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OFFICE OF
RESEARCH AND DEVELOPMENT

MEMORANDUM

SUBJECT: Draft Final Fate and Transport of Copper at Camp Edwards Small Arms Ranges
(**ERDC/CRREL TR-23-DRAFT**)

FROM: Chunming Su, Ph.D., Soil Scientist
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Per the request for technical assistance, the document titled “Draft Final Fate and Transport of Copper at Camp Edwards Small Arms Ranges” (dated February 2023) was reviewed. This technical review provides general comments on the draft document. The document describes field- and lab-based studies conducted by the Cold Regions Research and Engineering Laboratory under “Joint Base Cape Cod Cu Fate-and-Transport Study.” The document was prepared by a group of eight researchers from the Cold Regions Research and Engineering Laboratory, and Environmental Laboratory, of the U.S. Army Engineer Research and Development Center, and Dartmouth College.

The objective of this study was to assess the potential for copper (Cu) transport at Camp Edwards Small Arms Range (SAR) as a result of using Cu projectiles. Specifically, the soil adsorption and desorption behavior of Cu (as copper sulfate) was investigated to better understand the potential for Cu (as copper slugs and copper sulfate) transport in soils and surface water runoff at Camp Edwards SARs. A series of technical tasks were executed in this study including: 1) literature search on Cu fate-and-transport, 2) soil profiling and lysimeter sampling, 3) batch experiments, and 4) column experiments. The batch experiments provide baseline Cu adsorption and desorption equilibrium coefficients (i.e., Kd) to help understand Cu partitioning between the solid and aqueous phase. Laboratory-based column studies were planned to be conducted to investigate the potential for Cu mobilization under Camp Edwards geochemical conditions. The column study approach was designed to investigate the extent to which Cu can be transported in soil and surface water runoff under various solid-phase Cu matrices by monitoring Cu migration as a function of soil profile depth. The calculated site-specific sorption values for Cu are similar or higher than values obtained for Pb, dinitrotoluene (DNT), and nitroglycerin (NG). The document concludes that “Although, Cu jacketed lead projectiles have

been used for many years. Routine groundwater monitoring at Camp Edwards does not indicate the presence of anthropogenic Cu nor Pb, DNT, or NG. Given the Pb, NG, and DNT observations and the limited fate-and-transport behavior of Cu groundwater contamination of the aquifer is not expected.”

The following comments on the draft final report are provided for your consideration.

- 1) The Operation, Maintenance and Monitoring Plan (OMMP) developed for Camp Edwards requires soil and groundwater monitoring. The OMMP indicates Cu action levels of 10,000 mg/kg in soil, 1,300 µg/L in soil porewater, and 650 µg/L in groundwater. Dissolved copper from a lysimeter sample collected from India Range berm face was reported at 364 µg/L (28% of the action level for soil porewater). Soils from the Sierra, Tango, and India Ranges were analyzed by X-ray Fluorescence (XRF). Copper concentrations in soil ranged from below the level of detection to 3300 mg/kg in one sample collected at a depth of 8 inches from the India Range (33% of the action level for soil). Groundwater data for Cu were not evaluated in this report.
- 2) The literature review provides little insight about the processes and mechanisms of metallic copper (Cu(0)) oxidation and the subsequent transport & fate (attenuation/mobilization) of Cu(I, II) at variable pH conditions. It is stated that Cu(II) can be mobilized through soil at favorable pH and redox conditions. However, a clear description of the “favorable environmental conditions” and how these conditions might compare to those encountered at Camp Edwards is not defined in the report. Thus, the literature review is of limited value for making any predictions about Cu mobility at Camp Edwards, especially in a scenario where greater than 10⁶ rounds of ammunition are anticipated to be fired on an annual basis over decades.
- 3) The Approach is described as a series of tasks including: 1) literature survey; 2) soil profiling & lysimeter soil porewater sampling; 3) batch experiments; and 4) column experiments. The batch and column experiments were expected to be conducted at geochemical conditions that match those at Camp Edwards. The Approach outlined in Section 1.4 of the report generally coincides with the updated Statement of Work reviewed by EPA (SOW dated May 27, 2022). However, there are significant exceptions as noted in these review comments. A separate section of the report should have been developed to document differences in the planned effort with the work as-conducted, Quality Assurance/Quality Control deviations, explanations of confused sampling and laboratory analyses (e.g., as noted in Tables 6 & 11), and the application of data qualifiers.
- 4) There remains uncertainty about extrapolating the fate and transport behaviors of Cu, Pb, and Sb at the KD Range from the short-term laboratory batch tests (24 hours) and column experiments (28 days). The limitations of applying laboratory studies to the field performance were not discussed. For example, laboratory column tests do not account for preferential flow of percolating water with contaminants through cracks, root canals, and animal burrows to reach groundwater at a greater speed than assumed.
- 5) Section 2.3 – it is stated that HPLC was used for determination of ion concentrations, but it is not clear what ions were measured with this method. In general, a clear description of the methods used, analytes determined with each method, method reporting limits, and quality control procedures would have been helpful in the report.

