# The use of sewage sludge hydrochar for improving soil fertility in the Cerrado region of Brazil – scientific effects and social acceptance

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# Table of Content

# List of Figures

## List of Tables

## List of Abbreviations

| | |
|---|---|
| AAS | Atomic Absorption Spectroscopy |
| ABC | Brazilian program of Agriculture of Low Carbon Emission |
| ANOVA | Analysis of Variance |
| ASTM | American Society for Testing and Materials |
| BAM | Federal Institute for Materials Research and Testing |
| BRM | Biological Reference Material |
| BS | Base Saturation |
| BET | Brunauer Emmett and Teller |
| CAF | National Register of Family Agriculture |
| CEC | Cation Exchange Capacity |
| CETESB | Brazilian Environmental Sanitation Technology Company |
| CONAMA | National Environment Council |
| COP15 | Fifteenth session of the Conference of the Parties to the United Nations Framework Convention on Climate Change |
| DM | dry matter |
| DMA | Mercury Direct Analyzer |
| EC | Electrical Conductivity |
| EDA | Exploratory Data Analysis |
| EMBRAPA | Brazilian Public Agricultural Research Corporation |
| EPA | Environmental Protection Agency |
| FAO | Food and Agriculture Organization of the United Nations |
| FOB | Free On Board |
| FTIR | Fourier Transformed infrared spectroscopy |
| GC-MS-SIM | Gas Chromatography Mass Spectrometry – Selective Ion Monitoring |
| GDP | Gross Domestic Product |
| GHG | Greenhousegases |
| HMF | Hydroxymethylfurfural |
| HTC | Hydrothermal Carbonization |
| HTT | Highest Treatment Temperature |
| HWC | Hot Water extractable Carbon |
| H+Al | Potential Acidity |
| IAASTD | International Assessment of Agricultural Knowledge, Science and Technology for Development |
| IAF | International Association of Fertilizers |
| IBAMA | Brazilian Institute of Environment |
| IBGE | Brazilian Institute of Geography and Statistics |
| ICMS | Interstate and Intercity Transportation and Communication Services |
| IFAD | International Fund for Agricultural Development |
| IEA | Brazilian Agricultural Economics Institute |
| IFG | Federal Institute of Goiás |
| IMB | Mauro Borges Institute |
| INPE | Brazilian Institute for Space Research |
| IPEA | Brazilian Institute for Applied Economic Research |

| | |
|---|---|
| ISO | International Organization for Standardization |
| IUPAC | International Union of Pure and Applied Chemistry |
| KBr | Potassium bromide |
| LANAGRO-GO | National Laboratory of the Ministry of Agriculture, Livestock and Food Supply |
| LC50 | Median Lethal Concentration |
| MAPA | Ministry of Agriculture, Livestock and Food Supply |
| MDIC | Brazilian ministry of industry, foreign trade and services |
| MMA | Ministry of Environment |
| NIST | National Institute of Standards and Technology |
| OECD | Organization for Economic Cooperation and Development |
| PCA | Principal Component Analysis |
| PCDD | Polychlorinated dibenzoditoxins |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctanesulfonic acid |
| PV | Pore Volume |
| RSD | Relative Standard Deviation |
| SA | Surface Area |
| SANEAGO | Sanitation Unity of Goiás |
| SCBA | Sugarcane bagasse ash |
| SD | Standard Deviation |
| SEAD | Brazilian Special Secretariat for Familiy Farming and Agrarian Development |
| SEM | Scanning Electron Microscope |
| SiBCS | Brazilian Soil Classification System |
| SNIS | Brazilian National Information System on Sanitation |
| SOC | Soil Organic Carbon |
| UFG | Federal University of Goiás |
| UFPA | Family Agrarian Production Unit |
| UFN III | Brazilian Nitrogenated Fertilizer Unit III |
| UNCTAD | United Nation Conference on Trade and Development |
| TDM | Total Dry Matter |
| TOPV | Total Pore Volume |
| TPI | Terra Preta de Indio |
| TXRF | Total X-Ray Fluorescence Spectroscopy |
| UDDT | Urine Diversion Dehydration Toilet |
| USDA | United States Department of Agriculture |
| UV/VIS | Ultraviolet-visible |
| VFA | Volatile Fatty Acids |
| WFP | World Food Programme |
| WHC | Water Holding Capacity |
| WWTP | Wastewater Treatment Plant |
| XPS | X-ray photoelectron spectroscopy |

## Summary

Biosolids/sewage sludge are the product of the wastewater treatment. Hydrochar is the solid product resulting from hydrothermal carbonization (HTC). The HTC is a thermal treatment, which is reported to reduce biosolids volume, to promote nutrient bioavailability and to destroy pathogens. The conversion of waste biomass into hydrochars for agronomical purposes has been studied as an environmental sustainable alternative and potential supplement of mineral fertilizers. However, the previous studies about hydrothermal carbonized sewage sludge (Sewchar) as a soil amendment are still insufficient to understand its effects in agriculture and its acceptance by farmers.

Substantial knowledge gaps still exist regarding the Sewchar content produced in specific process parameters; the toxicity of Sewchar to biota; the optimal realistic concentration of Sewchar on growth of specific crops; and the residual effect of Sewchar as a soil amendment on soil properties and plant growth. Additionally, there is a dearth of information concerning what is considered important for the farmers when choosing a fertilizer and their acceptance about Sewchar as a soil amendment. Consequently, the effect of Sewchar as a soil amendment and its impact to environmental and human health can barely be estimated.

This thesis is based on results gained by laboratory and greenhouse experiments and the conduction of a survey among farmers in central Brazil. The general objective was to investigate the effect of Sewchar as a soil amendment. Therefore, the following experiments were performed. The toxicity of Sewchar was first assessed to earthworms, using application rates (0, 10, 20, 40 and 80 Mg $ha^{-1}$) up to four times the realistic field application rate (10-20 Mg $ha^{-1}$). Afterwards, the toxicity of the process water filtrate of the Sewchar to shrimps (*Artemia salina*) was measured using application rates (6.25% - 0.31 ml, 12.5% - 0.62 ml, 25% - 1.25 ml, 50% - 2.5 ml and 100% - 5 ml) up to 100% with and without the adjustment of the pH (chapter 2).

Subsequently, the residual effect of Sewchar as a soil amendment and its optimum application rate related to plant growth and soil properties was evaluated in a pot trial for bean (*Phaseolus vulgaris*) growth. Considering the results of the toxicity tests, the pot trial was performed in two crop harvests with Sewchar application rates (0, 4, 8, 16 and 32 Mg $ha^{-1}$) up to slightly exceeding the application rate used in realistic agronomic practice. Sewchar was applied in addition to phosphorous in the second crop harvest (chapter 3). The effect of Sewchar as a soil amendment was also assessed through a germination test using different plant crops additional to bean (*Phaseolus vulgaris*), such as radish (*Raphanus sativus*) and rice (*Oryza sativa*). The germination test was carried out applying higher Sewchar additions (0, 10, 20, 40 and 60 Mg $ha^{-1}$) than those used in the pot trials to confirm whether the best results related to the total dry biomass of the plant crops would exceed the range of the realistic agronomic application rate (chapter 4).

Various analyzes were carried out to identify the alterations of biosolids after HTC to complete the evaluation of the potential use of Sewchar as a soil amendment (chapter 4). In addition, the aim to these

analyses was a better understanding of the results of the toxicity (chapter 2), pot trial (chapter 3) and germination (chapter 4) tests and to identify the potential risks and promising Sewchar characteristics concerning its use as a soil amendment. To characterize the biosolids and Sewchar the following parameters were investigated: proximate analysis (moisture, mobile/volatile matter, ash content, and resident matter); chemical analyses (macronutrient and trace element concentrations, polycyclic aromatic hydrocarbons (PAHs), and chemical functionality, chemical surface and structural properties) and physical analyses (particle size distribution, surface morphology, surface area and pore volume). Finally, a survey was carried out to assess the decision criteria of farmers for choosing a soil amendment and their acceptance of using Sewchar in agriculture (chapter 4).

The results of the individual studies of this work can be summarized as follows: The Sewchar was not toxic to earthworms up to four times the reasonable field application rate. It is likely that the absence of the median lethal concentration of the Sewchar applications to earthworms was related to the legally satisfactory concentration of trace element content in the Sewchar. The process water filtrate of Sewchar caused lower toxicity to shrimps after the adjustment of its pH to 8.5. These results show that pH adjustment of the process water filtrate of Sewchar is crucial in case of discharging it in saline or fresh water (chapter 2).

The results of the pot trial experiment showed that the Sewchar application rate of 16 Mg $ha^{-1}$ had the best results regarding bean dry biomass, which was equivalent to the bean dry biomass of mineral fertilizer in both crop harvests. As results of the residual effect of this Sewchar dose there was an increase of the soil quality due to the input of organic carbon from Sewchar, absorbable nitrogen forms, and various nutrients to the soil (Ca, Cu, Fe, P and Zn). Additionally, Sewchar improved the cation exchange capacity, the water holding capacity and, the nutrients supply to beans (Ca, P and Zn). The increase of total dry matter of bean indicated the potential of Sewchar as a soil amendment for bean growth at a common Sewchar field application rate (chapter 3).

In absolute terms the germination experiment confirmed that an applicable Sewchar dose in agronomical field practice, 0.5% (10 Mg $ha^{-1}$) obtained the highest dry biomass yield for bean, which was 37% higher than that of the control. As to the rice growth the Sewchar dose about 3 times higher than normally used in agronomical field practice 3% (60 Mg $ha^{-1}$) showed the highest dry biomass yield for rice, which was 18% higher than that of the control. However, the dry mass data of bean and rice relative to the Sewchar doses did not show a tendency behavior between the total dry matter of these crops and the Sewchar doses. In addition, the dry mass data of radish relative to the Sewchar indicated a decrease of radish biomass with increasing Sewchar doses. The reason for the total dry matter decrease of radish can be explained due to the insufficient supply of nutrients (nitrogen, phosphorous and potassium) from the Sewchar additions in relation to the radish nutrient demand (chapter 4).

The chemical and physical analysis of biosolids and Sewchar evidenced chemical and physical modifications in the biosolids' properties through the HTC, resulting in promotion of pore structure development and increase of trace element and PAHs content. However, trace element values were below the threshold values of Brazilian National Environment Council (CONAMA 375 2006). Conversely, some PAHs values were above the standard limits preconized by CONAMA 375 (2006), indicating that a legal framework including standard methods of PAHs content analysis in hydrochars is of crucial importance (chapter 4). In addition, the chemical (Oxigen-containing functional groups, orderly arranged carbon structure, aliphatic and aromatic carbon content) and physical analyses (Sewchar porosity) of Sewchar performed in chapter 4 could explain the positive effects of Sewchar as a soil amendment described in chapter 3, such as improvement in the water holding capacity, cation exchange capacity and nutrient uptake by bean.

The results of the survey showed that younger farmers who had higher education were more prone to use Sewchar as a soil amendment. Additionally, farmers who would not use Sewchar as a soil amendment attributed the highest level of importance for economic criteria, such as fertilizer and freight prices. Finally, the results in this study showed that Sewchar would potentially be used by most interviewed farmers as a soil amendment (chapter 4).

Overall, this research showed that Sewchar applied in a common field practice application rate has a great potential to supplement mineral fertilizer due to the enrichment of nutrients in the soil, the increase of soil fertility indicators and the supply of nutrients to beans. The potential use of Sewchar as a soil amendment was also confirmed by most of the farmers of the survey. However, applications response varied in different crops. This study exposed various physicochemical properties of Sewchar that indicate a promising performance as a soil amendment. In addition, it revealed no toxicity of Sewchar to earthworms, and exposed the ecotoxicological risks of Sewchar process water to shrimps. It also revealed that further studies are required concerning the long-term application of Sewchar in the soil due to the high values of some PAHs in the Sewchar.

The knowledge gained can contribute to the design of the Sewchar production according to specific applications. Another advantage is to use the data of this research for the support of further studies in field trials exploring the long-term effects and interactions of Sewchar as a soil amendment in different ecosystems and plant crops to its agronomical efficiency and environmentally safe application. In future, further studies about the characterization and long-term effect of the field application of Sewchar produced under different process conditions and applied on diverse plant crops and ecosystems should be carried out. As result, our understanding about the interactions of Sewchar with the soil could be expanded. Consequently, enabling its safe use as a soil amendment to the environment and the human health. In addition, the dissemination of research information about the Sewchar as soil amendment should be provided to the farmers as knowledge transfer to subside their decision for using Sewchar in agriculture.

# Zusammenfassung

Bisolide/Klärschlämme sind das Produkt der Abwasserbehandlung. Hydrokohle ist das feste Produkt, das aus der hydrothermalen Carbonisierung (HTC) resultiert. Die HTC ist eine thermische Behandlung bei der das Volumen der Ausgangsmasse verringert wird. Als Bodenzusatzstoff fördert das Endprodukt die Bioverfügbarkeit von Nährstoffen. Weiterhin werden krankheitserregenden Stoffe im Klärschlamm zerstört. Die Umwandlung von Abfallbiomasse in Hydrokohlen für agronomische Zwecke wurde als eine umweltverträgliche, nachhaltige Alternative zur möglichen Substitution von Mineraldünger untersucht. Die bisherigen Forschungen über hydrothermal-karbonisierten Klärschlamm (Sewchar) als Bodenzusatzstoff reichen jedoch nicht aus, um die Auswirkungen auf die Landwirtschaft und deren Akzeptanz durch die Landwirte ganzheitlich zu verstehen.

Hinsichtlich der Sewcharbestandteile bestehen noch erhebliche Wissenslücken, die unter spezifischen Prozessparametern erzeugt werden; die Toxizität von Sewchar gegenüber Biota; die Auskirkung der optimalen realistischen Konzentration von Sewchar auf das Wachstum bestimmter Kulturen; die Residualwirkung von Sewchar als Bodenzusatzstoff auf Bodeneigenschaften und Pflanzenwachstum. Zusätzlich mangelt es an Informationen, welche Kriterien für die Landwirte bei der Auswahl eines Düngers und deren Akzeptanz für Sewchar als Bodenzusatzstoff wichtig sind. Infolgedessen sind die Auswirkungen dieser Wechselwirkungen noch nicht abschließend bekannt. Der Einfluss von Sewchar auf die Umwelt und die menschliche Gesundheit kann daher nur unzureichend abgeschätzt werden.

Im Rahmen dieser Arbeit wurden Labor- und Gewächshausexperimente sowie eine Umfrage unter Landwirten in Zentralbrasilien, den möglichen Andwender, durchgeführt. Das Hauptziel war es, die Wirkung von Sewchar als Bodenzusatzstoff zu untersuchen. Daher wurden die folgenden Experimente durchgeführt. Die Toxizität von Sewchar auf Regenwürmer (*Eisenia foetida*) wurde zuerst untersucht, wobei die Anwendungsmenge (0, 10, 20, 40 and 80 Mg $ha^{-1}$) bis zum Vierfachen der realistischen Feldanwendungsrate (10-20 Mg $ha^{-1}$) verwendet wurde. Danach wurde die Toxizität des Prozesswasserfiltrats der Sewchar auf Garnelen (*Artemia salina*) unter Verwendung von Anwendungsmengen (6.25% - 0.31 ml, 12.5% - 0.62 ml, 25% - 1.25 ml, 50% - 2.5 ml and 100% - 5 ml) bis zu 100% mit und ohne Einstellung des pH-Wertes gemessen (Kapitel 2).

Anschließend wurde die Residualwirkung von Sewchar als Bodenzusatzstoff und seine optimale Konzentration in Bezug auf das Pflanzenwachstum und die Bodeneigenschaften in einem Topfversuch anhand des Wachstums von Bohnen (*Phaseolus vulgaris*) untersucht. Unter Berücksichtigung der Ergebnisse der Toxizitätstests wurde der Topfversuch in zwei Ernten mit Sewchar-Anwendungsmengen (0, 4, 8, 16 und 32 Mg $ha^{-1}$) durchgeführt, bis die realistischen Anwendungsmenge in der agronomischen Praxis leicht übertroffen wurde. Bei der zweiten Ernte wurde Sewchar zusätzlich zu Phosphor angewendet (Kapitel 3). Die Wirkung von Sewchar als Bodenzusatzstoff wurde auch durch einen Keimungstest unter Verwendung von verschiedenen Pflanzenkulturen neben Bonhnen (*Phaseolus*

*vulgaris*), mit Rettich (*Raphanus sativus*) und Reis (*Oryza sativa*) bewertet. Der Keimungstest wurde unter Anwendung höherer Sewchar-Zugaben (0, 10, 20, 40 und 60 Mg $ha^{-1}$), als bei den Topfversuchen, durchgeführt um zu bestätigen, ob die besten Ergebnisse, in Bezug auf die Gesamttrockenbiomasse der Pflanzenkulturen, den Bereich der realistischen agronomischen Anwendungsmenge überschreiten würden (Kapitel 4).

Zur Vervollständigung der Bewertung der potenziellen Verwendung von Sewchar als Bodenzusatzstoff wurden verschiedene Analysen zur Identifizierung der Veränderungen von Klärschlamm durch HTC durchgeführt (Kapitel 4). Ziel dieser Analyse war außerdem die Ergebnisse der Toxizitäts- (Kapitel 2), Topfversuchs- (Kapitel 3) und Keimungsexperimente (Kapitel 4) besser zu verstehen sowie die möglichen Risiken und vielversprechende Sewchar-Eigenschaften hinsichtlich der Verwendung als Bodenverbesserung zu identifizieren. Zur Charakterisierung der verwendeten Biokohl und Klärschlamm wurden die folgene Parameter untersucht: Immediatanalysen (Feuchtigkeit, flüchtige Bestandteile, Aschegehalt und festen Kohlenstoff); chemische Analysen (Makronährstoff- und Spurenelementkonzentrationen, polyzyklische aromatische Kohlenwasserstoffe (PAK) und chemische Funktionalität, chemische Oberflächen- und Struktureigenschaften) und physikalische Analyse (Partikelgrößenverteilung, Oberflächenmorphologie, Oberfläche und Porenvolume). Im letzten Schritt wurde eine Umfrage durchgeführt, um die Entscheidungskriterien der Landwirte für die Auswahl eines Bodenzusatzstoffes zur Verbesserung der Bodeneigenschaften und ihre Akzeptanz gegenüber der Verwendung von Sewchar in der Landwirtschaft zu bewerten (Kapitel 4).

Die chemischen und physikalischen Analysen von Biosoliden und Sewchar zeigte chemische und physikalische Modifikationen der Eigenschaften der Biosoliden durch HTC, was zur Förderung der Porenstrukturentwicklung und zur Erhöhung des Gehalts an Spurenelementen und PAKs führte. Die Spurenelementwerte lagen unter den Schwellenwerten des brasilianischen Nationalen Umweltrates (CONAMA 375 2006). Im Gegensatz dazu lagen einige PAK-Werte über den Standardgrenzwerten, die durch CONAMA 375 (2006) vorgeschrieben sind. Dies deutet darauf hin, dass ein rechtlicher Rahmen für den PAK-Gehalt in Hydrochars von entscheidender Bedeutung ist (Kapitel 4). Darüber hinaus konnten die in Kapitel 4 durchgeführten chemischen (Sauerstoffhaltige-funktionelle Gruppen, geordnet angeordnete Kohlenstoffstruktur und aliphatischer und aromatiker Kohlenstoffgehalt) und physikalischen Analysen (Sewchar-Porosität) von Sewchar die positiven Effekte von Sewchar, die in Kapitel 3 beschriebene Bodenverbesserung, wie Verbesserung der Wasserhaltekapazität, Kationenaustauschkapazität und Nährstoffaufnahme durch Bohnen, bestätigen.

Die Ergebnisse der Umfrage zeigten, dass jüngere Landwirte, die eine höhere Ausbildung genossen haben, offener für den Einsatz von Sewchar als Bodenzusatzstoff waren. Landwirte, die Sewchar nicht als Bodenzusatzstoff verwenden würden, haben den höchsten Stellenwert hier für wirtschaftlichen Kriterien wie Dünger- und Frachtpreise zugeschrieben. Schließlich zeigten die Ergebnisse dieser Studie, dass Sewchar potentiell von den meisten befragten Landwirten als Mittel zur Bodenverbesserung verwendet werden würde (Kapitel 4).

Insgesamt zeigte diese Untersuchung, dass Sewchar in einer praktischen Anwendung ein großes Potenzial zur Ergänzung von Mineraldünger durch die erhöhte Anreicherung von Nährstoffen im Boden, der Erhöhung von Bodenfruchtbarkeitsindikatoren und der Nährstoffversorgung von Pflanzen (Bohnen) aufweist. Die mögliche Verwendung von Sewchar als Bodenverbesserung wurde auch von den meisten Landwirten der Umfrage bestätigt. Die Reaktion auf Sewchar-Anwendungen variierte jedoch in verschiedenen Pflanzenkulturen. Diese Studie zeigte verschiede physikalisch-chemische Eigenschaften von Sewchar, die eine vielversprechende Leistung als Bodenzusatzstoff nahelegen. Darüber hinaus zeigte sich keine Toxizität von Sewchar gegenüber Regenwürmern und die ökotoxikologischen Risiken von Sewchar Prozesswasser auf Garnelen (*Artemia salina*). Es zeigte sich auch, dass aufgrund der hohen Werte einiger PAK weitere Untersuchungen zur Langzeitanwendung von Sewchar im Boden erforderlich sind. Die gewonnenen Erkenntnisse können dazu beitragen, die Sewchar-Produktion anwendungsspezifisch zu gestalten. Ein weiterer Vorteil besteht darin, die Daten dieser Forschung zur Unterstützung weiterer Studien in Feldversuchen zu nutzen, damit die Langzeiteffekt sowie der Wechselwirkungen von Sewchar als Bodenzusatzstoff in verschiedenen Ökosystemen und Pflanzenkulturen auf seine agronomische Effizienz und umweltgerechte Anwendung untersucht werden können.

Künftig sollten weitere Studien zur Charakterisierung und der langsfristigen Wirkung der Anwendung von Sewchar unter verschiedenen Prozessbedingungen auf verschiedene Pflanzenkulturen und Ökosysteme durchgefürt werden. Als Ergebnis könnte unser Verständnis über die Wechselwirkungen von Sewchar mit dem Boden erweitet weden. Folglich ermöglicht es die sichere Nutzung von Sewchar als Bodenzusatzstoff für die Umwelt und die menschliche Gesundheit. Darüber hinaus muss ein Wissentransfer der Forschungsergebnisse über die Verwendng von Sewchar als Bodenzusatzstoff an die Landwirte erfolgen, um inhen die Entscheidungsgrundlagen zur Anwendung von Sewchar in der Landwirtschaft liefern zu können.

# 1 Introduction

Biosolids are the by-products of the treatment of the wastewater from domestic, and eventually contains industrial effluents (Kumar and Chopra 2016). Biosolids are generally called sewage sludge (Kumar et al. 2017). The biosolids are still an environmental liability for several municipalities worldwide, demanding treatment and disposal. The use of mineral fertilizers is environmentally and economically unsatisfactory due to, among other factors, the use of non-renewable resource as feedstock, toxic impurities content, high price and price fluctuation. In addition, in countries like Brazil, as opposed to domestic products, imported raw materials used in the formulation of fertilizers have zero tariffs and no incidence of Brazilian tax on the circulation of goods, Interstate and Intercity Transportation and Communication Services (ICMS). Consequently, the importation of fertilizers is stimulated, making the economy of these countries vulnerable, due to the dependency on imported fertilizers. Therefore, hydrothermal carbonization of biosolids is emerging as an innovative, renewable and economical alternative of soil amendment to improve soil fertility and promote the environmental and human health. However, before large scale application of Sewchar, it is of crucial importance to identify the effects of the hydrothermal carbonization (HTC) on the physical and chemical properties of the biosolids, to assess the toxicity of Sewchar for terrestrial and aquatic fauna, its effects on the soil properties and crop growth and to identify its acceptability by the farmers. Thus, to evaluate the potential of Sewchar as soil amendment the present research was directed to 1) identify the influence of Sewchar on the lethality of earthworms and the Sewchar process water filtrate on the lethality of shrimps, 2) assess the residual effect of Sewchar on plant growth, trace elements and other soil properties and to identify an optimum Sewchar application rate with respect to the plant biomass response in two consecutive pot trials 3) evaluate the effects of the HTC on the chemical and physical properties of biosolids and to compare the effect of different doses of Sewchar on germination of crops with diverse nutrient demand and life cycles (rice, bean and radish). Additionally, 4) identify the farmer's perception of Sewchar as soil amendment and the criteria utilized by the farmers for choosing a fertilizer.

## 1.1 Justification of the research

The justification of this research is showed in Figure 1-1. The amount of sewage sludge continuously increases demading treatment. In many countries wastewater management is neglected resulting in highly negative impacts on the sustainability of water supplies, the economy, the human health, and the environment (Koncagül et al. 2017). The basic sanitation is a public health issue, therefore a solution for recycling or treating the biosolids is of crucial importance; particularly in countries where there is no treatment for such residue. Currently there is no treatment or reuse of biosolids in the studied region (Goiânia-Goiás, Brazil), where 110 tons of biosolids are produced per day and the forecast for the year 2025 is 200 tons per day on a dry matter basis.

Concomitantly, governments around the world give input subsidies on fertilizers, energy, and water as some of the incentives aiming to increase agricultural production and food security (Kotschi et al. 2015). This incentive induces great demand for chemical fertilizer and fossil fuels, leading to pressure on natural resources, more greenhouse emissions and future challenges to a sustainable agricultural growth. Brazil, for example, is a world agricultural leader due to subsidized financial credit, agricultural research and rural extension - transformation of Cerrado - Brazilian tropical Savannah - into productive land (Pereira et al. 2012). Brazil is the fourth-largest consumer of fertilizer in the world and it depends on imported fertilizers (Vegro 2018).

The emergence of natural resources scarcity for agriculture is one of the projections to 2050 due to consumption patterns driven mainly by population growth, changing dietary patterns, industrial development, urbanization and climate change. Therefore, conservation of scarce natural resources and reduction of waste are some of the practices aligning climate goals and a sustainable agricultural development (FAO 2017). Consequently, based on a circular economy for nutrients (Gievers et al. 2017) the use of waste for nutrient recovery and reuse in agriculture can improve the nutrient management efficiency and, therefore, has been stimulated (Buckwell and Nadeu 2016; Prabhu et al. 2014). Within this context, HTC presents as a promising technology for biosolids treatment both from energetic and resource recovery point of view, because the hydrochar can be easily dried and palletized.

In addition, nutrients are reported to remain in plant available forms after HTC (Breulmann et al. 2014; Fühner et al. 2011) and trace elements content is reported to accumulate and to be immobilized in the Sewchar, leading to low environment risk (Huang and Yuan 2016; Zhang et al. 2014). Hence, hydrothermal carbonization appears to be either an option for the sewage sludge treatment as well as a sustainable alternative for the agricultural production. Results of the researches using sewage sludge biochar as a soil amendment indicate that Sewchar has also potential to replace or supplement the current economically and environmentally unsatisfactory use of high doses of mineral fertilizer (Deenik and Cooney 2016; Faria et al. 2017; Hossain et al. 2010), what can contribute to the environment and human health.

These results indicating benefits for agronomical applications of sewage sludge biochar are related to its physicochemical properties, such as porosity, feedstock content and presence of surface function groups (de la Rosa et al. 2011; Luo et al. 2018; Zhang et al. 2015). These biochar characteristics are reported to result in improvements on the soil physical, chemical and biological properties (Mierzwa-Hersztek et al. 2018; Vasilyeva and Butusov 2018; Woldetsadik et al. 2018), contributing to enhance plant nutrient availability (Hossain et al. 2010), soil organic matter, microbial activity (Mierzwa-Hersztek et al. 2018; Luo et al. 2018) and, consequently, better plant yield (Silva et al. 2017).

Previous researches have showed that Sewchar contains more nutrient plant available forms, Ca, Mg and P, (Breulmann et al. 2014), has higher nutrient capacity (Dieguez-Alonso et al. 2018), higher exchange capacity and lower enrichment of trace elements than sewage sludge biochar (Breulmann et al. 2017b).

Therefore, the use of Sewchar as a soil amendment is also expected to have positive effect on soil properties, resulting in plant yield improvements. However, there are relatively less studies about the application of Sewchar as a soil amendment (Breulmann et al. 2017a; Breulmann et al. 2014; Paneque et al. 2015) and they report negative and positive effects of Sewchar on plant growth. As to the Sewchar's toxicity, it was reported to have no changes on *V. fischeri*, significant decrease on *H. incongruens* toxicity (Mierzwa-Hersztek et al. 2018) and to be toxic to cress germination (Breulmann et al. 2017a). These different effects might also be related to the variety of process conditions, dose, plant crop and test organisms. As a result, knowledge about Sewchar physicochemical properties, its effect on different types of plant crop, and toxicity to biota is crucial before its land application. In addition, understanding the farmer's perception about the use of Sewchar as soil amendment it is very important to enable an appropriate biosolids management, Sewchar production and provide its use as a soil amendment from a save environmental and human health perspective.

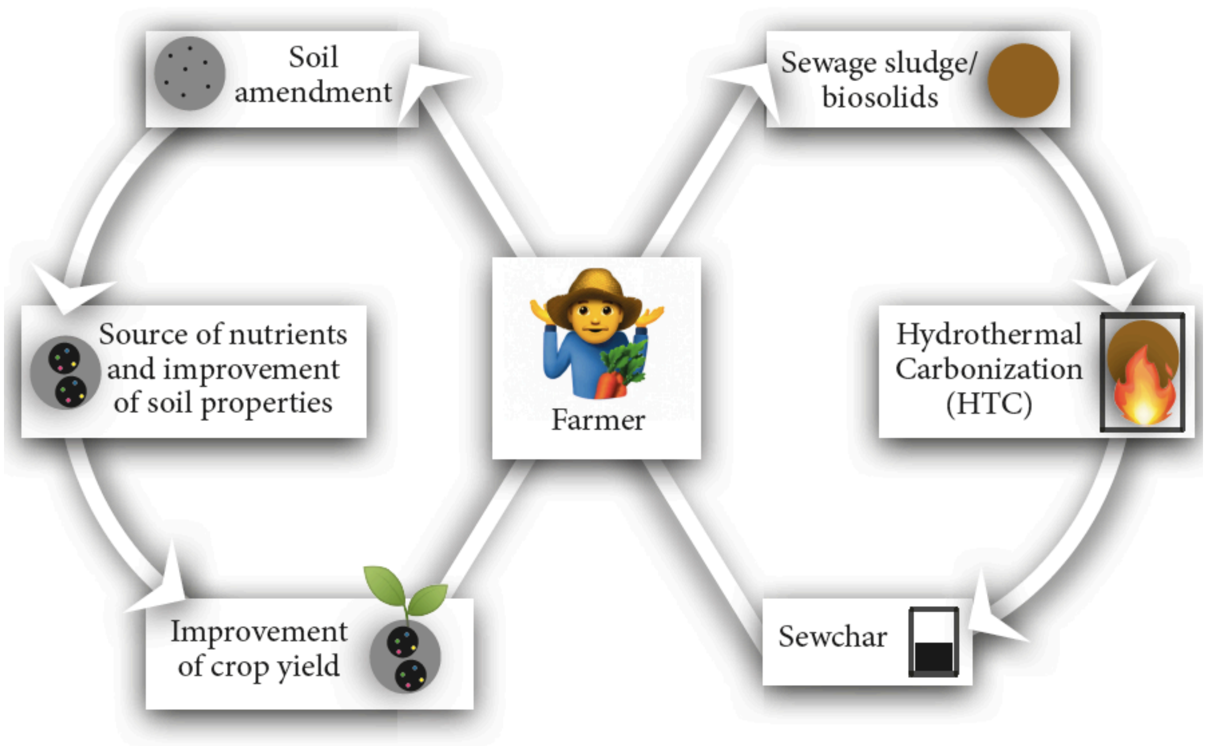


Figure 1-1 Graphic of the research justification

## 1.2 The Brazilian soil territory

The Brazilian territory reveals different soil types, due to the intensity of manifestation from different forms and kinds of topography, climate, source material, vegetation, and associated organisms, which conduct to different soil-forming processes. Ross 2013 describes the types of geological structures in sedimentary basins (64%), crystalline shields – Cratons/platforms (36%), and orogenic belts. Most of the

Brazilian territory is situated in sedimentary basins, which contain mineral deposits used as source of energy, such as coal and petroleum (Sephton and Hazen 2013; Tissot and Welte 1978). The Brazilian sedimentary basins (Amazônica, Paraíba or Maranhão, Paraná) are from the Phanerozoic (Paleozoic, Mesozoic and Cenozoic) period. Many phases of erosion contributed to the devastated and older lands (Pre-Cambrian Period) of the crystalline shields, such as Amazônica, São Francisco and Uruguaio-Sulriograndense platforms. The crystalline shields are composed of metamorphic and igneous rocks (de Almeida et al. 1981), which are the main source of Brazilian minerals, such as copper, diamonds, gold, iron, lead, etc. (Veblen et al. 2007). The orogenic belts are also very old and correspond to several stages along the Pre-Cambrian. In the past these lands were sedimentary basins that were folded many times by crust pressure. Numerous erosive phases deteriorated the three Brazilian old mountain chains (Atlantic, Brasilia and Paraguai-Araguaia). However, big extensions of land still preserve the mountainous characteristic (Ross et al. 2013).

Basically, the compartments of the Brazilian relief are defined considering these three great structures: Orogenic Belts, platforms or Cratons, and sedimentary basins. The geographer Jurandyr Ross (1995) compartmentalized the Brazilian relief in 28 geomorphological units: 11 plateaus, 6 plains, and 11 depressions. The Brazilian relief classification was elaborated based on radar images of the 80’s and 90’s. Plateaus are surfaces above 300 meters of altitude that suffer erosive wear. Plains are flat surfaces, with an altitude of less than 100 meters, formed by the accumulation of sediments of marine, fluvial and lacustrine origin. Depressions are surfaces between 100 and 500 meters in altitude, being flatter than the plateaus (it is a surface with a smooth slope) and lower than surrounding areas. In addition, the depressions have erosive erosion (formed by prolonged processes of erosion) and present residual elevations as inselbergs and residual plateaus. The plateaus are predominant in Brazilian territory mostly along southern and southeaster regions and the plain regions are situated along Amazon region (da Silva et al. 2011).

The first edition of the Brazilian Soil Classification System (SiBCS) was released in 1999 and its latest version is from 2013 (Embrapa 2013). The SiBCS is a hierarchic system, created considering morphogenetic soil attributes. The SiBCs has six categorical levels, which are structured as a key down to subgroup level: 13 orders, 43 suborders, 188 great groups, 447 subgroups, families and series (dos Anjos 2014). The lowest categorical levels (soil families and series) were not yet defined. Lepsch (2013) declares that his biggest concern is about the absence of large-scale soil maps related to the efficiency of soil surveys in Brazil. Figure 1-2 shows the map of the Brazilian soils.


