PNNL-16089

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An Alternative Treatment of Trace Chemical Constituents in Calculated Chemical Source Terms for Hanford Tank Farms Safety Analyses

J.L. Huckaby

September 2006

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Summary

Hanford Site high-level radioactive waste tank accident analyses require chemical waste toxicity source terms to assess potential accident consequences. Recent reviews of the current methodology used to generate source terms and the need to periodically update the sources terms has brought scrutiny to the manner in which trace waste constituents are included in the source terms.

This report examines the importance of trace constituents to the chemical waste source terms, which are calculated as sums of fractions (SOFs), and recommends three changes to the manner in which trace constituents are included in the calculation SOFs:

1. The SOF contribution of the organic constituents should be based solely on the BBI TOC inventory, thereby eliminating the redundant counting of the individual trace organic constituents (from sample analyses and default values) and the BBI TOC inventory. It is demonstrated in this study that SOFs calculated from the BBI TOC inventories, assumed to be in the form of oxalate, result in generally conservative (large) organic waste contributions to the SOFs.

2. Inorganic trace constituents that do not contribute significantly to the waste toxicity should be eliminated from the SOF calculations. The analysis presented identified 13 inorganic trace constituents (in addition to Ag) that, based on current toxicological parameters and 2002 characterization data, could individually contribute more than 1% of an SOF. These are As, Be, Cd, Co, Pd, Rh, Se, Sn, Te, Th, Tl, W and Zn.

3. In lieu of an established BBI-S inventory for a given trace constituent, its assigned concentration in each tank should be based on a total evaluation of the available data (e.g., sample analyses, process history, tank fill history), and not automatically assigned to be the highest reported concentration. This is expected to improve the accuracy of the assigned values, and reduce excessively large concentrations assumed by Cowley et al. for some constituents in some tanks

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Acronyms and Abbreviations

BBI	Best Basis Inventory
BBI-S	Best Basis Inventory – Supplemental
DST	Double-shell tank
EDTA	Ethylenediaminetetraacetate
HEDTA	Hydroxyethylethylenediaminetriacetate
IDA	Imimodiacetate
SOF	Sum of fractions
SST	Single-shell tank
TBP	Tributyl phosphate
TCD	Tank Characterization Database
TEEL	Temporary Emergency Exposure Limit
TOC	Total organic carbon

1.0 Introduction

Hanford Site high-level radioactive waste tank accident analyses require chemical waste toxicity source terms to assess potential accident consequences. The development and calculation of these source terms are given by Cowley et al. (2003). Recent reviews of that document and the need to update the sources terms has brought scrutiny to the manner in which trace waste constituents are included in the source terms. This report examines the importance of trace constituents to the chemical waste source terms, and makes specific recommendations for a modified approach.

2.0 Background

The high-level waste tank chemical and isotopic inventories are specified by the Best Basis Inventory (BBI). The BBI includes inventory estimates for 25 primary waste constituents in each of the 177 high-level radioactive waste tanks at the Hanford Site. These 25 primary constituents account for greater than 99% of the mass of waste stored in the tanks and similarly account for the majority of the wastes' chemical toxicity (Cowley et al. 2003). However, there are other waste constituents present at trace levels that can be important to the estimation of waste toxicity because they are significantly more toxic than the bulk waste.

The potential importance of trace constituents to toxicity estimates was recognized by Cowley et al. (2003). In that document the concentrations of trace constituents were based on solid and liquid waste sample characterization data and BBI Supplemental (BBI-S) data in the Tank Characterization Database (TCD). All trace constituents were included in the sum of fractions (SOFs) toxicity estimates, including those that had no significant impact on the SOFs. The lack of trace constituent concentration data for individual tanks (sample data do not exist for many trace constituents in many tanks) was addressed by assigning default concentrations based on the highest measured concentrations. This helped ensure the SOFs were conservatively high when sample data were unavailable for the trace constituents, but the methodology failed to include the non-sample based data. For example, the identities and concentrations of organic complexants in many tanks have not been determined by samples, but process knowledge and waste transfer histories indicate only a small number of tanks have significant organic complexant waste inventories (Sandgren 2003).

An additional issue with the treatment of trace constituents by Cowley et al. is that one of the BBI primary constituents, total organic carbon (TOC), is actually a summary measurement of many individual organic trace constituents. The BBI TOC inventories include the organic complexants and ions (e.g., citrate, cyanide, acetate, oxalate, dibutyl phosphate) and the covalent organic compounds of various origins (e.g., 1-butanol, normal paraffin hydrocarbons, tributyl phosphate, polychlorinated biphenyls). Cowley et al. assumed all the BBI TOC to be in the forms of oxalate and/or acetate ions, and all other organic waste species detected in waste samples were added to the SOF calculations independently. This effectively resulted in all reported organic species (other than acetate and oxalate) being included twice in the SOF calculations; once as oxalate or acetate, and once as the organic chemical named in the sample analysis. Furthermore, like other trace constituents, organic constituents were assumed to be present at their highest reported concentrations when BBI-S or actual sample results were unavailable (i.e., at their default concentrations). This led to the assignment of relatively high concentrations of organic complexants where process knowledge indicated otherwise, and to instances of tanks with default organic inventories larger than their BBI TOC inventories.