- 6) Biocide was not mentioned in the original Statement of Work (SOW) for Joint Base Cape Cod Science Advisory Committee Support dated September 13, 2021, but biocide was proposed to be used in the batch experiments in the updated SOW for Joint Base Cape Cod Science Advisory Committee Support dated May 27, 2022. It is stated in Section 2.4 that CRREL had originally proposed to run batch tests with and without biocide. Because of problems encountered during the work, data are only available for experiments with biocide added as an amendment. Thus, having data only from biocide-spiked experiments renders the batch experiments difficult to interpret and connect to the expected conditions at Camp Edwards. It is noted in the report that previous experiments (Clausen et al. 2010) found no difference between biocide-spiked and un-spiked batch tests. However, the previous testing was unrelated to Cu and focused on DNT and NG, very different contaminant species that would not be expected to behave like Cu.
- 7) Section 2.4 – it is unclear what electrolyte solution composition was used in the batch experiments, i.e., with respect to the major anion/cation composition. It is noted that calcium carbonate was added to the solution; the reason for the addition of calcium carbonate is unclear as is how the carbonate addition was accomplished. However, carbonate addition caused the pH to increase to 9, which is a deviation from the overall objective of matching experimental conditions with the geochemical conditions at Camp Edwards. It is noted that the increase in pH is “not likely” to affect Cu adsorption; however, this premise is not supported by information in the literature that indicates that pH is a fundamental control on Cu adsorption/desorption and solubility. Compare pH 9 with the results of soil pH in Table 1; pH ranges from 4.8 to 7.4 (mean = 5.9). Thus, the batch and column tests should have been conducted at pH ~5.5 to 6 in order to match the field pH conditions with the experimental pH.
- 8) Section 2.4.1 – it is not clear whether 24 hours was enough time to reach steady state in the batch experiments. The updated SOW proposed that a 24-hour equilibration time would be used in the batch adsorption experiments. It would have been appropriate to investigate time as an experimental variable. The original SOW indicated that experiments would be conducted over a 120-hour equilibration period. There is no explanation for this discrepancy (120 hours vs. 24 hours) in the experimental approach; please see point 3.
- 9) It is unclear why sample drying in an oven was used in some cases, whereas in other cases, samples were air-dried at room temperature. For desorption tests, elevated temperature can result in labile mineral forms converting to more refractory forms (i.e., leading to increased stability & lower solubility), and potentially less desorption as described in section 2.4.2. Sample drying in an oven is not a preferred method and can lead to experimental artefacts.
- 10) It would have been appropriate to provide a table documenting the electrolyte composition and a comparison to porewater composition from lysimeter data.
- 11) Table 2 indicates that dissolved cation and anion concentrations from a 24-h 1:10 soil/Milli-Q water equilibration are provided. Data on many metals including Cu, Pb, and Sb are missing in this table. The updated SOW indicated that 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) would be performed using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Additionally, Table 2 shows high levels of

extractable nitrate and phosphate which should have been mentioned, interpreted, and discussed.

- 12) Figure 6 shows a comparison of metals concentrations, not differences in concentrations as stated in the caption.
- 13) Table 3 – the units for TDS, OC, and IC should be mg/L, not g/kg.
- 14) Section 3.3 indicates that soil mineralogy using X-ray diffraction is needed to better understand Cu retention; agreed, this analysis should be completed.
- 15) Section 3.2 – it is unclear what a trip blank for pH represents. Trip blanks are used to evaluate whether sample bottles become contaminated during sample storage, sampling, or shipment to and from the field. Trip blanks are not expected to be relevant for pH; they are typically relevant for volatile species and dissolved gases. Same comment for conductivity.
- 16) The report is missing a QA/QC section. A QA/QC section would describe the quality control samples used in the field and the lab; it would describe data quality objectives and whether they were met in all cases or otherwise provided explanations where they were not met. Where any deviations from the Quality Assurance Project Plan noted (e.g., the missing experiments without biocide, uncertainties in sample analysis as noted in Table footnotes)? How were data qualifiers assigned? This report indicates uncertainty in data quality that should have been clearly documented in the report.
- 17) Tables 4 & 5 – the report should have provided information on what “ND” and “bd” refer to. What are the tags on Cu63 and Pb208, i.e., [1] and [2]? The elements Ca, Fe, Mg, K, and Na do not have mass numbers associated with them; was ICP-OES used for these elements or was ICP-MS used? It would have been appropriate to provide method quantitation levels and minimum detection levels for all the elements determined. The tables in the appendix indicate that Pb206 was used for ICP-MS quantitation. Was Pb208 (more abundant isotope) or Pb206 used, or both? The trip blank values reported for Na, NH₄, K, Mg, Cl, sulfate, and nitrate are elevated – what was the source of the trip blank water and why are these values so high? Concentrations of Sb in lysimeter samples should have been analyzed for and reported in Table 4. The unit in the title of Table 5 should be mg/L, not mg/kg. The potential effect of high dissolved phosphate concentration in the lysimeter sample for the India Range berm face (40.48 mg/L) on the fate and transport of Sb should have been discussed.
- 18) Section 3.3 – information is lacking on the composition and pH of the electrolyte solution.
- 19) Section 3.3 – a conclusion reached in this section is that Cu metal corrosion to Cu(II) followed by dissolution is the likely rate limiting step in the overall transport of Cu at Camp Edwards, and furthermore, that Cu is likely to migrate no more than several feet into the soil profile. This conclusion about Cu(0) oxidation is reasonable based on literature studies, however, it is unclear where the conclusion about “several feet” of migration comes from – this conclusion is speculative and does not provide any connection to time, i.e., 1 month, 1 year, decade, multi-decadal time periods.
- 20) Page 20, last paragraph, Clausen et al. 2010 should read Clausen et al. 2010b.
- 21) Page 22, the Report states “The batch tests indicate some limited Cu mobility, which likely translates to a few feet” – this statement is unsupported by any analysis in the report.