Figure 1-2 Map of Brazilian soils. Scale 1: 5,000,000. Legend according to the United States Department of Agriculture and National Cooperative Soil Survey (USDA) soil taxonomy. Adapted from Embrapa 2014

Latosol (Oxisol – U.S. Soil Taxonomy) is the most common type of soil in Brazil and is reported to cover about 65% of the Brazilian land mass, being predominant in the Southeast and Midwest Brazil (Ajayi et al. 2009). Latosols are soils from B horizon with general predominance of iron oxides, aluminum, silicon and titanium, low cation exchange capacity, strongly acid and with low base saturation. They usually have low fertility and are very porous, what contributes to the low water retention capacity (Embrapa 2013).

The fertility of the soil depends on the rock that gave rise to it and the conditions of weathering. In conditions of intense weathering, the minerals that contribute to the enrichment of soil fertility are eliminated from the system. The latosols are 'old' (more weathered) soils, which the intense bioclimatic activity over a long period of time allowed the development of a deep weathering mantle. Thus, elements easily removed as calcium and magnesium, responsible for fertility, were leached from the system, resulting in soils with low fertility (de Sousa and Lobato 2004).

The anthropogenic dark earth (terra preta de índio) is a fertile black soil found in the Amazon Basin, which is assumed to be created by the activities from the indigenous population in the pre-Columbian period (de Souza et al. 2016). This method of using ‘slash-and-char’ to improve the soil fertilize has been replicated in laboratory scales through the carbonization of several types of biomass to use those chars to: improve soil properties (Puccini et al. 2018), sequester carbon (Breulmann et al. 2017b), maximize greenhouse gas mitigation potential (Mandal et al. 2016), and generate renewable energy (Zhai et al. 2017).

Brazil comprises six continental biomes, where their total area in Brazil corresponds to Amazon (49.29%) in North Brazil, Cerrado (23.92%) in Central West Brazil, Atlantic Forest (13.04%) in Southeast Brazil, Caatinga (9.92%) in Northeast Brazil, Pampa (2.07%) in South Brazil, and Pantanal (1.76%) in Central West (Brazilian Institute of Geography and Statistics - IBGE 2004). The updated Brazilian Biome mapping should be published by IBGE still in 2018. In 2015 the Ministry of the Environment (MMA) established the Brazilian Biomes Environmental Monitoring Program. Through Ordinance No. 365/2015 the program focus is to map and to monitor the vegetation cover throughout the Brazilian territory. Additionally, the program emphases mapping and monitoring deforestation; vegetation cover and land use assessment; fire monitoring; vegetation restoration and selective logging. The fire outbreaks in the Brazilian biomes in 2018 were Cerrado (39.9%), Amazon (38%), Atlantic Forest (15.5%), Caatinga (4.1%), Pampa (1.5%), and Pantanal (1%) – (Brazilian Institute for Space Research (INPE 2018).

Cerrado is the biome of the Brazilian Midwest and it is more adapted to fires. The occurrence of natural fires helps soil nutrients recycling, stimulation of dormant seeds to sprout and flourishing of several endemic species (Damasco et al. 2018). Cerrado is the second largest Brazilian biome in area and represents the most extensive area of savanna-type vegetation in South America. The first largest Brazilian Biome is Amazon, which occupies an area of 420 million hectares - 49.29% of Brazil total area (The World Bank 2017). The Cerrado occupies an area of 204 million hectares (23% of the Brazil total area) and 22% of Brazil’s population (42.7 million) lives in Cerrado (The World Bank 2017). Cerrado is one of the two Brazilian "hotspots", with over than 4,800 species of plants and vertebrates that have been found nowhere else on the planet (Damasco et al. 2018).

Based on Köppen (1936) criteria for climate classification the main climate in Brazil is tropical moist climate, which occurs in all Brazil, except in the Southern region. This type of climate represents 84% of the Brazilian territory, with dry winter and short dry season. The dry climate is concentrated in the northeastern Brazil, representing the smallest part of the Brazilian territory (5%), where the average annual precipitations is less than 800 mm (Alvares et al. 2014). Warm oceanic/humid subtropical climate is moist with mild winter, which occurs in South and Southeast Brazil, and represents 11% of the Brazilian territory (Sparovek et al. 2007).

The States of the Midwest region of Brazil are Distrito Federal, Mato Grosso, Mato Grosso do Sul and Goiás. This region of Brazil has 1,612,077 km², comprises 18% of the national territory and is the less populous region in Brazil (it hosts 7.52% of the population of Brazil). The regional economy is based on agriculture and pasture. It is geopolitically important, because it has resources that are becoming increasingly scarce, such as agricultural soils and water (Fan et al. 2016).

Goiás is the most central State of Brazil, has 340,110.385 $km^2$ and is the 7th largest Brazilian State. Goiás land structure consists of 45.5% of land for pastures and 17.9% for agricultural production (Instituto Mauro Borges de Estatísticas e estudos socioeconômicos - IMB 2016). Goiás represents 4% of the Brazilian territory and is the seventh state of the country in territorial extension. According to the Brazilian Institute of Geography and Statistics (IBGE 2017), Goiás has 6,778,772 inhabitants with 17.65 inhabitants/$km^2$ and 90% of the inhabitants live in the cities (IMB 2018).

As to the physical and territorial characterization, the climate of Goiás is predominantly tropical, with two well defined seasons: rainy and dry. The highest rainfall occurs between the month of September and Abril, with annual rainfall between 1,200 and 2,500 mm. The territory of Goiás consists of rocks that vary in age from the Archaean to the Cenozoic and are represented by granite-gneiss, greenstone belts, sedimentary volcanic complexes, badly co-ultramafic complexes and sedimentary rocks (IMB 2014). As to the relief, the state has low altimetric amplitudes with mainly flat lands. The highest point of the State lies in the Serra do Pouso Alto (1,7676 meters above sea level). The fertility of the soil is variable according to the type of relief and the generating rock. The Latosol group (Brazilian Soil Classification System – SiBCS – dos Anjos et al. 2014) is prevalent, where the red Latosol occupies most of the territory followed by Cambisols and Yellow Red Latosol (IMB 2014).

## 1.3 Background information on agriculture in Brazil and Cerrado region

Human health and environmental sustainability has been threatening by our current food system. Intensification of the agriculture driven by a lucrative and inefficient food system has boosted the production, accelerating the soil degradation and food insecurity (United Nations 2017). The global demand for food is expected to increase between 59% to 98% by 2050 (Elferink and Schierhorn 2016). Agriculture occupies 34% of the total area of Brazil (284 million ha). The mainly use of the agricultural land in Brazil is for livestock pastures. Due to the increase in production Brazil may dominate the key agricultural commodities (Camargo et al. 2017).

The latest agricultural Census in Brazil was carried out by the Brazilian Institute of Geography and Statistics (IBGE 2006) and showed how strategic is the family farming segment for the Brazilian economy, being the basis of the economy for 90% of all Brazilian municipalities up to 20,000 inhabitants. The 2017 Brazilian census of agriculture was not published yet. The family farming accounts for 38% of the gross farming income, occupies about 70% of manpower field (Brazilian Special Secretariat for

Familiy Farming and Agrarian Development – SEAD 2017) and produces 36% of the national food production (Guanziroli and Di Sabbato 2014).

The family farmers officially emerge on the national scene in Brazil up to 2006 due to its recognition by the Law 11,326/2006. This law introduces guidelines and defines general objectives for the national policy on family farming and rural family units. In particular, it provides the principles undergoing the policy. This law was regulated in 2017 by the Decree 9,064, which also established the national register of family agriculture. Additionally, it stablished that public policies aimed at family agriculture and rural family enterprises should consider the Family Agrarian Production Unit – UFPA, rural family enterprises and the National Register of Family Agriculture - CAF.

Nevertheless, the family farmers in Brazil still face fundamental limitations that inhibits their progress. Medina et al. (2015) revealed that 12.77% of the Brazilian family farmers' benefits from agricultural policies, 33.81% adopt basic technologies as soil fertilization, 5.45% belong to cooperatives, 68.26% have access to electricity, 83.07% do not have sufficient land to be competitive, 24.46% are integrated into markets, and 42.92% began attending primary school.

Mineral fertilizer has been intensively used and subsidized from many countries to promote food security and agricultural production (FAO 2017). As consequense these subsidies induce greater demand of chemical fertilizers, leading to environmental negative impacts (Cordell and White 2014). The excessive application of mineral fertilizers worsens environmental negative effects, such as soil acidification (Liang et al. 2013), humus depletion (Kotschi 2015), $N_2O$ emissions (Ullah et al. 2016), and GHG emissions (FAO 2017), promoting global warming process. Another example of the soil degradation due to the use of mineral fertilizer is the declining of the world's phosphorus (P) and potassium (K) reserves, as result of the soil mining. The high cost, the use of unrenewable natural resource and the high energy consumption for its production are some other disadvantages related to the use of the mineral fertilizers (Kotschi 2015).

As reported by Tilman et al. (2002), the global use of nitrogen (N) and phosphorus fertilizers is expected to increase threefold by 2050, featuring a progressively conversion of agricultural practices towards intensive agriculture systems. Brazil accounts for almost 6% of world fertilizer consumption, being the fourth largest fertilizer consumer in the world, where only 30% of the fertilizer demand is provided by domestic production. The challenges for the Brazilian domestic fertilizer production are the high costs of fertilizer production due to logistical difficulties, lack of infrastructure and available mineral reserves (Inacio 2013).

In addition, there is no project for the expansion of national production. The Brazilian Nitrogenated Fertilizer Unit III (UFN III) was maintained by Petrobras and could reduce the need for fertilizer imports. However, it is paralyzed since December 2014 and currently Petrobras is negotiating the sale with the Russian company Acron. 70% of the Brazilian fertilizer demand is dependent on imports and global supply conditions. Also in Goiás the second most imported product in 2016 was fertilizer US$ free on board (FOB) 410,362,889 (IMB - 2016).

According to the Brazilian Ministry of Industry, Foreign Trade and Services (MDIC 2017) the Brazilian import of raw materials and intermediate products for fertilizers in 2017 was 20.17% higher compared to the previous year. In addtion, the agriculture and agribusiness sectors have been the biggest contributor to economy recovery in the difficult period of recession. However, this strong dependece on fertilizer and raw material imports for fertilizer production is reported to currently be the main fragility of Brazilian agribusiness (Vegro 2018).

Another concern about the Brazilian agricultural expansion is environmental sustainability (Brooks 2017; FAO 2015). The Brazilian government launched in 2010 a national program for Reducing Greenhouse Gas Emissions in Agriculture (ABC Program) and in 2016 a national plan for adaption to climate change, to reach the objectives defined by the United Nations Climate Change Conference (COP15) in 2009. The ABC Program prioritizes the increase of agricultural productivity with reduction of greenhouses gases (such as nitrous oxide - $N_2O$, methane – $CH_4$ and carbon dioxide – $CO_2$), responsible for global warming (Brazilian Public Agricultural Research Corporation - Embrapa 2016). Additionally, in 2012 the presidential decree n. 7,794 (2012) about the national policy for agroecoloy and organic production in Brazil was lauched.

The State of Goiás is very representative for the Brazilian agriculture, occupying the fourth place as agricultural producer state in Brazil. Soybean is the most important economic crop produced in the state (IMB 2018). This region of Brazil has the most agricultural development in grain production taking place, what contributes to global food security (Hosono et al. 2016). From the 1960s to the early 1980s the government-led industrialization process took place in Brazil, which began to transform the “unproductive” Cerrado into productive land to increase agricultural production and provide food at affordable prices for the growing urban population (Pereira et al. 2012). The replacement of Cerrado for agropastoral activities is resulting in negative effect on the biodiversity. Therefore, effort is expected from the Brazilian government on managing and intensifying previously cleared lands to preserve Cerrado (Spera 2017).

One example of the consequence of the agricultural expansion is showed in Figure 1-3. More than half of the Cerrado area has been converted into cash-crop agriculture, pasture, and other uses over the latest decades (Beuchle et al. 2015; da Silva et al. 2017). Françoso et al. (2018) have reported the critical protection of biodiversity in Cerrado, where the protected areas represent 3%. However, 17% was the target defined by the Convention on Biological Diversity. The vegetation of Cerrado encompasses the entire state of Goiás, where likewise most of the area is occupied per anthropic activities, such as agriculture and pasture, resulting in the region of Brazil with lowest fraction of the Cerrado original physiognomy (Maranhão et al. 2017). As result of the land degradation, soil compaction and erosion are current problems resulting in high costs of production and stimulation of the Cerrado aridity “aridification” (Pereira et al. 2018). In addition, the conversion of Cerrado vegetation to pasture was confirmed to cause the deterioration of the soil hydro-physical properties, to increase streamflow, and to reduce evapotranspiration (Nóbrega et al. 2017).

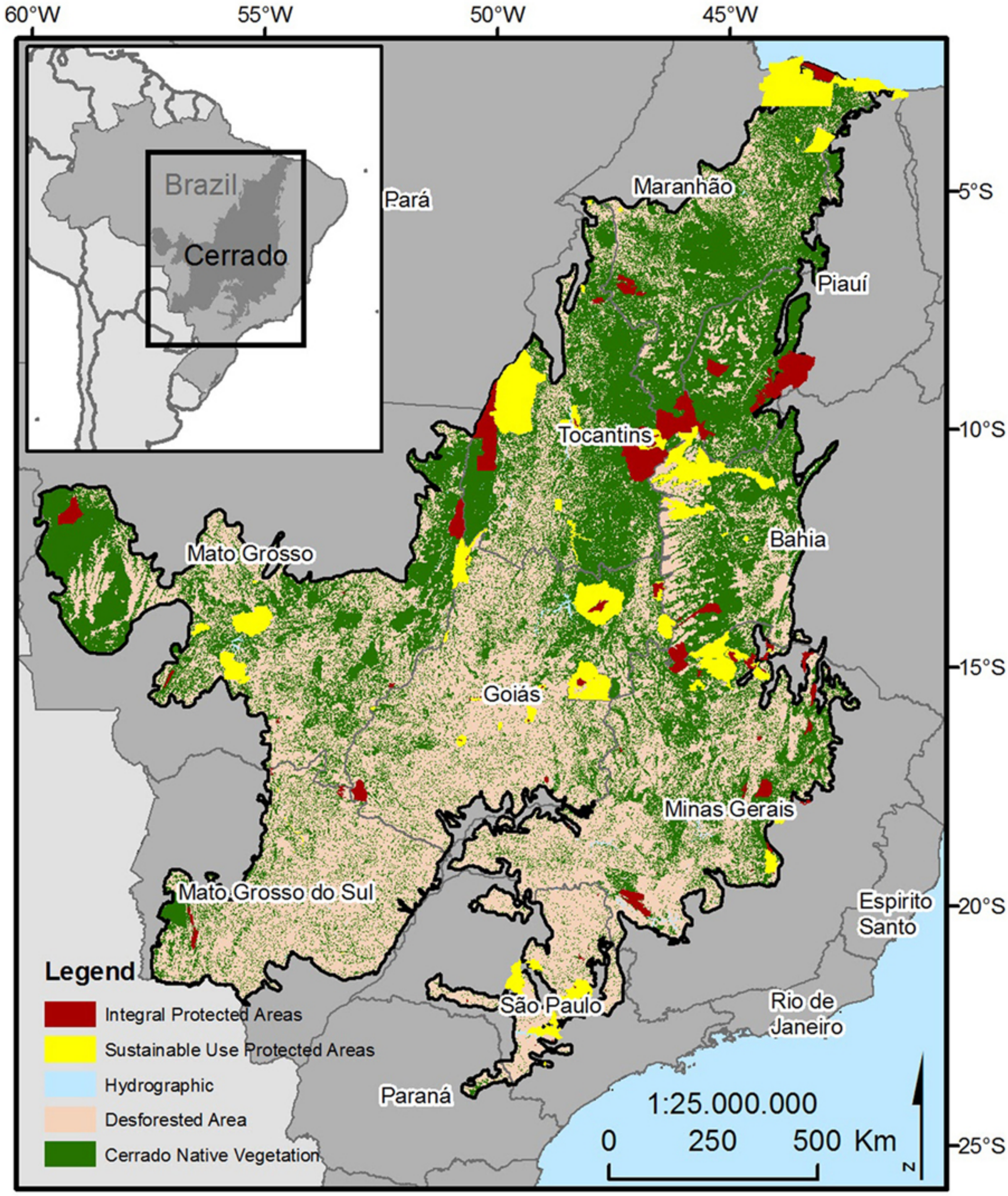


Figure 1-3 Cerrado deforestation. Source: Françoso et al. 2018.

## 1.4 Hydrothermal carbonization

The hydrous pyrolysis or hydrothermal carbonization (HTC) is a technique that involves heating biomass together with different types of acids, which act as a catalyst (Figure 1-4). This method of biomass processing was first used and described by the German chemist and Nobel prize winner Friedrich Bergius in the year 1913 as a means to simulate natural coalification of organic matter in the laboratory (Bergius 1913). In 2006 Professor M. Antonietti brought this process to light again and investigated it in more details (Titirici et al. 2007).

The HTC process is carried out manly in a closed vessel that contains the wet biomass and it is heated to temperatures until 250 °C and over a variable residence time (Fiori et al. 2014) and autogenous pressure (Fakkaew et al. 2015; Kambo and Dutta 2015; Titirici 2013). The solid products of HTC and pyrolysis are called respectively hydrochar and biochar.

The reaction mechanisms of hydrothermal carbonization are similar to those in dry pyrolysis and include hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization (Neethu and Dubey 2018; Titirici et al. 2008). Normally dehydration rate (elimination of hydroxyl groups) is higher than decarboxylation – elimination of carboxyl groups (Fuertes and Ziegler 2010). The HTC has also been shown to be exothermic in nature and in comparison with biochar produced by dry pyrolysis (Lucian and Fiori 2017; Titirici et al. 2007). The HTC-system has an advantage compared to other thermochemical processes, because it can convert wet input material into carbonaceous solids at relatively high yields without prior drying processes before or during the process (Fang et al. 2018; Libra et al. 2011; Ok et al. 2015). Additionally, some gases, such as $CO_2$, nitrogen oxides and sulfur oxides are dissolved in water, forming the corresponding acids and/or salts, making further treatment for air pollution possibly avoidable (Kalderis et al. 2014).

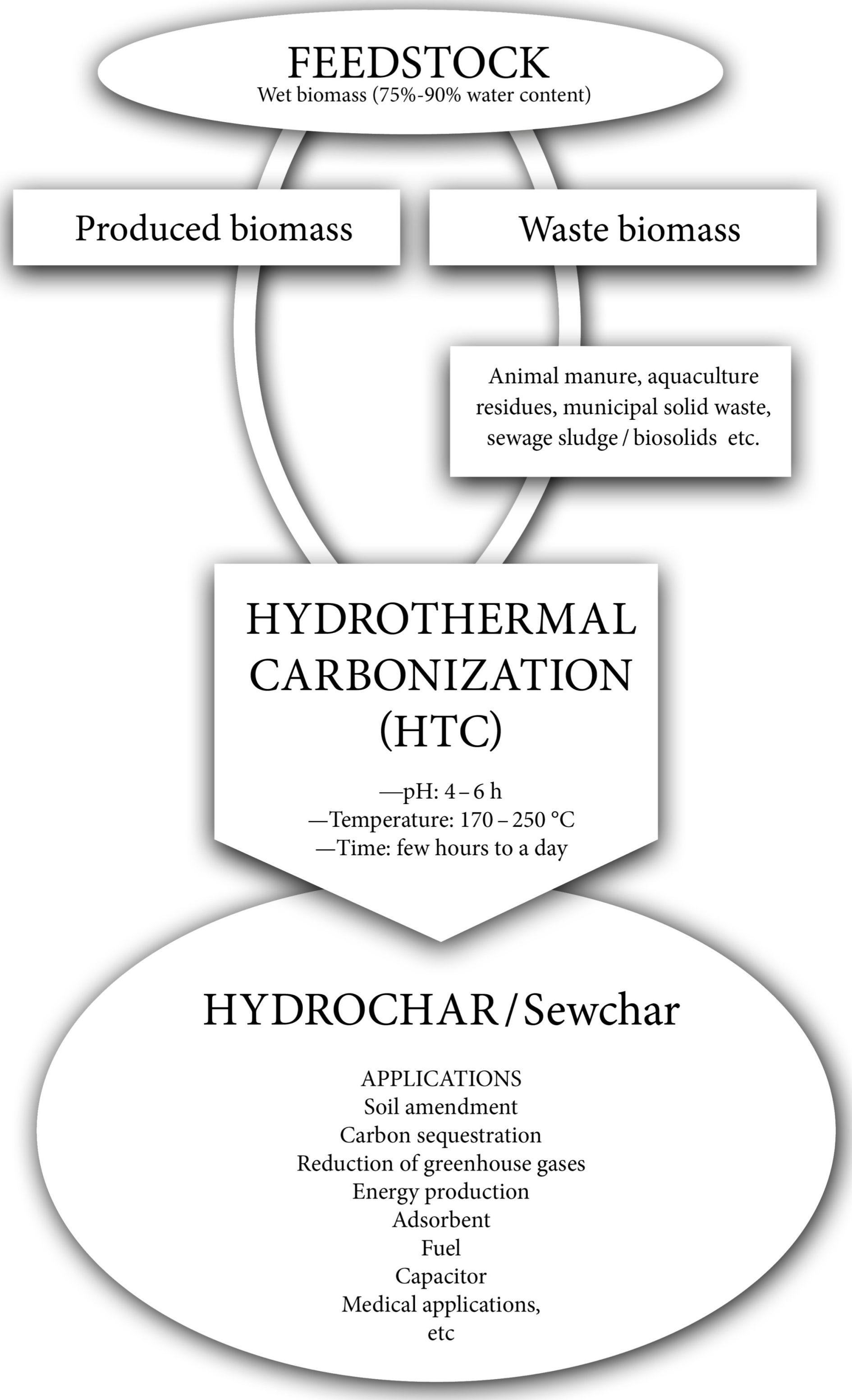


Figure 1-4 Hydrothermal carbonization process

Higher level of cation exchange capacity and lesser extent of trace elements accumulation were the advantages reported by the hydrothermal carbonization of sewage sludge compared with pyrolysis (Breulmann et al. 2017b). In general, hydrochar has been reported to have predominantly mesoporosity independently of feedstock and process conditions, having lower surface area, higher pore volume, higher oxygen-containing functional groups and nutrient availability than biochars (Dieguez-Alonzo et al. 2018). The physicochemical properties of chars result in their sorption potential, which may increase the CEC and reduce dissolved organic C content (Eibisch et al. 2015). Besides, hydrochar is reported to have a hydrophobic core and a hydrophilic outer surface (Chung et al. 2017), while most freshly biochars are reported to be hydrophobic (Lehmann and Joseph 2015).

Different process conditions of hydrothermal carbonization (Wirth et al. 2015) of several types of biomass have been studied for a variety of applications: eliminate micropollutants (Bestoem et al. 2018); anode in Li-ion battery (Fakkaew et al. 2016); phosphorus recovery (Takahashi et al. 2015); solid fuel (He et al. 2013; Kim et al. 2014; Lucian and Fiori 2017); energy recycling (Zhai et al. 2017); methane production (Danso-Boateng et al. 2015); soil amendment for reducing greenhouse gas emission and improve soil properties; medical applications; capacitor; adsorbent to the removal of trace element, bacterial contaminants, organic pollutant, pathogens and phosphate (Chung et al. 2017; Fang et al. 2018; Patra et al. 2017).

One of the advantages of the HTC is that it extents the potential use of a diversity of non-traditional biomass streams (Wang et al. 2018). Sewage sludge or biosolids are incessantly generated and renewable residues that are an environmental liability for several municipalities, where recycling it is still not a reality (Canedo et al. 2016). The challenge about the use of biosolids as feedstock for hydrochar production is that biosolids are spatial and temporal variable because the composition of the input material is very heterogenic and inconstant. In addition, the chemical characteristics of the biosolids are dependent upon local requirements and methods of treatments (Malinowska et al. 2015). Furthermore, a high level of sanitation and stabilization of organic matter is required for the agricultural utilization of municipal sewage sludge to maintain soil, water and air qualities and to effectively use these bioresidues as soil amendment and a source of nutrients for plants (Dumontet et al. 2012; Vasilyeva and Butusov 2018).

Wastewater treatment plants (WWTPs) are responsible for the appropriate destination of the sewage sludge in Brazil. Nowadays the wastewater in Goiânia goes to the treatment plant Dr. Hélio Seixo de Britto - WWTP-Goiânia – and receives only the advanced primary treatment (chemically assisted). 75% of the collected wastewater is treated and per day it is produced 110 tons of biosolids and the forecast for the year 2025 is 200 tons per day on a dry matter basis. The wastewater primary treatment consists of the removal of coarse materials and sand. After the addition of coagulants and polymers it is possible to reduce 50% of the organic matter and 80% of the total suspended solids (Bandeira et al. 2017).

Since 2005, after the treatment, the biosolids from the WWTP-Goiânia were used by farmers as soil amendment. The farmers must participate in a bidding process to be able to receive the biosolids. This bidding process is very bureaucratic and all the environmental agency requirements must be fulfilled.

Therefore, there are few farmers interested in the use of the biosolids as soil amendment. Consequently, the WWTP-Goiânia has a problem with the accumulation of biosolids.

Sewage sludge content includes plant nutrients (N and P), ashes, trace elements, pathogens, several pollutants (pathogens, persistent organic pollutants, etc) and the main organic compounds are carbohydrates, proteins, lipids, lignin (He et al. 2014). Application of sewage sludge to land was reported not currently to be a common agricultural practice for all vegetable farmers (Krogmann et al. 2001). The experience of sewage sludge application on the soils it is also not widespread in Brazil, because there are few cities, which have wastewater treatment units. The Brazilian National Information System on Sanitation (SNIS) states that 51.9% of the total wastewater is collected. 44.9% of the produced wastewater is treated and 74.9% of the collected wastewater is treated (SNIS 2016). Additionally, the high water content in biosolids (from 90 to 95 dag $kg^{-1}$) offered to the farmers as soil amendment in Brasília (Brazil) demanded high doses of biosolids application to have the equivalence to the commercial fertilizers (Silva et al. 2002). Consequently, the transport of a big volume might be very expensive for the farmers and it could limit the utilization of biosolids as soil amendment.

Studies about sewage sludge as soil amendments showed improvement on soil properties (El-Nahhal et al. 2014; Tsadilas et al. 2018), stimulated microbial activity (Wolna-Maruwka et al. 2018), increased the levels of macronutrients in plant and soil (Amadi et al. 2018; Soudani et al. 2017) and immobilized toxic elements in soil (Placek et al. 2016; Zhang et al. 2017). However, it may also contain potentially harmful substances, such as parasites, pathogens, trace elements, non-essential trace elements, organic contaminants, pharmaceutical drug residues, salts, and radioactive materials (Devi and Saroha 2017; Kumar et al. 2017; Paz-Ferreiro et al. 2018), limiting its agriculture use (Kirchmann et al. 2017).

## 1.5 Use of biosolids-derived chars as soil amendment

Carbonized biomass is an alternative that has being studied as soil conditioner in agricultural crops. Biochar is a charred matter, produced intentionally to be applied to soils to sequester carbon and to improve soil properties (Lehmann and Joseph 2015). When applied to sewage sludge, the HTC solid product is called Sewchar and it results both in sanitation of the sludge and in its stabilization (Danso-Boateng et al. 2015). In Brazil the criteria and procedures for the agricultural use of wastewater sewage sludge or derived product for agricultural purposes are defined by the National Environment Council (CONAMA 2006).

The Sewchar formation pathways are reported to occur due to the hydrolysis, dehydration, and Maillard reactions, where there is the dissolution of carbohydrates and proteins fractions and the formation of polyaromatic hydrochars. Afterwards, the undissolved fraction of sewage sludge is reported to undergo condensation, dehydration, and decarboxylation (He et al. 2013; Wang et al. 2018).

The studies about carbonization of sewage sludge for agronomical purposes are mostly about biochar and showed to improve plant growth (Deenik and Cooney 2016; Song et al. 2014; Yue et al. 2017); to increase nutrients in the soil and soil fertility indicators (Hossain et al. 2010; Sousa and Figueiredo 2015; Vasilyeva and Butusov 2018); to have potential to replace mineral fertilizers (nitrogen, phosphorus and micronutrients) for corn production (Faria et al. 2017); to enhance the immobilization of potentially toxic elements and to reduce their bioavailability and mobility in the soil (Bogusz et al. 2017; Méndez et al. 2012); to exceed the trace element threshold (Wesenbeeck et al. 2014), with low (Hossain et al. 2010; Khan et al. 2013; Yue et al. 2017) and increased (Yue et al. 2016) bioavailability; to increase soil respiration (Méndez et al. 2012); to mitigate potentially toxic elements and polycyclic aromatic hydrocarbons bioaccumulation (Wagas et al. 2014; Woldetsadik et al. 2016; Zielińska and Oleszczuk 2015); to reduce toxicity to *Heterocypris incongruens* and to increase microbial C use efficiency (Mierzwa-Hersztek et al. 2018); to remove Cr (VI) and As (V) from the aqueous solution (Agrafioti et al. 2014); to reduce $N_2O$ emissions and to stimulate the uptake of $CH_4$ (Khan et al. 2013); to reduce the toxicity of the sewage and leaching of nutrients from the amendment soil, stimulating effect on the tested organism (Kończak and Oleszczuk 2018); and to stabilize trace elements in soil (Zhang et al. 2013).

The fewer studies about the hydrothermal carbonization of sewage sludge have also suggested the Sewchar potential to be used as a soil amendment (Álvarez et al. 2017). However, these studies were restricted to show the potential of Sewchar to: recover phosphorus (Takahashi et al. 2015); maintain the bioavailability of the trace elements within the permitted concentrations (Zhang et al. 2014); immobilize trace elements through the combination of HTC followed by pyrolysis (Liu et al. 2018), have a positive effect on accumulating Pb, Ni, Cd and Zn in Sewchar due to the change in the feed-water pH (Zhai et al. 2016), remain nutrient in plant available forms during HTC (Breulmann et al. 2014; Fühner et al. 2011), degrade phytotoxic components of HTC in the field (Breulmann et al. 2014), increase ryegrass biomass (Paneque et al. 2015), improve soil quality due to the increase in soil microorganism and Cd immobilization in a contaminated soil (Ren et al. 2017).

Other studies concerning sewage sludge chars show that their effects on plant growth are very complex and reliant not only on variables, such as char dose and crop type, but also on process conditions, experimental setting, type of soil, char residual effects, and application of additional fertilizer. Breulmann et al. (2014) showed that HTC char stimulated plant growth of winter rape even at low application rates, while pyrolysis char improved plant growth only if applied at high rates together with mineral fertilizer. Furthermore, Fühner et al. (2011) stated that higher-temperature of HTC (180 x 200 ºC) contributed to higher plant tolerance, although Breulmann et al. (2017a) stated that increasing the temperature (180 x 200 ºC) and time (4 x 8 h) of the hydrothermal sewage sludge treatment increased the negative effects of the Sewchars on plant growth. Faria et al. (2017) used sewage sludge biochar produced at 300 and 500 ºC for corn yield, where biochar produced at 300 ºC was reported to have higher levels of N and biochar produced at 500 ºC had higher levels of P.

The residual effect of sewage sludge chars was also reported to improve plant biomass (Deenik and Cooney 2016; Woldetsadik et al. 2018). However, different results were reported using sewage sludge chars in field and pot trials. Sewage sludge chars have been reported to promote plant growth in field trials and suggested to have deleterious effects in small pots because of the unnatural settings (Butt 1999). Additionally, Woldetsakit et al. (2017) reported the highest absolute yield of fecal biochar addition (with or without N) in less fertile sandy loam soil. Some other studies have shown that the first application of sewage sludge biochars combined with mineral fertilizers has a better effect on the crop production performance than biochar alone (Deenik and Cooney 2016; Faria et al. 2017; Hossain et al. 2010). Furthermore, Breulmann et al. (2017a) stated that sewage sludge char treatment, such as pre-washing with water, loosened essential plant available nutrients, decreasing their possible value as a soil amendment.

Bioassays, additional to chemical analysis, contribute to better understanding about the potential Sewchar toxicity. Nevertheless, studies concerning bioassays using hydrochars from sewage sludge are limited to cress seed germination (Breulmann et al. 2017), spring barley germination (Bargmann et al. 2013), and genotoxicity assay (Busch et al. 2013). The addition of sewage sludge hydrochar to soil has been reported to increase the abundance of soil microorganism, to decrease soil pH and electrical conductivity, and to immobilize Cd in a contaminated soil (Ren et al. 2017).

The physicochemical properties of biochars have also been studied and helping to understand the effects of chars as a soil amendment (Li et al. 2017). Electrical conductivity (EC) is reported to predict salinity, where increasing conversion temperatures of biochar resulted in greater ash content, indicating higher EC and pH (Rehrah et al. 2014). Application of biochars with high EC as a soil amendment may increase soil salinity, resulting in plant water and salt stress and nutrient imbalances (Nazar et al. 2017). The high ash content is related to the presence of minerals and other inorganic compounds, which are full of micronutrients for plants, while volatile matter is a biodegradable constituent that shortly enhances soil organic carbon (Yuan et al. 2015). Aromaticity and polarity of biochars have been predicted by molar H/C and O/C ratios respectively (Uchimiya et al. 2010). Increasing conversion temperatures have been reported to reduce the molar O/C ration, resulting in less hydrophilic biochars (Ahmad et al. 2012). Pyrolysis is reported to reduce O-containing-containing functional groups, while HTC to create them (Dieguez-Alonso et al. 2018).

Generally, with gradual aging, biochar is reported to reduce in size, and to develop functional groups such as carboxyl, and carbonyl or hydroxyl on biochar surface, potentially increasing interactions between derived organic materials with soil minerals, nutrients, and contaminants. These interactions promote a higher ability to retain cations and to increase the bioavailability of anions such as phosphate and arsenate, increasing the stability in the soil (Mia et al. 2017). Formation of functional groups is reported to provide sites for surface negative charge in biochars, which increases with progressive oxidation (Cheng et al. 2008).

The oxygen-containing surface functional groups have been reported to increase sorption capacity of biochar (Jin et al. 2018; Mandal et al. 2017), because the adsorption is reported to be hydrogen-bonds (Pastor-Villegas et al. 2010). The oxygen-containing functional groups are also reported to decrease with increasing conversion temperatures of biochars (Dieguez-Alonso et al. 2018). The removal oxygen-containing functional groups is reported to increase surface area and hydrophobicity and to decrease the polarity of biochar, which together with the high aromaticity of biochar promoted its sorption capacity (Ahmad et al. 2012; Ahmad et al. 2013).

Cation exchange capacity has also been related to the negatively charged oxygen-containing functional groups on the biochar surface - carboxylate and hydroxyl functional groups (Lawrinenko et al. 2015; Mukherjee et al. 2011; Mukome and Parikh 2016). High conversion temperatures have resulted in decreased oxygen-containing functional groups and, therefore, decreased cation exchange capacity of biochars (Zhao et al. 2017). Increasing cation exchange capacity promotes available cation retention for the plant due to the negative surface charge, large surface area, and charge density of the feedstock char (Zhang and You 2013).

The chars surface area is also associated with the loss of organic compounds due to volatization of organic compounds in high temperatures, creating voids in the biochar matrix (Downie et al. 2009). Chars with a high surface area and charges have high adsorption ability. Likewise, the adsorption is related to take place in micropores, whilst meso- and macropores act as pathways of the adsorbate to the micropores (Zhang and You 2013). The surface area and porosity of chars indicate their potential to retain water, nutrients, contaminants, stimulate microbial activity in soil, reduce greenhouse gas emissions, and sequester carbon (Igalavithana et al. 2018; Mukome and Parikh 2016). The soil retention of water and nutrients is related to the improvement of bulk density, aggregation ability and water holding capacity of chars, what directly contributes to the soil fertility (Ding et al. 2016). The surface area and pore volume of biochar are reported to increase with increasing conversion temperatures up to a particular temperature is reached, when the biochar structure collapses and the microstructural rearrangement occurs (Dieguez-Alonso et al. 2018; Li et al. 2017).

The porosity of chars is related to the loss of water and aromatic C-groups in high conversion temperatures and depends on conversion temperature, pressure, feedstock (Downie et al. 2009; Gray et al. 2014; Rutherford et al. 2005). Biochars with small pore size are reported to have less sorption capacity because they cannot trap large sorbate, regardless their charges or polarity (Li et al. 2017). The volatile matter is reported to be released from chars' pore-infillings, increasing micropore surface area and decreasing acid functional group concentration with conversion temperature (Mukherjee et al. 2011).

Assessment of the farmer's acceptance in using product from sewage sludge as soil amendment is also a gap to be studied. Krogmann et al. (2001) reported that perceived risks, including negative public perception, odor complaints and increase of contaminants in the water supply outweighed economic incentives and soil improvement benefits. Differently, a mail survey of 467 Swiss farmers showed acceptability of the Swiss farmers about urine-based fertilizers and 42% willed to purchase such product (Lienert et al. 2003). Similarly, most urine diversion dehydration toilet (UDDT) users were applying UDDT products as fertilizers on their farms in Kenya (Uddin et al. 2012). Therefore, understanding farmers' perceptions and choices regarding land application of sewage sludge by-products is crucial to develop locally accepted strategies for managing biosolids and provide the use of Sewchar as soil amendment.

## 1.6 General and specific objectives

The general objective of this thesis was to evaluate the effect of the hydrothermal carbonization (HTC) as a treatment for biosolids and the use of Sewchar as soil amendment for Cerrado region of Brazil. The specific objectives were:

- to identify the effects of the HTC on chemical and physical properties of biosolids
- to assess the toxicity of Sewchar to earthworms and to three different crops and to assess the toxicity of Sewchar process water filtrate to shrimps
- to evaluate the residual effect of different Sewchar doses and to identify the optimal Sewchar application rate for bean cropping
- to identify the acceptance of Sewchar as soil amendment and the decision criteria of farmers for choosing a soil amendment.

## 1.7 Thesis structure

This thesis consists of five chapter exploring research conducted on preparation and use of a biosolids derived hydrochar as an environmentally sustainable alternative to be used as soil amendment. Figure 1-5 shows the thesis scope.

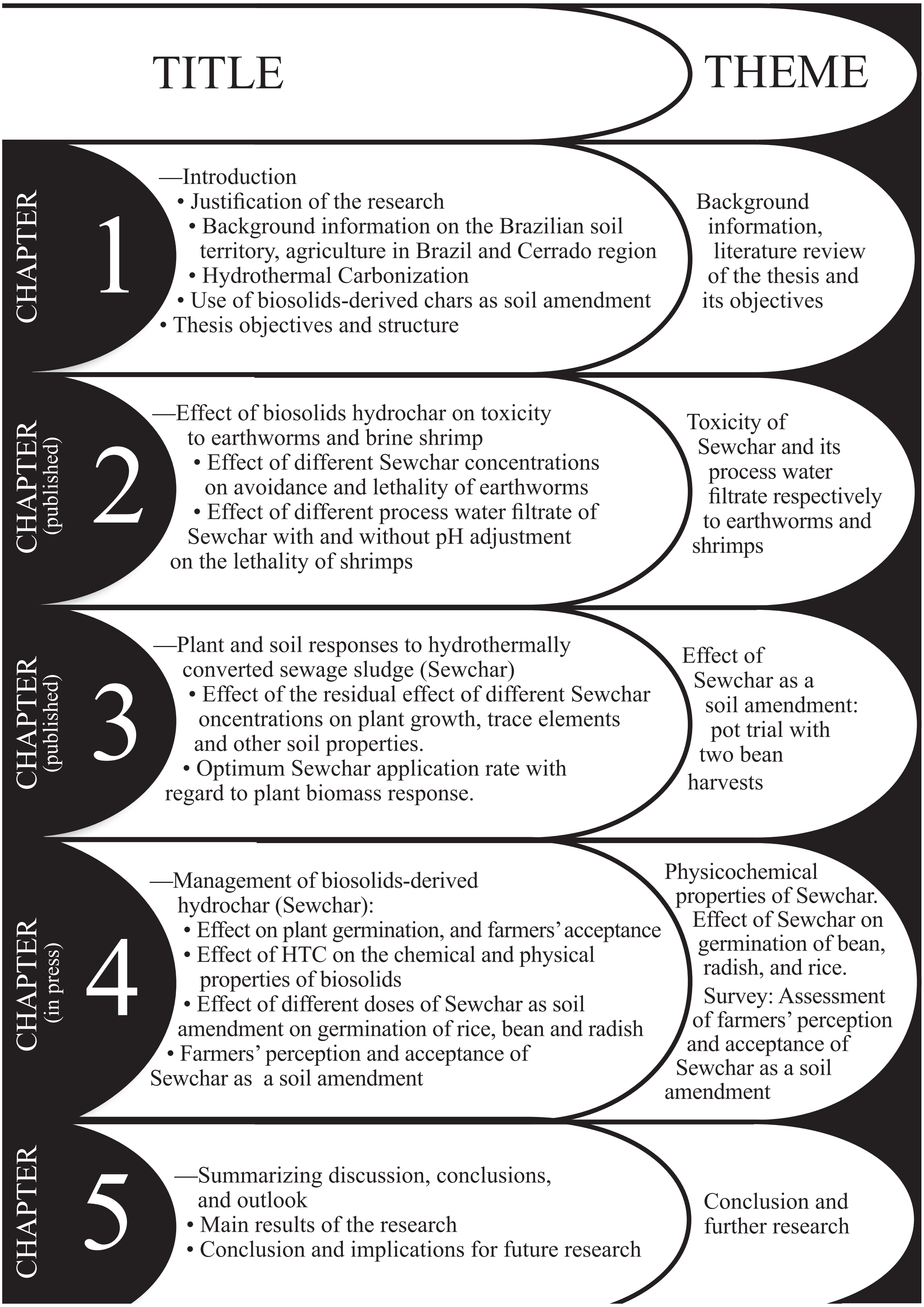


Figure 1-5 Thesis scope

Chapter 1 presents the background information concerning Brazilian soil territory and the agriculture in Brazil and Cerrado region. This chapter also reviews and analyzes limitations of researches concerning the application of Sewchar as soil amendment. In addition, it emphasizes the research objectives and summarizes the thesis structure.

Chapter 2 investigates the effect of Sewchar on the toxicity to earthworms and the effect of the Sewchar process water on the toxicity to shrimps. This chapter includes information related to the acute toxicity of Sewchar concentrations up to four times the reasonable field application rate to earthworms. This chapter also contains the median lethal concentration of the Sewchar process water filtrate with and without pH adjustment to shrimps. This chapter also investigates the chemical characterization of biosolis and Sewchar. This study consists of a paper accepted in Environmental Geochemistry and Health. 39, 1351-1364. (Melo, T.M., Bottlinger, M., Schulz, E., Leandro, W.M., de Aguiar Filho, A.M., Ok, Y.S., Rinklebe, J.). Effect of biosolid hydrochar on toxicity to earthworms and brine shrimp.

Chapter 3 explores the residual effect and the optimum Sewchar application rate in a pot experiment with two harvests on bean growth, trace elements and other soil properties. This study deals with the effect of Sewchar and mineral fertilizer on bean total dry matter; soil properties (cation exchange capacity, base saturation, potential acidity, water holding capacity); soil content (macro and micronutrients, C : N ratio, ammonium, mineral N, nitrate, total N, total organic carbon, hot water extractable carbon); nutrient uptake by beans; and threshold of Sewchar applications. This study consists of a paper accepted in Chemosphere. 206, 338-348. (Melo, T.M., Bottlinger, M., Schulz, E., Leandro, W.M., de Aguiar Filho, A.M., Wang, H., Ok, Y.S., Rinklebe, J.). Plant and soil properties to hydrothermally converted sewage sludge (sewchar).

Chapter 4 investigates the effect of HTC on the chemical and physical properties of biosolids and compare the effect of different doses of Sewchar as soil amendment on the germination of crops (rice, bean and radish) with diverse nutrient demands and life cycles. This chapter also explores the farmers' perceptions of Sewchar as a soil amendment, whether famers are prone to use Sewchar as soil amendment, and which criteria are utilized by farmers when choosing a fertilizer. This study consists of a paper accepted in Journal of Environmental Management. In press. (Melo, T.M., Bottlinger, M., Schulz, E., Leandro, W.M., de Aguiar Filho, A.M., Wang, H., Ok, Y.S., El-Naggar, A., Rinklebe, J.). Management of biosolids-derived hydrochar (Sewchar): physical and chemical properties, effect on plan germination, and farmers' acceptance

Chapter 5 summarizes the main research findings with respect to the potential use of Sewchar as a soil amendment, discussing the correlation between the chapters. This chapter also presents a general conclusion and suggests potential future studies to better understanding of subjects that require supplementary research or were beyond the scope of this study.

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# 2 Effect of biosolids hydrochar on toxicity to earthworms and brine shrimp

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## 2.1 Abstract

The hydrothermal carbonization of sewage sludge has been studied as an alternative technique for the conversion of sewage sludge into value-added products, such as soil amendments. We tested the toxicity of biosolids hydrochar (Sewchar) to earthworms. Additionally, the toxicity of Sewchar process water filtrate with and without pH adjustment was assessed, using brine shrimps as a model organism. For a Sewchar application of 40 Mg ha$^{-1}$, the earthworms significantly preferred the side of the vessel with the reference soil (control) over side of the vessel with the Sewchar treatments. There was no acute toxicity of Sewchar to earthworms within the studied concentration range (up to 80 Mg ha$^{-1}$). Regarding the Sewchar process water filtrate, the median lethal concentration (LC50) to the shrimps was 8.1% for the treatments in which the pH was not adjusted and 54.8% for the treatments in which the pH was adjusted to 8.5. The lethality to the shrimps significantly increased as the amount of Sewchar process water filtrate increased. In the future, specific toxic substances in Sewchar and its process water filtrate, as well as their interactions with soil properties and their impacts on organisms, should be elucidated. Additionally, it should be identified whether the amount of the toxic compounds satisfies the corresponding legal requirements for the safe application of Sewchar and its process water filtrate.

## 2.2 Introduction

Sewage sludge is typically considered as a suitable soil amendment because it contains valuable plant nutrients, such as high concentrations of nitrogen (N) and phosphorous (P) and small quantities of other nutrients (Roy et al. 2011). However, toxic pollutants, such as heavy metals and organic contaminants, as well as pathogenic organisms are often present in municipal sewage sludge (Apedaile 2001; Kim et al. 2015). In addition, its huge volume makes its treatment and disposal a challenge for municipalities worldwide. The high process temperatures of thermal treatments can destroy pathogens and potentially organic contaminants such as pharmaceutically active compounds (Bridle et al. 1990; Süterlin et al. 2007), thereby, such treatments appear as an opportune alternative for producing sewage sludge byproducts for agronomic purposes. Hydrothermal carbonization (HTC) is an example of a catalytic conversion process, where wet biomass, such as manures, digestate or sewage sludge, is heated to temperatures between 170 and 250°C (Funke and Ziegler 2010; Reza et al. 2014; Sevilla and Maciá-Agulló 2011) in a closed vessel over a period ranging from a few hours to a day. The aim is to imitate the natural coalification of the biomass, which occurs at a time scale of some hundreds (peat) to hundred million (black coal) of years (Titirici and Antonietti 2009). Hydrochar is the solid product resulting from the HTC process. The solid product of the HTC specifically of sewage sludge is called Sewchar. Biochar, in turn, is the solid product resulting from the pyrolysis process, which consists of thermal decomposition of a biomass with low water content under anaerobic conditions (Ahmad et al. 2014). The advantage of the HTC process as compared to other thermal systems is that wet feedstocks can be converted into carbonaceous solids without the need for energy-intensive drying before or during the process (Libra et al. 2011; Ok et al. 2015).

The different feedstocks, process conditions and production techniques resulting in large differences in hydrochar properties (Gao et al. 2013; Kalderis et al. 2014; Kambo & Dutta 2015) and the temperature seem to be the main drivers determining the chemical composition of hydrochars (Ahmad et al. 2012; Lynam et al. 2015, Wiedner et al. 2013). Previously, hydrochars from sugar beet pulp, beer draff (Gajić & Koch 2012), beet root chips (Jandl et al. 2013; Rillig et al. 2010; Salem et al. 2013), pig slurry (Schimmelpfennig et al. 2014), bagasse, hickory, peanut hull (Fang et al. 2015) and sewage sludge (Fühner et al. 2010) were studied as soil amendments. The process parameters for hydrochar production were shown to be more compatible with plants when produced at 200 °C and Sewchar when produced at shorter conversion times, i.e., 4 versus 8 hours (Fühner et al. 2010). Additionally, hydrochar from sewage sludge was found to increase biomass production (Paneque et al. 2015), while that from sugar beet pulp and draff were suggested to offer a moderate potential for carbon sequestration (Gajić et al. 2012). Still, the reduction of the average pore size of sewage sludge after the HTC process has further implications regarding its water and nutrient retention capacity (Paneque et al. 2015). Various authors have suggested that the process water of Sewchar is also suitable as a liquid fertilizer for agricultural proposes due to its heavy metal-free property (Verstegen 2015) and high concentration of plant food nutrients, especially nitrogen and potassium (Saetea and Tippayawong 2013; Sun et al. 2013).

Other studies have speculated that most of the toxic or harmful compounds are present in the liquid phase of hydrochar (George et al. 2012; Glasner et al. 2011; Libra et al. 2011), particularly at lower HTC reaction temperatures (Funke and Ziegler 2010; Hoekman et al. 2011; Yu et al. 2008). Furthermore, it has been reported that the solid phase of hydrochars may also contain several toxic substances, such as long C-chain aliphatic compounds (Jandl et al. 2013), organic acids, phenols, polychlorinated dibenzoditoxins (PCDD's) and hydroxymethylfurfural (HMF) (Bargmann et al. 2013; Kang et al. 2013 Wagner and Kaupenjohann 2014). When using sewage sludge as feedstock either for HTC or for pyrolysis, other common contaminants identified were hydrogen sulfide ($H_2S$), ammonia ($NH_3$), (Xue et al. 2015), perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Kim et al. 2015). However, the bioavailability reduction of mostly heavy metals was observed in the HTC of sewage sludge, although they accumulated in the Sewchar (Zhang et al. 2014). Furthermore, the total residual concentration of PFOA and PFOS in the sludge biochar does not significantly decrease after pyrolysis (Kim et al. 2015). Additionally, the conditions in the HTC process enable numerous not yet identified chemical reactions and the formation of unknown organic molecules (Busch et al. 2013). Some different process parameters have already been tested for Sewchar production, but no significant reduction of the heavy metals seems to be possible using that technical process configuration (Verstegen 2015).

To assess the ecotoxicological risks of hydrochars and biochars to biota, ecotoxicological tests with living organisms have been carried out using various methods as a complementary tool for chemical analysis.

Some of the organisms used for assessing the toxicity of hydrochars and biochars from different feedstocks have been plants for germination (Busch et al. 2012; Bargmann et al. 2013; Busch et al. 2013), plant growth (George et al. 2012; Jandl et al. 2013; Rillig et al. 2010) and genotoxicity assays (Busch et al. 2013; Sack 2014). Likewise, toxicity tests on soil fauna, such as earthworms (Chan et al. 2008), using *Eisenia foetida* (Busch et al. 2012; Van Zwieten et al. 2010 and Žaltauskaitė and Sodienė 2010), *Aporrectodea caliginosa* (Salem et al. 2013) and *Eisenia andrei* (Gonzalez et al. 2013; Matos-Moreira et al. 2011) as test organisms, have been performed. Other soil fauna, for example, arbuscular mycorrhiza fungi (Rillig et al. 2010; Salem et al. 2013), the free-living nematode *Caenorhabditis elegans* (Chakrabarti et al. 2015) and microarthropods, such as *Collembola* have also been used as test organisms for toxicity tests (Domene et al. 2015; Reibe et al. 2015). Moreover, brine shrimp such as *Artemia salina* have been used as marine fauna for toxicity tests of hydrochar (Sack 2014). Despite such studies, the carbonization process of sewage sludge as feedstock and its product development are still in their infancy (Libra et al. 2011; Saetea and Tippayawong 2013; Xue et al. 2015). Such knowledge is limited to different thermal treatments, such as pyrolysis (Bridle and Pritchard 2004) and thermocatalytic low-temperature conversion (Süterlin et al. 2007), or to the comparison of different thermal processes, such as between HTC and pyrolysis (Xue et al. 2015), or between low-temperature conversion (slow pyrolysis) and HTC (Fühner et al. 2010). Additionally, HTC at subcritical (<374°C) and supercritical (>374°C) temperatures has been used for the production and removal of volatile fatty acids and other hydrolyzed products from sludge (Shanableh 2000).

Studies regarding the HTC of sewage sludge have focused on the reaction conditions for optimum carbon recovery in the liquid by-product and optimal methane yields (Danso-Boateng et al. 2015), the energy efficiency of HTC as a drying technology for sewage sludge (Escala et al. 2013), different chemical properties and agronomic effects of Sewchar (Paneque et al. 2015), the effect of the HTC process on the characteristics of sewage sludge (Sun et al. 2013; Zhang et al. 2014) and a tradescantia genotoxicity assay (Busch et al. 2013). However, despite these contributions, little is known regarding the Sewchar toxic effects on the fauna of soil and water. Hence, the aim of this study was to evaluate i) the toxicity of Sewchar to earthworms (*Eisenia foetida*) over a concentration range up to 4% (80 Mg $ha^{-1}$) and ii) the acutely toxic concentration of Sewchar process water filtrate to shrimps (*Artemia salina*), with and without pH adjustments to the saline dilution water. In the case of the presented pollutants, we expected toxic effects on both test organisms, resulting in high mortality rates. Our overall aim was to identify the influence of Sewchar and its process water filtrate treatments on the lethality to earthworms and shrimps.

## 2.3 Material and Methods

### 2.3.1 Sewchar properties

The Sewchar was produced at a temperature of 190°C and pH 4.5 with a 4 h residence time in an 8 L lab autoclave at the Federal Institute of Goiás, Brazil. Biosolids from a wastewater treatment plant in

Goiânia/Goiás, Brazil was used as the input material for the HTC. The biosolids was sampled after the centrifugation process without the addition of lime. The chemical characterization of the biosolids and Sewchar was carried out based on Embrapa (2009), Table 2-1. The samples were homogenized, dried at 65°C for 16 h, milled and passed through a sieve with a mesh of 0.5 mm. The pH was measured using a pH electrode, with the samples in a suspension of 0.01 mol $L^{-1}$ $CaCl_2$ and distilled water (1:5). The samples were oxidized (digested) using 6 ml of nitric-perchloric acid and 20 ml of distilled water was thoroughly mixed with the oxidized sample. Subsequently, a mixture of 0.25 ml of the oxidized samples and 4.75 ml of distilled water was used for the chemical analysis.

Table 2-1 Biosolids and Sewchar chemical characterization

| Moisture content | pH | N | P | K | Ca | Mg | Cu | Fe | Mn | Zn | C | C:N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % | | g kg $^{-1}$ | | | | | | | | | | |
| Biosolids chemical characterization | | | | | | | | | | | | |
| 73.1 | 5.3 | 30.8 | 10.9 | 7.0 | 17.4 | 2.3 | 0.3 | 5.1 | 0.2 | 0.1 | 68.2 | 2.2 |
| Sewchar chemical characterization | | | | | | | | | | | | |
| 23.6 | 5.0 | 22.4 | 11.6 | 4.0 | 20.2 | 2.8 | 0.3 | 4.9 | 0.2 | 0.1 | 107.9 | 4.8 |

Phosphorus (P) was measured using the ascorbic acid method, where the molybdenum blue was measured spectrophotometrically at a wavelength of 660 nm (Spectronic 20, Bausch & Lomb). Potassium (K) was measured via flame photometry - SOP Flame photometer Corning 400. Copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) were measured via atomic absorption spectrophotometry (AAS) (Perkin Elmer AAnalyst 100), while calcium (Ca) and magnesium (Mg) were also measured via atomic absorption spectrophotometry after the addition of 4.75 ml of lanthanum at 0.22%. Organic carbon (C) was measured after wet oxidation of the samples using potassium dichromate and sulfuric acid, followed by the photometric determination of chromium III ($Cr^{3+}$), using an ultraviolet-visible (UV/VIS) spectrophotometric procedure at a wavelength of 660 nm (Spectronic 20 Bausch & Lomb). The total nitrogen (N) was measured using the Kjeldahl method, which involved oxidized sample, using sulfuric acid, followed by distillation and measurement of the released ammonia. The C/N relation was calculated by dividing the results, in mass percentage, obtained for the total C and N.

Additionally, biosolids and Sewchar trace element contents were assessed and compared with the threshold values according to CONAMA – Brazilian National Environment Council (2006), Table 2-2.

Table 2-2 Biosolids and Sewchar trace element content and threshold value according to CONAMA (2006)

| | As | Cd | Cr | Cu | Hg | Mo | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | mg kg$^{-1}$ | | | | |
| Biosolids | 18.18 | - | 57.48 | 159.00 | 0.55 | 8.20 | 26.59 | 19.01 | 491.50 |
| Sewchar | 26.44 | 0.89 | 79.70 | 362.80 | 1.34 | 11.40 | 72.58 | 23.45 | 1885 |
| CONAMA (2006) | 41 | 39 | 1000 | 1500 | 17 | 50 | 420 | 300 | 2800 |

The biosolids and Sewchar samples were digested in a microwave system (Milestone MLS 1200 Mega, Germany) using 37% HCl and 65% $HNO_3$ in a 1:3 ratio and analyzed for trace metals according to the US EPA Method 3051A (2007). The concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn) and molybdenum (Mo) were measured via inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Ultima 2 spectrometer (Horiba Jobin Yvon, Unterhaching, Germany). A 4-point calibration was performed using standard solutions (CertiPur, Merck) diluted in deionized water. Analyses of the multi-element standards (Merck, Darmstadt) were routinely included for quality control. Additionally, a test of recovery was performed at five different concentration levels as an internal quality control. The average relative standard deviation (RSD) was <4.5%. The detection limits were 53 µg L$^{-1}$ for As, 2.7 µg L$^{-1}$ for Cd, 7.1 µg L$^{-1}$ for Cr, 5.4 µg L$^{-1}$ for Cu, 12 µg L$^{-1}$ for Mo, 10 µg L$^{-1}$ for Ni, 6.6 µg L$^{-1}$ for Pb and 1.8 µg L$^{-1}$ for Zn. The maximum allowable RSD between replicates was set to 5%. Quality control of the extraction efficiency was performed using certified soil reference materials (BRM n. 13a and BRM n. 13b) obtained from the Federal Institute for Materials Research and Testing (BAM). The recovery ranged from 79% to 112% depending on the studied element. The measurement of mercury was performed using the mercury-direct-analyzer DMA 80, which is an AAS (MLS GmbH, Leutkirch, Germany). The following reference materials were used for Hg analysis: BRM N. 09b, 1.02 (0.85-1.19) mg kg$^{-1}$ Hg, BRM N. 12, 8.86 (8.48-9.24) mg kg$^{-1}$ Hg and National Institute of Standards and Technology (NIST) pine needle standard: 0.0399 (0.0392-0.0406) mg kg$^{-1}$ Hg. The recovery was, in all cases, within the allowed limits.

### 2.3.2 Earthworm acute toxicity test (*Eisenia foetida*)

- Acute avoidance toxicity test procedure

The experiment was carried out based on the Environment Canada (2004) methodology for an acute avoidance test and the ISO (2008) standard for an avoidance test. This biological test method uses adult earthworms as test organisms to measure their avoidance of test soils after their simultaneous exposure to the reference soil (control soil: soil without Sewchar) and test soil (soil with Sewchar) in a two-compartment vessel. *Eisenia foetida* is recommended as a test organism; it was used to study terrestrial ecotoxicology by the Organization for Economic Co-operation and Development (OECD) (2004) and in standardized toxicity tests of the chemical substances in temperate soil (OECD 1984) and in tropical regions (Brazilian Institute of the Environment and Renewable Natural Resources - IBAMA 1990). The reference and test soil sides were marked in each two-compartment vessel and 10 earthworms were placed between the two types of soils. The avoidance behavior was assessed 48 h after the exposure of earthworms between the two soils, where the number of animals on both sides of the vessel was determined. The percentage of avoidance was calculated according to Equation 1 (Environment Canada, 2004), where "n. in reference soil" is the number of live worms found in all compartments containing clean soil at the end of the test, "n. in test soil" is the number of live worms found in all compartments containing test soil at the end of the test, and "total number of worms" is the total number of live worms found in all compartments at the end of the test:

$$Avoidance\ (\%) = \frac{n. in\ reference\ soil - n. in\ test\ soil}{total\ number\ of\ worms}\ x\ 100 \qquad (1)$$

For the evaluation of soil toxicity, the 'habitat function' of soil was considered 'limited' if less than 20% of the test organisms (on average) were found in the test soil sample (ISO 2008). The earthworm toxicity tests were carried out using the solid phase of the HTC of the biosolids, i. e., the Sewchar. The experiment had a completely randomized block design, with the following treatments in duplicate: 4 concentrations of a Sewchar-test soil mixture, 0.5%, 1%, 2% and 4% (weight/weight - w/w), which correspond to 10, 20, 40 and 80 Mg $ha^{-1}$ plus the control (reference soil without the addition of Sewchar). Such Sewchar concentrations were used because usually the geometric sequence 0, 0.5, 1.0, 2 and 4 times the recommended concentration is applied. Soil amendments at concentrations above 1% represent the upper limits of reasonable field application rates therefore, unrealistic in agronomic practice (Bargmann et al. 2013). Likewise, high charcoal applications of > 100 Mg $ha^{-1}$ are also considered inadequate for practical use (Glaser et al. 2002), suggesting not increasing plant growth (Bargmann et al. 2013, Rillig et al. 2010, Rondon et al. 2007). Therefore, 1% Sewchar was used as reference concentration, consequently the range of Sewchar application up to 80 Mg $ha^{-1}$ was applied. The reference soil was prepared according to the Environment Canada (2004) methodology for the formulation of artificial soil and the OECD (1984) methodology for an artificial soil test substrate, with the moisture content maintained at 45% and the pH was adjusted to 6.0 via addition of calcium carbonate. During the test, the moisture content (%) of each test soil was maintained at 45 %. The statistical endpoints were the percentages of live earthworms per Sewchar treatment in each test unit at the end of the test.

- Acute lethality test procedure

The acute lethality test was carried out based on the methods described by the Environment Canada (2004) methodology for the conduction 14-day lethality test for soil toxicity using earthworms and the OECD (1984) guideline for an acute toxicity test, i. e., the testing of chemicals. The principle of the test involves keeping earthworms in samples of a precisely defined reference soil, to which a range of concentrations of the test substance is applied. Mortality is assessed 7 and 14 days after application. The test species used for this experiment was *Eisenia foetida*. The mean ±SD of the individual fresh weight of the adult earthworms used in the experiment was 0.897 ± 0.10 g at the start of the test. The reference soil was prepared similarly to that for the acute avoidance toxicity test, except that the pH was adjusted to 7.0-7.5 for this test. The moisture content (%) of each test soil was maintained at 45 % during the whole test via the addition of distilled water if required. The experimental design included a random combination of 4 concentrations of Sewchar (0.5%, 1%, 2% and 4% - w/w), which corresponded to 10, 20, 40 and 80 Mg $ha^{-1}$ plus the control with no Sewchar. Each treatment, including the control, had 3 replications. The statistical endpoints were earthworm weight, soil pH and earthworm lethality.

### 2.3.3 Brine shrimp (*Artemia salina*) acute toxicity test procedure

The toxicity test with brine shrimps was carried out based on the methods described by the EPA - US Environmental Protection Agency (2002) for acute toxicity test and Meyer et al. (1982), using *Artemia salina* as the test organism (Nunes et al. 2006) and the process water filtrate of Sewchar as the test substance. This acute toxicity test consists of the exposure of brine shrimp eggs to precisely defined artificial sea water (3.8% of sea salt), to which a range of concentrations of the test substance (Sewchar process water filtrate) is applied. At the end of the test, the median lethal Sewchar process water filtrate concentration (LC50) for nauplii is calculated. The experimental design consisted of 5 concentrations of Sewchar process water filtrate (6.25% - 0.31 ml, 12.5% - 0.62 ml, 25% - 1.25 ml, 50% - 2.5 ml and 100% - 5 ml) plus the control, which had no Sewchar process water filtrate. These concentrations were used according to the recommendation of the EPA for effluent test concentrations (US EPA 2002). Each treatment, including the control, was performed in triplicate. Additionally, a solution of 1 M NaOH was prepared and added to an additional replicate for each Sewchar concentration to adjust the pH to 8.5. This procedure was carried out, as suggested by the US EPA (2002), because mortality due to pH alone may occur if the pH of the sample falls outside the range of 6.0-9.0. Furthermore, legal requirements, which establish the conditions and effluent discharge standards, also require that the discharge of effluents in saline water not exceed the pH of the natural saline water (6.5 and 9) (CONAMA 2005; Levi Strauss & CO. 2007). After 48 h of exposure of shrimps to Sewchar process water filtrate, an animal was considered dead if no movement was observed after 5 minutes of observation and tapping against the dish. The statistical endpoint was Sewchar process water filtrate median lethal concentration (LC50) with and without pH adjustments.

### 2.3.4 Statistical analyses

For statistical analysis of the acute avoidance test and acute lethality test, the RStudio statistical program was used (version R 3.3.0, R Core Team 2016). Our data followed a normal distribution and showed homogeneity of variances. The results of all statistical analyses were considered significant at $p < 0.05$. The influence of increasing Sewchar concentrations on earthworm performance (avoidance, weight and lethality) was analyzed via one-way analysis of variance (ANOVA) and the significance of the differences between mean values was calculated using pairwise Student's t-test with Holm-Bonferroni p-value correction. The Holm-Bonferroni method was applied because it is considered a method that is applicable to the same cases as the Bonferroni procedure but is uniformly more powerful (Aickin and Gensler 1996).

A classical linear regression model was created according to Johnson and Wichern (2007) to assess the effect of Sewchar concentrations on soil pH values. ANOVA was also performed for the acute lethality test to evaluate whether applications of increasing amounts of Sewchar influenced earthworm lethality. For the mortality/concentration data a graph was plotted.

Statistical analysis for the shrimp acute toxicity test was performed using Minitab 16 software. ANOVA, followed by a normal distribution Probit regression, was performed, where the percentage data of dead brine shrimps were related to the increasing Sewchar process water filtrate concentration. The significance of model coefficients, evaluated using the Z-test, was used to estimate the Sewchar process water filtrate median lethal concentration (LC50), at which 50% of the shrimp died, and its confidence intervals.

## 2.4 Results and Discussion

### 2.4.1 Assessment of Sewchar in terms of acute toxicity to earthworms (*Eisenia foetida*)

- Avoidance behavior of earthworms after solid-phase Sewchar exposure

Comparing all treatments, earthworms preferred the control soil side of the vessel over the Sewchar side of the vessel. Sewchar treatments of 1% (20 Mg $ha^{-1}$) had exactly 80% of the total organisms in the control soil sample, therefore such treatment was not considered with soil habitat function limited. Sewchar treatments of 2% and 4% (40 and 80 Mg $ha^{-1}$) were considered with the soil habitat function limited because more than 80% of the total organisms were found in the control soil sample and less than 20% were found in the soil with Sewchar. However, for only the 2% concentration (40 Mg $ha^{-1}$) of Sewchar, the earthworms significantly preferred the side of the vessel with the reference soil over that with the Sewchar treatments, $p < 0.001$ (Figure 2-1).

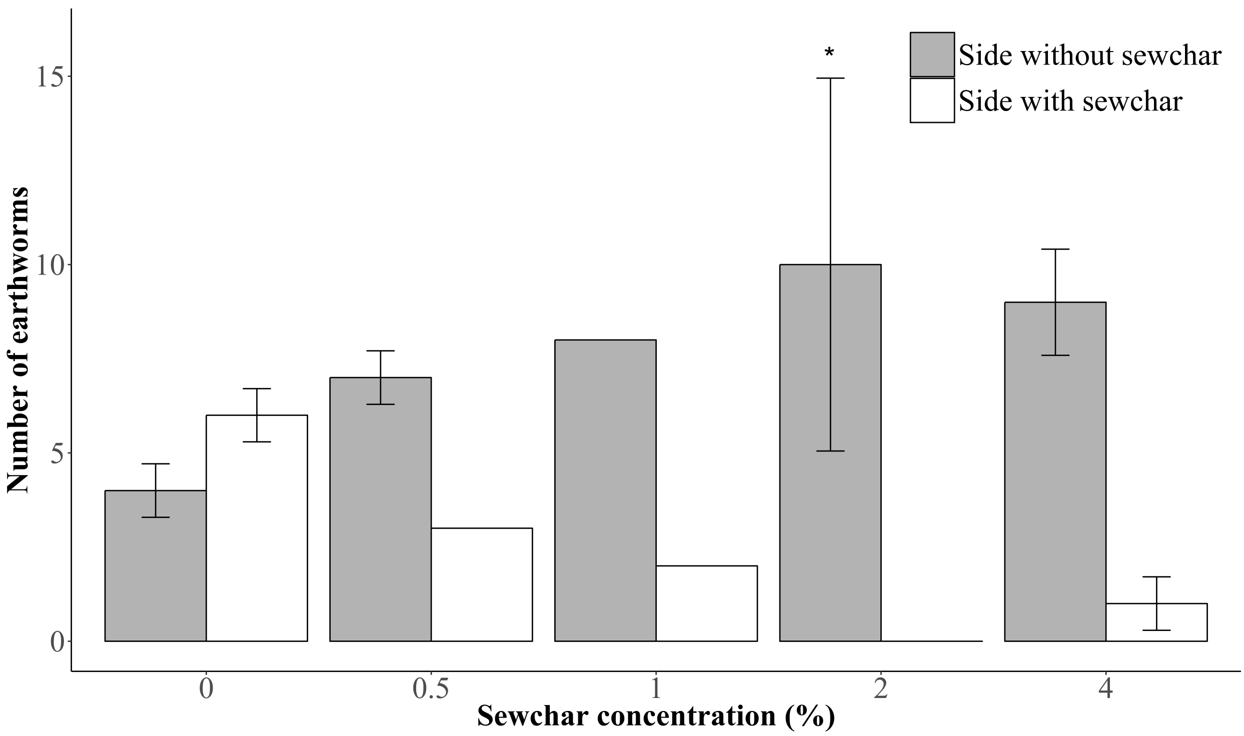


Figure 2-1 Acute earthworm avoidance test after 48 h of exposure of ten earthworms (*Eisenia fetida*) simultaneously to reference soil (side without Sewchar) and test soil samples (side with Sewchar) in a two-compartment vessel. Each vessel corresponded to the following treatments in duplicate: control/reference soil (0%) and test soil with Sewchar concentrations (w/w) of 10 Mg ha$^{-1}$ (0.5%), 20 Mg ha$^{-1}$ (1%), 40 Mg ha$^{-1}$ (2%) and 80 Mg ha$^{-1}$ (4%). *$p<0.05$.

Our results suggest that earthworm avoidance might be related to decrease of pH with increasing amount of Sewchar. The Sewchar addition concentration higher than 1% showed a quite large deviation, therefore better understanding is expected due to the lethality test. No-avoidance response of earthworms can be attributed to higher pH values and nutrient concentrations (mainly P and Ca) of the substance to which the earthworms are exposed (Edwards and Bohlen 1996). According to the authors, these were reported to be the more favorable properties for organism development in tested soils. However, chronic effects, such as reproduction and bioaccumulation might occur after longer exposure periods. Similarly, Busch et al. (2012), using hydrochar from wet beetroot chips (low pH: 4.4), explained that the avoidance of the earthworms was due to the change in pH in the soil, with the avoidance increasing with the hydrochar amount. Likewise, biochar from a paper mill significantly increased the pH of ferrosol, which earthworms preferred over the control soils (Van Zwieten et al. 2010).

- Lethality behavior of earthworms after solid-phase Sewchar exposure

The Sewchar concentration did not influence the earthworm weight. ANOVA suggested a significant difference in earthworm weight among Sewchar concentrations, $p < 0.05$ (Table 2-3); however, this hypothesis was refuted by the pairwise Student's t-test, $p > 0.05$ (Table 2-4). The results (p-values) in both statistic tests were very close to the reference (0.05), which indicates uncertainty. Therefore, we considered to be conservative, due the lack of strong evidence, what indicates no influence of Sewchar concentration on earthworm weight.

Table 2-3 Results of analysis of variance (ANOVA) regarding the influence of Sewchar concentrations on earthworm weight

| | Df[1] | Sum Sq[2] | Mean Sq[3] | F value | Pr (>F) |
|---|---|---|---|---|---|
| Treatment | 4 | 0.0545970 | 0.0136493 | 3.817381 | 0.0390287 |
| Residuals | 10 | 0.0357556 | 0.0035756 | - | - |

Table 2-4 Results of multiple t-test with Holm-Bonferroni correction to identify the influence of Sewchar concentrations on earthworm weight

| | Control | 0.5% Sewchar | 1% Sewchar | 2% Sewchar |
|---|---|---|---|---|
| 0.5% Sewchar | 0.6907289 | - | - | - |
| 1% Sewchar | 0.6907289 | 0.0507052 | - | - |
| 2% Sewchar | 1.0000000 | 0.6070483 | 0.7111664 | - |
| 4% Sewchar | 0.8182253 | 1.0000000 | 0.1239977 | 0.7808568 |

One consolidated reason for the E. foetida biomass increase is the presence of organic matter (Barley 1961; Teotia et al. 1950). Different feedstocks or a feedstock under different treatments yielded differences in earthworm weight. Domestic sewage sludge without the HTC process yielded a gain of earthworm (E. foetida) biomass in all treatments-100%, 75%, 50%, 25% and 10% (Dores-Silva et al. 2013). Conversely, the most digested sewage sludge amendment (12 Mg ha-1) had a negative effect on mass increase and the reproduction of earthworms of a different species - E. andrei (Moreira et al. 2008). The exposure of earthworms E. foetida to soil containing cadmium tended to yield a dose-related decrease, although a statistically significant decline was detected only in the case of the highest concentration, i.e., 100 µg Cd g-1 soil (Žaltauskaitė and Sodienė 2010). Earthworm (E. foetida) weight decrease was also observed when the worms were exposed to high concentrations of dry apple-wood-chip biochar, >100 g kg-1 (Li et al. 2011).

At the end of the experiment, the pH values of all Sewchar treatments increased in comparison with the pH of the treatments at the beginning of the test. However, the linear regression model showed that the pH values exhibited a decreasing pattern as Sewchar was added (Equation 2). The model was also significant for prediction, because $R^2 = 0.7$ and p-value was below 0.01 ($p = 0.0058$) for F test of

[1] Degrees of freedom

[2] Sum of squares

[3] Mean squares

significance. In addition, the model required the use of an ordinary least squares model, which has the following residuals for normality: p-value of the Shapiro-Wilk test above 0.05 (p-value = 0.4393).

$$pH = 8.04 - 0.070 * \text{Sewchar treatment dose} \qquad (2)$$

Our results showed an increase in pH value of soil mixtures after the addition of Sewchar. Similar results were reported for different hydrochar feedstocks, such as beet root chips by Bargmann et al. (2014), Rillig et al. (2010) and Salem et al. (2013); spent brewer's grains by Bargmann et al. (2014) and maize silage, food leftovers and digestates from a biogas plant by Busch et al. (2013). The increase in soil pH might have been due to the microbial reduction reactions, as reported by Rillig, et al. (2010). In such study such reactions were traced and led to a pH increase of the medium despite the quite acidic nature of the hydrochar itself.

Our results also showed that increasing Sewchar application rates decreased soil pH. Similar results were reported using hydrochar made of spent brewer's yeast (George et al. 2012), biochars made from pine chips (Gaskin et al. 2010) and peanut hulls. Such pH decrease might have occurred due to originate from the oxidation of the surface of the chars over time, which creates more carboxylic functional groups, as explained by Cheng et al. (2006).

The highest percentage of earthworm lethality (11%) was observed at a concentration of 0.5% after 14 days of earthworm exposure to different Sewchar concentrations (Figure 2-2). Furthermore, there was any influence of the Sewchar concentrations on the acute toxicity to earthworms, $p > 0.05$ (Table 2-5). None of the four Sewchar concentrations was lethal to 50% of the test organisms during the test. Therefore, Sewchar applications to soil did not present acute toxicity to earthworms. No acute toxicity of the Sewchar can be explained by the results of the analysis of its trace element content. The Sewchar trace element contents showed that HTC enhanced the concentrations of the trace element content (Table 2-2). Similar results were reported by Zhang et al. (2014). However, Sewchar trace element contents are still below the threshold values of CONAMA (Table 2-2). Therefore, Sewchar could be used as soil amendment.

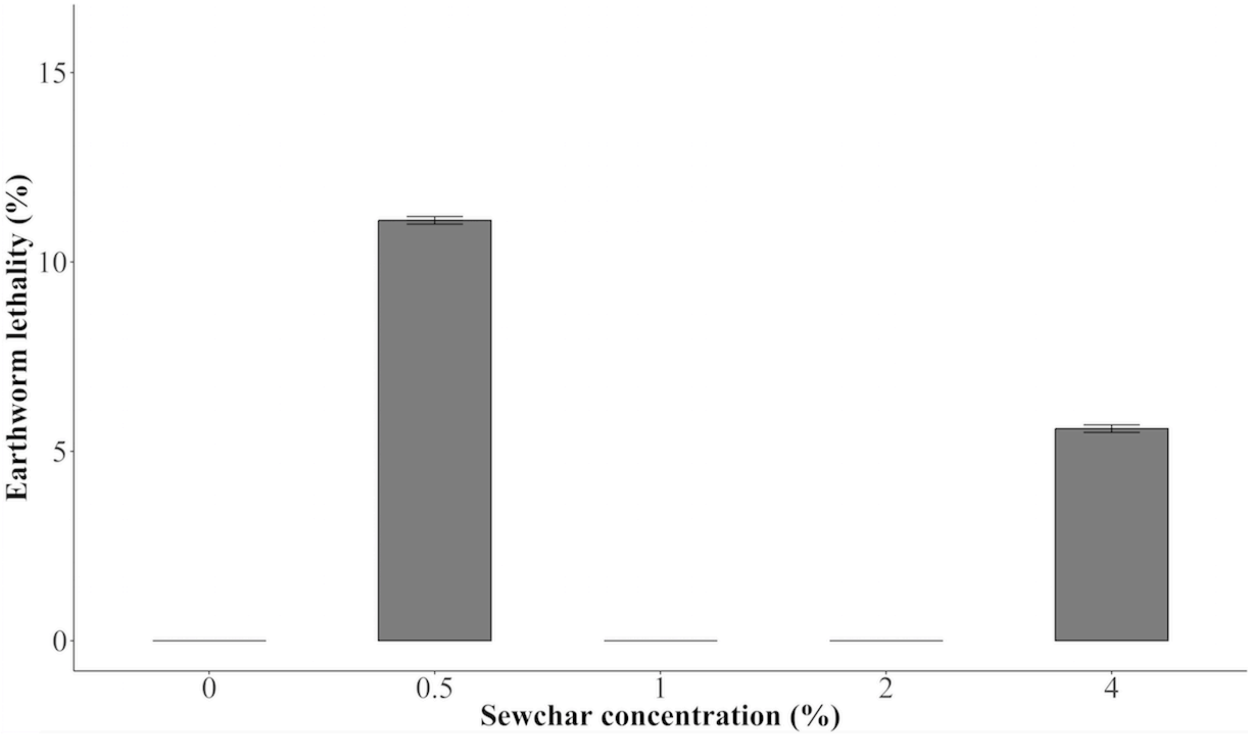


Figure 2-2 Acute earthworm lethality test after 14 days of exposure of six earthworms per vessel. Each vessel corresponded to the following treatments in triplicate: control/reference soil (0%) and test soil with Sewchar concentrations (w/w) of 10 Mg ha$^{-1}$ (0.5%), 20 Mg ha$^{-1}$ (1%), 40 Mg ha$^{-1}$ (2%) and 80 Mg ha$^{-1}$ (4%). *p<0.05.

Table 2-5 Results of analysis of variance (ANOVA) regarding the influence of Sewchar concentrations on earthworm lethality

| | Df[4] | Sum Sq[5] | Mean Sq[6] | F value | Pr (>F) |
|---|---|---|---|---|---|
| Treatment | 1 | 0.0037 | 0.00370 | 0.011 | 0.9181 |
| Residuals | 13 | 4.3778 | 0.33675 | - | - |

The use of domestic sewage sludge as a test substance without HTC also did not present acute toxicity to the earthworms at any of the sewage sludge concentrations (100%, 75%, 50%, 25% and 10%), i.e., all the exposed animals survived (Dores-Silva et al. 2013). In contrast, the risk of death of E. foetida increased with the concentration of lead ($\chi^2$= 28.64, p=0.00001), though there was no significant mortality at all cadmium concentrations (Žaltauskaitė and Sodienė 2010). It has been suggested that soil regulatory levels for lead are not meant to protect of worms in acidic soils (Wijayawardena et al. 2016). Furthermore,

[4] Degrees of freedom

[5] Sum of squares

[6] Mean squares

fluorine and α -endosulfan act synergistically with respect to their toxic effects on earthworms (Nam et al. 2016).

### 2.4.2 Lethality behavior of brine shrimps (*Artemia salina*) after Sewchar process water filtrate exposure

The median lethal concentration for the shrimps was higher (54.8%), when the pH of the Sewchar process water filtrate was adjusted compared to when it was not adjusted (8.1%) to 8.5. Application of the Z-test to the model coefficients demonstrated the significant effect of the treatments on the mortality of the nauplii ($p < 0.001$), Figure 2-3. The lethality analysis indicated an increase in the toxicity of the environment to the nauplii as the amount of Sewchar process water filtrate increased (Equations 3 and 4, where ϕ is the cumulative normal distribution function). pH seems to be an important cause of mortality for Artemia in salt water. This effect may be worse in soft fresh water, which has little buffering capacity to resist a change in pH, because the oceans generally have a higher alkalinity with regard to carbonate content and thus have a greater ability to buffer free hydrogens ions (Crone, 2004).

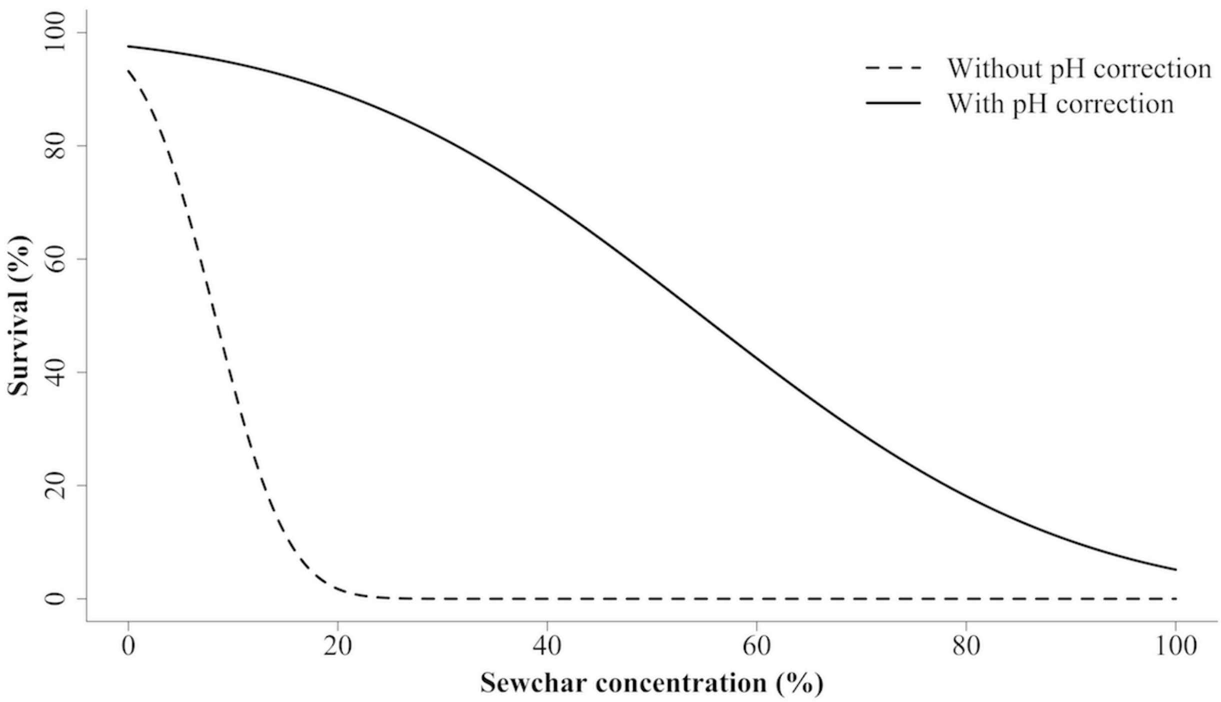


Figure 2-3 (LC50) – Lethal concentration to 50% of shrimps exposed to four different concentrations of Sewchar process water filtrate (25, 50, 75 and 100%) plus the control with and without pH adjustment

$$\text{Survival (without pH adjustment)} = 1 - \phi(0.18 \times \text{Dose} - 1.49) \quad (3)$$

$$\text{Survival (with pH adjustment)} = 1 - \phi(0.036 \times \text{Dose} - 1.97) \quad (4)$$

Our results showed that the liquid phase of the biosolids hydrothermal carbonization caused lower toxicity to shrimps when its pH was adjusted. Mortality may occur due to pH alone if the pH of the substance falls outside the range of 6.0-9.0 (US EPA 2002). Acid waters cause a disturbance of the balance of sodium and chloride ions in the blood of the aquatic fauna, where hydrogen ions may be taken into cells and sodium ions expelled (Morris et al 1989). The loss of sodium ions from the blood and loss of oxygen in the tissues is the primary causes of fish death in acid waters (Brown and Sadler 1989). Additionally, the heavy-metals are more soluble at lower pH (Li et al. 2013, Ukiwe and Oguzie 2008 ), what increases the risk of mobilized toxic metals that can be absorbed, even by humans, causing physiological damage. Differently, high pH levels can not be effectively disinfected with chlorine, causing indirect risks (Fink 2005) and can be toxic to aquatic organisms because the alkalinity will strip a fish of its slime coat. Additionally, the relative proportion of unionized ammonia form ($NH_3^0$) is the most toxic and it increases as pH rises (US EPA 2013) The presence of other forms of toxicity (metals and organics) in HTC byproducts may be masked by toxic effects of low or high pH, because the toxicity of HTC products seems to increase the LC50 of the respective feedstock. A lower LC50 32.44% for shrimps was found using the sewage sludge without HTC (dos Santos 2009). Sugarcane bagasse ash (SCBA) also resulted in lower mortality of shrimps compared to SCBA after HTC (Sack 2014). Due to the toxicity of hydrochars and respective process water, pre- and post-treatment detoxification strategies, such as physical strategies–washing (Bargmann et al. 2013; Chakrabarti et al. 2015; Flora et al. 2013), chemical strategies–hydrogen peroxide (Busch et al. 2013; Sack 2014), and biological strategies–composting (Busch et al. 2013), were studied, and different results were reported. Sack (2014) performed detoxification of hydrochar from SCBA using hydrogen peroxide and ozone to oxidize the hazardous substances. Such treatments did not produce an effective detoxification response, suggesting that such processes can emerge in more toxic products.

## 2.5 Conclusions

Our results suggest that the conversion of a biosolids to Sewchar can offer an attractive option for sanitation and minimizing the volume of sewage sludge for treatment. Concurrently, Sewchar seems to be beneficial as a soil amendment because its application to soil at concentrations up to four times the reasonable field application rate demonstrates no acute toxicity to earthworms. Therefore, the recycling of biosolids through HTC and further land application of Sewchar presents an agronomical and environmentally sound alternative, which surpasses a simple disposal of waste, while the residue byproduct can be used as a soil conditioner to potentially replace or supplement commercial fertilizer. However, to prevent potential negative effects on the environment, additional studies should be carried out, especially regarding the long-term impacts, before applying Sewchar at the agricultural scale. Moreover, the adjustment of the pH of Sewchar process water filtrate is necessary in the case of discharging it in saline and, particularly, soft fresh water. Complementary qualitative and quantitative chemical analyses are necessary to identify the toxic substances present in Sewchar and its process water filtrate, to understand their interactions with soil properties, to understand the impacts on organisms, and to determine if the amount of toxic compounds satisfies the corresponding legal requirements for the safe application of Sewchar process water filtrate.

## 2.6 Acknowledgment

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# 3 Plant and soil responses to hydrothermally converted sewage sludge (Sewchar)

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## 3.1 Abstract

This study compared the effects of Sewchar and mineral fertilizer on plant responses in beans (*Phaseolus vulgaris*, var. "Jalo precoce") and soil properties in a pot experiment in a completely randomized design with two harvests. The initial treatments consisted of a control, Sewchar doses of 4, 8, 16 and 32 Mg $ha^{-1}$ and mineral fertilizer (30 mg N, 90 mg $P_2O_5$ and 60 mg $K_2O$ $kg^{-1}$). The treatments (4 replications each) were fertilized with 135 mg $P_2O_5$ $kg^{-1}$ at the second harvest. The Sewchar application rates correlated positively with the CEC, the water holding capacity, the availability of Zn, Ca, Fe, Cu, and P, and the concentrations of nitrate, ammonium, total N, total organic carbon and hot water extractable carbon. They correlated negatively with the Mg availability and the soil C: N ratio. Additionally, they correlated positively with the P, Zn and Ca uptake from the soil. For both harvests, the 16 Mg $ha^{-1}$ Sewchar treatment had a total dry matter equivalent to that of the mineral fertilizer. After the second harvest, the 16 Mg $ha^{-1}$ Sewchar treatment revealed 96% higher plant biomass than the control and 79% higher biomass than it did during the first period. The positive effect of Sewchar in addition to phosphorous on the plant response and soil properties suggests that the residual effect of Sewchar could be a promising alternative as a soil amendment for partly replacing mineral fertilizers. In future, further studies are necessary to evaluate long-term residual effects of Sewchar in soil.

## 3.2 Introduction

Sewage sludge is a source of essential crop nutrients (Ferreiro-Domínguez et al. 2011; Roy et al. 2011; Smith and Tibbett 2004) that is not always used as a soil amendment due to the risk of contamination. Thermal treatment can destroy the pathogens in sewage sludge (Sütterlin et al. 2007), reduce its volume and immobilize some nutrients (Dai et al. 2015; Silva et al. 2017). Hence, the natural coalification of organic matter has been simulated by methods such as pyrolysis and hydrothermal carbonization - HTC (Funke and Ziegler 2010) to promote nutrient bioavailability (Glaser et al. 2001; Hilscher and Knicker 2011) and to sequester carbon (Glaser et al. 2002; Lehmann et al. 2003). Hydrochar is the solid product of the HTC (Libra et al. 2011). "Sewchar" in this study refers to the solid part of the HTC from biosolids. Its advantages are that HTC is suitable for processing feedstocks with high moisture contents (Benavente et al. 2015; Kim et al. 2014; Song et al. 2014) without requiring pre-drying (Kambo and Dutta 2015). Additionally, hydrochars retain more nutrients in a plant-available form (Libra et al. 2011) and had lower PAH contents (Bargmann et al. 2013) than biochars derived from pyrolysis or gasification (Libra et al. 2011; Ahmad et al. 2014). However, most of the available studies are about sewage sludge biochar (Faria et al. 2017; Marks et al. 2014; Ren et al. 2017). The few available studies about sewage sludge hydrochar have focused on the impact of its different production conditions (Xu and Jian 2017; Breulmann et al. 2017a, b; Paneque et al. 2015), optimal methane yields and carbon recovery from the resulting liquid by-product (Danso-Boateng et al. 2015). There have also been studies on the toxicity of Sewchar (Busch et al. 2013; Melo et al. 2017) and the chemical characteristics of its solid and liquid phases (Saetea and

Tippayawong 2013; Sun et al. 2013). Additional studies have reported that Sewchar addition to soil increased the concentrations of the total and bioavailable trace elements (Yue et al. 2017). However, its bioavailability in hydrochar (Melo et al. 2017; Zhang et al. 2014) and in food (Hossain et al. 2010) was within the permitted concentrations. These studies suggest that HTC appears to be a promising method for the biosolids treatment from an energetic (Escala et al. 2013; Xue et al. 2015) and resource recovery point of view (Saetea and Tippayawong 2013) as well as a sustainable soil amendment for enhancing soil fertility and productivity. Therefore, we expect that Sewchar can positively affect bean growth and soil properties by adding nutrients that were previously contained in biosolids to the soil. This alternative is very attractive for countries such as Brazil, where the economy is driven by agriculture. As the fourth-largest consumer of fertilizers in the world, Brazil imports a large amount of these compounds (da Cunha et al. 2014). Therefore, the agronomical effects of Sewchar should be assessed in view of its status as an alternative source of nutrients to replace or supplement mineral fertilizers before larger scale applications. However, there is no available published study about the changes in plant growth, nutrients and trace elements in soil as compared to mineral fertilizer after Sewchar application and its optimum application rate. This knowledge is crucial for a better understanding of the interactions among Sewchar, soil and plants for the safe and effective application of Sewchar. Consequently, the aim of this study was to assess the residual effect of Sewchar on plant growth, trace elements and other soil properties and to identify an optimum Sewchar application rate (w/w) with respect to the plant biomass response in two consecutive pot trials.

## 3.3 Material and Methods

### 3.3.1 Sewchar

The biosolids used as the feedstock material for the HTC were sampled following a centrifugation process without adding lime from a wastewater treatment plant in Goiânia/Goiás, Brazil. The biosolids chemical properties were as follows: pH: 5.3, phosphorus (P): 10.9, potassium (K): 7.0, calcium (Ca): 17.4, magnesium (Mg): 2.3, copper (Cu): 0.3, iron (Fe): 5.1, manganese (Mn): 0.2 and zinc (Zn): 0.1 g kg $^{-1}$. The trace element contents in the biosolids were: arsenic (As): 18.18, cadmium (Cd): -, chromium (Cr): 57.48, mercury (Hg): 0.55, molybdenum (Mo): 8.20, nickel (Ni): 26.59 and lead (Pb): 19.01 mg kg$^{-1}$. The Sewchar was produced at 190°C, pH 4.5, with the addition of sulfuric acid as a catalyst and 4 h residence time in an 8L lab autoclave at the Federal Institute of Goiás, Brazil. After the HTC process, the solid part of the Sewchar was separated from the liquid part using a sieve with a mesh size of 0.25mm. Afterwards, the solid part of the Sewchar was dried at 75ºC for 5 hours. The Sewchar had the following values: pH: 5.0, P: 11.6, K: 4.0, Ca: 20.2 Mg: 2.8, Cu: 0.3, Fe: 4.9, Mn: 0.2 and Zn: 0.1 g kg $^{-1}$. The trace element contents of Sewchar were: arsenic (As): 26.44, cadmium (Cd): 0.89, chromium (Cr): 79.7, mercury (Hg): 1.34, molybdenum (Mo): 11.4, nickel (Ni): 72.58 and lead (Pb): 23.45 mg kg$^{-1}$. The Sewchar trace elements were according to the threshold value of the Brazilian Resolution, which establishes criteria and procedures for using sewage sludge generated in sewage treatment plant and their derivate products in agriculture (CONAMA 375 2006). Details about the Sewchar chemical analysis methods are provided in Supplementary Information 1 (SI1).

### 3.3.2 Soil

The soil was collected from the 0-0.2 m layer of topsoil in the Cerrado biome in Goiânia/Goiás, Brazil and sieved to ≤ 2 mm to remove coarse stones and plant residues. The soil was a clay red yellow Oxisol. The Oxisols are reported to contain mainly aluminum oxides – gibbsite (Fink et al. 2016). Additionally, Alleoni and Camargo (1995) also showed that oxides hematite, goethite, maghemite and magnetite predominate in tropical and subtropical Oxisols. EMBRAPA-SNLCS (1988) stated that in yellow Oxisols goethite prevails in relation to hematite, where $Fe_2O_3$ content is between 7 and 11% in a clay Oxisol. Additionally, Canellas et al. (2000) reported that the same type of soil as that one used in our experiment had a balance between the reactive humid fractions, where the humic acid and fulvic acid ratio (HA/FA) was close to the unity. In our experiment one type of soil was used since Oxisol is the prevalent type of soil in the State of Goiás and we aimed to study the local use of Sewchar as soil amendment. A composite sample was collected, passed through a 1 mm sieve and analyzed before the start of the experiment (Table 3-1).

Table 3-1 Soil physical and chemical characteristics

| Clay | Silt | Sand | Cu | Fe | Mn | Zn | Organic Matter | pH $CaCl_2$ | P | K | Ca | Mg | H+Al | Al | CTC | BS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| g kg $^{1}$ | | | mg $kg^{-1}$ | | | | g $kg^{-1}$ | | mg $kg^{-1}$ | | | | $cmol_c$ $kg^{-1}$ | $mgkg^{-1}$ | $cmol_c$ $kg^{-1}$ | |
| 460 | 160 | 380 | 1.6 | 37.2 | 29.7 | 0.9 | 190 | 6.0 | 7.1 | 110 | 8.4 | 1.1 | 1.7 | 0.0 | 7.1 | 75.9 |

### 3.3.3 Pot experiment

The greenhouse pot experiment was performed in a completely randomized design with six treatments and four replications, using Phaseolus beans (*Phaseolus vulgaris*, var. "Jalo precoce"). The six treatments comprised four different Sewchar application doses (0.2%, 0.4%, 0.8% and 1.6% (weight/weight (w/w)), corresponding to field application amounts of 4, 8, 16 and 32 Mg $ha^{-1}$ at a soil depth of 20 cm), with one dose of mineral fertilizer and one control. The mineral fertilizer was a soil mixture containing NPK 10-30-20 as follows: urea $(NH_2)_2CO$ (46% total N), thermophosphate (Yoorin - 18% $P_2O_5$) and potassium chloride (60% $K_2O$). The doses of mineral fertilizer used per pot were equivalent to 132 kg Urea (46% N), 996 kg Yoorin (18% $P_2O_5$) and 192 kg potassium chloride (60% $K_2O$) $ha^{-1}$. For the second crop harvest, 3.75 g of thermophosphate per pot corresponding to 135 mg $P_2O_5$ $kg^{-1}$was added to all the treatments from the first crop harvest. At the end of the first crop harvest (T1), the shoots and roots were removed from the pots and soil samples were taken for chemical analysis. The remaining soil was left in the pots and used again in the second crop harvest (T2) to assess the residual effects of Sewchar on plant growth and soil fertility. Details about the methods used for the pot experiment are provided in Supplementary Information 1 (SI1).

### 3.3.4 Soil sampling and analysis

For T1, soil composite sampling of the replicates for each treatment was performed. A soil composite sample of a treatment consisted in the all the replicates of the same treatment. For T2, soil was sampled from each single replication, air-dried, sieved to 2 mm and analyzed for its pH, P, K, Ca, Mg, Cu, Fe, Mn, Zn, CEC, (potential acidity) H+Al, (base saturation) BS, water holding capacity (WHC), hot water extractable carbon (HWC), C: N ratio, N mineral, total organic carbon (TOC) and N total contents, nitrate and ammonium. Details about the methods of soil analysis are given in Supplementary Information 1 (SI1).

### 3.3.5 Plant tissue sampling and analysis

Plant tissue sampling was performed during the early bloom and the full bloom of the two plant crop harvests. The uppermost fully developed trifoliate leaf of each replicate was sampled, dried to a constant weight at 80°C and finely ground (1 mm). At the end of the two trials, the plants were harvested from each pot, oven-dried at 80°C to constant weight before weighing to determine their total dry matter (TDM) and analyzed for N, Cu, Fe, Mn, Zn, K, Ca, and Mg. The results of the elemental plant biomass and soil chemical analysis were compared to the respective sufficiency thresholds of nutrients for beans in the Brazilian savannah (Cerrado) soil, according to de Sousa and Lobato (2004), to identify nutritional disorders. Details about the methods used for soil plant tissue analysis are provided in Supplementary Information 1 (SI1).

### 3.3.6 Statistical analyses

Statistical analyses were performed with the RStudio program (version R 3.3.0, R Core Team 2016) with a significance level of alpha = 0.05. For each plant crop harvest, Pearson's correlation coefficient (r) was used to evaluate the linear correlation between increasing Sewchar application doses and the relative response to plant growth, tissue nutrients and soil properties. A one-way analysis of variance (ANOVA) followed by a Student's t-test were performed to compare the results (TDM, tissue nutrients and soil properties) of the same treatment (control, Sewchar application doses and mineral fertilizer) between the T1 and T2. One-way analysis of variance (ANOVA) followed by a comparison of means (Tukey-HSD) was applied as a post hoc test to compare the results of the treatments for each harvest.

## 3.4 Results and Discussion

### 3.4.1 Effect of Sewchar and mineral fertilizer on plant growth

The results showed that Sewchar has the potential to be used as a soil amendment, however its effects on the TDM depended on the harvest and the Sewchar doses. The control and Sewchar treatments displayed no significant differences in T1 with regards to the TDM. In T2, the residual effect of Sewchar indicated that nutrients were being supplied to the plants, resulting in higher TDM. Mineral fertilizer had a higher TDM in T1 than the control and 32 Mg $ha^{-1}$ Sewchar. In T2, mineral fertilizer had no significant difference related to TDM compared to all the other treatments (Figure 3-1).

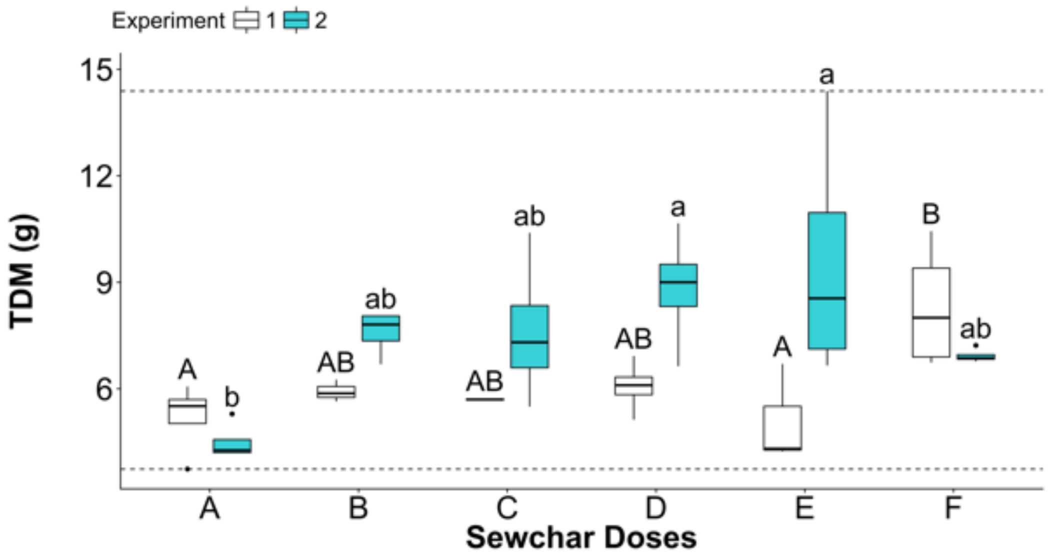


Figure 3-1 Results of the comparison of means (Tukey-HSD) of the total dry matter (TDM) for the treatments (A: 0.0, B: 4 Mg $ha^{-1}$, C: 8 Mg $ha^{-1}$, D: 16 Mg $ha^{-1}$, E: 32 Mg $ha^{-1}$ Sewchar doses and F: mineral fertilizer) after the first and the second plant crop harvests (Experiments). Whiskers represent ± the standard errors of the mean (n = 5). Different letters indicate significantly different values at $\alpha < 0.05$.

Additionally, the mineral fertilizer and control showed no significant differences regarding the TDM between T1 and T2 (Table 6-2). Increasing Sewchar doses correlated positively with the increasing TDM of beans in T2 alone (Table 3-2). Better results related to the TDM in T2 were obtained for Sewchar doses of 16 and 32 Mg $ha^{-1}$ (which were 96% and 112% higher than the control, respectively). The results of the pot trial indicated that Sewchar can improve the TDM of beans, especially when it is incorporated into the soil for three months prior to sowing. However, the effects of chars as soil amendments seem to be very complex and dependent on many variables, such as the type of soil, type of crop, char doses, char process conditions, feedstock, time in the soil and experiment setting (field/pot). Other studies using the same feedstock (sewage sludge) under different process conditions and doses also reported positive results related to plant growth in pot (Deenik and Cooney 2016; Hossain et al. 2010; Khan et al. 2013; Sousa and Figueiredo 2016) and field experiments (Butt 1999; Faria et al. 2017). However, deleterious effects were reported in pots due to the non-natural conditions (Butt 1999). Differently, positive and negative results related to plant growth were reported in a small plot field experiment depending on the Sewchar process conditions, doses and type of crop (Breulmann et al. 2014). Our results indicated that the residual effect of Sewchar improved plant growth, suggesting a slow release of nutrients. However, other studies using sewage sludge as feedstock reported many different results, because of the variability in the process conditions, doses, experiment setting (field/pot), types of soil and crop. For example, Deenik and Cooney (2016) reported better effects on corn growth in the first crop cycle in a greenhouse experiment with 50 Mg $ha^{-1}$ flash carbonized sewage sludge biochar applied to an infertile Oxisol due to increases in the extractable base cation concentrations of the soil. Whereas Faria et al. (2017) applied 15 Mg $ha^{-1}$ of sewage sludge biochar (pyrolysis) in a Red-Yellow Latosol during a two-year field experiment and reported higher corn yield during the second cropping season due to the higher total rainfall in this period. Studies about the variations in Sewchar process conditions confirmed that they changed its chemical properties and hence its agronomic effect. Sewchar was shown to have higher plant biomass production when produced at 200°C (Fühner et al. 2011; Paneque et al. 2015). Furthermore, residence times of 30 minutes and 1 hour did not affect the plant biomass productivity, while using a conversion time of 4 instead 8 hours tended to be more compatible with plants (Fühner et al. 2011). The effects of the storage or soil incubation of different hydrochars prior to sowing appeared to remove toxic substances (Busch et al. 2012) due to the microbial decomposition of carbohydrates and phytotoxic substances (Bargmann et al. 2013). Additionally, hydrochar incubation was shown to reduce the N-immobilization effect, because while aging hydrochar is biodegraded and its surface is loaded with nutrients. Therefore, to reduce the risks of negative effects on plant growth, hydrochar application was suggested for after different pretreatments such as aging or co-composting with fresh organic materials such as crop residues or farm fertilizers from animal manure (Bargmann et al. 2014).

Table 3-2 Results of the r and p-values of the Pearson's correlation coefficient used to evaluate the linear correlation between increasing Sewchar application rates and the relative response to soil properties and total dry matter in the first and second plant crop harvests

| First crop harvest | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ca | Cu | Fe | K | Mg | Mn | P | Zn | pH | CEC[7] | H+Al[8] | BS[9] | TDM[10] |
| r | 0.86 | 0.81 | **0.99** | 0.39 | 0.56 | **0.94** | **0.96** | **0.89** | 0.24 | 0.71 | -0.72 | 0.87 | -0.10 |
| p-value | 0.06 | 0.10 | 0.00 | 0.51 | 0.32 | 0.01 | 0.00 | 0.04 | 0.69 | 0.17 | 0.16 | 0.05 | 0.71 |

| Second crop harvest | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ca | Cu | Fe | K | Mg | Mn | P | Zn | pH | CEC | H+Al | BS | TDM | WHC | $NH_4$ | $NO_3$ | Mineral N | Total N | C:N | TOC |
| r | **0.91** | **0.61** | **0.85** | 0.24 | **-0.58** | 0.41 | **0.58** | **0.94** | -0.30 | **0.88** | **0.68** | **0.52** | **0.58** | **0.66** | **0.89** | **0.94** | **0.98** | **0.87** | **-0.77** | **0.83** |
| p-value | 0.00 | 0.00 | 0.00 | 0.30 | 0.01 | 0.07 | 0.01 | 0.00 | 0.20 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

[7] Cation Exchange Capacity

[8] Potential acidity

[9] Base Saturation

[10] Total Dry Matter

### 3.4.2 Effect of Sewchar and mineral fertilizer on soil properties

The enrichment of soil-available nutrients displayed different responses depending on the crop harvest and Sewchar doses. Bais et al. (2001) explain that the compounds secreted by plant roots play an important role as chemical attractants and repellants in the rhizosphere. In the pot experiment an earlier nutrient exhaustion due to the acceleration of the nutrient solubilization process could occur. Therefore, the close ratio between soil and root system is generally one of the drawbacks of the pot experiments compared to field conditions, However, pot experiments are cheaper in comparison to field experiments and conditions can be better controlled allowing the isolation of variables more effectively than in field experiments (Sparks, 1996). The results of the pot experiments should therefore be confirmed at the field scale. In T1, increasing Sewchar doses were positively correlated with the soil contents of Fe, P, Zn and Mn (Table 3-2). However, nutritional imbalances, such as insufficiency of K, Mg and low CEC, additional to the excess of Cu and Zn in the Sewchar treatments in T1 can explain the higher TDM average of the Sewchar doses in T2 (Table 6-1, Figures 3-2 and 3-3).

The higher TDM in T1 for mineral fertilizer related to the soil properties might be due to the pH (Table 6-1, Figure 3-3g), H+Al, base saturation (Table 6-1, Figure 3-3h) and soil K concentration (Table 6-1, Figure 3-2b). In T1, mineral fertilizer had a higher pH (6.6) than all the other treatments, and the BS was higher than the sufficient level for Cerrado soil in T1 and T2 (67.1 and 61.5%). Although the mineral fertilizer had soil K concentrations a little below the sufficiency threshold for K in Cerrado soil (50 mg $dm^3$), it displayed the highest average soil K concentration of all the treatments in T1. Additionally, K concentrations in the soil and bean tissue were below the sufficiency threshold for bean in Cerrado soil for all the Sewchar treatments in both bean harvests. These results can be explained because all the Sewchar treatments had higher Ca content in the soil than the sufficiency threshold for Cerrado soil, what may facilitate K leaching (Tammeorg et al. 2014). Previous researches also reported similar results using sewage sludge biochar, suggesting the addition of raw material rich in K for the co-production of biochar as alternative to make it a more complete source of plant nutrients (Faria et al. 2017; Sousa and Figueiredo 2016). In T2, our results showed that the soil Mg concentration of mineral fertilizer was the only nutrient within the sufficiency threshold for bean growth in Cerrado soil. Nutrients such as P, K, Ca Cu, Mn and Zn were above the adequate levels. This soil nutritional disorder might have hindered improvements concerning the total dry matter of the mineral fertilizer treatment in T2 (Table 6-1, Figures 3-2 and 3-3).

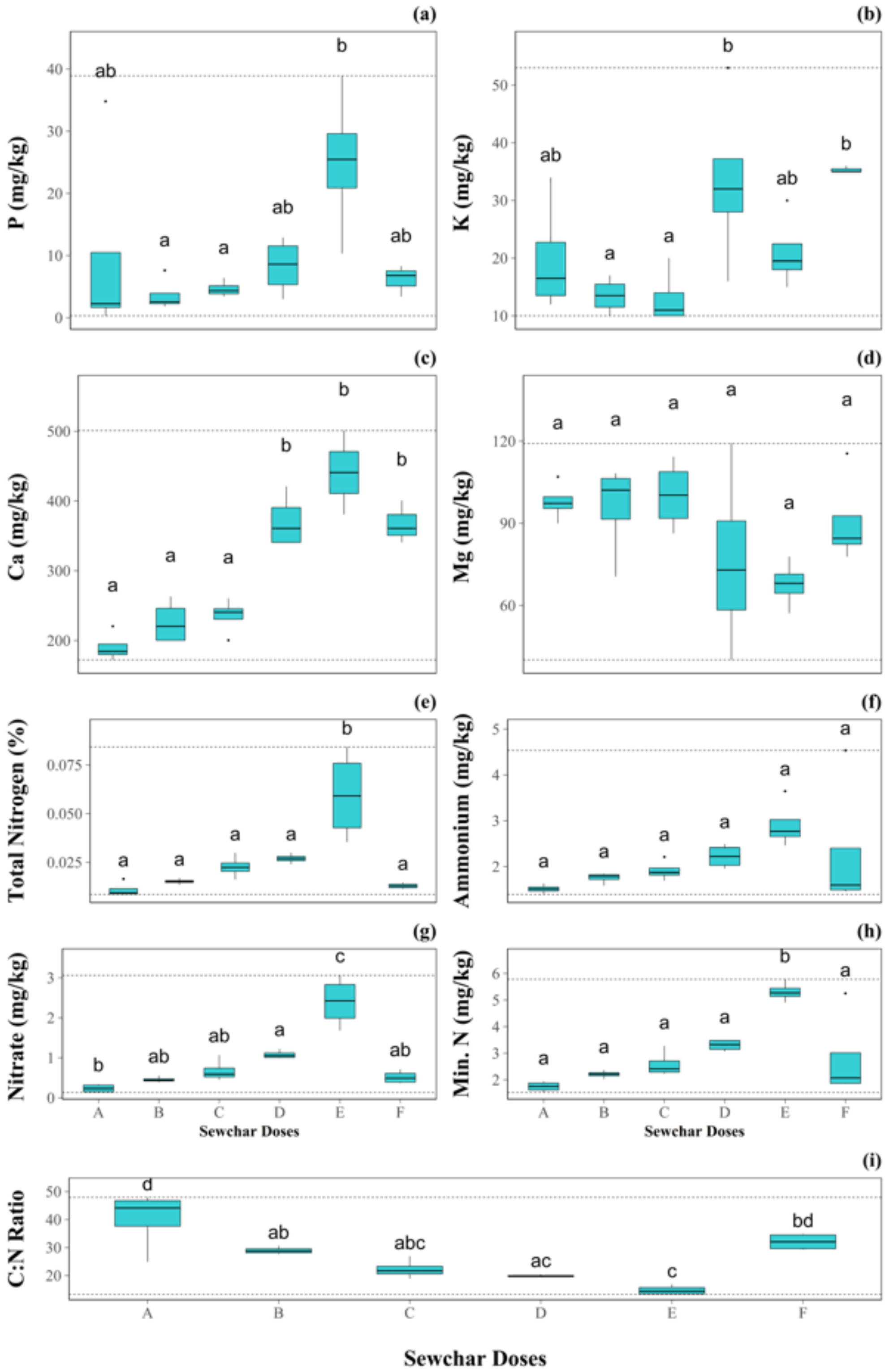


Figure 3-2 Results of the comparison of means (Tukey-HSD) for element concentrations of macronutrients (a) P, (b) K, (c) Ca and (d) Mg and different forms of N: (e) Total N, (f) Ammonium, (g) Nitrate, (h) Mineral N and (i) the C: N ratio in soil of the treatments (A: 0.0, B: 4 Mg ha$^{-1}$, C: 8 Mg ha$^{-1}$, D: 16 Mg ha$^{-1}$, E: 32 Mg ha$^{-1}$ Sewchar doses and F: mineral fertilizer) at the end of both crop harvests. Whiskers represent ± the standard errors of the mean (n = 5). Different letters in the same experiment indicate significantly different values at $\alpha < 0.05$.

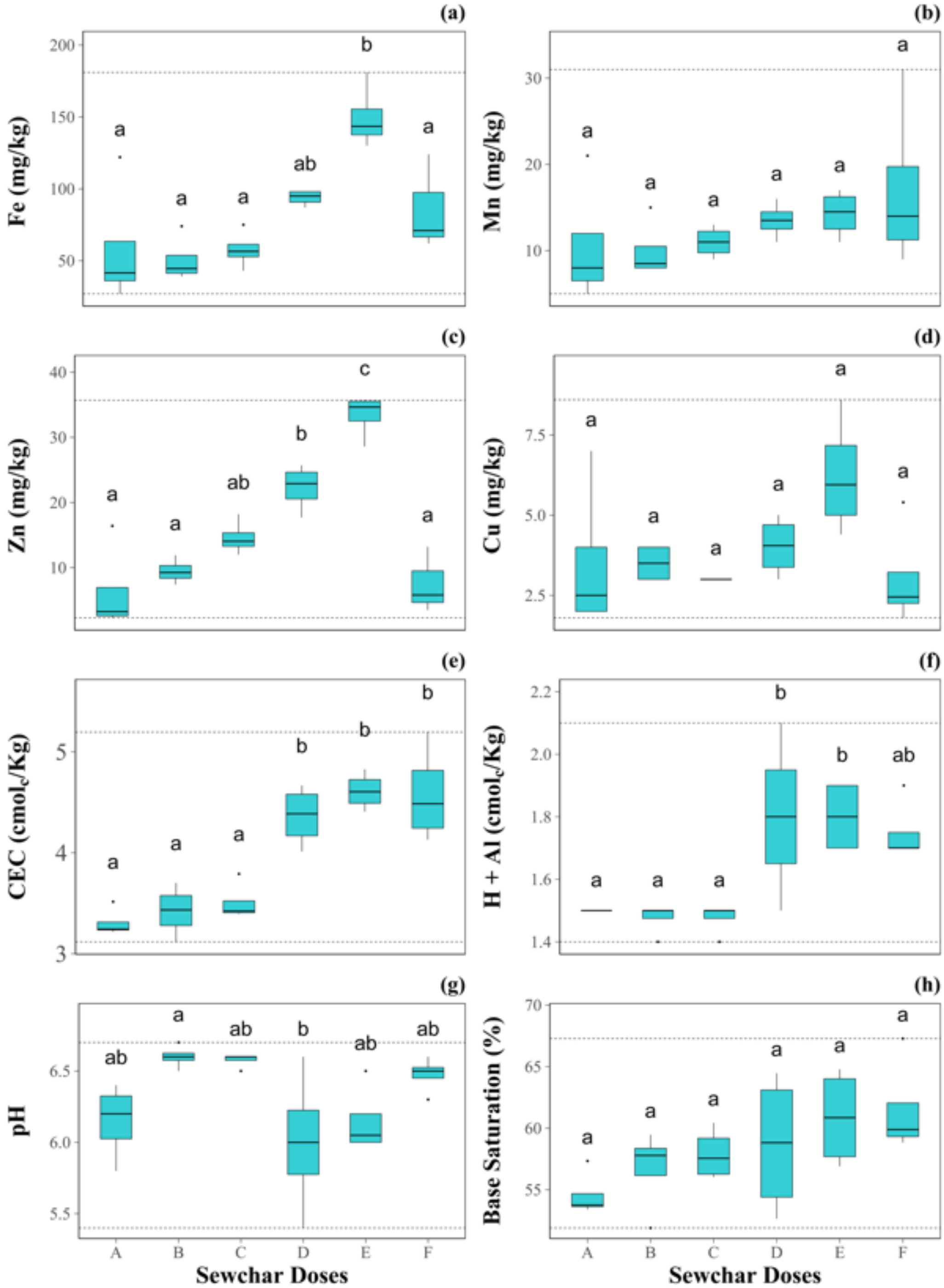


Figure 3-3 Results of the comparison of means (Tukey-HSD) for the elemental concentration of micronutrients (a) Fe, (b) Mn, (c) Zn and (d) Cu and other soil properties, namely, the (e) cation exchange capacity - CEC, (f) potential acidity - H+Al, (g) pH and (h) base saturation, in the treatment soils (A: 0.0, B: 4 Mg ha$^{-1}$, C: 8 Mg ha$^{-1}$, D: 16 Mg ha$^{-1}$, E: 32 Mg ha$^{-1}$ Sewchar doses and F: mineral fertilizer) at the end of both crop harvests. Whiskers represent ± the standard errors of the mean (n = 5). Different letters in the same experiment indicate significantly different values at $\alpha < 0.05$.

At the end of the pot experiments, fewer Sewchar treatments than the ones in T1 were not within the sufficiency threshold of nutrients for Cerrado soil, and more treatments exceeded the sufficiency threshold of nutrients for Cerrado soil (Table 6-1, Figures 3-2 and 3-3). These results suggest that the Sewchar interacted with the soil due to various processes including redox reactions, where its decomposition supplied electrons to more oxidized species presented in the soil system. For example, Mn(II) and Fe(II) are reduced forms reported to be required for uptake (Fox and Guerinot 1998) and were within the sufficiency threshold of nutrients for Cerrado soil in our experiment. Additionally, Fe and Mn bioavailability increased from T1 to T2 in most of the treatments. In T2, increasing the Sewchar doses correlated positively with the soil contents of Zn, Ca, Fe, Cu, P, nitrate, ammonium, total N, mineral N, TOC, HWC, WHC and CEC and correlated negatively with the C: N ratio and Mg (Table 3-2). These results indicated that applications of Sewchar promoted soil fertility and improved soil nutrients, suggesting that mineralization instead of immobilization occurred. The N mineralization is the biological conversion of organic N to inorganic forms, such as nitrate and ammonium, and it shows itself in low C : N ratios, while the microbial immobilization of N increases with the C : N ratio of the soil amendment (Jansen et al. 1998). In T2, our results indicated that adding Sewchar to the soil released the available N, because increasing the Sewchar doses correlated positively with the total N and mineral N. Therefore, the application of Sewchar into soil indicated an increase in the soil N content, reflecting in increased readily absorbable N forms, such as nitrate and ammonium in the soil, which contributed to the decrease in the C : N ratio. As the Sewchar C : N ratio of our study (4.8) is considered low, the addition of Sewchar into soil tends also to decrease the soil C : N ratio. Another possibility is that the application of Sewchar increased mineralization of native soil N, changing the decomposition rate of the organic matter, as result of the positive priming effect (Kuzyakov 2010). The availability of N in the soil may be explained due to the N availability in the Sewchar and the low temperature of HTC. Our results also showed that increasing Sewchar doses increased TOC and HWC, which may indicate that the application of Sewchar into soil increased the soil quality. Körschens et al. (1990) reported that the HWC well reflects the level of organic matter supply of the soil and the ability of soils to release N. Additionally, the HWC is recommended as an integrated indicator of soil organic matter quality (Ghani et al. 2003) and it is reported to correlate well with component of the labile soil organic matter, soil microbial biomass and mineralizable nitrogen and carbon (Körschens et al. 1990; Schulz 1990). Another study applying Sewchar for a short-term experiment reported humified Sewchar C and its transference into stabilized soil organic carbon (SOC), indicating its potential for soil C sequestration (Breulmann et al. 2017a). Our results also showed that increasing the Sewchar applications increased the available P in the T2. However, the P sufficiency threshold was a little excessive at 16 Mg $ha^{-1}$ Sewchar (8.3 mg $dm^3$), more excessive at 32 Mg $ha^{-1}$ Sewchar (25 mg $dm^3$) and was not reached in the other Sewchar treatments (Table 6-1, Figure 3-2a). It has already been reported that sewage sludge biochar applications in a field (Faria et al. 2017) and in a greenhouse experiment (Deenik and Cooney 2016; Sousa and Figueiredo 2016) improved the availability of P and major cations. The P bioavailability increase can be explained by the fact that the thermochemical treatment of sewage sludge leads to P release from biochar directly in soluble forms (Deluca et al. 2009). Additionally, P losses from sewage sludge by volatilization were reported only at pyrolysis temperatures above 700ºC (Gaskin et al. 2008; Hossain et al. 2010), in which HTC is no included (Funke and Ziegler 2010; Sevilla et al. 2011). Therefore, the P availability from hydrochar is crucial for Oxisols, the predominant tropical soils in Brazil, in which P deficiency is the major limiting factor for crop production (Fageria et al. 1988). Our results related to exchangeable cations showed that the soil Ca content increased with increasing Sewchar applications and the Ca sufficiency threshold for bean growth in Cerrado soil was exceeded in all the treatments (Table 6-1, Figure 3-2c). An increased soil Ca content was also reported when using biochar from sewage sludge (Hossain et al. 2010; Sousa and Figueiredo 2016). Our results also showed that increasing Sewchar concentrations increased CEC and WHC. Likewise, the CEC was reported to increase with the addition of biochars produced under pyrolysis (Jeffery et al. 2011; Méndez et al. 2013; Shenbagavalli and Mahimairaja 2012). However, the soil CEC showed changes depending upon the feedstock from chars, the amount applied to soil (Bicalho 2012; Cely et al. 2015; Schulz and Glaser 2012), process conditions (Breulmann et al. 2017b) and biochar age (Liang et al. 2006). Biochar on contact with air and water is supposed to form carboxylate and other ionizable functional groups on its surface, which are hydrophilic (Basso et al. 2013). These chemical changes on the surface of Sewchar particles may explain the increase in CEC and WHC with Sewchar applications. The potential of the Sewchar to increase soil WHC suggests that soil amended with Sewchar could retain more water from rainfall and improve the crop production, due to the enhancement of the water availability to crops and reduction of the plant water stress. Additionally, soils with a great WHC are less subject to nutrient leaching and waste of water for the grow of crops specially in irrigated regions. Regarding trace elements, although the soil Zn, Mn and Cu thresholds for Cerrado soil were exceeded for all the treatments in T1 and T2, no phytotoxic effects were observed in the beans.

### 3.3 Effect of Sewchar and mineral fertilizer on nutrient uptake by beans

Increasing Sewchar doses were positively correlated with the Mn, Mg, N, Zn and P uptake of beans and negatively correlated with K in T1 (Table 6-3). However, in T1, no correlation between increasing Sewchar applications and the TDM was observed. One possible reason might be the insufficiency of the N, P, K, Mg and Cu for beans in Cerrado soil. The higher TDM of mineral fertilizer related to nutrient uptake by beans in T1 might be due to the sufficiency of Ca, Fe, Mn and K for beans in Cerrrado soil. Mineral fertilizer was the only treatment that provided a K concentration within the sufficiency threshold for beans in Cerrado soil (Table 6-1 and Figure 3-4f). The mineral fertilizer had lower TDM in T2, although it was not significant (Table 6-2 and Figure 3-1). This result might be due to the insufficient Cu, P, and Mg for bean growth in Cerrado soil (Table 6-1 and Figure 3-4d, e, h) and the leaching of the applied mineral contents within one growth period after application. Only mineral fertilizer did not provide a Cu concentration within the sufficiency threshold for Cerrado soil (Table 6-1 and Figure 3-4d). Similarly, biochars were reported to reduce nutrient leaching (Gunes et al. 2014; Uzoma et al. 2011).

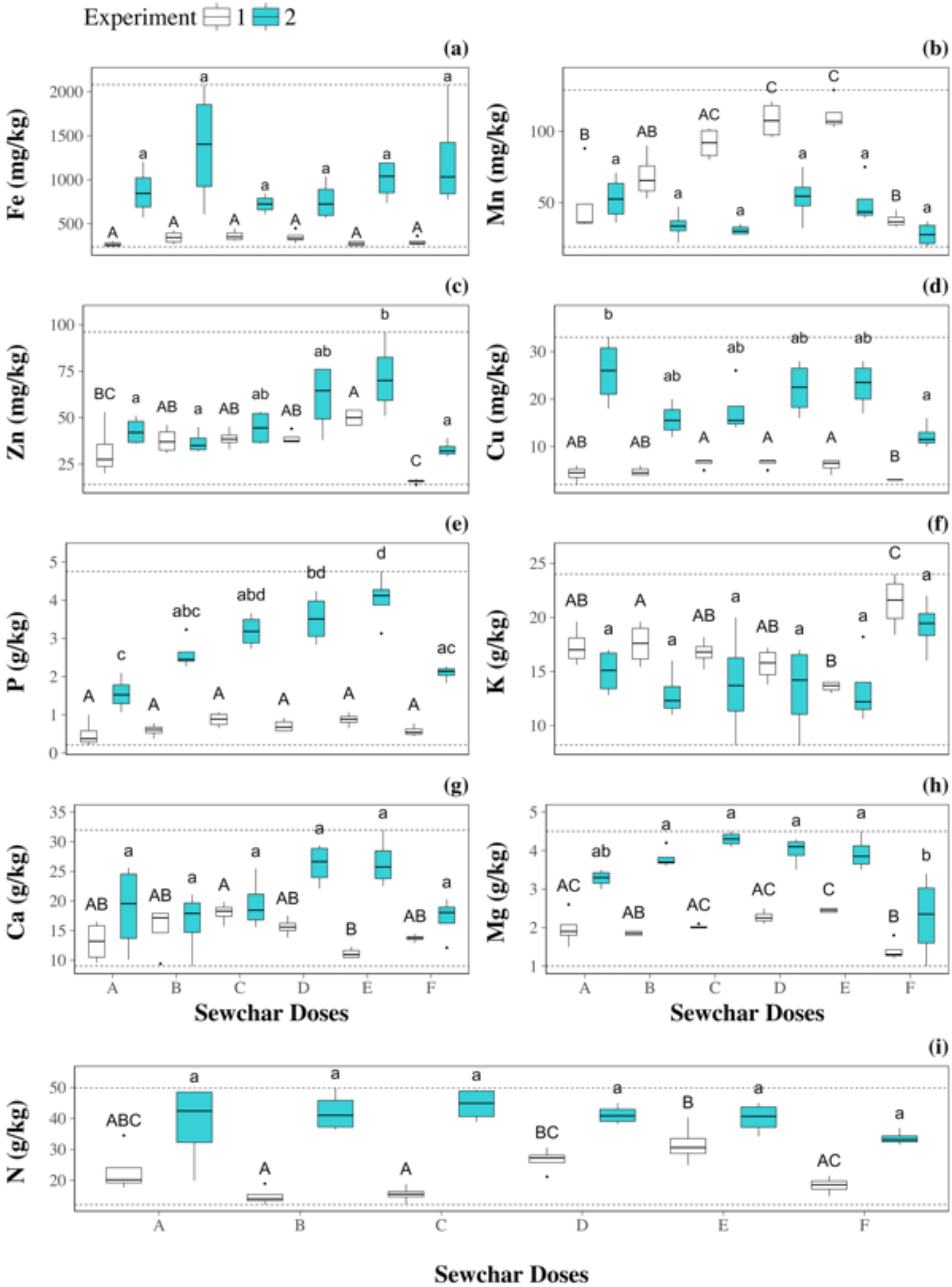


Figure 3-4 Results of the comparison of means (Tukey-HSD) for the uptake of (a) Fe, (b) Mn, (c) Zn, and (d) Cu, (e) P, (f) K, (g) Ca and (h) Mg and (i) N from soil treatments (A: 0.0, B: 4 Mg ha$^{-1}$, C: 8 Mg ha$^{-1}$, D: 16 Mg ha$^{-1}$, E: 32 Mg ha$^{-1}$ Sewchar doses and F: mineral fertilizer) after T1 and T2. Whiskers represent ± the standard errors of the mean (n = 5). Different letters in the same experiment indicate significantly different values at $\alpha < 0.05$.

Our results confirmed that Sewchar has nutritional value for agricultural purpose and better nutrient uptake by beans was observed with longer residence time of Sewchar in the soil. Some explanations for the positive correlation between the increasing Sewchar doses and TDM in T2 are the positive correlation between increasing Sewchar doses and the uptake of P, Zn and Ca (Table 6-3). Additionally, the sufficient plant thresholds of P, Ca, N, Mg, Cu, Mn, and Zn for beans in Cerrado soil were provided (Table 6-1 and Figure 3-4). The P uptake by beans had a strong correlation with increasing Sewchar applications, which was expected due to the fertilization with phosphate in T2. The understanding about the effect of sewage sludge chars on nutrient availability is not entirely clear, because increasing and decreasing uptake of different nutrients have been reported (Faria et al. 2017; Khan et al. 2013; Sousa and Figueiredo 2016). Different process conditions showed that nutrients remained in plant available forms during HTC (Fühner et al 2011). Also, Breulmann et al. (2014) demonstrated that Sewchar contain more nutrient plant available forms (P, Ca and Mg) than biochar. Other studies confirmed that thermochemical conversion could improve plant tolerance to sewage sludge, however, biochar from activated sewage sludge seems to have higher plant compatibility and plant nutritional value than Sewchar from raw sludge (Fühner et al. 2011). We also found that increasing Sewchar applications had a moderate correlation to Ca uptake by bean. Additionally, contrasting to Sousa and Figueiredo (2016), our results did not confirm the inhibition relationship between Cu and Zn. In our study Cu and Zn uptake raised with increasing Sewchar doses. However, Cu was a little exceeded in the Sewchar doses 16 and 32 Mg ha$^{-1}$ and Zn was still within the sufficiency threshold for bean growth in Cerrado soil for all the treatments. Another explanation of the higher TDM with increasing Sewchar doses in T2 might be a better nutritional balance. The N uptake increased from T1 to T2 in all the Sewchar treatments except the 32 Mg ha$^{-1}$ Sewchar and control treatments (Table 6-2), and it was within the N sufficiency plant threshold for bean growth in Cerrado soil for all the Sewchar treatments. One explanation for the plant N sufficiency might be the HTC temperature in our study (190ºC), in which lower N losses are expected (Tian et al. 2014). Our results indicated that Sewchar application promoted mineralization, but no correlation between increasing Sewchar doses and increased N uptake was observed. Nevertheless, the soil analysis of total N, mineral N, ammonium, nitrate and the C : N ratio at the end of our experiment confirmed the ability of Sewchar to release available N into the soil via mineralization.

### 3.4.3 Threshold of Sewchar applications

The Sewchar applications up to 32 Mg ha$^{-1}$ was chosen because doses above 20 Mg ha$^{-1}$ are unrealistic in agronomic practice (Bargmann et al. 2013). Additionally, charcoal applications higher than 100 Mg ha$^{-1}$ were reported to show no increase in plant growth (Bargmann et al. 2013; Rillig et al. 2010; Rondon et al. 2007). In this study, doses of 10 - 20 Mg ha$^{-1}$ (Bargmann et al. 2013) were suggested to be more suitable in agronomic practice. The TDM of the 16 Mg ha$^{-1}$ Sewchar had the best results compared with the other Sewchar treatments, because it exhibited no significant difference compared to the TDM of mineral fertilizer and 32 Mg ha$^{-1}$ in T1 and T2. In T2, the TDMs of 16 and 32 Mg ha$^{-1}$ Sewchar were higher than the control TDM (Figure 3-1). Other study applying 15 Mg ha$^{-1}$ of biochar from sewage sludge produced under two different temperatures (300 and 500ºC) in a two-year field experiment also reported corn growth similar to the addition of mineral fertilizer in both cropping seasons (Faria et al. 2017). In our study the 16 Mg ha$^{-1}$ Sewchar dose had a TDM increase (79% higher) in T2 than in T1, which was not observed neither for mineral fertilizer nor for 32 Mg ha$^{-1}$ Sewchar (Table 6-2). The TDM increase in T2 for 16 Mg ha$^{-1}$ Sewchar might be due to its higher P availability compared to the lower Sewchar additions. Additionally, unlike the 32 Mg ha$^{-1}$ treatment, the 16 Mg ha$^{-1}$ Sewchar treatment had higher plant-available N in T2 than in T1 (Table 6-2, Figure 3-4i). Likewise, unlike the mineral fertilizer, the 16 Mg ha$^{-1}$ treatment had higher plant-available Ca in T2 than in T1 (Table 6-2, Figure 3-4g). Moreover, 16 Mg ha$^{-1}$ Sewchar had a lower C: N ratio than the control and mineral fertilizer in T2 (Figure 3-2i). In general, our results showed that the Sewchar dose 16 Mg ha$^{-1}$ was able to supply nutrients to beans, promoting TDM of beans equivalent to mineral fertilizer. Similarly, several studies applying different doses (up to 60 Mg ha$^{-1}$) and process conditions of sewage sludge biochar as soil amendment reported positive effects, indicating its potential to replace mineral fertilizer by means of maintaining the same productivity (Deenik and Cooney 2016; Faria et al. 2017; Hossain et al. 2010). However, 50 Mg ha $^{-1}$ Sewchar and (60-100 Mg ha$^{-1}$) sewage sludge biochar were reported to have negative effects on the growth of spring barley (Breulmann et al. 2014) and radish (Sousa and Figueiredo 2016) respectively. The reported negative effects of sewage sludge biochars were the limitation of K availability, excess of nutrients that limit the development of plant at higher doses (Sousa and Figueiredo 2016), increase of Cd and Zn bioaccumulation, and decrease of N and K bioaccumulation by rice (Khan et al. 2013). However, Breulmann et al. (2014) stated Sewchar potential to recycle plant availability of N, Ca and Mg and to degrade phytotoxic components in the field. In our study, the optimum Sewchar dose 16 Mg ha$^{-1}$ is a realistic dose in agronomic practice. Additionally, this dose increased soil fertility indicators, enriched most of the nutrients in the soil and supplied nutrients to plants, except for K, promoting the increased TDM of beans. The Zn, Mn and Cu availabilities in the soil exceeded the sufficiency threshold for Cerrado soil. However, the Zn and Mn uptake were within the sufficiency threshold for beans in Cerrado soil, while Cu uptake exceeded it a little. Nevertheless, no phytotoxic effects were observed in the beans. Other studies also showed that sewage sludge chars promise in mitigating the negative effects of soil Mn toxicity (Deenik and Cooney 2016) and phyto-available Cd (Ren et al. 2017). Additionally, the level of the other trace elements in bean tissue was within the Brazilian threshold for beans in Cerrado soil. These results support the potential use of Sewchar as a soil amendment from a safety perspective. Consequently, applying 16 Mg ha$^{-1}$ to soil seems to be a sustainable alternative that will be help in facing the decline in soil fertility and productivity, reducing the current fertilizer requirements of agriculture.

## 3.5 Conclusions

This study indicates that HTC can be a promising alternative for recycling biosolids and enhancing soil fertility and productivity. Sewchar can potentially replace or supplement the current economically and environmentally unsatisfactory use of high doses of mineral fertilizer. The reduction of mineral fertilizer demand decreases the emissions of greenhouse gases from the fertilizer industry, making Sewchar likewise environmentally attractive. Applying Sewchar to soil led to no phytotoxic effect in beans, and the short residual effect of Sewchar could improve nutrient uptake by these plants. However, the growth responses vary in different soils, crops, residence times and field settings. Therefore, knowledge about the longevity of Sewchar benefits on soil fertility and nutrient cycling is still quite limited. In the future, field studies about the effect of the optimum Sewchar dose over multiple crop cycles trials should be performed to confirm if the interaction among Sewchar, soil biota, and plants continue to be positive and environmentally safe over the long-term.

## 3.6 Acknowledgment

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## 4 Management of biosolids-derived hydrochar (Sewchar): effect on plant germination, and farmers' acceptance

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## 4.1 Abstract

Hydrothermal carbonization is a promising approach of biosolids management and its utilization as a soil amendment. This study evaluated the physical and chemical properties of hydrothermally converted biosolids (Sewchar) and its effect as a potential soil amendment on the growth of rice, beans, and radish. The germination experiment was conducted in a greenhouse in a randomized design using five Sewchar doses (0, 10, 20, 40 and 60 Mg ha$^{-1}$). The results showed that hydrothermal carbonization influences the physicochemical properties of the biosolids, such as promoting pore structure and trace elements below the threshold values for use in agriculture. The spectroscopic techniques demonstrated higher presence of oxygen-containing functional groups (e.g., C-O/O-H) on surfaces of Sewchar than that of biosolids. The Sewchar doses of 10 Mg ha$^{-1}$ and 60 Mg ha$^{-1}$ yielded the highest dry biomass for beans and rice respectively. Increasing Sewchar doses negatively correlated with radish dry biomass, as indicated by linear regression equation fitting. Thus, biomass responses to Sewchar application into the soil varied with Sewchar dose and type of plant. For a proper environmental management, a survey was conducted to assess farmers' perception and acceptance of Sewchar as a soil amendment. The survey revealed that younger farmers who had higher education qualifications were more prone to use Sewchar as soil amendment. Additionally, farmers who would not use Sewchar as soil amendment attributed the highest level of importance to economic criteria, such as fertilizer and freight prices. In the future, studies on a longer term under field conditions should be performed to elucidate the interactions between Sewchar and soil properties on plant growth and to ensure the safe use of Sewchar as a soil amendment.

## 4.2 Introduction

Hydrochars and biochars have been studied as soil amendment to imitate the natural coalification of biomass based on man-made soils – known as Anthrosols or *Terra Preta de Índio (TPI)*, the Amazonian Dark Earth. TPI is a soil with an archeo-anthropogenic horizon, which is presumed to be created by chance or by deliberately adding large quantities of charred residue, excrement, organic waste, and bones by pre-Columbian native populations (Glaser 2007; Haubold-Rosar et al. 2016; Oliveria et al. 2018). This type of soil has been reported to have a high content of plant nutrients and highly fertile charcoal particles as a result of the adsorption of nutrients on charcoal surfaces (Glaser and Birk 2012). The solid byproduct from hydrothermal carbonization (HTC) is called hydrochar, and the solid byproduct from pyrolysis is called biochar. HTC is a process of converting wet feedstock into carbonaceous product, which can then be used as a soil amendment (Libra 2011). Therefore, one of the pathways to achieving sustainable agriculture in the twenty-first century is beneficial utilization of chars from waste biomass as soil amendment (Glaser 2007). However, the production process of biochar and the respective influences on biochar properties have not yet been described by the European Biochar Certificate (EBC) or the International Biochar Initiative – IBI (Dieguez-Alonso et al. 2018). The absence of definition for parameters related to specific applications is one of the current challenges for the use of hydrochars as a soil amendment.

The use of chars in field trials indicated that the influence of hydrochar application on plant growth depends, among others, on the feedstock, production conditions, application rate location, specific factor and the plant crop tested (O'Connor et al. 2018). This variabilitiy of results was also observed in pot experiments, such as a decrease in plant biomass yield was observed after hydrochar application into soil using beet root chips (Bargman et al. 2014), spent brewer's grains (Bargmann et al. 2013; Bargmann et al. 2014), sugar beet pulp, beer draff (Gajić and Koch 2012), maize silage (Busch et al 2013), and orange peel (Kalderis et al. 2018) as feedstocks for leek, barley, phaseolus bean, sugar beet, mustard, and maize growth.

Conversely, also in greenhouse experiments an increase in plant biomass yield was observed after hydrochar application into soil using beet root chips and spent brewer's grains as feedstock for the growth of phaseolus bean (Bargman, et al. 2014) and dandelion plants (Rillig et al. 2010). Likewise, the deleterious effect of hydrochars from spent brewer's grains and beet root chips on barley germination was mitigated by washing these hydrochars (Bargmann et al. 2013). Aged hydrochar from municipal woody and herbaceous pruning has been reported to have the lowest concentration of polyphenols and volatile fatty acids (VFAs), resulting in higher radicle length and higher germination percentage for lettuce compared with fresh and washed hydrochars (Puccini et al. 2018).

The product derived from HTC of sewage sludge or biosolids is called in this study Sewchar. Sewage sludge has plant nutrients and hazardous compounds, of which polycyclic aromatic hydrocarbons (PAH), furans and dioxins, endocrine disruptors, pesticides, and aliphatic hydrocarbons are significant (Eriksson et al. 2008). Studies on the HTC of sewage sludge have shown pharmaceuticals compounds in Sewchar (Vom Eyser et al. 2015). Other studies have demonstrated that PAHs and phenols are phytotoxic compounds formed during carbonization (Hilber et al. 2012), which are likely to hinder germination (Rogovska et al. 2011). However, hydrochars have been reported to have lower PAH contents than biochars (Bargmann et al. 2013) and to contain trace elements below the threshold values for use in agriculture (Zhang et al 2014; Melo et al 2017). In addition, HTC of sewage sludge followed by pyrolysis has been reported to yield a more alkaline material, with higher immobilization potential of trace elements than hydrochar from raw sludge pyrolysis (Liu et al. 2018).

Sewage sludge biochar has also been considered for risk mitigation of toxic metal accumulation in fruits (Hossain et al. 2015) and for soil remediation and reduction of the mobility of trace elements in co-contaminated soil (Zhou et al. 2017). HTC also exposed P for interaction with various minerals/metals, with the final P speciation closely associated with the speciation/composition of metals and their affinities to P (Huang and Tang 2016). Similarly, the ash from sewage sludge after monoincineration shows P content comparable with phosphate rock-based mineral fertilizers applied in Germany, as well as lower Cd and U contents (Krüger et al. 2014). Likewise, liquefaction and pyrolysis of sewage sludge reveal reduction of trace elements toxicity (Shao et al. 2015). Therefore, the HTC appears to be an attractive alternative for wet waste treatment, regarding sanitation, volume reduction (Saetea and Tippayawong 2013), and nutrient immobilization (Dai et al. 2015; Silva et al. 2017a).

Positive results have been reported using several doses of sewage sludge carbonized under diverse settings and used in various crop species (Deenik and Cooney 2016; Faria et al. 2017; Paneque et al. 2015). Conversely, negative effects have also been reported in pot (Butt 1999) and plot field experiments (Breulmann et al. 2014). Sewchar treatments, such as washing, has been reported to reduce element concentration, biodegradable compounds, phytotoxic effects, and plant available nutrients (Breulmann et al. 2017a). In germination tests with cress, the wet oxidation of the process water from hydrothermal carbonization of sewage sludge resulted in higher toxicity than untreated process water (Weiner et al. 2018). The different reported effects of sewage sludge chars as soil amendment are due to the large variation in Sewchar properties with respect to the process conditions, application rate, and types of crop and soil. Hence, knowledge about the physicochemical characterization of Sewchar and the effects of various doses of Sewchar on different types of plant crops are needed before it can be used as a soil amendment in large-scale applications.

In addition, understanding farmers' opinions and choices concerning land application of sewage sludge by-products is crucial to develop customary approaches for managing sewage sludge and locally using its byproducts. Personal, telephone, and on-line interviews are often used to collect information about knowledge, attitudes, and perceptions regarding a specific theme. In particular, this method can help determine rules, values, and principles that are not presented in secondary data sources. A fundamental aim of interviews is to reveal possible answers to the impacts of new practices for adoption under field conditions (Colten and Hemmerling 2014). The objective of this study was to assess the effects of HTC on the physicochemical properties of biosolids and compare the effect of different doses of Sewchar as soil amendment on the germination of crops (rice, bean and radish) with diverse nutrient demands and life cycles. Additionally, we aimed to identify farmers' perceptions of Sewchar as a soil amendment, whether farmers are prone to use Sewchar as soil amendment, and which criteria are utilized by farmers when choosing a fertilizer.

## 4.3 Material and Methods

### 4.3.1 Sewchar preparation

The feedstock material for HTC was the biosolids from a wastewater treatment plant in Goiânia/Goiás, Brazil, which was sampled after the centrifugation process without the addition of lime. The Sewchar was produced in an 8-L lab autoclave with the addition of sulfuric acid, pH 4.5 and 4 h residence time at the Federal Institute of Goiás, Brazil. The means ± SD of the temperature and bar pressure were 190 ± 4.6 °C and 12 ± 1.7 bar pressure, respectively. Afterwards, a 0.25-mm mesh size sieve was used to separate the solid part of the Sewchar from the liquid part, and the solid part was dried at 75 °C for 5 hours.

### 4.3.2 Chemical properties of biosolids and Sewchar

a) Proximate analysis, pH, macronutrient, trace element concentrations, and polyclyc aromatic hydrocarbons (PAHs)

Biosolids and Sewchar proximate analysis was performed according to American Society for Testing and Materials (ASTM) method D5142. Moisture was measured by heating the samples at 105 °C for 24 h. Afterwards the samples were heated in a furnace at 450 °C for 1 h to determine their mobile matter according to weight loss. Ash content was measured after heating the samples in uncovered crucibles at 750 °C for 1 h. The resident matter was calculated by the difference between the initial weight and the summed weight of moisture, mobile matter and ash contents.

The chemical characterization of the biosolids and Sewchar was performed as described by Melo et al. (2017). Analysis of pH, calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), nitrogen (N), phosphorus (P) and zinc (Zn) were measured based on Embrapa (2009). Analysis of arsenic (As), molybdenum (Mo), nickel (Ni), and lead (Pb) contents was performed in accordance with the US EPA Method 3051A (2007), and mercury (Hg) was measured via atomic absorption spectrophotometry using a mercury direct analyzer DMA 80 (MLS GmbH, Leukirch, Germany).

PAHs were measured after ultrasonic extraction with hexane and identified by gas chromatography- mass spectrometry (GC-MS, SIM mode). Samples of 0.5 g (DM) were extracted twice with 3 ml of n-hexane, followed by centrifugation. The solution was evaporated under a gentle $N_2$ stream at 30 ºC (TurboVap II) to remove the solvent. After that, the dry residue from extraction of biosolids as well as Sewchar samples was re-diluted in hexane. Finally, 500 ng of an internal standard was added (16 EPA PAH in cyclohexane, PAH Mix 9, Dr. Ehrenstorfer) and PAHs were measured in GC-MS-SIM mode. Quantification was carried out according to the internal standard. Naphthalene was not included because a great amount of blanks from the extraction solvent as well as from potential evaporation loss during concentration occurred.

b) Surface characterization using spectroscopic techniques

The molecular bonds within biosolids and Sewchar were analyzed by Fourier transformed infrared spectroscopy analysis (FTIR). The samples were dried at 70 °C for 4 h, and their chemical functional groups were studied with a Fourier transformed infrared spectroscopy analysis via the identification of bond vibrations at designated wavelengths. The sample was dispersed in a matrix of KBr using a weight ratio of sample/KBr = 1/100. Afterwards, the sample was pressed to form a transparent pellet and the FTIR spectra were recorded at room temperature in the 400-4000 $cm^{-1}$ wave number range with 2 $cm^{-1}$ resolution on a Shimadzu FTIR-8400S.

The chemical compounds and chemical bonds on the biosolids and Sewchar surface were characterized using an X-ray photoelectron spectroscopy (XPS) K-Alpha, ThermoFisher, USA. This analysis was performed to distinguish the functional groups and the chemical composition of surfaces of biosolids and Sewchar. The calibration of C binding energy was done using the C1s peak at 284.5 eV. A Gaussian–Lorentzian sum function was applied for the interpretation of XPS spectra.

The structural properties of the biosolids and Sewchar surfaces have also been characterized using a Raman spectrometer (ARAMIS, Horiba Jobin, Japan) at a resolution more than 2 $cm^{-1}$ at room temperature.

### 4.3.3 Physical properties of biosolids and Sewchar

Particle size distribution analysis was carried out at Umwelt-Campus Birkenfeld of the University of Applied Sciences using a Laser Particle Sizer "Analysette 22 Micro Tec Plus" from Fritsch company with a wet dispersion unit. The method of analysis was laser diffraction. The samples were measured three times, and the distribution width was shown for three values on the x-axis, the D10, D50, and D90. The D10, D50, and D90 are defined as the diameters where respectively 10%, 50% and 90% of the population lies below this value. The equipment used was suitable for all typical measurements tasks in the range of 0.08 to 2000 microns. Only the particle size distribution of the Sewchar sample was possible to determine, because the particles of biosolids sample were too small and were agglomerated even after addition of wetting agent (tenside) and an ultrasound bath. Therefore, biosolids sample could not be analyzed using this equipment.

The surface morphology was studied using a Scanning Electron Microscope (SEM, FEI Quanta FEG 250 series, Japan) to elucidate porous properties of the biosolids and Sewchar samples. The samples of biosolids and Sewchar were dried at 105 °C for 4 h and sieved to 500 µm. Biosolids and Sewchar samples areas were selected during the SEM analysis and imaged randomly to minimize bias. The magnifications used was between 8,000 and 20,000x.

For the surface area (SA) and pore volume (PV) the Sewchar sample was dried at 70 °C for 4 h. The SA and PV analyses were performed by $N_2$ sorption on a Micrometrics ASAP 2020, with $N_2$ at 77 K and $CO_2$ at 273 K. Prior to analysis, the samples were degassed under vacuum for at least 12 h at 180 °C. SA-$N_2$ was calculated according to the Brunauer-Emmet-Teller (BET) equation, using adsorption data in the 0.05 – 0.3 relative pressure range (Brunauer et al.1938). The final result is a curve obtained by plotting the quantity of adsorbate at constant temperature against the concentration of the substance in the original gas or solution. Total pore volumes (PV-$N_2$) were calculated from a single point at P/Po = 0.97574624. Average pore width was calculated as 4V/A BET (V: total pore volume and A: BET surface area).

### 4.3.4 Soil properties

The soil used in this study was a composite sample of different types of soils from the 0-0.2 m layer of topsoil in the Cerrado biome in Goiânia/Goiás, Brazil. The soil texture was sandy loam. The soil was prepared according to the OECD (2006) methodology for natural soil. Briefly, the soil sample was heat-treated by autoclaving for 20 min at 120 °C to reduce the effect of soil pathogens and passed through a 2-mm sieve to remove coarse stones and plant residue. Prior to the experiment, a composite sample was collected and analyzed to determine pH; Ca, Cu, Fe, K, Mg, Mn, P, and Zn contents; potential acidity (H+Al); and cation exchange capacity (CEC); as described by Melo et al. (2018) (Table 4-1).

Table 4-1 Soil chemical characteristics

| Clay | Silt | Sand | Cu | Fe | Mn | Zn | Organic Matter | pH $CaCl_2$ | P | K | Ca | Mg | H+Al | Al | CTC | BS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | g kg $^{1}$ | | | mg $kg^{-1}$ | | | g $kg^{-1}$ | | | mg $kg^{-1}$ | | | $cmol_c$ $kg^{-1}$ | mg $kg^{-1}$ | $cmol_c$ $kg^{-1}$ | % |
| 68 | 112 | 820 | 1.8 | 51.3 | 12.0 | 2.0 | 3 | 5.0 | 44.4 | 80.0 | 1.5 | 0.8 | 2.5 | 0.0 | 5.0 | 50.0 |

### 4.3.5 Germination experiment

The germination experiment was conducted in a greenhouse in a randomized design containing five treatments, four replicates per treatment, and three crop species (rice – *Oryza Sativ*, phaseolus bean – *Phaseolus vulgaris*, radish – *Raphanus sativus*). The experiment was carried out based on the OECD (2006b) methodology for terrestrial plant test: seedling emergence and seedling growth test, a guideline for testing of chemicals. The three crop species were chosen because they have different nutrient demands, in this order (radish>bean>rice), and growth periods (rice>bean>radish). The five treatments included various treatments with Sewchar doses (0%, 0.5%, 1%, 2%, and 3%), which correspond to (10, 20, 40, and 60 Mg $ha^{-1}$ at a soil depth of 20 cm); 0 level (without Sewchar amendment) was used as the control. The Sewchar doses up to three times the realistic field application rate (1%) were chosen to confirm whether the best results related to the biomass of different crops with diverse nutrient demands and life cycles are observed in a realistic application rate in agronomic practice (Bargmann et al. 2013). Commercial plastic pots 7.5 cm in height x 10 cm in diameter were used containing 400 g of dry matter of soil plus the amendment. A fine gauze was placed in the holed bottom of the pots to hinder particulate matter loss. Three seeds of beans, six seeds of rice, and seven seeds of radish per pot were used. The pots were watered daily up to the field water capacity, according to the plant requirements. The trials were held under natural long-day tropical weather conditions of lighting and temperature. Plants were collected after 21 days of growth and shoot and root biomass were dried to constant weight at 60 °C, fined-ground (1 mm), and weighed.

### 4.3.6 Survey

Structured qualitative research interviews using a questionnaire were conducted to investigate family farmers' perceptions of choosing a fertilizer and of land applications of Sewchar. The survey questionnaire was designed based on general questionnaire survey guidance (Saris and Gallhofer 2007). The questionnaire included questions about the knowledge, attitudes and perceptions of the farmers related to Sewchar and general characteristics of the farmers, such as age, gender, and education (primary education, secondary education, first stage of tertiary education, second stage of tertiary education). In addition, there were questions about the state of the art related to their current soil amendment used, such as the type of soil amendment currently used (organic, inorganic, or both), the reason for using the present soil amendment, and whether what is produced is also commercialized. Furthermore, there were questions with respect to the living standard of the farmers, such as size of the owned land, belonging to settlement, access to governmental assistance, access to capacitation, and access to credit. Three types of exploratory variables concerning the factors considered important by the farmers for choosing a fertilizer were embedded into this survey, such as agronomic, economic, and environmental variables. This conceptual framework was built upon the principles of a sustainable agriculture (FAO 2017) and circular economy for nutrients (Gievers et al. 2017). The agronomic, economic, and environmental criteria for choosing a fertilizer were evaluated using a 5-point Likert scale, where 1: not at all important, 2: slightly important, 3: important, 4: fairly important, 5: very important. We expected that the fertilizer choice may be influenced by the characteristics of the farmer, such as gender, age, education (measured in terms of the number of schooling years and access to capacitation). Additionally, we supposed that economic situation of the farmers (living standards), such as belonging to settlement, access to credit or social government assistance, commercialization of their crop, and land size could also play a role in choosing a fertilizer. The last part of the survey concerned the knowledge and the acceptance of Sewchar as soil amendment, such as knowledge about the source of biosolids/seage sludge and about the HTC technology. Furthermore, farmers were asked if they would use Sewchar as a soil amendment. In case the farmers would use Sewchar as a soil amendment, they were asked for each type of crop (edible and inedible, only inedible, or none) and for which purpose (own consumption and commercial, just commercial, or none). In case the farmers would not use Sewchar as a soil amendment, they were asked the reason(s) for their response.

A pilot questionnaire test was conducted personally on March 6th, 2015 with 10 members of the group of family farmer women from Canudos, settlement association, Brazil "Associação Guerreira de Canudos". According to feedback from participating farmers, the questionnaire was revised to improve the precision of the language used. On April 27th and 29th, 2016 a finalized survey questionnaire was conducted with family farmers at a family farmers' fair "Feira Agro Centro-Oeste Familiar" in a municipality called Urutaí in southeast Goiás state in Brazil. The questionnaire of the survey had 25 questions and was applied to a total of 55 rural producers (Supplementary Table S2). The farmers present at the fair were randomly chosen, informed of the objective of the survey and consented to participation, and a face-to-face interview was performed. The response rate was 100%.

### 4.3.7 Data analyses and statistics

Statistical analyses were performed with the program RStudio (version R 3.4.2, R Core Team 2018).

For the germination experiment, homogeneity and normality were tested using Bartlett's test and the Shapiro-Wilk test, respectively. Assuming a significance level of 0.05, the influence of different Sewchar doses on the germination of the three crop species was evaluated via one-way analysis of variance (ANOVA), according to Johnson and Wichern (2007). Additionally, the parametric model was attempted to be adjusted to the data to obtain the dry mass behavior of each crop germination regarding to the increasing Sewchar doses. The total dry biomass (TDM) data were converted to a percentage as a function of Sewchar 0%. Moreover, the continuous endpoints (effective dose – EDx or effective application rate) were calculated according to the increasing Sewchar doses. The effective dose relates to an effect predicted on x% of the test plant at a given dose (OECD 2006a). The aim was to adjust the dry mass data relative to the Sewchar doses of each culture in a linear regression to the experimental data. Additionally, the effective dose was estimated in relation to the dry mass of the control.

For the results of the survey, the answers were analyzed using exploratory data analysis (EDA). The analytic techniques of principal component analysis (PCA) are used to reduce the number of variables and to detect structure in the relationships between variables – Shlens (2005). Therefore, PCA was used to identify which variables were related to the farmers' decision concerning using Sewchar as a soil amendment. The most important variables were identified through the order of magnitude of the loadings of the first principal components, which means the minimum number of components that accounted for the maximum possible variance (Johnson and Wichern 2007). Subsequently, the PCA with the variable "would use" isolated was carried out to indentify the variables, which had a strong correlation with the answers "yes" and "no" for the use of Sewchar as a soil amendment. Spearman's correlation coefficient (r) was used to evaluate the correlation between the ordinal variable in each group. Spearman's correlation coefficient (r) was used because we would like to determine the strength and direction of the monotonic relationship between two variables rather than the strength and direction of the linear relationship between the two variables.

## 4.4 Results and Discussion

### 4.4.1 Biosolids and Sewchar chemical properties

a) Proximate analysis

HTC increased the ash content of biosolids from 30.48% to 36.98%, decreased moisture content from 4.22 % to 2.59 %, mobile matter from 25.18 % to 23.69 % and resident matter from 40.11 % to 36.75%. Previous study has also shown higher ash content and lower fixed carbon after hydrothermal carbonization of sewage sludge (Parshetti et al. 2013). Different feedstock content and process conditions result in different moisture content, ash content, volatile matter and resident matter o chars (Al-Wabel et al. 2013).

b) Macronutrient and trace element concentrations

The results of the chemical characterization of biosolids and Sewchar are shown in Table 2. The HTC increased the concentration of the trace elements (Cr>Ni>As>Pb>Mo). As previously reported by Melo et al. (2017), although Sewchar had trace element contents higher than those of biosolids, these values met the threshold value of CONAMA 375 (2006). The CONAMA 375 (2006) is the Brazilian Resolution that establishes criteria and procedures for using sludge generated in wastewater treatment plant and their derivative products in agriculture. The explanation for the accumulation of trace elements on Sewchar may be related to the concentration effect. The trace elements ended up concentrated in the Sewchar because of the HTC. Similar results have been reported using sewage sludge as feedstock for carbonization processes at higher temperatures (Chen et al. 2018) and longer reaction times (Zhang et al. 2014). In addition, the introduction of rice straw and sawdust for the co-pyrolysis of sewage sludge has been reported to reduce the total content of some trace elements contents, such as Cu, Zn, and Ni (Huang et al. 2017). However, it has also been reported the increase of total and bioavailable trace elements in soil with Sewchar application, where oxidable and residual fractions of trace elements transformed into acid-soluble and reducible fractions during incubation (Yue et al. 2016).

c) Polycyclic aromatic hydrocarbon content

With respect to PAH concentration (Table 4-2), the main components of the samples were fatty acids, esters, and cholesterol derivatives. Our results showed that the PAH amount increased in Sewchar, when compared with the original biosolids feedstock. Similar outcomes have been reported by Wiedner et al. (2013), where the PAH amount increased with increasing HTC temperature. Paraíba et al. (2011) stated that the levels of PAH concentration found in sewage sludge could potentially contaminate the soil. Currently, there is not yet a legal framework for PAH threshold values for neither hydrochar nor for biochar. The current limits are in regard to biosolids, compost, and soil. Our results showed the values of benzo(a)anthracene and benzo(a)pyrene in biosolids and Sewchar, and the value of benzo(k)fluoranthene in Sewchar exceeded the threshold values defined by the Brazilian National Environment Council - CONAMA 375 (2006). However, the sum of the PAHs in the biosolids of our study complied with the limits ($\sum$9PAHs 6 mg kg$^{-1}$) set by the Council of European Community (CEC 2000). In our study, the sum of the PAHs in the Sewchar was within the range of maximum allowed threshold ($\sum$16PAHs 6-300 mg kg$^{-1}$) set by the International Biochar Initiative (IBI 2015) PAHs for biochar. However, the sum of the PAHs in the Sewchar in our study was above the maximum threshold ($\sum$16PAHs < 12 mg kg$^{-1}$) defined by the European Biochar Certificate for basic grade (EBC 2012). PAHs are considered to be persistent in the environment and have mutagenic, carcinogenic and teratogenic effects on human health (Wang et al. 2017). The impact of PAHs in chars on microbial populations and plant growth is still unknown. In addition, several methods have been used to measure PAHs in chars resulting in different accuracy of PAHs content in biochars (Dutta et al. 2017). Therefore, PAHs threshold values are reported to be eloquent, only if they are related to the permitted PAH analysis methods (Meyer et al. 2017). However, there is no standard method for quantitative analysis of PAHs content in chars. Therefore, further research on the release of these compounds from chars in soil is essential to provide a legal framework and standardize the most accurate analytical method including extraction to measure total and bioavailable PAHs in Sewchar before its use as a soil amendment.

Table 4-2 Biosolids and Sewchar chemical characteristics

| Moisture content | pH | N | P | K | Ca | Mg | Cu | Fe | Mn | Zn | As | Cd | Cr | Hg | Mo | Ni | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % | g kg $^{-1}$ | | | | | | | | | | mg kg $^{-1}$ | | | | | | |
| Biosolids chemical characteristics | | | | | | | | | | | | | | | | | |
| 73.1 | 5.3 | 30.8 | 10.9 | 7.0 | 17.4 | 2.3 | 0.3 | 5.1 | 0.2 | 0.1 | 18.2 | - | 57.5 | 0.5 | 8.2 | 26.6 | 19.0 |
| Sewchar chemical characteristics | | | | | | | | | | | | | | | | | |
| 23.6 | 5.0 | 22.4 | 11.6 | 4.0 | 20.2 | 2.8 | 0.3 | 4.9 | 0.2 | 0.1 | 26.4 | 0.9 | 79.7 | 1.34 | 11.4 | 72.6 | 23.4 |

| PAHs. Content mg kg $^{-1}$ | PAHs. Content in Biosolids | PAHs. Content in Sewchar |
|---|---|---|
| Acenaphtylene | 0.1041 | 1.0863 |
| Acenaphthene | 0.419 | 0.7868 |
| Fluorene | 0.0139 | 0.3749 |
| Phenanthrene | 0.8003 | 5.0317 |
| Anthracene | 0.1677 | 0.9284 |
| Fluoranthene | 0.0295 | 3.0364 |
| Pyrene | 0.5915 | 3.2538 |
| Benzo(a)antracene | 0.3363 | 0.7522 |
| Crysene | 0.3641 | 0.8856 |
| Benzo(b)fluoranthene | 0.1272 | 0.4615 |
| Benzo(k)fluoranthene | 0.331 | 2.4772 |
| Benzo(a)pyrene | 0.4365 | 2.1636 |
| Sum PAH | 3.7212 | 21.2385 |

d) Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of biosolids and Sewchar are shown in Figure 4-1. Biosolids and Sewchar had different FTIR profiles, demonstrating the influence of the HTC treatment on the chemical structure of both materials. The main alteration observed between biosolids and Sewchar was the dissimilar peaks intensities for different functional groups. The different FTIR profiles were identified using several references, including Zakaria et al. (2016). A small peak observed at 3287 $cm^{-1}$ can be attributed to O-H stretching vibration, resulting from hydroxyl and carbonyl groups as well as the presence of water in the sample (Nakason et al. 2017). The presence of bands at 2912 and 2850 $cm^{-1}$ can be accredited to C-H stretching vibration (aliphatic C-H bond). The decreased intensity of the peaks at 2912 and 2850 $cm^{-1}$ suggests an increase in the contents of nonpolar groups (Wang et al. 2013). The bands at 1580, and 1540 $cm^{-1}$ were assigned to C=C stretching vibrations from aromatic rings. The band at 1382 $cm^{-1}$ was accredited to C-O bending from ether, carboxylic acids, or aldehydes. The band at 1022 $cm^{-1}$ was attributed to C-H bending from the absorption from C-H bridge of aliphatic carbon, methylene, and methyl. The band at 820 $cm^{-1}$ was due to C-O-C stretching vibration from ether, open ring ether and cyclic ether. The decreased intensity of the peak at 820 $cm^{-1}$ after HTC indicates dehydrogenation reactions (Liu et al. 2018). The band at 550 $cm^{-1}$ was assigned to M-X stretching vibrations in both organic and inorganic halogens compounds (Hossain et al. 2011).

The information obtained from FTIR can help to understand how Sewchar added to soil will affect the soil pH and interact with inorganic and organic compounds. The results of our study showed the presence of functional groups in Sewchar, such as carboxyl, hydroxyl, and phenols, which are associated with the surface oxidation capacity of Sewchar and its potential to enhance the adsorption of dissolved organic carbon, positively or negatively charged nutrients, minerals, and trace elements (Dieguez-Alonso et al. 2018; Liu et al. 2015b; Zhang et al. 2015). Mukome and Parikh (2016) explains that biochar with significant contributions from carboxyl and hydroxyl groups are thought to have higher CEC and high sorption capacity for cations and metals.

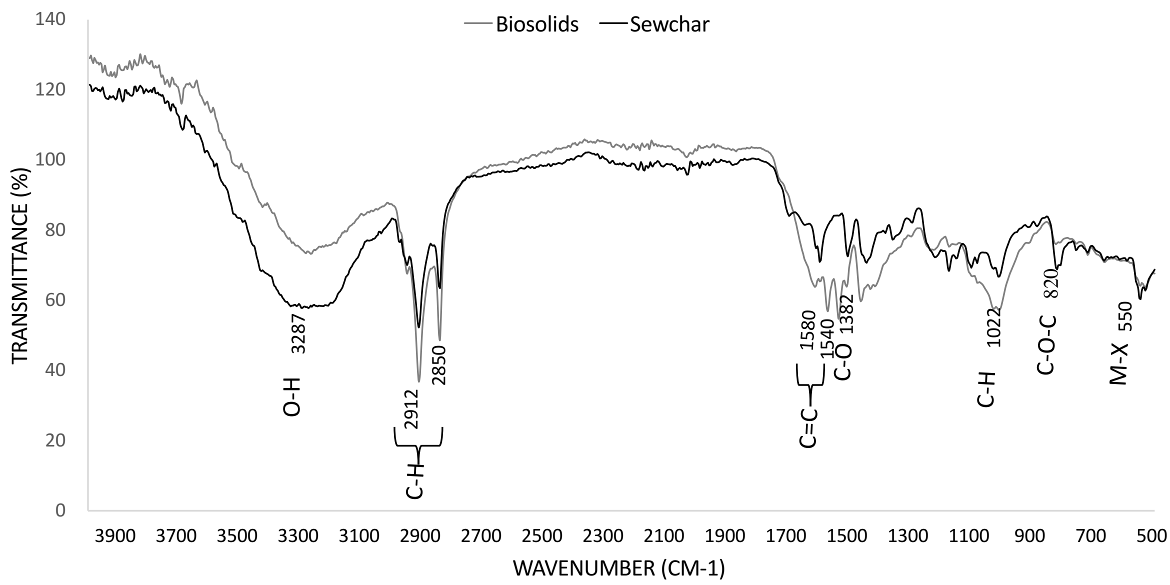


Figure 4-1 FTI spectra of Sewchar at 190 °C and 4 h residence time

e) X-ray photoelectron spectroscopy (XPS) analysis

The XPS results showed that biosolids and Sewchar surfaces have functional groups, including C-OH/C-O, hydroxyl C; C-C/C-H, aliphatic/aromatic C; and sp$^2$ C. The curve fitting results for the XPS spectra revealed that C-H, C-C, followed by C-OH/C-O, were the major C-bonding states (Figure 4-2). Sewchar contained higher proportions of oxygen-rich functional groups (carbon groups in oxidized states, such as C-OH/C-O) than biosolids. These results indicate a potential surface oxidation and an increased adsorption ability because the sorption potential of biochars are related to the presence of oxygen-containing functional groups (Jin et al. 2018). The oxidation process on biosolids surfaces during the HTC treatment might cause a decrease in basic sites, consequently, it might create new acidic functional groups on the surfaces of Sewchar. The cation exchange capacity is reported to be influenced by factors including the oxygen-containing functional groups on the biochar surface, which were shown to decrease with increasing conversion temperatures of biochars (Dieguez-Alonso et al. 2018). Our results also showed that the aliphatic and aromatic C components increased in Sewchar as compared to biosolids, indicating the impact of the HTC on the surface functionality. The higher aliphatic/aromatic C contents in the Sewchar might facilitate higher surface activity in soil (El-Naggar et al. 2018a,b). The results of the XPS analysis are according to the FTIR spectrum, where the presence of aromatic/ aliphatic carbon and oxygen-contained functional groups were evidenced in Sewchar.

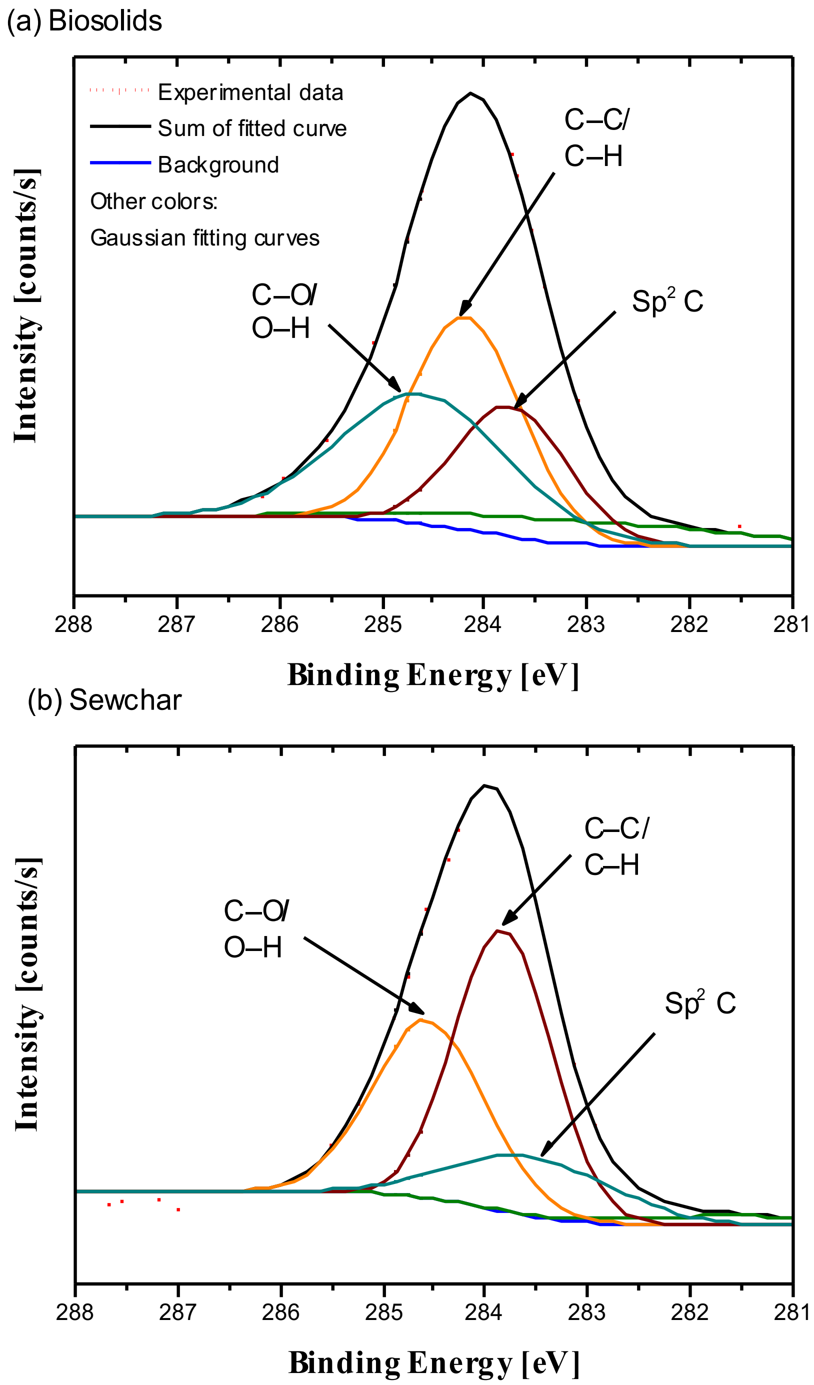


Figure 4-2 Curve fitting of C1s peaks in the XPS spectra of the biosolids (a) and Sewchar (b) samples

f) Raman spectroscopy analysis

The Raman spectra of the biosolids and Sewchar exhibited D and G bands at 1320-1350 cm$^{-1}$ and 1540-1590 cm$^{-1}$, respectively (Figure 4-3), indicating the presence of aromatic hydrocarbons and graphitic carbon structures (El-Naggar et al. 2018c; Igalavithana et al. 2018; Parikh et al. 2014). We estimated the intensity ratio of the D and G bands ($I_D/I_G$) based on the peak area value. The $I_D/I_G$ ratio is considered as an index for the amorphous or disordered graphite and the crystalline carbon or graphitic crystallites structures (Igalavithana et al. 2018; Zhang et al. 2015). The $I_D/I_G$ ratio of biosolids was higher than that observed in Sewchar, suggesting that it has lower aromaticity and an irregular arrangement (less stable) of carbon structure. Sewchar showed low $I_D/I_G$ ratio, indicating higher orderly arranged carbon structure (higher stability) than biosolids (Jin et al. 2018). Hydrochars are reported to become more stable and recalcitrant with progression of the HTC reaction (Zhu et al. 2015). When biochars are stored in the field environment, their high aromatization and recalcitrance are supposed to help C sequestration in soil (Zhang et al. 2015). Results of FTIR, XPS and Raman demonstrate that Sewchar might have higher recalcitrant nature than biosolids and hence, suggesting long turnover time in soil as compared to the biosolids. Orderly arranged structure is reported to be related to the microporosity in chars (Verheijen et al. 2010). Highly aromatic biochars are known to be more hydrophobic and to have high affinity for a wide range of organic compounds, particularly those with low aqueous solubility. However, hydrochar is reported to have a hydrophobic core and a hydrophilic outer surface (Chung et al. 2017), what can result in higher nutrient retention (Dieguez-Alonso et al. 2018).

