	Experiment title: Do organic waste treatments alter copper speciation ?	**Experiment number**:
Beamline:	**Date of experiment**: from: 29 October 2020 to: 03 November 2020	**Date of report**: 08/02/2021
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Report:

There is now a global consensus among scientists, economists, politicians and civil society stakeholders on the necessity to recycle resources and close loops in a circular economy. Agricultural recycling makes it possible to effectively and synergistically use livestock, urban and agro-industrial **organic waste** (OW). From a waste management standpoint, composting and anaerobic digestion are the most obvious and operational processes for OW treatment prior to soil application. **Composting** OW is seen as an effective method for reducing the waste volume, eliminating pathogens and creating a stable product suitable for application in crop fields. **Anaerobic digestion** has also significantly increased in several countries and represents an opportunity to convert OW into biogas and organic fertilizer (digestate).
The choice of using either raw OW, compost or digestate as fertilizer and soil amendment should be based on a comprehensive assessment of potential benefits and negative effects. However, the lack of understanding regarding the impact of treatments on contaminant speciation make comprehensive assessments difficult.

Copper (Cu) is a potentially toxic trace element present in large amounts in organic wastes (OWs) spread on agricultural lands as fertilizer. Cu, a growth promoter, is supplemented at low levels in animal diets. Only a small portion of this Cu is metabolised, then a substantial amount of Cu is excreted in the livestock manure, i.e. agricultural OW. Sources of Cu in urban or industrial OW are multiple and difficult to resolve (steel corrosion, contamination by soil particles, etc.)

Cu speciation in OW is a crucial parameter to understand its fate in soil after spreading and to assess the risk associated with agricultural recycling of OW. Here, we conducted a systematic study to investigate the speciation of Cu, a potentially toxic element, in raw and treated OWs sampled in a wide range of full-scale OW treatment plants chosen to represent the most common origins of OW (agricultural, urban, industrial OW) and treatment processes (AD, composting).

The normalization and data reduction is performed according to standard methods using Athena software. The procedure to determine Cu species in the OW samples is based on a combination of principal component analysis (PCA), target transformation (TT), and least-squares linear combination fitting (LCF). PCA and TT is performed using the SIXPack interface to the IFEFFIT XAFS analysis package whereas LCF of the XAFS data will be performed using the Athena software. The data treatment is still under progress but an overview of the first results is presented below.

The Cu K-edge X-ray absorption near edge structure (XANES) spectra for the organic wastes were compared with Cu standards characterized by different Cu oxidation states and ligands (Figure 1). The raw and digestate featured a distinctive rising-edge peak at 8986 eV, similar to CuS. This indicates that Cu^{+1}-sulfides were most likely the predominant Cu species in these OW. Compost showed edge energy and shape similar to that for Cu^{+2}-malate. This indicates that Cu^{+2} in octahedral-like symmetry, surrounded by O atoms in the first coordination shell was predominant in compost.

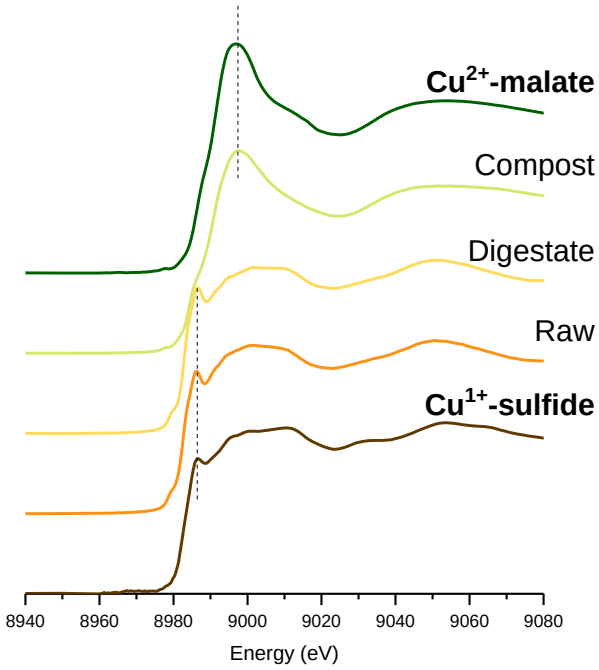
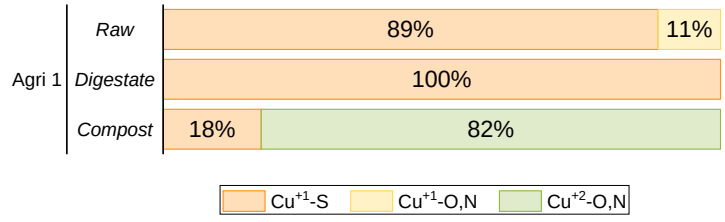


Figure 1. Cu K-edge XANES spectra for Agricultural organic wastes (raw, digestate and compost) and selected references containing Cu^{+1} and Cu^{+2} with different coordination and ligands (sulfide and carboxylic).

Figure 2. Cu speciation determined from the linear combination fitting of the Cu K-edge XANES spectroscopy data.



The first quantitative least square linear combination fitting (LCF) results (expressed as a percentage of each Cu species obtained for agricultural OW are shown in Figure 2.

Cu^{+1}-S speciation was found to be the main Cu species in the raw OWs (89%). The main Cu speciation in the composts was Cu^{+2}-O,N (82%) whereas Cu^{+1}-S speciation was only present as minor species (18%) in composts. This means that a significant fraction of Cu^{+1}-S and Cu^{+1}-O,N initially present in raw OW was oxidized during composting. Cu^{+1}-S accounted for 100% of Cu speciation in digestates regadless of their origin.
It is worth noting that these trends are observed for all the OW regardless of their origin (agricultural, urban or central).