

### ***Supplemental information:***

*Table 1. Field Surrogate Spiking Protocol – Incubation & Lysimeter Trials 2020*

|  |
|--|
| <p><u>Materials:</u></p> <ul style="list-style-type: none"> <li>- 15 mL centrifuge tubes (for soil and crop samples)</li> <li>- 50 mL centrifuge tubes (for urine samples)</li> <li>- 500 mL amber glass bottles (for water samples)</li> <li>- Sulfuric acid (for water samples)</li> <li>- 250 µL syringe</li> <li>- 250 µg/L spiking mix (made and supplied by UB)</li> <li>* Please store upright in coldest freezer available (-20 °C) with parafilm wrap to prevent evaporation</li> <li>*Spiking mix used is not toxic - though it is not encouraged to spike without proper PPE, the mix does not contain dangerous substances, and the concentration is well below the average daily dose</li> <li>- 2 mm sieve</li> <li>- Methanol for syringe wash</li> </ul>   |
| <p><u>Syringe Protocol:</u></p> <p><i>Note:</i> It is important to do all the spiking samples at the same time, and not be interrupted or stop in the middle of this process. Prepare all of the samples to be spiked before you start. Don't talk to someone when they are spiking!</p> <p>If you forget whether you have spiked something, it is better to double-spike than not at all – Please take note of possible discrepancies</p> <ol style="list-style-type: none"> <li>1. Take spiking mix out of the freezer and allow it to reach room temperature. Variation in temperature through the spiking process can affect concentrations. Once finished, place back in the freezer. Using a pipette, remove an aliquot of the surrogate spike that will cover the day's samples + some extra, and place in a 15 mL centrifuge tube. Always replace the cap immediately when not actively spiking.</li> <li>2. Prepare 3 methanol wash tubes (3, 15 mL wash tubes should last through the season)</li> <li>3. Prior to use, wash the syringe by drawing methanol to the full volume of the syringe (past the 250 mark) then discarding the methanol to waste. This should be done in each wash tube in triplicate, a total of 9 washes. There should be no air bubble in the syringe when washing.</li> <li>4. With the syringe, draw up a small amount of air (~5 µL in the 250 µL syringe is sufficient) followed by drawing up the spiking mix. This air pocket helps to accurately read the syringe to the correct spiking volume, as well as to fully dispel the mix from the syringe and into the sample.</li> <li>5. When expelling the liquid, do so in one fluid motion rather than drips or starting and stopping.</li> <li>6. Tap the top of the syringe several times to knock off the drop that forms on the tip when expelling. If the syringe comes in contact with the sample or the sample tube please repeat the methanol washing process.</li> <li>7. Finally, after all samples are spiked, rewash the syringe using the same procedure as step 2.</li> <li>**The syringe does not need to be washed in between each sample if it remains clean. If the syringe touches the sample or is otherwise contaminated, please rewash using the same procedure.</li> <li>8. The syringe may be placed down on a clean/sterile paper towel in between samples, to allow for re-capping and opening tubes.</li> </ol> <p><b>** Spike volume for all samples = 200 µL with a 250 µL syringe of 250 ppb spiking mix (1ppm for</b></p> |

|   |
|---|
| urine)**  |
| <p><u>Soil:</u><br/> <i>Optimized extraction mass (dry weight) = 1.0 g</i><br/> <i>Approximate soil moisture content = 21%*</i><br/> <i>Wet weight required = 1.21 g +/- 5%</i></p> <ol style="list-style-type: none"> <li>1. Sieve soil using a 2 mm sieve (this is for field soil samples in lysimeter trial only; incubation soil was 2 mm sieved prior to setting up the experiment)</li> <li>2. Stir soil (for incubation) 20 times with flat spatula</li> <li>3. Weigh 15 mL centrifuge tube empty without cap and record the weight</li> <li>4. Weigh 1.21 g (+/- 0.05g) of wet soil into centrifuge tube and record the weight</li> <li>5. When all samples have been prepared and are ready for spiking, spike in <b>200 µL of 250 ppb spiking mix</b> (100 ppb final concentration) to each sample using the syringe. It is ok to leave the cap off the surrogate container during spiking. Only replace it if you need to clean the syringe frequently, to prevent excessive evaporation.</li> <li>6. Once spike is added, please recap the sample and agitate from side to side. Avoid allowing the sample to come in contact with the cap as this causes loss of sample to the cap. Once the sample is visibly homogenized (roughly 10 shakes from side to side) you can move onto the next sample.</li> <li>7. Place sample upright on ice or in the freezer prior to shipment.</li> </ol> <p>*Sample weight is based on soil moisture, so the wet weight of the sample must be calculated for each sampling time using the current soil moisture level. This will always be 21% for the incubation but may be different for the lysimeter samples;</p> |
| <p><u>Crop:</u><br/> <i>Optimized extraction mass (dry weight) = 250 mg</i><br/> <i>Approximate moisture content = 95% (carrot is 88% moisture)</i><br/> <i>Wet weight required = 5g</i></p> <ol style="list-style-type: none"> <li>1. Grind lettuce</li> <li>2. Weigh empty 15 mL centrifuge tube without cap and record</li> <li>3. Weigh 5g (+/- 0.05g) of ground crop into the pre-weighed tube and record weight</li> <li>4. Using syringe, spike in <b>200 µL of 250 ppb spiking mix</b></li> <li>5. Close tube and shake sample side to side to homogenize and incorporate. Tubes should be shaken for approx. 1 minute. Do not let the sample touch the cap of the tube.</li> <li>6. Store samples upright on ice or in freezer prior to shipment</li> </ol>  |
| <p><u>Water Samples:</u><br/> <i>Optimized extraction volume = 500 mL</i></p> <ol style="list-style-type: none"> <li>1. Collect water in 500 mL amber vials, filling but careful to not overfill</li> <li>2. Spike in <b>200 µL of 250 ppb spiking mix</b> (spike can be before or after acid)</li> <li>3. Acidify to pH <math>2 \pm 0.2</math> using sulfuric acid (estimated ~1 mL)</li> <li>4. Store upright in on ice or in fridge prior to shipping</li> </ol>   |
| <p><b>Shipping note:</b><br/> - All samples must be shipped upright</p>   |

Figure 1. Soil dissipation study design:

