

From: [Baganha, Paulo A CW3 USARMY NG MAARNG \(USA\)](#)
To: [Downing, Jane](#)
Cc: leonard.pinaud@state.ma.us; [Springborg, Denise](#); [Driscoll, Keith J NFG \(USA\)](#)
Subject: RE: Two Items
Date: Wednesday, July 27, 2022 1:01:51 PM
Attachments: [Copper F&T Study Bibliography.pdf](#)

Good afternoon Jane,

It was a pleasure to meet you and the team in person on Monday. I believe we were able to get a lot more accomplished meeting in person with all the stakeholders there. I've attached the literature search that we've received for your review.

To answer your question about the overall status of the Copper F&T Study, we are slightly behind on some laboratory analysis of field samples (waiting on delivery of argon for the metals analysis of the samples). Other testing is underway/complete (pH and anion analysis). Samples are being shipped for organic/organic carbon analysis and TDS. Batch tests start this week and column tests will start next Monday, 1 August 2022. Although we are slightly behind on the start of the lab testing and analysis, USACE are conducting many of these tests concurrently in order to make up for lost time. Overall, they are on schedule for 30 September 2022 draft report. At this time we have no problems meeting and discussing the literature search, but it may be more prudent to wait until the results of the metals analysis is complete (mid August). That way we could discuss field observations, batch test results and initial column results. If you have any further questions, please do not hesitate to contact us. We look forward to hearing from you.

Regards,

Mr. Paulo A. Baganha
Environmental Program Manager

JFHQ-MA CFMO
2 Randolph Road
Hanscom AFB, MA 01731
Office: 339-202-3960
Cell: 508-958-2709

From: Downing, Jane <Downing.Jane@epa.gov>
Sent: Tuesday, July 19, 2022 9:42 AM
To: Driscoll, Keith J NFG (USA) <keith.j.driscoll.nfg@army.mil>
Cc: Baganha, Paulo A CW3 USARMY NG MAARNG (USA) <paulo.a.baganha.mil@army.mil>;

leonard.pinaud@state.ma.us; Springborg, Denise <Springborg.Denise@epa.gov>

Subject: [Non-DoD Source] FW: Two Items

Hi Keith

This is to follow up on 2 items:

~ Unless I missed it, we are still waiting for the literature search, conducted as part of the copper leaching study project. As you know, this project will be critical to meeting our overall project review goal. Please provide this product and the status of other facets of the copper leaching study.

~ This Monday, the EPA team is planning to be on site. We appreciate the information and logistics provided by Paulo. It looks like you are suggesting we come in through the main gate and travel to the Welcome Center. One fundamental question is – what should we put into the GPS for an address of the main gate opening.

That's it for now

Looking forward to our future visit and discussion

Thanks

Jane

From: Driscoll, Keith J NFG (USA) <keith.j.driscoll.nfg@army.mil>

Sent: Thursday, June 23, 2022 3:45 PM

To: Downing, Jane <Downing.Jane@epa.gov>

Cc: pinaud.leonard@state.ma.us; Wilkin, Rick <Wilkin.Rick@epa.gov>; Su, Chunming <Su.Chunming@epa.gov>; Springborg, Denise <Springborg.Denise@epa.gov>

Subject: RE: Two Items

Hi Jane-

Yes I think we should have a call next week to discuss the test fire. Our goal is to present a scenario that simulates the operational conditions of the proposed MPMG as close as possible. I will speak to the Camp Edwards Plans and Training Officer who is arranging this test fire for his availability for a call next week and get back to you with some dates and times.

And yes the literature search is one of the questions we had directed at the ACOE. Once acquired we will send it to you.

Keith

From: Downing, Jane <Downing.Jane@epa.gov>

Sent: Thursday, June 23, 2022 2:59 PM

To: Driscoll, Keith J NFG (USA) <keith.j.driscoll.nfg@army.mil>
Cc: pinaud.leonard@state.ma.us; Wilkin, Rick <Wilkin.Rick@epa.gov>; Su, Chunming <Su.Chunming@epa.gov>; Springborg, Denise <Springborg.Denise@epa.gov>
Subject: [Non-DoD Source] RE: Two Items

Hi Keith

Sounds like a plan to settle on July 25 for the site visit – we will definitely need to work with you on logistics. Since I will be out the first two weeks in July, to settle on details sooner may be better than later. Send me the list of questions/info you will need.

Also, we are interested in the response to the following question covered in my previous email:
As per your SOW, the literature search should be complete. See below. Is this something you can send us for review, with a follow up summary call, and/or should we schedule a call with appropriate experts?

Finally, I want to discuss with you and your team , the option of a test fire that as closely as possible simulates the operational conditions of the proposed multi-purpose machine gun range. Len and I have previously discussed this in some detail, This may or may not be feasible for the July 25 visit. Let me know your thoughts on this idea and if a call next week may be warranted to explore logistics on both topics.

Thanks
Jane

Jane Downing
Chief, Drinking Water and Municipal Assistance Branch
EPA Region 1
617-918-1571

From: Driscoll, Keith J NFG (USA) <keith.j.driscoll.nfg@army.mil>
Sent: Thursday, June 23, 2022 1:41 PM
To: Downing, Jane <Downing.Jane@epa.gov>
Cc: pinaud.leonard@state.ma.us; Wilkin, Rick <Wilkin.Rick@epa.gov>; Su, Chunming <Su.Chunming@epa.gov>; Springborg, Denise <Springborg.Denise@epa.gov>; Baganha, Paulo A CW3 USARMY NG MAARNG (USA) <paulo.a.baganha.mil@army.mil>
Subject: RE: Two Items

Good afternoon Jane-

The MAARNG is available for hosting a tour at Camp Edwards on Monday July 25. Len Pinaud will be available for the tour as well. As we get closer to the date we can decide upon the best time to meet. Camp Edwards is a secure base which will require a list of all participants ahead of time in which each will need to undergo a brief security review conducted by the base. A list of all vehicles that will be entering the base that day will be needed to provide a seamless access through the base

security gate as well.

As for the requested information in regard to the copper study we have a call and an email in to the Army Corps of Engineer (ACOE) to confirm that the July 5/8 sampling event is still on track but we have not heard back as of yet. We do know that the ACOE has started the study but we didn't want to confirm the sampling was on track until we heard it from them. Once we hear back I will let you know.

We also have sent a follow up request for information to the U.S. Army Joint Munitions Command to help answer the some of the questions that came up during our teams call. We have received a portion of the answers but not all as of yet. I will send a follow up email that has some of the answered information.

Keith

From: Downing, Jane <Downing.Jane@epa.gov>
Sent: Thursday, June 16, 2022 4:43 PM
To: Driscoll, Keith J NFG (USA) <keith.j.driscoll.nfg@army.mil>
Cc: pinaud.leonard@state.ma.us; Wilkin, Rick <Wilkin.Rick@epa.gov>; Su, Chunming <Su.Chunming@epa.gov>; Springborg, Denise <Springborg.Denise@epa.gov>
Subject: [Non-DoD Source] Two Items

Hi Keith

This is to follow up on two items:

1. If Len P is available, we tentatively propose Monday July 25, as the date for a site visit. Does that work for you and the team? The logistics and agenda items can be developed at a future time.
2. As you know, the scope, quality, and schedule for completion of interim and final tasks of the Copper Study are critical to EPA's review of the proposed machine gun range. As per your SOW, the literature search should be complete. See below. Is this something you can send us for review, with a follow up summary call, and/or should we schedule a call with appropriate experts? Also, as a reminder the field sampling is scheduled for early July – let us know if any problems/questions

| | | | | |
|----|------------------------------------|--------|--------|-----|
| 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 |

ing on comments to the Monitoring Plan which we hope to submit by end of

June

Let me know if questions/concerns

Thanks

Jane

Jane Downing
Chief, Drinking Water and Municipal Assistance Branch
EPA Region 1
617-918-1571

Cu F&T Annotated Bibliography
01 July 2022

References

- Bannon, Desmond I., John W. Drexler, Genevieve M. Fent, Stan W. Casteel, Penelope J. Hunter, William J. Brattin, and Michael A. Major. "Evaluation of small arms range soils for metal contamination and lead bioavailability." *Environmental science & technology* 43, no. 24 (2009): 9071-9076.
- Bravin, Matthieu N., Cédric Garnier, Véronique Lenoble, Frédéric Gérard, Yves Dudal, and Philippe Hinsinger. "Root-induced changes in pH and dissolved organic matter binding capacity affect copper dynamic speciation in the rhizosphere." *Geochimica et Cosmochimica Acta* 84 (2012): 256-268.
- Cavallaro, N., and M. B. McBride. "Zinc and copper sorption and fixation by an acid soil clay: effect of selective dissolutions." *Soil Science Society of America Journal* 48, no. 5 (1984): 1050-1054.
- Chen, Liwei, Jun Wu, Jian Lu, Chulin Xia, Michael A. Urynowicz, Zaixing Huang, Li Gao, and Mingying Ma. "Speciation, fate and transport, and ecological risks of Cu, Pb, and Zn in tailings from Huogeqi Copper Mine, Inner Mongolia, China." *Journal of Chemistry* 2018 (2018).
- Cornu, Jean-Yves, David Huguenot, Karine Jézéquel, Marc Lollier, and Thierry Lebeau. "Bioremediation of copper-contaminated soils by bacteria." *World Journal of Microbiology and Biotechnology* 33, no. 2 (2017): 1-9.
- de Boer, Tjalf E., Neslihan Tas, Martin Braster, Erwin JM Temminghoff, Wilfred FM Röling, and Dick Roelofs. "The influence of long-term copper contaminated agricultural soil at different pH levels on microbial communities and springtail transcriptional regulation." *Environmental science & technology* 46, no. 1 (2012): 60-68.
- Dumestre, A., S. Sauve, M. McBride, P. Baveye, and J. Berthelin. "Copper speciation and microbial activity in long-term contaminated soils." *Archives of Environmental Contamination and Toxicology* 36, no. 2 (1999): 124-131.
- Fang, W. A. N. G., P. A. N. Genxing, and L. I. Lianqing. "Effects of free iron oxyhydrates and soil organic matter on copper sorption-desorption behavior by size fractions of aggregates from two paddy soils." *Journal of Environmental Sciences* 21, no. 5 (2009): 618-624.
- Gnecco, I., J. J. Sansalone, and L. G. Lanza. "Speciation of zinc and copper in stormwater pavement runoff from airside and landside aviation land uses." *Water, Air, and Soil Pollution* 192, no. 1 (2008): 321-336.
- Grigalaviciene, I., Rutkoviene, V., & Marozas, V. (2005). The Accumulation of Heavy Metals Pb, Cu and Cd at Roadside Forest Soil. *Polish Journal of Environmental Studies*, 14(1).
- Heier, Lene Sørli, Sondre Meland, Marita Ljønes, Brit Salbu, and Arnljot Einride Strømseng. "Short-term temporal variations in speciation of Pb, Cu, Zn and Sb in a shooting range runoff stream." *Science of the total environment* 408, no. 11 (2010): 2409-2417.
- Hermann, Robert, and Peter Neumann-Mahlkau. "The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH." *Science of the total environment* 43, no. 1-2 (1985): 1-12.
- Hutchinson, T. C., & Whitby, L. M. (1977). The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. *Water, Air, and Soil Pollution*, 7(4), 421-438.
- Ho, Y. S., and G. McKay. "Sorption of copper (II) from aqueous solution by peat." *Water, Air, and Soil Pollution* 158, no. 1 (2004): 77-97.

- Jarvis, S. C. "Copper sorption by soils at low concentrations and relation to uptake by plants." *Journal of Soil Science* 32, no. 2 (1981): 257-269.
- Jing, Ran, and Birthe V. Kjellerup. "Biogeochemical cycling of metals impacting by microbial mobilization and immobilization." *Journal of Environmental Sciences* 66 (2018): 146-154.
- Karlsson, Hanna L., Johanna Gustafsson, Pontus Cronholm, and Lennart Möller. "Size-dependent toxicity of metal oxide particles—a comparison between nano-and micrometer size." *Toxicology letters* 188, no. 2 (2009): 112-118.
- Kiaune, Lina, and Nan Singhasemanon. "Pesticidal copper (I) oxide: environmental fate and aquatic toxicity." *Reviews of Environmental Contamination and Toxicology Volume 213* (2011): 1-26.
- Kieber, Robert J., Stephen A. Skrabal, Cliff Smith, and Joan D. Willey. "Redox speciation of copper in rainwater: Temporal variability and atmospheric deposition." *Environmental science & technology* 38, no. 13 (2004): 3587-3594.
- Komy, Zanaty R., Ali M. Shaker, Said EM Heggy, and Mohamed EA El-Sayed. "Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid." *Chemosphere* 99 (2014): 117-124.
- Kuo, S., and A. S. Baker. "Sorption of copper, zinc, and cadmium by some acid soils." *Soil science society of America journal* 44, no. 5 (1980): 969-974.
- Kurdi, Fuad, and H. E. Doner. "Zinc and copper sorption and interaction in soils." *Soil Science Society of America Journal* 47, no. 5 (1983): 873-876.
- Laporte-Saumure, Mathieu, Richard Martel, and Guy Mercier. "Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges." *Environmental technology* 32, no. 7 (2011): 767-781.
- Laporte-Saumure, Mathieu, Richard Martel, and Guy Mercier. "Pore water quality in the upper part of the vadose zone under an operating Canadian small arms firing range backstop berm." *Soil and Sediment Contamination: An International Journal* 21, no. 6 (2012): 739-755.
- Mariussen, Espen, Ida Vaa Johnsen, and Arnljot Einride Strømseng. "Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires." *Environmental Science and Pollution Research* 24, no. 11 (2017): 10182-10196.
- Martin, W. A., Lee, L. S., & Schwab, P. (2013). Antimony migration trends from a small arms firing range compared to lead, copper, and zinc. *Science of the total environment*, 463, 222-228.
- McBride, M. B., and D. R. Bouldin. "Long-term reactions of copper (II) in a contaminated calcareous soil." *Soil Science Society of America Journal* 48, no. 1 (1984): 56-59.
- Najafi, Sarvenaz, and Mohsen Jalali. "Effects of organic acids on cadmium and copper sorption and desorption by two calcareous soils." *Environmental monitoring and assessment* 187, no. 9 (2015): 1-10.
- Okkenhaug, Gudny, Andreas Botnen Smebye, Thomas Pabst, Carl Einar Amundsen, Hilmar Sævarsson, and Gijs D. Breedveld. "Shooting range contamination: mobility and transport of lead (Pb), copper (Cu) and antimony (Sb) in contaminated peatland." *Journal of soils and sediments* 18, no. 11 (2018): 3310-3323.
- Payne, Kay, and W. F. Pickering. "Influence of clay-solute interactions on aqueous copper ion levels." *Water, Air, and Soil Pollution* 5, no. 1 (1975): 63-69.
- Pérez-Novo, C., M. Pateiro-Moure, F. Osorio, J. C. Nóvoa-Muñoz, E. López-Periago, and M. Arias-Estévez. "Influence of organic matter removal on competitive and noncompetitive adsorption of copper and zinc in acid soils." *Journal of Colloid and Interface Science* 322, no. 1 (2008): 33-40.

- Pérez-Novo, C., A. Bermúdez-Couso, E. López-Periago, D. Fernández-Calviño, and M. Arias-Estévez. "The effect of phosphate on the sorption of copper by acid soils." *Geoderma* 150, no. 1-2 (2009): 166-170.
- Ponizovsky, Alexander A., Herbert E. Allen, and Amanda J. Ackerman. "Copper activity in soil solutions of calcareous soils." *Environmental Pollution* 145, no. 1 (2007): 1-6.
- Qiu, Rongliang, Benliang Zhao, Jinling Liu, Xiongfei Huang, Qingfei Li, Eric Brewer, Shizhong Wang, and Ning Shi. "Sulfate reduction and copper precipitation by a *Citrobacter* sp. isolated from a mining area." *Journal of Hazardous Materials* 164, no. 2-3 (2009): 1310-1315.
- Rader, Kevin J., Richard F. Carbonaro, Eric D. van Hullebusch, Stijn Baken, and Katrien Delbeke. "The fate of copper added to surface water: field, laboratory, and modeling studies." *Environmental toxicology and chemistry* 38, no. 7 (2019): 1386-1399.
- Rodriguez-Rubio, P., E. Morillo, Luis Madrid, T. Undabeytia, and C. Maqueda. "Retention of copper by a calcareous soil and its textural fractions: influence of amendment with two agroindustrial residues." *European Journal of Soil Science* 54, no. 2 (2003): 401-409.
- Roque-Álvarez, Isela, Fabiola S. Sosa-Rodríguez, Jorge Vazquez-Arenas, Miguel A. Escobedo-Bretado, Israel Labastida, José Javier Corral-Rivas, Antonio Aragón-Piña, Ma Aurora Armienta, Patricia Ponce-Peña, and René H. Lara. "Spatial distribution, mobility and bioavailability of arsenic, lead, copper and zinc in low polluted forest ecosystem in North-western Mexico." *Chemosphere* 210 (2018): 320-333.
- Sanderson, Peter, Ravi Naidu, Nanthi Bolan, Mark Bowman, and Stuart McLure. "Effect of soil type on distribution and bioaccessibility of metal contaminants in shooting range soils." *Science of the total environment* 438 (2012): 452-462.
- Sharma, S. K., N. S. Sehkon, S. Deswal, and Siby John. "Transport and fate of copper in soils." *International Journal of Civil and Environmental Engineering* 3, no. 3 (2009): 145-150.
- Sipos, Péter, Tibor Németh, Viktória Kovács Kis, and Ilona Mohai. "Sorption of copper, zinc and lead on soil mineral phases." *Chemosphere* 73, no. 4 (2008): 461-469.
- Sodré, Fernando Fabríz, Vanessa Egea dos Anjos, Ellen Christine Prestes, and Marco Tadeu Grassi. "Identification of copper sources in urban surface waters using the principal component analysis based on aquatic parameters." *Journal of Environmental Monitoring* 7, no. 6 (2005): 581-585.
- Sodré, Fernando F., and Marco T. Grassi. "Changes in copper speciation and geochemical fate in freshwaters following sewage discharges." *Water, Air, and Soil Pollution* 178, no. 1 (2007): 103-112.
- Stone, M., and I. G. Droppo. "Distribution of lead, copper and zinc in size-fractionated river bed sediment in two agricultural catchments of southern Ontario, Canada." *Environmental Pollution* 93, no. 3 (1996): 353-362.
- Strømseng, Arnljot Einride, Marita Ljønes, Loella Bakka, and Espen Mariussen. "Episodic discharge of lead, copper and antimony from a Norwegian small arm shooting range." *Journal of Environmental Monitoring* 11, no. 6 (2009): 1259-1267.
- Uchimiya, Minori, K. Thomas Klasson, Lynda H. Wartelle, and Isabel M. Lima. "Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations." *Chemosphere* 82, no. 10 (2011): 1431-1437.
- Wicke, Daniel, Tom Cochrane, and A. D. O'Sullivan. "Contaminant sources, transport and fate in stormwater runoff in Christchurch, New Zealand." (2010).
- Wu, J. I. G. A. N. G., D. A. Laird, and M. L. Thompson. Sorption and desorption of copper on soil clay components. Vol. 28, no. 1. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1999.

Xu, J., X. Han, S. Sun, F. Meng, and S. Dai. "Leaching Behavior of Copper (II) in a Soil Column Experiment." *Bulletin of Environmental Contamination & Toxicology* 75, no. 5 (2005).

Fang, W. A. N. G., P. A. N. Genxing, and L. I. Lianqing. "Effects of free iron oxyhydrates and soil organic matter on copper sorption-desorption behavior by size fractions of aggregates from two paddy soils." *Journal of Environmental Sciences* 21, no. 5 (2009): 618-624.

Background:

1. Soil aggregates are strongly bound soil particles by organic matter. Studies have shown that SOM and heavy metals are more concentrated in coarse sand and clay than smaller fractions, which can lead to differences in the soil's chemical composition.
2. The sorption and desorption capacity of heavy metals by soil aggregates is hypothesized to be driven by particle size dependent environmental factors such as SOM and free iron oxyhydrates. The sorption capacity of heavy metals by coarse sand/clay is higher than that of their soil counterparts.

Mission:

1. Evaluate the influence of SOM and free iron oxyhydrates on the sorption capacity of heavy metals by soil aggregates in paddy soils.

Methodology:

I. Soil collection

A. Sample Collection

1. Samples from two locations with different chemical properties were collected in triplicates from 0-15 cm. Soil samples were either stored in the refrigerator or air-dried. Refrigerated samples were then separated into various size fractions, while air-dried samples were ground to <0.25 mm.

B. Characterization of Soil Properties

1. Soil pH → water:soil ratio of 2.5:1
2. Cation exchange capacity → 1 mol/L ammonium acetate (pH 7)
3. Soil organic carbon measured → digestion with $K_2Cr_2O_7$

II. Sorption-desorption studies

A. Adsorption

1. 1 g sample added to 20 mL of 40 mol/L $CuCl_2$ and 0.01 mol/L $CaCl_2$ solution in a centrifuge tube.
2. The centrifuge tube was shaken at 180 r/min/ 25°C for 24 hr.
3. The suspension was then centrifuged at 3600 r/min for 10 min
4. The solution ran through a 0.45 μm filter paper.
5. Cu^{2+} concentration analyzed using Atomic Adsorption Spectroscopy
6. adsorbed Cu^{2+} = total Cu^{2+} added – Cu^{2+} remaining in solution

B. Desorption

1. Adsorbed residues were weighed
2. 20 mL of 0.01 mol/L $CaCl_2$ (pH 6.0) solution was added to the centrifuge tube and shaken at 180 r/min/ 25°C for 24 hr.

3. The suspension was centrifuged at 3600 r/min for 10 min
4. The supernatant ran through a 0.45 μm filter paper.

Results and Key Findings:

- Absence of SOM and free iron oxyhydrates significantly decreased Cu^{2+} adsorption capacity
- Desorption rates increased by SOM removal but were not affected by free iron oxyhydrate removal
- Adsorption of heavy metals by coarse sand dominated as negative surface charge increased

Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid

Komy, Zanaty R., Ali M. Shaker, Said EM Heggy, and Mohamed EA El-Sayed. "Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid." *Chemosphere* 99 (2014): 117-124.

Background:

1. Hematite is abundant in soil and has a large surface area with a negative charge. These intrinsic properties drive adsorption of heavy metals by hematite in soil.
2. Humic acid has strong complexing sites and adsorbs onto surface of soil minerals, increasing adsorption capacity for Cu.
3. Cu adsorption kinetics explain Cu retention in water and soil.

Mission:

1. Determine the chemical characteristics of soils
2. Evaluate the role of soil properties on the rate of Cu adsorption.

Methodology:

I. Cu^{2+} adsorption quantification

A. Suspension preparation

1. Cu^{2+} stock solution (concentration: 75 mg/L) prepared using anhydrous copper chloride at pH 5, 6, 7 and at different ionic strengths
2. Samples were centrifuged, and 5 mL supernatant was discarded and replaced with Cu^{2+} at matching pH and ion strength (10 mL total)
3. Suspensions were shaken for 24 hr and then centrifuged at 20000 rpm for 5 min

B. Cu^{2+} adsorption calculation

1. initial concentration of Cu^{2+} – Cu^{2+} equilibrium concentration in supernatant

Results:

- Adsorption of Cu by soils increased after HA addition
- A pH from 5-7 increased Cu adsorption
- Cu and soil suspension time positively correlated to adsorption capacity

Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges

Laporte-Saumure, Mathieu, Richard Martel, and Guy Mercier. "Characterization and metal availability of copper, lead, antimony and zinc contamination at four Canadian small arms firing ranges." *Environmental technology* 32, no. 7 (2011): 767-781.

Background:

1. Cu contamination at small arms firing ranges in Canada is caused by the degradation of Cu-Zn jackets from 5.56 mm calibre bullets. Though each bullet is composed of only 4.5% Cu relative to other metal contaminants, the accumulation of Cu within the backstops can pose a threat to both humans and plants if the contaminant is available.

Mission:

1. Assess the soil mineralogy and chemical composition of backstop soils
2. Determine Cu availability

Methodology:

I. Field-Sampling methodology for IA-ID

- A. composite samples from impact compartments
 1. composite samples (100 sub-samples) from 0-30cm depth
- B. 2 composite samples were combined, homogenized on plastic tarps, and then divided into two groups
- C. 1 kg sample from each bucket (taken from top, middle, and bottom) to represent SAFR backstop (2 kg)

II. Field sampling methodology to assess the vertical distribution of contamination

- A. backstop sampled at 0–15cm, 15–30cm, 30–50cm and 50–90cm using manual auger that was rinsed with DI water and 10% concentrated HCl between each interval
- B. 2-3 subsamples were collected from 15 impact compartments

III. Characterize backstop soils of 4 SAFR

- A. quantification of total Cu and Cu in various size fractions
 1. 2 kg sample dried for 24 hr at 105C
 2. sieved at >2 mm, 0.5–2.0 mm, 53–500µm, <53µm (soil size fractions, SF)
 3. samples from each SF passed through sample splitter to obtain 30-40 g sample. Quartz (SiO₂) was crushed in between samples to prevent cross-contamination.
 4. samples from each SF then digested and diluted in ultra-pure water for ICP-AES analysis

B. chemical properties

1. TC, TOC, TIC, pH
2. Carbon quantification using Leco CHNS-932 analyzer. Total carbon analyzed → washed with 0.1 N H₂SO₄ → reanalyzed for TOC → difference is TIC
3. pH measured using Fisher Scientific AR 25 Dual Channel pH/ion meter (1:2 soil/distilled water ratios)

II. Assess Cu availability via leaching tests

A. leaching test: SPLP → acid rain leachate.

1. This method is used to determine the potential of Cu mobility from unsaturated soil to the groundwater table.

Results and Key Findings:

- Leachate tests: final leachate pH explained Cu abundance
- no correlation between backstop soil mineralogy and Cu availability

Sorption and Desorption of Copper on Soil Clay Components

Wu, J. I. G. A. N. G., D. A. Laird, and M. L. Thompson. *Sorption and desorption of copper on soil clay components*. Vol. 28, no. 1. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1999.

Background:

1. The adsorption and desorption behavior of Cu by soil directly relates to the abundance of Cu in soil. Studies have shown that organic matter and free Mn oxide are most influential in relation to adsorption and desorption capacity as they have abundant binding sites and a strong binding affinity for Cu. However, studies indicate that removal of organic matter can in fact create new negative sorption sites due to soil heterogeneity.

Mission:

1. Determine the impact of soil clay components on Cu sorption and desorption capacities
2. Assess the spatial variance of soil properties and their effect on Cu adsorption/desorption.

Methodology:

I. soil properties measured

- A. pH → 1:1 soil/water slurry
- B. TOC → quantification via combustion
- C. CEC → quantification via exchange with NH₄OAc (pH 7)
- D. exchangeable Ca, Na, K, Mg → AAS

II. Sorption/desorption studies

- A. Sorption (in duplicate)

1. 0.1 g clay combined with CuCl_2 at concentrations from 2.5×10^{-6} to 1.25×10^{-3} M. 0.01 M CaCl_2 was added to provide the suspension with a background electrolyte
2. solution pH adjusted to 6 to achieve a total volume of 20 mL.
3. suspensions shaken for 24 hr at 23°C and then centrifuged for 20 min at 18000 rpm.
4. Cu content of 10 mL supernatant was measured via ICP-AES

B. Desorption

1. 10 mL 0.01 M CaCl_2 added to samples with the highest concentration of equilibrated Cu from IIA.
2. samples were vortexed to create suspensions and then shaken for 24 hr at room temp.
3. Supernatant removed and analyzed via ICP-AES

Results:

- The coarse clay fraction = strongest binding affinity for Cu
 - Coarse fraction had a high CEC and carbon content
- Organic matter removal decreased Cu sorption by coarse clay fractions to such a degree that they sorbed less Cu than finer soil components

Transport and Fate of Copper in Soils

Sharma, S. K., N. S. Sehkon, S. Deswal, and Siby John. "Transport and fate of copper in soils." *International Journal of Civil and Environmental Engineering* 3, no. 3 (2009): 145-150.

Background:

1. Copper is a highly reactive, non-biodegradable element that is often a wastewater contaminant. The movement of copper through the soil, using wastewater as a medium, often leads to groundwater (via percolation) and soil (precipitation/adsorption) contamination.

Mission:

1. Measure copper transport through a semi-pervious soil layer.
2. Plot breakthrough curves (a measure of adsorption) at different soil depths.

Method of Analysis:

1. Copper percolation through the soil column.
2. Measure Cu diffusion across varying soil depths.

Results:

- Breakthrough times ($T_{1/2}$) increase with depth when initial $[\text{Cu}] = 50 \text{ mg/L}$

- Copper outflow decreases as depth increases
- Cu is present at smaller depths for more extended periods; thus, adsorbing larger [Cu].

Key Findings:

- Copper has a greater affinity for percolation than adsorption.
- Copper flows faster in the soil (reaches the groundwater table sooner).

Speciation, Fate and Transport, and Ecological Risks of Cu, Pb, and Zn in Tailings from Huogeqi Copper Mine, Inner Mongolia, China

Chen, Liwei, Jun Wu, Jian Lu, Chulin Xia, Michael A. Urynowicz, Zaixing Huang, Li Gao, and Mingying Ma. "Speciation, fate and transport, and ecological risks of Cu, Pb, and Zn in tailings from Huogeqi Copper Mine, Inner Mongolia, China." *Journal of Chemistry* 2018 (2018).

Background:

Mining waste products can exist in a liquid form (effluents) and a solid form (tailings). Mining waste has a high metal concentration and poses a significant threat to the environment as oxidation of these metals will lead to transformation into mobile forms, leading to potential ionization. Therefore, determining heavy metal speciation (Cu focused) is an essential factor in the assessment of fate (toxicity) and transport (active and passive).

Mission:

1. Chemical speciation of tailings (quantify distribution).
Exchangeable, carbonate, deoxidize, oxidizable, silicate
2. Assess migration potential (quantification).

Method of Analysis:

1. Concentration of Cu measured using Atomic Absorption Spectrophotometer after acid digestion.
2. Acid potential and neutralization potential quantified using respective counting methods.
3. Leaching Di water (pH 4-8) through a column loaded with tailings to quantify migration.
 - Percolation rate
 - Leachate (water that percolated through water column)—analyzed pH and [Cu]
4. Speciation by the classical sequential extraction technique

Results and Key Findings:

- Migration
 - The concentration of [Cu] decreased over time
 - Lower pH = higher [Cu]
 - [Cu] varies greatly depending on pH

- Speciation
 - Copper is predominantly present in the oxidizable form (>60%)
 - Concentration can decrease under acidic conditions

Oxidizable copper (Cu^{2+}) → copper oxide, cuprous/cupric oxide, copper carbonate →
Oxidized **Transform**
 exchangeable form → Mobilized (dissolved) and a threat to the ecosystem
Cation exchange

- Silicate second highest form
 - Stable → will not cause harm under normal environmental conditions

The Fate of Copper Added to Surface Water: Field, Laboratory, and Modeling Studies

Rader, Kevin J., Richard F. Carbonaro, Eric D. van Hullebusch, Stijn Baken, and Katrien Delbeke. "The fate of copper added to surface water: field, laboratory, and modeling studies." *Environmental toxicology and chemistry* 38, no. 7 (2019): 1386-1399.

