

Updated Statement of Work for Joint Base Cape Cod Science Advisory Committee Support

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The following statement of work (SOW) is a proposal for a series of studies to improve the fate-and-transport (F&T) understanding of copper (Cu) at Joint Base Cape Cod (JBCC) small arms ranges (SAR). The SOW involves four tasks: 1) Literature search on Cu F&T, 2) Soil profiling and lysimeter sampling, 3) Batch Experiments, 4) Column Studies, and 5) SAR Science Advisory Committee (SAC) support for attendance at two virtual meetings for FY22. A technical report summarizing each of the four tasks will be provided at the end of the project.

Background

SAR activities at DOD sites lead to heavy-metal contamination of the soil through the deposition of ammunition residues (Laporte-Saumere et al. 2011). Small arms bullets are composed of copper-zinc jackets that corrode over time and release Cu into the soil (Laporte-Saumere et al. 2011, Laporte-Saumure, Martel, and Mercier 2010). Cu is a highly reactive, non-biodegradable contaminant that can be toxic to living organisms at high concentrations (Sharma et al. 2009). Cu introduced to the soil through anthropogenic activities has a greater affinity for the aqueous phase, known as Cu in its 2^+ oxidative state (Rader et al. 2019; Cornu et al. 2017). Cu^{2+} can transform into different phases of matter when bound to ligands within the soil and porewater (Rader et al. 2019). Changes in Cu speciation through geochemical processes dictate the bioavailability and transport of the contaminant through the system (Rader et al. 2019; Sodr  and Grassi 2007).

Cu partitioning between the aqueous and solid phases can occur via adsorption of Cu^{2+} by soils (Perez-Novo et al. 2008). One mechanism of interest to this study is adsorption by cation exchange, a process driven by soil pH (de Bor et al. 2012; Tangtong 2014). pH directly impacts cation exchange capacity (CEC) by governing the abundance of negatively charged surface sites, i.e., sorption sites (Tangtong 2014; de Bor et al. 2012). Ca^{2+} ions simultaneously increase the abundance of negatively charged surfaces by replacing other cations adsorbed by soil and forming bridged bonds to other anionic species (Tangtong 2014). There is an increase in sorption sites and complex stability at high pH, thus increasing metal adsorption by soils (Tangtong 2014; Xu et al. 2005). Another mechanism of adsorption is covalent bonding to negatively charged functional groups present on organic and inorganic matter (Rader et al. 2019). Each metal has a different affinity for varying particles which creates a competitive environment for Cu^{2+} covalent bonding in the presence of other metal cations (Bansal 2009; Perez-Novo et al. 2008). Cu is known to have a greater affinity than other metal ions, such as zinc, for organic substances (Perez-Novo et al. 2008). Fang, Genxing, and Lianqing 2008 found through sorption/desorption experiments that Cu^{2+} sorption capacity decreased after removing soil organic matter. As a result, organic matter content is another crucial factor in the assessment of Cu F&T (Sodr  and Grassi 2007; Tangtong 2014).

Aqueous Cu^{2+} can be transported to off-site locations and/or the groundwater table during rain events via percolation through the soil column under favorable pH and redox conditions (Xu et al. 2005). The relative abundance and depth of Cu migration in the soil column depend on the amount of adsorbed Cu within the column (Sharma et al. 2009; Xu et al. 2005). Sharma et al. 2009 and Xu et al. 2005 performed column experiments to assess copper transport and found an inverse relationship between Cu outflow and depth as adsorption affects the level of Cu exposure at greater depths. The relationship between Cu transformation and environmental factors as a function of soil depth must be understood to effectively explain current Cu transport at JBCC SARs (Rader et al. 2019; Xu et al. 2005). These findings can be integrated with the assessment of Cu distribution and abundance at JBCC to predict Cu F&T.

Task 1 – Literature Search on Copper (Cu) Fate-and-Transport

A detailed literature search on the fate-and-transport behavior of Cu will be conducted. Also, we will look through prior data collected from SARs at JBCC such as soil profiles and shallow pore-water lysimeters and see if there is any indication of Cu movement. We will also glean any site-specific information on soil metal, cation, anion, inorganic and organic carbon, and pH levels as well as soil pore water concentrations of metals, cations, anions, inorganic and organic carbon, and total dissolved solids (TDS). Calcium (Ca), anions, metalloids, inorganic and organic carbon, and pH are the key variables have bearing on Cu fate-and-transport behavior. Previous studies at JBCC have not indicated groundwater impacts from SAR activities related to lead or antimony transport (Clausen et al. 2017).

The information gathered from Task 1 will be summarized in a joint call with MAARNG, USEPA, and State regulators. Following the completion of Task 2 a short letter report will be prepared that will summarize the Task 1 findings specific to the conditions at JBCC.

