Attachment II

Rationale for Selection of Pesticides, Herbicides, and Related Compounds from the Hanford SST/DST Waste Considered for Analysis in Support of the Regulatory DQO (Privatization) (PNNL-12039)

PNNL-12039

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Rationale for Selection of Pesticides, Herbicides, and Related Compounds from the Hanford SST/DST Waste Considered for Analysis in Support of the Regulatory DQO (Privatization)

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P. Daling
K. Meier

December 1998

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Pacific Northwest National Laboratory
Richland, Washington

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1.0 Introduction

The Hanford Site has 177 underground storage tanks that contain 54 million gallons of high-level radioactive waste. The U.S. Department of Energy (DOE), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) have entered into the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) under the *Resource Conservation and Recovery Act of 1976 (*RCRA) and the Washington *Hazardous Waste Management Act of 1976* (HWMA). Under the RCRA and HWMA, the tank waste is designated as listed, characteristic, and criteria waste. Characterization data are needed for the tank waste to ensure compliant treatment, storage, and disposal of the waste, including requirements for meeting land disposal restrictions, delisting, and risk assessment. The DOE and Ecology through the Regulatory Data Quality Objectives (DQO) process have defined and documented (Wiemers et al. 1998c) characterization needs for the Hanford Site single-shell tank (SST) and double-shell tank (DST) waste.

The DQO process included selection of regulated analytes to be measured in Hanford DST and SST waste. The analyte selection process was completed through a series of technically defensible logic steps that are described by Wiemers et al. (1998c). An overview of the logic steps is provided in Appendix A. The detailed logic flowsheets are provided in Appendix B. The logic steps and associated terminology presented in Appendix A and Appendix B are referenced in this report. The analyte selection logic begins with a large universe of regulated compounds compiled from a number of applicable regulatory-related compound lists. These input lists include the Underlying Hazardous Constituents and Universal Treatment Standards (40 CFR 268.48) and the Toxic Air Pollutant (TAP) Class A (WAC 173-460-150) and Class B (WAC 173-460-160). In the analyte selection logic, each of the regulated compounds was evaluated, in part, with respect to the plausibility of existing in the Hanford Site SST and DST waste. One of the plausibility decisions addressed the need for analysis of regulated herbicides, pesticides, miticides, and fungicides.[1]

The objective of this report is to provide a description of the activities completed to answer the question: "What pesticides, herbicides, miticides, and related reagents[2] should be considered for analysis of compounds from the Hanford SST/DST waste in support of the Regulatory DQO for privatization?"

Pesticides and herbicides have been used on the Hanford Site since the early 1940s. During early site operations, these reagents consisted primarily of chlorinated compounds. The effort would be significant to recover historical procurement records and site use information for pesticides and herbicides. In addition, there exists a large uncertainty as to the quality and usefulness of such records. DOE and Ecology have therefore agreed to retain the chlorinated pesticides and herbicides for further consideration in the DQO analyte selection logic.

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[1]Decision steps preceding the pesticide, herbicide, etc., decision may have resulted in dismissal of regulated compounds from further consideration in the analyte selection logic. The list of compounds used as input to the pesticide, herbicide, etc., decision represents a subset of the initial regulatory input list.

[2]Hereafter, the different forms of "ides" (miticides, fungicide, insecticide, etc.) are referred to as "pesticides and herbicides."

Additional efforts were undertaken to further assess which pesticides and herbicides from the Regulatory DQO analyte input list should be considered for analysis. These efforts included review of:

- Historical Hanford Site technical documents
- Hanford Site Operation Procurement Records, 1990 to present
- Columbia River Comprehensive Impact Assessment
- a list of pesticide and herbicide compounds routinely analyzed by the Manchester Environmental Laboratory

Some reviewers of the Regulatory DQO have asked why pesticides and herbicides are a consideration in the source tank waste. No records indicate that pesticides and herbicides were purposely placed in the tanks. Pesticides and herbicides were applied in controlled concentrations and for specific reasons. Herbicides were more commonly used than pesticides because of the need to prevent growth of foliage over the tank farm area. Few locations in the tank farms exist where rainwater pools, forming puddles that could potentially come in contact with tank structures and allowing migration through the tank confinement into the tank. However, all tank farms contain sump pumps where accumulated water is pumped into the tank farm system. Therefore, pesticides and herbicides might have migrated into the tanks from the outside. To address this uncertainty, a limited number of chlorinated pesticides and herbicides were identified for further assessment.

Results of the recent assessments of pesticide and herbicide compound inputs and their applicability to the Regulatory DQO are described in Section 2.0. The regulated pesticide and herbicide compounds are tracked through the Regulatory DQO analyte selection logic in Section 3.0.

2.0 Assessments of Pesticide and Herbicide Uses at the Hanford Site

2.1 Historical Hanford Technical Documents

A historical inventory from the E.I. DuPont De Nemours & Co., Inc. (Hanford Engineer Works) was reviewed for information related to pesticide and herbicide use during early Hanford Site operations. This report lists the quantities of general classifications of chemicals. For example, pesticides and herbicides are grouped together as "agricultural, insecticide" or "agricultural, herbicide." This information was not useful for the identification of specific compounds to be considered in the analyte selection logic.

2.2 Hanford Site Operations Procurement Records, 1990 to Present

Grounds maintenance and procurement record summaries were obtained for chemical products used at the Hanford tank farm area since 1990. The inventory consisted of trade names only. The associated Material Safety Data Sheets (MSDS) and the Merck Index were used to identify individual chemical compounds. These compounds were compared to the Regulatory DQO analyte input list. Eight

pesticides and herbicides from the 1990 to present procurement list were common to the Regulatory DQO input list (Table 1). These compounds were retained in the analyte selection logic for further assessment.

2.3 Columbia River Comprehensive Impact Assessment (CRCIA)

A screening assessment in support of the CRCIA was prepared in April 1997 (Pacific Northwest National Laboratory 1997). This study lists over 550 constituents measured in the Columbia River, the groundwater near the Columbia River, and in soil and sediments in those areas. Assuming that Hanford Site-wide operations may have used pesticides and herbicides common to those used in the surrounding areas of the Hanford Site, this report provides an indication of potential past usage of pesticides and herbicides near the waste tanks. Three pesticide/herbicide compounds are reported as detected (Table 2) and were further considered in the analyte selection logic. In the subsequent logic steps, two of the three compounds (endrin aldehyde and chlordane) were assigned as unstable in the tank waste matrix. The third compound (4,4′-DDE) had a toxicity ranking below the cutoff and was dismissed from further consideration. Based on the analyte selection logic, the three compounds reported as detects in the CRCIA were not considered further.

2.4 Manchester Environmental Laboratory Pesticide and Herbicide Compound List

As a crosscheck, Ecology provided a list of pesticide and herbicide compounds (28 analytes, Table 3) that have been frequently analyzed for by the Manchester Environmental Laboratory[3]. The Manchester list includes 11 regulatory compounds also included on the Regulatory DQO analyte input list. Ecology agreed that compounds not on the Regulatory DQO input list should not arbitrarily be added for analysis in tank waste. Therefore, compounds from the Manchester list not on the Regulatory DQO input list were not evaluated as part of the Regulatory DQO.

2.5 Use of Pesticides and Herbicides During Early Hanford Site Operations

Due to the inconsistent record keeping for pesticides and herbicides during the early Hanford Site Operations, Ecology and DOE agreed to consider the chlorinated pesticides and herbicides that are listed in EPA SW-846, methods 8081A and 8151A. These analytes are included as input to subsequent analyte selection logic steps in the Regulatory DQO input list (35 analytes, Table 4).

[3]The Manchester Environmental Laboratory supports theWashington State Department of Ecology. The laboratory is located in Manchester, Washington.

3.0 Regulatory DQO Analyte Selection Logic Application to Pesticides and Herbicides

The Regulatory DQO analyte selection logic (refer to Appendix A and Appendix B) was applied to the regulated pesticide, herbicide, and related compounds. The following text explains the results of the relevant decision logic steps. References made to items such as "Q2, Q3, Q5-4, etc." refer to the individual queries in the database, and are marked as such on the Regulatory DQO analyte selection logic flowchart, Figures 4.1 through 4.6 (also provided in Appendix B).

There are 120 compounds on the analyte input list of the Regulatory DQO which may be classified as pesticides and herbicides (Table 5). Table 5 also identifies overlaps between the Regulatory DQO input list and input assessments described in Section 2.0. In the analyte selection logic, the regulated compounds were divided into those detected in the DST/SST waste and those that were non-detected. Because not all the compounds were analyzed in the DST/SST waste, non-detected compounds were reviewed to determine their plausible use during early Hanford Site operations. Compounds that are likely to have been used during early operations and those currently used and non-detected were assessed for stability in the tank waste environment and their relative level of toxicity and carcinogenicity (Wiemers et. al 1998c). Regulated pesticide and herbicide compounds detected 10 or more times are included for potential analyses.

3.1 Detected Compounds Not Considered for Analysis

From the list of regulated pesticides and herbicides in Table 5, the two compounds listed in Table 6 are not considered for further analysis since they have been detected in the DST/SST waste less than 10 times and have lower toxicity and carcinogenicity (Figure 4.2, Q5-4).

3.2 Non-Detected Compounds Removed During "Used in Industries Potentially Unrelated to Hanford" Evaluation

As part of the analyte selection logic, a review of compounds potentially unrelated to Hanford was performed, Figure 4.3, Q16-2. The process of determining whether the pesticides and herbicides were likely to have been used at Hanford is described by Wiemers et al. (1998b).

The Regulatory DQO input list contains 75 pesticides and herbicides that were assigned to "Used in industries potentially unrelated to Hanford activities" (Table 7). These 75 compounds were dismissed from further consideration in the analyte selection logic. Excluded from the "Used in industries potentially unrelated to Hanford activities" list are all chlorinated pesticides and herbicides (refer to Section 2.5), pesticides and herbicides reported in the 1990 to present procurement records (refer to Section 2.2), and any pesticides and herbicides reported as a detect in the SST/DST waste. These three groups of compounds were further considered in the analyte selection logic.

One example of the logic used to assess the use of a pesticide and herbicide at Hanford follows.

An MSDS for Ethion (CAS# 563-12-2) was found at the website for the Cooperative Extension Offices of Cornell University, Michigan State University, Oregon State University, and University of California at Davis (**http://ace.ace.orst.edu/info/extoxnet/pips/ethion.p93**). The information provided in the MSDS states: "Ethion is an organophosphate pesticide used to kill aphids, mites, scales, thrips, leafhoppers, maggots and foliar feeding larvae."

The Tank Waste Information Network System (TWINS) Tank Characterization Database and vapor database do not report any detections in the DST/SST waste for organophosphate compounds (OPC), but documentation is not available to see if analyses were performed for these compounds. The OPCs are not listed in the historical Hanford inventories for pesticides and herbicides, however, these inventories were based primarily on process chemicals, not site maintenance records. The reviewers concluded this pesticide would be used in an agricultural setting and control of the pests listed in the MSDS was not a Hanford Site-wide priority. Therefore, the compound Ethion was listed as "Used in industries potentially unrelated to Hanford."

3.3 Non-Detected Compounds, Considered Unstable in Tank Waste Matrix

The next step in the Regulatory DQO analyte selection logic was to evaluate the pesticides and herbicides for stability in the tank waste environment (Figure 4.4, Q18R). The basis for the stability assessment is provided by Wiemers et al. (1998a). Eighteen of the regulated pesticides and herbicides were considered unstable in the tank waste environment (Table 8) and did not continue through in the analyte selection logic.

3.4 Non-Detected, Stable Compounds with Lower Toxicity and/or Carcinogenicity

The remaining non-detected, stable, and potentially used at Hanford pesticides and herbicides were then evaluated for their specific toxicity and carcinogenicity (Figure 4.4, Q24). The toxicity and carcinogenicity ranking criteria is described by Wiemers et al. (1998c), Appendix C. Thirteen compounds were found to have toxicity and carcinogenicity rankings below the analyte selection cutoff (Table 9) and did continue through the analyte selection logic.

3.5 Priority Regulated Compounds for Characterization

Applying the final analyte selection logic steps shown in Figure 4.6 results in a list of compounds assigned as "priority-regulated compounds" for characterization. Table 10 lists the 12 pesticide and herbicide compounds included in the final priority list. An accounting of the regulated pesticide and herbicide pathway through the Regulatory DQO analyte selection logic is provided in Table 11.

4.0 Conclusion

Regulated pesticides, herbicides, miticides, and fungicides were evaluated for their potential past and current use at the Hanford Site. The starting list of these compounds is based on regulatory analyte input lists discussed in the Regulatory DQO. Twelve pesticide, herbicide, miticide, and fungicide compounds are identified for analysis in the Hanford SST and DST waste in support of the Regulatory DQO. The compounds considered for additional analyses are non-detected, considered stable in the tank waste matrix, and of higher toxicity/carcinogenicity.

5.0 References

40 CFR 268.48. "Land Disposal Restrictions." *U.S. Code of Federal Regulations*, as amended.

EPA. 1997. *Test Methods for Evaluation Solid Waste Physical/Chemical Methods*. SW-846, 3rd Edition, as amended by Updates I (July, 1992), IIA (August, 1993), IIB (January, 1995), and III (Dec 1997). U.S. Environmental Protection Agency, Washington, D.C.

Hanford Engineer Works. HAN-73214. Traffic and Transportation Departments. Memorandum to File. E.I. DuPont De Nemours & Co., Inc., Explosives Department, Wilmington, Delaware.

Hazardous Waste Management Act of 1976. Ch. 70.105 RCW.

Pacific Northwest National Laboratory. 1997. *Screening Assessment and Requirements for a Comprehensive Assessment - Columbia River Comprehensive Impact Assessment*. PNNL-11540, DOE/RL-96-16, Rev. 0. Pacific Northwest National Laboratory, Richland Washington.

WAC 173-460. "Controls for New Sources of Toxic Air Pollutants." *Washington Administrative Code*, as amended.

Wiemers KD, H Babad, RT Hallen, LP Jackson and ME Lerchen. 1998a. *An Assessment of the Stability and the Potential for In-Situ Synthesis of Regulated Organic Compounds in High Level Radioactive Waste Stored at Hanford, Richland, Washington*. PNNL-11943. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, RT Hallen, H Babad, LK Jagoda and K Meier. 1998b. *A Compilation of Regulated Organic Constituents Not Associated with the Hanford Site, Richland, Washington*. PNNL-11927. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, ME Lerchen, M Miller, and K Meier. 1998c. *Regulatory Data Quality Objectives Supporting Tank Waste Remediation System Privatization Project*. PNNL-12040, Rev. 0. Pacific Northwest National Laboratory, Richland, Washington.

Table 1. Hanford Procurement Records, Pesticides and Herbicides, 1990 to Present (8 compounds).

CAS #	Constituent
1582-09-8	Trifluralin
22781-23-3	Bendiocarb
2921-88-2	Chlorpyrifos
314-40-9	Bromacil
330-54-1	Diuron
8003-34-7	Pyrethrum
94-75-7	2,4-D
98-01-1	Furfural

Table 2. Detected, Regulated Pesticide and Herbicide Compounds from the Columbia River Comprehensive Impact Assessment (CRCIA) (3 compounds).

CAS #	Constituent
57-74-9	Chlordane
72-55-9	4,4'-DDE
7421-93-4	Endrin aldehyde

Table 3. Manchester Environmental Laboratory Pesticide and Herbicide List (28 compounds).