Background:

Metals are unique in their ability to react with the functional groups of both organic and inorganic matter. Dissolved copper in its 2+ oxidative state is the most common form of copper in surface waters that, when bound to ligands within the water, soil, and sediment, can take on different phases of matter. The transformation of copper into other forms (high K_D) creates a ripple effect where fate and transport are ultimately affected. To effectively predict copper fate and transport, researchers must understand the interplay between copper transformation and environmental factors, including pH and redox potential. Determining copper fate includes a detailed evaluation of copper "degradability." Here, researchers understand that though copper does not degrade in the environment, it can undergo changes in speciation that affect bioavailability, including but not limited to bioavailability change over time, copper ion percolation, residence time in the water column, and interactions at the water-sediment interface.

Reactions including complexation, precipitation, and adsorption change the chemical nature of copper (speciation) as all reactions involve covalent bonding. Copper speciation is a determinant of its bioavailability and is commonly used to reduce toxicity and lower environmental risk.

Mission:

1. Assess the fate of copper after being added to surface water.

Method of Analysis:

1. Field/Laboratory studies to investigate the final [Cu] in eluents from a water column in the event that a high concentration of Cu is loaded to the top of the column.

Results:

- [Cu] decreases in/removed from a water column due to adsorption, precipitation, sediment processes, diffusion into the sediment, washout.
- Continuous flow: sudden increase of [Cu], which leads to a steady-state concentration.

Key Findings:

- Copper had a higher affinity for the solid phase, becoming less bioavailable
- Copper remobilization is unlikely due to strong binding of copper by particulate phases.

COMPETITIVE ADSORPTION OF HEAVY METALS BY SOILS OF ALIGARH DISTRICT

Bansal, O. P. "Competitive adsorption of heavy metals by soils of Aligarh district." *Int. J. Chem. Sci* 7, no. 2 (2009): 1439-1446.

Background:

Copper and other heavy metals are introduced to the environment via fertilizers, sewage sludge composts, and industrial waste materials. When various heavy metals are abundant in the soil, the bioavailability and transport of each metal differ. The fate of a metal can be predetermined by taking a closer look into how the distribution coefficient (K_D) can affect Cu mobility.

Mission (focus on Copper):

1. Study selectivity sequence
2. Approximate Cu competitive adsorption

Method of analysis:

1. For the adsorption study, solutions containing varying volumes of a (50 mg L⁻¹) solution (Pb, Cr, Cu, Zn, Cd, Ni) were added to each soil sample.
 - $K_d = \text{metal concentration adsorbed} / \text{metal concentration in solution}$

Results and Key Findings:

- The distribution coefficient for copper was higher than other metal species
- K_d decreases with increasing metal concentration
- Increase pH = decrease adsorption

Changes in copper speciation and geochemical fate in freshwaters following sewage discharges

Sodré, Fernando F., and Marco T. Grassi. "Changes in copper speciation and geochemical fate in freshwaters following sewage discharges." *Water, Air, and Soil Pollution* 178, no. 1 (2007): 103-112.

Background:

Sewage in developing countries is not treated before being released into nearby water reservoirs. Neglect to treat sewage before it is discharged creates many complications in aquatic environments, the food chain, and public health. In addition, continuous input of raw sewage into nearby waters dramatically affects the water quality (pH, suspended solids, organic matter, dissolved oxygen), where poor water quality alters metal speciation.

Speciation can be broken down into two types: physical and chemical. Physical speciation refers to “the distribution of an analyte according to physical properties... controls the overall physical transport...” where chemical speciation is characterized by the effect of dissolved metals on aquatic biota. Dissolved metals are more bioavailable, thus posing a greater risk to the environment.

Mission:

1. Research factors that influence copper speciation in two rivers to evaluate the effect raw discharge has on copper fate in receiving waters.

Raw sewage → river 1 → river 2
Speciation changes

Method of Analysis:

1. Water samples were collected each month from two different rivers, both upstream and downstream, to evaluate copper behavior in different ranges.

River 1: Irai (upstream)
 Less polluted

River 2: Iguacu (downstream)
 Anoxic, polluted

Receiving raw sewage and discharges from sewage treatment works
 Look at fate throughout the entire watershed

Results:

- Cu most abundant in particulate form and in Iguacu river
- Partitioning coefficient (K_D) (ratio organic layer to aqueous layer)
 - K_D decreases = suspended solid concentration increases
- Irai = % copper in aqueous phase most abundant
- Iguacu river = % copper in solid-phase most abundant

Key Findings:

- Change in copper speciation from upstream aqueous phase to downstream solid phase is likely to be caused by the increase in organic matter downstream.
- Dissolved copper readily complexes with organic matter and precipitate out (at high pH).

Identification of copper sources in urban surface waters using the principal component analysis based on aquatic parameters

Sodré, Fernando Fabríz, Vanessa Egea dos Anjos, Ellen Christine Prestes, and Marco Tadeu Grassi. "Identification of copper sources in urban surface waters using the principal component analysis based on aquatic parameters." *Journal of Environmental Monitoring* 7, no. 6 (2005): 581-585.

Background:

It is essential to recognize that urban run-off introduces copper and other heavy metals to the water column intermittently (rivers, lakes, streams, groundwater, etc.). Copper can be transported into reservoirs during heavy rainfall as copper-coated roofs and car brakes can dissolve due to passing water. Non-point sources occurring due to storm-water events lead to an increase in copper in aquatic systems. Research involving non-point heavy metal sources has taken the approach of studying individual sources of contamination, rather than taking the top-down approach by identifying sources of contamination through the examination of the receiving water.

Mission:

1. Researched the effects on copper levels in receiving urban waters as a function of distribution and season.
2. Evaluated the water status at two points in a watershed.

Method of analysis:

1. Water samples were collected upstream (Irai) and downstream (Iguacu).
2. Chemical analysis included alkalinity, pH, suspended solids, dissolved chloride

Results:

- Increase in copper levels downstream river and decreased levels in the upstream river during periods of low rainfall.
- There was not a significant difference in copper levels between two rivers following periods of heavy rainfall.
- Total suspended solids increased during rainy period in the downstream river – increased water flow affects residence time in the water column (increased)
- TSS did not change in the upstream river due to the presence of a reservoir (controls the water flow).
- During low precipitation period, sedimentation rates increased in the upstream river (expected).
- During the rainy period from September to October, TSS and copper concentration increased in both rivers.

Key Findings:

- Non-point sources affected both rivers during periods of high precipitation.
- 50% of copper in the urban run-off was associated with adsorbed Cu.

The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH

Hermann, R., & Neumann-Mahlkau, P. (1985). The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. *Science of the total environment*, 43(1-2), 1-12.

Background:

Heavy metals are deposited into river soils as contaminated sediments settle on the riverbed. The groundwater table is located 10-80 cm below surface and can move up into these contaminated surface zones, posing a threat to drinking water. Two factors that influence whether or not the drinking water is at risk are pH and redox potential, where these environmental conditions can vary spatially but typically remain stable. Heavy metals change pH and redox potential, thus influencing their mobility through the column and their threat to the groundwater table.

The groundwater table is between an upper soil horizon and a lower one but does not always stay within these boundaries; the upper region has an oxidizing environment, whereas the lower region exhibits a reducing environment.

Mission:

1. Assess the mobility and concentrations of heavy metal contaminants in groundwater.

Method of analysis:

1. Redox potential (Eh) measured in groundwater
2. pH
3. Heavy metal concentration determined using AAS

Results:

- The concentration of copper in the upper horizon was high, whereas the copper concentration in the lower horizon was low.
- **pH**
 - Copper is more soluble at a low pH in an oxidizing environment
- **Redox Potential**
 - Oxidizing environment = more soluble = more significant threat to drinking water
 - High redox potential
 - The degree of solubility depends on pH; lower pH = greater solubility
 - Reducing environment = less soluble
 - Copper complexes with sulfide = immobile = decrease threat
 - Low redox potential

Key Findings:

- Redox potential has a significant effect on Cu solubility
 - Effect of redox potential dependent on pH

Influence of organic matter removal on competitive and noncompetitive adsorption of copper and zinc in acid soils

Pérez-Novo, C., M. Pateiro-Moure, F. Osorio, J. C. Nóvoa-Muñoz, E. López-Periago, and M. Arias-Estévez. "Influence of organic matter removal on competitive and noncompetitive adsorption of copper and zinc in acid soils." *Journal of Colloid and Interface Science* 322, no. 1 (2008): 33-40.

Background:

The concentration of heavy metals in contaminated soils is dependent on their mobility through the soil. Heavy metal mobility differs by soil type as it is affected by particulate adsorption – reactions that occur more frequently in a high pH environment. Adsorption onto surface sites is competitive in the presence of other metals as each element has a different affinity for varying particles.

Mission:

1. Evaluate competitive and non-competitive adsorption of Cu and Zn as a function of organic matter content.

Method of analysis:

1. Untreated soil and experimental soil treated with acid to remove organic matter were saturated with water and acid, respectively, and centrifuged. The supernatant was measured for Cu and Zn via AAS. This amount was subtracted by the initial amount to calculate the adsorbed metal concentration.

Results and Key Findings:

- Copper adsorption greater than zinc
- The removal of organic matter significantly decreased copper adsorption.

Factors that affect covalent bonding to organic matter:

- Adsorption of Cu by soil influenced by electronegativity
Copper more electronegative than zinc = higher retention rate
- Cu has a lower pKa = more strongly adsorbed at neutral and acidic pH

Influence of clay-solute interactions on aqueous copper ion levels

Payne, K., & Pickering, W. F. (1975). Influence of clay-solute interactions on aqueous copper ion levels. *Water, Air, and Soil Pollution*, 5(1), 63-69.

Background:

Clay is one of the most adsorbent species in soil and sediment. Copper can adsorb to clay binding sites through both cation exchange and specific bonding. Adsorbent reactions are affected by environmental conditions, such as pH. The potential for copper to complex with ligands present in the water does not necessarily reduce adsorption capacity; however, little research has been done on this topic of interest.

