Journal of Cleaner Production 157 (2017) 22-29

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Use of industrial diatomite wastes from beer production to improve soil fertility and cereal yields



^a Department of Environmental Health Science & Technology, Jimma University, P.O.Box 378, Jimma, Ethiopia

^b Department of Horticulture and Plant Sciences, Jimma University, P.O. Box 307, Jimma, Ethiopia

^c Department of Natural Resources, Cornell University, Ithaca, NY, USA

ARTICLE INFO

Article history: Received 16 August 2016 Received in revised form 5 April 2017 Accepted 7 April 2017 Available online 20 April 2017

Keywords: Cereal yield Diatomite sludge Trace metal Soil guality Organic fertilizer

ABSTRACT

One promising way to reuse and recycle brewery spent diatomite sludge (BSDS) is by direct application to croplands as a soil amendment. This paper assesses the value of BSDS as a soil amendment and organic fertilizer. BSDS samples of different ages were analyzed to determine physicochemical properties and trace metal concentrations. All BSDS samples were alkaline (pH 8.3-8.7) with high concentrations of available phosphorus (373–416 mg kg⁻¹) and potassium (883–3297 mg kg⁻¹). Organic carbon and total nitrogen content were also found to be relatively high (3.1% and 0.22%, respectively) in the freshly dumped BSDS. The total porosity and available water holding capacity of BSDS were found in the range of 71-73% and 145-176 mm m⁻¹, respectively, which indicate favorable conditions for plant growth. Concentrations of potentially toxic trace metals in BSDS were much lower than the standards set for land application, implying that BSDS is safe for use as organic fertilizer. In addition, field trials with teff (Eragrostis abyssinica Zucc.) and wheat (Triticum aestivum L.) were conducted to measure the effects of BSDS amendments on grain yield as compared to recommended inorganic fertilizers and farmyard manure. For both cereals, application of BSDS resulted in two-fold higher grain yields than the control and 50% increases over farm yard manure. Post-harvest analysis also revealed an improvement in physicochemical properties of soil. Wheat and teff grown in fields treated with BSDS showed higher grain protein content than controls, and nearly as high as those treated with recommended inorganic fertilizers. In conclusion, BSDS has great potential to be used as a soil amendment to increase crop productivity and nutritional quality.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

By volume, beer is the fifth most consumed beverage in the world after tea, carbonated drinks, milk, and coffee (Fillaudeau et al., 2006). The brewing process for beer generates large amounts of wastewater effluent and solid wastes that must be disposed of without negatively affecting soil and water quality. Solid wastes from breweries include spent grains, spent diatomite, waste yeast and hot trub, all of which form a layer of residual sediment on the bottom of the fermenter (Mathias et al., 2014). Diatomite (also known as diatomaceous earth) is a mineral ore composed of fossilized diatoms, which are microscopic silicaceous marine organisms deposited during the Tertiary period (Johnson,

Corresponding author. E-mail address: desalewgashaw@gmail.com (G. Dessalew). 1997). The use of diatomite in beer filtration has been an industry standard for more than 100 years, but has been increasingly scrutinized from economic, environmental and technical standpoints (Fillaudeau et al., 2006). During filtration, haze active substances (the proteins, tannins and yeasts that make beer cloudy) are removed, and the biological and colloidal stability of beer is increased (Fontana and Buitti, 2009; Clemens, 2010). Beer production produces brewery spent diatomite sludge (BSDS), which consists diotomite as well as yeast residues and suspended solids. On average, during the production of 1 L of beer, a brewery requires 1–2 g of raw diatomite and produces 17.14 g of BSDS (Iliescu et al., 2009). According to a report by Access Capital Research (2011), breweries in Ethiopia have the potential to produce more than 4 million hL of beer per year. Since all Ethiopian breweries use diatomite for clarification, the total amount of BSDS produced each year is estimated to be about 69,000 metric tons.

Diatomite waste is a major challenge for all breweries due to its





CrossMark



Cleane Production

Abbreviations				
BD	Bulk density			
BGI	Borland Graphics Interface			
BSDS	Brewery spent diatomite sludge			
DAP	Diammonium Phosphate			
FYM	Farmyard manure			
PD	Particle density			
RIF	Recommended inorganic fertilizer			
TN	Total nitrogen			

economic and environmental consequences (Kanagachandran and Jayaratne, 2006). The cost for treatment and disposal of sludge is expensive, comparable to the total cost of the filtration process. Consequently, BSDS is often dumped in landfills or open fields. Dumping of BSDS on open field releases carbon monoxide and carbon dioxide to the atmosphere, which does not only contribute to global climate change, but also promote the growth of microbes (Iliescu et al., 2009). Moreover, the high moisture content of BSDS (approximately 70%) and its chemical composition lead to rapid degradation, so that the open dumping produces unpleasant odors and attracts animals (Mathias et al., 2014).

