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Zinc and copper distribution in swine wastewater treated by anaerobic digestion

André Cestonaro do Amaral [a], Airton Kunz [b,*], Ricardo Luís Radis Steinmetz [b], Karin Cristiane Justi [a]

[a] Midwestern State University – Unicentro, 85040-080 Guarapuava, PR, Brazil
[b] Embrapa Swine and Poultry, 89700-000 Concórdia, SC, Brazil

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ABSTRACT

Swine wastewater contain high levels of metals, such as copper and zinc, which can cause a negative impact on the environment. Anaerobic digestion is a process commonly used to remove carbon, and can act on metal availability (e.g., solubility or oxidation state). The present study aimed to evaluate the influence of anaerobic digestion on total Zn and Cu contents, and their chemical fractioning due to the biodegradation of the effluent over different hydraulic retention times (HRTs). The sequential extraction protocol proposed by the Community Bureau of Reference (BCR), plus two additional fractions, was the method chosen for this study of Cu and Zn distribution evaluation in swine wastewater. The Zn and Cu concentrations in raw swine manure were 63.58 ± 27.72 mg L^{-1} and 8.98 ± 3.99 mg L^{-1}, respectively. The metal retention capacity of the bioreactor decreased when the HRT was reduced from 17.86 d to 5.32 d. Anaerobic digestion had a direct influence on zinc and copper distribution when raw manure (RM) and digested manure (DM) were compared. The reducible fraction showed a reduction of between 3.17% and 7.84% for Zn and between 2.52% and 11.92% for Cu when DM was compared with RM. However, the metal concentration increased in the oxidizable fraction of DM, viz. from 3.01% to 10.64% for Zn and from 4.49% to 16.71% for Cu, thus demonstrating the effect of anaerobic conditions on metal availability.

1. Introduction

The main environmental impacts caused by intensive swine production are due to the large volume of concentrated wastewater applied to the soil without a good agronomic management practice. The manure composition may change according to the animal growth phase and diet. These waste matters are rich in organic matter, nutrients and metals that have high pollution potential for water, air and soil (Steinmetz et al., 2009).

Anaerobic digestion is an important and effective treatment alternative for organic matter (mainly biodegradable matter) and reduces greenhouse gas emission (Kunz et al., 2009; Tauseef et al., 2013; Zaman, 2013). Metal species that are present in manure cannot be removed in the same way as organic carbon and will be present in the digestate and can accumulate in the soil when used as a biofertilizer (Achiba et al., 2010; Vries et al., 2012; Montoneri et al., 2014).

The availability of metals for microbial uptake and growth depends on the metal speciation, which is governed by the reactor conditions (e.g., pH, temperature, hydraulic retention time (HRT) and redox potential). The metal concentration and distribution are dependent on the chemical processes inside the reactor, such as precipitation and complexation and can affect the biochemical reactions (Aquino and Stuckey, 2008; Mudhoo and Kumar, 2013).

Changes in the biodigester parameters can significantly affect the initial stages of anaerobic digestion, mainly hydrolysis, by altering the characteristics of the generated products from the anaerobic digestion that can affect the metal distribution in the digestate (Evans and Furlong, 2011).

Several metals are found in swine manure, such as aluminum, iron, manganese, zinc and copper, reaching different concentrations in the swine wastewater. Among these metals, copper (Cu) and zinc (Zn) are found in higher concentrations, up to 15 mg L^{-1} and 40 mg L^{-1}, respectively, due to their use in swine diet (Steinmetz et al., 2009; Kim et al., 2010). Zn is an important component of enzymes, e.g., hydrogenase, formate dehydrogenase

* Corresponding author. Tel.: +55 49 34410481.
E-mail addresses: andrec.doamaral@gmail.com (A. Cestonaro do Amaral), airton.kunz@embrapa.br (A. Kunz), Ricardo.steinmetz@embrapa.br (R.L. Radis Steinmetz), kcjusti@hotmail.com (K.C. Justi).

