



	Experiment title: Investigation of speciation of Cu in organic wastes used for market gardening	Experiment number: EC-836
Beamline: BM30B	Date of experiment: from: 05/05/2011 to 10/05/2011	Date of report: 13/02/2012
Shifts: 18	Local contact(s): Vincent RANIERI	<i>Received at ESRF:</i>
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Report:

Introduction

The agricultural recycling is recognized as an alternative to stockpiling or incineration. However, the benefits of the use of organic wastes as fertilizers and soil amendments should be assessed together with potential environmental and toxicological impacts due to the presence of heavy metals. A part from problems of accumulation and risks of crops toxicity, the main challenge in organic waste recycling is to ensure that there is no transient or disseminated pollution to natural environment. While total concentrations of metals are not sufficient to assess their potential ecological risks, the knowledge of heavy metals speciation is crucial and essential to fully understand their behavior after spreading of organic wastes and to predict their bioavailability. Therefore we proposed to study the speciation of Cu in various composts, from sewage sludge, household refuses, animals manure and garden rubbish, and used in market garden in fringe of cities in geographical various countries (Yvelines and Reunion-France, Mahajanga-Magagascar, Dakar-Senegal). Spectroscopy (XAS) has been combined with different analytical approaches to determine speciation.

Experimental details

The study involved a combination of techniques to investigate the speciation of Cu in wastes. Size fractionation was first performed to account for the complexity of composts and X-ray absorption. On several type of wastes (fine fraction from municipal solid waste compost (FF-MSWC), MSWC, manure compost (MC) and sewage sludge (SS)), previous analysis of copper content in particle-size fractions revealed accumulation in some fractions. Thus, raw samples and the most concentrated particle-size fractions were ground and compacted into pressed pellets and analyzed.

Cu K-edge XANES measurements on wastes and reference compounds were performed between 5 and 10 K (helium cryostat), to avoid any possible dehydration or oxidation of samples. They were carried out on beamline BM30B/FAME with a Si(220) crystal monochromator operating at 6 GeV and 90 mA. The XAS spectra were all recorded in fluorescence mode, using a thirty-element solid-state germanium detector (Canberra, CT, USA).

Results

Further insight into the oxidation state of Cu was obtained by XANES.

Cu K-edge XANES spectra of raw wastes and their fines or coarse particles fractions are reported in Figure 2. For FF-MSWC, XANES spectrum in the raw sample is similar to that of its fine-particles fractions, where Cu is accumulated. We can identify different maximum of adsorption on the first derivative similar to those reported for Cu(II) reference compounds (dipole-forbidden electronic transitions $1s \rightarrow 3d$ from 8977 to 8978 eV; $1s \rightarrow 4p$ transition at 8985 eV and $1s \rightarrow$ continuum transition at 8995 eV). Consequently, copper in all particles of FF-MSWC was found mainly as Cu(II). Conversely, XANES spectrum of copper in raw MC(poultry) is clearly different to that of its fine particles fractions, where Cu is accumulated. However, it is similar to those of its coarse-particles fraction, where Cu is also accumulated. For fine particles of MC(poultry), we observed the additional presence of feature at 8982 eV on first derivative is characteristic of $1s \rightarrow 4p$ transitions of Cu(I) compounds. These results indicate that Cu was found as Cu(I) and Cu(II) in MC(poultry) and the oxidation state differs according to size of particles. Similar XANES feature were found for others samples.

To resume, Cu was found as Cu(I) and Cu(II) in organic wastes and the oxidation state could differ according to size of particles.