Mission:

1. Study the effects of ligands on the sorption of copper by purified kaolin (type of clay).

Method of analysis:

1. Amount of copper adsorbed per gram of kaolin was measured using an atomic absorption spectrophotometer at 324.8 nm.

Results and Key Findings:

- pH < 3.5 = no Cu ion uptake
- pH < 5 = competition for sorption sites
- pH > 6 = total removal of Cu ions

- As pH increases, adsorption increased, and Cu ion concentration decreased.
- Presence of adsorbed species (H₂PO₄⁻): increased uptake of Cu ion.
- EDTA: commonly complexes with copper.
 - If the ligand is in contact with clay before copper is present, Cu uptake is reduced.
 - If the clay is added after complexed ligand – copper, no adsorption occurs.

The Accumulation of Heavy Metals Pb, Cu and Cd at Roadside Forest Soil

Grigalavičienė, I., Rutkoviėnė, V., & Marozas, V. (2005). The accumulation of heavy metals Pb, Cu and Cd at roadside forest soil. *Pol. J. Environ. Stud*, 14(1), 109-115.

Background:

The roadside environment is constantly polluted by heavy metals in the air from “...traffic, domestic heating, and long-range transport.” Copper present in the soil can have adverse effects on forest soil fertility and subsequent productivity. Copper influences biological turnover through alterations to biological, chemical, and physical properties. When living organisms take up bioavailable copper, it is propagated through the food chain. Bioavailable copper exists in the soluble, or easily mobile, form.

Mission:

1. Evaluate forest soil contamination by distance from the highway
2. Measure total and soluble copper concentrations in contaminated roadside soils.

Method of analysis:

1. Samples were collected between 5-100 m from the highway and analyzed for organic matter, particle size, pH, and metal concentration.
2. Strong acids used to determine the total metal concentration
3. Soluble metal concentration was analyzed using EDTA (pH 4.65) and DTPA (pH 7.31).
 - EDTA is a chelating agent
 - Examine the distribution of soluble and exchangeable forms

Results:

- Total copper concentration decreased with increasing distance from the highway.
- Extractable copper concentration decreased with increasing distance from the highway.

Key Findings:

- Forest ecosystems act as a barrier to heavy metal infiltration.

Biogeochemical cycling of metals impacting by microbial mobilization and immobilization

Jing, R., & Kjellerup, B. V. (2018). Biogeochemical cycling of metals impacting by microbial mobilization and immobilization. *Journal of Environmental Sciences*, 66, 146-154.

Background:

Heavy metals mainly exist in aquatic environments as sediments from various sources, including but not limited to urban wastewater, precipitation, weathering, atmospheric transport, and sewage. Copper is characterized as a class B metal, which means that it can form stable complexes with soft acids and methyl-/alkyl- substances (biological systems). $\text{Cu}(\text{OH})^+$, $\text{Cu}_2(\text{OH})_2^{2+}$ and CuCO_3 are highly toxic in large concentrations. Cu^{2+} is the most toxic copper form most prevalent in the aqueous phase (soluble). Microorganisms have been used in soil bioremediation efforts to alter copper's oxidation state, thus affecting its mobility and further toxicity. Biofilm and extracellular polymeric substances (EPS) affect mobility, where enzymes in EPS can decrease copper mobility via the transport of copper into cells.

Key Terms that **increase** metal bioavailability:

Bioremediation: microorganisms dissolving metals (can be used as a method of extraction) from ores.

- Low pH environment (1.5-3)
- Metal dissolves into cations, thus oxidizing sulfide
- Cost-effective
- Contact leaching – bacteria attach to ore and oxidize sulfide to sulfur and sulfate
- Non-contact leaching – bacteria oxidize dissolved Fe (II) and Fe (III), which then oxidize sulfide
- Chalcopyrite (CuFeS_2) most important copper mineral
 - Some microorganisms gain energy from oxidizing sulfide minerals
 - Obtain energy from sulfur in chalcopyrite

Bioweathering: decomposition, erosion, decay of rocks and minerals – free copper in sediment

Methylation: adding a methyl group to metal

Bacterial extracellular polymers: bind to copper and increase bioavailability.

Redox: microorganisms can alter redox as they are oxidizing agents, and oxidizable copper is readily mobile. When copper loses electrons, it becomes mobile.

pH: low pH = increase bioavailability

Key Terms that **decrease** metal bioavailability:

Microorganisms: immobilize metals by gaining energy through redox reactions – transforming metals into less toxic forms – (CrVI) reduced to Cr (III), which is less soluble and forms chromium oxide (removed from contaminated water).

pH: high pH = alter the charge of functional groups which change binding site on microbial surfaces.

- Most bacteria have net negative surface charge = increase (-) charge, increase # binding sites.

Biosorption:

- Step 1. Metal binds to the cell wall of a living organism
- Step 2. Metal is transported through the membrane

Biofilms: Metals adsorb to EPS (cation sink due to anionic nature) on biofilm matrix

Microbial cell covered soil: metals have higher adsorption affinity here than with clay.

- Mechanisms for immobilization:
 1. microprecipitation
 - Mechanism of biosorption taking place at the cell surface
 - Binding between the cell surface and metal does not occur
 - Metals form insoluble aggregates
 - Hydrogen sulfide strong reducing agent that forms a metal-sulfide complex
 - Low solubility
 - Sulfate reduction at low pH
 - Essential to reduce sulfate prior to release in wastewater as optimal conditions need to be met before reactions take place.
 2. physical adsorption
 - Adsorption to microorganism cell walls (functional groups hydroxyl, sulfate, phosphate) involve Van der Waals forces and electrostatic interactions.
 - Passive process that takes energy (1 kcal/g mol)– dependent on metabolism
 3. ion-exchange
 - Bacterial cell walls contain cations that can be exchanged for metals
 4. complexation
 - Metals combine with ligands – form coordinate complex
 - 1+ metal cation surrounding central atom (microorganism) with ligands
 - Chelate: one ligand binds to metal cation through two+ atoms
 - The complex binds to the cell surface due to metal-ligand-active groups on cell wall interactions.

Mission:

1. Evaluate the role of microorganisms in metal biochemical cycling.
2. Evaluate microorganism mobilization and immobilization processes.

The influence of long-term copper contaminated agricultural soil at different pH levels on microbial communities and springtail transcriptional regulation

de Boer, Tjalf E., Neslihan Tas, Martin Braster, Erwin JM Temminghoff, Wilfred FM Rölting, and Dick Roelofs. "The influence of long-term copper contaminated agricultural soil at different pH levels on microbial communities and springtail transcriptional regulation." *Environmental science & technology* 46, no. 1 (2012): 60-68.

Background:

Copper is a necessary trace element for microorganisms as it acts as a catalyst for many enzymes involved in redox reactions. However, copper is toxic to soil biota even at small concentrations. Agricultural soils are continuously contaminated by pig manure and fungicides, which can have long-term, irreversible effects on soil biota and even lead to heavy metal resistance. Microorganisms, in particular, are more sensitive to copper than other living organisms in the soil. The fate of copper is mainly dependent on the pH conditions of the soil that affect cation exchange capacity, thus dictating copper bioavailability.

Mission:

1. Evaluate the influence of copper and pH on soil quality and toxicity by taking two approaches.
 1. In-situ analysis on microbial community structure – history on conditions and toxicity over time
 2. Transcriptional profiling of one species via lab incubation under controlled conditions—actual pollution status

Method of analysis:

1. Initial soil samples were collected on-site and measured for [Cu] and pH.
 - 1a. The site was divided into blocks that were applied with varying [Cu] and pH
 - Total reactive [Cu] determined using ICP-AES
 - Bioavailable [Cu] extracted by introducing acid CaCl₂
 - pH measured and [Cu] measured by HR-ICP-MS (after centrifugation)
2. RNA extraction and RNA microarray hybridization (measure RNA transcripts for gene expression – transcription and translation)
 - 2a. DNA extraction, PCR amplification, gel electrophoresis (DNA separation)

Results:

- Increase in pH caused a decrease in total and bioavailable [Cu]
- No effect of exposure to Wildekamp soil reproduction/growth
 - pH and [Cu] did not have lethal effects on yeast
- No significant difference in gene expression (total [Cu])
- Bioavailable copper (CuCaCl₂) significantly affected genes responsible for secretion—overexpression

- Low pH affected gene expression of nucleotide and protein metabolism and acute inflammatory response

Key Findings:

- Copper bioavailability influenced by soil pH
- pH changes cause general distress to yeast; bioavailable copper causes a specific response
 - Transcriptional changes are evidence of physiological response to detox
- Long-term effects of pH (more evident) and Cu on community composition of bacteria and fungi (Cu effects are related to bioavailable copper)
- Community composition stabilized overtime after Cu contamination – resistance to metal (changes to the membrane)
- High [Cu] complexed with dissolved organic carbon (DOC) – reduce bioavailable copper content
- [Cu] decreased over time, especially in low pH environments (?)

Copper speciation and microbial activity in long-term contaminated soils

Dumestre, A., S. Sauve, M. McBride, P. Baveye, and J. Berthelin. "Copper speciation and microbial activity in long-term contaminated soils." *Archives of Environmental Contamination and Toxicology* 36, no. 2 (1999): 124-131.

Background:

US EPA and CEC regulations for heavy metal toxicity in the soil are based on total [Cu]; it is not the total [Cu] that determines toxicity but the bioavailable concentration. To date, the bioavailable concentration of heavy metals in soil has been determined through extraction methods using chemical extractants such as weak salts, weak acids, and chelating agents (EDTA). Though these methods prove successful in quantifying heavy metals, they do not produce comparable results as confounding variables (environmental and metal properties) persist.

Two factors that indicate heavy metal contamination in the soil are the C-mineralization process and metal tolerance of soil microbes. Microbes metabolize carbonaceous material into carbon dioxide via oxidation, a process that is disrupted by heavy metal contamination. The delay in this process, referred to as the lag time, can be used as an indicator of contamination – where a high lag time correlates to an increase in contamination. The metal tolerance of soil microbes can be used to assess contamination—an increase in resistance corresponds to an increase in contaminated levels. These two factors provide concentrations that are not influenced by other factors and can accurately assess toxicity.

Mission:

1. Understand the long-term effects of copper concerning speciation on microorganisms

Method of analysis:

1. C-mineralization potentials measured using modified substrate-induced respiration technique
 - 1a. Quantify pH, organic matter, soil metal speciation
2. Evaluated prevalence of metal-resistant microbes via plate counting

Results:

- Curves for C-mineralization vs. time soil samples varied
- Soil containing the highest Cu concentration did not have the highest lag period (LP)
 - Total Cu concentration insufficient in predicting toxicity
- No direct relationship between LP and pH – evidence for sensitivity and specificity
- Correlation between Cu^{2+} and LP is high at each site
 - Better predictor for toxicity (than total Cu) when comparing sites

Key Findings:

- Copper contamination affects C-mineralization processes 50 years after the introduction of copper to the soil.
- Evidence to suggest lag period is the most sensitive indicator of copper contamination.
 - Not affected by pH, organic matter, or soil humidity
 - Increase LP = increase copper contamination
- LP of Cu^{2+} ions (incorporate OM and pH) is a better indicator of copper contamination than total copper as it accounts for bioavailable copper.
 - Total copper speciation influenced by pH and organic matter – overall adsorption capacity. Total copper concentration does not take physicochemical characteristics into account.
 - Metal ions can be used to compare heavy metal concentrations across sites.
- Max mineralization rate best associated with soil organic matter content (directly influenced). Toxic metals reduced the mineralization rate.

Sulfate reduction and copper precipitation by a *Citrobacter* sp. isolated from a mining area

Qiu, R., Zhao, B., Liu, J., Huang, X., Li, Q., Brewer, E., ... & Shi, N. (2009). Sulfate reduction and copper precipitation by a *Citrobacter* sp. isolated from a mining area. *Journal of Hazardous Materials*, 164(2-3), 1310-1315.

Background:

The mining industry is known to create waste in the form of acid mine drainage (AMD). AMD is a metal-rich leachate formed when sulfides in mining waste are oxidized into metal-sulfides upon exposure to water and air. Efforts to reduce the toxicity of AMD include pH neutralization (using lime to raise pH) to form heavy metal precipitates. A more cost-effective approach has been proposed to use sulfur-reducing bacteria (SRB) to biologically reduce sulfur

into hydrogen sulfide and carbon dioxide as a byproduct (anaerobic conditions). Hydrogen sulfide increases pH, thus neutralizing AMD; at a neutral pH, hydrogen sulfide is insoluble and can be extracted from the liquid medium.

Mission:

1. Evaluate the sulfur-reducing ability of a sulfate-reducing strain of *citrobacter* sp.
2. Assess its suitability as an AMD treatment

Method of analysis:

1. Sediment samples collected from the top layer of sediment from a river exposed to acid mine drainage.
2. Samples prepared under anaerobic conditions (normal conditions).

Results:

- pH increased in anaerobic and aerobic conditions from DBM growth – carbon source oxidation.
- Anaerobic conditions yielded fast sulfate reduction
- DBM growth triggered a decrease in Cu and sulfate concentration (sulfate □ reduced to sulfide).
- Sulfate reduction stopped when [Cu] over 0.6mM

Key Findings:

- Strain DBM facultative anaerobe
 - Anaerobic – sulfate reduction release CO₂ → increase pH
 - Aerobic – lactate oxidation release CO₂ → increase pH
- Heavy metals compete for active sites on cells, interfering with enzyme activity in AMD where DMB ceases to reduce sulfate into hydrogen sulfide and metal sulfide.

Speciation of zinc and copper in stormwater pavement runoff from airside and landside aviation land uses

Gnecco, I., J. J. Sansalone, and L. G. Lanza. "Speciation of zinc and copper in stormwater pavement runoff from airside and landside aviation land uses." *Water, Air, and Soil Pollution* 192, no. 1 (2008): 321-336.

Background:

Urban rainwater runoff can accumulate high concentrations of heavy metals, thus posing a significant threat to receiving waters. The toxicity of copper relies on metal partitioning between the aqueous and particulate phase as speciation impacts both the biological cycle (accumulation, availability) and geochemical processes (transport, adsorption/absorption, precipitation). Metals present in the particulate phase are considered chronic toxicity sources due

to their ability to transform into the aqueous phase. Metals in the aqueous phase can take on the form of an acid through their ability to complex with anywhere from four to eight water molecules. Hydrated metal ions can then complex with organic or inorganic ligands via substitution of the complexed water molecule. Therefore, it is vital to assess speciation in runoff waters in order to predict toxicity effectively.

Mission:

1. To study the effects of pavement (impervious) on the relationship between rainfall and runoff in aviation and port environments.

Coupled build-up and wash-off pollutant load?
Influence metal speciation?

Method of analysis:

1. Characterize the runoff from two aviation land-use catchments – assess hydrology and water chemistry.

2. Determine zinc and copper speciation in relation to hydrology.

3. Assess the influence of hydrology and land use activity on pollutant wash-off.

Results and Key Findings:

- Predominant carbonate copper complexes at the airside site (TSS mass limited)
65-85% CuCO_3 . Next dominant species: free Cu^{2+}
- Acidic environment and ligand deficient – airside site
- Lower pH values at the landside site due to asphalts' inability to buffer acidic rainfall compared to concrete— complexation at landside site reduced.
- Delivery of free copper ions proportionate to runoff volume.

Root-induced changes in pH and dissolved organic matter binding capacity affect copper dynamic speciation in the rhizosphere

Bravin, Matthieu N., Cédric Garnier, Véronique Lenoble, Frédéric Gérard, Yves Dudal, and Philippe Hinsinger. "Root-induced changes in pH and dissolved organic matter binding capacity affect copper dynamic speciation in the rhizosphere." *Geochimica et Cosmochimica Acta* 84 (2012): 256-268.

Background:

Metal contaminant bioavailability is influenced by root-induced physical-chemical factors, such as pH and sorbents in the solid-phase (SPOM/oxides) and aqueous phase (DOM). DOM's binding affinity and concentration are inversely related to the amount of free copper (Cu^{2+}) in a solution. In addition, the binding affinity of DOM is dictated by the pH of the solution at a given time (increase in pH = higher binding affinity).

Copper bioavailability must be assessed at the soil-root interface (rhizosphere), where the plant organism can absorb the contaminant via physiological processes. Plants absorb copper as free copper ions at the soil-root interface in more significant amounts than present in the soil, suggesting that copper in labile pools (complexed but have the potential to re-mobilize) is a source of re-supply to the rhizosphere. The concentration of copper in labile pools and its diffusion through the soil factor kinetics into metal speciation and can be referred to as **dynamic speciation**.

Mission:

1. Study the effects of root-induced pH and DOM changes on copper dynamic speciation at the soil-root interface.

Method of analysis:

1. Plants were grown in soil samples over a wide range of pH.
2. Root-induced chemical changes were measured by comparing each trial to the control.
3. Mobile copper (Cu^{2+}) and DOC were then quantified.

Results and Key Findings:

- Durum wheat roots induce changes to pH (through alkalization increase up to 2.8 pH).
 - Alkalization is a plant survival mechanism that reduces the toxicity of manganese and aluminum.
- Durum wheat roots cause an increase in DOM concentration as rhizodeposition (waste excretion) increase enhances microbial activity (SOM turnover).
- Copper lability decreases with increasing pH. Increase ability = increase in plant uptake.
- Quantity and binding properties of DOM (root-induced change through alkalization and rhizodeposition) influence Cu speciation to a greater extent than pH.

Bioremediation of copper-contaminated soils by bacteria

Cornu, Jean-Yves, David Huguenot, Karine Jézéquel, Marc Lollier, and Thierry Lebeau. "Bioremediation of copper-contaminated soils by bacteria." *World Journal of Microbiology and Biotechnology* 33, no. 2 (2017): 1-9.

Background:

Copper is necessary for the survival of living organisms in trace amounts and is typically present in the soil at concentrations ranging from ~13-24 ppm. Copper that is naturally present in the soil as a result of soil formation on igneous rocks (higher [Cu])/sedimentary rocks (lower [Cu]) has a greater affinity for the solid phase and has a high partitioning coefficient (K_D). Conversely, copper present in the soil due to anthropogenic activities has a greater affinity for the aqueous phase (increased bioavailability). Consequently, plants have evolved to perform

survival strategies in the face of dangerous metal concentrations to either tolerate or resist these contaminants. Such tolerance can be enhanced by the presence of specific bacteria and can ultimately be used as a natural way to reduce the toxicity of contaminants in the soil.

Mission:

1. This article is a thorough review of the processes involved in the mobilization and immobilization of copper by bacteria in the soil.

Metal immobilization

Biosorption:

- Metabolically independent
- Utilizes ion exchange, surface complexation, physical adherence
 - Ion exchange prominent (metal ion and negative cell wall)
 - In bacteria, functional groups lose a proton, which are then sites open to fix Cu^{2+}
 - pH influences ion exchange
 - Increase pH = increase (-) charged sites on cell wall
- Bacteria excrete exopolysaccharides (EPS) to recover nutrients that can sorb metal ions (high-affinity Cu)

Bioaccumulation:

- Metabolism dependent
- Absorption of Cu ions at a faster rate than excreted

Biomining:

- Bacteria can supersaturate localized positions on the cell wall, which causes metal ions to precipitate with anions released when exposed to the cell wall (ex. phosphate).
- Metal ions (Cu^{2+}) can be incorporated into the lattice of microbial-induced precipitates via substitution.

pH:

- Bacteria can enhance alkalization, increasing the pH of the soil by +2 pH units
- Indirect immobilization

Metal mobilization, in-situ

Microbes oxidize structural components of minerals and decrease the pH of the soil.

Redoxolysis

- Specific bacteria use electrons from immobilized, solid compounds involving metal as a source of energy.
- The metal is oxidized and thus mobile.

Acidolysis

- Microbes can secrete protons that exchange for metals bound to mineral surfaces.
 - Protons are secreted via nitrification and sulfur oxidation

Complexolysis

- Microbial chelators complex with metals on the surface of minerals and the mineral lattice (solid phase).

Metal mobilization, ex-situ

Bioleaching

- Microorganisms used to extract metals from solid-phase matter.
- Chemolithotrophic bacteria can mobilize metals via acidolysis and redoxolysis
 - Sulfide-rich material at low pH
- Heterotrophic bacteria mobilize Cu^{2+} in glass/slugs by releasing organic acids/polysaccharides
 - Low yield

Leaching behavior of copper (II) in a soil column experiment

Xu, J., X. Han, S. Sun, F. Meng, and S. Dai. "Leaching Behavior of Copper (II) in a Soil Column Experiment." *Bulletin of Environmental Contamination & Toxicology* 75, no. 5 (2005).

