

# Characterizing the fate of poorly soluble metal oxide nanoparticles in soils

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## Objectives:

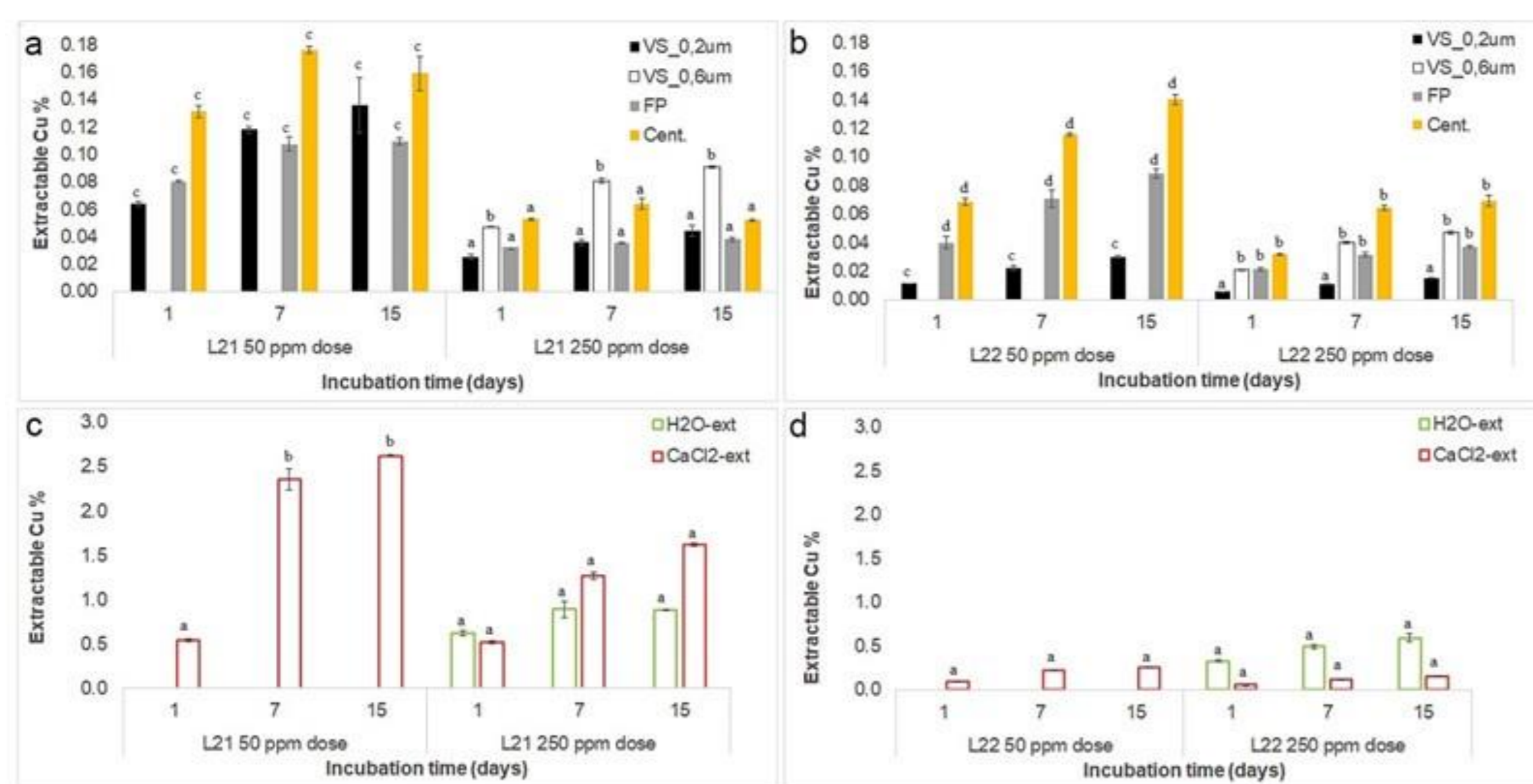
In soil, metal oxide nanoparticles (NPs) can be dispersed in pore water or retained in the soil solid matrix. The accurate characterization of the fate of NPs in soils is crucial for characterizing the complete pool of Cu that may be potentially bioavailable for plants or organisms. **The main objectives of this study were to:**

- Determine the Cu recovery efficiency from soils amended with CuO NPs, using four pore water and soil extraction methods commonly applied in soil metal studies;
- Understand which phases of Cu are recovered from soil using the four methods and assess the advantages and limitations of each method for soil risk evaluations..

Two standard agricultural soils LUFA 2.1 and LUFA 2.2 (loamy sand soil and sandy loam soil respectively) were dosed with either CuO NPs at 50 or 250 mg Cu kg<sup>-1</sup> dw at 50% Water Holding Capacity (WHC).

Pore water collection and analysis of Cu recovery was performed at days 1, 7 and 15 after amendment, using four different methods (Fig. 1):

- 1. Vacuum subsampling** using two membrane filter pore sizes < 0.2 μm, and < 0.60 μm (VS\_0,2um and VS\_0,6um respectively) [1];
- 2. Pressure filtering** using a FANN® filter press pressurized with N<sub>2</sub> at 50 psi for 30 minutes. Extracted solution was filtered with 25 mm, PTFE (0.45 μm) syringe filters (FP);
- 3. Batch soil extraction using CaCl<sub>2</sub> 0.01M or DI-H<sub>2</sub>O** at a 1:10 soil to volume ratio. Supernatant was filtered with 25 mm, PTFE (0.45 μm) syringe filters (CaCl<sub>2</sub>-ext and H<sub>2</sub>O-ext respectively) [2];
- 4. Centrifugation.** Saturated soil (85% WHC) placed on a 10 mL syringe plugged with borosilicate glass wool (pre-moistened with MilliQ water), suspended from the top of a 50 mL centrifuge tube. Centrifugation at 1000 rpm for 8 min the extracted solution was filtered with 25 mm, PTFE (0.45 μm) syringe filters (Cent.) [3].



**Fig. 2** - Percentage of extractable Cu (%wt. relative to total Cu concentration dosed, in dry weight) recovered from soils dosed with CuO NPs at 3 incubation times by: vacuum sampling (VS), filter pressing (FP), centrifugation (Cent.) for soil L21 (a) or soil L22 (b); and, by CaCl<sub>2</sub> 0.01M (CaCl<sub>2</sub>-ext) or distilled water extraction (H<sub>2</sub>O-ext) for soil L21 (c) or soil L22 (d). Different letters indicate statistically significant differences ( $p < 0.05$ ).

## Conclusions:

- Traditional pore water collection methods are efficient to characterize the pool of ionic Cu<sup>2+</sup> dissolved from CuO NPs that partitions into pore water.
- The pool of Cu that is readily available to plant or to soil organisms in soils dosed with CuO NPs (at a concentration up to 250 mg kg<sup>-1</sup>) as determined by pore water extraction is small.
- The use of pore water sampling methods to assess the fate of CuO NPs nanoparticles in soil is associated with a very low recovery of particles and may not be representative of the population of NPs present in pore water or of the pool of Cu that is prone to transport in soils or uptake by plants and organisms.
- The understanding of the potential for remobilization of weakly attached NPs can also be relevant for environmental risk assessment or for testing the efficacy of time-dependent and controlled-release nanoscale fertilizers. Thus, robust methods to characterize this pool of NPs in soil are needed.

