Estimating Solubility for Modeling the Fate of Heavy Metals with the Training Range Environmental Evaluation and Characterization System (TREECS™)

by Mark S. Dortch

PURPOSE: The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed by the U.S. Army Engineer Research and Development Center (ERDC) for the Army with varying levels of capability to forecast the fate of munitions constituents (MC), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and groundwater. The overall purpose of TREECS is to provide environmental specialists with tools to assess the potential for MC migration into surface water and groundwater systems and to assess range management strategies to ensure protection of human health and the environment. Modeling the fate of heavy metals on ranges is especially challenging due to uncertainties in estimating metal dissolution from solid phase metal to the more mobile aqueous phase. Metal dissolution rate is affected by metal oxidation rate, metal oxidation products, and the solubility of the oxidation products. The purpose of this technical note is to provide guidance for estimating the solubility needed to compute heavy metal dissolution fluxes within TREECS.

BACKGROUND: With Tier 2 of TREECS™, each MC initially exists as a solid phase particle residue following loading to the soil area of interest (AOI), such as a range impact area or the backstop embankment of a small arms firing range. Heavy metal residue can be the result of high explosive ordnance and projectiles as well as small arms projectiles. Solid phase metal MC residues gradually corrode or oxidize, forming oxidation products that dissolve into water where they can potentially be transported from the surface soil to the vadose zone, groundwater, and surface water. TREECS contains models to represent fate/transport within each of these media as described by Dortch et al. (2009, 2011a). The dissolution rate is computed within the soil model and is dependent on the MC aqueous solubility (mg/L) and solid phase initial particle diameter (μm), both of which are input by the user. The model is a simplification of the real world, particularly as associated with the metal oxidation processes and resulting oxidation products. For example, the metal solubility actually refers to the solubility of the oxidation products, which vary with the specific metal and site soil chemistry.

Dissolution rates and subsequent MC fate can be quite sensitive to the two inputs (metal solubility and residue particle size), and solubility is difficult to determine and highly uncertain for metals and their oxidation products (Dortch et al. 2011b, Dortch 2012). There is some guidance for MC residue particle size for both HE (Pennington et al. 2005, Taylor et al. 2004) and metals (Larson et al. 2005). There are also solubility values for HE compounds within the TREECS constituent databases. There is also a utility within the soil model user interface to calculate solubility of TNT and RDX given the temperature of the soil-water matrix.

The distribution coefficients, K_d (L/kg), used to partition water-dissolved metals onto soils and sediments in surface waters are also highly variable and uncertain, while having a substantial effect on metal fate (Dortch et al. 2011b, Dortch 2012). Another modeling challenge is estimating the metal K_d, which in the real world is related to the particular species and compounds of the dissolved metal and the site soil chemistry. Again, the model is a simplification of the real world, and the applied metal K_d is assumed to be representative for the metal species/compounds present and the site soil chemistry. There is information on K_d values for heavy metals in soil (U.S. Environmental Protection Agency (USEPA) 1999), and there is also a utility within the TREECS models to empirically estimate soil K_d for metals given the pH and percent by weight of the combined organic matter, clay, and iron and aluminum oxy-hydroxides content in the soil. Additionally, there is information within the TREECS *Help* files on K_d values for surface water sediments based on the report by Allison and Allison (2005).

For the reasons outlined above, this technical note addresses only metal solubility. The solubilities of the metals lead, copper, zinc, antimony, and uranium 238 are addressed in this technical note since these are the metals that have been modeled thus far with TREECS. The solubility of each of these five metals is discussed below.

Lead: Estimating the solubility of lead received considerable attention in the study by Dortch et al. (2011b). In that study, lead and copper solubility were computed, due to the absence of measured values, using two models, an equilibrium chemistry spreadsheet from the Stevens Institute of Technology (SIT) (*http://personal.stevens.edu/~dvaccari/metals.html*) and the equilibrium chemistry software Visual MINTEQ ((*http://www.lwr.kth.se/English/OurSoftware/vminteq/*), or VM for short. The application of these two models to lead and copper is discussed in considerable detail in Appendix A of the report by Dortch et al. (2011b). The spreadsheet models for lead and copper are included as a utility under *Tools* in the TREECS user interface. VM is not included due to the complexity of applying this model compared with the spreadsheets. VM is a far more complete equilibrium modeling approach with less underlying assumptions, and VM takes into account soil background ionic chemical concentrations. Both models consider soil pH and alkalinity when computing solubility; however, VM allows soil pH and alkalinity to vary due to exposing the system to atmospheric CO_2 and computing pH from component mass balance. VM allows specification of solid phase metal concentrations or assuming an infinite supply of metal, but the chemical compound form of the metal must be specified. VM also allows for precipitation of metal compounds. These capabilities allow the pH to be affected by the amount of metal concentration, where the addition of lead can elevate the soil-water pH above background. This pH increase has been observed in small arms firing range berms and has been attributed to the oxidation and transformation of the elemental lead in the lead bullets followed by the carbonation of the lead oxide (Larson et al. 2007). The spreadsheet model requires inputting the soil-water pH, which should be measured in the AOI where the metal resides rather than using background pH.

The weathering crust around lead projectiles is the result of oxidation and carbonation and typically results in a mixture of lead hydroxide [$Pb(OH)_2$], hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], cerussite ($PbCO_3$), anglesite ($PbSO_4$), and massicot (PbO) (Clausen et al. 2007). These crusts can further react with soil-water and associated anions resulting in equilibrium reaction products. The sum of the dissolved Pb^{+2} components is the lead solubility.

Calculations with VM were performed (Dortch et al. 2011b) using the background component ionic concentrations shown in Table 1, treating the system as open to atmospheric CO_2, calculating pH from mass balance, and allowing precipitation. Without lead present, the background pH was computed to be 5.62, which is close to the observed background pH of 5.5 for the test case at Fort A.P. Hill.

Table 1. Ion concentrations (mg/L) for background soil-water conditions.					
Cl^-	SO_4^{-2}	Ca^{+2}	Mg^{+2}	K^+	Al^{+3}
36	19	20	4	2	0.01

Adding a fixed concentration of 60 µmol/L of lead hydroxide or an infinite amount of hydrocerussite provided the same results, including: pH = 6.59, ionic strength (I) = 0.0022, charge difference = 1.15 %, Pb^{+2} = 1.08 E-5 mol/L, or 2.24 mg/L, and the solid hydrocerussite precipitated.

The spreadsheet model requires pH, total dissolved solids (TDS), and alkalinity as $CaCO_3$ as input. The input pH was set to 6.59 as computed by VM. The input TDS was 88 mg/L based on I of 0.0022 as computed by VM. The alkalinity, which was calculated using the VM-computed molal concentrations of carbonate, bicarbonate, hydrogen ion, and hydroxide, was 2.34 E-5 mol/L, or 1.17 mg/L as $CaCO_3$. With these inputs, the spreadsheet model computed lead solubility of 3.03 mg/L, which is quite close to the value of 2.24 computed by VM. The problem with using the spreadsheet model is that the value of pH with the presence of lead was not known without applying VM. Additionally, the spreadsheet model does not account for metal precipitation.

Higher, but more conservative, estimates are obtained with the spreadsheet model if background values for inputs are used. For example, using the background value for pH = 5.5 and VM-computed value for I = 0.0022 or TDS = 88 mg/L, and associated alkalinity of zero (for pH values this low, alkalinity is expected to be negligible), the spreadsheet model calculates a lead solubility of 251 mg/L, which is two orders of magnitude greater than the estimates with VM or the spreadsheet model using conditions computed by VM. VM is considered to be more accurate than the spreadsheet model, since it includes more reactions, precipitation, free CO_2, and floating pH. However, to apply VM requires more information in terms of major ion concentrations and the compound form of the solid metal. Therefore, the spreadsheet model provides a quick, yet conservative, estimate.

Copper: After much testing with VM using various forms of solid copper as finite and infinite amounts and with the same ionic components as those listed in Table 1, it was determined that consistent results could be obtained using a finite amount of either copper hydroxide, $Cu(OH)_2$, or tenorite (CuO). The same results were obtained with either of these copper solids set within the range of 9 to 120 µmol/L; these results included pH = 6.42, I = 0.0022, charge difference = 1.15 %, and Cu^{+2} = 7.81 E-6 mol/L, or copper solubility of 0.5 mg/L. The amount of precipitated tenorite increased as solid copper was increased to values between 9 and 120 µmol/L.

The SIT spreadsheet for copper was applied using the pH, TDS, and alkalinity calculated from VM as inputs. The SIT spreadsheet model computed a copper solubility of 18.4 mg/L. It is recognized that the spreadsheet model will provide higher solubility estimates than can actually exist, although inflated estimates are more conservative for modeling metal fate. As an example, the spreadsheet model estimates copper solubility of 440 mg/L for the background soil pH of 5.53 compared to the estimate of

0.5 mg/L for copper solubility computed with VM. The two primary reasons for the inflated estimates with the spreadsheet model are that it does not consider metal precipitation, and the soil-water pH can be greater than the background pH with the presence of lead or copper. However, the spreadsheet model can be easily applied to provide a quick and conservative estimate of copper solubility in the absence of measured values.

Zinc: Zinc carbonate ($ZnCO_3$) and zinc hydroxide ($Zn(OH)_2$) are two important solid phases that can control zinc solubility (Zn^{+2}) in water. As with other metals, Zn solubility varies with pH, and it can also be highly dependent on alkalinity and water hardness. Literature data and modeling (Dyer et al. 1998) indicate that Zn solubility in pure water varies from high to low values and back up to high values as pH varies from 7 to 13. At a pH of 7, the solubility is in the range of 100 to 1000 mg/L. For a pH of 13, solubility is in the range of about 50 to 500 mg/L. Solubility is near the minimum of about 0.2 to 0.7 mg/L for a pH of 10. Most computed Zn solubility values discussed in the literature are for pure water, and thus are higher than for natural waters that have alkalinity and hardness, both of which tend to reduce Zn solubility.

Modeling of Zn was conducted with VM to gain a better understanding of Zn solubility for varying background conditions. All tests were for an ambient temperature of $15\,^{\circ}C$. The first modeling case consisted of using the same conditions as discussed for modeling Pb above using the same concentrations of ionic components (see Table 1) and infinite solid hydrocerussite. The only difference is that finite amounts of solid $ZnCO_3$ were added. For a fixed concentration of $ZnCO_3$ of 100 μmol/L, Zn saturation or solubility was obtained with a Zn^{+2} = 6.0 mg/L and 7 % of Zn precipitated. The computed values for pH, I, and charge difference were 7.41, 0.0025, and 1.03 %, respectively. Nearly the same result was obtained by removing the hydrocerussite. This same test was repeated with the hydrocerussite included, but instead of $ZnCO_3$ as the fixed solid, $Zn(OH)_2$ (amorphous) was fixed. In this case, the saturated Zn concentration or solubility was computed to be 7.1 mg/L, but the computed values for pH, I, and charge difference were 4.78, 0.0034, and 0.7 %, respectively. The same results were obtained for this case with the removal of hydocerusite except that the pH dropped to 4.19.

A VM test case was conducted where the pH was specified, and I was computed. The system was not exposed to atmospheric CO_2, alkalinity was not specified, and no other ionic components were included (thus pure water). Varying amounts of fixed solid $Zn(OH)_2$ (amorphous) were added until reaching saturation when the zincite precipitate formed. For a pH of 7, the computed Zn solubility was 300 mg/L, which is within the range noted above from Dyer et al. (1998). The computed I was 0.0091, and there was a large charge imbalance due to not having any other ionic components. This same test case was run again with pH = 8. The computed solubility was 2.5 mg/L, which agrees with literature values reported by Dyer et al. (1998) for pH = 8.

Varying amounts of the components Na^+ and Cl^- were added to bring the charge into near balance for the previous test case with pH = 7 and fixed $Zn(OH)_2$. A charge difference of 2 % was obtained for 250 mg/L of Cl^- and 1.0 mg/L of Na^+, resulting in I = 0.01. The computed Zn solubility for these conditions was 237 mg/L, which is still within the range reported by Dyer et al. (1998). This test of pH = 7 was repeated, but with $ZnCO_3$ as the fixed solid and $Zn(OH)_2$ removed. The ion component concentrations were adjusted to Na^+= 25 mg/L and Cl^- = 45 mg/L. The computed values were I = 0.0017, charge difference = 3.4 %, and Zn solubility = 15.5 mg/L. Thus, a much lower Zn solubility resulted when $ZnCO_3$ was used for the fixed solid, probably because of the carbonate. For pH = 8, with

$Zn(OH)_2$ as the fixed solid, and with ions adjusted to $Na^+ = 14$ mg/L and $Cl^- = 25$ mg/L, the computed values were $I = 0.0008$, charge difference $= 2.8\%$, and solubility $= 5.1$ mg/L, which is still within the range of literature data report by Dyer el al. (1998) at a pH of 8.