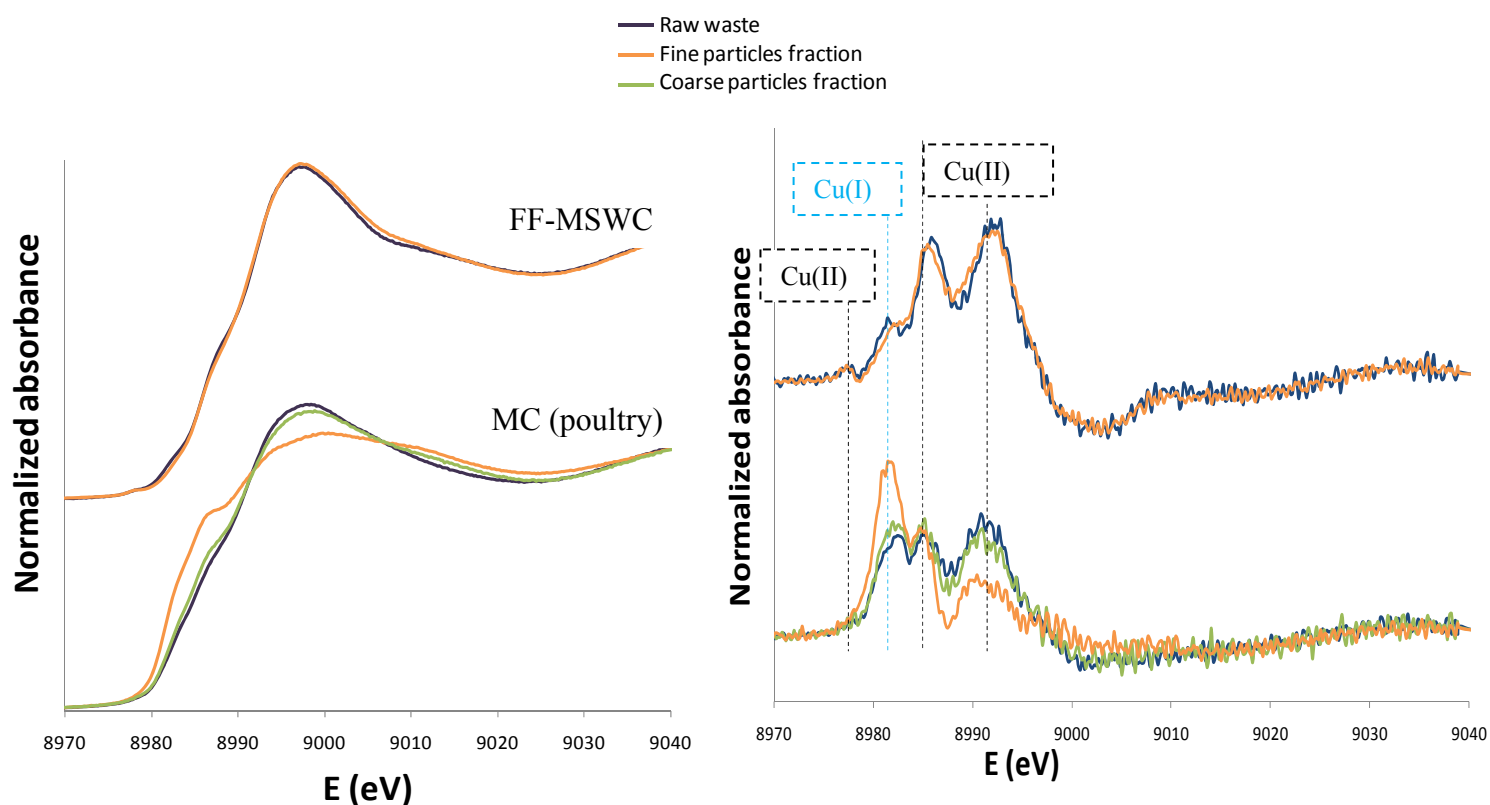


Figure 2. Normalized Cu K-edge XANES spectra of various raw wastes and their fines or coarse particles fractions

Further insight into the speciation of Cu was obtained by EXAFS.

We first compared the Cu K-edge EXAFS spectra of raw organic wastes and size fraction samples with two reference minerals that have different coordination shells: Cu_2S and Cu(II)-histidine. For Cu_2S , copper was surrounded by six S atoms around the central atom (Cu-S binding), whereas for Cu(II)-histidine, Cu was bound to six O atoms (Cu-O binding). For example, the FF-MSWC_0.2-20 EXAFS spectrum (Fig. 3) showed oscillations similar to Cu(II)-histidine species and the MC(poultry)_0.2-20 presented oscillations similar to Cu_2S . Similar observations could be realized with the others samples. To resume, in organic wastes, Cu was surrounded by S and O atoms in the first atomic shell.