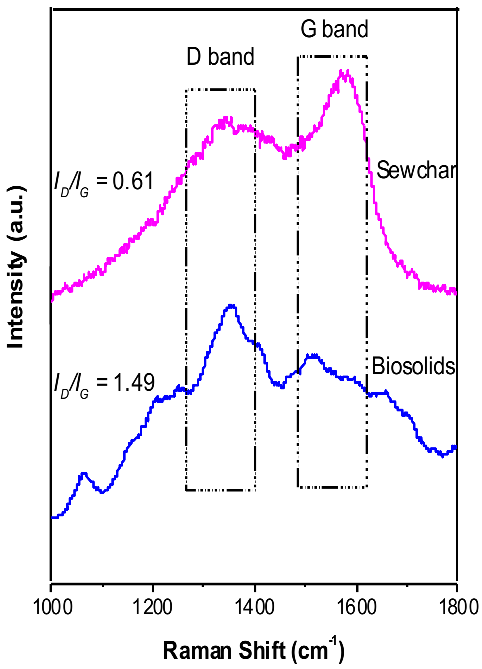


Figure 4-3 Raman spectra of the biosolids and Sewchar samples

### 4.4.2 Biosolids and Sewchar physical properties

a) Particle size distribution

The particle size distribution determined by laser scattering is shown as a volume distribution. A total of 90% of the complete Sewchar sample volume contained particles smaller than 59.7 µm (Supplementary Figure 6-1 in Supplementary Information 2). It has also been reported that sewage sludge biochar had a homogeneous structure, where the most frequent particle sizes were from 10 to 100 µm (Glazunova et al. 2018). Determining the particle size of a material is an important indicator of performance and quality process because it influences many material properties, such as rate of reaction, potential to dissolve, packing density, sedimentation, product appearance, and texture. However, according to Horiba (2012) transforming a volume distribution into either a surface area or number basis requires caution. The author explains that the conversion provided in the software is for comparison with other methods, such as microscopic techniques. Therefore, Sewchar samples were characterized using a scanning electron microscope (SEM) to compare the results from the two technologies.

b) Surface morphology

The SEM images of biosolids and Sewchar are shown in Figure 4-4. The images showed that HTC treatment resulted in the disintegration of the biosolids. However, remaining fibrous structure could still be seen in the Sewchar, indicating that they were not completely carbonized by HTC. These results were according to the FTIR results, where the decrease of –OH and aliphatic groups were also observed in Sewchar, suggesting formation of pores (Zhang et al. 2015). Similar results were reported by Saetea and Tippayawong (2013), suggesting that the rupture of the structure may contribute to degradation of the residual lignocellulosic contents of the biosolids. Knowledge of the surface properties of hydrochar is crucial because these properties determine the potential role of hydrochar in the reduction of greenhouse gas emissions, water retention, sorption of contaminants and metal(loid)s, microbial activity and community size in soil, and C sequestration (Igalavithana et al. 2018; Mukome and Parikh 2016). Insignificant physical alterations of the morphologies of hydrochar from sewage sludge and hydrochar from sewage sludge activated with potassium hydroxide were also reported by Chung et al. (2017) using SEM analysis.

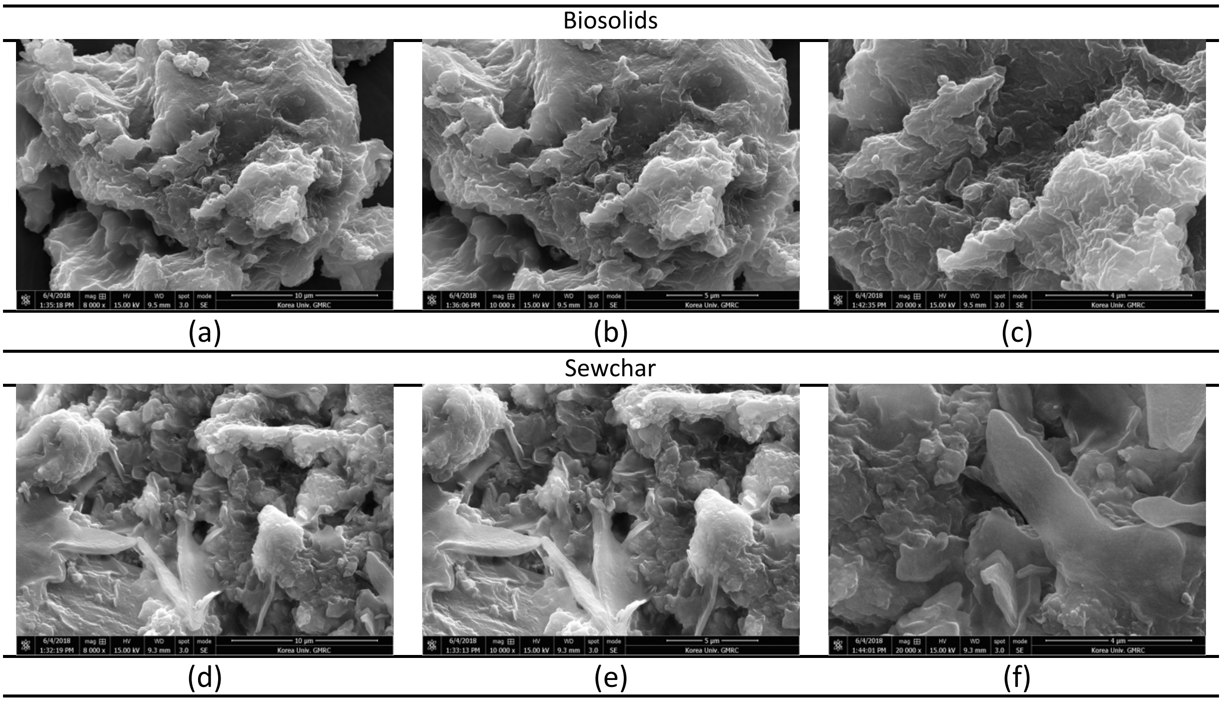


Figure 4-4 SEM images of biosolids with magnifications of 8,000x (a), 10,000x (b) and 20,000x (c) and Sewchar samples with magnifications of 8,000x (d), 10,000x (e) and 20,000x (f)

c) Surface area and pores

The isotherm of the Sewchar fell within type II according to IUPAC classification group, with a type H3 hysteresis loop (Figure 4-5). The reversible type II isotherm is characteristic of aggregates or agglomerates of non-porous or macroporous solids - porous size > 50 nm (Chang et al. 2009). Type H3 hysteresis is reported to be found usually on solids containing aggregates or agglomerates of particles forming slit-shaped pores – plates or edges particles like cubes, with non-homogeneous size and/or shape (Leofanti et al. 1998). The same classification type of isotherms was obtained by Kalderis et al. (2014) for hydrothermal carbonization of rice husk at 200 ºC and 300 ºC and 6 h residence time.

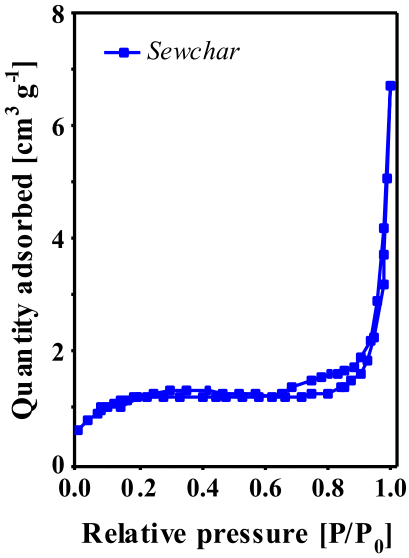


Figure 4-5 Adsorption isotherm determined by nitrogen adsorption (77K) of Sewchar

Previous studies suggest that micropores act as a habitat, protecting the microorganisms from grazers and/or desiccation (Steinbeiss et al. 2009). In addition, the ability to provide microbial habitats and soil aggregation nuclei, retain water and added nutrients, reduce denitrification, and remove contaminants are reported to be dependent on surface area (Mukome and Parikh 2016; Zhang et al. 2015). Likewise, the porosity indicates the sorption potential capacity, for example: retention of water, gases, trace elements, organics and nutrients. In addition, it provides microhabitats for microorganisms, promoting the biodiversity (Mukome and Parikh 2016). In general, high porosity in hydrochar is obtained with HTC low conversion temperature and retention time (Zhu et al. 2015).

According to the International Union of Pure and Applied Chemistry (IUPAC), in catalysis, a pore diameter < 2 nm is defined as a micropore, while pore diameters between 2 nm and 50 nm, and > 50 nm are described as mesopores and macropores, respectively. In our study, the structural properties of Sewchar were: BET surface area: 21 m$^2$ g$^{-1}$, Langmuir surface area: 30 m$^2$ g$^{-1}$, total pore volume: 0.0373 cm$^3$ g$^{-1}$ and average pore width: 7.0907 nm. Our results indicate the potential of Sewchar to retain nutrients and water available to plants. Previous studies have reported the importance of pores in the size range 2-10 nm for retaining nutrients and pores in the size range 100-10,000 nm for retaining water available to plants (Liu et al. 2015a). The average pore width of the Sewchar in our study (7.0 nm) was smaller than that (380 nm) reported by Zhang et al. (2014), who produced Sewchar at the same temperature (190 ºC) but longer residence time (6 h) than those used in our study (Zhang et al. 2014). In our study, the surface area and pore measurement of biosolids was not carried out. However, the results of Raman (orderly arranged structure) and FTIR (decrease in –OH and aliphatic groups) analysis indicated that HTC in acid pH promoted pore formation, which could be confirmed by SEM images.

### 4.4.3 Germination experiment

The application of Sewchar led to different plant growth responses, depending on the type of crop and Sewchar dose (Table 4-3).

Table 4-3 Results of analysis of variance (ANOVA) regarding the influence of Sewchar concentrations on the growth of radish, rice and bean. The dry mass of the treatments was normalized based on the dry mass of the control

| | | | Radish | | | |
|---|---|---|---|---|---|---|
| | Df[11] | Sum Sq[12] | Mean Sq[13] | F value | Effect | Pr (>F) |
| Model | 1 | 5660 | 5660 | 14.44 | -17.44±4.59 | 0.00158 |
| Error | 16 | 6274 | | | | |
| | | | Rice | | | |
| | Df | Sum Sq | Mean Sq | F value | Effect | Pr (>F) |
| Model | 1 | 26 | 25.71 | 0.095 | 1.129±3.674 | 0.762 |
| Error | 17 | 4625 | 272.04 | - | | - |
| | | | Bean | | | |
| | Df | Sum Sq | Mean Sq | F value | Effect | Pr (>F) |
| Model | 1 | 152060 | 152060 | 4.71 | -82.01±37.79 | 0.0454 |
| Error | 16 | 516606 | 32288 | - | | - |

In absolute terms, a Sewchar dose of 0.5% (10 Mg $ha^{-1}$), which is a realistic amount in agronomical field practice, had the highest dry biomass yield for bean, 37% higher than that of the control. Also in absolute terms, a Sewchar dose about three times higher than normally used in agronomical field practice, 3% (60 Mg $ha^{-1}$), showed the highest dry biomass yield for rice, 18% higher than that of the control. The data for the radish germination was the only one that fit a linear regression equation, where Y = -17.44x + 91.6, indicating a decrease in radish biomass with increasing Sewchar doses (Figure 4-6). The model followed the requirement of an Ordinary Least Square model, which is the normality of the residuals, p-value of the Shapiro-Wilk test greater than 0.05 (0.8734), and homogeneity of variance (p-value of Bartlett test greater than 0.05 – 0.5817). The EDx for radish was y = EDx/5.25, where y is the dry mass variation of radish in relation to the dry mass of the control. Conversely, because of the high variability of data for the dry mass of rice and bean, the dry mass data of these two crops was not able to be fitted using a linear regression method.

[11] Degrees of freedom

[12] Sum of squares

[13] Mean squares

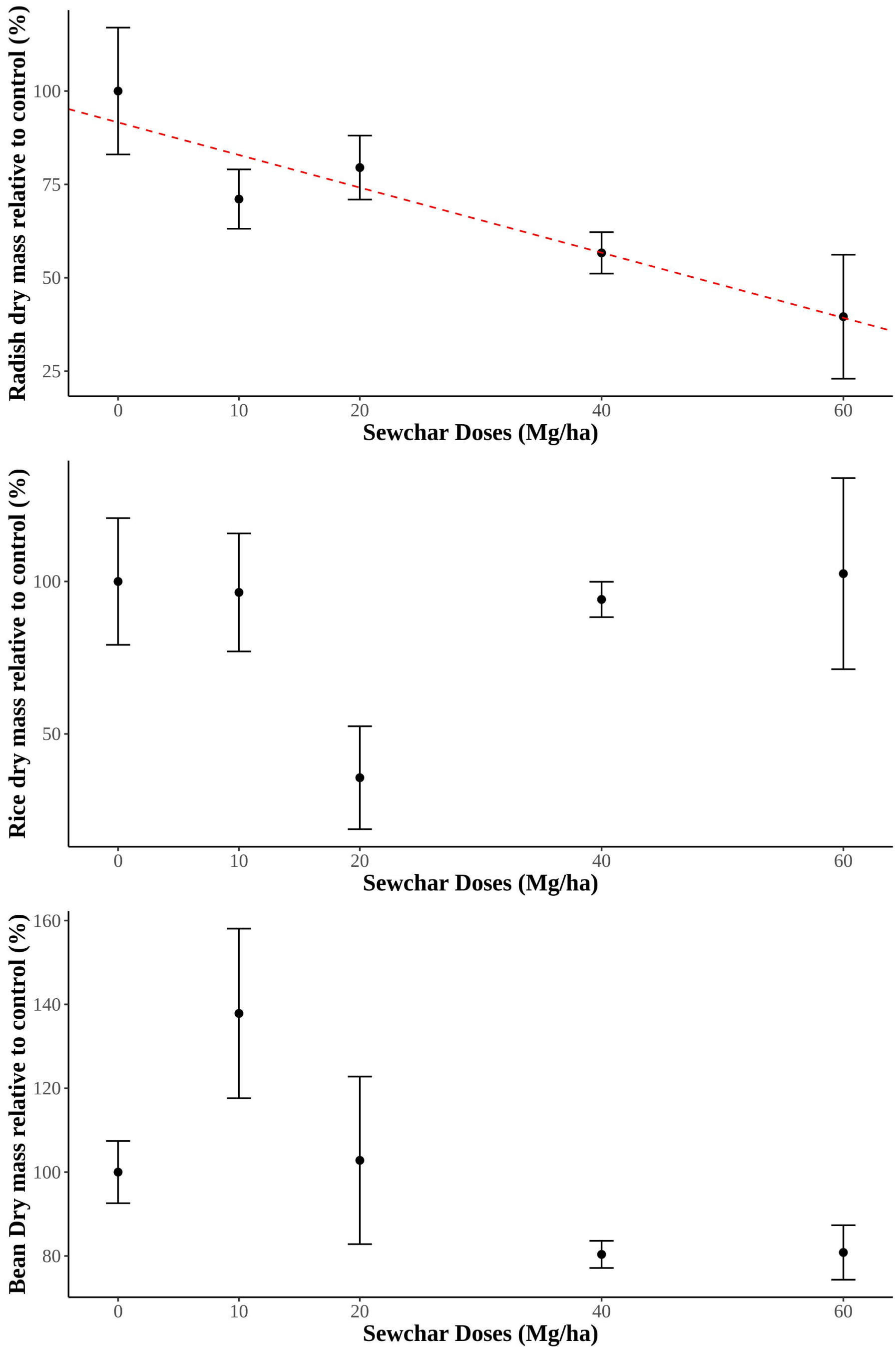


Figure 4-6 Results of the treatments with control, 0.5%, 1%, 2% and 3% Sewchar for germination and growth testing of radish, bean and rice

Better results than what we found using 10 Mg $ha^{-1}$ of Sewchar for bean growth was reported by Hossain et al. (2010) with application of the same amount of wastewater sludge biochar, where the production of cherry tomatoes was improved by 64% compared with the control (acidic chromosol). Sewage sludge biochar addition (20 to 40 Mg $ha^{-1}$) have also been reported to increase radish and common meadow-grass biomass (Mierzwa-Herstek et al. 2018; Sousa and Figueiredo 2016). Likewise, increased plant biomass and yield have also been reported with higher sewage sludge biochar doses (100 and 200 Mg $ha^{-1}$) than those used in our research (Khan et al. 2013). In other studies, the effect of chars from sewage sludge included increases in plant growth in additional different cultures, such as bean (Melo et al. 2018), corn (Faria et al. 2017), lettuce (Woldetsadik et al. 2016; Woldetsadik et al. 2018), cherry tomato (Hossain et al. 2010; Hossain et al. 2015), common meadow-grass (Mierzka-Hersztek, et al. 2018), winter rape (Breulmann et al. 2014), ryegrass (Álvarez et al. 2017; Vasilyeva and Butusov 2018), and eucalyptus (Silva et al. 2017b). However, sewage sludge chars have also been reported to have negative effects on the growth of spring barley (Breulmann et al. 2014) and cress (Breulmann et al. 2017a). As for the radish, Haag and Minami (1987) reported that this cultivar species demands a high amount of nutrients in a relatively short time. Additionally, Nunes et al. (2014) reported the best results related to the number of leaves, chlorophyll index Falker, height, tuber diameter, tuber fresh weight, and TDM of radish at values of P higher (490 and 568 kg $ha^{-1}$) than the P value of the Sewchar doses of our study (Table 4-4). Therefore, our results showed that the TDM decrease for radish with the addition of Sewchar may have occurred because Sewchar was not able to supply the radish demand for N, P, and K.

Table 4-4 NPK content of Sewchar doses used in the germination test according to the chemical analysis of Sewchar

| Sewchar doses ($Mg\ ha^{-1}$) | N | $P_2O5$ | $K_2O$ |
|---|---|---|---|
| 10 | 224 | 116 | 40 |
| 20 | 448 | 232 | 80 |
| 40 | 896 | 464 | 160 |
| 60 | 1344 | 695 | 240 |
| | N | P | K |
| 10 | 224 | 266 | 48 |
| 20 | 448 | 532 | 96 |
| 40 | 896 | 1,063 | 193 |
| 60 | 1344 | 1,595 | 289 |

Coutinho Neto et al. (2010) reported the maximum TDM efficiency for radish when plants were supplied with N and K values (360,000 and 260,000 kg $ha^{-1}$ respectively) much higher than the N and K values of the Sewchar doses used in our study (Table 4-4). In addition to the type of crop, the effects of sewage sludge chars on plant growth seem also to differ according to the dose. In our experiment, the application of Sewchar with a dose of 10 Mg $ha^{-1}$ yielded higher bean plant biomass in absolute terms. Melo et al (2018) used the same Sewchar used in this study and confirmed that a similar dose (16 Mg $ha^{-1}$) led to a TDM of bean comparable with that of the inorganic fertilizer, although the Zn and Cu availabilities in the soil were surpassed. Therefore, in our experiment, higher doses of Sewchar (40 and 60 Mg $ha^{-1}$) showed a lower TDM of bean, probably because of an excess of nutrients and trace elements, which may have been toxic for bean growth. Other studies have shown positive effects of sewage sludge biochar on plant growth when applied up to 50 Mg $ha^{-1}$ (Deenik and Cooney 2016; Faria et al. 2017; Hossain et al. 2010) and negative effects with application of greater than 50 Mg $ha^{-1}$ (Breulmann et al. 2014; Sousa and

Figueiredo 2016). Further studies are necessary to provide a world database and enable a future standard production method and application rate of Sewchar according to the specific type of crop and soil.

### 4.4.4 Survey

Table 4-5 shows the general results of the Survey. When identifying the reasons for using their current fertilizer, 73% of the farmers tended to think first of the agronomic benefits, such as better productivity and soil fertility. A total of 27% of the respondents named the cost of the fertilizer, and none of them mentioned the environmental benefits. However, when the farmers were directly questioned about the importance of the agronomic, environmental, and economic criteria for choosing a fertilizer, most of them tended to select the environmental criteria as the most important. Analogous results were described by Krogmann et al. (2001), where in an interview with fruit and vegetable farmers from New Jersey concerning application of sewage sludge in agriculture, most of the farmers tended to think foremost of their land and their crop when discussing the benefits and drawbacks of the application of sewage sludge in agriculture, while the environmental benefits and risks were only discussed when the farmers were directly questioned about them. Therefore, educational strategies about Sewchar should primarily address the farmers' direct interests, such as productivity and soil fertility first; afterwards, environmental matters can be discussed.

With respect to the knowledge of the source of Sewchar, 56% of the respondents answered that they know that sewage sludge is made of human excrement, but most of them (56%) have never heard of hydrothermal carbonization. Nevertheless, most of the respondents (51%) would use Sewchar as a soil amendment and for both edible and inedible plants. Similar results have been reported by Zapparoli (n.d), where 87 % of the asked rural producers in Paraná would use biosolids as a soil amendment. On the contrary, our results also showed that many of the farmers (48 %) would use Sewchar neither for commercial nor for personal consumption crops. This result shows uncertainty from the farmers, suggesting that complementary research would be very important to identify the consumer preferences related to crops cultivated on land where Sewchar has been applied. Some authors showed that trust is a very important factor for consumers' support of a land application method (Rodriguez and Peterson 1996; Zimmerman et al. 1991), being more important than level of knowledge (Rodriguez and Peterson 1996). Trust is very important to consider, especially in situations where institutions are not considered reliable. Giogliotti (1991), for example, showed that the interviewers did not considered sewage sludge management entities to be very trustworthy. Reliability with respect to wastewater treatment plants is very important because the production of hydrochar from sewage sludge byproducts requires a monitored supply network to ensure a sustainable managed feedstock to address the risks related to agricultural recycling of sewage sludge byproducts.

Table 4-5 Results of the questionnaire given to the rural producers

| | | | | | |
|---|---|---|---|---|---|
| General characteristics of the rural producers | | | | | |
| 1.Gender | | Male | | Female | |
| | | 51% | | 49% | |
| 2.Age | 18-25 | 26-35 | 36-45 | 46-55 | >56 |
| | 4% | 11% | 24% | 33% | 29% |
| 3.Education | None | Primary | Secondary | FSTertiary[14] | SSTertiary[15] |
| | 5% | 40% | 38% | 4% | 13% |
| State of the art of the soil amendment currently used | | | | | |
| 4.Type of fertilizer | | Organic | Inorganic | | Both |
| | | 42% | 20% | | 38% |
| 5.Reason for using current fertilizer | | Agronomic | | Economic | |
| | | 73% | | 27% | |
| 6.Commercialization of the production | | Commercialized | | Own consume | |
| | | 55% | | 45% | |
| Living standard of the rural producers | | | | | |
| 7.Land size | <5ha | 5-20 ha | | 21-50 ha | > 50 ha |
| | 8% | 32% | | 51% | 9% |
| 8.Belong to settlement | | Yes | | No | |
| | | 54% | | 46% | |
| 9.Receive social assistance | | Yes | | No | |
| | | 33% | | 67% | |
| 10.Access to capacitation | | Yes | | No | |
| | | 89% | | 11% | |
| 11.Access to credit | | Yes | | No | |
| | | 65% | | 35% | |
| Criteria for choosing a fertilizer | | | | | |
| Agronomic | | | | | |
| 12.Productivity | 5 | 4 | 3 | 2 | 1 |
| | 54% | 31% | 15% | - | - |
| 13.Fertility | 59% | 28% | 7% | 6% | |
| Economic | | | | | |
| 14.Fertilizer price | 5 | 4 | 3 | 2 | 1 |
| | 41% | 19% | 20% | 4% | 17% |
| 15.Freight price | 41% | 15% | 22% | 7% | 15% |
| Environmental | | | | | |
| | 5 | 4 | 3 | 2 | 1 |
| 16.Residue as feedstock | 74% | 19% | 7% | - | - |
| 17.Local production | 89% | 7% | 4% | - | - |
| 18.Reduction of GHG | 81% | 8% | 6% | 2% | 4% |
| Knowledge and acceptance of Sewchar | | | | | |
| 19.Knowledge about the Sewchar source | | Yes | | No | |
| | | 56% | | 44% | |
| | | Yes | | No | |
| 20.Heard of sewage sludge chars | | 44% | | 56% | |
| 21.Would use Sewchar | | Yes | | No | Maybe |
| | | 51% | | 35% | 15% |
| 22.Type of crop | | Edible and inedible | | Inedible | None |
| | | 51% | | 15% | 35% |
| 23. Purpose of use | | Only commercialize crops | | Commercialize and own consumption | None |
| | | 46% | | 6% | 48% |
| 24.Why would not use | | Unfamiliarity | | Disgust | Disinformation |
| | | 12% | | 39% | 49% |

[14] First stage of tertiary education
[15] Second stage of tertiary education

For the PCA, the set of variables was updated to determine the most representative variables for dimension reduction. The results of the PCA showed two groups of Data respectively for the respondents who would use Sewchar as a soil amendment (left side of Supplementary Figure 6-2 in Supplementary Information 2) and for respondents who would not use Sewchar as a soil amendment (right side of Supplementary Figure 6-2 in Supplementary Information 2). The two first components (accumulated) retained 99% of explained variance. The first principal component of the PCA showed that age was the most determinant variable for a positive answer related to the use of Sewchar as a soil amendment.

The exploratory data analysis showed that respondents younger than 42 years old were more prone to use Sewchar as a soil amendment. Furthermore, according to the exploratory data analysis, it could be inferred that as the education level increased, the more likely the farmers were to use Sewchar as a soil amendment (Figure 4-7). These results show that education of the farmers plays an essential role in the choice of a fertilizer. Therefore, investments in knowledge transfer are of crucial importance.

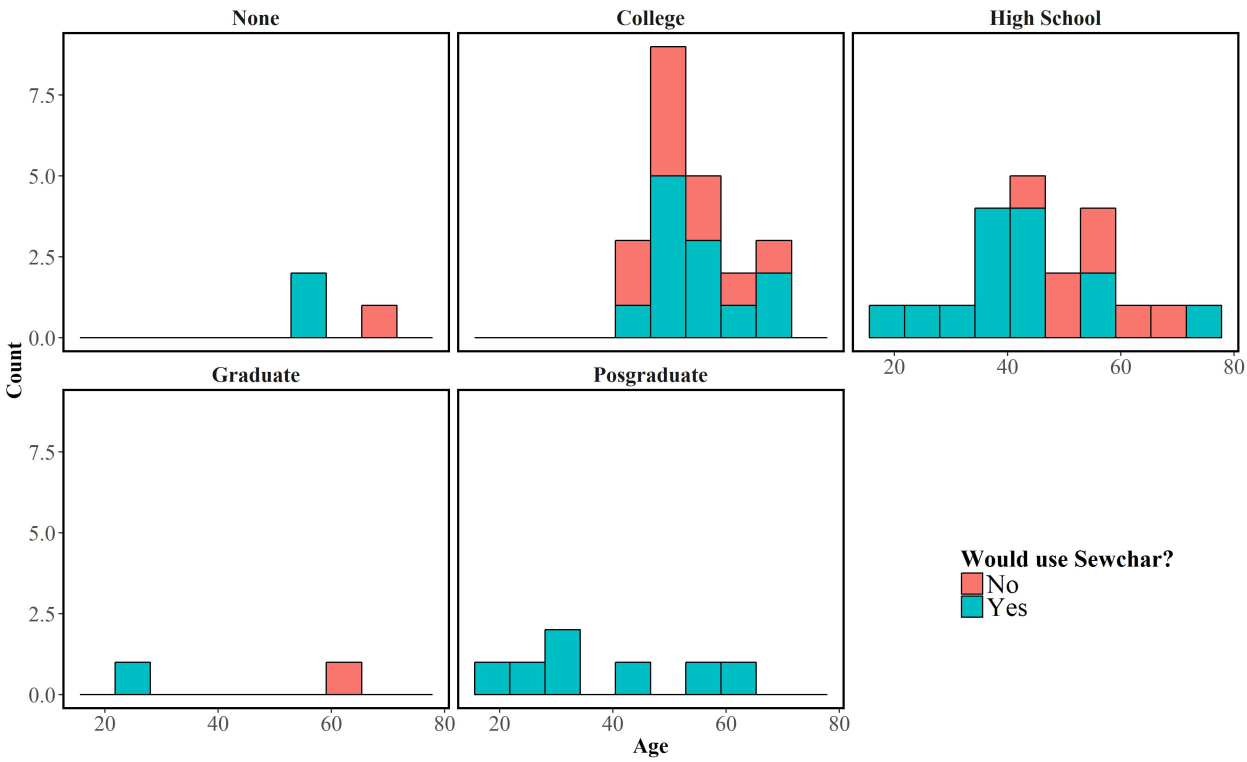


Figure 4-7 Results of the exploratory data analysis (EDA) concerning the relationship between education and age of the respondents of the Survey, who would use or not use Sewchar as a soil amendment

The second principal component of the PCA showed that the variables freight and fertilizer prices were the most determinant variables related to not using Sewchar as a soil amendment. The respondents who would not use Sewchar and attributed the highest importance to fertilizer price, also attributed the highest value of importance to freight price (r: 0.89, p-value $< 0.0001$). The environmental and the agronomical criteria are correlated and considered as very important criteria by the farmers, who would not use Sewchar. The farmers who would not use Sewchar as a soil amendment and considered productivity very important criteria for choosing a fertilizer also considered fertility of the soil (r: 0.52, p-value $< 0.05$) and the use of residues as feedstock (r: 0.61, p-value < 0.01) as very important. Likewise, the importance of soil fertility was also correlated with the importance of the local production of fertilizer (r: 0.50, p-value < 0.05). Environmental criteria were also considered very important criteria by the farmers for choosing a fertilizer. The farmers who would not use Sewchar as a soil amendment and elected the local production of fertilizer as very important, also attributed the reduction of greenhouse gas (GHG) emissions (r: 0.84, p-value: < 0.0001) and residue as feedstock as very important criteria (r: 0.71, p-value: < 0.0001).

The respondents who would use Sewchar attributed similar importance to the economic and agronomic criteria with respect to choosing a fertilizer as a soil amendment as did the respondents who would not use Sewchar. The respondents who would use Sewchar and credited the highest value of importance to fertilizer price, also attributed the highest value of importance to freight price (r: 0.71, p-value < 0.05). As for the agronomic criteria, the respondents attributed the highest value of importance likewise to soil fertility of the soil and productivity (r: 0.59 p-value < 0.01). The economic, environmental, and agronomic criteria were elected as very important by the farmers who would not use Sewchar as a soil amendment, although these criteria are fulfilled by Sewchar. Thinking of economic criteria when choosing a fertilizer is very understandable because the farmers must feed their families with their work. Sewchar uses waste biomass as feedstock, which might contribute to the cheaper price of Sewchar compared with mineral fertilizers. This advantage of Sewchar may arouse the interest of farmers who indicated that the economic criteria are very important when choosing a fertilizer.

From the environmental perspective, Sewchar may reduce fertilizer requirements and stabilize organic carbon, providing a sustainable way to reduce and treat biosolids. HTC Sewchars have been reported to be more appropriate for improving soils' nutrients, while pyrolysis Sewchars are superior for increase long-term carbon sequestration (Breulmann et al. 2017b). With respect to GHG emissions, pyrolysis Sewchar has been reported to reduce $N_2O$ emissions (Khan et al. 2013; van Zwieten et al. 2010). These results indicate that Sewchar is a potential favorable alternative for reducing the concentrations of GHGs, considering that approximately 60% of the global anthropogenic $N_2O$ emissions are derived from agriculture because of the intensive use of nitrogen fertilizer (Millar et al. 2018).

As for the agronomic criteria for choosing a fertilizer, Sewchar also can promote the yield of various crops, comparable with mineral fertilizer (Deenik and Cooney 2016; Faria et al. 2017; Melo et al. 2018). Moreover, it has been reported that the addition of chemical fertilizers does not contribute to the maintenance of crop yields into a third consecutive growing season (Kumarathilaka et al. 2016). The use of renewable and local resources as input for Sewchar systems might also contribute to the economic development of local impoverished communities. Currently, smallholders in developing countries rely on mineral fertilizer subsidy programs (Kotschi 2015). In summary, the combination of the economic, socio-environmental, and agronomical outcomes from the use of sewage sludge as a soil amendment is expected to lead to the sustainable development of the agriculture and therefore meet the criteria for choosing a fertilizer of farmers who would not use Sewchar as a soil amendment.

The general results also showed that, among the reasons why the respondents would not use Sewchar as a soil amendment, 49% of the total answers were because of disinformation, followed by disgust (39%) and unfamiliarity (12%). One alternative would be providing information to the farmers about the economic, agronomic, and environmental advantages of Sewchar as a soil amendment. However, Chess (1998) explains that offering information does not inevitably alter perception or behavior. Still, the problem with the 'unknowns' of Sewchar could be solved through confirmation of the advantages of Sewchar in further studies. One example is a mobile game created by the Singapore National Water Agency, which translated technical information about the use of treated wastewater into simple language to reduce negative public perceptions (Koncagül et al. 2017). Additional alternatives are the exemption of the agricultural sewage sludge spreading from the activities subjected to strict liability under the Environmental Liability Directive (European Union 2004). Furthermore, the creation of insurance fund systems similar to the liability fund of lower Austria and Germany (European Communities 2001) or the fund suggested by Goldfarb et al. (1999) for the United States, which would compensate for any loss of profits, damages, or other costs related to the land application of Sewchar.