With pH $= 6$ and no other fixed species, $ZnCO_3$ as the fixed solid, and sodium and chloride as the only specified ionic components, the computed results were $I = 0.0039$, charge balance $= 0.6\%$, and Zn solubility $= 86$ mg/L. When $Zn(OH)_2$ was used as the fixed solid, unrealistic values of I resulted before Zn^{+2} saturation could be achieved.

Tests were run to evaluate the effects of allowing atmospheric CO_2 versus specifying alkalinity. For these tests, the pH was fixed to 7.0, and ionic strength was calculated. Varying amounts of the sodium and chloride ions were added to bring the charge balance within 5%. Fixed amounts of the solid $Zn(OH)_2$ were added to determine the Zn solubility. These tests indicated that about the same Zn solubility is computed regardless of whether the alkalinity is specified or the system is exposed to atmospheric CO_2. For example, allowing the system to be exposed to the gas resulted in a computed Zn solubility of 36 mg/L. The computed alkalinity based on summing the components contributing to alkalinity was 3.45 mg/L as $CaCO_3$. By not exposing the system to CO_2 gas and specifying an alkalinity of 3.45 mg/L, the computed Zn solubility was 37 mg/L. In both cases, the computed I was 0.0017. The remaining tests were conducted by not exposing to atmospheric CO_2 but specifying the alkalinity.

Tests were run to evaluate the effects of alkalinity on Zn solubility. The first test consisted of setting fixed pH $= 7$, alkalinity fixed to 100 mg/L as $CaCO_3$, no exposure to atmospheric CO_2, and fixing varying amounts of $ZnCO_3$. Ionic components Na^+ and Cl^- were adjusted to 45 and 3 mg/L, respectively, to force a charge difference of less than 5%. For these conditions, Zn saturation or solubility of 1.6 mg/L was obtained with computed $I = 0.0021$ and charge difference $= 3.0\%$. This compares to a Zn solubility of about 13 mg/L computed by O'Conner et al. (1964) for the same pH and alkalinity. These same conditions were run again with fixed $Zn(OH)_2$ instead of $ZnCO_3$. The computed results were $I = 0.0021$, charge difference $= 2.4\%$, and Zn solubility $= 1.6$ mg/L. Thus, the same solubility was computed regardless of which solid form of Zn was used. With an alkalinity of 10 mg/L and fixed $ZnCO_3$, the computed results were $I = 0.0011$, charge difference $= 5.1\%$, and Zn solubility $= 6.9$ mg/L. The concentrations of sodium and chloride were adjusted to 20 mg/L each to bring the charge balance down to near 5%. This result illustrates how decreasing alkalinity increases Zn solubility.

Tests similar to the ones above were run, in which the pH was set, varying amounts of alkalinity were specified, I was computed, the solid phase Zn was fixed for either zinc hydroxide or zinc carbonate, and the Zn solubility was determined. Varying amounts of Na^+ and Cl^- were added to balance charges within 5%. Results of these tests are summarized in Table 2. As pH increases from 6 to 8, and as alkalinity increases for any given pH, Zn solubility decreases. There is also dependency on the type of solid Zn. Zinc hydroxide results in greater solubility than zinc carbonate in most cases.

In the absence of measured values, Zn solubility in natural waters with some level of alkalinity and hardness and with neutral pH is expected to be in the range of about 1 to 100 mg/L depending on the amount of alkalinity and hardness. For a pH of 8, the solubility should be considerably less and within the range of about 0.1 to 10 mg/L. For a pH of 6, the solubility is expected to increase about ten-fold above the solubility at pH $= 7$ to a range of about 10 to several hundred mg/L.

Table 2. VN results for fixed pH, alkalinity, and solid Zn.			
pH	Alkalinity input, mg/L	Type of solid Zn input	Computed Zn solubility, mg/L
6	none	Zn(OH)2	No solution
6	10	Zn(OH)2	195
6	100	Zn(OH)2	16.4
6	none	ZnCO3	86
6	10	ZnCO3	28.1
6	100	ZnCO3	13.4
7	none	Zn(OH)2	237
7	3.45	Zn(OH)2	37.5
7	10	Zn(OH)2	13.7
7	100	Zn(OH)2	1.6
7	none	ZnCO3	15.5
7	10	ZnCO3	6.9
7	100	ZnCO3	1.6
8	none	Zn(OH)2	5.1
8	10	Zn(OH)2	0.64
8	100	Zn(OH)2	0.23
8	none	ZnCO3	1.48
8	10	ZnCO3	0.64
8	100	ZnCO3	0.23

Antimony: Antimony (Sb) is often an alloy in lead bullets. Antinomy forms compounds in the +III, +V, and –III oxidation states, with the +III and +V being the most stable and prevalent at environmentally relevant conditions. Antimony reacts with oxygen under controlled conditions to give the oxides Sb_2O_3, Sb_2O_4 and Sb_2O_5. Sb(III) is remarkably inert with respect to oxidation under oxic conditions and is found in substantial portions in many natural, oxic systems (Biver 2011). Thus, Sb_2O_3 is considered to be the primary solid-phase form of Sb expected on firing ranges. The solubility of Sb_2O_3 is reported by the World Health Organization (WHO) (2003) to be about 0.017 mg/L, but the soil characteristics and chemistry were not reported.

In aqueous solution, both Sb(III) and Sb(V) are extensively hydrolyzed, but between pH 2 and 11, the electrically neutral $Sb(OH)^3$, or Sb(III) prevails (Biver 2011). VM was applied for Sb as follows. The pH was fixed at 7.0 with I computed. The only ionic components added were 6 mg/L of Na^+ and 10 mg/L of Cl^-. The solid Sb_2O_3 was added in fixed amounts to determine the saturated concentration of the product $Sb(OH)^3$, which was determined to be 0.27 mg/L with I = 0.0003 and charge difference = 3.9%. The same results were obtained with pH values of 6 and 8.

These results support the rather low solubility of Sb cited above from WHO (2003). Thus, the value for Sb solubility is expected to be within the range of about 0.02 to 0.2 mg/L. It is emphasized that this expected solubility is for Sb(III). If oxidation to Sb(V) occurs, Sb can become more soluble.

Uranium: Uranium is a naturally occurring, ubiquitous, heavy metal found in various chemical forms in all soils, rocks, seas, and oceans. Natural uranium consists of a mixture of three radioactive isotopes, which are identified by the mass numbers [238]U (99.27% by mass), [235]U (0.72%), and [234]U (0.0054%). Uranium is used primarily in nuclear power plants; most reactors require uranium in which the [235]U

content is enriched from 0.72% to about 3%. The uranium remaining after removal of the enriched fraction is referred to as depleted uranium. Depleted uranium (DU) typically contains about 99.8% ^{238}U, 0.2% ^{235}U, and 0.0006% ^{234}U by mass. For the same mass, DU has about 60% of the radioactivity of uranium (WHO 2001). DU has the same Chemical Abstract Service Registry Number (CASRN) (7440611) as uranium and ^{238}U, and chemically behaves the same.

Uranium oxidizes as it weathers, producing uranyl oxides and salts, evident as black and yellow coatings on the solid surface. The black substance has been identified as uraninite, UO_2, while a possible further oxidation product was tentatively identified as U_3O_8 (Mellini and Riccobono 2005). The amorphous yellow coating is an oxidized corrosion product (possibly from uraninite) composed of uranyl ions, and hydroxyl compounds and/or water, producing a compound that is possibly schoepite, $UO_3 \cdot 2H_2O$, which has relatively high solubility in water (Mellini and Riccobono 2005).

Uranium occurs in the environment predominantly as U(IV) in reducing systems and U(VI) in oxic systems. In reducing waters, U(IV) forms insoluble phases and thus is relatively immobile. In oxic waters, U(VI) forms many soluble hydroxide and carbonate complexes, which lead to increased solubility and mobility (Curtis and Davis 2006).

Jang et al. (2006) measured the solubility of schoepite at pH values of 5.9, 6.9, and 7.8 and with exposure to $10^{-3.5}$ atmosphere of CO_2. The results compared most accurately with computed solubility by using the hydrolysis constants from Langmuir (1978) with schoepite as the solubility limiting phase and with a log solubility product constant of 5.39. The solubility of DU is best described by the solubility plot of U(VI) versus pH shown in Figure 1. U(VI) solubility in mol/L can be converted to mg/L by multiplying the inverse log ($10^{ordinate\ value}$) by 238,000 mg/mol. Thus, for pH = 7, the solubility is about 0.12 mg/L. Note that solubility increases substantially as pH drops below 7. For example, for pH = 6, DU solubility is expected to be about 3.8 mg/L.
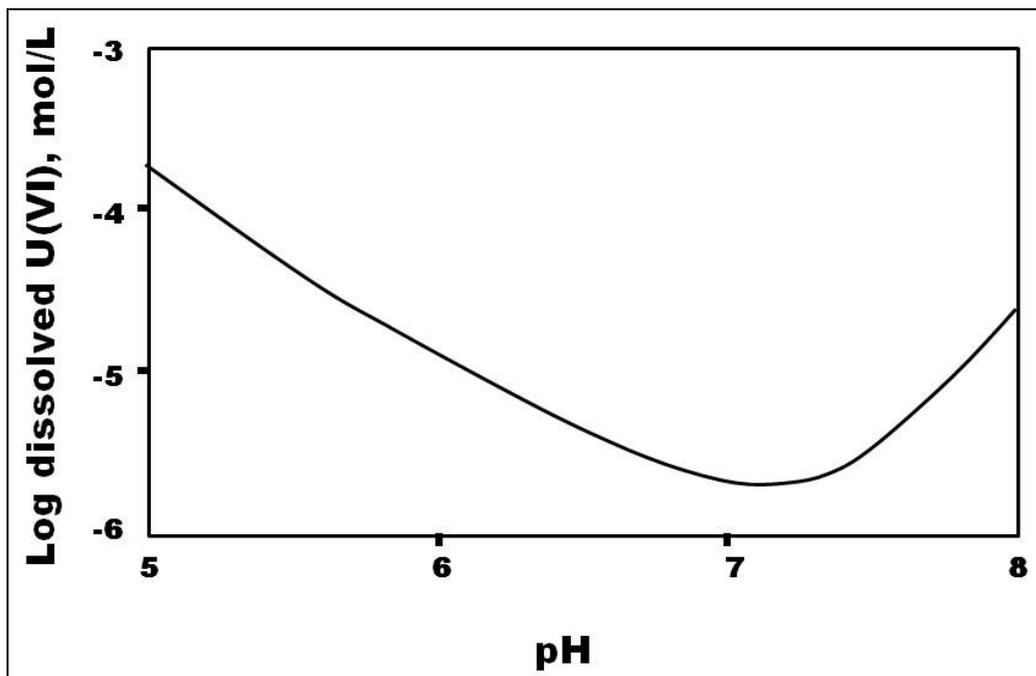
Figure 1.   U(VI) solubility versus pH (modified from Jang et al. (2006)).

CONCLUSIONS AND RECOMMENDATIONS: The dissolution of solid phase MC is an important process simulated within TREECS™ to predict fate/transport of MC from firing ranges to receiving waters. Dissolution with the model is dependent on the input solubility of the MC. Solubility of metal MC can be highly variable and difficult to estimate since it is affected by the local geochemistry and metal oxidation products. Review of literature and modeling with VM have been used to gain insights into the solubility of lead, copper, zinc, antimony, and DU. This technical note provides an overview of these insights resulting in values that can be considered during modeling with TREECS™.

Given the complexity and variability in metal solubility, it is recommended that the sensitivity/uncertainty (S/U) analysis feature within TREECS™ be used to place confidence limits on model results as impacted by solubility. The TREECS™ S/U feature uses Monte Carlo simulation with Latin Hypercube sampling to generate probabilistic output. This feature requires the user to input the statistical properties of the uncertain input variable, including the expected upper and lower bounds. It is intended that the results of this technical note will help in setting these bounds for metal solubility.

POINTS OF CONTACT: For additional information, contact Mark Dortch (601) 634-3517, _Mark.S.Dortch@usace.army.mil_. This technical note should be cited as follows:

> Dortch, M. S. 2012. Estimating solubility for modeling the fate of heavy metals with the Training Range Environmental Evaluation and Characterization System (TREECS™). EQT Technical Notes Collection. ERDC TN-EQT-12-1. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

REFERENCES

Allison, J. D., and T. L. Allison. 2005. _Partition coefficients for metals in surface water, soil, and wastes_. EPA/600/R-05/074. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development.

Biver, M. 2011. Some kinetic aspects of the mobilization of antimony from natural sources. Ph.D. diss., Ruprecht – Karls University, Heidelberg, Germany.