Task 2 – Soil Profiling and Lysimeter Sampling

Soil Sampling

This task will involve soil profile and lysimeter sampling at several SAR locations at Camp Edwards. Copper munitions have been used on India and Sierra Ranges for close to 10-years and for approximately two months on Tango Range.

Three soil borings are each planned at India and Sierra Ranges and will be completed to 4 feet, or refusal using a hand auger. The soil will be sampled on 4-inch intervals in the field using a hand-held X-ray fluorescence (XRF) unit using an analysis time of 120 seconds per location at 3 locations per sample to principally measure Cu and Ca as well as the standard list of XRF measurable metals. We have previously used a 120 second counting interval for successful XRF analysis of JBCC soils for Cu. If the in-field XRF soil measurements for Cu are below the detection limit of the instrument we will collect sample material in a 4oz glass jar for transport and later analysis back at the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH. Sample preparation will involve drying the soil for 24-hrs followed by digestion using USEPA Method 3050. Metal analysis for Cu and the standard metal analytes (Ag, Al, As, Ba, Be, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, and Zn) will be performed using Inductively Coupled Plasma - Optical Emission Spectrography (ICP-OES) following U.S.

Environmental Protection Agency Method 6010. A pH meter, YSI meter, Model 556 MPS, will be used to measure soil pH using a soil: water ratio of 1:2. The pH of soil at the T Range was measured to be 5.37 in 2010, prior to the lime amendment (Clausen et al. 2017). Following lime addition, the soil pH increased from 7.6 to 8.7.

A subset of a dozen soil samples will be additionally analyzed for cations, anions, CEC, inorganic and organic carbon. Six samples will be obtained from near the soil surface and six at depth. Organic carbon will be measured by USEPA Method 9060, and CEC measured by USEPA Method 908.1.

In addition, we will use the XRF Cu results to identify an area where a larger volume of Cu contaminated soil can be collected for Tasks 3 and 4. Our goal is to collect material with the highest observed Cu concentrations for our batch and column experiments. We will also collect a larger volume of uncontaminated soil, outside of the SAR north of Gibbs Road, determined to be judgmentally similar in grain size, texture, and mineralogy as the contaminated soil. The uncontaminated soil will be utilized for the Tasks 3 and 4 batch and column experiments.

Lysimeter Sampling

At the present time we are aware that there are three functioning shallow lysimeters present on India Range, two on Sierra Range, and two on Tango Range. These are pan lysimeters installed in 2010 to monitor heavy metals and metalloids in soil porewater and have been monitored periodically for evidence of metalloid mobilization. The Best Management Practices and Operation, Maintenance and Monitoring Plan (OMMP) developed for JBCC indicates the following Cu action levels; soil = 10,000 mg/kg, porewater = 1,300 ug/L, and groundwater = 650 ug/L.

We will sample any existing functioning lysimeters on India, Sierra, and Tango Ranges and collect the water for later analysis at CRREL. We will attempt to collect up to 500 ml of liquid using pre-acidified sample containers. The samples will be kept at 4°C upon transport back to the EREDC-CRREL laboratory. Half of the liquid sample will be filtered with a 0.45 micron Millex FH filter prior to digestion for metals analysis. The other half of the unfiltered sample will be used for pH, TDS and inorganic/organic carbon analysis. The analyte list will include Cu and metalloids using ICP-OES, pH, cations, anions, TDS, and inorganic/organic carbon. Previous porewater measurements in 2011 indicated a pH level of 7.0.

The information gathered from Task 2 will be summarized in a joint call with MAARNG, USEPA, and State regulators. Also, following the completion of Task 2 a short letter report will be prepared that will summarize the Task 1 and 2 findings.

Task 3 – Batch Experiments

Sorption Tests

This task involves a series of batch adsorption/desorption experiments to better understand the behavior of Cu. The purpose of the sorption/desorption experiments is to derive the equilibrium

distribution coefficient (K_d) for Cu, which will provide an indication of Cu mobility. K_d determines the maximum quantity of contaminant adsorbed to (or desorbed from) a specified mass of contaminated soil and volume of liquid and is defined as follows:

$$Kd = \frac{S}{C_e} = \frac{C_0 - C_e}{C_e} * V/m$$

where:

K_d = soil-to-water partition coefficient for a given substance (L/kg)

S = mass of sorbed contaminant per mass of soil (mg/kg)

C_e = equilibrium liquid phase concentration (mg/L)

C_0 = initial liquid phase concentration (mg/L)

V = volume of the liquid phase (L)

m = mass of soil (kg)