## 4.5 Conclusions

Hydrothermal carbonization of sewage sludge presents the potential alternative of using Sewchar as a soil amendment, which is a sustainable option for minimizing and treating waste and reducing the costly transport of wet biomass. The results of this study showed that HTC affected the physicochemical properties of biosolids, such as promoting pore structure development, as demonstrated by SEM analysis. Surface of Sewchar exhibited higher O-containing functional groups, as well as aliphatic/aromatic C than biosolids. These results demonstrate higher Sewchar surface activity, with higher potential of water and nutrient retention and cation exchange capacity than biosolids. The chemical analysis results also showed trace elements threshold values according to the limits for use in agriculture. Additionally, detailed research on the migration mechanism of PAHs is crucial for drawing up a legal framework regarding PAH threshold values before Sewchar can be used in agrosystems. The results of the germination experiment indicate that Sewchar, with a reasonable field application rate, has good potential as a soil amendment. However, crops demanding different amounts of nutrients showed different results with respect to the effect of Sewchar dose on plant growth. The survey showed results confirming that Sewchar is likely to be accepted by farmers as a soil amendment and that it fulfills the farmers' most important criteria for choosing a fertilizer. The PCA results showed that younger farmers are more likely to use Sewchar as a soil amendment and that economic criteria, such as fertilizer and freight prices, were the most important criteria for not using Sewchar as a soil amendment. Field studies over longer time periods are likewise necessary to elucidate the interactions between Sewchar and soil properties on plant growth and the safe use of Sewchar in agriculture. Standardization of the HTC process for the production of hydrochar (e.g., Sewchar) is required. An international database would allow the creation of a control mechanism to accurately predict the longevity and durability of Sewchar on the yield of individual crops and soil types.

## 4.6 Aknowledgment

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# 5 Summarizing discussion, conclusions, and outlook

This research investigated an innovative soil amendment to address the potential of recycling a renewable and theoretically unlimited source (sewage sludge/biosolids) and help moving toward the enrichment of nutrients in the soil, nutrient supply to plants, and improvement of soil properties. This chapter presents the relevant results related to the objectives of this study and the interlinkage among the chapters, the conclusions, and the outlook.

This thesis investigated the effect of Sewchar as a renewable soil amendment. Particularly, the effect of Sewchar on (a) the toxicity of Sewchar and its process water filtrate on the lethality respectively to earthworms and shrimps was assessed. In addition, the potential of Sewchar use as a soil amendment (b) was evaluated through pot trials with beans and germination tests with three different types of plants (bean, radish and rice). The effect of the HTC on (c) the physical and chemical properties of biosolids was also investigated. Finally, (d) the farmers' acceptability of using Sewchar as a soil amendment and their criteria for choosing a fertilizer were explored through a survey. The results of the individual studies of this work can be summarized as follows:

## 5.1 Main research results

In chapter 2 the results of the acute toxicity tests showed no median lethal concentration of Sewchar to earthworms (*Eisenia fetida*) within the studied concentration range (up to 80 Mg ha$^{-1}$). It was indicated the favorable potential use of Sewchar as a soil amendment. As to the Sewchar process water filtrate, the lethality of shrimps increased with Sewchar's process water filtrate additions and decreased with its pH adjustment. It was evidenced that the pH of the Sewchar's process water filtrate play a decisive role on the lethality of shrimps. Therefore, the pH of the Sewchar's process water might be adjusted before its disposal to reduce mortality of freshwater and marine organisms. Still in chapter 2 the results of the chemical analyses showed that HTC promoted a relative enrichment of some macro- and micronutrient content in Sewchar. In addition, the trace elements in Sewchar were within the Brazilian threshold values for application in agriculture.

Pot experiments were carried out in chapter 3 to confirm the potential use of Sewchar as a soil amendment as indicated in the results of chapter 2. The chemical analyses of the soil used in the pot experiment showed that Sewchar met the bean nutrient demand. The pot experiment with two harvests with respect to effects of different application rates of Sewchar on soil properties and plant responses to bean growth revealed that Sewchar application rates (4, 8, 16 and 32 Mg ha$^{-1}$) fertilized with 135 mg kg$^{-1}$ $P_2O_5$ enriched nutrients in the soil (Ca, Cu, Fe, P and Zn), increased the soil fertility indicators (nitrate, ammonium, total N, total organic carbon and hot water extractable carbon), improved soil properties (CEC and WHC), and supplied nutrients to beans (Ca, P, and Zn). The results of this chapter also demonstrated that Sewchar applied in a habitual field application rate (16 Mg ha$^{-1}$) had a total dry matter equivalent to that of the mineral fertilizer in both crop harvests. Especially, the effect of Sewchar showed better plant response in the second crop harvest, suggesting an optimal residual effect of the Sewchar dose 16 Mg $ha^{-1}$ as a promising sustainable alternative for partly replacing mineral fertilizers for bean growth.

The chapter 4 investigated whether the results of chapter 3 were also applicable to other crop plants and other Sewchar doses. The findings of chapter 4 showed that Sewchar had different plant response depending on the type of crop and on the Sewchar doses. In absolute terms it could be confirmed that a realistic Sewchar dose in agronomical field practice, 10 Mg $ha^{-1}$, have the highest dry biomass yield for bean. For rice, a dose about 3 times higher than usually used in agronomical field practice (60 Mg $ha^{-1}$) had the highest dry biomass yield. However, no tendency between the dry mass data relative to the Sewchar doses of rice and bean was found. For radish, there was a decrease of biomass with increasing Sewchar doses.

Further studies in chapter 4 explored physical and further chemical analysis of Sewchar to understand its properties for agricultural use and to examine its potential contaminants. The Sewchar chemical analysis showed that Sewchar has plant nutrients. However, the value of some PAHs contents (benzo(a)anthracene, benzo(a)pyrene, and benzo(k)fluoranthene) in Sewchar exceeded the Brazilian threshold values for the application of biosolids derivative products in agriculture. These results require detailed research with respect the safe use of Sewchar as a soil amendment. The positive effects of Sewchar as a soil amendment, such as enrichment of soil nutrients, cation exchange capacity, and water holding capacity shown in chapter 3 could be explained through the Sewchar physicochemical analysis performed in chapter 4.

The evidence of chemical functional groups by FTIR in chapter 4, such as carboxyl and hydroxyl in Sewchar; the surface area and porosity of Sewchar shown by BET and SEM explains the effect of Sewchar as enrichment of nutrients and trace elements due to the Sewchar adsorption capacity (Dieguez-Alonso et al. 2018; Liu et al. 2015b; Zhang et al. 2015). The oxygen-contained functional groups in Sewchar observed by XPS and FTIR analyses could explain the positive effect of Sewchar on CEC of the bean growth described in chapter 3. The ability of Sewchar to retain water reported in chapter 3 could justified due to its porosity explored in chapter 4 (Liu et al. 2015a) Furthermore, the aromatic and recalcitrant structure of Sewchar (Raman) indicates future studies regarding its potential for C sequestration (Zhang et al. 2015).

Additional results of the survey in chapter 4 showed that the economic, environmental and agronomic criteria were elected as very important by the farmers who would not use Sewchar as a soil amendment. However, the most important criteria for choosing a fertilizer by the farmers who would not use Sewchar as a soil amendment were the economic criteria, such as fertilizer and freight prices. Contrariwise, younger farmers had higher education and were more prone to use Sewchar as a soil amendment. In general, Sewchar fulfills the farmer’s most important criteria for choosing a fertilizer. Figure 5-1 shows the theme of each chapter, linking the main results among the chapters and presents questions to be answered in future researches.

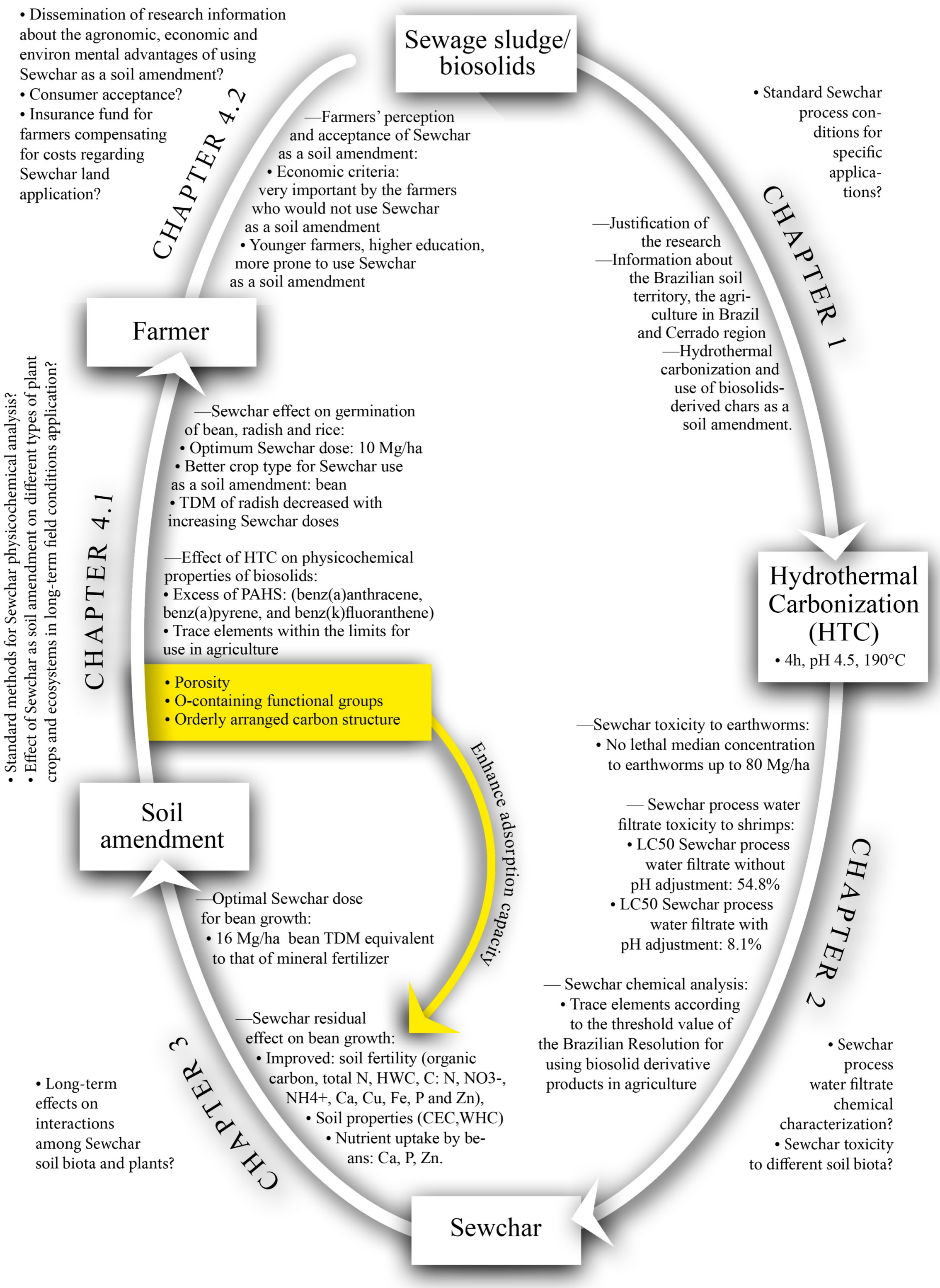


Figure 5-1Visualization of interlinkage among the chapters. Inner circle: Theme of each chapter and main results. Outside circle: questions for future researches.

## 5.2 Conclusions and outlook

The results of the present study lead to the conclusion that biosolids recycled through HTC (190°C, pH 4.5 and 4 h residence time) have the potential to be used as a soil amendment. Using Sewchar in a realistic field dose application rate is not toxic to earthworms and caused a better plant growth of bean cultivation. Sewchar's physicochemical properties, such as trace elements threshold values according to the limits for use in agriculture, porosity, O-containing functional groups and orderly arranged carbon structures explained the positive effect of Sewchar on bean growth, such as enrichment of soil nutrients, nutrient uptake by beans (except for K), cation exchange capacity, and water holding capacity. These results elucidated the higher TDM of bean due to the residual effect of Sewchar compared to mineral fertilizer. Therefore, Sewchar has potential to be used as a renewable soil amendment to partially replace mineral fertilizer. However, correction of the pH of the Sewchar process water filtrate is indicated before its disposal in fresh or marine waters. Attention should also be payed to the PAHs in the Sewchar. Broad knowledge transfer to the farmers about the use of Sewchar as a soil amendment is particularly important to improve their understanding and help their decision for the use of Sewchar in agriculture.

In future, further studies about the characterization and land application of Sewchar produced under different process conditions could broad our understanding about the complex interaction and the long-term effect between Sewchar and soil properties. Detailed research on the migration mechanism of PAHs is crucial for drawing up a legal framework regarding PAH threshold values and respective standard methods of analysis. Supplementary toxicity tests using Sewchar and its process water filtrate over the long-term to different organisms are needed to identify its toxic effects to the biota. Likewise, chemical characterization of the Sewchar process water filtrate may be carried out to identify and avoid possible contaminants to receiving waters. It is also recommended the verification of the potential use of Sewchar as a soil amendment exposed in this study in field trials exploring the long-term effects on different plant crops and ecosystems. The dissemination of research information about the economic, agronomic and environmental advantages of Sewchar as soil amendment must be provided as knowledge transfer to the farmers to subside their decision for using Sewchar in agriculture. Complementary research about the consumer preference with respect to crops cultivated with application of Sewchar is also important to investigate the social acceptance of Sewchar before its commercial use as a soil amendment. These studies could help to predict the Sewchar agronomical efficiency, cost/benefit compared with mineral fertilizer, social acceptance, and environmentally safe application. All those studies could feed an international database and support the standardization of parameters regarding methods for Sewchar physicochemical analysis and process conditions according to individual applications. Based on this database a discussion about the creation of an insurance fund to compensate for costs regarded to the land application of Sewchar could be initiated.

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# 6 Appendix

**Supplementary Information to**

**Plant and soil responses to hydrothermally converted sewage sludge (Sewchar)**

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**Supplementary Information 1**

**Methodological details: Sewchar chemical analysis**

The samples of biosolids and Sewchar were homogenized, dried at 65 ºC for 16 h, milled and passed through a sieve with a mesh of 0.5 mm. The pH was determined on a (1:5) Sewchar:0.01 mol $L^{-1}$ $CaCl_2$ suspension and measured with a pH electrode. The samples were oxidized with 6 ml of nitric–perchloric acid, and 20 ml of distilled water. The chemical analysis was carried out with a mixture of 0.25 ml of the oxidized samples and 4.75 ml of distilled water. The Phosphorus (P) was determined through the ascorbic acid method, where the molybdenum blue was determined spectrophotometrically at a wavelength of 660 nm (Spectronic 20, Bausch and Lomb). Potassium (K) was determined via flame photometry—SOP Flame photometer Corning 400. Copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) were determined via atomic absorption spectrophotometry (AAS) (PerkinElmer AAnalyst 100). After the addition of 4.75 ml of lanthanum at 0.22% calcium (Ca) and magnesium (Mg) were also determined via atomic absorption spectrophotometry. The chemical analysis was carried out according to the methodology of Embrapa (2009). The samples of the biosolids and Sewchar samples were digested in a microwave system (Milestone MLS 1200 Mega, Germany) using 37% HCl and 65% $HNO_3$ in a 1:3 ratio and the concentration of the trace elements, such as arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and molybdenum (Mo) analyzed via inductively coupled plasma atomic emission spectrometer (Horiba Jobin-Yvon, Unterhaching, Germany) according to the US EPA Method 3051A (2007). The measurement of mercury (Hg) was performed via AAS, using the mercury direct analyzer DMA 80 (MLS GmbH, Leutkirch, Germany). Details about the biosolids and Sewchar chemical analyses are described at Melo et al. (2017).

**Methodological details: Pot experiments**

Phaseolus beans (*Phaseolus vulgaris*, var. "Jalo precoce") was grown for being a typical grain of Brazil of short life cycle (from 65 to 100 days). Commercial plastic pots 17 cm height x 22 cm diameter containing 5 kg dry matter of the soil plus the amendments were used. Sewchar was previously mixed to the soil to get a homogeneous mixing before placing the mixtures to the pots. The perforated bottom of the pots was sealed with fine gauze to hinder the loss of particulate matter. The trials were held under natural long-day tropical weather conditions of lighting and temperature. The average temperature during the study was 31°C varying from 24 to 38 °C. The pots were watered manually 4 to 7 times a week according to plant requirement up to the field water capacity throughout the duration of the pot trial. Sowing was done with 5 seeds per pot. If necessary, after germination plants were thinned to three plants per pot. The incubation period after addition of the Sewchar was 60 days. For the first crop harvest, mineral fertilizer doses corresponded to 0.33 g urea, 2.49 g thermophosphate and 0.48 g potassium chloride or 30 mg N, and 90 mg $P_2O_5$ and 60 mg $K_2O$ $kg^{-1}$ respectively per pot. The doses were calculated and adapted to pots based on the soil chemical analysis and the fertilization recommendations for bean crop (de Sousa and Lobato 2004, Embrapa 2006). The 'Thermophosphate' used as part of the mineral fertilization is a phosphate fertilizer produced by fusing phosphate rock with magnesium silicate minerals, which is reported to be effective on some tropical soils (McCune 1924). After the first crop harvest the level of P, K, Ca and Mg in the soil samples of some Sewchar treatments were below the optimal needs for bean growth in Cerrado soil. However, for the second crop harvest (T2) just one variable was changed. Therefore, only P was added in the soil samples because P deficiency is the major limiting factor for crop production in highly weathered Oxisols (Fageria et al. 1988) like large expanses of Latin American soils (McCune 1924). For the second crop harvest, thermophosphate (Yoorin - 18% $P_2O_5$, 18% Ca, 7% Mg, 0.1% B, 0.05% Cu, 0.3% Mn, 10% Si and 0.55% Zn) was added to all the treatments from the first crop harvest.

**Methodological details: Soil chemical analysis**

Roots and other plant remnants were removed and the soil was sampled at the end of the first and the second crop harvests in a random manner. Soil pH was potentiometically measured in a 1:2,5 soil: solution ratio 0.01 mol $L^{-1}$ $CaCl_2$, using air-dried soil samples. Potential acidity (hydrogen + aluminum) was estimated by the Shoemaker-McLean-Pratt (SMP) buffer method (Shoemaker et al. 1961). The CEC was calculated by the sum of exchangeable cations. Plant available nutrients, such as P, K, Cu, Fe, Mn and Zn were extracted by Mehlich I double acid procedure (0.025 N $H_2SO_4$ + 0.05 N HCl). Afterwards, Cu, Fe, Mn, Zn were determined by atomic absorption spectrophotometry (Perkin Elmer AAnalyst 100), while K was measured by flame photometry (SOP Flame photometer Corning 400). The P was measured by spectrophotometry at 660 nm wave-length (Spectronic 20 Bausch & Lomb) after the addition of 10 ml of ammonium molybdate solution (4%) and 0.2g of ascorbic acid. The Ca, Mg and Al were extracted by potassium chloride 1N. The Ca, Mg were also measured by atomic absorption spectrophotometry, after the addition of 4.75 ml of oxide lanthanum at 0.22%. The percent Base Saturation was calculated from the sum of cations (K, Mg, Ca, Na) divided by the CEC. The water retention characteristics of the samples (WHC) were determined using the method WHC60, which measures the maximum volume amount of retained water by the samples after saturation and draining, when the samples are subjected to a 60.0 cm column of water (6kPa) The soil analyses were carried out according to Embrapa (2009) and Embrapa (1997). The amount of total N and organic carbon in the soil samples was determined by C/H/N analyzer (Vario EL III, Elementar, Hanau, Germany). For mineral nitrogen, samples were extracted with 1 M KCl (1:4; w/v) by shaking horizontally for 1.5 h and then filtered (Schleicher & Schuell 595 ½, Dassel, Germany). The extracts were analyzed for ammonium -N (NH4+ - N) and nitrate - N (NO3- - N) immediately after filtration with a flow injection analyzer (FIAstar 5000, Foss GmbH, Rellingen, Germany). The hot water extractions (HWC) were performed to determine the samples' contents of readily decomposable C and N compounds. Dry samples of 10 g were boiled in 50 ml of deionized water for 1 h under a reflux condenser. After cooling to room temperature, 0.1 ml of 1 M $MgSO_4$ was added to each suspension, which was then centrifuged for 10 min at 2000 rpm to obtain a clear extract. The extracts were filtered using RC 25 Minisart single–use syringe membrane filter units with a 0.45 µm pore size (Sartorius AG, Göttingen, Germany). All extracts were analyzed for their total C and N concentrations (HWC and HWN) using an elemental analyzer for aqueous samples (Micro N/C and Multi N/C, Analytik Jena, Jena, Germany). At the end of each crop harvest the results of the chemical analysis of the soil samples and tissue bean were compared with the sufficiency threshold of nutrients for Brazilian savannah (Cerrado) soil and bean tissue, according to de Sousa and Lobato (2004). The values above the range are supposed not likely increase crop growth and could even be toxic to the crop. While values below the range can indicate a nutrient deficiency that is not yet visible in the plant (Table 6-1).

Table 6-1 Tissue and soil sufficiency threshold for bean in Brazilian savannah (Cerrado) soil

| Tissue sufficiency threshold | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| N | P | K | Ca | Mg | Fe | Mn | Zn | Cu |
| g kg$^{-1}$ | | | | | mg kg$^{-1}$ | | | |
| 30-50 | 2.5-4.0 | 20-25 | 10-25 | 2.5-5.0 | 100 – 450 | 30-300 | 20-100 | 10 – 20 |

| Soil sufficiency threshold | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| P | K | CEC | Ca | Mg | Fe | Mn | Zn | Cu |
| mg dm$^{-3}$ | | cmol$_c$ dm$^3$ | | | mg dm$^{-3}$ | | | |
| 5.1-8.0 | 51-80 | 9.1-13.5 | 0.1-0.5 | 0.5-2.0 | - | 2.0-5.0 | 1.1-1.6 | 0.5-0.8 |

Data from de Sousa and Lobato (2004)

**Methodological details: Plant tissue chemical analysis**

At the end of each plant growth period shoots were clipped off, dried (60°C) and weighed. Afterwards, the plant materials were analyzed for N by Kjeldahl method (Bremmer 1965) after acid digestion with sulfuric acid and copper sulfate in the presence of a catalyst. For the other analyses the samples were oxidized (digested) with nitric-perchloric acid, in a 2:1 acid nitric : acid perchloric ratio and Cu, Fe, Mn and Zn were determined by atomic absorption spectrophotometry (Perkin Elmer AAnalyst 100). The P was measured by spectrophotometry at 660 nm wave-length (Spectronic 20 Bausch & Lomb) and K was measured by flame photometry (SOP Flame photometer Corning 400). After the addition of lanthanum at 0.22% to the oxidized samples, Ca and Mg were also measured by atomic absorption spectrophotometry. Roots were also removed from soil by hand, washed, dried (80°C) and weighed.

Table 6-2 p-values of the Student's t-test to compare the total dry matter and plant elemental concentration of the treatments between the two crop harvests

| | Control | 4 Mg ha$^{-1}$ Sewchar | 8 Mg ha$^{-1}$ Sewchar | 16 Mg ha$^{-1}$ Sewchar | 32 Mg ha$^{-1}$ Sewchar | Mineral fertilizer |
|---|---|---|---|---|---|---|
| Ca p-value | 0.242 | 0.765 | 0.562 | **0.004** | **0.004** | 0.149 |
| Cu p-value | **0.006** | **0.005** | **0.025** | **0.010** | **0.004** | **0.006** |
| Fe p-value | **0.022** | 0.054 | **0.002** | **0.027** | **0.007** | 0.051 |
| K p-value | 0.145 | **0.020** | 0.336 | 0.367 | 0.870 | 0.262 |
| Mg p-value | 0.055 | **0.048** | 0.058 | 0.067 | 0.060 | **0.020** |
| Mn p-value | 0.792 | **0.015** | **0.001** | **0.003** | **0.001** | 0.104 |
| N p-value | 0.112 | **0.001** | **0.003** | **0.001** | 0.082 | **0.000** |
| P p-value | **0.010** | **0.011** | 0.051 | **0.023** | **0.016** | **0.023** |
| TDM p-value | 0.279 | **0.007** | 0.156 | **0.036** | 0.080 | 0.220 |
| Zn p-value | 0.252 | 0.834 | 0.327 | 0.099 | 0.110 | **0.002** |

Table 6-3 Results of the r and p-values of the Pearson's correlation coefficient used to evaluate the linear correlation between increasing Sewchar application rates and the relative response to nutrient uptake from soil in the first and second crop harvests

| | First crop harvest | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ca | Cu | Fe | K | Mg | Mn | N | P | Zn |
| r | -0.36 | 0.39 | -0.17 | **-0.74** | **0.7** | **0.73** | **0.63** | **0.45** | **0.62** |
| p-value | 0.11 | 0.09 | 0.47 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 |
| | Second crop harvest | | | | | | | | |
| | Ca | Cu | Fe | K | Mg | Mn | N | P | Zn |
| r | **0.58** | 0.13 | -0.06 | -0.10 | 0.32 | 0.21 | -0.02 | **0.77** | **0.7** |
| p-value | 0.00 | 0.58 | 0.79 | 0.66 | 0.17 | 0.38 | 0.94 | 0.00 | 0.00 |

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**Supplementary Information to**

# Management of biosolids-derived hydrochar (Sewchar): effect on plant germination, and farmers' acceptance

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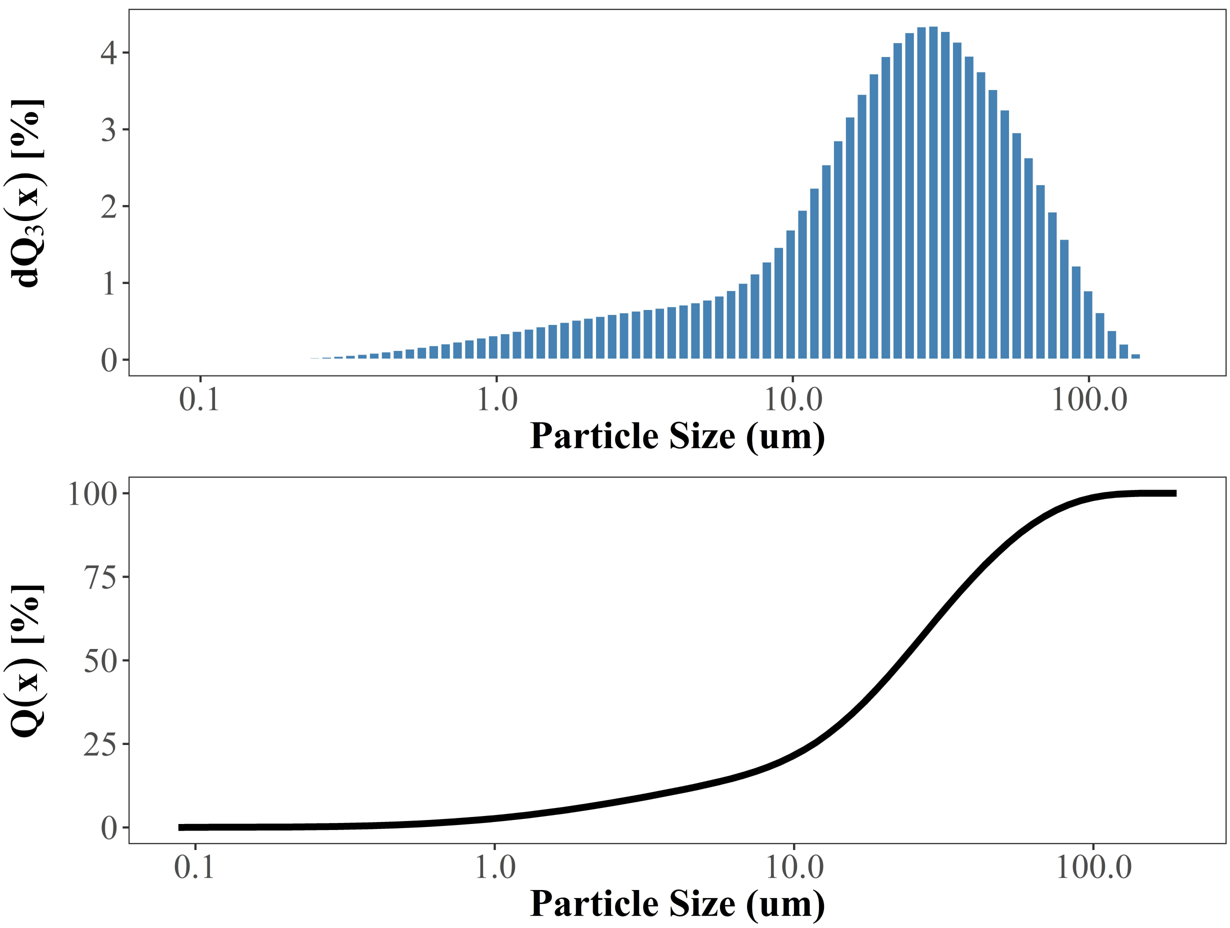
**Supplementary Information 2**

Table 6-4 Questionnaire given to the farmers

| |
|---|
| 1. What is your name? |
| 2. What is your gender? |
| 3. What is the date of your birth? |
| 4. What is the highest educational qualification you have acquired? |
| 5. What is the type of fertilizer you currently use? |
| 6. What is the reason for using the type of fertilizer that you currently use? |
| 7. Do you commercialize the crops your growth in your property? |
| 8. How big is the land you own? |
| 9. Do you belong to a settlement? |
| 10. Have you ever received social assistance from the government? |
| 11. Have you ever received capacitation related to the farm activities? |
| 12. Have you ever had access to credit? |
| 13. How important (from 1 to 5) do you consider the variable productivity for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 14. How important (from 1 to 5) do you consider the variable soil fertility for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 15. How important (from 1 to 5) do you do you consider the variable fertilizer price for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 16. How important (from 1 to 5) do you consider the variable freight price for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 17. How important (from 1 to 5) do you consider the variable residue as feedstock for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 18. How important (from 1 to 5) do you consider the variable local production for your decision on choosing to buy a fertilizer? 1 is the less important and 5 is the most important |
| 19. How important (from 1 to 5) do you consider the variable reduction of greenhouse gases for your decision on choosing a fertilizer? 1 is the less important and 5 is the most important |
| 20. Do you know what municipal sewage sludge is made from? |
| 21. Have you ever heard about chars produced from sewage sludge? |
| 22. Would you use Sewchar as soil amendment? |
| 23. If yes, for each type of crop would you use Sewchar (edible, inedible, both or none)? |
| 24. If yes, for each purpose would you use Sewchar (commercialize crops, consume crops, both, none)? |
| 25. If no, why is the reason you would not use Sewchar as soil amendment? |




| Q3(x) % | x (µm) | First measurement | Second measurement | Third measurement |
|---|---|---|---|---|
| 10 | 3.7 | 3.6 | 3.8 | 3.8 |
| 50 | 22.9 | 23 | 22.9 | 22.8 |
| 90 | 59.7 | 60.9 | 60 | 58.1 |

Figure 6-1 Particle size distribution for Sewchar produced from biosolids at 190 °C and 4 h residence time

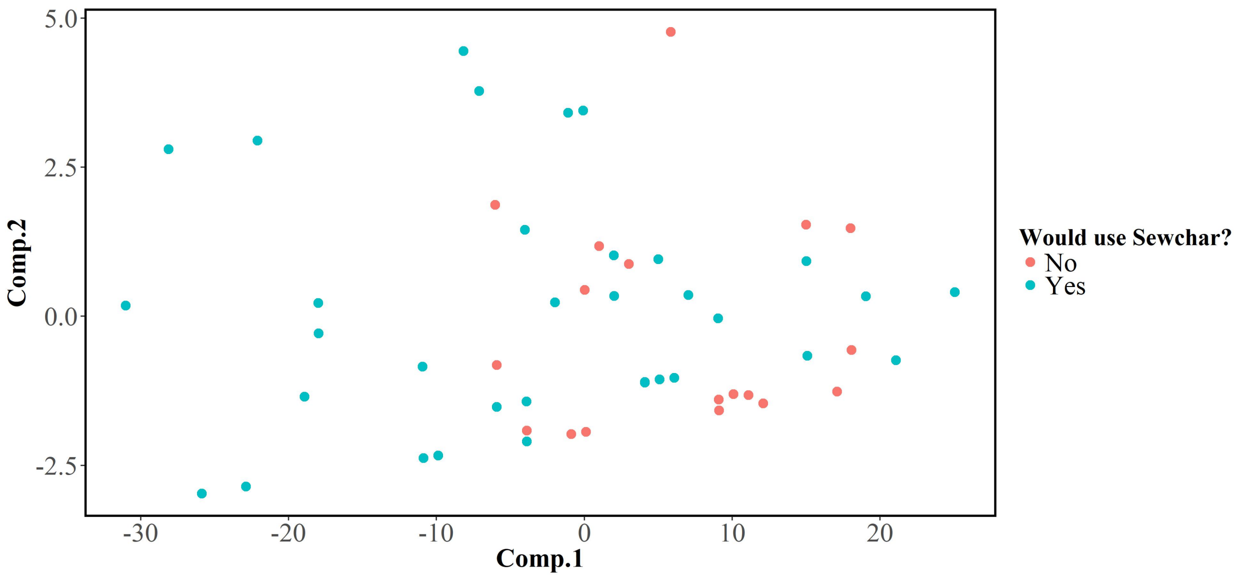



Figure 6-2 Results of the Principal Component Analyses (PCA) related to the Survey about the farmers' criteria for choosing a fertilizer

**Proof of individual contribution**

| **Manuscript included in the thesis** | **Author (Melo, T.M.)** | **Co-authors** |
|---|---|---|
| **Melo, T.M.,** Bottlinger, M., Schulz, E., Leandro, W.M., de Aguiar Filho, A.M., Ok, Y.S., Rinklebe, J., 2017. Effect of biosolids hydrochar on toxicity to earthworms and brine shrimp. Environ. Geochem. Health. 39, 1351-1364.<br>**Chapter 2** | Generating research idea, generating and evaluating the data, writing the manuscript | **Bottlinger, M.**<br>Supervisor, assistance during generation of research idea, correcting the manuscript<br>**Schulz, E.,**<br>Assistance during generation of research idea, correcting the manuscript<br>**Leandro, W.M.,**<br>Assistance during generation of research idea, correcting the manuscript<br>**de Aguiar Filho, A.M.,**<br>Assistance during statistical data evaluation, correcting the manuscript<br>**Ok, Y.S.,**<br>Correcting the manuscript<br>**Rinklebe, J.**<br>Supervisor, assistance during generation of research idea, correcting the manuscript |
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| 04/2009 – 03/2013 | Environmental Manager<br>Goiarte – Pre-cast concrete industry Goiás Artefatos de Cimento Limitada – Goiânia/Goiás – Brazil |
| 06/1998 – 03/2008 | Civil servant<br>Secretary of Health of Goiás State – Goiânia/Goiás - Brazil |

### Education

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| 03/2005 – 06/2006 | Graduate school (specialization course) in Treatment and Final Disposal of Solid and Liquid Waste<br>Federal University of Goiás UFG - Goiânia/Goiás – Brazil<br>Final publication: Overview of construction residues in Goiânia |
| 01/2002 – 06/2005 | Graduation in Environmental Management<br>Federal Center of Technological Education of Goiás – CEFET-GO - Goiânia/Goiás – Brazil |
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## Declaration of primary authorship

### Declaration of primary authorship

I declare that I have written the present thesis entitled for doctorate by myself and without the help of others. Other than the present references were not used and quote results were always marked with the relevant reference. The present thesis was never either abroad or in Germany submitted for examination in the present or similar version.

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Wuppertal, October 05, 2018