Use of BSDS as a soil amendment and for bioremediation of contaminated soils is a relatively recent practice. Although chemical analysis of spent diatomaceous earth has high nutrient content, particularly of organic nitrogen (Johnson, 1997), the environmental risks associated with its application are not well known. As for CO₂ release, the IPCC (2006) has reported that CO₂ from biodegradable waste does not pose a significant risk to the environment. Moreover, nitrate production from BSDS is released slowly; hence, it has a lower leaching risk and advantages for crop production (Snyman and van der Waals, 2004).

Treatment of organic solid wastes is a growing area of investigation, and new technologies are replacing conventional treatment systems. Environmental concerns have led to more stringent regulations and increased incentives to utilize byproducts without unintended environmental consequences (Stocks et al., 2002; Kanagachandran, 2004). Research that explores opportunities to reuse and recycle wastes, including brewery byproducts, is important to improve the efficiency of production and consumption, and thereby make progress toward sustainable development goals (UN, 2015).

The use of other types of biowaste as agricultural soil amendments in place of inorganic fertilizer is relatively well researched (Tarraso'n et al., 2008; Delibacak et al., 2009), and fertilizer advice is available for many similar materials (Rigby and Smith, 2014). For example, the nutrient value of paper-mill sludge (Madejo'n et al., 2003; Price et al., 2009) and other industrial biowastes resulting from food and beverage production and processing are well defined, and guidelines for the use of these byproducts in agriculture as fertilizers have already been developed (Rigby and Smith, 2014). By comparison, information regarding the value of BSDS as a potential fertilizer is limited, despite the strategic importance of recycling BSDS to improve agricultural production. A few previous studies indicate that BSDS has high potential to increase the availability of nutrients to plants (Mbagwu and Ekwealor, 1990; Johnson, 1997; Mathias et al., 2014). Other wastes from breweries, including spent grains, have been combined with additional organic materials (e.g., sawdust and horse manure) and used to produce compost, which has been shown to increase yields of crops such as kale (Crosier, 2014). Field research is necessary to characterize the value of BSDS as an organic fertilizer, and thereby enhance the efficient utilization and management of this industrial waste material as an alternative fertilizer in agriculture.

Borland Graphics Interface (BGI) Brewery Limited Company is located in Kombolcha town in the South Wollo Zone of Ethiopia. While BSDS from BGI is said to pose a major threat to the surrounding environment, little is known about the potentially toxic properties of the brewery's BSDS or its potential to improve soil fertility and thereby improve crop growth and yield on local farms. The aim of this study is to characterize the nutrient composition of BSDS from BGI and evaluate how its use as an organic fertilizer affects the yields of teff (*Eragrostis abyssinica* Zucc.) and wheat (*Triticum aestivum* L), two of the most important crops within the study area and the country at large.

2. Materials and methods

2.1. BSDS samples collection and characterization

Time since dumping (i.e. the age of BSDS) was expected to affect the physicochemical properties of BSDS. Therefore, three composite 1 kg samples were collected from dumping sites close to the BGI factory, including one that had been dumped two years earlier, one that had been dumped two months earlier, and another that had been recently used for filtration. The samples were dried prior to characterization of their physicochemical properties.

2.2. Physical characterization of BSDS

The bulk density (BD) of each BSDS sample was measured with a core sampler (Rowell, 1997). Particle density (PD) was determined using a pychnometer (Sahlemedhin and Taye, 2000). Total porosity was calculated from the values of BD and PD (Equation (1)).

Total porosity(%) =
$$\left(1 - \frac{BD}{PD}\right) \times 100$$
 (1)

Available water holding capacity was calculated as the percent difference between moisture content at field capacity and wilting point (Klute and Dirksen, 1986).

2.3. Chemical characterization of BSDS

The pH of each BSDS sample was determined by mixing 10 g with 50 mL of distilled water potentiometrically using a glass-calomel combination electrode. The solution was left for two hours at room temperature prior to measurement with a digital pH meter (Hatch HQ40d). Organic Carbon (OC) was measured by wet combustion, otherwise known as dichromate oxidation (Walkley and Black, 1934). Total nitrogen (TN) was determined by the Kjedahl method (Black, 1965), and available phosphorus (P) by extraction with NaHCO₃ (Olsen et al., 1954). Soluble cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺) and anions (Cl⁻, CO₃²⁻, HCO₃⁻ and SO₄²⁻) were measured following standard procedures (Sahlemedhin and Taye, 2000). BSDS samples were analyzed for trace metals (Cd, Pb, As and Ni) using Atomic Absorptions Spectrophotometer.

2.4. Physicochemical characterization of the field experimental soil

Before sowing and applying treatments with BSDS, three composite soil samples were collected from the experimental sites, which were located on agricultural land on the west side of the Kombolcha airport. Soil samples were collected from a depth of 20 cm using a soil auger. Composite soil samples were analyzed for multiple physicochemical properties. Bulk density, particle density and total porosity were measured following the procedures described for BSDS. In addition, soil texture was determined using a hydrometer (Day, 1965). Soil pH was measured in a suspension of 1:2.5 soils to potassium chloride (Chopra and Kanwar, 1976). Total N was determined following the micro-Kjedahl method (Jackson, 1958), and available P by extraction with the Bray II method (Bray and Kurtz, 1945) using 0.03M NH₄F and 0.1M HCl solution. Soil cation exchange capacity was measured by extracting exchangeable Ca, Mg, K and Na with 1M NH₄OAc at pH 7. Exchangeable Ca and Mg in these extracts were analyzed using an Atomic Absorption Spectrophotometer, while Na and K were analyzed by flame photometer (Chapman, 1965; Rowell, 1994). After crop harvest, a second set of soil samples were collected from plots to assess change in the physicochemical properties of the soil as a result of BSDS application.

2.5. Field trials to measure yield following application of BSDS

To evaluate BSDS as an organic fertilizer, field trials were conducted for two years during the main cropping season (June to November in 2014 and 2015). Fresh BSDS was selected because chemical characterization had indicated that it had more desirable qualities than older BSDS. Older BSDS samples were found to have high concentrations of bicarbonates, which are known to have adverse effects on nutrient availability. Test crops included teff (Eragrostis abyssinica Zucc.) and wheat (Triticum aestivum L.), two of the cereal crops most commonly grown within the study area. Four treatments consisting of a control (i.e. no fertilizer or manure application). 100% farm vard manure (FYM) at 3 t ha^{-1} . 100% BSDS at 0.5 t ha⁻¹ and 100% recommended inorganic fertilizer (RIF), which consisted of 64 kg N and 46 kg P ha⁻¹, were laid out in a randomized complete block design with three replicates. Urea (46% N) and Diammonium Phosphate (DAP; 18% N and 46% P₂O₅) were used as sources of N and P. The FYM and BSDS treatments were broadcast and thoroughly incorporated into the top 15 cm of the soil 20 days before sowing. Teff was grown on 3×3 m plots at a raw spacing of 20 cm. Seeds were drilled in 15 rows, each 3 m long for a seeding rate of 60 kg ha⁻¹. Wheat was grown on 4 \times 5 m plots at a raw spacing of 20 cm apart. Seeds were drilled in 20 rows, each 5 m long, for a seeding rate of 60 kg ha^{-1} . Plots were more than 1 m apart and blocks (replications) more than 2 m apart. The full dose of P_2O_5 (46 kg P) and half of the dose N (32 kg) were applied during sowing; the remaining N dose (32 kg) was applied during heading initiation. Both crops were harvested at grain maturity. Grain yield, biomass yield (kg ha⁻¹), and protein content from nitrogen were determined.

2.6. Data analysis

Statistical analysis was conducted in STATISTICA 8.0 (StatSoft, Inc). Student's t-tests were used to evaluate differences in the yields between treatments, and an ANOVA to test differences among treatment groups. Spider charts were used to visualize concentrations of cations and anions and evaluate changes in ion balance within BSDS over time.

3. Results and discussion

3.1. Physicochemical characteristics of BSDS

3.1.1. Water holding capacity and porosity of BSDS

The porosity of BSDS ranges between 71 and 77% and water holding capacity of 145–176 mm m⁻¹ (Table 1). Water holding capacity and porosity are important agronomic characteristics that affect transport, storage and availability of water, air and nutrients

Table 1

Physicochemical analysis of the three age groups of brewery spent diatomite sludge (BSDS) immediately after dumping, after two months, and after two years.

Parameters	Age of Brewery S (BSDS)		omite Sludge
	Fresh	Two months	Two years
Organic Carbon (g kg ