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Potential for Evaporation and *In Situ* Reaction of Organic Compounds in Hanford Supplemental LAW

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January 2022

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EXECUTIVE SUMMARY

The presence of regulated organic species in Hanford nuclear tank waste is assessed in this report, along with fate of the organics and possible evaporative treatment. A narrowed list of regulated organic species of concern is developed based upon published analyses, chemical properties like aqueous solubility, and chemical reactivity under alkaline conditions. Published analyses include tank headspace and liquid samples, review of chemical reagents formerly used at Hanford, and the Tank Waste Information Network System (TWINS). This work supports possible stabilization of Hanford Supplemental Low Activity Waste (SLAW) by grouting.

Revision 1 of this report includes information on a regulatory and processing Land Disposal Restriction (LDR) treatment variance strategy termed “Sample-and-Send”. The Hanford Tank Operating Contractor, Washington River Protection *Solutions, LLC* (WRPS) has been developing this regulatory and processing LDR treatment variance strategy that relies, in part, on demonstrating that in situ decomposition reactions along with historic evaporation of tank waste has destroyed or removed many of the LDR organics (SRNL-STI-2020-00582, SRNL-STI-2021-00453). Under the Sample-and-Send concept, Hanford tank waste would be prepared to create a feed candidate tank that would then be sampled to confirm the waste acceptance criteria is met for a supplemental LAW cementitious treatment facility.

Regulated organic species under the Environmental Protection Agency’s Resource Conservation and Recovery Act (RCRA) LDR program in 40 Code of Federal Regulations (CFR) Part 268 are important to understand because of the dilution prohibition in 40 CFR 268.3. EPA established the dilution prohibition to prevent owner and operators of hazardous waste management units from intentionally diluting waste to avoid treatment. EPA typically requires that regulated organic species are “removed” or “destroyed” to meet the LDR program requirements. EPA also does not regard stabilization through using cementitious reagents to provide adequate treatment for organics but has provided some guidance that stabilization of low concentration organics may be acceptable [Federal Register, 2001]. Therefore, the information evaluated in this report is important for the U.S. Department of Energy to be able to finalize the LDR strategy for addressing regulated organic species in stabilization of SLAW by a non-thermal technology such as grouting.

This task included first reviewing and summarizing published works on the topic of organic species in Hanford waste tanks to identify a list of chemicals that may be present. The second activity was to examine the ability of an evaporator to remove the organic chemicals based on known chemical properties. The third activity examined the published literature for information on reactivity of the chemicals, particularly looking at degradation due to alkaline hydrolysis.

Many of the organic species are known to preferentially separate to the aqueous condensate stream during evaporation, where they would be treated at the permitted 200-Area Hanford Effluent Treatment Facility (ETF). Previous work had found that Henry’s Law values for organic species indicate more favorable separation by evaporation when high (molar) concentrations of sodium are present in solution and when the solution temperature is high. This evaluation of organic chemicals that are present in Hanford tank waste has provided a list for further evaluation. These chemicals are considered likely present in tanks at measurable concentrations and may require treatment to remove them. Evaporation is practical for the removal of many of the chemicals, and in addition, reactivities have been identified that may explain why some chemicals were not measured in tanks. It is evident that a large number of organic chemicals, and particularly those that are most commonly measured (acetone, butanone, and n-butyl alcohol), can be readily removed by evaporation as demonstrated in prior work. Removing the volatile species eliminates one impediment that may enable producing a grout waste form that can be disposed in a permitted facility.

Reactivity by alkaline hydrolysis in particular was assessed since several classes of chemicals react in the strongly alkaline waste solutions. While hydrolysis may still yield regulated organic products, they would be of lower molecular weight than the original chemical, likely enhancing treatment by evaporation. Hydrolysis of both individual and classes of chemical species was evaluated.

The compounds that, if present, are expected to be difficult to remove by evaporation are shown in Table E-1. Five of these have been found in the Tank Waste Inventory System (TWINS) database to be above the wastewater limits in at least one liquid tank sample.

Table E-1. Compounds Expected Difficult to Remove by Evaporation ^a

LDR Organic species	CAS#
p-Nitrophenol	100-02-7
Phenol	108-95-2
2,4-Dinitrotoluene	121-14-2
Cresols (m,p,o) phenol, 2-methyl ^a	1319-77-3 95-48-7
2,4-Dinitrophenol*	51-28-5
morpholine, N-nitroso*	59-89-2
Pentachlorophenol*	87-86-5
4,6-Dinitro-o-cresol*	534-52-1
N-nitrosodiethylamine	55-18-5
2,4,6-Trichlorophenol	88-06-2
2-Nitrophenol*	88-75-5
2-Naphthylamine	91-59-8
2,4,5-Trichlorophenol	95-95-4
a. o-cresol is also known as phenol, 2-methyl but is shown here in both nomenclatures	
*Identified in TWINS as present above WW limit in at least one tank	

Based on the information available, the data indicate that some tanks do contain regulated organics at low concentrations. Using an evaporator can remove the majority of those organic species from the aqueous tank waste so that they are captured in the condensate and treated at the ETF. Although there are some organic species present in some tanks that may not be removed by evaporation.

A companion FY21 activity at WRPS has been focused on documenting additional process knowledge through a review of past LDR notification forms for waste transfers into the Hanford DSTs, and that work has added more compounds that will need to be assessed in the manner described here. A summary of the compounds identified by WRPS at the close of FY21 is provided in Appendix C. Follow-on work at SRNL in FY22 is planned to complete such an effort. Confirmatory testing of evaporation and degradation are also planned.

^a Phthalates may be present but are excluded from this list for reasons discussed in the document

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LIST OF ABBREVIATIONS

a	separation factor, dimensionless
atm	atmospheres
C	Celsius
BHEP	bis(2-ethylhexyl)phthalate
DST	Double-shell tanks
CAS#	Chemical Abstracts Service identification number
CFR	Code of Federal Regulations
EPA	Environmental Protection Agency
EPI	Estimated Programs Interface
ETF	200-Area Effluent Treatment Facility
g	grams
H	Henry's Law coefficient, units atm-m ³ /mol
hr	hour
L	Liter
LAW	Low Activity Waste
LDR	Land Disposal Restriction
mg	milligram
mL	milliliter
mm	millimeter
mM	millimolar
NIH	National Institute of Health
NIST	National Institute of Standards and Technology
Non-WW	Non-Wastewater
PCB	Polychlorinated biphenyl
pKa	acid dissociation constant, dimensionless
ppm	Parts per million
RCRA	Resource Conservation and Recovery Act
SLAW	Supplemental Low Activity Waste
SOW	Statement of work
SRNL	Savannah River National Laboratory
SST	Single-shell tanks
TCDD	Tetrachlorodibenzodioxin
TWINS	Tank Waste Information System
UHC	Underlying hazardous constituents

WRPS	Washington River Protection Solutions
wt %	Weight percent
WTP	Waste Treatment and Immobilization Plant
WW	Wastewater
x	liquid phase mole fraction
y	gas phase mole fraction

1.0 Introduction

At the U.S. Department of Energy's Hanford Site in southeastern Washington State the Waste Treatment and Immobilization Plant (WTP) is being built to treat Hanford nuclear waste, including high-level waste (HLW) and low activity waste (LAW). After processing by filtration and ion exchange to remove ^{137}Cs from the aqueous waste, this decontaminated LAW will initially be immobilized by vitrification using a joule heated melter in WTP. However, the current LAW vitrification facility is predicted to not have the capacity to solidify all of the LAW. A second process, referred to as Supplemental LAW (SLAW), will be needed to expand the immobilization capacity. One option under investigation for immobilization is to solidify LAW in a cementitious waste form that meets Resource Conservation and Recovery Act (RCRA) and DOE O 453.1 requirements. As stated in Bates et al. (2019),

“Supplemental Low Activity Waste (SLAW) is treated Hanford liquid radioactive waste that cannot be treated and solidified by the currently planned first Low Activity Waste (LAW) systems within the Waste Treatment and Immobilization Plant (WTP) without extension of processing and tank storage durations. Under current planning expectations, the projected volume of SLAW (~54,000,000 gallons) will be similar to the volume of waste currently stored in the tanks due to the need to add water while removing the waste from the tanks, transferring it, and pretreating to remove key radionuclides.”

One issue with the proposed use of a non-thermal immobilization method which does not rely on vitrification is that there may be small amounts of a variety of RCRA regulated organic chemicals in the aqueous waste. These regulated organics must be removed or destroyed to sufficient levels to meet the disposal requirements of the grout waste form. One treatment method that has been proposed is to remove the organics from the aqueous stream by evaporation with subsequent treatment of the aqueous condensate containing the removed organics in the RCRA-permitted Hanford Effluent Treatment Facility (ETF). This would enable disposal of the LAW in a cementitious waste form (Skeen et al., 2020). This method is like the current evaporative volume reduction of tank waste performed by the Hanford 242-A evaporator. Note that the 200-Area ETF is an existing permitted facility that already treats the aqueous evaporator condensate from the 242-A evaporator, including some dissolved organics. The overall conceptual flowsheet is shown in Figure 1 using the WTP baseline configuration (without Direct Feed Low Activity Waste), with the baseline shown in black, and the alternate evaporator and condensate pathway shown in red. The HLW and LAW are to be separated in the Pretreatment Facility. This task focuses on the future supplemental low activity waste immobilization process.

This evaluation includes three tasks to support SLAW evaporation and relies on previous works that examine the inventory of organics in tanks. The first task was to examine analytical databases and organic chemical usage information to determine which regulated organic chemicals are to be considered for removal in an evaporation process. This task included reviewing recent published works on the topic and brings in the newest available information. The second task was to examine the ability of an evaporation process to remove the named organic chemicals from a high sodium, high alkaline liquid SLAW stream. The third task is to examine the literature and reports on reactivity of the considered chemicals, with alkaline hydrolysis being a primary reaction mechanism. The third task provides another method to address regulated organics. Through chemical reactions, organics can be shown to be destroyed in situ in the tank waste storage environment. The removal or destruction of organics from regulated waste is EPA's primary method to address treatment of organics under the LDR program.

Waste Treatment and Immobilization Plant (WTP) Processes

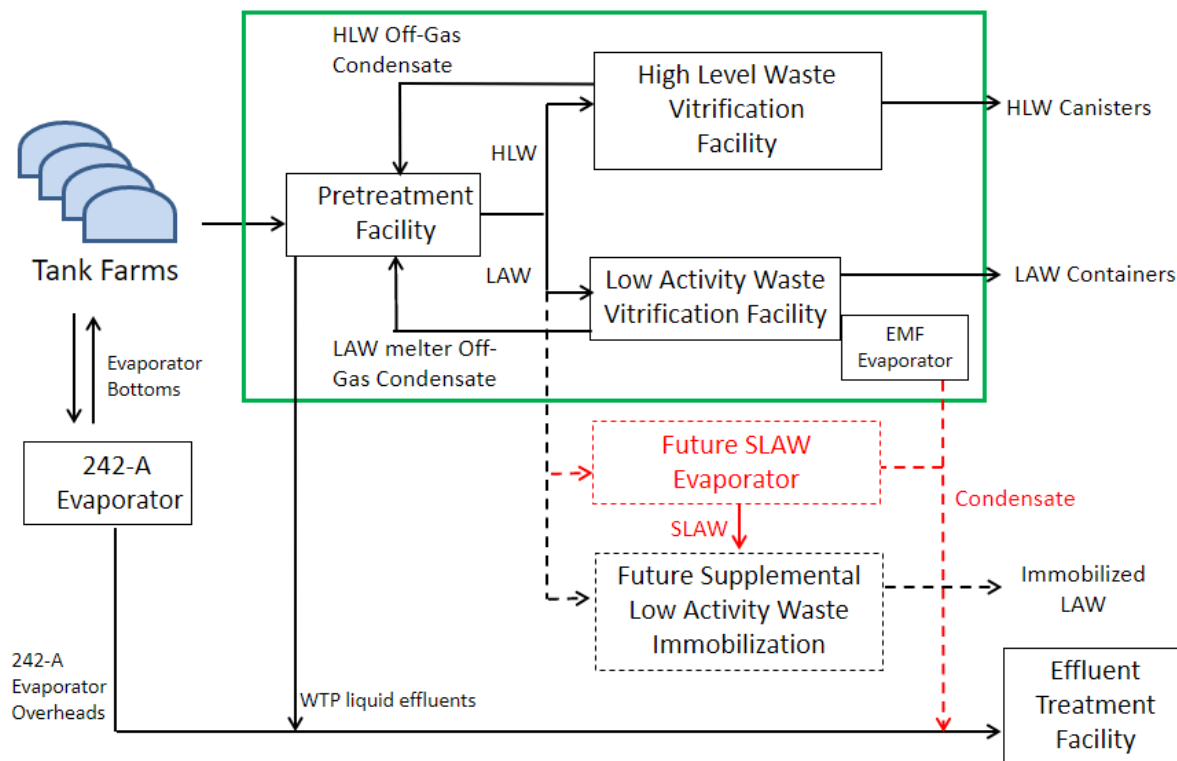


Figure 1. Simplified Proposed WTP Flowsheet

1.1 Testing Basis and Objective

The scope of this task is to continue the evaluation of using SLAW stream evaporation for removing regulated organic chemicals as documented in the earlier work [Nash et al., 2021]. This would eliminate one impediment to enable a possible cementitious waste form. The work was authorized by WRPS after receipt of a Scope of Work (SOW) from SRNL, [McCabe and Nash to Dorsey, 2021].

2.0 Assessment of Regulated Organic Species of Concern

This section draws upon past work along with current efforts to narrow a list of LDR organic species to be considered for treatment of Hanford SLAW (Skeen et al, 2020).

2.1 Assessment and Selection of Regulated Organic Species for Evaluations

The list of LDR organics to be assessed in this work was generated from Table 3-5 in a recent report [Skeen et al., 2020]. This table represents a compilation of chemical compounds and elements associated with the RCRA F and D waste codes on the Hanford single shelled tanks (SST) and double shelled tanks (DST) RCRA Part A permit applications. The table also includes a complete list of underlying hazardous constituents (UHC) listed in 40 CFR 268.48 that could apply to Hanford. As stated in the source document, it is an over-estimation to assume all the constituents listed in the table will apply to Hanford tank waste immobilized in a supplemental treatment system and WRPS staff worked parallel tasks developing and documenting the information needed to refine the list to include only compounds that:

1. Are Hanford tank farm F001-F005 constituents, or
2. Are RCRA Part A “D” codes: D018, D019, D022, D028, D029, D030, D033, D034, D035, D036, D038, D039, D040, D041, D043, or
3. Were used at Hanford including identified components in commercial products (Prior to May 8, 1992), or
4. Are detected in the SSTs or DSTs samples (Past and Future), or
5. Are identified as decomposition reaction end products formed in tanks, or
6. Are identified on an LDR notification form from past and future transfers into the DSTs that:
 - a. were detected at or above the LDR wastewater standard, or
 - b. have no analytical data to indicate concentration, or
 - c. process knowledge cannot be developed to support the constituent is not in the waste when reported as <MDL but MDL is greater than LDR wastewater standard.

The information for all six parameters above was not sufficiently mature at the time this work was started to shorten the list. However, the work has progressed, and Appendix C provides the resulting list of 130 LDR organic compounds that are retained as regulated species based on the preceding six screening criteria [Skeen, 2021].