CAS #	Constituent	Included on Regulatory DQO Input List
100-02-1	4-Nitrophenol	
118-79-6	2,4,6-Tribromophenol	
120-36-5	Dichloroprop	
133-90-4	Chloramben	x
1689-83-4	Ioxynil	
1689-84-5	Bromoxynil	
1861-32-1	Dacthal (DCPA)	
1918-00-9	Dicamba (I,II)	
1918-02-1	Picloram	x
25057-89-0	Bentazon	
4901-51-3	2,3,4,5-Tetrachlorophenol	
50594-66-6	Acifluorfen (Blazer)	
51338-27-3	Diclofop-ME	
51-36-5	3,5-Dichlorobenzoic Acid	
58-90-2	2,3,4,6-Tetrachlorophenol	x
75-99-0	Dalapon (DPA)	x
7600-50-2	5-Hydroxydicamba	
87-86-5	Pentachlorophenol	x
88-06-2	2,4,6-Trichlorophenol	x
88-85-7	Dinoseb	x
933-78-8	2,3,5-Tetrachlorophenol	
93-65-2	MCPP	
93-72-1	2,4,5-TP (Silvex)	x
93-76-5	2,4,5-T	x
94-74-6	MCPA	
94-75-7	2,4-D	x
94-82-6	2,4-DB	
95-95-4	2,4,5-Trichlorophenol	x

Table 4. Regulated, Chlorinated Pesticides and Herbicides Potentially Used During Early Hanford Site Operations (35 compounds).

CAS #	Constituent
1024-57-3	Heptachlor Epoxide
1031-07-8	Endosulfan Sulfate
118-74-1	Hexachlorobenzene
133-06-2	Captan
133-90-4	Chloramben
1582-09-8	Trifluralin
1836-75-5	Nitrofen
1918-02-1	Picloram
2385-85-5	Mirex
2425-06-1	Captafol
309-00-2	Aldrin
319-84-6	alpha-BHC
319-85-7	beta-BHC
319-86-8	delta-BHC
33213-65-9	Endosulfan II
465-73-6	Isodrin
50-29-3	4,4-DDT
510-15-6	Chlorobenzilate
57-74-9	Chlordane
58-89-9	gamma-BHC (Lindane)
60-57-1	Dieldrin
72-20-8	Endrin
72-43-5	Methoxychlor
72-54-8	4,4'-DDD
72-55-9	4,4'-DDE
7421-93-4	Endrin aldehyde
75-99-0	2,2-Dichloropropionic acid
76-44-8	Heptachlor
77-47-4	Hexachlorocyclopentadiene
8001-35-2	Toxaphene
87-86-5	Pentachlorophenol
88-85-7	2-sec-Butyl-4,6-dinitrophenol; syn Dinoseb
93-76-5	2,4,5-T
94-75-7	2,4-D
959-98-8	Endosulfan I

Table 5. Comparison of Regulatory DQO Analyte Input List for Pesticides and Herbicides and Input Assessments[1] (120 compounds). (3 Sheets)

CAS #	Constituent	CRCIA	Pre 1990	Manchester	1990 Inventory
101-27-9	Barban				
1024-57-3	Heptachlor Epoxide		x		
1031-07-8	Endosulfan Sulfate		x		
10605-21-7	Carbendazim				
1114-71-2	Pebulate				
114-26-1	Propoxur				
115-29-7	Endosulfan				
115-90-2	Fensulfothion				
118-74-1	Hexachlorobenzene		x		
121-75-5	Malathion				
122-42-9	Propham				
13121-70-5	Cyhexatin				
133-06-2	Captan		x		
133-90-4	Chloramben		x	x	
136-78-7	Sesone				
137-30-4	Ziram				
140-57-8	Aramite				
141-66-2	Dicrotophos				
143-50-0	Kepone				
14484-64-1	Ferbam				
1563-38-8	Carbofuran phenol				
1563-66-2	Carbofuran				
1582-09-8	Trifluralin		x		x
16752-77-5	Methomyl				
17804-35-2	Benomyl				
1836-75-5	Nitrofen		x		
1912-24-9	Atrazine				
1918-02-1	Picloram		x	x	
1929-77-7	Vernolate				
1929-82-4	Nitrapyrin				
2008-41-5	Butylate				
2032-65-7	Methiocarb				
2104-64-5	EPN				
21087-64-9	Metribuzin				
2212-67-1	Molinate				
22224-92-6	Fenamiphos				
22781-23-3	Bendiocarb				x
2303-17-5	Triallate				
23135-22-0	Oxamy				
23564-05-8	Thiophanate-methyl				
2385-85-5	Mirex		x		
23950-58-5	Pronamide				

Table 5. Comparison of Regulatory DQO Analyte Input List for Pesticides and Herbicides and Input Assessments[1] (120 compounds). (3 Sheets)

CAS #	Constituent	CRCIA	Pre 1990	Manchester	1990 Inventory
2425-06-1	Captafol		x		
2631-37-0	Promecarb				
2921-88-2	Chlorpyrifos				x
2971-90-6	Clopidol				
298-00-0	Methyl parathion				
298-02-2	Phorate				
298-04-4	Disulfoton				
299-84-3	Ronnel				
299-86-5	Crufomate				
300-76-5	Naled				
30558-43-1	A2213				
309-00-2	Aldrin		x		
314-40-9	Bromacil				x
315-18-4	Mexacarbate				
319-84-6	alpha-BHC		x		
319-85-7	beta-BHC		x		
319-86-8	delta-BHC		x		
330-54-1	Diuron				x
33213-65-9	Endosulfan II		x		
333-41-5	Diazinon				
3383-96-8	Temephos				
3424-82-6	o,p'-DDE (2,4'-DDE)				
35400-43-2	Sulprofos				
3547-04-4	DDE (p,p'-Dichlorodiphenyldichloroethylene)				
3689-24-5	Tetraethyldithiopyrophosphate (TEDP)				
465-73-6	Isodrin		x		
4685-14-7	Paraquat				
50-29-3	4,4'-DDT		x		
510-15-6	Chlorobenzilate		x		
53-19-0	o,p'-DDD (2,4'-DDD)				
55-38-9	Fenthion				
555-84-9	1-(5-Nitrofurfurylidene)amino)-2-imidazolidinone				
56-38-2	Parathion				
563-12-2	Ethion				
57-24-9	Strychnine				
57-74-9	Chlordane	x	x		
58-89-9	gamma-BHC (Lindane)		x		
58-90-2	2,3,4,6-Tetrachlorophenol			x	
59669-26-0	Thiodicarb				
60-57-1	Dieldrin		x		

Table 5. Comparison of Regulatory DQO Analyte Input List for Pesticides and Herbicides and Input Assessments[1] (120 compounds). (3 Sheets)

CAS #	Constituent	CRCIA	Pre 1990	Manchester	1990 Inventory
61-82-5	Amitrole				
62-44-2	Phenacetin				
62-73-7	Dichlorvas				
63-25-2	Carbaryl				
6923-22-4	Monocrotophos				
72-20-8	Endrin		x		
72-43-5	Methoxychlor		x		
72-54-8	4,4'-DDD		x		
72-55-9	4,4'-DDE	x	x		
7421-93-4	Endrin aldehyde	x	x		
75-99-0	2,2-Dichloropropionic acid		x	x	
759-94-4	EPTC				
76-44-8	Heptachlor		x		
77-47-4	Hexachlorocyclopentadiene		x		
7786-34-7	Mevinphos				
78-34-2	Dioxathion				
789-02-6	o,p'-DDT (2,4'-DDT)				
8001-35-2	Toxaphene		x		
8003-34-7	Pyrethrum				x
8022-00-2	Methyl demeton				
8065-48-3	Demeton				
81-81-2	Warfarin (>0.3%)				
81-81-2a	Warfarin (<0.3%)				
83-26-1	Pindone				
83-79-4	Rotenone				
85-00-7	Diquat				
86-50-0	Azinphos-methyl				
87-86-5	Pentachlorophenol		x	x	
88-06-2	2,4,6-Trichlorophenol			x	
88-85-7	2-sec-Butyl-4,6-dinitrophenol; syn Dinoseb		x	x	
92-84-2	Phenothiazine				
93-72-1	Silvex (2,4,5-TP)			x	
93-76-5	2,4,5-T		x	x	
94-75-7	2,4-D		x	x	x
944-22-9	Fonofos				
95-95-4	2,4,5-Trichlorophenol			x	
959-98-8	Endosulfan I		x		
98-01-1	Furfural				x

[1]Input assessments are described in Section 2.0.

Table 6. Regulated, Detected Pesticides and Herbicides with Lower Toxicity and Less Than Ten Hits (2 compounds).