Background:

Heavy metals in industrial sludge can percolate through the soil to groundwater – a process referred to as solution elution (removal of adsorbed metal by washing with solvent). Wastewater irrigation transports heavy metals to groundwater at a faster rate than industrial sludge percolation as wastewater metals are already in the aqueous phase. However, the concentration of percolated heavy metals depends on their adsorption through the column.

Mission:

1. Assess Cu^{2+} migration through a soil column
2. Evaluate the influence of different leaching solvents on copper migration

Method of analysis:

1. Concentration of Cu in leachates quantified using DIW (DI water, Millipore Ultra-Pure Water System), TCLP (Toxicity Characteristic Leaching Procedure), SPLP (Synthetic Procedure Leaching Condition), and DOC as solution elutions in soil columns at consistent pH of 7.11 at varying volumes.
2. Concentration of Cu in leachates quantified at different depths using the same solutions for elution to assess vertical distribution.
3. Concentration of Cu in leachates at varying pH 1,3,5,7,9 vs soil depth and cumulative volume.

Results and Key Findings:

- Eluent type has an effect on percolation rate.
- SPLP increases the rate of percolation through a soil column – greater risk to groundwater.
 - SPLP simulates rainfall conditions—transport chemicals from recycled waste to groundwater.
- Cu leaches at higher concentrations at the beginning of eluent exposure (50mL) than final concentrations (400 mL).
- [Cu] decreases with increasing soil depth.
- Cu retention high in DOC exposed soils (metal-DOC complex) – reduce mobility.
- Increase pH = decrease copper mobility (adsorption, ion exchange, precipitation).

Retention of copper by a calcareous soil and its textural fractions: influence of amendment with two agroindustrial residues

Rodriguez-Rubio, P., E. Morillo, Luis Madrid, T. Undabeytia, and C. Maqueda. "Retention of copper by a calcareous soil and its textural fractions: influence of amendment with two agroindustrial residues." *European Journal of Soil Science* 54, no. 2 (2003): 401-409.

Background:

Copper retention in the soil is dictated by physicochemical properties that lead to adsorption, complexation, and precipitation changes. The adsorption processes (occurring more often at small concentrations) and precipitation (dominating at large concentrations) occur naturally between heavy metals and calcium carbonate surfaces. When copper is present in calcareous soils, it is often precipitated out as carbonate or hydroxide. Calcium carbonate is positively correlated to copper retention in the soil and has a greater influence on retention than pH alone. Immobile copper is most abundant in the upper 15 cm of soil.

Mission:

1. Copper has a strong binding affinity for organic matter. This study aimed to evaluate the influence of calcium carbonate particle size on copper retention and release by the soil.

Method of analysis:

1. Amendments (composted olive mill sludge (A) and vinasse (V)) were added to topsoil and treated each year with either A or V, and radish was planted within the soil for a total of 3 years.
2. Soils were further dried, homogenized, and sieved for analysis after the 3 years.
3. Soil samples were analyzed for particle-size distribution, organic matter content, pH, total carbonate content, and cation exchange capacity.

Results and Key Findings:

- Calcareous samples: silt, clay, and sand fractions
 - no desorption
 - sorption was higher in V and even higher when A was added
 - sorption highest on silt fraction
 - high in quartz, calcite, organic matter, and carbonate
 - 2x the amount of carbonate as clay/sand fractions
 - no pH change → carbonate acts as buffer
 - Clay fraction: add carbonate = increases adsorption
- Addition of A
 - metal sorption increased to greater extent than addition of V
 - Higher organic matter content than V
 - increase calcite content in silt fraction
 - No desorption → high carbonate content
- Addition of V
 - increase metal sorption (not due to pH change)
 - increase organic matter content
 - increased calcite content in clay fraction
 - Cu desorption in clay double than unamended clay
 - lower pH from V addition
- Carbonate-free samples
 - adsorption lower than carbonate containing soil
 - metal retained on carbonate surface
 - enhance copper mobility
 - increase adsorption=increase desorption
 - strong adsorption = small surface area covered

CONTAMINANT SOURCES, TRANSPORT, AND FATE IN STORMWATER RUNOFF IN CHRISTCHURCH

Wicke, Daniel, Tom Cochrane, and A. D. O'Sullivan. "Contaminant sources, transport and fate in stormwater runoff in Christchurch, New Zealand." (2010).

Background:

Copper from brake linings can accumulate on the pavement and take on both mobile and immobile forms (sediment and particulate matter). Stormwater transports copper and other heavy metal contaminants to urban waterways in high concentrations and poses a threat to aquatic life in these waterways.

Mission:

1. To produce a model that can be used to efficiently quantify contaminant sources and their spatial variability as a function of wash-off and surface roughness.

Method of analysis:

1. Thin constructed boards of varying material (concrete or asphalt) were arranged in a grid in an urban catchment consisting of roads, paths, and carparks.
2. The boards were exposed to rainfall and traffic and then placed in a rainfall simulator to quantify wash-off rates and runoff concentration.

Results and Key Findings:

- Higher copper and TSS wash-off concentrations on concrete boards than asphalt
Concrete = smoother
 - Asphalt = higher retention
- Spatial variability of copper among the same type of board in close proximity
 - Factors that influence this include age of the cars on the board, number of cars, parked vs empty boards during rainfall, etc.

Spatial distribution, mobility and bioavailability of arsenic, lead, copper and zinc in low polluted forest ecosystem in North-western Mexico

Roque-Álvarez, Isela, Fabiola S. Sosa-Rodríguez, Jorge Vazquez-Arenas, Miguel A. Escobedo-Bretado, Israel Labastida, José Javier Corral-Rivas, Antonio Aragón-Piña, Ma Aurora Armienta, Patricia Ponce-Peña, and René H. Lara. "Spatial distribution, mobility and bioavailability of arsenic, lead, copper and zinc in low polluted forest ecosystem in North-western Mexico." *Chemosphere* 210 (2018): 320-333.

Background:

Copper contamination to forest soils by anthropological activity can negatively affect the protection forests provide for biodiversity. These contaminants are bioavailable for uptake by pine and oak trees given proper physicochemical conditions. However, little research has been

conducted on these contaminants' mineralogy (chemical behavior), mobility, and bioaccumulation in a low polluted forest.

Mission:

1. Understand the pollution process in low polluted forest ecosystems.

Methods:

1. Spatial analysis of copper concentrations in pine stem wood, pine foliage, and soil.
2. Evaluate the relationship between copper concentration in the soil and mobility and bioavailability using a systematic approach to assess the distribution of copper from low-heavy polluted ecosystems and their influence on bioaccumulation.

Results and Key Findings:

- Copper Oxide-like compound (5-10 um) only copper compound identified in forest ecosystem.
 - Solubility higher than other copper sulfides
 - Distribution of CuO nanoparticles in depth soil profiles
 - Mineral phase → potential chemical weathering and biological oxidation
 - Greater concentration in surface soil
 - Accumulation is also due to complexation with primary sulfides
 - General low mobility
 - Ability to form stable metal-organic complex
- Forest elevation had no effect on spatial distribution.
- Background copper levels above 24 ppm are due to pollution and can be toxic to the ecosystem.
- Bioaccumulation of copper found to be <4 ppm
 - Resembles bioaccumulation in heavily polluted forests
 - Phytotoxic bioaccumulation levels are 3-30 ppm
 - Significant bioaccumulation despite sluggish mobility

Pesticidal copper (I) oxide: environmental fate and aquatic toxicity

Kiaune, Lina, and Nan Singhasemanon. "Pesticidal copper (I) oxide: environmental fate and aquatic toxicity." *Reviews of Environmental Contamination and Toxicology Volume 213* (2011): 1-26.

Background:

Copper oxide is an effective biocide that has become increasingly popular since the late 1980s. It is evident that the increasing use of copper in the environment can accumulate and pose a threat to non-target organisms in the water. Copper primarily exists as Cu (II) in water but can transform into Cu (I) or a solid (elemental form) based on how copper oxide's physicochemical

properties interact with the water's pH and organic content. Copper oxide is only soluble in strong acids, ammonium hydroxide, and aqueous ammonia.

Environmental Fate in Surface Waters

- Copper oxide dissociates in water → prevalent as Cu (II), which has the greatest influence on toxicity
 - Dissolved Cu = pass through 0.45 um filter pore size
- Cu (II) can adsorb to both dissolved molecules and particulate matter → strong interaction between Cu (II) and dissolved matter.
- Total dissolved copper (TDCu) = labile copper and copper bound to organic ligands (DOM/DOC).
- Organically complexed Cu = sources can be natural (humic/fluvic substances) or anthropogenic (EDTA/NTA)
 - Includes bioavailable copper and nonbioavailable copper.
 - Ligands can be weak or strong
 - Weak binding affinity $\sim 10^9$
 - Strong binding affinity $\sim 10^{13}$
- Labile copper (LCu) = Cu (II) and Cu bound to inorganic ligands
 - Bioavailable

Environmental Fate in Freshwater

- Least studied
- Each freshwater location has a different geochemistry, which has a great effect on the water's characteristics
 - Water properties (pH, hardness, alkalinity) affect speciation, and this changes from location to location.
- Copper speciation is primarily dependent on Cu bound to organic ligands
 - 99.99% TDCu bound strongly to organic ligands (organic ligand concentration higher than TDCu).
 - Organic ligand binding stability/affinity = above 10^{13}
 - Higher affinity for copper than other metals → copper-specific ligand?
- pH significantly affects copper speciation
 - Low pH = Dissolved
 - High LCu
 - High pH = particulate form
- Alkalinity = “capacity to neutralize strong acids”
 - HCO₃⁻ and CO₃²⁻
 - Carbonate-buffered water
 - High pH, CuCO₃ predominant species
- Water hardness = Ca²⁺ and Mg²⁺ ion concentration
- Alkalinity and water hardness have a direct relationship
- Copper is toxic in soft, less alkaline water
 - Bioavailable

Copper Speciation in Sediment

- Sediment pore water = water that fills gaps between sediment grains
- Accumulation of heavy metals can remobilize in sediment pore water
- Copper speciation is influenced by diagenetic processes (chemical, physical, biological process affecting sedimentary material) and oxygen levels/temperature.
 - Break Cu-POM complexes
 - Oxygen influences whether copper is precipitated out or recycled into water column.
 - Oxidic conditions (0-2 cm) = copper recycling
 - Anoxic conditions (2-15 cm) = copper precipitation
 - Temperature -- changes oxygen levels
 - Higher temperatures = more copper is precipitated out of pore water into sediment
 - Colder temperatures = more copper is accumulated in the sediment
 - Sediment type -- varying surface area
 - finer sediments = higher surface area, greater adsorbance

Copper Speciation in Soil

- Copper speciation is influenced by pH, organic and inorganic content.
- Copper accumulates in upper 15 cm of soil (topsoil).
- Copper speciation is strongly associated with organic matter content
 - Direct adsorption → inner sphere complexation
 - Copper distribution = not uniform
- Researchers have not yet agreed on the determinant in calcareous soils yet
 - Organic matter adsorption vs. precipitation as CuCO_3
- Copper transport influenced by soil pH

The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada

Hutchinson, T. C., and L. M. Whitby. "The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada." *Water, Air, and Soil Pollution* 7, no. 4 (1977): 421-438.