For the purpose of this effort, the list of 207 organic compounds in Table 3-5 of Skeen et al. (2020) was narrowed to the list of considered compounds to include those that were:

- a) used at Hanford (based on information in RPP-RPT-61301), or
- b) measured in waste tank liquids or vapors (based on RPP-RPT-61301), or
- c) measured in liquids or solids and reported in RPP-21854, or
- d) estimated in Table 4 of SRNL-RP-2018-00687 to exceed the Wastewater treatment standard based on analysis of tank vapors and Henry’s Law, or
- e) added to the list based on an evaluation of potential chemicals present by WRPS regulatory subject matter experts as chemicals suspected of being present, or
- f) degradation products of listed chemicals identified by analysis (e.g., n-butanol from tributyl phosphate)

This results in the list of organics shown in Table 1. The first column of Table 1 below provides the chemical name and is highlighted in green if records indicate that it was used at Hanford. The Chemical Abstracts Service identification number (CAS#) is shown in the second column. The third column indicates the number of detectable measurements in DST vapor samples as previously reported [Tables 7 & 8 in Lindberg et al., 2019]. The fourth column shows those chemicals identified in DST supernate samples that did not pass the QC controls and the fifth column shows those that did pass the QC controls [Tables 11 & 12 in Lindberg et al., 2019]. The sixth column shows the Henry’s Law coefficient (H) in water from the literature. The seventh column shows the acid dissociation constant, pK_a . The H and pK_a values provided in Table 1 were used to determine if the chemical could be readily removed from the tank waste using evaporation. Prior testing showed that methanol ($H = 4.55E-06 \text{ atm}\cdot\text{m}^3/\text{mol}$ at 25°C) was readily removed by differential evaporation from a Hanford LAW simulant [Nash et al., 2021]. This indicates that the methanol and any species with a higher H will likely be removed by evaporation. The pK_a is important for evaporation because even if the H indicates that a species can be separated by evaporation from water, it would not be separable if it is ionized in the strongly alkaline tank waste. This is particularly true for some alcohols. The eighth column indicates an “x” if the pK_a is below 14 (equivalent to 1.0 M hydroxide ion, typical of tank waste) or if the H is less than $1.4E-06 \text{ atm}\cdot\text{m}^3/\text{mol}$ in water at vacuum evaporation conditions of 60 torr and about 42°C . An “x” in this column indicates that this chemical is NOT likely to be removable by evaporation. If an “~x” appears, then the H for this chemical is between $4.55E-06$ and $1.4E-06 \text{ atm}\cdot\text{m}^3/\text{mol}$, so is below the proven limit for methanol but above the estimated limit value for separable by evaporation and further evaluation is needed to verify that it is removable by evaporation. Finally, the

column on the far right indicates the water solubility of the compound at near ambient temperature obtained from the National Institute of Health (NIH) or Environmental Protection Agency (EPA) websites. The yellow or blue colors indicate the reference for the information if a value was not obtained from the source indicated in the column heading. In the Table, H is the Henry's Law coefficient and pKa is the acid dissociation constant for each organic chemical.

Table 1. LDR Organic Chemicals Identified in Hanford Tank Waste

Table 3-5 from SRNL-STI-2020-00228; only Used at Hanford; Measured in DST Headspace or Liquid; or Reported as Detected in DST Liquid or Solid in RPP- 21854	CAS#	Number of Detectable Measurements in DST Vapor Table 7 & 8 Lindberg	TWINS DST supernate detected organic (incl. NOT passing QC) Tables 11 & 12 Lindberg	TWINS DST supernate with measurable organic w/passing QC Tables 11 & 12 Lindberg	NIH Henry's Law coeff (atm- m ³ /mole)	Reported Temperature for NIH Henry's Law coeff, °C	pKa	H or pKa indicates cannot remove w/ evaporation	NIH water solubility (mg/L)
p-Nitrophenol	100-02-7	0	2	0	4.15E-10	20	7.13	x	>100
Ethylbenzene	100-41-4	9			1.00E-02	25			>100
cis-1,3-Dichloropropylene	10061-01-5	1			2.38E-03	20			>100
trans-1,3-Dichloropropylene	10061-02-6	1			2.37E-03	20			>100
Heptachlor epoxide	1024-57-3				2.10E-05	20			0.23
1,4-Dichlorobenzene	106-46-7	0	2	0	2.41E-03	20			81
2-propenal	107-02-8				1.22E-04	25			>100
1,2-Dichloroethane	107-06-2	0			1.18E-03	25			>100
Propanenitrile	107-12-0				3.70E-05	25			1.88
4-Methyl-2-pentanone	108-10-1	33	1	0	1.38E-04	25			>100
Toluene	108-88-3	61	58	37	6.64E-03	25			>100
Chlorobenzene	108-90-7	0	8	8	3.11E-03	25			>100
Phenol	108-95-2	3			3.33E-07	25	9.99	x	>100
Pyridine ^a	110-86-1	25	8	8	1.10E-05	25			>100
bis(2-ethylhexyl)phthalate*	117-81-7	1	33	10	2.70E-07	25		x	0.000099

Table 3-5 from SRNL-STI-2020-00228; only Used at Hanford; Measured in DST Headspace or Liquid; or Reported as Detected in DST Liquid or Solid in RPP-21854	CAS#	Number of Detectable Measurements in DST Vapor Table 7 & 8 Lindberg	TWINS DST supernate detected organic (incl. NOT passing QC) Tables 11 & 12 Lindberg	TWINS DST supernate with measurable organic w/passing QC Tables 11 & 12 Lindberg	NIH Henry's Law coeff (atm-m ³ /mole)	Reported Temperature for NIH Henry's Law coeff, °C	pKa	H or pKa indicates cannot remove w/ evaporation	NIH water solubility (mg/L)
Di-n-octylphthalate	117-84-0		3	3	2.57E-06	25		~x	0.000021
1,2,4-Trichlorobenzene	120-82-1	0	2	0	1.42E-03	25			49
2,4-Dinitrotoluene	121-14-2				5.44E-08	25		x	>100
Tetrachloroethylene	127-18-4	5			2.00E-02	25			>100
Pyrene	129-00-0		5	0	1.19E-05	25			0.135
Cresols ^b (m,p,o)	1319-77-3	4			~1.E-06	25	10.3	x	21.5
Xylene(m,p,o)	1330-20-7	16	42	17	1.00E-02	25			>2100
All Aroclors	1336-36-3		4	3	see below	Not avail			see below
Ethylacetate	141-78-6	7			1.34E-04	25			>100
Fluoranthene	206-44-0		1	0	9.45E-06	20			0.00025
Aldrin	309-00-2				4.40E-05	Not avail			0.05
alpha-BHC	319-84-6				5.14E-06	25			2.3
beta-BHC	319-85-7				5.14E-06	25			2.7
2,4-Dinitrophenol	51-28-5		24	12	8.60E-08	25	4.09	x	>100
4,6-Dinitro-o-cresol	534-52-1		2	0	1.40E-06	25		x	>100
1,3-Dichlorobenzene	541-73-1		3	0	2.83E-03	25			>100
N-Nitrosodiethylamine	55-18-5				3.60E-06	25		~x	>100
Carbon tetrachloride	56-23-5	1			2.76E-02	25			>100
morpholine, N-nitroso	59-89-2				1.35E-06	25		x	>100
Ethyl Ether	60-29-7				1.23E-03	25			>100
N-Nitroso-di-n-propylamine	621-64-7	3	3	2	5.38E-06	37			~100
N-Nitrosodimethylamine	62-75-9				3.65E-05	25			>100

Table 3-5 from SRNL-STI-2020-00228; only Used at Hanford; Measured in DST Headspace or Liquid; or Reported as Detected in DST Liquid or Solid in RPP- 21854	CAS#	Number of Detectable Measurements in DST Vapor Table 7 & 8 Lindberg	TWINS DST supernate detected organic (incl. NOT passing QC) Tables 11 & 12 Lindberg	TWINS DST supernate with measurable organic w/passing QC Tables 11 & 12 Lindberg	NIH Henry's Law coeff (atm- m ³ /mole)	Reported Temperature for NIH Henry's Law coeff, °C	pKa	H or pKa indicates cannot remove w/ evaporation	NIH water solubility (mg/L)
Methanol	67-56-1	31			4.55E-06	25			>100
Acetone	67-64-1	100	185	128	3.50E-05	25			>100
Chloroform	67-66-3	1	1	1	3.67E-03	24			>100
Hexachloroethane	67-72-1				3.89E-03	25			50
n-Butyl alcohol	71-36-3	148	116	105	8.81E-06	25	15.6		>100
Benzene	71-43-2	15	32	18	1.00E-02	25			>100
1,1,1-Trichloroethane	71-55-6	0	17	1	2.00E-02	25			>100
Chloromethane	74-87-3				1.00E-02	24			>100
Vinyl chloride	75-01-4	0			2.78E-02	25			>100
Acetonitrile	75-05-8				3.45E-05	25			>100
Methylene chloride	75-09-2	31	58	35	3.25E-03	25			>100
Carbon disulfide	75-15-0	3			1.44E-02	24			>100
1,1-Dichloroethane	75-34-3	0			5.63E-02	24			>100
1,1-Dichloroethylene	75-35-4	0			2.61E-02	24			>100
Trichlorofluoromethane	75-69-4	36			9.70E-02	25			>100
Heptachlor	76-44-8				2.94E-04	25			0.18
Isobutyl alcohol	78-83-1				9.78E-06	25	>14		>100
2-Butanone	78-93-3	52	96	70	4.67E-05	25			>100
1,1,2-Trichloroethane	79-00-5	0			8.24E-04	25			>100
Trichloroethylene	79-01-6	0	2	1	9.00E-03	25			>100
1,1,2,2-Tetrachloroethane	79-34-5	1			4.20E-04	25			>100

Table 3-5 from SRNL-STI-2020-00228; only Used at Hanford; Measured in DST Headspace or Liquid; or Reported as Detected in DST Liquid or Solid in RPP- 21854	CAS#	Number of Detectable Measurements in DST Vapor Table 7 & 8 Lindberg	TWINS DST supernate detected organic (incl. NOT passing QC) Tables 11 & 12 Lindberg	TWINS DST supernate with measurable organic w/passing QC Tables 11 & 12 Lindberg	NIH Henry's Law coeff (atm- m3/mole)	Reported Temperature for NIH Henry's Law coeff, °C	pKa	H or pKa indicates cannot remove w/ evaporation	NIH water solubility (mg/L)
Butylbenzylphthalate	85-68-7		6	2	1.26E-06	25		x	0.002
Diethylphthalate*	84-66-2	32	1	1	6.10E-07	25		x	1.04
di-n-Butylphthalate*	84-74-2		5	4	1.81E-06	25		~x	0.011
Propane, 2-nitro	79-46-9				1.20E-05	25			>100
Acenaphthene	83-32-9				1.84E-04	25			3.9
9H-fluorene	86-73-7				9.62E-05	25			1.90
Hexachlorobutadiene	87-68-3				1.03E-02	20			3.2
Pentachlorophenol	87-86-5		7	1	2.45E-08	22	4.7	x	14
2,4,6-Trichlorophenol	88-06-2		1	0	4.20E-06	25	6.23	x	>100
2-Nitrophenol	88-75-5		1	0	1.28E-05	20	7.15	x	>100
Naphthalene	91-20-3	0	2	0	4.40E-04	25			31
2-Naphthylamine	91-59-8				8.10E-08	25		x	6.4
phenol, 2-methyl (o-cresol) ^b	95-48-7				1.20E-06	25	10.2	x	>100
2,4,5-Trichlorophenol	95-95-4		1	0	2.21E-06	25	7.43	~x	>100
1-phenylethanone (acetophenone)	98-86-2				1.04E-05	25	18.3		>100
Nitrobenzene	98-95-3	0	2	1	2.40E-05	25			20
green highlight = used at Hanford					Ref: NIH: https://pubchem.ncbi.nlm.nih.gov/				
*identified in PNNL-15646 as a plasticizer					Ref: EPA: https://comptox.epa.gov/dashboard/dsstoxdb/				
a. Laboratory chemical used Procedure LA-695-102					Ref: Chemical Book: https://www.chemicalbook.com/				
b. Not identified in reference as used onsite but F004 is included in the DST System part A permit application with cresols and cresylic acid as the basis for the listing.									
NR = Not Reported, and NA = not applicable									

Note the H value listed is for the chemical at ambient temperature, typically in the range of 20 to 25° C, and not the 42° C associated with the previously reported evaporation limit ($1.4\text{E-}06 \text{ atm-m}^3/\text{mol}$) [Nash et al., 2021]. However, since data at 42° C is not readily available for these compounds, the H at 25° C was used to compare with the limit to evaluate if a compound is expected to be removed by evaporation. This would be conservative, since the H value should be higher at 42° C than at 25° C, so using the 25° C value would tend to underestimate the volatility.

The data in Table 1 clearly show that although many samples indicate the presence of organic compounds, most of the organics in Hanford tank waste are highly volatile with 55 of 74 having a Henry's Law coefficient above the estimated limit. It is expected that the 55 volatile species could be readily removed by evaporation. The most common chemicals identified in Lindberg et al., [2019] (reproduced in columns 3, 4, 5 of Table 1 above) were acetone, butanone, n-butyl alcohol, toluene, benzene, xylenes, and methylene chloride. These all can be readily removed by evaporation as previously shown in prior work or by comparison with the Henry's Law coefficient from chemicals tested in prior work.

The TWINS database contains the most up-to-date inventory of Hanford tank sample analysis results available. The list of compounds in Table 1 above that were identified as challenging to remove by evaporation are shown in Table 2. WRPS performed a screening of the challenging organics versus the primary aqueous sample analysis results in the TWINS database. Table 2 shows the Hanford tanks that have at least one detected sample value in the TWINS database that exceeds the corresponding wastewater (WW) and non-wastewater (non-WW) treatment standards from 40 CFR 268.40 or §268.48. If no tanks are listed in columns four or five, then no tank waste samples are reported to exceed the associated standards. The sixth column in the table shows the year of the most recent sample that exceeded one of the standards.

Table 2. Screening of Low Volatility LDR Organic Chemicals from TWINS for Detected Constituents

LDR Organic species	CAS#	WW/non-WW treatment standard (mg/L)	Tank liquid >WW standard	Tank liquid > non-WW standard	Latest year sampled
p-Nitrophenol	100-02-7	0.12/29	AW-104 TX-116		2017 2003
Phenol	108-95-2	0.039/6.2			
bis(2-ethylhexyl)phthalate	117-81-7	0.28/28	AP-103 AP-104 AW-101 AW-104 AY-101 B-111 B-201 B-202 BX-107 SY-101 T-104 TX-116		1991 2015 1991 2017 2016 1991 1991 1991 1992 2018 1992 2003
Di-n-octyl phthalate	117-84-0	0.017/28	AW-102 AY-101		2017 1997
2,4-Dinitrotoluene	121-14-2	0.32/140			
Cresols (m,p,o)	1319-77-3	0.88/11.2			

LDR Organic species	CAS#	WW/non-WW treatment standard (mg/L)	Tank liquid >WW standard	Tank liquid > non-WW standard	Latest year sampled
2,4-Dinitrophenol	51-28-5	0.12/160	AN-107 AP-107 AW-102 AW-104 AW-106		2019 2017 2018 2017 2018
4,6-Dinitro-o-cresol	534-52-1	0.28/160	AW-104		2017
N-Nitrosodiethylamine	55-18-5	0.4/28			
morpholine, 4-nitroso	59-89-2	0.4/2.3	AN-107 AW-102	AN-107	2019 2018
Diethyl phthalate	84-66-2	0.2/28	SY-101		1991
di-n-Butyl phthalate	84-74-2	0.057/28	AN-107 SY-101		2019 1991
Butyl benzyl phthalate	85-68-7	0.017/28	AP-103 AP-104 AW-104 SY-101		1991 2015 2017 2018
Pentachlorophenol	87-86-5	0.089/7.4	AP-103 AP-104 AW-104 AY-101		2015 2015 2017 2016
2,4,6-Trichlorophenol	88-06-2	0.035/7.4			
2-Nitrophenol	88-75-5	0.028/13	TX-116		2003
2-Naphthylamine	91-59-8	0.52/NA			
phenol, 2-methyl (a.k.a. o-cresol)	95-48-7	0.11/5.6			
2,4,5-Trichlorophenol	95-95-4	0.18/7.4			
Gray highlight indicates a phthalate					

The aroclors (polychlorinated biphenyls) were previously reviewed [Lindberg et al., 2019]. The aroclors are expected to partition almost entirely to the solids or a separate organic liquid phase because of their low water solubility. Of those aroclors measured in DST liquids, the highest value was 8.6 µg/L which was expected to be below any applicable limits [Lindberg et al., 2019]. Furthermore, the range of H for individual polychlorinated biphenyls (PCB) is 2.1E-5 to 2.0E-4 atm-m³/mole,¹ which is well above the value that indicates that they could be removed by evaporation. For these reasons, the aroclors were eliminated from further consideration in this evaluation and are not shown in Table 2.

