iron	6010B	58.6 (J)^B	62.2 (J)^B	32.4 (J)^B	42.0 (J)^B	48.8
Lead	6020	<1.1	<1.1	<1.1	<1.1	–
	6020	<0.23	<0.23	<0.23	<0.23	–
Manganese	6010	0.8	0.7	<0.5	0.7	
	6020 (analyzed on 11/2/00)	1.5	1.4	0.85	1.0	1.2
	6020 (reanalyzed on 12/4/00)	1.2	1.1	0.70	0.76	0.94
Nickel	6010B	5.6 (J)^B	7.2 (J)^B	3.6 (J)^B	4.3 (J)^B	5.2
Thallium	6010	<4.9	<4.9	<4.9	<4.9	<4.9
	6020 (analyzed on 11/2/00)	<0.1 (UJ)	<0.1 (UJ)	<0.1 (UJ)	<0.1 (UJ)	–
	6020 (reanalyzed on 12-4-00)	<0.02	0.034 (U)	<0.02	<0.02	–
Vanadium	6020	<1	<1	<1	<1	–
	6020	<0.2	<0.2	<0.2	<0.2	–

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.
J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).
UJ = This analyte was not detected, but the detection limit is probably higher due to a low bias identified during the quality assurance review.
R = Unusable result – analyte may or may not be present in this sample.
^{B} = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.
^{Q} = LAB FOOTNOTE: STL and ES did not define this qualifier.

Constituent of Concern	Analysis	Table 11: Oxidation Wastewater (intermittent) – RIN 11 – Edge Moor				
		OWW-1	OWW-2	OWW-3	OWW-4	Average
Total Dissolved Solids – 160.1 (mg/L)		779	1070	630	324^{G}	701
Total Suspended Solids – 160.2 (mg/L)		261	834	1490	5450^{Q}	2009
	Total	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L (Validation Qualifier)	ug/L
Antimony	6010	4.54	6.6	7.7	5.4	
	6020	0.85 (U)	0.65 (U)	0.74 (U)	1.0 (U)	0.81
Arsenic	6010	<3.6	<3.6	<3.6	<3.6	<3.6
	6020	0.42 (J)	0.39 (J)	0.51 (J)	0.73 (J)	0.51
Barium	6010B	86.3	102	243	156	147
Boron	6010B	19.9 $(J)^{B}$	19.5 $(J)^{B}$	19.7 $(J)^{B}$	18.1 $(J)^{B}$	19.3
Chromium	6020	21.5	18.8	68.4 (J)	76.6	46.3
Cobalt	6010B	<1	<1	<1	<1	–
Iron	6010B	3380	2630	6930 (J)	7870	5202
Lead	6020	6.5	4.7	15.4	26.3	13.2
Manganese	6010	34.5	26.7	71.9	49.9	
	6020	43.9	32.5	87.5 (J)	63.1	56.8
Nickel	6010B	33.5 $(J)^{B}$	28.1 $(J)^{B}$	93.8	59.6	53.7

Constituent of Concern	Analysis	Table 11: Oxidation Wastewater (intermittent) – RIN 11 – Edge Moor				
		OWW-1	OWW-2	OWW-3	OWW-4	Average
Thallium	6010	<4.9	<4.9	<4.9	<4.9	<4.9
Thallium	6020	<0.02 (UJ)	0.048 (U)	0.034 (U)	0.036 (U)	0.039
Vanadium	6020	25.0	31.2	68.4 (J)	51.6	44.0

U = This analyte should be considered " not-detected" because it was detected in a blank at a similar level.

J = Quantitation is approximate due to limitations identified during the quality assurance review (data validation).

UJ = This analyte was not detected, but the detection limit is probably higher due to a low bias identified during the quality assurance review.

^{B} = LAB FOOTNOTE: The lab result should be considered qualitatively questionable due to blank contamination. The numerical value will be used for comparison purposes.

^{G} = LAB FOOTNOTE: Severn Trent Lab and Environmental Standards did not define this qualifier.

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