Background:

Rain in Sudbury, Canada, near nickel-copper smelters, has been profoundly acidic due to the constant release of sulfur dioxide into the air. Researchers have inferred that acid rainfall alone is unlikely to result in acidic soil less than pH 3 under the soil's standard buffering

capacity. However, the impact of acid rainfall coupled with heavy metal accumulation in the soil has not been thoroughly documented.

Mission:

1. Evaluate the coupled effect of heavy metals and acid rainfall on naturally acidic soil.

Method of analysis:

1. Soil, vegetation, and rainfall samples were collected from 25 uninhabited hilltops 100 m from the main roads to mitigate confounding variables (i.e., glacial contamination, traffic).
2. Vegetation samples were mixed and washed with detergent, rinsed 5x in Di water, and dried at 60 degrees Celsius.
3. Rainfall samples for metal analysis were collected in polyethylene containers and treated with nitric acid to prevent metal deposition.
4. Soil samples for pH analysis were mixed 1:1 water to soil
 - 4a. Soil samples for conductivity analysis were mixed 2:1 water to the soil.
 - 4b. Soil samples for metal analysis were dried, sieved through 0.2 mm mesh, homogenized, digested using sulfuric and nitric acid, diluted, and analyzed via atomic absorption spectrophotometry (AAS).
5. Soil-water extracts were made by filtering a 1:3 soil to Di water ratio.

Results and Key Findings:

- pH increased with increased distance from smelters (measured for total and available Cu content)
Caused by dry (wind) and wet precipitation of sulfur dioxide in air
- pH increased with increasing depth
- Conductivity and sulfur concentration decreased with increased distance from smelters
- Profoundly acidic rainfall
- Copper deposited/rescrubbed in higher concentrations closer to the smelter
- Copper particulates dispersed over a greater range during dry periods
- Copper transport into the soil is significantly impacted by acid rainfall
Acidity leads to copper mobility = more toxic
- Long-distance dispersal of metal particulates
- Copper concentration in foliage decreased with increased distance from smelters
- Chain of effects caused by smelters induce conformational changes in organic matter
 - With respect to fulvic acid, sulfur replaced C atoms in -COOH and phenolic -OH groups. S=O then dictates the behavior of the benzene ring and there are changes to fulvic acids ability to act as a nutrient reservoir.

Size-dependent toxicity of metal oxide particles—A comparison between nano- and micrometer size

Karlsson, Hanna L., Johanna Gustafsson, Pontus Cronholm, and Lennart Möller. "Size-dependent toxicity of metal oxide particles—a comparison between nano- and micrometer size." *Toxicology letters* 188, no. 2 (2009): 112-118.

Background:

Particulate matter (PM) in the air ranges in size from fine particles (<2.5 μm) to ultrafine particles (nanoparticles <100 nm). While fine particles contribute to the bulk of PM mass in the air, ultrafine particles are present in larger quantities. Nanoparticles have a larger surface area to mass ratio and often have a different chemical composition than their fine particle counterparts. Particles inhaled into the lungs of humans can be toxic, where toxicity is influenced by particle size.

Mission:

1. Metal oxides in the air have been shown to cause oxidative stress. The purpose of this study is to evaluate the effect of CuO particle size on the severity of oxidative stress by monitoring mitochondrial and DNA damage.

Method of analysis:

1. Expose a human epithelial cell line (A549) to micrometer and nanometer CuO of the same composition and note differences in cell death, mitochondrial and DNA damage, and oxidative DNA lesions.

Results and Key Findings:

- Nonviable cell, mitochondrial depolarization, and DNA damage percentage from highest to lowest: exposed to CuO nanoparticles (40 $\mu\text{g}/\text{cm}^3$), exposed to CuO fine particles (40 $\mu\text{g}/\text{cm}^3$), control.
- Cells exposed to lower concentrations (20 $\mu\text{g}/\text{cm}^3$) had an increased percentage of nonviable cells.
- Mitochondrial depolarization dose-response curves from 5-40 $\mu\text{g}/\text{cm}^3$ CuO show significant dose-response patterns.
- Nanometer CuO particles can cause oxidative stress (indicated by oxidative DNA damage).

Long-Term Reactions of Copper(II) in a Contaminated Calcareous Soil

McBride, M. B., and D. R. Bouldin. "Long-term reactions of copper (II) in a contaminated calcareous soil." *Soil Science Society of America Journal* 48, no. 1 (1984): 56-59.

Background:

Copper contaminated soils that harbor low concentrations of soluble/chemically extractable Cu^{2+} initially can still pose a toxicity threat. Changes to the physicochemical

properties of the soil, through incubation specifically, can lead to an increase in extractable Cu^{2+} . Long-term copper contaminated soils consist of copper found in the readily-extractable form, often bound to organic matter.

Mission:

1. Observe the long-term changes to Cu speciation in calcareous soils that were highly contaminated 50 years ago.

Method of analysis:

1. Measure total and free Cu^{2+} in water extracts from topsoil without maintaining consistent pH.

Results and Key Findings:

- Over half of total Cu was able to be extracted by chemical agents that work to dissolve inorganic and organically complexed metals.
- The highest percentage of total copper was found in the complexed form.
- Copper adsorbed in the soil = abundantly to inorganic matter.
- Copper in soil solution = abundantly complexed to organic matter.
- Decrease soil pH = increase free copper in soil solution (not significant).

Redox Speciation of Copper in Rainwater: Temporal Variability and Atmospheric Deposition

Kieber, Robert J., Stephen A. Skrabal, Cliff Smith, and Joan D. Willey. "Redox speciation of copper in rainwater: Temporal variability and atmospheric deposition." *Environmental science & technology* 38, no. 13 (2004): 3587-3594.

Background:

Copper is a trace element found in the atmosphere that directly influences redox potential in the troposphere (lowest region of atmosphere). Copper plays a role in the conversion of sulfur dioxide to sulfur trioxide, a highly reactive compound that increases the acidity of the troposphere. It is imperative that copper in atmospheric water is measured in terms of its speciation to integrate the influence of speciation on the level of reactivity.

Mission:

1. Evaluate the role of time and seasons on total copper, total dissolved Cu (II), and total dissolved Cu(I) in rainwater.
2. Evaluate the impact of anthropological activities on copper speciation in rainwater.
3. Evaluate the effectiveness of rainwater and wet deposition as a method of atmospheric Cu removal.

Method of analysis:

See article for methodology

Results and Key Findings:

- Rainwater total Cu levels are lower than fog and cloud water since Cu in the clouds is diluted when they are formed into rain droplets.
- 25% of total Cu is present in the Cu(I) form in rainwater, which is significantly lower than that in fog and cloud water.
 - Large abundance of Cu(I) due to rainwater's reducing environment
 - Can attribute to either photoreduction or H₂O₂ acting as reducing agent
- Total dissolved Cu concentrations > strong ligand concentrations
 - Not all dissolved Cu can be complexed
- The effect of Cu speciation on the redox potential of the troposphere depends on how long Cu exists in precipitation
 - Thermodynamically theorized, dissolved Cu in rainwater most abundantly present as Cu (II). However, the presence of Cu(I) shows that Cu (II) is reduced and stabilized via oxidation or complexation with stabilizing ligands (prevent oxidation and maintain levels of Cu (I) in rainwater).
- Total dissolved Cu (II) is higher than total dissolved Cu (I) in the summer months (June to September).
 - Cu (I) oxidation to Cu (II)
- Total dissolved CU (I) is higher than total dissolved Cu (II) in the winter months (December to February).
 - Cu (II) reduction to Cu (I) caused by increased production of oxidizing agents.
- Total dissolved Cu is not affected by season.
- Cu concentrations are higher in storms of continental origin, rather than coastal origin, due to anthropological activity.
- Increased rainfall (diluted)= increased Cu washout from atmosphere

Distribution of lead, copper and zinc in size-fractionated river bed sediment in two agricultural catchments of southern Ontario, Canada

Stone, M., and I. G. Droppo. "Distribution of lead, copper and zinc in size-fractionated river bed sediment in two agricultural catchments of southern Ontario, Canada." *Environmental Pollution* 93, no. 3 (1996): 353-362.

Background:

The mobility of copper through pore water and the water column found in riverbed sediment is dictated by the size and texture of sediment particles. Particle size influences both the percolation and deposition rate of suspended solids in the water. There is typically an inverse relationship between the concentration of heavy metals and grain size, where a high concentration is associated with a small grain size.

Mission:

1. This study focuses on riverbed sediments in agricultural watersheds as a reservoir for toxic levels of heavy metals. This study aims to evaluate copper partitioning in sediment of varying grain size.

Method of analysis:

1. Sediment surface samples from two different catchments were collected and analyzed for particle size (2, 10, 15, 24, 38 and 45 μm) and separated.
2. Copper contaminated solutions were passed through specific particle size columns so that the Cu present in the leachates could be quantified.

Results and Key Findings:

- Organic matter predominantly accumulates in the $<8 \mu\text{m}$ size fraction
 - Increase grain size = decrease concentration
 - Influence copper mobility through complexation
 - 50% Cu bound to organic matter in $<12 \mu\text{m}$ size fraction
- Copper complexes with carbonates in the three largest size fractions in the summer.
 - Less Fe/Mn and organic matter competition.
- Copper is most abundant in the 8-12 μm size fraction of one creek and $<8 \mu\text{m}$ size fraction of the other creek.
 - Increase grain size = decrease copper concentration
- Sediment transported from storms is most abundant in particle sizes smaller than 63 μm .
 - Sediment less than 31 μm accounts for 80% of this yield
 - Vector for copper transport
- Small particles = high metal concentrations = longer time in the water column
- Copper transport in the exchangeable form is not influenced by grain size
- pH has a greater effect on Cu mobility than grain size