While it is not verified, the presence of phthalates in tank waste samples is often likely due to contamination from sampling and laboratory equipment. Phthalates are common plasticizers used in many polymers and most are nearly insoluble in water. They are commonly found in tubing, plastic bottles, O-rings, and other components used for sampling and analyzing liquids.

¹Henry's Law coefficients for PCBs 011, 019, 026, 045, 118, 121, 126, 138, 152, and 153 obtained from the EPA website <https://comptox.epa.gov/dashboard/dsstoxdb/>

A previous report discussed that their presence in Hanford tank vapor samples is likely due to contamination from the sampling equipment. The work, however, was unable to prove this assertion because the original equipment was no longer available [Huckaby, 2006]. More recently, the analysis report of a sample from SY-101 indicates that both prep blanks contained butylbenzylphthalate and bis(2-ethylhexyl)phthalate above the Minimum Detection Limit but beneath the measured sample values [Kirchner, 2020]. The phthalates are also shown in gray highlights in Table 2. While it cannot be proven that sampling and handling originated all of the phthalate species in historical samples, future tank sample analyses should consider using specialized sampling and analysis techniques to fully resolve the true concentration of phthalates and avoid blank contamination.

The compounds that are expected to be present in some number of tanks and likely not removable by evaporation alone are shown in Table 3. These are derived from Table 2 as being identified at potentially significant concentrations in some tanks and not sufficiently volatile for removal according to their pKa, or Henry's Law coefficient. They are also not reactive in alkaline solution. The phthalates are excluded until more analytical analyses are performed.

Table 3. LDR Organics Likely Not Removable by Evaporation

LDR Organic species	CAS#
p-Nitrophenol	100-02-7
Phenol	108-95-2
2,4-Dinitrotoluene	121-14-2
Cresols (m,p,o) phenol, 2-methyl ^a	1319-77-3 95-48-7
2,4-Dinitrophenol*	51-28-5
morpholine, N-nitroso*	59-89-2
Pentachlorophenol*	87-86-5
4,6-Dinitro-o-cresol*	534-52-1
N-nitrosodiethylamine	55-18-5
2,4,6-Trichlorophenol	88-06-2
2-Nitrophenol*	88-75-5
2-Naphthylamine	91-59-8
2,4,5-Trichlorophenol	95-95-4
a. o-cresol is also known as phenol, 2-methyl but is shown here in both nomenclatures	
*Identified in TWINS as present above WW limit	

It should be noted that the compounds in Table 2 is not a complete list of the difficult to evaporate regulated organic compounds that are likely to be in Hanford tank waste. This results from the fact that the starting list (Table 1) is a subset of the possible LDR organic compounds, although it was derived from previous comprehensive reports. The companion FY21 activity at WRPS has focused on documenting additional process knowledge through a review of past LDR notification forms for waste transfers into the Hanford DSTs, and that work has added more compounds that will need to be assessed in the manner described here (See Appendix C). Follow-on work at SRNL in FY22 is planned to complete such an effort.

Since the selection criteria included only those compounds specifically identified as used or detected, a “secondary list” of chemicals was also created to include additional chemicals listed in Table 3 of RPP-RPT-54699. These chemicals are not proven to actually be present in Hanford tank samples by analysis of samples or by records of their use. This secondary list shows UHCs but excludes: (a) those that are in Table 1 of this report; (b) those unrelated to Hanford; and (c) those believed unstable in caustic and radiation.² Those compounds were evaluated for their susceptibility to be removed by evaporation based on their Henry’s Law coefficient and their pKa. This list is shown in Appendix A. Like the screening process for Table 1, only seven (7) of the 46 compounds listed in Appendix A are expected to persist at an appreciable concentration in tank waste after evaporation if they are actually present in the waste.

One of the chemicals on the secondary list that is a UHC but has not been measured is phthalic acid. If the phthalates listed in Table 1 above were present in tank waste, it is expected that they would decompose to phthalic acid, which is water soluble. Since phthalic acid is not reported in tank sample analysis reports, it is either further decomposed in tank waste, is not identifiable by the analytical methods, or the original phthalates were not actually present in the tanks in measurable quantities.

3.0 Reactivity of Organic Chemicals

A screened list of organic chemicals regulated under RCRA LDRs are listed in this report in Appendix B. The list was drawn from Table 1. Hydrolysis rates and half-lives listed in the table were generated using the EPA Estimation Programs Interface (EPI) suite and are listed within the table. HYDROWIN v2.00 is the module under the Chemical Property and Fate Programs in EPI Suite that was used to derive this information. The software provides a second order rate constant under basic conditions (K_b ; pH >8) in L/mol-sec and a half-life at pH 8 in years. The details of the results for the organic chemicals are shown in the table in Appendix B.

Compounds not listed in the database either do not contain functional groups that hydrolyze or are missing from the database. Based on prior Hanford Tank Waste reports [Wiemers et al., 1998, Lindberg, 2019], a column appears in the Appendix B table that lists the likely primary reaction of the compound such as hydrolysis, substitution/elimination, oxidation, or no/slow hydrolysis (expected to survive in the heated, caustic tank waste). The rate constants in Appendix B were used to order compounds in terms of base hydrolysis reactivity for saponification or substitution/elimination reactions (Figure 2). The results are summarized in Figure 3 with a line to indicate what compounds will have longevity within the SLAW stream.

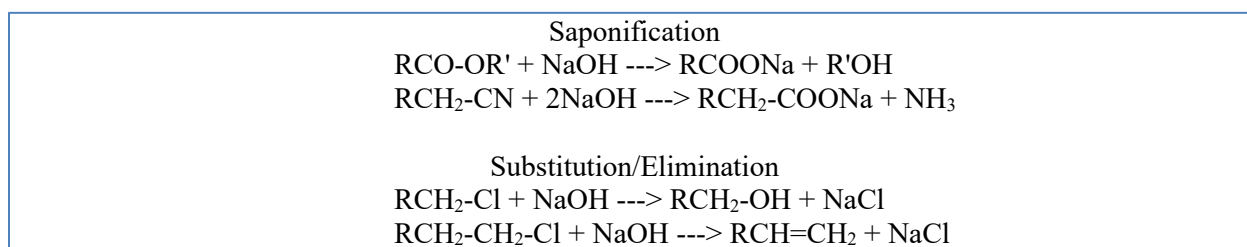


Figure 2. Hydrolysis Reactions [Wiemers et al., 1998]

Additionally, a series of reports [Ellington et al. 1986, Ellington et al. 1987, Ellington, et al. 1988, Ellington et al. 1989] and literature [Jeffers et al.; Keller et al.] were used when compounds were not found in the EPI suite and information is listed in the comment’s column of the Appendix B table. Three of the Ellington

² Criteria b and c were used to generate Table 3 in RPP-RPT-54699

reports are a 3-volume series (1986, 1987, and 1988) that examines the hydrolysis of regulated organic compounds for Hazardous Waste Land Disposal. The 1989 work is a summary report. These volumes were used to supplement the data in EPI Suite and to confirm the reactivity trend of Saponification>Substitution/Elimination>Aromatic halides shown in Figure 3.

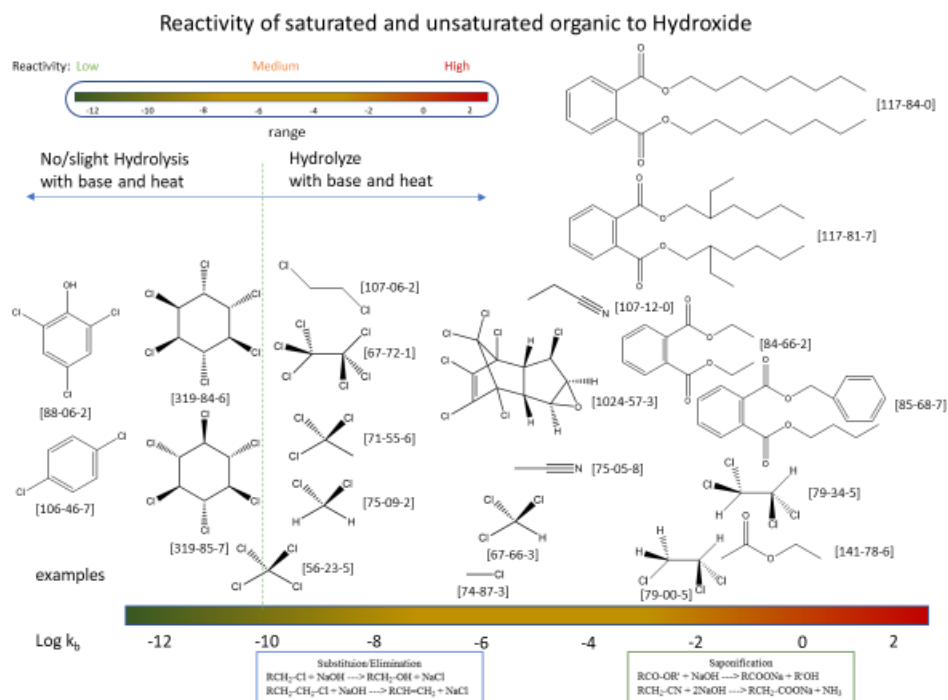


Figure 3: Regulated Organic Chemicals Listed in order of Hydrolysis Reactivity Based on Reaction Rates for the EPI suite.

Several chlorinated methanes, ethanes, ethenes, and propanes on the regulated organic compound list did not have hydrolysis rates in the EPI suite. These types of compound are addressed in the literature [Jeffers et al. 1989]. Under highly basic conditions, the reactivity is dependent on the most acidic proton. Thus, perchlorinated compounds and chlorinated unsaturated compounds without an extractable hydrogen do not easily hydrolyze while unsaturated chlorinated alkanes with an abstractable alpha hydrogen on the same carbon do hydrolyze. Figure 4 summarizes the relative reactivity of the organic chlorinated compounds.

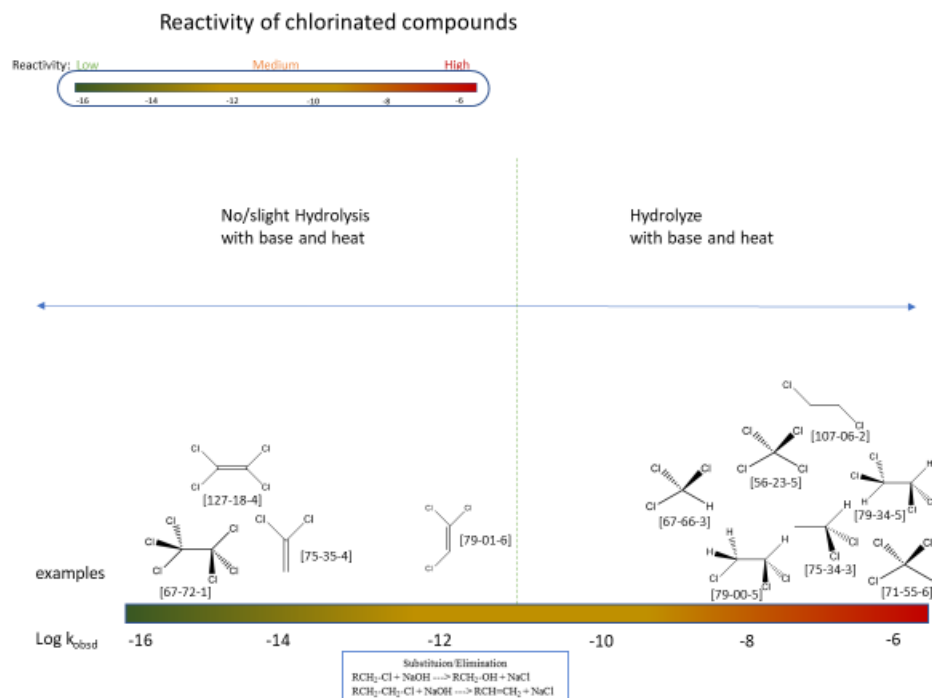


Figure 4: Regulated Halogenated Compounds in Order of Reactivity Based on Hydrolysis ($k_{\text{obsd}} = k_{\text{neut}} + k_{\text{b}}$) Rates from Jeffers et al. (1989).

4.0 Treatment of Organics in SLAW Streams by Evaporation

4.1 Specific Chemical Evaporation from Published Literature

Laboratory evaporator experimentation over many years has revealed the extent of evaporative removal of specific regulated organic chemicals. This section reviews specific works, with most supporting Hanford treatment of trace regulated organic chemicals. While most experiments employed simulant feeds, an actual waste test is also included below. The last 3 works are from the general literature on evaporation and do not use Hanford evaporator conditions.

Saito et al. (2000) spiked a processed complexant simulant of Hanford Tank AN-107 with 14 different regulated organic chemicals. The benchtop vacuum evaporator was operated at 60 torr absolute for about 75 hours in a steady and continuous mode, concentrating the feed by about 1.5 x. The total liquid feed volume for the bench work was 38.9 liters and the sodium molarity was 5.5 M. The concentration factor was limited to 1.5 x to minimize solids formation in evaporation. The feed was taken from a pilot scale experiment (100 gallons of feed) using the complexant simulant formulated by Eibling et al. (2001). The 100-gallon test ran the simulant through the strontium – TRU permanganate process and filtered and produced filtrate, part of which was used for the bench scale work here. The regulated organic spike was added to the filtrate product of the process before evaporation. Acetone was used as the base solvent for introduction of the spike into the aqueous solution.

In original planning, acrylonitrile, 1-chloroethene, 1,1-dichloroethene and dichloromethyl ether were to be included in the work. Use of PCBs and dioxin/furan were initially considered as well. However, these

were not used due to awareness of rapid chemical breakdown in caustic Hanford River Protection Project waste or off-gas sampling/analysis capability issues. Experimental toxicity hazard concerns for the work led to the selection of bis(2-ethylhexyl)phthalate (BEHP), a 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) toxicity equivalent, as an indicator for both PCB and dioxin/furan chemical groups based on thermal stability and vapor pressure criteria.

The following list of 14 organic chemicals and their results were found. Table 4 shows that most of the selected organic chemicals were removed by evaporation. Substantial removal here was for more than 97% of the feed mass of the organic chemical to be evaporated and not found in the concentrate. Some of the chemicals degraded in the caustic solution as indicated in the first note for the table. The report noted that the analyses of hexachlorobenzene and 1,2,3-trichloropropane especially were unreliable.