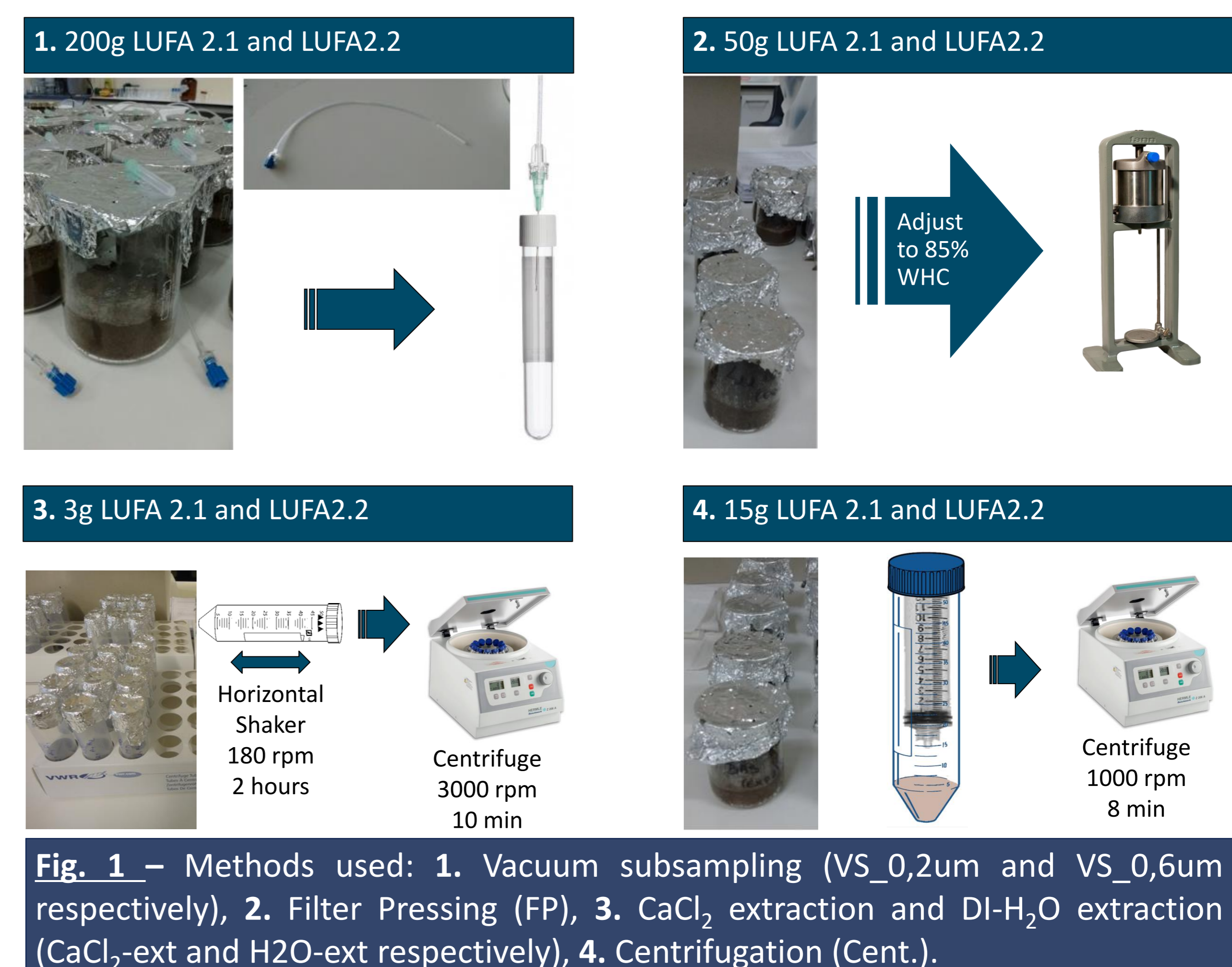
## Acknowledgments:

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## References:

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- [2] Gao et al (2017) Environ. Sci. Technol. 51, 2226–2234. <https://doi.org/10.1021/acs.est.6b04705>
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## Methods and Results:



**Fig. 1** – Methods used: 1. Vacuum subsampling (VS\_0,2um and VS\_0,6um respectively), 2. Filter Pressing (FP), 3. CaCl<sub>2</sub> extraction and DI-H<sub>2</sub>O extraction (CaCl<sub>2</sub>-ext and H<sub>2</sub>O-ext respectively), 4. Centrifugation (Cent.).

**Results obtained (Fig. 2) showed that most of the dosed Cu remained in the solid matrix (> 97%)..**

- Pore water collection recovered low levels of Cu < 0.18 ± 0.01% , regardless of soil type or Cu dose).
- Soil extraction by either CaCl<sub>2</sub> or DI-H<sub>2</sub>O led to higher Cu recovery than pore water collection, but still < 2.6 ± 0.1% of total dose.
- The higher Cu extractability in LUFA 2.1 soil compared to LUFA 2.2, was associated with lower SOM (decreasing Cu retention in the solid phase) and lower pH (increasing the exchangeable Cu concentration).

**The Cu-extractable pool extracted by all methods is representative of the fraction of ionic Cu<sup>2+</sup> in soils that partitions into pore water.**