CAS #	Constituent
88-06-2	2,4,6-Trichlorophenol
95-95-4	2,4,5-Trichlorophenol

Table 7. Regulated, Non-detected Pesticides and Herbicides Used in Industries Not Associated with Hanford (75 compounds). (2 Sheets)

CAS #	Constituent
101-27-9	Barban
10605-21-7	Carbendazim
1114-71-2	Pebulate
114-26-1	Propoxur
115-29-7	Endosulfan
115-90-2	Fensulfothion
121-75-5	Malathion
122-42-9	Propham
13121-70-5	Cyhexatin
136-78-7	Sesone
137-30-4	Ziram
140-57-8	Aramite
141-66-2	Dicrotophos
143-50-0	Kepone
14484-64-1	Ferbam
1563-38-8	Carbofuran phenol
1563-66-2	Carbofuran
16752-77-5	Methomyl
17804-35-2	Benomyl
1912-24-9	Atrazine
1929-77-7	Vernolate
1929-82-4	Nitrapyrin
2008-41-5	Butylate
2032-65-7	Methiocarb
2104-64-5	EPN
21087-64-9	Metribuzin
2212-67-1	Molinate
22224-92-6	Fenamiphos
2303-17-5	Triallate
23135-22-0	Oxamy
23564-05-8	Thiophanate-methyl
23950-58-5	Pronamide
2631-37-0	Promecarb
2971-90-6	Clopidol
298-00-0	Methyl parathion
298-02-2	Phorate
298-04-4	Disulfoton
299-84-3	Ronnel
299-86-5	Crufomate

Table 7. Regulated, Non-detected Pesticides and Herbicides Used in Industries Not Associated with Hanford (75 compounds). (2 Sheets)

CAS #	Constituent
300-76-5	Naled
30558-43-1	A2213
315-18-4	Mexacarbate
333-41-5	Diazinon
3383-96-8	Temephos
3424-82-6	o,p'-DDE (2,4'-DDE)
35400-43-2	Sulprofos
3547-04-4	DDE (p,p'-Dichlorodiphenyldichloroethylene)
3689-24-5	Tetraethyldithiopyrophosphate (TEDP)
4685-14-7	Paraquat
53-19-0	o,p'-DDD (2,4'-DDD)
55-38-9	Fenthion
555-84-9	1-(5-Nitrofurfurylidene)amino)-2-imidazolidinone
56-38-2	Parathion
563-12-2	Ethion
57-24-9	Strychnine
59669-26-0	Thiodicarb
61-82-5	Amitrole
62-44-2	Phenacetin
62-73-7	Dichlorvas
63-25-2	Carbaryl
6923-22-4	Monocrotophos
759-94-4	EPTC
7786-34-7	Mevinphos
78-34-2	Dioxathion
789-02-6	o,p'-DDT (2,4'-DDT)
8022-00-2	Methyl demeton
8065-48-3	Demeton
81-81-2	Warfarin (>0.3%)
81-81-2a	Warfarin (<0.3%)
83-26-1	Pindone
83-79-4	Rotenone
85-00-7	Diquat
86-50-0	Azinphos-methyl
92-84-2	Phenothiazine
944-22-9	Fonofos

Table 8. Regulated, Non-detected Pesticides and Herbicide Compounds Considered Unstable in SST/DST Waste Environment (18 Compounds).

CAS #	Constituent
1024-57-3	Heptachlor Epoxide
1031-07-8	Endosulfan Sulfate
133-06-2	Captan
133-90-4	Chloramben
1918-02-1	Picloram
22781-23-3	Bendiocarb
2425-06-1	Captafol
2921-88-2	Chlorpyrifos
314-40-9	Bromacil
330-54-1	Diuron
33213-65-9	Endosulfan II
510-15-6	Chlorobenzilate
57-74-9	Chlordane
7421-93-4	Endrin aldehyde
77-47-4	Hexachlorocyclopentadiene
8003-34-7	Pyrethrum
959-98-8	Endosulfan I
98-01-1	Furfural

Table 9. Regulated, Non-detected, Stable Pesticide and Herbicide Compounds With Lower Toxicity and Carcinogenicity Rankings (13 Compounds).

CAS #	Constituent	UHC Tox Category	TAP Tox Category	Slope Factor Ranking
1582-09-8	Trifluralin		V	
1836-75-5	Nitrofen[a]			
2385-85-5	Mirex[a]			
319-86-8	delta-BHC	D		
50-29-3	4,4'-DDT	C		BC
58-90-2	2,3,4,6-Tetrachlorophenol	C		
72-43-5	Methoxychlor	D	III	
72-54-8	4,4'-DDD	C		
72-55-9	4,4'-DDE	D		
75-99-0	2,2-Dichloropropionic acid		III	
93-72-1	Silvex (2,4,5-TP)	D		
93-76-5	2,4,5-T		III	
94-75-7	2,4-D	C		

(a) Toxicity and carcinogenicity unknown.
UHC = Underlying Hazardous Constituents
TAP = Toxic Air Pollutant

Table 10. Prioritized Pesticides and Herbicide Compounds for Analysis (12 compounds, Query Q42).

CAS #	Constituent	UHC Tox Cat	TAP Tox Cat	Slope Factor Ranking
118-74-1	Hexachlorobenzene	C		v
309-00-2	Aldrin	A		iv
319-84-6	alpha-BHC	C		v
319-85-7	beta-BHC			v
465-73-6	Isodrin	B		
58-89-9	gamma-BHC (Lindane)	B		
60-57-1	Dieldrin	X		iv
72-20-8	Endrin	A	I	
76-44-8	Heptachlor	B		v
8001-35-2	Toxaphene	C		v
87-86-5	Pentachlorophenol	B		
88-85-7	2-sec-Butyl-4,6-dinitrophenol; syn Dinoseb	B		

UHC = Underlying Hazardous Constituents
TAP = Toxic Air Pollutant

Table 11. Summary Accounting of Regulated Pesticides and Herbicides in the Regulatory DQO.

Table	Contents	Count
5	Total number of regulated pesticides/herbicides in Regulatory DQO input list	**120**
6	Detected compounds with lower toxicity and less than 10 hits	2
7	Non-detected compounds assigned to Industries not associated with Hanford	75
8	Non-detected compounds considered unstable in tank waste environment	18
9	Non-detected, stable compounds with lower toxicity and carcinogenicity ranking	13
10	Prioritized pesticides and herbicide compounds for analysis	12

Appendix A

Regulatory Data Quality Objective Analyte Selection Logic Summary

A1.0 Background

The DOE and Ecology through the Regulatory Data Quality Objectives (DQO) process have defined and documented (Wiemers et al. 1998) generator characterization needs for the Hanford Site single-shell tank (SST) and double-shell tank (DST) waste.

The Regulatory DQO process included selection of regulated analytes to be measured in Hanford DST and SST waste. The analyte selection process was completed through a series of technically defensible logic steps described by Wiemers et al. (1998). An overview of the logic steps is provided in this Appendix. The detailed logic flowsheets are provided in subsequent Appendix B.

A2.0 Overview of Logic

A2.1 Logic Construct

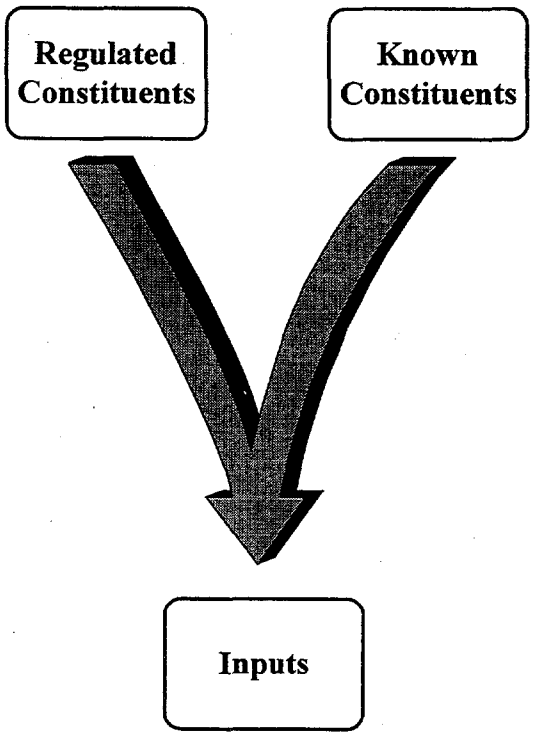
An analyte selection logic was developed that focuses on the data users needs and relies on technically defensible decisions for determining the final list of compounds for characterization. First, the input list of regulated and known compounds was created by:

- Identification of regulated compounds:
  - -- toxic air pollutants (TAP) (*Washington Administrative Code* [WAC] 173-460),
  - -- underlying hazardous constituents (UHC) (40 *Code of Federal Regulations* [CFR] 268.48)
  - -- universal treatment standards (UTS) (40 CFR 268.2(i)), and
  - -- Double-Shell Tank System RCRA Permit Application, Part A Form 3.
- Identification of known constituents:
  - -- Tank Waste Information Network System (TWINS) Tank Characterization Database and Vapor Database,
  - -- 242-A Campaign (1994-1996),
  - -- Historical inventories, and
  - -- Waste Stream Profile Sheets (WSPS).

These regulated and known constituents create the input list for the Regulatory DQO Analyte Selection Logic (see Figure A.1).

To manage these compounds in a logical fashion, constituents were grouped together into organic constituents, and non-organic constituents, which included organometalics, inorganic, radionuclides and test parameters. The analyte selection logic in Figure A.2 applies to the organic compounds. Organic constituents were evaluated to determine whether the analytes were likely to be used at the Hanford Site and evaluated for chemical stability in tank waste.

Figure A.1. Input List for Analyte Selection Logic.



Compounds that were retained include:

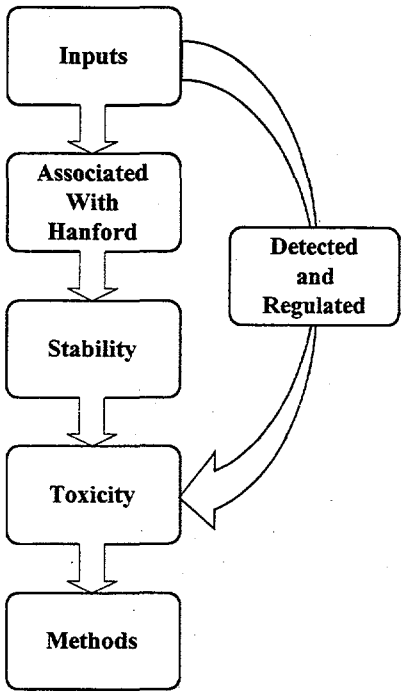
- polyaromatic hydrocarbons (due to tar in the tanks),
- chlorinated pesticides and herbicides used historically at the Hanford Site (Wiemers et al. 1998a),
- compounds reported in historical inventories, and
- compounds where a technical defensible decision to remove the constituent could not be made.

The technical decisions can be summarized in the following sections. Figure A.2 presents a simplified overview of the selection logic for the organic compounds and the technical evaluations performed.

A2.2 Other Industries

The regulated organic compounds were evaluated to assess potential use at the Hanford Site (Wiemers et al. 1998b). This evaluation was based on published information on predominant uses from a number of commercial databases and best professional judgment. Compounds identified as potentially never used at the Hanford Site were eliminated from the selection of regulated organic compounds. Compounds previously identified in tank waste were not removed in Industry use evaluation.

Figure A.2. Simplified Analyte Selection Logic for Organic Regulated Compounds.



A2.3 Stability

The Hanford tank waste is an aqueous alkaline, oxidative, radioactive matrix. Not all chemical compounds exist in this kind of environment, and many decompose or undergo chemical reactions in the tank.

Regulated compounds may be generated through degradation of solvents and/or complexants existing in the tank waste (Wiemers et al. 1998c). The stability evaluation was based on reaction chemistry of functional groups of the analytes in question and chemical reaction rates. To be considered unstable, one or more functional groups must react producing compounds with a half-life of less than one year. Therefore, the regulated organic compounds were reviewed for their possible instability in the tank environment and unstable compounds were eliminated from the list of regulated organic compounds. Compounds previously identified in tank waste were considered stable. Stable compounds were evaluated for toxicity and potential methods of analysis.

A2.4 Toxicity

The regulated organic compounds were also reviewed for their possible toxicity and carcinogenicity (Wiemers et al. 1998, Appendix C). Information was collected from US Environmental Protection Agency (EPA) databases and WAC regulations to allow ranking of compounds by level of toxicity/

carcinogenicity. Ranking the degrees of toxicity/carcinogenicity allows selection of higher toxicity/carcinogenicity compounds.

The final regulated organic compounds were grouped as follows:

- non-detected, considered stable in the waste matrix and of higher toxicity/carcinogenicity;
- detected and of higher toxicity/carcinogenicity; and
- detected more than 10 times and of lower toxicity.

The organic compounds from the list were screened against the above criteria. The remaining compounds were evaluated to determine whether SW-846 methods or modified SW-846 methods could be used for analysis (EPA 1997).

A2.5 Methods

An approach to methods selection and validation was agreed to by the DOE and Ecology. This approach requires the performing laboratory(ies) to verify MDLs, target EQLs and QC, and to conduct a holding time and storage condition study. Details of the methods assessment are provided by Wiemers et. al 1998d.

A3.0 Regulated Inorganic Analyte Selection Logic

The regulated inorganic and organometalic compounds removed at the beginning of the Regulatory DQO Organic Analyte Selection Logic were considered separately. For inorganic compounds, a comparison by CAS# is not possible, since these compounds disassociate to the ions in solution during analysis and are measured as ions in the appropriate analytical methods. Therefore, a unique list of anions and cations of the regulated inorganic and organometalic compounds was prepared.

This list was then reviewed against historical records and evaluated for potential use in Industries unrelated to Hanford activities. After deselecting ions not used at the Hanford Site, the final table of cations and anions of potential regulatory concern was prepared.

A4.0 References

40 CFR 268. "Land Disposal Restrictions." *Code of Federal Regulations*, as amended.

EPA. 1997. *Test Methods for Evaluation Solid Waste Physical/Chemical Methods*. SW-846, 3rd Edition, as amended by Updates I (July, 1992), IIA (August, 1993), IIB (January, 1995), and III (Dec 1997). US Environmental Protection Agency, Washington, D.C.

WAC 173-460. "Controls for New Sources of Toxic Air Pollutants." *Washington Administrative Code*, as amended.

Wiemers KD, ME Lerchen, M Miller, and K Meier. 1998. *Regulatory Data Quality Objectives Supporting Tank Waste Remediation System Privatization Project*. PNNL- 12040, Rev. 0. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, P Daling, and K Meier. 1998a. *Rationale for Selection of Pesticides, Herbicides and Related Compounds from the Hanford SST/DST Waste Considered for Analysis in Support of the Regulatory DQO (Privatization)*. PNNL-12039. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, RT Hallen, H Babad, LK Jagoda, and K Meier. 1998b. *A Compilation of Regulated Organic Constituents Not Associated with the Hanford Site, Richland, Washington*. PNNL-11927. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, H Babad, RT Hallen, LP Jackson, and ME Lerchen. 1998c. *An Assessment of the Stability and the Potential for In-situ Synthesis of Regulated Organic Compounds in High Level Radioactive Waste Stored at Hanford, Richland, Washington*. PNNL-11943. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers KD, ME Lerchen, and M Miller. 1998d. *An Approach for the Analysis of Regulatory Analytes in High Level Radioactive Waste Stored at Hanford, Richland, Washington*. PNNL-11942. Pacific Northwest National Laboratory, Richland, Washington.