Table 4. Organic Chemicals Added to Simulant for Evaporation, Saito et al (2000).

Species Substantially (>97% of mass) Removed by Evaporation		
benzene	toluene	1,2-dibromoethane*
4-methyl-2-pentanone	chlorobenzene	1,2,3-trichloropropane*
1,2,4-trichlorobenzene	naphthalene	pentachlorophenol*
Species Substantially Retained in the Concentrate		
pyrene**	benzo(a)pyrene	
Aldrin**	bis(ethylhexyl)phthalate (BEHP)*, **	
hexachlorobenzene*		

* Report explains poor mass balance due to hydrolysis of these chemicals

**Poor mass balance possibly due to second liquid phase impacting sampling

The work bounded the performance of the evaporator process by including heavy chemicals that remained in the concentrate phase. Pyrene in particular is a heavy and chemically stable species that cannot be removed to a practical extent with vacuum evaporation.

In another work, actual Tank AN-107 “Envelope C” liquid was evaporated, and organic species were identified in the condensate. Work by Crowder et al. (2000) identified 4-methyl-3-hexanol, 5-butyl-5-nonanol, and 4,5 dichlorophenylenediamine in the concentrate after evaporation. Tributylphosphate and 2,7 naphthalenediol were also identified in the evaporator concentrate. They would not be stripped in a practical evaporative treatment from a SLAW feed stream. Henry’s Law data for all of these were not found in PubChem [PubChem, 2021] and do not appear to be available for an independent assessment of removal by evaporation. The report also mentions detection of unidentified nitrophthalate esters. None of the named organic species in this work are regulated under 40 CFR 268.40 or §268.48.

Taylor-Pashow et al. (2019) operated a bench scale vacuum evaporator in batch mode to examine the partitioning of spikes of iodide, acetone, acetonitrile, acrylonitrile, and methylene chloride. The evaporator was operated at 60 torr absolute to be consistent with the operation of the Hanford 242-A evaporator. The target concentration factor for the work was 5 to 6X, i.e., increase the concentration of salt in the tank waste by a factor of 5-6.

The aqueous simulant was alkaline (pH ~12) and was about 0.27 M in sodium. The simulant mimicked feed to the WTP Effluent Management Facility evaporator. Practically no acetonitrile, acrylonitrile, or

methylene chloride were recovered from the bench scale evaporator samples. Hydrolysis likely played a major role in decomposing these chemicals, effectively treating them. The report provides the reactions for the nitriles, yielding ammonia and an organic acid. A small amount of methyl isocyanate was found in some knockout pot samples. Acetone was found in condensate samples. This indicates the chemical stability of acetone along with its ability to be recovered in the sampling method. No acetone, acetonitrile, acrylonitrile, or methylene chloride were found in concentrate products, demonstrating efficient removal by evaporation and/or reaction. The nitriles did not appear in the condensate samples. The level of removal of nitriles seemed to be much more efficient than implied by the alkaline hydrolysis rates for nitriles given in Section 3 above. It is not clear why the nitriles disappeared so easily in the Taylor-Pashow et al. (2019) work. That report focused on hydrolysis and losses as explanations. In follow-on work here, the literature was searched for alkaline reactions of nitriles with other components in the simulant. No alkaline reactions with zinc, nitrite, chromate, or iodide were found that would provide reasoning for reactive removal of nitriles. The overall conclusion is still that these two organic nitriles are easily removed by evaporation.

Nash et al. (2021) operated the same bench scale vacuum evaporator equipment as was used by Taylor-Pashow et al. In this case methanol, acetone, n-butyl alcohol, acetophenone, and pyridine were spiked into a caustic high sodium aqueous simulant. Evaporator operation was essentially similar to that of Taylor-Pashow et al. All five of these species were effectively removed from the feed by the vacuum evaporation (60 torr absolute). No chemical degradation of these five chemicals was detected in the work which is consistent with the information provided in Appendix B.

Bowman (1996) performed calculations that provide organic chemical limits on feed to the 242-A Hanford evaporator. The work is relevant because it uses Henry's Law values (related to chemical activity coefficients and pure component vapor pressures) to calculate removal of specific organic chemicals from hot condensate (water). The primary temperature considered was 75 °C. The goal of the work was to set evaporator feed limits for the specific organic chemicals so that 40 CFR 264 air emission restrictions could be met. The evaluation included chemicals under consideration in the current work. These chemicals are acetone, n-butanol, methyl ethyl ketone, phenol, and pyridine. These chemicals were shown to have low feed limits, reflective of easy evaporation and air emission. It is to be noted that phenol is not easily removed in the current work because alkaline solutions would deprotonate it and greatly reduce its partial vapor pressure. The Bowman report found that tridecane, tetradecane, and tributyl phosphate are not easily evaporated from water. However, those chemicals are not listed in 40 CFR 268.40 or §268.48 and are not considered here.

Agnihotri and Cobiella (1989) patented a use of flash vacuum evaporation to remove organic chemicals from an aqueous stream. The patented process uses an absolute pressure range of 1 to 5 psia (52 to 260 torr). The Hanford 242-A evaporator operates at 1.15 psia (60 torr) in comparison. The patent states,

“The methods are particularly adapted for removing volatile organic chemicals including both halogenated and non-halogenated compounds from water. Suitable volatile organic chemicals which may be removed from water using the methods of the present invention include, but are not limited to, tri- and tetrachloroethylene, cis- and trans-1,2-dichloroethylene, 1,1-dichloroethylene, vinyl and methylene chloride, 1,1,1-tri-chloroethane, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, 1,2-, 1,3- and 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene.”

This statement is consistent with the evaporative screening criteria discussed for the Table 1 compounds, since all the indicated organics have a H value greater than 1.4E-06 atm-m³/mol. The heaviest of these would be the 1,2,4-trichlorobenzene and its H value exceeds 1.4E-06 atm-m³/mol by three orders of magnitude, indicating an expectation of easy stripping by evaporation for all organic chemicals named in this reference.

Allen et al. (1988) studied the use of thin film evaporators and, separately, atmospheric pressure steam stripping, to remove organic chemicals from wastewater and petroleum refining waste sludges. Steam stripping of wastewater readily removed more than 99.9% of 1,2-dichloroethane, 1,1-dichloroethane, 1,2-dichloroethene, vinyl chloride, 1,2-trichloroethane, methylene chloride, carbon tetrachloride, and chloromethane. It should be noted that 96.5% of incoming chloroform was removed. While the thin film evaporator testing was at the relatively high temperatures of 150 and 320 °C, it was found that 2-methylnaphthalene and naphthalene were still partly removed, but with difficulty. Only 16 to 59 percent of the 2-methylnaphthalene was removed, and only 32 to 79 percent of the naphthalene was removed in runs at 150 °C. This is at some variance with Table 1, where the H value for naphthalene is high enough for an expectation of removal by evaporation. This is also at variance with the result for naphthalene in Table 4. Possibly the sludge matrix at the high temperature was retaining these chemicals by providing solvent properties that are very different from an aqueous fluid and possibly impacting the partitioning from the supernate stream. The sludge matrix may have been producing these components at the higher temperatures. No H values could be found in the literature for the 2-methylnaphthalene.

Harkins et al. (1988) examined air stripping of trace organic aromatic chemicals from wastewater. They found that Henry's Law coefficients were reasonably predictive of extent of removals. They also found that when several poorly water-soluble chemicals were present, they were removed reasonably well without interference from each other.

4.2 Henry's Law Coefficients and Practical Separation of Organic Species

Henry's Law coefficients are commonly published for environmental work as shown on the NIST, EPA CompTox, and NIH websites [NIST, 2021, EPA, 2021, and PubChem/NIH, 2021]. The coefficients are often referred to as "constants" in research literature when they are actually strong functions of both temperature, salt content, and sometimes pH in the liquid phase. Furthermore, they are published in a wide range of units, including [pressure], [dimensionless] and [pressure/molarity]. Given the complex chemistry of nuclear waste and simulants, the use of Henry's Law coefficients need to consider solvent chemistry and temperature.

In work supporting SLAW evaporation, Henry's Law coefficients are used in the units of atm/(moles per cubic meter). The concentration unit (moles per cubic meter) is equivalent to millimolar. The pressure (atm) is the partial pressure of the trace volatile chemical. It is thus the product of total pressure and vapor phase mole fraction of that chemical. Henry's Law coefficients in the units of atm/(moles per cubic meter) are the units found on many government websites like the US National Library of Medicine "PubChem" site [PubChem/NIH, 2021].

For batch distillation, Rayleigh's equation describes the amount of depletion of the more volatile of two components assuming relative volatility of that component is constant over the composition range [Robinson and Gilliland, 1950]. Relative volatility "a" is the ratio of the "K values" or mole ratios of the volatile and less volatile components and is provided in Equation (1).

$$a = \frac{(\frac{y}{x} \text{ more volatile component})}{(\frac{y}{x} \text{ heavier component})} \quad (1)$$

where "y" is gas phase mole fraction and "x" is liquid phase mole fraction. "a" is the Henry's Law coefficient in proper units when concentration of the volatile chemical in the system is very low. When the

concentration of the more volatile component is very low in a binary system, x and y of the heavier component approach their limits of unity. This is because the denominator of the Equation (1) is unity in that case. Water is the heavier and also the much more prevalent chemical in the current discussion.

To give an example with methanol, its reported H is $4.55\text{E-}06 \text{ atm}\cdot\text{m}^3/\text{mol}$ at 25°C (PubChem, 2021]. Its pure component vapor pressure exceeds 100 torr at 25°C while the vapor pressure of pure water is 23.76 torr [CRC Handbook, 1975]. Methanol is thus more volatile than water. To make the x of water close to unity, assume that the x of methanol is $1.0\text{E-}04$ making that of water to be $1.0 - 1.0\text{E-}04 = 0.9999$. In that case methanol in the vapor phase would have a partial pressure of $4.55\text{E-}06 * 5.5 \text{ moles}/\text{m}^3$ because a cubic meter of liquid water would have about 55,000 moles of water and the methanol concentration is one ten-thousandth of this. The partial pressure of methanol in the vapor would thus be $25.0\text{E-}06 \text{ atm}$ or 0.019 torr. The total pressure would be dominated by the vapor pressure of water which is 23.76 torr at the given temperature. The mole fraction of methanol in the vapor phase would be $0.019/23.76 = 8.0\text{E-}04$. This is eight times its mole fraction in the liquid phase, so separation by evaporation for methanol is expected at 25°C .

For the volatile chemical, x and y in a binary system are given by [Robinson and Gilliland, 1950]:

$$y = \frac{a*x}{(1+(a-1)*x)} \quad (2)$$

There would be no evaporative separation if the separation factor is unity. From equation (2) it can be noted that the denominator is unity in the cases that are relevant to the current analysis where x is arbitrarily small. This is in line with the Henry's Law assumption of low concentration of the volatile species. In that case the denominator approaches unity and $y = a * x$. If a is unity, then there is no separation that would change the concentration of the volatile chemical in either the concentrate or condensate of an evaporation process. Equation (2) shows that $x = y$ in that case.

It is also to be noted that if the product $a*x$ is a large number, such as if " a " is much larger than unity, y approaches unity. This makes sense as the organic chemical being evaporated would form much of the vapor phase and would be readily removed from the liquid phase.

Henry's Law coefficients (H) in the units of $\text{atm}/(\text{moles per cubic meter})$ can be related to the separation factor being unity. By way of example, if the total vapor pressure is 60/760 or 0.079 atmospheres, the vapor pressure of the trace organic species is the product of total pressure and y . If there is no separation by evaporation, $x = y$ for the organic chemical, and the ratio (y/x) would be unity. The H coefficient would be $1.4\text{E-}06 \text{ atm}\cdot\text{m}^3/\text{mol}$ since the concentration of water would predominate in the aqueous phase. Approximately 55,000 moles of water occupies one cubic meter as shown in Equation (3).

$$(y / x) * 0.079 \text{ atm} / (55,000 \text{ moles} / \text{m}^3) = 1.4\text{E-}06 \text{ atm}\cdot\text{m}^3/\text{mol} \quad (3)$$

If the pressure is instead atmospheric pressure, H would be $1.4\text{E-}06 * (760/60)$ or $1.7\text{E-}05 \text{ atm}/(\text{atm}\cdot\text{m}^3/\text{mol})$. Likewise, if an evaporator operated at 25°C its absolute pressure for aqueous feed would be about 0.031 atm absolute or 23.76 torr. An H of $5.5\text{E-}07 \text{ atm}\cdot\text{m}^3/\text{mol}$ would be the boundary value where a chemical would be equally volatile as, and would not separate from, water. An evaporator running at atmospheric pressure requires a higher H for good separation than a vacuum evaporator as shown here. However, the higher-pressure evaporation operates at a higher boiling temperature. This leads to the Henry's Law coefficient also being higher as is presented in tables in the next section.

In a continuous evaporator the heated pot contains liquid at the effluent composition. Feed is introduced while vapor from the boiling liquid exits the pot vessel. If the operation boiled down 4 M sodium solution feed to 8 M sodium liquid effluent, approximately half of the water volume would be evaporated.

This is obtained using Equation 2 above. It is assumed that the separation factor $a=2$. For small x Equation (2) provides $y = 2 * x$. The vapor phase thus carries away 2 moles of volatile component for every mole of water vaporized. A separation factor of 2 would thus send 2/3 of the chemical in the feed to condensate. By mass balance a feed concentration of 0.01 millimolar would be reduced to 0.0067 millimolar in the pot concentrate. If the separation factor was instead 10 ($H = 1.4\text{E-}05 \text{ atm-m}^3/\text{mol}$ for vacuum evaporation at 60 torr), the liquid exiting the pot would instead contain 0.0018 millimolar of the organic chemical.

For a batch evaporator with two components (water and a trace organic chemical) Rayleigh's equation is :

$$\ln\left(\frac{M}{M_0}\right) = \left(\frac{1}{a-1}\right) \cdot \ln\left(\frac{x(1-x_0)}{x_0(1-x)}\right) + \ln\left(\frac{1-x_0}{1-x}\right) \quad (4)$$

where "M's" are total moles in the pot, subscript zeroes are initial values, and "M" and "x" are values after removal of some moles by batch distillation.

Figure 5 shows two hypothetical cases for batch distillation. Only moles of water removed are considered for the "M's" in Equation (3) because water removal is the bulk of the evaporated moles. The separation factor "a" is set to 2 in Equation (3) and then also to 10 (unitless). The initial concentration of trace organic chemical starts at $1.0\text{E-}04$ mole fraction. When $a=2$ the mole fraction only goes down by a factor of 2 when half of the water is boiled away. In contrast, the mole fraction is reduced to about 1/450 of its initial value when the separation factor is 10. Since Henry's Law coefficients vary over orders of magnitude and are proportional to the separation factor, evaporation can become practical very quickly if H is much above $1.4\text{E-}06 \text{ atm-m}^3/\text{mol}$. The preceding example in the text before Equation (2) with methanol in water shows that methanol's $H = 4.55\text{E-}05 \text{ atm-m}^3/\text{mol}$ provides a vapor that is eight times richer in methanol (mole fraction) than is seen in the liquid phase for equilibrium at 25°C and its corresponding pressure of 0.031 atm or 23.76 torr, (not 0.079 atm which is more typical of the Hanford 242-A vacuum evaporator).