Since the EXAFS spectrum of the unknown sample is a weighted sum of all species spectra present, the atomic fraction of each metal species can be obtained by linear combination fits (LCF) of this spectrum to reference spectra. The minimum number of reference spectra needed to fit the unknown sample was determined by principal component analysis (PCA). Relevant reference compounds were identified via target transformation and the SPOIL function in a large collection of pure inorganic or organic Cu minerals and species. Results indicated that, in all organic wastes, Cu oxidation state and chemical environment were observed as: Cu(I)-S, Cu(II)-S, Cu(I) or Cu(II) associated with organic matter(OM), and Cu(II)-O in inorganic species. As conclusion, in all type of wastes and size-fractions Cu is mainly presents as Cu(II) oxidation state and associated with organic matter, except for one MSWC and fine particle-fraction of MC(poultry) were Cu(I) is bound to S predominantly.

XANES and EXAFS data analyses are done for all samples and publication with these results is currently in progress.

Communication: *Goldschmidt Conference 2011*, 14-19 August, Prague, Czech Republic. **Tella M.**, Chataing S., Collin B., Diot M.-A., Bravin M.N., Doelsch E., Copper speciation in organic wastes: an X-ray absorption spectroscopy study.

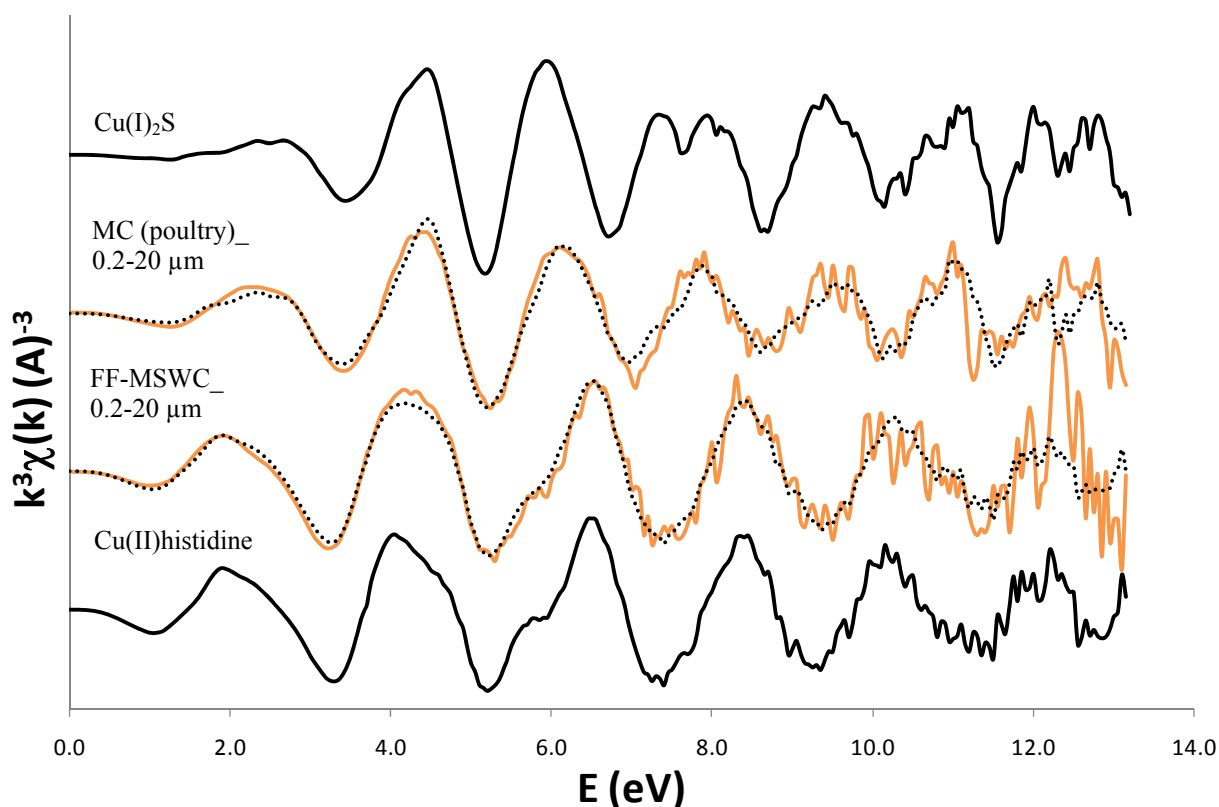


Figure 3. Cu K-edge EXAFS of two references spectra (black lines) and fine particles fractions of FF-MSWC and SS (orange lines) and LCF with references components (dotted line).