The batch sorption experiments will consist of the following 1) a control with no Cu added, 2) clean sand spiked with Cu chloride at three different concentrations (1, 100, and 100 ppm), 3) a clean sand spiked with eluent from zero-valent Cu immersed in DI water for 24-hours, and 4) clean sand spiked with eluent from JBCC Cu-contaminated soil immersed in DI water for 24-hour for a total of 6 batch tests. Cu chloride was found in literature to be commonly utilized in Cu sorption/desorption batch experiments (Fang, Genxing, and Lianqing 2009; Komy, Shaker, Heggy, and EL-Sayed 2014; Wu, Laird, and Thompson 1999). Two of the batch tests 1) clean sand spiked with Cu chloride and 2) clean sand spiked with eluent from JBCC Cu-contaminated soil immersed in DI water for 24-hour will be repeated with a biocide added, consisting of mercuric chloride (0.02%) and glutaraldehyde (1%). This biocide mixture has been successfully used in prior sorption/desorption batch and column experiments (Clausen et al. 2010). The biocide greatly reduces the biological activity within the soil. So, there will be a total of 10 tests. Each experiment will be conducted in duplicate for a total of 20 tests. One set of ten samples will be sacrificed for subsequent soil analysis at the end of the experiment and the other set of ten will be utilized for the following desorption tests.

The sorption experiments will follow the guidelines of ASTM with a 24-hr equilibration time. We propose to run “batch-type” sorption equilibration tests using a soil: solution ratio of 1:20. The adsorption reactions tests will utilize a 100 mL solution containing ~200 ppm Cu equilibrated with 5 g of “uncontaminated” soil from JBCC. The bottles will be shaken using a tumbler at approximately 60 rpm at room temperature. DI water will be used as the aqueous medium unless rainwater from JBCC is available and the test will be conducted using standard labware and an ICP-OES for analysis. For each soil sample the Cu solution will be added at the start of the equilibration interval. After 24-hrs the sample jars will have the liquid decanted (centrifuged) followed by filtration through a 0.45- μ m Millex FH filter and transferred to a 7-mL amber glass vial. An aliquot of liquid will then be sampled for analysis using ICP-OES following USEPA Method 6010 for Cu and a standard suite of metals. If Cu levels are below the reporting limit for ICP-OES analysis the samples will be shipped to the ERDC-Environmental Laboratory in Vicksburg, MS for ICP-MS analysis. The ICP-MS has an order of magnitude lower detection limit than the ICP-OES. We will also measure the Cu adsorbed to the soil using an XRF and if

levels are below the reporting limit, we will re-analyze the samples using ICP-MS. The sorption test results will provide a baseline K_d .

Desorption Test

The desorption experiments will utilize the same materials used for the sorption test. The soil samples will be measured for their Cu concentration prior to the desorption experiment. A solution of DI water and/or simulated JBCC rainwater will be allowed to equilibrate with 5 g of “Cu contaminated” soil from JBCC as well as the material from the adsorption tests for 24 hrs. The bottles will be shaken using a tumbler at approximately 60 rpm at room temperature. We will use a soil: solution ratio of 1:20. At the end of the experiment the liquid will be decanted (centrifuged), filtered through a 0.45- μm Millex FH filter, and analyzed for Cu as will the remaining soil. The information from this test will be provide the susceptibility for Cu desorption from JBCC soil following sorption.

The information gathered from Task 3 will be summarized in a joint call with MAARNG, USEPA, and State regulators. Following the completion of Task 3 a short letter report will also be prepared that will summarize the Task 3 findings.

Task 4 – Column Experiments

Laboratory-based column studies will be conducted to investigate the potential for Cu mobilization under Camp Edwards geochemical conditions. The objective is designed to investigate the extent to which Cu can be transported in soil and surface water runoff under a variety of conditions.

Acrylic columns (four total) will be packed individually with 5 g native soil (pristine) and Cu contaminated native soil to monitor the mobility Cu and establish any potential for off-site migration. Uncontaminated JBCC derived sand will be used to pack the columns. Soil will be characterized for Cu concentrations prior to packing columns. One column, Column A, will consist of a control filled with clean JBCC sand, i.e., no anthropogenic Cu present. Columns B, C, and D will consist of clean sand obtained from JBCC. Column B will have a thin layer of Cu-contaminated soil obtained from JBCC applied to the top. A third column, Column C, will consist of zero-valent copper added to the top of the column. The purpose of this augmentation is to test a Cu form like what is being introduced into the environment at JBCC. A fourth column, Column D, will consist of layer of Cu chloride added to the top of the column. Column D is intended to ensure sufficient Cu loading to observe Cu breakthrough. Column D is expected to represent a worse case scenario as the Cu is a mobilized form, whereas the Cu in columns B and C are not expected to be in a sufficiently mobilized form. For column experiments B, C, D the mass of C contaminated material will be sufficient to generate aqueous Cu concentrations in the ten to hundreds ppm, if Cu is mobile. The exact mass/volume of the uncontaminated soil and Cu-contaminated material will be determined prior to the start of the experiment.