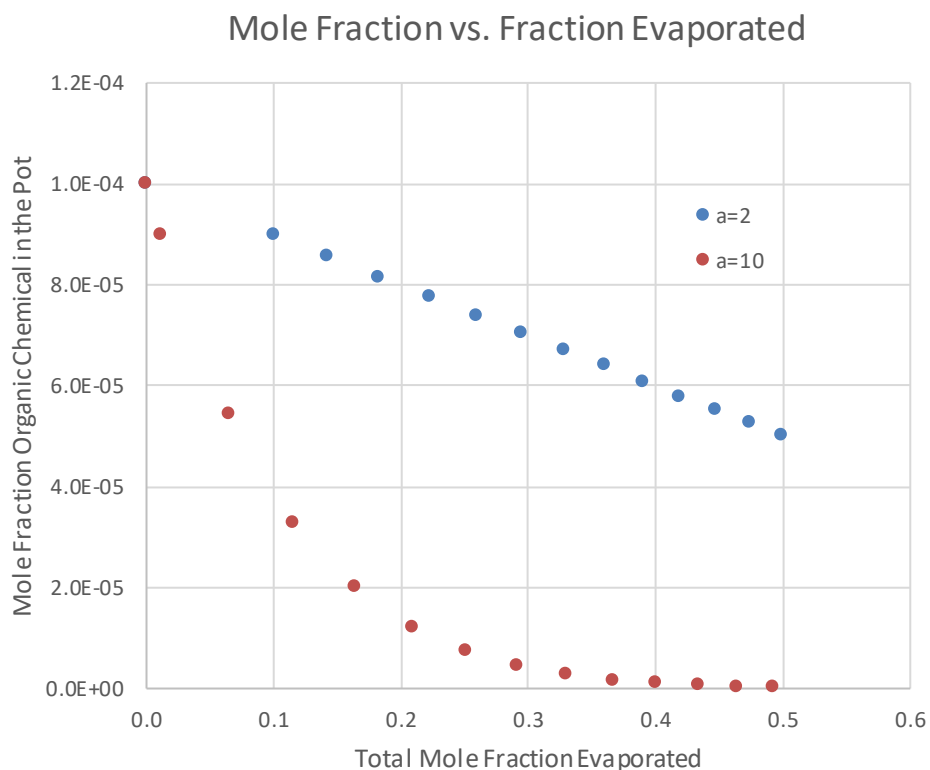


Figure 5. Use of Rayleigh's Equation for Modeling Batch Distillations

4.3 Practical Evaporation of Organic Species using OLI Software

OLI Systems, Inc. chemical thermodynamic software programs are used in calculating aqueous electrolyte chemistry. The OLI Studio software program is produced by OLI Systems, Inc. and was procured by SRNL. One of the components of this software system, the Studio, can be used to reconcile chemical analyses, calculate thermodynamic parameters, and predict component phase splits. Studio provides complete speciation of all phases that are in the databank for a given aqueous chemistry composition, along with the thermodynamic parameters (only the Studio component of the software was used in this work). The software program is a chemical thermodynamic simulator using the OLI Engine, which is used for approximating aqueous electrolyte chemistry. The results from this software can be used in many ways, such as estimating aqueous waste chemistry for development of flow sheets and material balances. The OLI databanks (which are part of the OLI Engine and used by Studio) have been evaluated and used previously by Nash et al., (2020) to estimate removal in an evaporator. For this work, the Studio software was utilized by SRNL to calculate the expected speciation and behavior of organic chemicals during evaporation. The prior work has shown that the partitioning of the organics measured during simulant testing and the model agree, indicating that the OLI software could be used in future flowsheet modeling efforts to predict partitioning of other organics during evaporation. This software models solution chemistry and includes a simulation of the increase of Henry's Law coefficients for organic volatiles with both increasing temperature and salt concentration.

The OLI databanks contain thermodynamic parameters on thousands of chemicals, with the parameters derived primarily from open technical literature. These fundamental parameters are then used by the software in a thermodynamic framework based on the Revised Helgeson Equation of State to predict

the physical and chemical properties of aqueous or multiphase systems. Calculation of the composition and phases is accomplished by solving the equilibrium equations with parameters from the included databanks. SRNL used this software and databanks without modification. OLI Studio version 10.0 was used for this work.

4.3.1 Aqueous Phase Composition Basis

The inorganic and ionic composition of the aqueous phase was based on simulants previously developed for Cast Stone testing [Russell et al., 2017] and used in the earlier simulant evaporation testing. Table 5 below (reproduced from Table 1-1 in [Nash et al., 2021]) shows the target composition for the “LAWPS 4.0 M Na Simulant Initial Liquid Phase Composition” formulation after accounting for charge-balancing and solubility and eliminating the trace amount of Cs and adding chromate. The amount of chromate is based on the original “HTWOS Overall Average” simulant formulation [Russell et al., 2013], adjusted for 4.0 M $[\text{Na}^+]$. Nitrate ion is reduced to compensate for the ion balance. The removal of fluoride and cesium, and addition of chromate per the reference [Russell et al., 2013] concentration was consistent with the earlier work [Nash et al., 2021].

Table 5. SLAW Evaporator Simulant Target Composition

(based on LAWPS 4.0M Na Simulant)

Constituent	Concentration (M)
Na^+	4.00E+00
K^+	8.71E-02
Al^{+3}	1.19E-01
Cl^-	8.71E-02
SO_4^{-2}	4.72E-02
PO_4^{-3}	3.09E-02
NO_2^-	7.29E-01
NO_3^-	1.25E+00
CO_3^{-2}	3.34E-01
oxalate	9.07E-03
CrO_4^{-2}	1.16E-02
Free OH^-	1.01E+00

4.3.2 OLI Modeling

The composition of the aqueous phase was input into OLI Studio 10.0. The “public” or “AQ” aqueous databank was used since it contained many of the organic species of interest from Table 2. The MSE databank was also checked but had very few of the organic chemicals of interest. Initial absolute pressure was set to 0.079 atmospheres (60 torr) to examine the distribution of organics to the vapor phase, which is the typical conditions in the 242-A evaporator. Runs were also performed at 1.0 atmospheres to provide a comparison. The temperature was adjusted to achieve evaporation of the target amount of water to leave the evaporator bottoms at the target sodium ion concentration, typically $\sim 7.4 \text{ M } [\text{Na}^+]$.

The primary test objective of the modeling was to determine partitioning of trace organic chemicals from the aqueous salt solution feed to an evaporator. Evaporation was historically performed to reduce the

volume of waste in the tanks, but it is also effective at removing the volatile organic species with the overhead (condensate) stream. At Hanford the low activity aqueous condensate is primarily composed of water, but also contains the organic compounds and is directed to the Effluent Treatment Facility, which is permitted for treating the organics.

OLI Studio was used to calculate the condition of a single evaporation step, i.e., the liquid and vapor produced in a single equilibrium condition. This is considered a conservative estimate of what would be expected in a continuous evaporator where only a small amount of fresh feed is continuously introduced into the evaporator pot and the condensate is continuously removed.

Each organic compound was input at an arbitrary concentration of 1.0E-5 M. The organic compounds that were in the databank, and their OLI identifier, are shown in Table 6.

Table 6. OLI Species Names

OLI Species	CAS #	OLI formula	OLI name
4-Nitrophenol *	100-02-7	C ₆ H ₅ NO ₃	NITPHENOL4
Pyridine	110-86-1	C ₅ H ₅ N	PYRIDINE
2-Ethylhexylphthalate	117-81-7	C ₂₄ H ₃₈ O ₄	BETHXPHTH2
Di-n-octylphthalate	117-84-0	C ₂₄ H ₃₈ O ₄	DOPHTH
2,4-Dinitrotoluene *	121-14-2	C ₇ H ₆ N ₂ O ₄	NITOLUEN24
Pyrene	129-00-0	C ₁₆ H ₁₀	PYRENE
m-Cresol *	108-39-4	C ₇ H ₈ O	MCRESOLE
p-Cresol *	106-44-5	C ₇ H ₈ O	PCRESOLE
Fluoranthene	86-73-7	C ₁₆ H ₁₀	FLUANTHEN
Alpha-1,2,3,4,5,6-Hexachlorocyclohexane (alpha-BHC)	319-84-6	C ₆ H ₆ Cl ₆	ALPHABHC
Beta-1,2,3,4,5,6-Hexachlorocyclohexane (Beta-BHC)	319-85-7	C ₆ H ₆ Cl ₆	BETABHC
2,4-Dinitrophenol *	51-28-5	C ₆ H ₄ N ₂ O ₅	NIPHENOL24
n-Butanol (a.k.a. n-butyl alcohol)	71-36-3	C ₄ H ₁₀ O	BUTYALCHOL
2-Methyl-1-propanol (isobutyl alcohol)	78-83-1	C ₄ H ₁₀ O	ISBUALCHOL
Diethyl-o-phthalate	84-66-2	C ₁₂ H ₁₄ O ₄	DIETPHTHL
Di-n-butyl phthalate	84-74-2	C ₁₆ H ₂₂ O ₄	DIBUTYPHTL
Butyl benzyl phthalate	85-68-7	C ₁₉ H ₂₀ O ₄	BUBNZPHTHA
Pentachlorophenol *	87-86-5	C ₆ HCl ₅ O	CL5PHENOL
2,4,6-Trichlorophenol	88-06-2	C ₆ H ₃ Cl ₃ O	CLPHENL246
2-Nitrophenol	88-75-5	C ₆ H ₅ NO ₃	NITPHENOL2
2,4,5-Trichlorophenol	95-95-4	C ₆ H ₃ Cl ₃ O	CLPHENL245
1-phenyl-1-ethanone	98-86-2	C ₈ H ₈ O	ACETPHENON
Phenol *	108-95-2	C ₆ H ₅ OH	C6H5OH

* Compound is in Table 3.

4.3.3 OLI Modeling Results

Results of the OLI Studio calculation for the evaporator pot liquid and the vapor phase are shown in Table 7. Note that for convenience of calculating the partitioning, this calculation was based on an initial volume of 1 L of liquid, as calculated at 25° C. Initial calculations showed that at atmospheric pressure and 25° C, the 1.0E-5 M concentration of organics exceeded the solubility of several species from Table 6, primarily the phthalates and pyrene, so were excluded from subsequent calculations. The diethyl phthalate was calculated to be soluble to over 1.0E-5 M under this condition so was included in the calculation. The calculated soluble concentration of those organics in the aqueous phase is shown in Table 8. The results of the calculation shown in Table 7 excluded these species. The calculation conditions adjusted the temperature of this mixture to 47.7° C to achieve the target amount of liquid phase remaining, ~0.54 L, which would correspond to a concentration of ~7.4 M [Na⁺]. The pressure of the isothermal calculation was 0.079 atmospheres.

Table 7. OLI Evaporation Calculation Organic Compound Partitioning Results

			Aqueous	Vapor
Species	Name	CAS#	% of Total	% of Total
C6H5O(-1)	Phenol	108-95-2	99.9	6.86E-04
CL5PHENT(-1)	Pentachlorophenol	87-86-5	7.91	92.1
MCRESOL	m-cresol	108-39-4	4.99	95.0
PCRESOL	p-cresol	106-44-5	6.78	93.2
BUTYLALCHOL	n-butyl alcohol	71-36-3	0.605	99.4
ISBUALCHOL	Isobutyl alcohol	78-83-1	0.0487	99.9
PYRIDINE	Pyridine	110-86-1	3.14	96.9
ACETOPHENON	1-phenyl-1-ethanone	98-86-2	1.31	98.7
DIETPHTHL	Diethyl-o-phthalate	84-66-2	20.7	79.3
CLPHENL245	2,4,5-Trichlorophenol	95-95-4	5.42	94.6
CLPHENL246	2,4,6-Trichlorophenol	88-06-2	5.54	94.5
NIPHENOL24	2,4-Dinitrophenol	51-28-5	100	4.38E-06
NITPHENOL2	2-Nitrophenol	88-75-5	17.5	82.5
NITPHENOL4	4-Nitrophenol *	100-02-7	99.9	0.0925
NITOLUEN24	2,4-Dinitrotoluene *	121-14-2	27.1	72.9

Table 8. Solubility of organic species in 4.0 M Salt Solution

Organic	CAS#	Solubility (M)
2-Ethylhexylphthalate	117-81-7	7.38E-08
Di-n-butyl phthalate	84-74-2	1.79E-06
Fluoranthene	86-73-7	8.37E-08
Pyrene	129-00-0	5.64E-08
Alpha-BHC	319-84-6	4.62E-07
Beta-BHC	319-85-7	5.93E-08
Butyl benzyl phthalate	85-68-7	6.04E-07
Di-n-octylphthalate	117-84-0	1.01E-10

The results of the calculation show that the phenol (shown as C6H5O(-1) in the table above) is almost completely ionized as phenoxide and remains in the aqueous phase, as expected with a small fraction in the vapor as phenol. The pentachlorophenol (CL5PHENT(-1)) is partitioned mostly to the vapor phase, with a small amount remaining in the aqueous phase as the ionized phenoxide. It is not known if this would happen in an evaporator, but the software is accounting for the ionization of the species.

The results for the phenolic compounds are not as expected, and no other ionized phenolics, other than the parent phenol, are in the output file. Evidently, the OLI software does not account for the ionization of the cresols and substituted phenolics that would occur in this high pH solution. It is expected that these species would remain in the aqueous phase as the corresponding phenoxide ions. Table 1 shows the pK_a of these species, which range from 4.09 to 10.3.

The diethyl phthalate is calculated to partition between the aqueous and vapor phases. This indicates that at least some of it may be removable by evaporation. Similarly, the dinitrotoluene is calculated to partition mostly to the vapor phase.

The pyridine, acetophenone, and butanol appear to partition mostly to the vapor phase, consistent with testing that was previously performed. The pK_a of these alcohols is high, as shown in Table 1, and they would not be expected to ionize in the solution. The isobutyl alcohol was also calculated to partition mostly to the vapor phase, as expected.

OLI Software databases have some of the regulated organic chemicals of interest in this report. Henry's Law coefficients (H) have been calculated for cases of 4 M sodium and 7.4 M sodium feed solution. Tables 9 and 10 show the results, but interpretation is added because OLI does not properly deprotonate the substituted phenols and the cresols as shown in blue. Blue indicates behavior if the chemical were a neutral species. However, at the alkaline conditions expected, they are likely not removed to a practical extent by evaporation. Chemicals in rows with red highlighting are indicated by OLI to not be significantly removed by evaporation, and these are reasonable. The rows with no highlighting are chemicals that are expected to be volatile enough to be treated by evaporation. Of the seven compounds present in the OLI data base and listed in Table 3 as being hard to evaporate based on H at 25 C and 1 atm pressure, only 2,4-dinitrotoluene is predicted by OLI to have the potential to be removed by evaporation. The other six compounds are still predicted to not be significantly removed by evaporation.

The comparison of the two Henry's law values in each table show that OLI predicts an increase in H with temperature and pressure. The variation in pressure does not change any conclusions about what is or is not treatable by evaporation.

Comparing cells across Table 9 vs. 10 shows the salting out effect that OLI predicts. H's are higher in Table 10 vs. Table 9 values. Table 9 values are appropriate for batch distillation processes where 4 M sodium feed is charged to an evaporator pot and batch evaporation commences. Table 10 is appropriate for continuous evaporation where the sodium concentration is a constant value equivalent to the final product concentration. In practice that final sodium concentration would be about 7.4 M. The continuous process would add feed to a pot operating at that higher sodium concentration (and slightly higher temperature – see table headings) while water is being boiled out. Product would be withdrawn at a rate to keep the pot volume constant.

In Tables 9 and 10 it must be noted that phenol is a special case where OLI does deprotonate the chemical correctly in the alkaline solution, causing H to be very low. OLI includes phenolate as an aqueous species and this must be counted as phenol still in the liquid phase. Phenol would be expected to not be removed by evaporation from alkaline solutions.