- 22) Section 3.4 – the SOW indicated that column data would simulate natural rainwater compositions and that the redox environment would be characterized; these expectations from the SOW were not met.
- 23) Table 8/Figure 8 – are the units supposed to be mass based units “concentrations in soil fractions”? The data are reported in units of mg/L, please clarify.
- 24) Tables 8 and 9 – these tables were not mentioned nor discussed in the report.
- 25) Page 26 – the report states that XRF provided a soil Cu concentration of ~544 mg/kg. This contaminated soil was used in column tests. Soil fraction analysis indicated a maximum Cu value of ~16.8 mg/kg. Was the Cu leached? If not, what is the cause of this concentration discrepancy?
- 26) Page 26 – the text states that Table 10 indicates that Cu in Column C effluents measured by ICP-MS were up to 0.211 ppm. Table 10 shows no sample Cu concentration at 0.211 ppm. Please explain the discrepancy; this text appears to be pointing to Column B effluents.
- 27) Tables 7, 8, 9, 10, and 11 – at what pore volume or leaching time were the analyte concentrations for?
- 28) Page 27 – the statement here implies that munitions are recovered, i.e., there are “few Cu slugs that remain in soil after munition recovery”. Please provide the basis for this statement and describe the frequency at which slugs will be recovered at the KD Range.
- 29) Page 29 – again the statement here indicates that the influent pH for the column tests was pH 9. This pH is unreflective of the pH conditions at the site. Thus, results from this study should be qualified. The report refers to a study by Xu et al. (2005) about experiments conducted at pH from 1 to 11; however, the experiments in this study were intended to reflect conditions at Camp Edwards. Thus, the experimental work is a significant departure from what was initially planned.
- 30) Page 35 – the recommendations “We recommend continued periodic groundwater and soil porewater monitoring (lysimeters) for Cu” should also include Pb and Sb.
- 31) Page 35 – three references were not cited or discussed in the text: Clausen et al., 2010a, 2011, 2007b.
- 32) Page 35 – Sodr e et al. was not cited or discussed in the text.

In summary, we reviewed the draft final copy of the Copper Fate and Transport Study of Copper provided by MAARNG. Our review indicates uncertainty about the main conclusion of the MAARNG study that “Cu groundwater contamination of the aquifer is not expected”. We acknowledge that copper has a propensity to sorb to soil and does not easily dissolve and migrate to groundwater, however, this short-term study is inconclusive. For example, it is unclear what electrolyte solution composition was utilized in the batch experiments. Carbonate addition caused the test solution pH to increase to 9, which is a deviation from the overall objective of matching the experimental conditions with the geochemical conditions at Camp Edwards. Camp Edwards soils have a pH typically in the range from ~5.5 to 6. Antimony was not analyzed for in the copper study; antimony has been noted as a contaminant of concern in various media. It is not clear whether 24 hours was enough time to reach steady state in the batch experiments. There remains uncertainty about extrapolating the fate and transport behaviors of Cu, Pb, and Sb at the KD Range from the short-term laboratory batch tests (24 hours) and column experiments (28 days) to years or decades of bullet accumulation. The limitations of applying laboratory studies to the field performance were not discussed. For example, laboratory column tests do not account

for preferential flow of percolating water with contaminants through cracks, root canals, and animal burrows to reach groundwater at a greater speed than assumed. Furthermore, copper was detected in pore water at 364 µg/L for the India Range berm face soil. Copper has been detected at active SARs in all media including soil, soil pore water, and groundwater. There remains uncertainty about the fate and transport of copper in the various environmental media over many decades, and as a result of the proposed operations of MPMGR, including the annual use of 1.3 million bullets.

If you have any questions concerning these comments and recommendations, please do not hesitate to contact me at your convenience via phone (580-436-8638, Chunming Su; 580-436-8874, Rick Wilkin), email, or MS Teams.

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