Appendix B

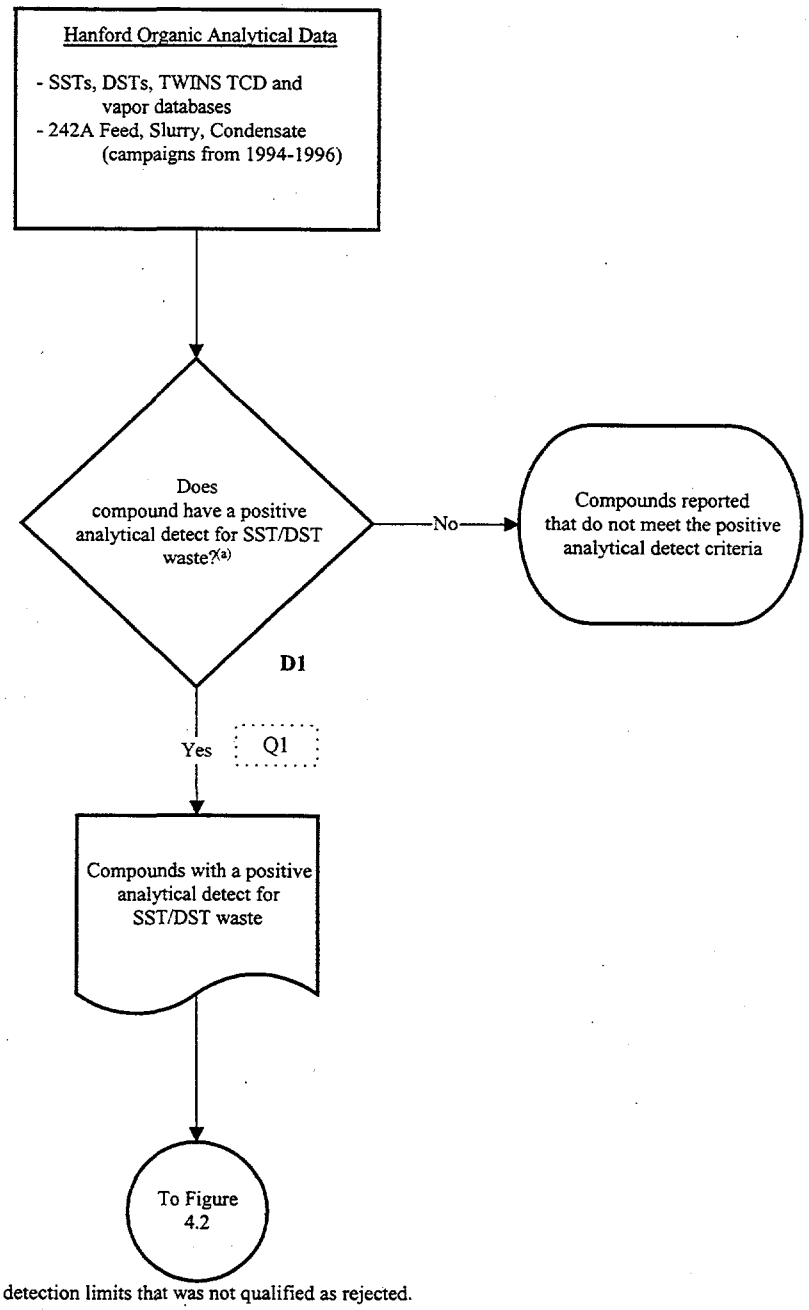
Regulatory Data Quality Objective Detailed Logic Flowsheet

Figures 4.1 through 4.6 were developed for the Regulatory DQO (Wiemers et al. 1998) and are provided for reference only.

Reference

Wiemer KD, ME Lerchen, M Miller, K Meier. 1998. *Regulatory Data Quality Objectives Supporting Tank Waste Remediation System Privatization Project.* PNNL-12040, Rev. 0. Pacific Northwest National Laboratory, Richland, Washington.

Figure 4.1. Development of Potential Organic Single-Shell Tank/ Double-Shell Tank Waste Positive Detect List.

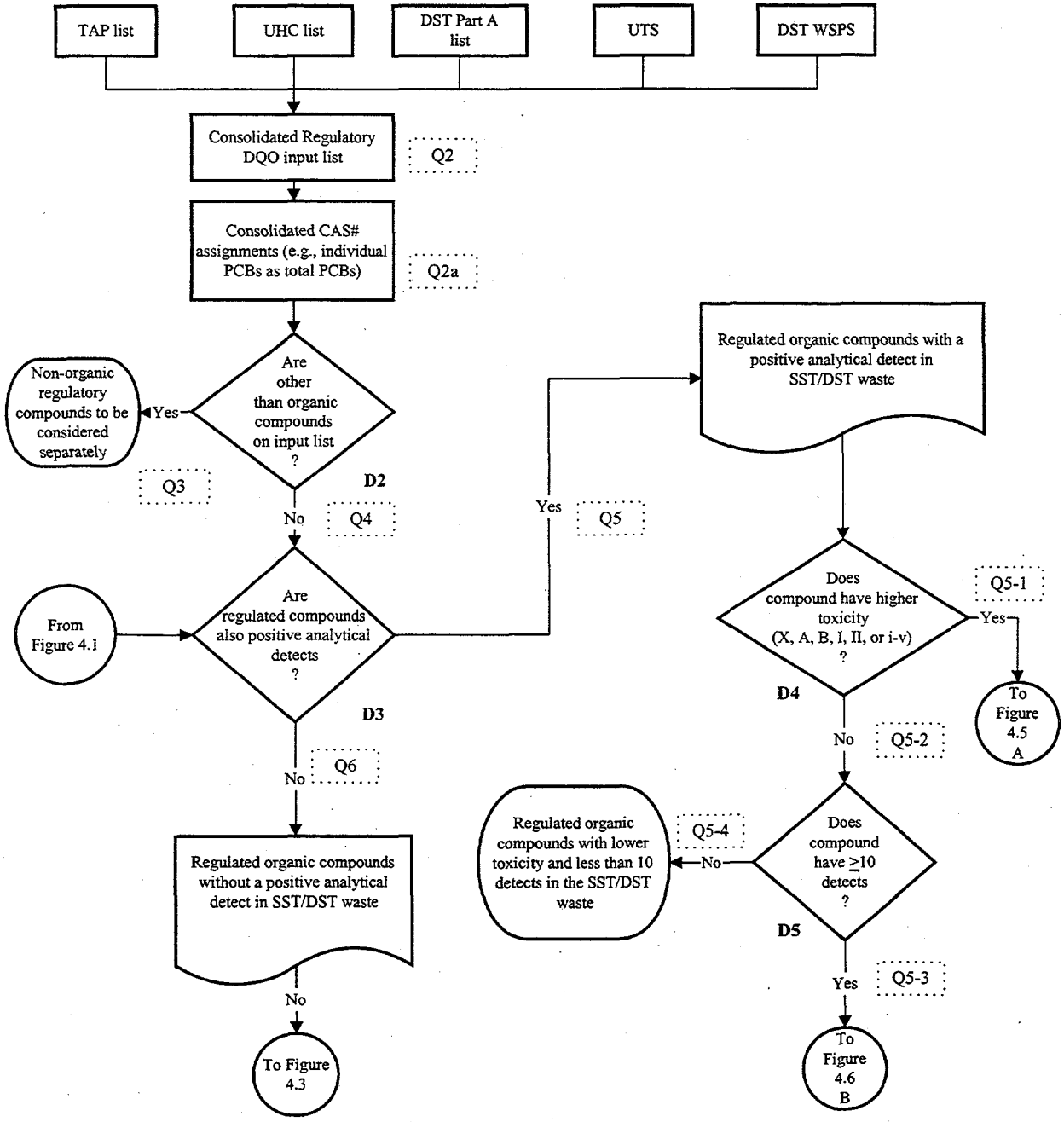


(a)Any vapor, solid, or liquid sample result above detection limits that was not qualified as rejected.

Where duplicate results existed, and one result was detected, a detected was included. Where duplicate results were presented and one result was rejected, the results were considered a positive detect.

DST = double-shell tank.
SST = single-shell tank.
TWINS = Tank Waste Information Network System
TCD = Tank Characterization Database.

Figure 4.2. Regulatory Data Quality Objective Input List and Logic to Segregate Regulated Detected and Non-detected Compounds and Evaluate Detected Compounds for Toxicity and Carcinogenicity.



CAS# = chemical abstract service number.
DQO = data quality objective.
DST = double-shell tank.
PCB = polychlorinated biphenyl.
SST = single-shell tank.
TAP = toxic air pollutant.
UHC = underlying hazardous constituents.
UTS = universal treatment standards.
WSPS = waste stream profile sheet.

Figure 4.3. Logic to Assess Non-detected, Regulated Compounds from Industries Not Associated with Hanford.

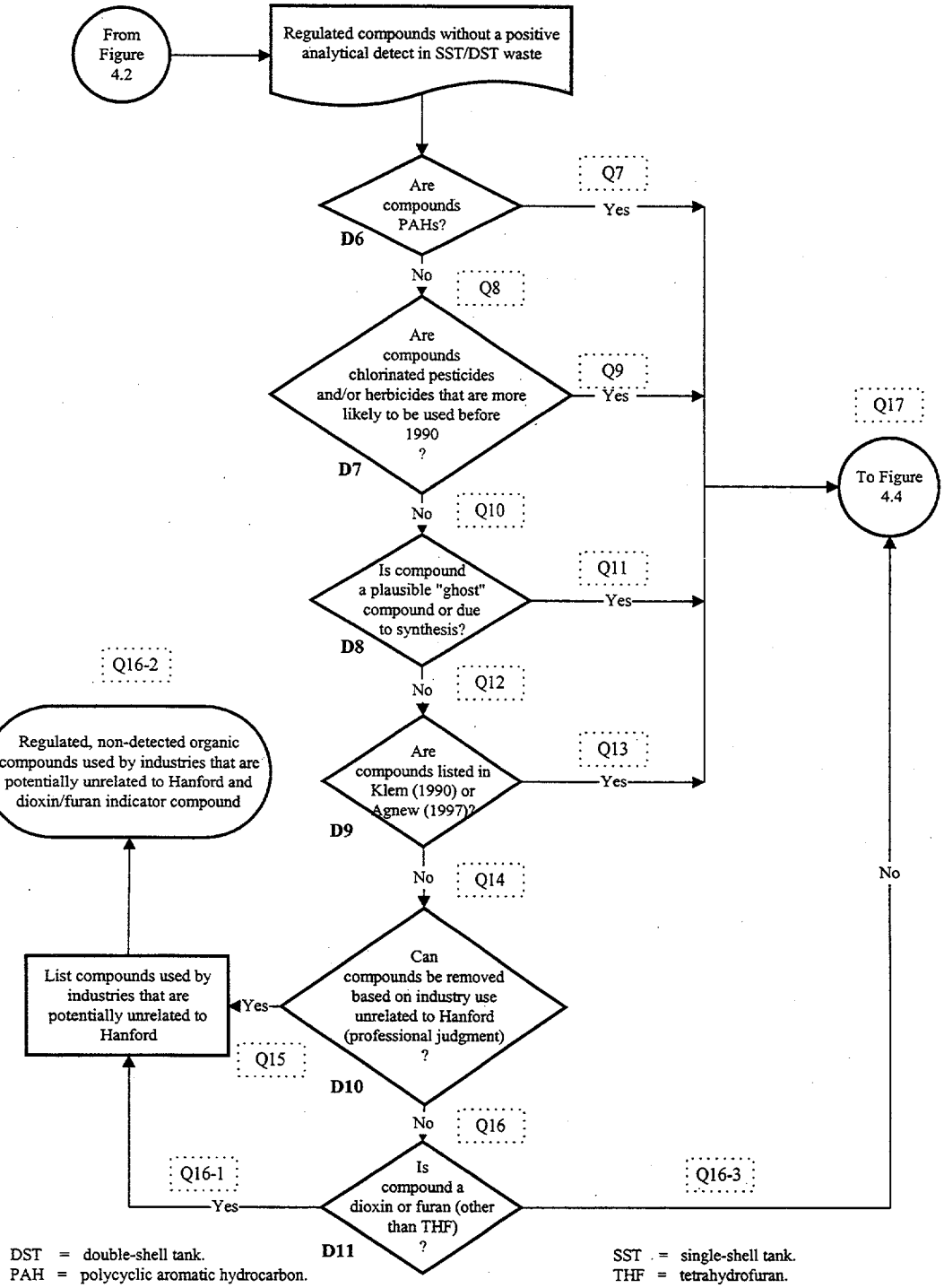


Figure 4.4. Logic for Stability, Toxicity, and Carcinogenicity Assessments.

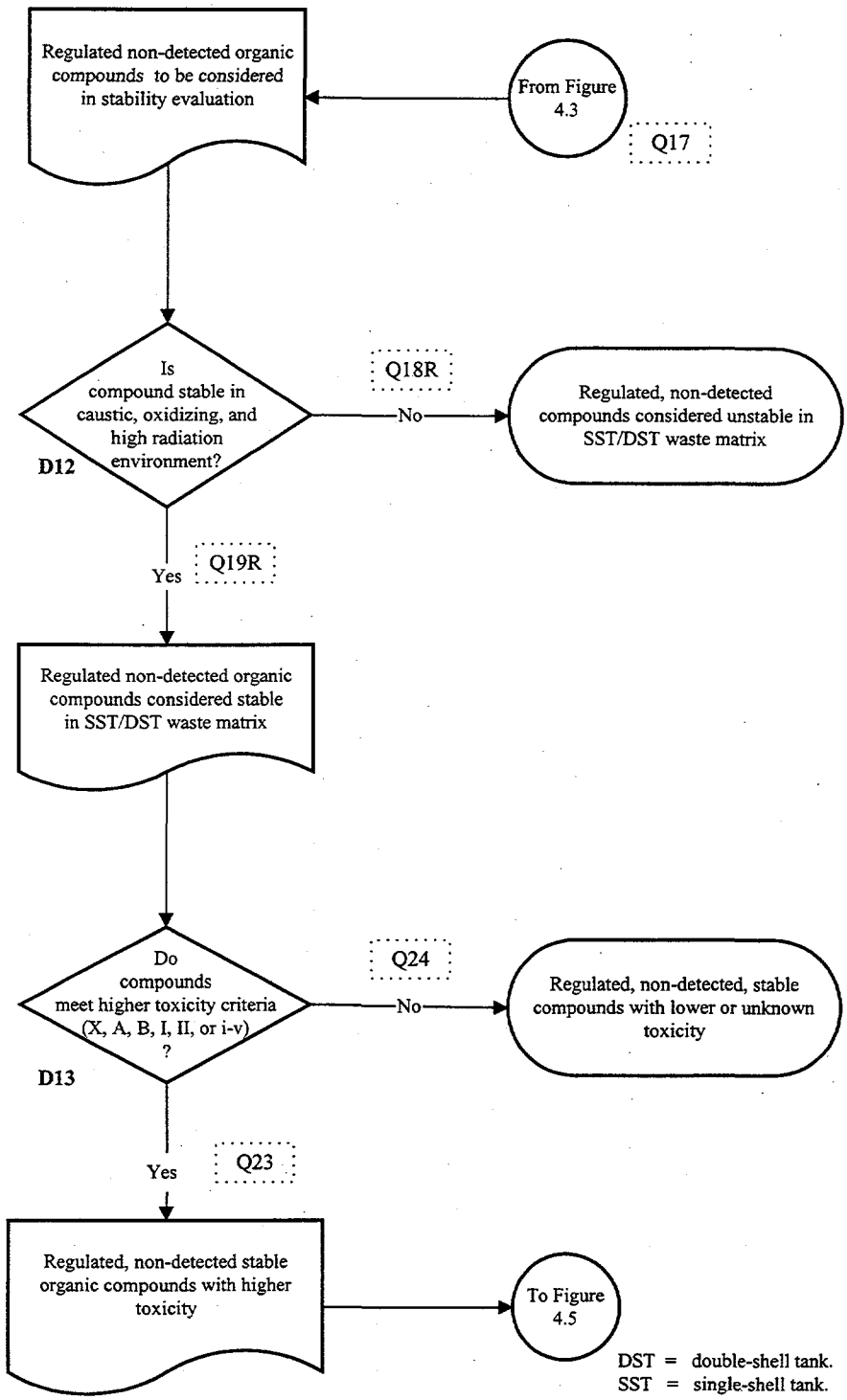
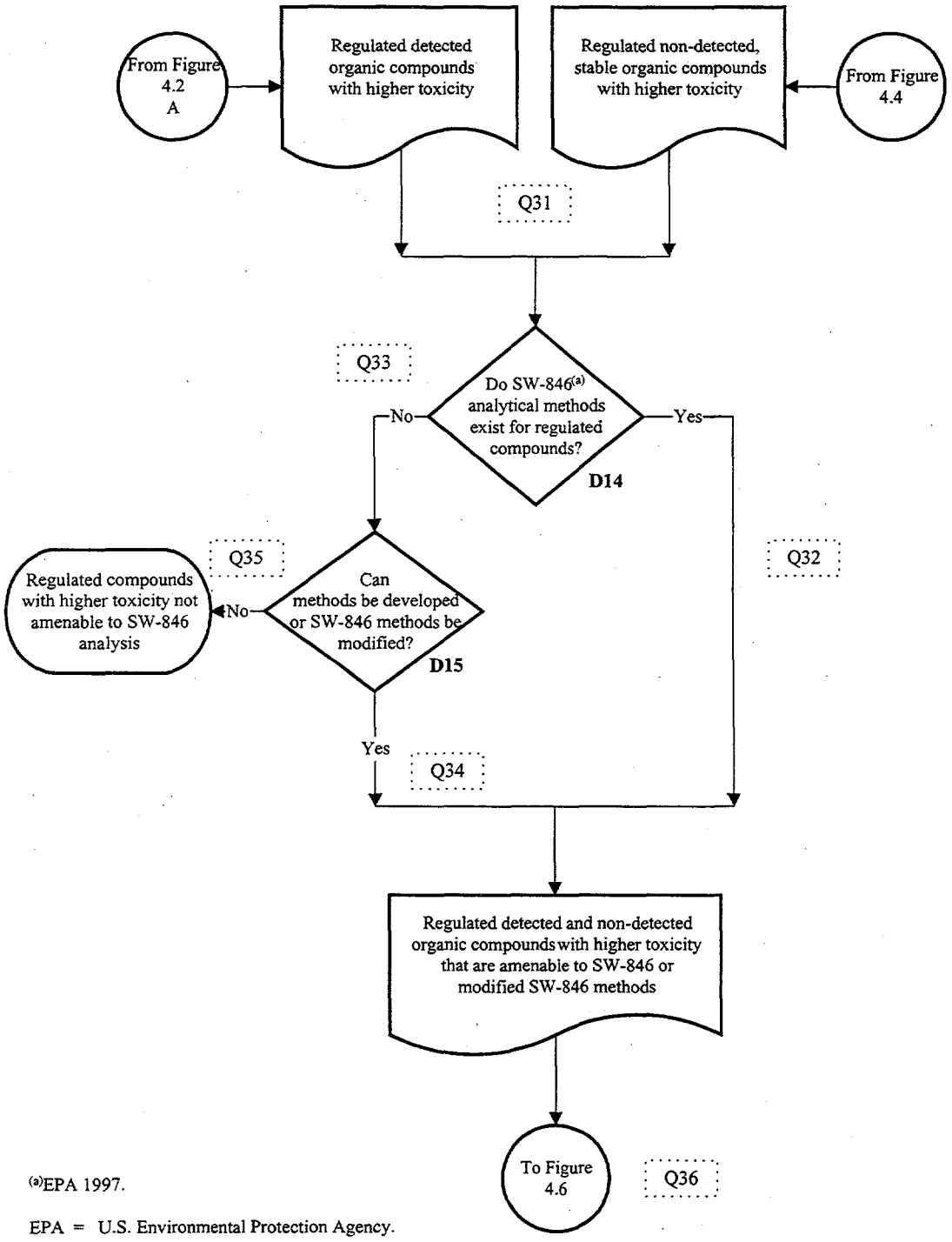


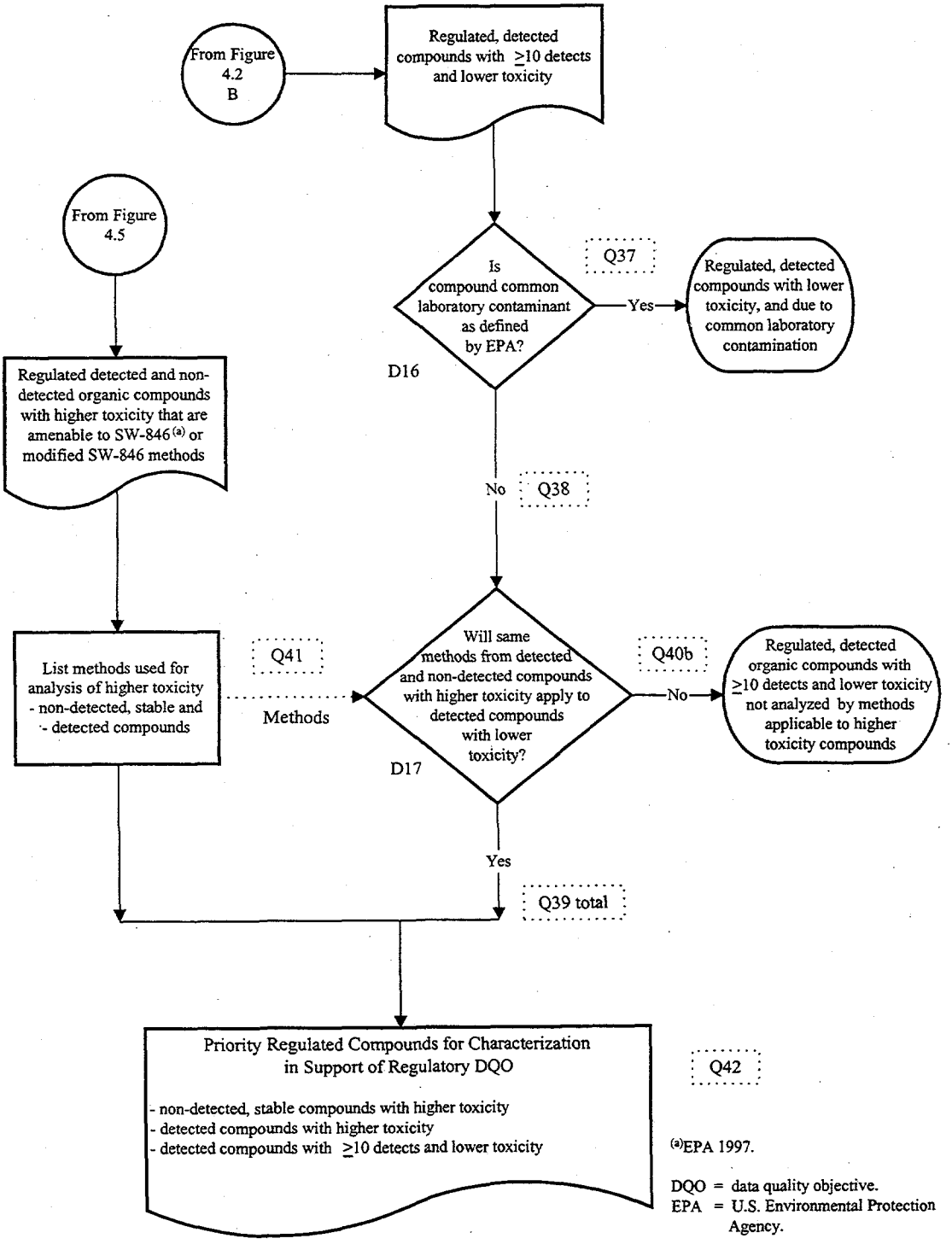
Figure 4.5. Analytical Methods Assessment for Compounds with Higher Toxicity.



[a]EPA 1997.

EPA = U.S. Environmental Protection Agency.

Figure 4.6. Analytical Methods Assessment for Compounds with Lower Toxicity and Priority Regulated Compounds for Characterization in Support of the Regulatory Data Quality Objective.



[a]EPA 1997.

DQO = data quality objective.
EPA = U.S. Environmental Protection Agency.

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