Table 9. Henry's Law Coefficients for 4 M Sodium Aqueous Feed

Chemical	CAS#	Formula	H* (OLI, 44 °C)	H* (OLI, 104 °C)
Pentachlorophenol**	87-86-5	C ₆ HCl ₅ O	5.72E-06	2.98E-04
m-cresol**	108-39-4	C ₇ H ₈ O	1.03E-05	5.31E-05
p-cresol**	106-44-5	C ₇ H ₈ O	7.31E-06	3.93E-05
n-butanol	71-36-3	C ₄ H ₁₀ O	8.93E-05	5.80E-04
isobutanol	78-83-1	C ₄ H ₁₀ O	1.37E-03	5.78E-04
Pyridine	110-86-1	C ₅ H ₅ N	1.74E-05	2.61E-04
Acetophenone	98-86-2	C ₈ H ₈ O	4.10E-05	3.46E-04
Fluoranthene	206-44-0	C ₁₆ H ₁₀	2.17E-04	2.17E-02
Alpha BHC	319-84-6	C ₆ H ₆ Cl ₆	3.30E-03	1.14E-02
Beta BHC	319-85-7	C ₆ H ₆ Cl ₆	2.58E-02	5.39E-02
2,4,5 trichlorophenol	95-95-4	C ₆ H ₃ Cl ₃ O	8.34E-06	3.74E-04
2,4,6 trichlorophenol	88-06-2	C ₆ H ₃ Cl ₃ O	8.58E-06	1.99E-04
2,4 dinitrophenol**	51-28-5	C ₆ H ₄ N ₂ O ₅	1.59E-14	1.95E-11
2-Nitrophenol	88-75-5	C ₆ H ₅ NO ₃	2.36E-06	3.05E-05
4-Nitrophenol**	100-02-7	C ₆ H ₅ NO ₃	5.63E-10	6.69E-09
2,4 dinitrotoluene**	121-14-2	C ₇ H ₆ N ₂ O ₄	1.23E-06	1.00E-04
Phenol**	108-95-2	C ₆ H ₆ O	3.03E-11	3.73E-08

* Units of Henry's Law coefficients in this table are atm-m³/mol.

** Table 3 compound

Red highlighting: Component is not practically removed by evaporation per OLI

Blue highlighting: OLI does not properly deprotonate these, overestimating H.

Table 10. Henry's Law Coefficients for 7.4 M Sodium Aqueous Feed

Chemical	CAS#	Formula	H* (OLI, 48 °C)	H* (OLI, 108 °C)
Pentachlorophenol**	87-86-5	C ₆ HCl ₅ O	1.85E-05	1.89E-03
m-cresol**	108-39-4	C ₇ H ₈ O	3.03E-05	2.75E-04
p-cresol**	106-44-5	C ₇ H ₈ O	2.19E-05	2.01E-04
n-butanol	71-36-3	C ₄ H ₁₀ O	2.61E-04	3.08E-03
isobutanol	78-83-1	C ₄ H ₁₀ O	3.27E-03	2.66E-03
Pyridine	110-86-1	C ₅ H ₅ N	4.91E-05	1.66E-03
Acetophenone	98-86-2	C ₈ H ₈ O	1.20E-04	1.93E-03
Fluoranthene	206-44-0	C ₁₆ H ₁₀	7.61E-04	1.38E-01
Alpha BHC	319-84-6	C ₆ H ₆ Cl ₆	8.85E-03	6.31E-02
Beta BHC	319-85-7	C ₆ H ₆ Cl ₆	6.65E-02	2.93E-01
2,4,5 trichlorophenol	95-95-4	C ₆ H ₃ Cl ₃ O	2.78E-05	2.29E-03
2,4,6 trichlorophenol	88-06-2	C ₆ H ₃ Cl ₃ O	2.72E-05	1.18E-03
2,4 dinitrophenol**	51-28-5	C ₆ H ₄ N ₂ O ₅	6.97E-14	1.36E-10
2-Nitrophenol	88-75-5	C ₆ H ₅ NO ₃	7.48E-06	1.71E-04
4-Nitrophenol**	100-02-7	C ₆ H ₅ NO ₃	1.47E-09	5.03E-08
2,4 dinitrotoluene**	121-14-2	C ₇ H ₆ N ₂ O ₄	4.27E-06	6.28E-04
Phenol	108-95-2	C ₆ H ₆ O	1.09E-11	2.26E-08

* Units of Henry's Law coefficients in this table are atm-m³/mol.

** Table 3 compound

Red highlighting: Component is not practically removed by evaporation per OLI

Blue highlighting: OLI does not properly deprotonate these, overestimating H.

4.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

5.0 Conclusions

An evaluation of organic chemicals that are likely to be present in Hanford tank waste has provided a list for further consideration. These chemicals are considered likely present in tanks at measurable concentrations and may require treatment to remove them. In addition, the reactivity of the chemicals was assessed against alkaline solution where possible. Evaporation is practical for the removal of many of the chemicals, and in addition, reactivities have been identified that may explain why some chemicals were not measured in tanks. It is evident that a large number of organic chemicals, and particularly those that are most commonly measured (acetone, butanone, and n-butyl alcohol), can be readily removed by evaporation. Removing the volatile species eliminates one impediment that may enable producing a grout waste form that can be disposed in a permitted facility.

The compounds that, if present, are expected to be difficult to remove by evaporation are shown in Table 11. Five of these have been found in the TWINS database to be above the wastewater limits in at least one liquid tank sample.

Table 11. Compounds Expected Difficult to Remove by Evaporation

LDR Organic species	CAS#
p-Nitrophenol	100-02-7
Phenol	108-95-2
2,4-Dinitrotoluene	121-14-2
Cresols (m,p,o)	1319-77-3
phenol, 2-methyl ^a	95-48-7
2,4-Dinitrophenol*	51-28-5
morpholine, N-nitroso*	59-89-2
Pentachlorophenol*	87-86-5
4,6-Dinitro-o-cresol*	534-52-1
N-nitrosodiethylamine	55-18-5
2,4,6-Trichlorophenol	88-06-2
2-Nitrophenol*	88-75-5
2-Naphthylamine	91-59-8
2,4,5-Trichlorophenol	95-95-4
a. o-cresol is also known as phenol, 2-methyl but is shown here in both nomenclatures	
*Identified in TWINS as present above WW limit in at least one tank	

6.0 Recommendations, Path Forward or Future Work

It is recommended to test evaporator partitioning of representative chemicals that are expected to be resistant to evaporation and that may be unreactive (stable) in warm alkaline solution. Examples include cresols, substituted phenols, and other hydrocarbons shown in Table 3. Completion of the FY21 activity by WRPS that focused on documenting additional process knowledge through a review of past LDR notification forms for waste transfers into the Hanford DSTs may add more compounds that will need to be assessed in the manner described here. Follow-on work in FY22 should be performed to complete such an effort. Additional analyses of tank samples are recommended to quantify the comprehensive list of regulated compounds, and to specifically analyze for phthalates, phthalic acid, and phenolic compounds.

7.0 References

40 CFR 268.48, “Universal Treatment Standards,” *Code of Federal Recommendations*, as amended.

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Appendix A. Underlying Hazardous Constituents

The table below is based on Table 3 of Appendix A in RPP-RPT-54699. This is a list of Underlying Hazardous Constituents, excluding those that are in Table 1 of this report and are unrelated to Hanford and those believed unstable in caustic and radiation (per criterion 4 and 5 in Appendix A Table 3 of RPP-RPT-54699). The third column shows the Henry's Law coefficient from the EPA website, and the fourth column shows the water solubility from the EPA website.³ The right-most column shows those that can be removed by evaporation or are insoluble (x) or are near the limit for removable by evaporation (~x) for those compounds with H between 4.55E-06 and 1.4E-06 atm-m³/mol, so is below the proven limit for methanol but above the estimated limit value for separable by evaporation.

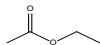


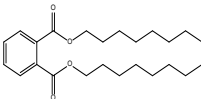
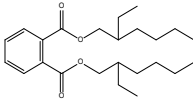
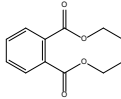
Chemical Compound	CAS#	EPA Henry's Law coeff (atm-m ³ /mole)	EPA water solubility (mg/L)	Removed by Evap or Not soluble
Phthalic acid	100-21-0	1.63E-09	1.50E+01	
4-Bromophenyl phenyl ether	101-55-3	1.42E-04	NR	x
1,2-Dibromoethane/Ethylene dibromide	106-93-4	6.50E-04	3.96E+03	x
Acrolein	107-02-8	1.22E-04	2.10E+05	x
3-Chloropropylene	107-05-1	1.60E-02	3.34E+03	x
Ethyl cyanide/Propanenitrile	107-12-0	3.70E-05	1.04E+05	x
Acrylonitrile	107-13-1	1.38E-04	7.48E+04	x
Anthracene	120-12-7	5.56E-05	6.02E-02	x
2,4-Dichlorophenol	120-83-2	1.33E-06	4.52E+03	x
Diphenylamine	122-39-4	7.36E-08	4.59E+01	
1,4-Dioxane	123-91-1	4.80E-06	1.00E+06	x
Methacrylonitrile	126-98-7	1.09E-05	2.54E+04	x
trans-1,2-Dichloroethylene	156-60-5	6.73E-03	4.69E+03	x
Benzo(g,h,i)perylene	191-24-2	3.31E-07	2.60E-04	x
Dibenz(a,e)pyrene	192-65-4	3.08E-07	7.71E-04	x
Indeno(1,2,3-c,d) pyrene	193-39-5	3.48E-07	1.91E-04	x
Benzo(b)fluoranthene	205-99-2	6.57E-07	2.37E-03	
Benzo(k)fluoranthene	207-08-9	5.84E-07	8.07E-04	x
Acenaphthylene	208-96-8	1.14E-04	1.64E+01	x
Chrysene	218-01-9	5.23E-06	2.79E-03	x
delta-BHC	319-86-8	3.18E-06	5.87E+00	~x
Isodrin	465-73-6	4.41E-05	1.39E-02	x
Benzo(a)pyrene	50-32-8	4.57E-07	2.12E-03	x
Dibenzo(a,h)anthracene	53-70-3	9.24E-07	1.20E-03	x
3-Methylcholanthrene	56-49-5	7.99E-04	2.98E-03	x

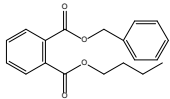
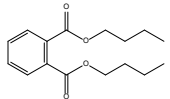





³ <https://comptox.epa.gov/dashboard/dsstoxdb/>

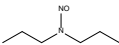







Chemical Compound	CAS#	EPA Henry's Law coeff (atm-m ³ /mole)	EPA water solubility (mg/L)	Removed by Evap or Not soluble
Benz(a)anthracene	56-55-3	1.20E-05	1.19E-02	x
gamma-BHC	58-89-9	3.18E-06	7.36E+00	~x
2,3,4,6-Tetrachlorophenol	58-90-2	5.58E-07	2.31E+01	
p-Chloro-m-cresol	59-50-7	1.13E-06	3.84E+03	
1,1,1,2-Tetrachloroethane	630-20-6	2.50E-03	1.08E+03	x
Hexachloroethane	67-72-1	3.89E-03	5.02E+01	x
Bromomethane	74-83-9	7.34E-03	1.42E+04	x
Chloromethane	74-87-3	8.82E-03	5.76E+03	x
Chloroethane	75-00-3	1.11E-02	6.00E+03	x
Bromodichloromethane	75-27-4	2.12E-03	3.88E+03	x
Dichlorodifluoromethane	75-71-8	3.43E-01	5.98E+02	x
1,2-Dichloropropane	78-87-5	2.82E-03	2.79E+03	x
Pentachloronitrobenzene	82-68-8	9.39E-04	4.43E-01	x
Acenaphthene	83-32-9	1.84E-04	7.15E+00	x
Phenanthrene	85-01-8	4.23E-05	1.13E+00	x
Hexachlorobutadiene	87-68-3	1.03E-02	3.18E+00	x
2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	6.29E-08	7.16E+01	
2-Chloronaphthalene	91-58-7	3.20E-04	1.18E+01	x
Silvex/2,4,5-TP	93-72-1	1.60E-09	1.01E+02	
1,2-Dichlorobenzene	95-50-1	1.92E-03	1.44E+02	x
2-Chlorophenol	95-57-8	1.12E-05	1.12E+04	x






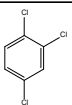

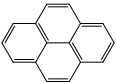
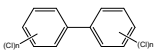
Appendix B. Reactivity of Organic Chemicals

The following table gives information on the expected reactivities or lack thereof of many organic chemicals. Reactions included hydrolysis, air oxidation, reaction with nitrite, and substitution of a halide bonded to an aromatic.



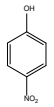


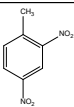
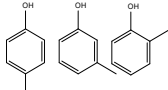
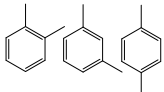
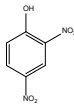
CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pKa (estimated) ² , ³	Comments
141-78-6	Ethyl acetate		Hydrolysis (esters)	Saturated	Ester		1.21E-01	66.387 days	25	Saponification to acetic acid and ethanol
75-05-8	Acetonitrile		Hydrolysis (esters)	Saturated	Nitrile		0.00567 M-1 hr-1	>17.5 hours		Estimated pKa is 25. Hydrolyses to acetic acid and ammonia. From reference 4, pH 10+ 23 C no hydrolysis after 17.5 hours, at 66 oC t 1/2 = 32 days, and at 85.5 C t 1/2 5.5 days. Rate in table is from Peskoff, N; Meyer, J. Zur Kenntnis der Folgereaktionen. III Die Hydrolyse von Saureamiden und Nitrile. Z. Phys. Chem. 1913, 82, 129-163. Also, hydrolysis has been estimated to be 100 hr at pH 13 @ 165 F and 100 hr at pH 14 @ 120 F in Keller, B. K. et al Decomposition of Select Volatile Organic Compounds by Caustic Hydrolysis for Effluent Management Facility, Washington River Protection Solutions, RPP-RPT-61542, Hanford, May 2019.
107-12-0	Propionitrile		Hydrolysis (esters)	Saturated	Nitrile				25	Hydrolysis to propanoic acid and ammonia.
117-84-0	Di-n-octylphthalate		Hydrolysis (esters)	Unsaturated	Ester	Benzene	2.85E-02	281 days	>30	Saponification to phthalic acid and octanol. In ref. 5 as 7.4 M ⁻¹ hr ⁻¹ and a half life of 107 years at pH 7 25 deg C
117-81-7	bis(2-ethylhexyl)phthalate (DEHP)		Hydrolysis (esters)	Unsaturated	Ester	Benzene	4.12E-02	194 days	>30	Saponification to phthalic acid and ethylhexanol
84-66-2	Diethyl phthalate		Hydrolysis (esters)	Unsaturated	Ester	Benzene	7.55E-02	106 days	>30	Saponification to phthalic acid and ethanol. Also in Ref 5 as 36 M ⁻¹ hr ⁻¹ and a half life at pH 7 of 22y