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and superoxide dismutase, and has an essential role in protein, carbohydrate and lipid metabolism. Cu is related to the increment in the body's defense against oxidative stress because it is necessary for hemoglobin synthesis, and it also plays an important role in the animal immune system (Shao et al., 2012; Kim et al., 2012).

Assessment of the behavior of metals present in complex matrices such as swine wastewater could be a very important tool to avoid losses in biogas generation efficiency. It has been shown that the determination of total metal content is not enough to indicate its bioavailability, mobility and toxicity (Amir et al., 2005). In fact, the bioavailability and toxicity of metals are more often dependent on the chemical form of the metals (He et al., 2009). The mobility and bioavailability of Cu and Zn can provide important information for the understanding of microorganism inhibition mechanisms in anaerobic digestion (Guillén et al., 2010). An understanding of the distribution of metals in swine manure is necessary to predict and avoid negative effects on the anaerobic digestion process and to help choose the best management practices for the digestate (Wang et al., 2005).

Several sequential chemical speciation schemes have been applied; however, the results obtained by these different techniques were not comparable. This led the Community Bureau of Reference (BCR) to develop a three-step protocol of sequential chemical extraction (Ure et al., 1993) to standardize and harmonize the results. The protocol divides the metals into different phases, viz. exchangeable or bound to carbonates, reducible (bound hydrated oxides of Fe and Mn) and oxidized (linked to organic matter and sulfide).

The original BCR extraction protocol was developed for dry sediments; however, this causes oxidation of the samples, which can change the original metal speciation (Bordas and Bourg, 1998). When the extraction procedure is performed in wet samples to maintain the original partitioning, the water-soluble fraction is considered the supernatant water (Buykx et al., 2000). As an internal check on the procedure, it is also recommended that the residue from the organic fraction be digested and the total amount of metal extracted (i.e., sum of Step 1 + Step 2 + Step 3 + Step 4 + Residue) and compared with the values obtained from the total metal analysis (Sutherland, 2010).

Considering these facts, the present study aimed to evaluate the influence of anaerobic digestion on total Zn and Cu contents as well as the effect of their chemical fractioning on the digestate through changes in the hydraulic retention time using the BCR sequential extraction protocol plus two additional fractions.

2. Material and methods

2.1. Swine wastewater

Wastewater was collected from the homogenization tank (HT) at a swine manure treatment plant (SMTP) at the experimental facilities of Embrapa Swine and Poultry, Concordia, SC, Brazil (Kunz et al., 2009).

2.2. Biodigester

A 10 m^3 fiberglass upflow biodigester with an internal heating system to keep the biomass temperature at a constant 36 (±2) °C was used in this study (Fig. 1). The bioreactor was fed according to the desired flow rate (Table 1). A recirculation system was turned on twice a day for 2 min to prevent biomass clogging. Sludge discharges of 2% (v sludge/v influent) were performed during all of the experiments. The biodigester influent and effluent samples were collected, representing raw manure (RM) and digested manure (DM), respectively. Fig. 1

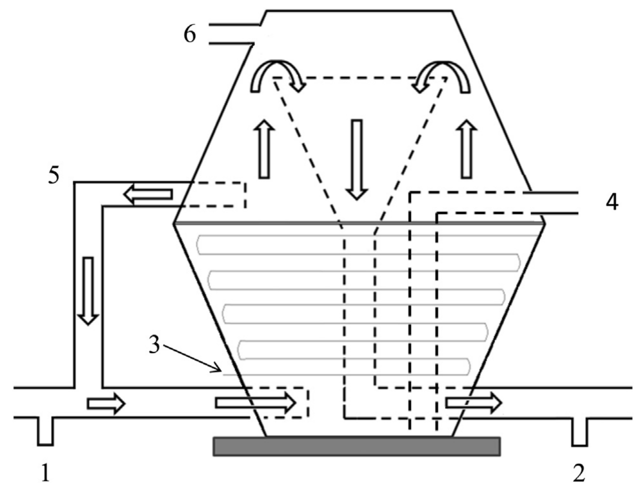

Fig. 1. Schematic representation of fiberglass 10 m^3 biodigester. The sampling points of raw manure (1) and digested manure (2), heating system (3), sludge discharge (4), agitation system (5) and biogas output (6) are indicated.

