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Heavy metal assessment in vineyard sludge. Copper lixiviation and recovery studies.

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Abstract

The use of copper-based compounds to prevent fungi diseases in vineyards have contributed to heavy metal accumulation in soil, vegetation and waste, causing a serious environmental and agro-industrial problem. One main issue is the waste generated both during and after wine production. This waste must undergo through aerobic/anaerobic digestions, so a safe disposal is possible. As a result, a main final sludge waste is generated, characterized by the presence of significant nutrients for soil fertilization and regeneration, so the return of sludge to vineyard soils would provide a sustainable solution for this waste. However, its hazardous copper (Cu) and zinc (Zn) content hinders its use in soils. The risk associated to its use, does not depend on the total heavy metal content but to the retention phases and metal speciation present in the sludge, which will determine the mobility and bioavailability of the metals. In this research, Cu and Zn availability assessment is determined by applying sequential speciation methodologies to determine both the risk associated with the use of this sludge as a soil improver and fertilizer, and the metal distribution in the sludge phases to accomplish for a most appropriate and environmentally safe treatment process for their recovery and re-use.

Keywords: Sludge, copper, zinc, operational speciation, waste management.

1. Introduction

There is an increasing trend towards recycling sludge as a fertilizer for a more sustainable approach to waste management and agriculture. Sludge represents a potential source of nutrients and organic matter that can encourage plant and crops growth, promote soil regeneration and fertilization, increase water retention capacity, while reducing the need for chemical fertilizers and enhancing soil carbon capture. However, sludge may contain heavy metals (HMs), organic contaminants, pathogens, among other pollutants, that can pose risks to human health and to the environment, leading to long-term negative impacts (Fagnano et al., 2020). Therefore, the use of sludge as a fertilizer requires proper management and adherence to regulatory guidelines to ensure its safety and effectiveness. Vineyard sludge is a significant issue for the wine industry, as it represents both a waste management challenge and a potential resource for soil enrichment. In that regard, initiatives have been undertaken to explore the potential use of vineyard sludge as a fertilizer in the vineyards themselves, providing winegrowers full circularity in the wine-making process (Bustamante et al., 2008). Unfortunately, the presence of copper in high concentrations hinders compliance with regulations for its use. Copper residues appears in the sludge as a result of multiple and prolonged applications, for over a century, of copper-based products such as Bordeaux mixture and, more recently Cu oxychloride, to combat fungal growth in the vine (Mackie et al., 2012).

Therefore, to address the use of sludge in vineyards, rather than assessing the risk imposed by the total heavy metal content, it is important to investigate the speciation and retention phases of copper present in sludge since it determines the mobility and bioavailability of the metals. In addition, the possibility of recovering copper and regenerating copper-based compounds to be reuse as fungicides in the vineyards must be tacked so that resources are use as long as possible, promoting a circular economy strategy in the wine sector (Niculescu and Ionete, 2023).

The aim of this research project is to identify the various chemical forms in which copper is present in the sludge, such as free ions, complexes, or bound to organic matter, to provide a first approach to the hazards associated with the use of sludge in vineyards. Based on these results, and in a subsequent step, the recovery of copper for reuse can be considered. This research pretends to serve as a trigger for developing sustainable waste management practices that protect human health and the environment while supporting agricultural productivity.

2. Materials and methods

2.1. Sampling and sample pre-treatment

Sludge samples were collected from a waste treatment plant located in Vilafranca del Penedès, Barcelona, Spain, in which around six thousand tons of sludge are generated every year due to grape pomace and wastewater treatments. In this plant, residues are pre-treated in anaerobic digestors for several months until its volume and chemical oxygen demand (COD) are reduced to a minimum. Later, sludge is dewatered so that a manageable and consistent solid is obtained for further management. Sludge was collected, immediately dried at 105°C to constant weight, grounded and stored in a desiccator until analysis.

2.2. Experimental

Sludge physicochemical parameters. pH, moisture content (%), organic matter (% O.M.) and electrical conductivity (EC), were obtained for general characterization. pH was measured following the test method EPA9045D described for solid and waste materials. 20 g of sludge where place in a 50-mL beaker and 20 mL of deionized water was added and continuously stirred for 5 min. Then, the mixture was centrifuged for pH determination. Conductivity measurements were performed mixing 20 g of sludge with 200 mL of deionized water and shaked for 2 h at 20±1ºC. Dry matter was determined after 48 h at 105ºC so that all data is informed on a dry weight basis. Total Organic Matter (%) was determined by the difference in weight of sludge before and after placing it in a muffle at 550°C for 4h.

Metal content determination. Major component determination was performed using Field Portable-X Ray Fluorescence (FP-XRF) in the dry and grounded sludge. Precise measurement of total metal content was determined after Microwave Assisted (MW) digestion of 0.20 ± 0.01 g of sludge, by increasing the temperature to 180°C in 5 minutes at 960 W power. The samples were left for 20 minutes at this temperature and then allowed to cool. The digested solution was filtered with 0.22 µm and analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Operational Speciation techniques. A first approach to understand distribution, mobility, and potential bioavailability of HMs in the sludge was performed following several single extraction techniques commonly used in metal speciation studies. Typical single extractions involve the use of strong acids such as hydrochloric acid (HCl), weak acid extraction often performed using acetic acid (CH_3COOH), reducing agents like hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), among salts like calcium chloride ($CaCl_2$) and sodium nitrate ($NaNO_3$). In addition, two conventional indirect Speciation Extraction Schemes (SES) methods, BCR (Bureau of Community Research) and Tessier(Tessier et al., 1979), were addressed. These methods involve a series of selective extraction steps that target different forms or fractions of metals present in the sample.
To validate experimental procedures, single extractions were done as described in the BCR 484 reference material (RM) report. As for the sequential steps, those of the BCR 701 RM report were followed, while the Tessier method was applied as described in Tessier et al. work. After each extraction, the suspension was centrifuged, the supernatant was separated from the solid phase by filtering with a 0.22 µm, and HM content was evaluated with ICP-MS technique. All extractions and digestions were performed in triplicate.

3. Results

Sludge characterization plays a crucial role in determining the appropriate treatment and disposal methods for sludge, as well as in complying with environmental regulations. It helps in optimizing treatment processes, assessing the potential for its reuse, and ensuring safe handling and management of sludge.
Table 1 shows edaphological parameters measured for sludge. Slightly alkaline pH and moderate conductivity level were obtained, which are an advantage when applied to soil, as it can provide pH balanced, promoting optimal nutrient uptake and a healthier soil environment. Also, the relatively high moisture content and significant amount of OM, can contribute to enhance soil fertility and structure and to conserve water.

Table 1. *Sludge edaphological parameters*

Parameter	Value
pH	7,82 ± 0,04
Conductivity (mS/cm)	7,37 ± 0,22
% O.M.	48,35 ± 0,56
% Moisture	77,27 ± 9,1

FP-XRF analysis was carried out to obtain a fast-screening elemental determination of heavy metals in dry-sludge samples, following SW-846 Test Method 6200. Also, to achieve a more precise and comparability of these results, sludge MW digestion with HNO_3 (70%) was performed, in line with EPA3051A method, followed by ICP-MS concentration analysis. It should be noted that, despite the strong acid MW digestion, solid residues remained, which can be attributed to silicate phases, accounting for 3,43±0,4% of the total initial mass of sludge treated. To completely dissolve this silicate phase, the solid should be treated with hydrofluoric acid, but for practical purposes and risk assessment it was not considered, as this phase is classified as unavailable to plants and soils (Zimmerman and Weindorf, 2010).
In table 2, concentrations of metals obtained through both techniques are compared. Special attention was paid to the analysis of Cd, Cu, Ni, Pb, Zn, Hg and Cr total content, which must be considered when sludge application in agricultural soils is pretended, according to EU directive (86/278/EEC)(European Commission, 1986). As it can be observed, sludge in composed of high content of copper and zinc, while other harmful metals are below the detection limits (LOD) measured with FP-XRF technique, but analysis with ICP-MS showed that they are below the maximum limits stablished by EU directives. The presence of copper in such high concentrations is a consequence of the use of copper-based fungicides to combat fungal growth in the vineyard, meanwhile, the presence of zinc may appear as a concomitant residue in fungicides or due to the use of fertilizers with high Zn content, as Zn is a

determinant trace element affecting the final size of the grape (Todeschini et al., 2011).

Table 2. *Heavy metal content analyzed with FP-XRF and ICP-MS*

	FP-XRF	ICP-MS
	mg/kg	
Cu	177,33 ± 4,24	160,56 ± 21,11
Zn	107 ± 7,07	91,48 ± 3,13
Ni	<LOD	4,84 ± 0,30
Cr	<LOD	1,71 ± 0,08
Cd	<LOD	0,16 ± 0,01
Pb	<LOD	0,33 ± 0,02
Hg	<LOD	0,081 ± 0,002

Based on these results, simple and sequential extractions methodologies were carried out, mostly focused on Cu and Zn, which are the metals which render this sludge unsuitable for its use as fertilizers. Analyzing the retention phases of these metals in the solid matrix will give us a first insight to the type of risk associated with their use in vineyards.

Simple extractions have been performed with $CaCl_2$, $NaNO_3$, CH_3COOH and HCl, values shown in Figure 1. On one hand, extraction with $CaCl_2$ and $NaNO_3$ targets metals that are easily exchangeable, representing the fraction that could be uptaken by plants or released into soil. The difference observed between extraction with $CaCl_2$ or $NaNO_3$ may be due to the ability of chlorides to complex with copper and zinc (Pérez et al., 2008). However, the amount of metals extracted with these salt solutions is very low, so considered negligible. On the other hand, extraction capacity of CH_3COOH is relatively mild compared to HCl, as CH_3COOH can extract 10% of the total copper extracted with HCl, and less than 30% of zinc. This gives us preliminary evidence that there is a difference in the retention phases of the two metals, since CH_3COOH primarily targets metals that are loosely bounded, such as those adsorbed on the surfaces or held by weak electrostatic forces and HCl can solubilize metals associated with minerals, crystalline structures, or OM, representing metals that may become available under certain conditions.

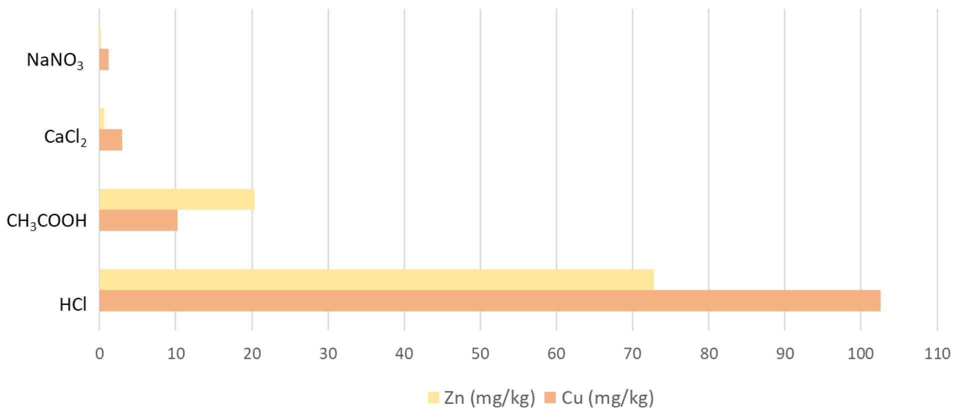

Figure 1. *Amount of Cu and Zn (mg/kg) obtained through simple extractions treatments.*

The percentages of Cu and Zn extracted in each step of BCR and Tessier methods are shown in Figure 2. A similar pattern is observed with both methods. The extraction percentages were calculated based on results in table 2, obtained with ICP-MS.

In the initial steps, both methods aim to extract the more labile exchangeable forms of these metals, weakly sorbed or adsorbed onto the surfaces of the sample matrix. This is achieved using salt solutions and weak acids, such as $MgCl_2$ + sodium acetate solution (pH 5) in the first two extraction steps of Tessier or acetic acid (0,1 mol/L) in the case of BCR extraction, which help in selectively leaching the exchangeable and carbonate fraction of metals. In this regard, step (1+2) of Tessier reached 5,31% Cu and 2,58% Zn extraction while BCR showed 7,69% for Cu and 2,19% for Zn, which demonstrates that only a small portion of metal labile or in the form of carbonates would dissolve at weak acid conditions.