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² ,3	Comments
85-68-7	Butyl benzyl phthalate		Hydrolysis (esters)	Unsaturated	Ester	Benzene	1.59E-01	50.6 days	>30	Base catalyzed saponification to butanol, benzyl alcohol, and phthalic acid.
84-74-2	Dibutyl phthalate (DBP)		Hydrolysis (esters)	Unsaturated	Ester				>30	Base catalyzed saponification to butanol and phthalic acid.
75-15-0	Carbon disulfide	$S=C=S$	Slow/No Hydrolysis	S or P	Sulfide				>30	Can react with amines. No hydrogen for pK _a measurement
108-10-1	4-Methyl-2-pentanone (Methyl isobutyl ketone)		Slow/No Hydrolysis	Saturated	Ketone				20	aldol reaction
55-18-5	Diethylnitrosoamine (N-Nitrosodiethylamine, NDEA)		Slow/No Hydrolysis	Saturated	Amine				>30	
56-23-5	Carbon tetrachloride		Slow/No Hydrolysis	Saturated	Halogen				>30	No hydrogen for pK _a measurement
59-89-2	N-Nitrosomorpholine		Slow/No Hydrolysis	Saturated	Nitroso				>30	
60-29-7	Diethyl ether (Ethyl ether)		Slow/No Hydrolysis	Saturated	Ether				>30	

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² ,3	Comments
621-64-7	Dipropylnitrosoamine (N-Nitroso-di-n-propylamine)		Slow/No Hydrolysis	Saturated	Nitroso				>30	
62-75-9	N-Nitrosodimethylamine (N-Nitroso-N,N-dimethylamine)		Slow/No Hydrolysis	Saturated	Nitroso				>30	
67-56-1	Methanol		Slow/No Hydrolysis	Saturated	Carboxylic acid				16	
67-64-1	2-Propanone (Acetone)		Slow/No Hydrolysis	Saturated	Ketone				20	Aldol reaction
71-36-3	n-Butyl alcohol (1-Butanol)		Slow/No Hydrolysis	Saturated	Alcohol	Alkane			16	
78-83-1	Isobutyl alcohol		Slow/No Hydrolysis	Saturated	Alcohol				16	
78-93-3	2-Butanone (MEK)		Slow/No Hydrolysis	Saturated	Ketone				20	Aldol reaction
79-46-9	2-Nitropropane		Slow/No Hydrolysis	Saturated	Nitro				10	



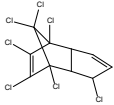

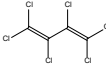

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² , ₃	Comments
106-46-7	1,4-Dichlorobenzene		Slow/No Hydrolysis	Unsaturated	Benzene				>30	Ref 5 at basic conditions <0.9 M-1 hr-1 and a half life at pH 7 25 deg C of >900 y
107-02-8	2-Propenal (Acrolein)		Slow/No Hydrolysis	Unsaturated	Alkene	Aldehyde			>30	
108-90-7	Chlorobenzene		Slow/No Hydrolysis	Unsaturated	Benzene				>30	
108-95-2	Phenol		Slow/No Hydrolysis	Unsaturated	Alcohol				10	nitrite can nitrate. May also form quinone
110-86-1	Pyridine		Slow/No Hydrolysis	Unsaturated	Pyridine				>30	
120-82-1	1,2,4-Trichlorobenzene		Slow/No Hydrolysis	Unsaturated	Benzene				>30	
127-18-4	Tetrachloroethylene (PCE)		Slow/No Hydrolysis	Unsaturated	Halogen				>30	
129-00-0	Pyrene		Slow/No Hydrolysis	Unsaturated	Polyaromatic				>30	
1336-36-3	Aroclors (Total PCB)		Slow/No Hydrolysis	Unsaturated	Benzene				>30	

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² ,3	Comments
206-44-0	Fluoranthene		Slow/No Hydrolysis	Unsaturated	Polyaromatic				>30	
309-00-2	Aldrin		Slow/No Hydrolysis	Unsaturated	Halogen				>30	
541-73-1	1,3-Dichlorobenzene		Slow/No Hydrolysis	Unsaturated	Benzene				>30	
71-43-2	Benzene		Slow/No Hydrolysis	Unsaturated	Benzene				>30	
83-32-9	Acenaphthene		Slow/No Hydrolysis	Unsaturated	Polyaromatic				>30	
86-73-7	9H-fluorene		Slow/No Hydrolysis	Unsaturated	Polyaromatic				>30	
91-20-3	Naphthalene		Slow/No Hydrolysis	Unsaturated	Naphthalene				>30	
91-59-8	2-Naphthylamine		Slow/No Hydrolysis	Unsaturated	Amine	Naphthalene			>30	

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pKa (estimated) ² 3	Comments
98-86-2	Acetophenone		Slow/No Hydrolysis	Unsaturated	Ketone	Benzene			16	Stable aromatic with mildly acidic ketone (Novak, M.; Loudon, G. M. The pKa of Acetophenone in Aqueous Solution <i>J. Org. Chem.</i> 1977 , <i>42</i> , 2494-2498)
98-95-3	Nitrobenzene		Slow/No Hydrolysis	Unsaturated	Benzene	Nitro			>30	Stable aromatic with no acid hydrogens
100-02-07	4-Nitrophenol (p-Nitrophenol)		Oxidation (aromatics)	Unsaturated	Alcohol	Benzene			7	para position blocked for quinone formation
100-41-4	Ethylbenzene		Oxidation (aromatics)	Unsaturated	Benzene	Alkane			>30	alpha carbon susceptible to oxidation
108-88-3	Toluene		Oxidation (aromatics)	Unsaturated	Benzene				>30	methyl group susceptible to oxidation to benzoic acid
121-14-2	2,4-Dinitrotoluene		Oxidation (aromatics)	Unsaturated	Benzene				>30	
1319-77-3	Cresol (o, m, p)		Oxidation (aromatics)	Unsaturated	Alcohol				10	methyl group susceptible to oxidation to benzoic acid
1330-20-7	Xylene (o, m, p)		Oxidation (aromatics)	Unsaturated	Benzene				>30	methyl group susceptible to oxidation to benzoic acid
51-28-5	2,4-Dinitrophenol		Slow/No Hydrolysis	Unsaturated	Alcohol				5	

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² ₃	Comments
534-52-1	4,6-Dinitro-2-methylphenol (4,6-Dinitro-o-cresol, DNOC)		Slow/No Hydrolysis	Unsaturated	Alcohol				5	Methyl could be oxidized
87-86-5	Pentachlorophenol		Oxidation (aromatics)	Unsaturated	Alcohol				5	
88-06-2	2,4,6-Trichlorophenol		Oxidation (aromatics)	Unsaturated	Alcohol				7	at neutral pH 2.3 +/- 3.5 E-7 M-1 hr-1 and a half life at pH 7 25 deg C of >300 years
88-75-5	2-Nitrophenol		Oxidation (aromatics)	Unsaturated	Alcohol				7	
95-48-7	2-Methylphenol (o-Cresol)		Oxidation (aromatics)	Unsaturated	Alcohol	Benzene			10	Acidic phenol with oxidizable methyl group
95-95-4	2,4,5-Trichlorophenol		Oxidation (aromatics)	Unsaturated	Alcohol	Benzene			7	Acidic phenol
319-84-6	α-1,2,3,4,5,6-hexachlorocyclohexane (BHC)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	6.17E-12	3558000000 years	>30	
319-85-7	β-1,2,3,4,5,6-hexachlorocyclohexane (BHC)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	6.17E-12	3558000000 years	>30	
75-34-3	1,1-Dichloroethane (11-DCA)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	9.16E-10	23980000 years	>30	Hydrolysis forms vinyl chloride or less likely acetic acid through aldehyde
75-09-2	Dichloromethane (Methylene Chloride)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	5.10E-09	4311000 years	>30	Hydrolysis forms formaldehyde

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² ,3	Comments
71-55-6	1,1,1 Trichloroethane (111-TCA)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	7.43E-09	2954000 years	>30	Reactive with base. Could undergo elimination to dichloroethene or less likely substitution to form acetic acid.
74-87-3	Chloromethane (Methyl chloride)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	9.78E-06	2245 years	>30	Converts to methanol
67-66-3	Chloroform		Substitution/elimination (halides)	Saturated	Halogen	Alkane	6.45E-05	340 years	16	Slowly air oxidizes to phosgene. A faster reaction is alpha elimination to form dichlorocarbene that goes to carbon monoxide and formate. Substitution to form an alcohol is also likely to occur make formate.
79-00-5	1,1,2-Trichloroethane (112-TCA)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	1.88E-02	1.171 years	upper 20s to lower 30s	Hydrolysis forms dichloroethene through elimination or glycolic acid through aldehyde
79-34-5	1,1,2,2-Tetrachloroethane (1122-TCA)		Substitution/elimination (halides)	Saturated	Halogen	Alkane	1.469	5.462 days	upper 20s to lower 30s	Hydrolysis forms trichloroethene or less likely oxalic acid
67-72-1	Hexachloroethane (HCA)		Substitution/elimination (halides)	Saturated	Halogen		4.3E-7 M ⁻¹ hr ⁻¹	1.8E9 years	>30	No abstractable hydrogen so very unreactive. In ref. 5 at basic conditions at 4.3E-7 M ⁻¹ hr ⁻¹ and a half life at pH 7 25 deg C of 1.8E9 years.
75-69-4	Trichlorofluoromethane		Substitution/elimination (halides)	Saturated	Halogen				>30	No abstractable hydrogen so very unreactive
1024-57-3	Heptachlor epoxide		Substitution/elimination (halides)	Unsaturated	Halogen	Ether	6.86E-05	3204 years	>30	EPA EPI only had acid catalyzed case at pH = 7. Our case would be faster and end with diol formation
10061-01-5	cis-1,3-Dichloropropene		Substitution/elimination (halides)	Unsaturated	Halogen				upper 20s to lower 30s	Can form the alcohol at sp3 carbon.
10061-02-6	trans-1,3-Dichloropropene		Substitution/elimination (halides)	Unsaturated	Halogen				upper 20s to lower 30s	Can form the alcohol at the sp3 carbon

CAS #	Chemical Constituent	Structure	Reactions	Saturated/ Unsaturated	Functional group #1	Functional group #2	Hydrolysis ¹ (K _b), L/mol-sec	K _b ¹ Half-Life pH 8	pK _a (estimated) ² 3	Comments
75-01-4	Vinyl chloride		Substitution/elimination (halides)	Unsaturated	Halogen				>30	
75-35-4	1,1-Dichloroethylene (11-DCE)		Substitution/elimination (halides)	Unsaturated	Halogen				>30	
76-44-8	Heptachlor		Substitution/elimination (halides)	Unsaturated	Halogen				>30	
79-01-6	Trichloroethene (Trichloroethylene, TCE)		Substitution/elimination (halides)	Unsaturated	Halogen				>30	
87-68-3	Hexachlorobutadiene (HCBd)		Substitution/elimination (halides)	Unsaturated	Halogen				>30	
107-06-2	1, 2-Dichloroethane (12-DCA)		Substitution/elimination (halides)	Saturated	Halogen		1.1E-06 M-1 hr-1	72 years	>30	Can form vinyl chloride by elimination. In ref. 5 at neutral conditions at 1.1E-6 M-1 hr-1 and a half life at pH 7 25 deg C of 72 years.

1. Total K_b for pH>8 at 25 deg C for US EPA EPI Suite

2. Hans Reich's Collection, Bordwell pK_a Table, https://organicchemistrydata.org/hansreich/resources/pka/#pka_water_compilation_williams

3. Molecular Orbital Package (MOPAC), <http://openmopac.net/index.html>

4. Ellington, J. J.; Stancil, F. E.; Payne, W. D.; Trusty, C. Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal Volume 2. Data on 54 Chemicals, US EPA, August 1987

5. Ellington, J. J. Hydrolysis Rate Constants for Enhancing Property-Reactivity Relationships, US EPA.

6. Wiemers, K. D.; Babad, H.; Hallen, R. T.; Jackson, L. P.; Lerchen 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, December 1998.

7. White, T. L. Notes Describing the Work Product and References on EMF Profile to LERF-ETF Forecast, SRNL-L4130-2020-00006, Memorandum for Savannah River National Laboratory: Aiken, SC 29808.

8. Ellington, J. J.; Stancil, F. E.; Payne, W. D. Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal Volume 1. Data on 54 Chemicals, US EPA, August 1986

9. Ellington, J. J.; Stancil, F. E.; Payne, W. D.; Trusty, C. Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal Volume 3. Data on 54 Chemicals, US EPA, August 1988

10. Jeffers, Peter M.; Ward, Lisa M.; Woytowitch, Lisa M.; Wolfe, N. L. Homogeneous Hydrolysis Rate Constants for Selected Chlorinated
Methanes, Ethanes, Ethenes, and Propanes Environ. Sci. Technol. 1989, 23, 965-969.

11. Smith, M. B.; March, J. March's Advanced Organic Chemistry, Wiley-Interscience: United States of America, 6 th ed., pp 360-364. Note: pK_a tables

Appendix C. Results of WRPS FY21 LDR Organics Chemical Screening

The Hanford Tank Operating Contractor, Washington River Protection *Solutions*, LLC (WRPS) has been developing a regulatory and processing LDR treatment variance strategy termed “Sample-and-Send” that relies, in part, on demonstrating that in situ decomposition reactions along with historic evaporation of tank waste has destroyed or removed many of the LDR organics (SRNL-STI-2020-00582, SRNL-STI-2021-00453). Under the Sample-and-Send concept, Hanford tank waste would be prepared to create a feed candidate tank that would then be sampled to confirm the waste acceptance criteria is met for a supplemental LAW cementitious treatment facility. If it can be shown that LDR organics have been removed (by historic evaporation) or destroyed (by in situ decomposition) sufficiently to preclude additional organic treatment technology prior to creating a cementitious final waste form, the concept of Sample-and-Send would be proposed to establish a non-rulemaking site-specific treatment variance using the specified method of treatment “STABL” to remove sampling requirements of the waste form after treatment. Waste not meeting the waste acceptance criteria would be routed to the Hanford Waste Treatment and Immobilization Plant for LAW vitrification.

A key component in implementing the Sample-and-Send strategy is identifying which of the 207 LDR organic compounds associated with the Part A permit application waste codes for the Double Shell Tanks (DST Part A permit application) (DOE 2009, Ecology 2009) and any applicable Underlying Hazardous Constituents (UHCs) from 40 CFR 268.48 should be considered as possibly present and thus subject to regulation. In addition, it is also necessary to identify which of the possibly present LDR organic compounds are likely to have been removed by historic evaporation or destroyed by *in situ* decomposition reactions. WRPS document RPP-RPT-63493 provides a description of the outcome of the application of six decision rules to the list of 207 LDR organic compounds. These decision rules retain compounds on the list of possibly present LDR organics if they:

1. Are Hanford tank farm F001-F005 constituents, or
2. Are RCRA Part A “D” codes: D018, D019, D022, D028, D029, D030, D033, D034, D035, D036, D038, D039, D040, D041, D043, or
3. Were used at Hanford including identified components in commercial products (Prior to May 8, 1992), or
4. Are detected in the SSTs or DSTs samples (Past and Future), or
5. Are identified as decomposition reaction end products formed in tanks, or
6. Are identified on an LDR notification form from past (and future) transfers into the DSTs and:
 - a. were detected at or above the LDR wastewater standard, or
 - b. have no analytical data to indicate concentration, or
 - c. process knowledge cannot be developed to support the constituent is not in the waste when reported as <MDL but MDL is greater than LDR wastewater standard.

The following table lists the currently identified 130 possibly present LDR organic compounds in Hanford tank waste. The compounds are identified with an “X” in the fifth column of the table. The table also indicates the 73 compounds that were included in the analysis outlined in this report with an “X” in the sixth column. Note that all 73 compounds are included in the list of 130 possibly present LDR organics.

Table C-1: List of 207 LDR organic compounds associated with the Part A permit application waste codes for the Hanford double shelled tanks. The 130 possibly present LDR organic compounds and 73 compounds included in this work are identified in Column 5 and 6, respectively.