2.3. Biodigester HRT changes

The study was divided into three phases by increasing the flow rate in the biodigester (Table 1). The bioreactor was fed intermittently using a pump submerged in HT. The feeding pump was activated for 3.2 min every 2 h (23.34 L h^{-1}) during phase 1, for 3.2 min every hour (55.00 L h^{-1}) during phase 2 and for 4.8 min each hour (78.33 L h^{-1}) during phase 3. Table 1

2.4. Total Cu and Zn sequential extraction and quantification

The total metal concentration was obtained by using a nitric acid/hydrogen peroxide mixture by the following method. First, 5 mL of concentrated HNO_3 was added to 5 mL of the sample, and the mixture was then heated under reflux for 5 h. After cooling, 500 μL of H_2O_2 30% (v/v) was added and the solution was heated again under reflux for 1 h, or until the solution became transparent. Finally, the solution was cooled and quantitatively transferred to graduated polypropylene vials and diluted to 25 mL using purified water (Steinmetz et al., 2009).

The sequential extraction scheme developed by BCR (Ure et al., 1993) plus two additional fractions was conducted as shown in Fig. 2. All Zn and Cu analyses were performed by flame atomic absorption spectrometry (VarianSpectr AA 220) in an air/acetylene flame (Cu 324.75 nm and Zn 213.86 nm). Fig. 2

2.5. Accompaniment of total solids

These analyses were performed according to APHA (2012). The samples were dried at 105 °C for the determination of total solids.

Table 1
Description of the three stages of the study, with their flow rate and Hydraulic Retention Time (HRT).

Phase	Flow rate (m^3 d^{-1})	HRT (d)
1	0.56 ± 0.01	17.86 ± 0.10
2	1.32 ± 0.01	7.57 ± 0.06
3	1.88 ± 0.01	5.32 ± 0.03

value ± standard deviation.