These issues were appreciated and documented by Cowley et al. (2003). The principle results of that document, the limiting toxic chemical source terms, were reviewed and determined to not be unduly affected. However, given that toxic chemical source terms for individual tanks (instead of the limiting source terms given by Cowley et al.) may be needed in certain accident analyses, more accurate tank-specific estimates have been sought for the trace constituent concentrations. In the interest of efficiency, there is also a need to limit the trace constituents included in the SOF calculations to those that actually contribute significantly to the SOFs.

3.0 Recommended Methodology Changes

To improve the accuracy of the trace constituent component of the SOFs and eliminate unnecessary effort when updating the SOFs, the following changes to the methodology employed by Cowley et al. (2003) are recommended.

1. The SOF contribution of the organic constituents should be based solely on the BBI TOC inventory, thereby eliminating the redundant counting of the individual trace organic constituents (from sample analyses and default values) and the BBI TOC inventory.

2. Inorganic trace constituents that do not contribute significantly to the waste toxicity should be eliminated from the SOF calculations.

3. In lieu of an established BBI-S inventory for a given trace constituent, its assigned concentration in each tank should be based on a total evaluation of the available data (e.g., sample analyses, process history, tank fill history), and not automatically assigned to be the highest reported concentration.

The first and second recommendations are considered and elaborated in Sections 3.1 and 3.2, respectively. One aspect of the third recommendation, namely that the highest reported concentration of a trace constituent should not automatically be used when the TCD lacks data for that constituent in a particular tank, is employed in Section 3.1 but not otherwise considered in this report.

3.1 Trace Organic Constituents

It is recommended here that the BBI TOC inventories be used with a suitably conservative set of toxicological parameters to represent all organic constituents in the SOFs. Specifically, it is recommended that the TOC be assumed to be in the form of oxalate[1] and that individual trace organic

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[1] To be consistent with the SOF calculation methodology otherwise, the oxalate would be sodium oxalate in the solid wastes, and a mixture of sodium and potassium oxalate, based on the abundance of these cations, in the liquid wastes.

constituents be eliminated from the solid and liquid waste SOF calculations. This recommendation is supported by the following analyses.

First, the individual trace organic waste constituents that contributed 1% or more to the liquid and solid waste SOFs were identified. This was done by running the SOF program (Cowley et al. 2003) using the May 13, 2002 BBI, BBI-S and characterization data with the latest (Revision 21A[2]) TEELs (DOE 2006). When a trace organic constituent had neither BBI-S nor TCD characterization data in a given tank, a "default" concentration equal to the highest reported concentration for that constituent in that tank class was assigned, so that the SOFs generated were equivalent to those in Cowley et al. except that they were based on the latest published TEEL values. The maximum fractional contribution of each organic trace constituent was then calculated for the TEEL-1, TEEL-2 and TEEL-3 SOFs. Eight trace organic constituents were found to contribute 1% or more of an SOF. These are listed in Table 1.

Table 1. Trace Organic Constituents Contributing > 1% of an SOF
Using Methodology and Data of Cowley et al. (2003)

Chemical	Waste Phase SOF
Imimodiacetate (IDA)	Liquid
Sodium citrate ($Na_3C_6H_5O_7$)	Liquid and Solid
Sodium hydroxyethylethylenediaminetriacetate (Na_3HEDTA)	Liquid and Solid
Sodium ethylenediaminetetraacetate (Na_4EDTA)	Liquid and Solid
Sodium formate ($NaCHO_2$)	Liquid
Sodium cyanide (NaCN)	Liquid and Solid
Tetradecane	Solid
Tributyl phosphate (TBP)	Liquid

Note that the first six chemicals are organic complexants. The distribution of complexants in tank farms was extensively studied in the 1990s to resolve waste storage safety issues, and samples have been collected from all tanks thought to contain significant concentrations of organic complexants (Meacham et al. 1996 and Sandgren 2003). The remaining two organic constituents listed in Table 1, tetradecane and tributyl phosphate, have also been targeted in waste samples for storage safety issues and their distribution among tanks has been studied (Cowley et al. 2000). On the bases that the relatively high default concentrations for the organic constituents were unwarranted, the SOFs used in the analyses below used the same methodology and composition data of Cowley et al., but with all trace constituent default concentrations removed.