Line Number	Name	CAS Number	Waste code/UHC	Retained as Possibly Present LDR Organics Using the Six Decision Rules (RPP-RPT-63493)	Included in This Work
1	Phthalic acid	100-21-0	NA/UHC	X	--
2	Methapyrilene	91-80-5	NA/UHC	--	--
3	4,4-Methylene bis(2-chloroaniline)	101-14-4	NA/UHC	--	--
4	2-Acetylaminofluorene	53-96-3	NA/UHC	--	--
5	Phenacetin	62-44-2	NA/UHC	--	--
6	1,3-Phenylenediamine	108-45-2	NA/UHC	--	--
7	Acrylamide	79-06-1	NA/UHC	--	--
8	Silvex/2,4,5-TP	93-72-1	NA/UHC	X	--
9	5-Nitro-o-toluidine	99-55-8	NA/UHC	--	--
10	Famphur	52-85-7	NA/UHC	--	--
11	Phthalic anhydride	85-44-9	NA/UHC	--	--
12	2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	NA/UHC	--	--
13	N-Nitrosomorpholine	59-89-2	NA/UHC	X	X
14	2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	NA/UHC	--	--
15	Dibenz(a,e)pyrene	192-65-4	NA/UHC	X	--
16	N-Nitrosopyrrolidine	930-55-2	NA/UHC	--	--
17	Kepone	143-50-0	NA/UHC	--	--
18	Chlorobenzilate	510-15-6	NA/UHC	--	--
19	2-Naphthylamine	91-59-8	NA/UHC	X	X
20	4-Aminobiphenyl	92-67-1	NA/UHC	--	--
21	Methyl parathion	298-00-0	NA/UHC	--	--
22	Aramite	140-57-8	NA/UHC	--	--
23	Methoxychlor	72-43-5	NA/UHC	--	--
24	1,4-Dinitrobenzene	100-25-4	NA/UHC	--	--
25	p-Dimethylaminoazobenzene	60-11-7	NA/UHC	--	--

Line Number	Name	CAS Number	Waste code/UHC	Retained as Possibly Present LDR Organics Using the Six Decision Rules (RPP-RPT-63493)	Included in This Work
26	Parathion	56-38-2	NA/UHC	--	--
27	Endosulfan sulfate	1031-07-8	NA/UHC	--	--
28	Benzo(g,h,i)perylene	191-24-2	NA/UHC	X	--
29	bis(2-Chloroethoxy)methane	111-91-1	NA/UHC	X	--
30	2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	NA/UHC	X	--
31	1,2-Diphenylhydrazine	122-66-7	NA/UHC	--	--
32	p-Cresidine	120-71-8	NA/UHC	--	--
33	N-Nitrosopiperidine	100-75-4	NA/UHC	--	--
34	o-Anisidine (2-methoxyaniline)	90-04-0	NA/UHC	--	--
35	N-Nitrosodimethylamine	62-75-9	NA/UHC	X	X
36	4,6-Dinitro-o-cresol	534-52-1	NA/UHC	X	X
37	Cresols (m,p,o)	1319-77-3	F004/NA	X	X
38	N-Nitrosomethylethylamine	10595-95-6	NA/UHC	--	--
39	Disulfoton	298-04-4	NA/UHC	--	--
40	2,4-Dimethylaniline (2,4-xylidine)	95-68-1	NA/UHC	--	--
41	Diphenylamine	122-39-4	NA/UHC	X	--
42	gamma-BHC	58-89-9	NA/UHC	X	--
43	N-Nitrosodiethylamine	55-18-5	NA/UHC	X	X
44	Methyl methanesulfonate	66-27-3	NA/UHC	--	--
45	2,6-Dichlorophenol	87-65-0	NA/UHC	--	--
46	Endrin aldehyde	7421-93-4	NA/UHC	--	--
47	Phorate	298-02-2	NA/UHC	--	--
48	Methanol	67-56-1	NA/UHC	X	X
49	1,4-Dioxane	123-91-1	NA/UHC	X	--
50	beta-BHC	319-85-7	NA/UHC	X	X
51	delta-BHC	319-86-8	NA/UHC	X	--
52	3-Methylcholanthrene	56-49-5	NA/UHC	X	--

Line Number	Name	CAS Number	Waste code/UHC	Retained as Possibly Present LDR Organics Using the Six Decision Rules (RPP-RPT-63493)	Included in This Work
53	Toxaphene	8001-35-2	NA/UHC	--	--
54	p,p'-DDD	72-54-8	NA/UHC	--	--
55	o,p'-DDT	789-02-6	NA/UHC	--	--
56	n-Butyl alcohol	71-36-3	NA/UHC	X	X
57	alpha-BHC	319-84-6	NA/UHC	X	X
58	o,p'-DDD	53-19-0	NA/UHC	--	--
59	Pyridine	110-86-1	D038/UHC	X	X
60	Cyclohexanone	108-94-1	NA/UHC	X	--
61	Safrole	94-59-7	NA/UHC	--	--
62	Endrin	72-20-8	NA/UHC	--	--
63	Dieldrin	60-57-1	NA/UHC	--	--
64	Isobutyl alcohol	78-83-1	NA/UHC	X	X
65	Aldrin	309-00-2	NA/UHC	X	X
66	Acetonitrile	75-05-8	NA/UHC	X	X
67	o,p'-DDE	3424-82-6	NA/UHC	--	--
68	Heptachlor epoxide	1024-57-3	NA/UHC	X	X
69	tris-(2,3-Dibromopropyl) phosphate	126-72-7	NA/UHC	--	--
70	p,p'-DDT	50-29-3	NA/UHC	--	--
71	Ethyl cyanide/Propanenitrile	107-12-0	NA/UHC	X	X
72	p,p'-DDE	72-55-9	NA/UHC	--	--
73	Isodrin	465-73-6	NA/UHC	X	--
74	Chlordane (alpha and gamma isomers)	57-74-9	NA/UHC	--	--
75	Endosulfan I	959-98-8	NA/UHC	--	--
76	Endosulfan II	33213-65-9	NA/UHC	--	--
77	Acenaphthylene	208-96-8	NA/UHC	X	--
78	Acrolein	107-02-8	NA/UHC	X	X
79	1,2-Dibromo-3-chloropropane	96-12-8	NA/UHC	X	--

Line Number	Name	CAS Number	Waste code/UHC	Retained as Possibly Present LDR Organics Using the Six Decision Rules (RPP-RPT-63493)	Included in This Work
80	Ethylene oxide	75-21-8	NA/UHC	--	--
81	Ethyl acetate	141-78-6	NA/UHC	X	X
82	Methacrylonitrile	126-98-7	NA/UHC	X	--
83	Heptachlor	76-44-8	NA/UHC	X	X
84	Methyl methacrylate	80-62-6	NA/UHC	--	--
85	bis(2-Chloroisopropyl)ether	39638-32-9	NA/UHC	--	--
86	Benzal chloride	98-87-3	NA/UHC	--	--
87	Isosafrole	120-58-1	NA/UHC	--	--
88	Ethyl methacrylate	97-63-2	NA/UHC	--	--
89	Bromoform	75-25-2	NA/UHC	X	--
90	1,2-Dibromoethane/Ethylene dibromide	106-93-4	NA/UHC	X	--
91	Dibromomethane	74-95-3	NA/UHC	--	--
92	Ethyl Ether	60-29-7	NA/UHC	X	X
93	Pentachloroethane	76-01-7	NA/UHC	--	--
94	1,1,1,2-Tetrachloroethane	630-20-6	NA/UHC	X	--
95	trans-1,3-Dichloropropylene	10061-02-6	NA/UHC	X	X
96	Hexachloropropylene	1888-71-7	NA/UHC	--	--
97	Xylene(m,p,o)	1330-20-7	NA/UHC	X	X
98	Iodomethane	74-88-4	NA/UHC	--	--
99	2-Chloroethyl vinyl ether	110-75-8	NA/UHC	--	--
100	3-Chloropropylene	107-05-1	NA/UHC	X	--
101	2-Chloro-1,3-butadiene	126-99-8	NA/UHC	--	--
102	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	NA/UHC	X	--
103	1,1,1-Trichloroethane	71-55-6	F001/NA	X	X
104	1,1-Dichloroethylene	75-35-4	D029/UHC	X	X
105	1,2-Dichloroethane	107-06-2	D028/UHC	X	X
106	2,4,5-Trichlorophenol	95-95-4	D041/UHC	X	X

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107	2,4-Dinitrotoluene	121-14-2	D030/UHC	X	X
108	2-Butanone	78-93-3	F005/D035	X	X
109	4-Methyl-2-pentanone	108-10-1	F003/NA	X	X
110	Acetone	67-64-1	F003/NA	X	X
111	All Aroclors	1336-36-3	NA/UHC	X	X
112	Benzene	71-43-2	D018/UHC	X	X
113	Butyl benzyl phthalate	85-68-7	NA/UHC	X	X
114	Carbon tetrachloride	56-23-5	D019/UHC	X	X
115	Chloroform	67-66-3	D022/UHC	X	X
116	di-n-Butyl phthalate	84-74-2	NA/UHC	X	X
117	Hexachlorobutadiene	87-68-3	D033/UHC	X	X
118	Hexachloroethane	67-72-1	D034/UHC	X	X
119	Methylene chloride	75-09-2	F002/NA	X	X
120	Nitrobenzene	98-95-3	D036/UHC	X	X
121	Tetrachloroethylene	127-18-4	D039/UHC	X	X
122	Trichloroethylene	79-01-6	D040/UHC	X	X
123	Vinyl chloride	75-01-4	D043/UHC	X	X
124	1,1,2,2-Tetrachloroethane	79-34-5	NA/UHC	X	X
125	1,1,2-Trichloroethane	79-00-5	NA/UHC	X	X
126	1,1-Dichloroethane	75-34-3	NA/UHC	X	X
127	1,2,4-Trichlorobenzene	120-82-1	NA/UHC	X	X
128	1,2-Dichlorobenzene	95-50-1	NA/UHC	X	--
129	1,2-Dichloropropane	78-87-5	NA/UHC	X	--
130	1,3-Dichlorobenzene	541-73-1	NA/UHC	X	X
131	1,4-Dichlorobenzene	106-46-7	NA/UHC	X	X
132	2,4,6-Trichlorophenol	88-06-2	NA/UHC	X	X
133	2,4-Dichlorophenol	120-83-2	NA/UHC	X	--

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134	2,4-Dimethyl phenol	105-67-9	NA/UHC	X	--
135	2,4-Dinitrophenol	51-28-5	NA/UHC	X	X
136	2-Chloronaphthalene	91-58-7	NA/UHC	X	--
137	2-Chlorophenol	95-57-8	NA/UHC	X	--
138	2-Nitroaniline	88-74-4	NA/UHC	X	--
139	2-Nitrophenol	88-75-5	NA/UHC	X	X
140	4-Bromophenyl phenyl ether	101-55-3	NA/UHC	X	--
141	4-Chloroaniline	106-47-8	NA/UHC	X	--
142	4-Nitroaniline	100-01-6	NA/UHC	X	--
143	Acenaphthene	83-32-9	NA/UHC	X	X
144	Anthracene	120-12-7	NA/UHC	X	--
145	Benz(a)anthracene	56-55-3	NA/UHC	X	--
146	Benzo(a)pyrene	50-32-8	NA/UHC	X	--
147	Benzo(b)fluoranthene	205-99-2	NA/UHC	X	--
148	Benzo(k)fluoranthene	207-08-9	NA/UHC	X	--
149	bis(2-Chloroethyl)ether	111-44-4	NA/UHC	X	--
150	bis(2-ethylhexyl)phthalate	117-81-7	NA/UHC	X	X
151	Bromodichloromethane	75-27-4	NA/UHC	X	--
152	Bromomethane	74-83-9	NA/UHC	X	--
153	Carbon disulfide	75-15-0	NA/UHC	X	X
154	Chlorobenzene	108-90-7	NA/UHC	X	X
155	Chloroethane	75-00-3	NA/UHC	X	--
156	Chloromethane	74-87-3	NA/UHC	X	X
157	Chrysene	218-01-9	NA/UHC	X	--
158	cis-1,3-Dichloropropylene	10061-01-5	NA/UHC	X	X
159	Dibenzo(a,h)anthracene	53-70-3	NA/UHC	X	--
160	Dibromochloromethane	124-48-1	NA/UHC	X	--

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161	Dichlorodifluoromethane	75-71-8	NA/UHC	X	--
162	Diethyl phthalate	84-66-2	NA/UHC	X	X
163	Dimethyl phthalate	131-11-3	NA/UHC	X	--
164	Di-n-octyl phthalate	117-84-0	NA/UHC	X	X
165	Ethyl benzene	100-41-4	NA/UHC	X	X
166	Fluoranthene	206-44-0	NA/UHC	X	X
167	Fluorene	86-73-7	NA/UHC	X	X
168	Hexachlorobenzene	118-74-1	NA/UHC	X	--
169	Hexachlorocyclopentadiene	77-47-4	NA/UHC	X	--
170	Indeno(1,2,3-c,d) pyrene	193-39-5	NA/UHC	X	--
171	Naphthalene	91-20-3	NA/UHC	X	X
172	N-Nitroso-di-n-propylamine	621-64-7	NA/UHC	X	X
173	Pentachlorophenol	87-86-5	NA/UHC	X	X
174	Phenanthrene	85-01-8	NA/UHC	X	--
175	Phenol	108-95-2	NA/UHC	X	X
176	p-Nitrophenol	100-02-7	NA/UHC	X	X
177	Pyrene	129-00-0	NA/UHC	X	X
178	Toluene	108-88-3	NA/UHC	X	X
179	Trichlorofluoromethane	75-69-4	NA/UHC	X	X
180	Diphenylnitrosamine	86-30-6	NA/UHC	--	--
181	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	NA/UHC	--	--
182	1,2,3,4,6,7,8-Heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	NA/UHC	--	--
183	1,2,3,4,7,8,9-Heptachlorodibenzofuran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	NA/UHC	--	--
184	HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	NA/UHC	--	--
185	HxCDFs (All Hexachlorodibenzofurans)	NA	NA/UHC	--	--
186	N-Nitroso-di-n-butylamine	924-16-3	NA/UHC	--	--
187	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	NA/UHC	--	--

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188	1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)	39001-02-0	NA/UHC	--	--
189	Pentachlorobenzene	608-93-5	NA/UHC	--	--
190	PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	NA/UHC	--	--
191	PeCDFs (All Pentachlorodibenzofurans)	NA	NA/UHC	--	--
192	Pentachloronitrobenzene	82-68-8	NA/UHC	X	--
193	Pronamide	23950-58-5	NA/UHC	--	--
194	1,2,4,5-Tetrachlorobenzene	95-94-3	NA/UHC	X	--
195	TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	NA/UHC	--	--
196	TCDFs (All Tetrachlorodibenzofurans)	NA	NA/UHC	--	--
197	2,3,4,6-Tetrachlorophenol	58-90-2	NA/UHC	X	--
198	1,2,3-Trichloropropane	96-18-4	NA/UHC	--	--
199	Acetophenone	98-86-2	NA/UHC	X	X
200	Acrylonitrile	107-13-1	NA/UHC	X	--
201	Aniline	62-53-3	NA/UHC	--	--
202	p-Chloro-m-cresol	59-50-7	NA/UHC	X	--
203	o-Cresol	95-48-7	F004/NA	X	X
204	m-Cresol	108-39-4	F004/NA	X	--
205	p-Cresol	106-44-5	F004/NA	X	--
206	trans-1,2-Dichloroethylene	156-60-5	NA/UHC	X	--
207	2,6-Dinitrotoluene	606-20-2	NA/UHC	--	--

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