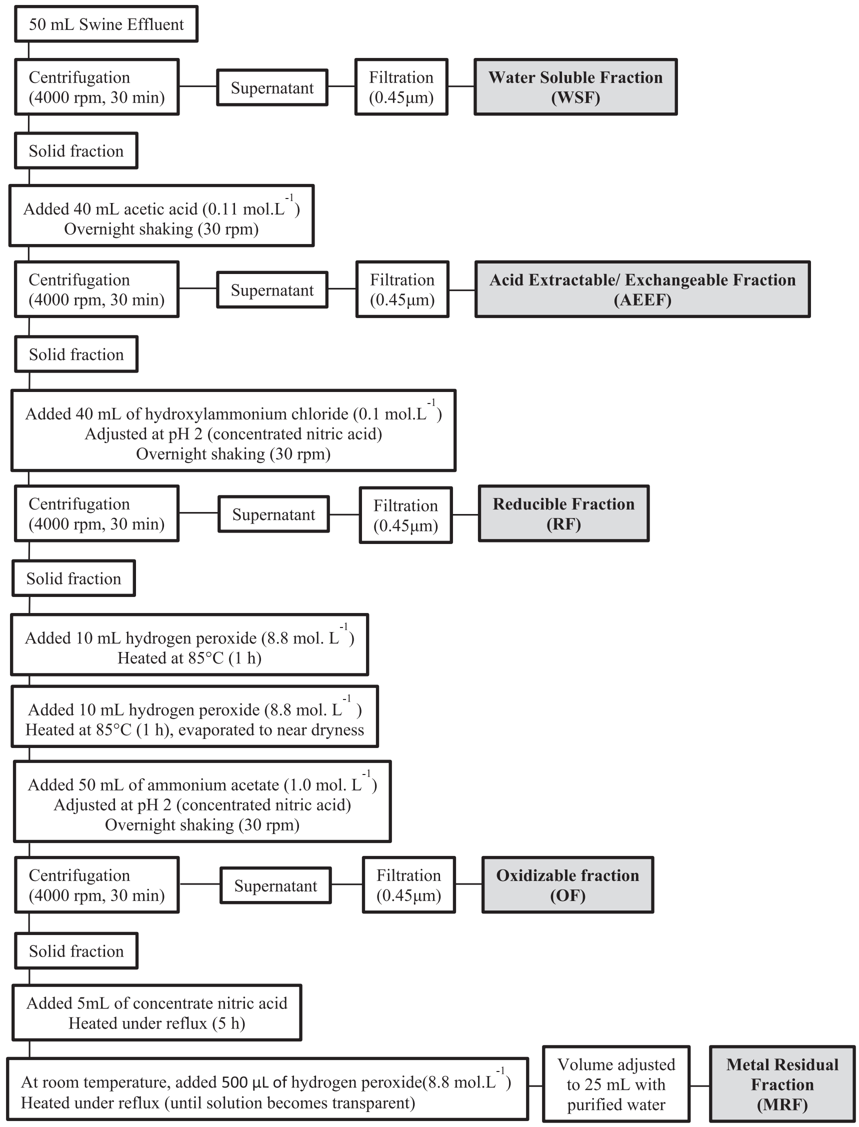

Fig. 2. BCR sequential extraction scheme for the swine wastewater samples, plus two additional steps (water soluble fraction and metal residual fraction).

2.6. Statistical analysis

All statistical analyses were performed using the GraphPad Prism ver. 3.02 software package. *P*-values below 0.05 were considered statistically different (Fongaro et al., 2012).

3. Results and discussion

3.1. Metals occurrence in swine manure

3.1.1. Total Cu and Zn concentration

The first purpose of this study was to determine and understand the behavior of the metals when subjected to biodigestion. The Cu and Zn total concentrations found in swine manure before and after treatment under the three HRT conditions are shown in Table 2. To facilitate comparison with Brazilian and international literature and regulations, the concentrations of the metals in RM and DM were presented in two forms: (a) dry matter (mg.g^{-1}) and (b) liquid manure (mg L^{-1}). Table 2

During phase 1 (HRT – 17.86 d) and phase 2 (HRT – 7.57 d), the bioreactor exhibited the capacity to retain Zn and Cu in anaerobic sludge, as evidenced by higher RM and lower DM concentrations (Table 2). This can be attributed to a reaction between the reduced sulfur species (e.g., H_2S) produced in anaerobic digestion with copper and zinc compounds, forming highly insoluble copper and zinc sulfides (Vivan et al., 2010; Gonzalez-Gil et al., 2012; Gustavsson et al., 2013). The H_2S concentration in biogas was 420 ± 245 mL m^{-3}, during this study. The reduction of sulfur compounds to H_2S in an anaerobic environment occurs in

Table 2
Zinc and copper total concentration in raw manure (RM) and digested manure (DM), during three phases of the study.

Metal	Phase	Liquid – mg L^{-1}		Solid – mg g^{-1}	
		RM	DM	RM	DM
Zn	1	94.00 ± 2.00	64.00 ± 2.00	6.77 ± 0.14	6.58 ± 0.20
	2	57.00 ± 1.00	49.00 ± 1.00	6.21 ± 0.11	5.66 ± 0.12
	3	39.75 ± 1.29	47.25 ± 0.53	3.41 ± 0.36	7.55 ± 0.09
Cu	1	13.55 ± 0.10	9.05 ± 0.10	0.98 ± 0.01	0.93 ± 0.01
	2	7.27 ± 0.23	6.58 ± 0.08	0.79 ± 0.02	0.76 ± 0.01
	3	6.13 ± 0.23	6.70 ± 0.04	0.55 ± 0.02	1.07 ± 0.01

approximately two days, indicating that over longer HRTs the metal species present will precipitate (Guo et al., 2012). In phase 3 (5.32 d), DM exhibited a higher concentration of metals than RM. This was due to an increased flow rate, generating greater internal agitation of biomass in the digester and providing the dragging of solids.

No significant difference was found between the concentrations of total solids during phase 1 (6.03 g $L^{-1} \pm 0.60$) and phase 2 (6.46 g $L^{-1} \pm 0.56$). Phase 3 showed an increase of total solids concentration in DM (10.12 g $L^{-1} \pm 1.26$). This increase was significant when compared to either phase 1 ($p = 0.0051$) or phase 2 ($p = 0.0308$).

Based on Cu and Zn concentrations expressed in mg L^{-1} in Table 2, there were significant differences between the concentrations of Zn in RM during phases 1 and 2 ($p = 0.0036$), 1 and 3 ($p < 0.0001$) and 2 and 3 ($p = 0.0002$). With regard to the Zn concentrations in DM, there were significant differences between phases 1 and 2 ($p = 0.0215$) and 1 and 3 ($p = 0.0002$). The Cu concentrations in RM also presented significant differences between phases 1 and 2 ($p = 0.0015$), 1 and 3 ($p < 0.0001$) and 2 and 3 ($p = 0.0085$). For DM, significant Cu concentration differences occurred between phases 1 and 2 ($p = 0.0025$) and 1 and 3 ($p < 0.0001$).

These differences in metal concentrations in RM during the three phases of the study can be attributed mainly to changes in the composition of swine food during the various stages of animal growth (Gopalan et al., 2013). The metal concentration can also be influenced by variation in animal numbers in different stages of production during the study. Changes in the volume of generated effluent can be attributed to differences in swine water consumption, cleaning of the facilities and water leakage that cause changes in the effluent metal concentration (Steinmetz et al., 2009). Changes in storage conditions before the anaerobic treatment can also cause differences in the concentrations of Cu and Zn present in swine manure (Popovic and Jensen, 2012).

It is important to understand the regulations regarding land application when considering the total metal concentration in the digestate.

The Brazilian resolution CONAMA 375 (2006) establishes criteria for the use of sewage sludge generated at the sewage treatment plant as soil conditioner for agriculture, where the limits for Zn and Cu are 2.8 mg g^{-1} and 1.5 mg g^{-1}, respectively. During the three phases of the study, the Cu concentration was below the limit established by this resolution; however, the Zn concentration (Table 2) was above this limit (22%–135%). The European Union recommends maximum levels for metals in anaerobically digested sludge for land application. The maximum values for Zn and Cu are 4.00 mg g^{-1} and 1.75 mg g^{-1}, respectively (Nordber, 2010). The values found for Zn in this study (Table 2) exceed the limits established by this guideline by 65% and 41% in phases 1 and 2, respectively. The zinc concentration in phase 3 and the copper concentration during all phases were lower than the limits previously mentioned. The United States Environmental Protection Agency (EPA) proposed limits to the metal concentration in biosolids applied on land, with Zn and Cu concentration limits of 7.50 mg g^{-1} and 4.30 mg g^{-1}, respectively (EPA, 2004). The metal concentrations contained in swine wastewater were lower than the limits imposed by this legislation, except during phase 3 for DM, when Zn surpassed the limit by only 0.70%.

3.1.2. Metal distribution and HRT

After studying the total metal concentrations in raw and digested manure, an evaluation was made of the zinc (Fig. 3a) and copper (Fig. 3b) distribution in different chemical fractions of RM and DM using the procedure described in Fig. 2. Fig. 3

The Water Soluble Fraction (WSF) is mainly composed of free metal ions and complexed ions with soluble organic material (Ure and Davidson, 2001). Free metal ions in swine manure can be adsorbed by the biomass present in the digester. Once adsorbed, metals are displaced to the oxidizable fraction (Gerardi, 2003). Due to the presence of H_2S inside the biodigester, Cu and Zn can precipitate as sulfides (Kafle and Kim, 2013), which is another reason for the low metal concentration in WSF. With regard to Zn, this fraction was negligible in RM and DM. In phase 2, Cu was present at 8.20% in RM, but after anaerobic digestion was reduced to 2.15%.

The Acid Extractable/Exchangeable Fraction (AEEF) includes metals weakly adsorbed to the surface of solids present in swine manure as a result of weak electrostatic interactions. These metals are often released by ionic exchange processes and may be co-precipitated as carbonates or bicarbonates. Carbonates can be an important adsorbent for many trace metals, this fraction being directly related to the alkalinity in the biodigester (Filgueiras et al., 2002). The AEEF fraction remained nearly constant during the anaerobic digestion. During phases 1 and 2 it was reduced by 0.85% and 1.75% (Zn) and by 0.56% and 0.49% (Cu), respectively, whereas in phase 3 it increased by 0.89% (Zn) and 0.20% (Cu), comparing RM and DM.

The reducible fraction (RF) represents the fraction where metals are bonded to iron and manganese hydrated oxides (Filgueiras et al., 2002). This fraction decreases between RM and DM and is thermodynamically unstable under strictly anaerobic conditions (P-RedOx < −200 mV), which causes fraction dissolution after passing through the biodigester (Marin et al., 1997). During phases 1, 2 and 3, the Zn concentration in the RF decreased by 6.40%, 7.84% and 3.17%, respectively, when comparing RM and DM. Copper had similar characteristics, decreasing by 11.92% in phase 1 and by only 2.52% in phase 3. A smaller influence of anaerobic digestion can be observed in phase 3, which corresponds to the shortest HRT (Table 1). The subsequent steps of the anaerobic digestion process are directly related to HRT. The reduction of HRT has significant

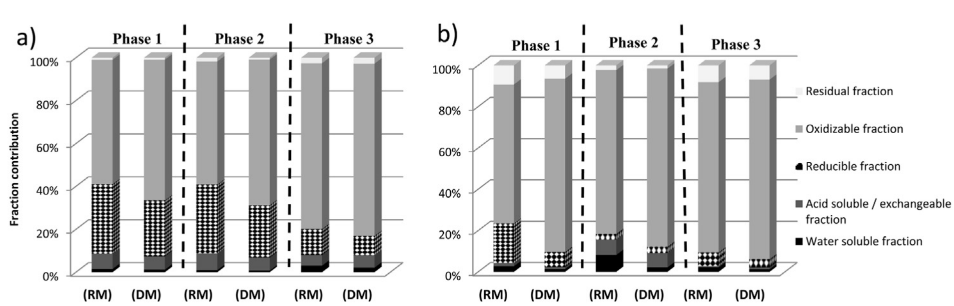

Fig. 3. a) Zinc distribution in five different chemical speciation during three phases, in raw manure (RM) and digested manure (DM). b) Copper distribution in five different chemical speciation during three phases, in raw manure (RM) and digested manure (DM).

impacts on the initial steps of anaerobic digestion and is directly related to substrate availability and biodegradability (Deublein and Steinhauser, 2008; Kim et al., 2012).

The oxidizable fraction (OF) comprises the metals linked to organic matter and/or a sulfide. With the dissolution of the fractions previously discussed, the metallic ions are precipitated as sulfides ($K_{s\ CuS} = 8.0 \times 10^{-37}$ and $K_{s\ ZnS} = 1.2 \times 10^{-23}$) in anaerobic environments and under high H_2S concentration conditions (Peu et al., 2012).

The Zn concentration (mg L^{-1}) for RM and DM in OF were 48.94 and 40.00 (phase 1), 29.64 and 29.25 (phase 2) and 28.96 and 31.61 (phase 3). The Cu concentration (mg L^{-1}) for RM and DM in OF were 7.78 and 7.96 (phase 1), 5.04 and 4.63 (phase 2) and 4.35 and 4.76 (phase 3). There was an increase of 7.60% (Zn) and 16.71% (Cu) in phase 1, 10.64% (Zn) and 6.93% (Cu) in phase 2 and 3.01% (Zn) and 4.49% (Cu) in phase 3. Artola et al. (2000) proposed that the anaerobic biomass has a high affinity for metals, particularly Cu. This fact can also be observed in Fig. 3b, where the largest portion of the metals is found in the oxidizable fraction, thus demonstrating high affinity. Theis and Hayes (1978) showed that anaerobic conditions (redox potential around −300 mV and neutral pH) favor the formation of carbonates and the precipitation of sulfides. However, they also cause an increase in the oxidizable fraction (Fig. 3), which indicates that precipitation in the form of sulfides prevailed during this study once the fraction containing the carbonates was insignificant.

The metal residual fraction (MRF) contains residual metals, especially primary and secondary minerals (Filgueiras et al., 2002).

We studied swine wastewater before and after anaerobic biodigestion, using the sequential chemical speciation method as proposed by Stover et al. (1976) and modified by McGrath and Cegarra (1992) and Marcato et al. (2009). The results described by these authors are very different from those obtained during the present study. The Cu concentration was found to be highest in the oxidizable fraction and decreased after anaerobic digestion as a result of an increase in the carbonate fraction. However, Zn was found mainly in the carbonate fraction for both raw and digested manure, while both metals have significantly increased concentrations in the residual fraction after anaerobically reaching levels near 25%.

The internal procedure control on the results of the BCR sequential extraction was performed by comparing the sum of the five fractions with the total concentration of metals from the digestion procedure (Rauret et al., 1999). The sum of the five steps was in good agreement with the total metal concentration, with satisfactory recoveries, viz. 87.74%–99.19% for Zn and 81.60%–104.73% for Cu. This indicates that the present BCR protocol with two additional fractions is reliable (Chen et al., 2008).

3.2. The biodigester and its environmental implications

The trace elements contained in WSF are relatively labile and thus have a high bioavailable potential for anaerobic microorganisms. These free and complexed ion species and ions complexed with soluble organic matter and other constituents, constitute the most mobile and potentially the most available metal and metalloid species.

AEEF contains metals that are precipitated or co-precipitated with carbonate and weakly adsorbed metals retained on the surface of solids by weak electrostatic interactions. The carbonate form and adsorbed metals are liable to change with environmental conditions (Filgueiras et al., 2002).

In RF, the metals are bonded to iron and manganese hydrated oxides. This fraction presents greater mobility because the metals associated with this fraction are thermodynamically unstable. The reduction of Fe(III) and Mn(IV) under anoxic conditions and their subsequent dissolution could release adsorbed trace metals. The dissolution of RF in biodigester bulk is due to negative values of the redox potential.

When DM or RM is applied to the soil, the WSF, AEEF and RF can be easily absorbed by organisms present in the environment. Thus, these fractions can be identified as having a direct environmental effect (Chen et al., 2008).

OF is only mobilized in oxidizing conditions, being transformed into WSF, AEEF and RF. However, the ecotoxic potential of should not be ignored. Depending on the characteristics of the soil in which it is applied, OF can be identified as a fraction with pollution potential (Yao et al., 2010). OF dominates trace metal distribution in anaerobic environments, especially through the presence of metallic sulfides that are not susceptible to biodigestion, as they do not interact with microorganisms (Guo et al., 2012).

Fraction MRF, viz. metals bound to stable inorganic structures, is inert to organisms and is identified as a stable fraction (Fuentes et al., 2008). The metals are not expected to be found in solutions in a reasonable time under the regular conditions found in natural systems (Lasheen and Ammar, 2009).

4. Conclusion

The highest concentrations of the two metals were bound to the oxidizable fraction in both raw (RM) and digested manure (DM). The process of anaerobic digestion changed the distributions of Zn and Cu in phase 1(HRT − 17.86 d) and phase 2 (HRT − 7.57 d). There was a minor influence on the distribution of Zn and Cu in RM and DM during phase 3 (HRT − 5.32 d). The metal concentrations in the fractions that were more bioavailable to the environment were always smaller than the oxidizable fraction. This shows that most metals are not readily bioavailable to anaerobic microorganisms, or during land application when digestate is used as an organic fertilizer.

The information derived from the present study can be used to assess the potential mobility or bioavailability of these metals in the biodigester, and to provide evidence for the suitability and feasibility of the digested swine manure for agronomic applications.

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