Clausen, J. L., N. Korte, B. Bostick, B. Rice, M. Walsh, and A. Nelson. 2007. _Environmental assessment of lead at Camp Edwards, Massachusetts, small arms ranges_. ERDC/CRREL TR-07-11. Hanover, NH: U.S. Army Engineer Research and Development Center.

Curtis, G. P., and J. A. Davis. 2006. _Tests of uranium (VI) adsorption models in a field setting_. Report NUREG/CR-6911. Prepared for Division of Fuel, Engineering, and Radiological Research, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, Washington, DC. Menlo Park, CA: U.S. Geological Survey.

Dortch, M. S., J. A. Gerald, and B. E. Johnson. 2009. _Methods for Tier 1 modeling with the Training Range Environmental Evaluation and Characterization System_. Technical Report ERDC/EL TR-09-11. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dortch, M. S., B. E. Johnson, Z. Zhang, and J. A. Gerald. 2011a. _Methods for Tier 2 modeling within the Training Range Environmental Evaluation and Characterization System_. Technical Report ERDC/EL TR-11-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dortch, M. S., B. E. Johnson, J. A. Gerald, Z. Zhang, and A. P. Simmons. 2011b. _Proof-of-concept application of Tier 2 modeling approach within the Training Range Environmental Evaluation and Characterization System_. Technical Report ERDC/EL TR-11-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dortch, M. S. 2012. Validation applications of the Training Range Environmental Evaluation and Characterization System (TREECS™). Technical Report ERDC/EL TR-12-3. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dyer, J. A., N. C. Scrivner, and S. K. Dentel. 1998. A practical guide for determining the solubility of metal hydroxides and oxides in water. *Environmental Progress* 17(1):1-8.

Jang, J. H., B. A. Dempsey, and W. D. Burgos. 2006. Solubility of Schoepite: Comparison and selection of complexation constants for U(VI). *Water Research* 40(24):2738-2746.

Langmuir, D. 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42: 547–569.

Larson, S., B. Tardy, K. Rainwater, and J. Tingle. 2005. *Rainfall lysimeter evaluation of leachability and surface transport of heavy metals from six soils with and without phosphate amendment*. Technical Report ERDC TR-05-9. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Larson, S. L., C. L. Teeter, V. F. Medina, and W. A. Martin. 2007. *Treatment and management of closed or inactive small arms firing ranges*. Technical Report ERDC/EL TR-07-06. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Mellini, M., and F. Riccobono. 2005. Chemical and mineralogical transformations caused by weathering in anti-tank DU penetrators ("the silver bullets") discharged during the Kosovo war. *Chemosphere* 60:1246-1252.

O'Conner, J. T., C. E. Renn, and I. Wintner. 1964. Zinc concentrations in rivers of the Chesapeake Bay region. *J. Am. Water Works Assoc*. 56(3):280-286.

Pennington, J. C. T. F. Jenkins, S. Thiboutot, G. Ampleman, J. Clausen, A. D. Hewitt, J. Lewis, M. R. Walsh, M. E. Walsh, T. A. Ranney, B. Silverblatt, A. Marois, A. Gagnon, P. Brousseau, J. E. Zufelt, K. Poe, M. Bouchard, R. Martel, D. D. Walker, C. A. Ramsey, C. A. Hayes, S. L. Yost, K. L. Bjella, L. Trepanier, T. E. Berry, D. J. Lambert, P. Dubé, and N. M. Perron. 2005. *Distribution and fate of energetics on DoD test and training ranges: Interim Report 5*. Technical Report ERDC TR-05-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Taylor, S., J. Lever, M. Walsh, M. E. Walsh, B. Bostick, and B. Packer. 2004. *Underground UXO: Are they a significant source of explosives in soil compared to low- and high-order detonations?* Technical Report ERDC/CRREL TR-04-23. Hanover, NH: U.S. Army Engineer Research and Development Center.

U.S. Environmental Protection Agency (USEPA). 1999. *Understanding variation in partition coefficients, K_d, values, Volume II: Review of geochemistry and available K_d values for cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium*. Report EPA402-R-99-004B. Washington, DC: Office of Radiation and Indoor Air.

World Health Organization (WHO). 2001. *Depleted uranium, sources, exposure, and health effects*. Report WHO/SDE/PHE/01.1. Geneva, Switzerland.

World Health Organization (WHO). 2003. *Antimony in drinking water, background document for developing who guidelines for drinking water quality*. Report WHO/SDE/WSH/03.04/74. Geneva, Switzerland.