To determine whether treating the TOC as oxalate results in a conservative representation of the toxicity of all organic constituents, the liquid and solid waste SOFs for each tank were calculated by two methods and compared. First, the SOFs were calculated by converting the BBI TOC inventories to oxalate and omitting all individual (TCD) organic constituents.[3] Second, new SOFs were calculated by including all

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[2] There is some ambiguity regarding the name of the current version of TEELs. They were obtained from a website that calls them "Revision 21" but the spreadsheet of TEELs is called "TEELs_Rev21A_publ.xls". In this report this set of TEELs are referred to as Rev. 21A.

[3] The conversion of all TOC to oxalate was done after Environmental Simulation Program® had been applied to distribute TOC between the liquid and solid waste phases. See Cowley et al. (2003) for a

individual organic constituents (including archived May 13, 2002 BBI-S values for oxalate and August 23, 2006 TCD values for acetate[4]) and omitting any contributions from the BBI TOC inventories. Individual SOFs for each phase and tank for these two methods were then paired and the percent relative difference for each pair was calculated as defined by

$$\%RD \quad = \quad 2\times\frac{SOF_{TOC/Oxalate} - SOF_{\Sigma(TCD\ organics)}}{SOF_{TOC/Oxalate} + SOF_{\Sigma(TCD\ organics)}}$$

Table 2 summarizes the results. As indicated by the table entries, the differences are generally very small, and tend to indicate (i.e., when the entries are > 0) that SOFs calculated by assuming the TOC is oxalate (and omitting all individual organic constituents) gives conservative SOFs.

Table 2. *%RD* for SOFs by Two Organic Constituent Methods

	Average %RD			**Minimum %RD**		
	DSTs	100-series SSTs	200-series SSTs	DSTs	100-series SSTs	200-series SSTs
Liquids TEEL-1	0.1%	0.1%	0.6%	-0.03%	-0.3%	0.003%
Liquids TEEL-2	0.4%	0.3%	2.3%	-0.01%	-0.1%	0.01%
Liquids TEEL-3	9.6%	7.8%	30%	-0.1%	0%	0.06%
Solids TEEL-1	0.6%	0.2%	-0.03%	-0.1%	-2.7%	-0.7%
Solids TEEL-2	2.0%	0.5%	0.2%	-0.2%	-0.6%	-0.05%
Solids TEEL-3	9.4%	4.3%	1.4%	-0.6%	-0.3%	-0.3%

The comparison is favorable in part because TEELs for the oxalate salts are relatively small (and lead to corresponding large, conservative, SOF contributions). Table 3 lists the TEEL-1, TEEL-2 and TEEL-3 values for the eight chemicals from Table 1 plus sodium oxalate and sodium acetate. In this table the units of the TEEL values have been adjusted to mg of carbon/m^3 to make them directly comparable. On this basis the toxicities of these organic constituents are shown to be similar, with the all values for a given TEEL level being less than a factor of 100 apart. Compared to the others listed, sodium oxalate has lower than average TEEL-1 and TEEL-2 values, and the lowest TEEL-3 value. It is thus a reasonably conservative choice.

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description of that process. Environmental Simulator Program is a registered trademark of OLI Systems, Inc., Morris Plains, New Jersey.

[4] TCD acetate concentrations were not downloaded or archived with other May 13, 2002 data by Cowley et al.

Table 3. Adjusted TEEL Values for Selected Organic Waste Constituents

Constituent	TEEL-1 (mg of C/m3)	TEEL-2 (mg of C/m3)	TEEL-3 (mg of C/m3)
Sodium cyanide (NaCN)	1.2	1.2	10
Tributyl phosphate	3.2	5.4	162
Tetradecane	0.85	6.4	8,476
Imimodiacetate (IDA)	1.1	7.2	36
Sodium oxalate ($Na_2C_2O_4$)	**5.4**	**9.0**	**9.0**
Sodium ethylenediaminetetraacetate (Na_4EDTA)	1.3	9.5	47
Sodium hydroxyethylethylenediaminetriacetate (Na_3HEDTA)	1.4	10	52
Sodium citrate ($Na_3C_6H_5O_7$)	8.4	14	140
Sodium acetate ($NaCH_3CO_2$)	12	88	146
Sodium formate ($NaCHO_2$)	22	88	88

3.2 Trace Inorganic Constituents

An analysis was conducted to determine which, if any, trace inorganic chemicals were important to the SOFs. Like the trace organic constituent analyses described in the preceding section, these analyses were based on the methodology and data of Cowley et al. (2003), but with the latest (Revision 21A) TEELs. As done by Cowley et al., when the concentration of a constituent was not known for a given tank, a default concentration equal to the highest reported concentration for that constituent in that tank class was assigned, so that the SOFs were equivalent to those developed by Cowley et al. except that they are based on Rev. 21A TEELs. The resulting SOFs were examined to identify all inorganic trace constituents that contributed 1% or more to a TEEL-1, TEEL-2 or TEEL-3 SOF. Table 4 lists the constituents meeting that criterion and indicates the waste phase of the SOF.