As the extraction proceeds, step 3 in Tessier and step 2 of BCR target metals bound to iron and manganese oxides/hydroxides, solubilized by reductants like hydroxylamine hydrochloride. It can be noticed that the presence of zinc in these fractions is relatively high compared to that of copper, indicating its greater tendency to bind with iron and manganese phases. The distribution obtained in each case is 4,46% of Cu and 56,25% Zn with Tessier method and 7,59% of Cu and 54,66% Zn with BCR treatment, results that are quite similar as both methods use the same chemical reagent, differing only in concentration. While copper can form associations with these oxides, it tends to exhibit stronger affinity towards other fractions, like OM, including humic substances and other organic ligands present capable of forming stable complexes with copper ions. Step 4 in Tessier method extracted 63% Cu and 29% Zn, like BCR oxidizable step with almost 74% Cu and 15% Zn.

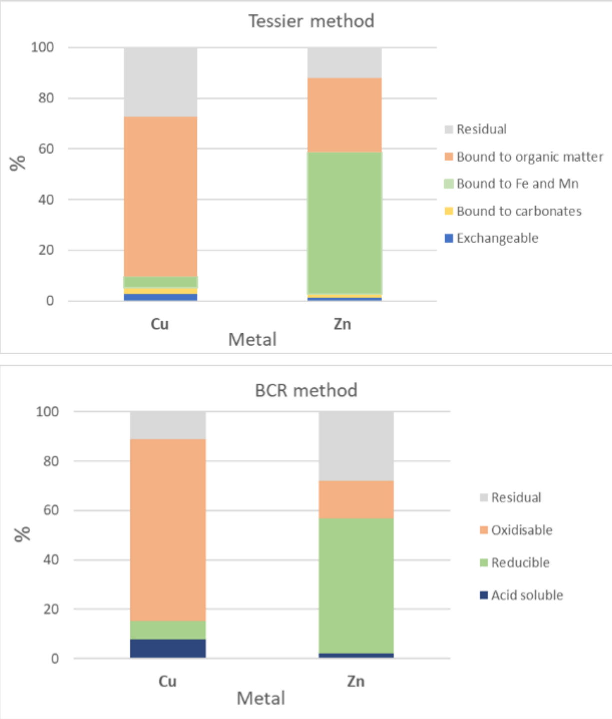

Figure 2. *Distribution of metal content in different phases of the solid matrix*

Although OS experiments offer an approach to metal speciation, there is still some controversy regarding (a) re-distribution of analytes among phases during extraction; (b) non-selectivity of reagents for target phases; (c) incomplete extraction and (d) precipitation of other kind of minerals (Zimmerman and Weindorf, 2010). To overcome these limitations, OS studies should be complemented with direct speciation experiments to obtain a more precise identification of the chemical state and local coordination environment of Cu and Zn regarding the nature of the sludge constituents involved in metal retention.

In this work, sequential extraction techniques were employed to evaluate the distribution and potential mobility of heavy metals in sludge with possibility of being used as a fertilizer, with a particular focus on copper and zinc. The results revealed distinctive patterns of heavy metal association within the sludge matrix. Copper was predominantly found in the organic matter phase, suggesting its strong affinity towards organic compounds present in the sludge. This implies that, even though Cu total concentration exceeds legislation limits, Cu may exhibit relatively low mobility and bioavailability in the environment, reducing its potential to leach into groundwater or be taken up by plants. On the other hand, zinc was primarily bounded to iron and manganese oxides, indicating that Zn may have a higher likelihood of being released and potentially affecting plants, soil, or water systems.

The sequential extraction approach employed in this study intends to provide a first insight into the speciation and potential environmental behavior of Cu and Zn in sludge when applied as a fertilizer in vineyards, which can help to guide appropriate management strategies and, in a subsequent step, to design methodologies to recover and reuse copper as fungicides so that a sustainable and integrated usage of winery wastes is achieved.

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