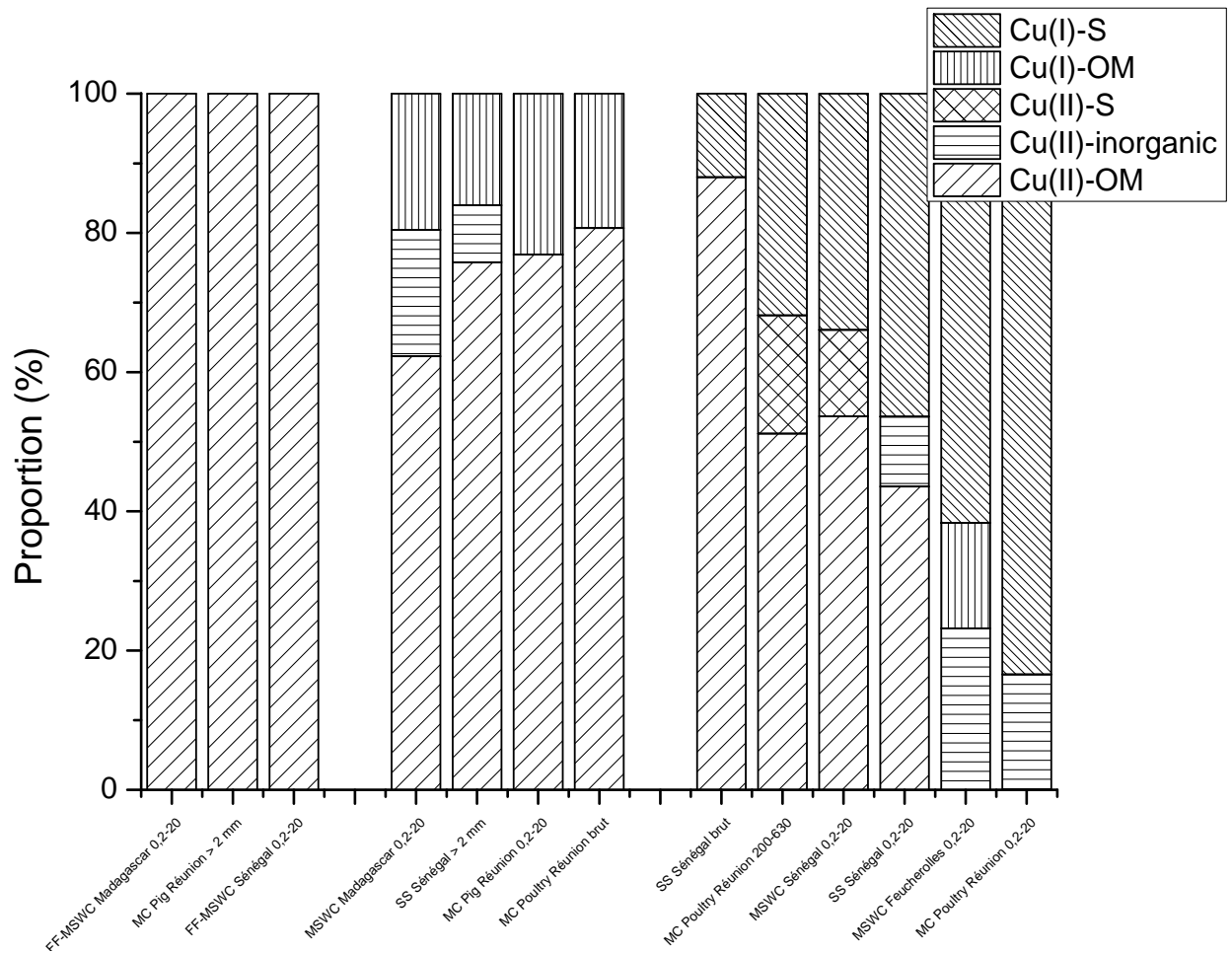


Figure 4. Proportions (%) for each type of reference compounds determined by LCF.