To verify that removing the trace constituents with less than a 1% contribution to any SOF has an acceptably small effect on the SOFs, the SOFs were recalculated with only the Table 4 trace constituents. This was accomplished by setting all default inorganic trace constituent concentrations to zero except for the constituents (by phase) listed in Table 4. Concentration data derived from the BBI-S, sample analyses or the calculated default values were included for the analytes and specific phases identified in Table 4, but not otherwise. Additionally, all individual trace organic constituents were omitted from the SOF calculations, to be consistent with the proposed removal of these discussed in the previous section. The SOFs with all inorganic trace constituents were compared directly to the corresponding SOFs with only the trace constituents in Table 4. Removal of the inorganic trace constituents not listed in Table 4 resulted in negligible decreases in the SOFs. Table 5 lists the impacts by TEEL level and tank class. As indicated by Table 5, all changes in the SOFs are less than 2%, and the average changes are less than 1% for all three TEEL levels and tank classifications.

Table 4. Inorganic Constituents that Contribute At Least 1% To a SOF[5]

Constituent	Solid	Liquid
Arsenic, As	Yes	Yes
Beryllium, Be	Yes	Yes
Cadmium, Cd	Yes	Yes
Cobalt, Co	Yes	Yes
Palladium, Pd	Yes	
Rhodium, Rh		Yes
Selenium, Se	Yes	Yes
Tin, Sn	Yes	
Tellurium, Te	Yes	
Thorium, Th	Yes	
Thallium, Tl	Yes	
Tungsten, W		Yes
Zinc, Zn		Yes

Table 5. Differences in SOFs Due to Removal of Inorganic Trace Constituents that Contribute < 1% To Any SOF

	Maximum SOF Change			**Average SOF Change**		
	DSTs	100-series SSTs	200-series SSTs	DSTs	100-series SSTs	200-series SSTs
Liquids TEEL-1	0.1%	0.9%	0.3%	0.03%	0.1%	0.1%
Liquids TEEL-2	0.4%	1.3%	0.7%	0.07%	0.2%	0.2%
Liquids TEEL-3	0.4%	1.9%	0.9%	0.1%	0.3%	0.3%
Solids TEEL-1	0.5%	1.5%	0.7%	0.1%	0.4%	0.2%
Solids TEEL-2	1.7%	1.8%	1.4%	0.5%	0.8%	0.3%
Solids TEEL-3	0.6%	1.4%	0.6%	0.1%	0.5%	0.1%

4.0 Discussion

Analysis of SOFs generated by the methodology of Cowley et al. (2003) using current TEEL values indicates that the largest percentage contributions from trace constituents tend to occur when the concentrations of the trace constituent are based on a default value. This was not a significant issue for Cowley et al. because the goal of their study was to develop limiting toxicological source terms, and these were not unduly affected by the trace constituents. Given the desire to have tank-specific toxicological source terms for all tanks, there is a recognized need to improve the accuracy and reduce excessively conservative treatment of trace constituents.

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[5] Silver, Ag, was not treated as a trace constituent in RPP-8369 Rev. 2 (i.e., was not assigned default concentrations when its concentration in a tank was not given) even though it was not actually a main BBI constituent. Silver compounds contribute greater than 1% of the RPP-8369 Rev. 2 SOFs (in both solids and liquids) and it is assumed here Ag will be treated as a trace constituent in future SOF calculations.

This study recommends three changes to the manner in which trace constituents are included in the calculation toxicological source terms:

4. The SOF contribution of the organic constituents should be based solely on the BBI TOC inventory, thereby eliminating the redundant counting of the individual trace organic constituents (from sample analyses and default values) and the BBI TOC inventory.

5. Inorganic trace constituents that do not contribute significantly to the waste toxicity should be eliminated from the SOF calculations.

6. In lieu of an established BBI-S inventory for a given trace constituent, its assigned concentration in each tank should be based on a total evaluation of the available data (e.g., sample analyses, process history, tank fill history), and not automatically assigned to be the highest reported concentration.

The first recommendation was considered in Section 3.1, where it was shown that SOFs calculated from the BBI TOC inventories, assumed to be in the form of oxalate, resulted in generally conservative (large) organic waste contributions. The second recommendation was examined in Section 3.2, where it was found that omitting all but 14 trace constituents (plus silver) resulted in negligible reductions (< 2%) of the SOFs. The third recommendation, though partially employed in the analyses of organic trace constituents, would be applied when updating trace constituent concentrations, which is outside the scope of this study.

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