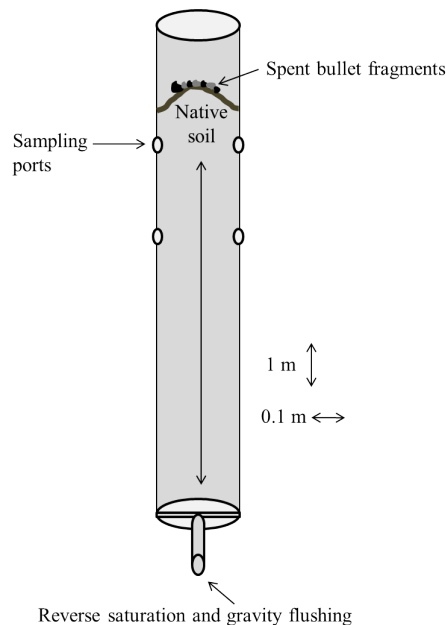
Columns will be initially reverse saturated (bottom to top) and flushed with a weak electrolyte solution mirroring the local rainwater or rainwater obtained from JBCC following soil packing to remove any unsaturated voids. Columns will be fully saturated and allowed to sit for at least 24 hours before commencing the column experiments. Columns B, C, and D will commence once

the Cu contaminated material is added to the top of the column. An image of the column design is shown in Figure 1.

Once the Cu contaminated material is added the column experiments will begin using a flow rate of approximately 2 mL/min. Water samples from the base of the column will be collected at approximately 0.5, 1, 2, 4, 8, 16, 48, 96, 168, 336, and 672 hours. After 1 month of aqueous sampling the experiment will be stopped and the soil removed from the columns as an intact core.

The soil cores will be sliced horizontally into thirds (upper, middle, lower) and two types of analysis will take place. First, the pore water will be squeezed from the soil sections using a centrifuge for metal(loid) analysis and second, the soil will be characterized for solid-phase Cu content as a function of soil profile depth. Understanding Cu partitioning between the solid and aqueous phase and monitoring Cu migration as a function of soil profile depth will provide a detailed understanding of the potential Cu to migrate off-site and/or into the groundwater table at shooting range sites.

Figure 1. Column design.



Sampling Schedule: Columns will be sampled for 1 month total and include a minimum of 11 aqueous samples for Cu characterization from each column for a total of 44 aqueous samples.

Analysis: Soils will be characterized for Cu concentrations prior to packing columns and after aqueous leaching experiment is complete using X-ray fluorescence analyzer.

Aqueous Cu concentrations will be analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES). In the event Cu levels are below the ICP-OES reporting limit the

samples will be sent to EL for ICP-MS analysis. Chemical conditions will be analyzed in-situ, including major ions (ion chromatography), pH, redox environment, and simulated rainwater composition.

Following Task 4 completion a technical report will be prepared that summarizes the results from all 4 tasks. MAARNG, USEPA, and State regulators will have the opportunity to review and comment on the draft report. It is the intent that draft/final report will incorporate responses to the reviewers' comments and then be provided to all stakeholders. As this will not be a final technical report, we ask that all stakeholders refrain from dissemination beyond the individuals provided the draft/final report. The draft/final report will be issued by the end of FY22. The technical report will be finalized through ERDCs editing organization; however, this review process can take up to 3 to 6 months beyond the initial submittal. We will request additional FY23 funds from MAARNG for finalization and publication of the final report in FY23.

Schedule

The following is the schedule of tasks activities including milestones and deliverables assuming a project start date of 23 May 2022.

Task	Activity	Start Date	End Date	Duration (weeks)
Pre-kickoff	Update SOW	23 May	3 June	2
Kickoff	Internal CRREL Meeting	23 May	23 May	
1a	Literature search	23 May	3 June	2
1b	Summary call w/USEPA, MAARNG	TBD	TBD	
2a	Field sampling at JBCC	5 July	8 July	1
2b	Laboratory analysis of field samples	11 July	22 July	2
2c	Summary letter report of findings	25 July	29 July	1
2d	Summary call w/USEPA, MAARNG	TBD	TBD	
3a	Batch testing	11 July	15 July	1
3b	Batch analysis	18 July	22 July	1
3c	Summary letter report of findings	25 July	29 July	1
3d	Summary call w/USEPA, MAARNG	TBD	TBD	
4a	Column Testing	18 July	5 Aug	4
4b	Column Analysis	8 Aug	12 Aug	1
4c	Summary call w/USEPA, MAARNG	TBD	TBD	
4d	Prepare draft report of all Tasks	15 Aug	19 Sep	4
4e	Review of draft report	19 Sep	23 Sep	1
4f	Draft/final report	26 Sep	30 Sep	1
4g	Final report	1 Oct	TBD	12 to 24

Note activities extending beyond FY22, such as Task 4g, will require additional funding to complete.

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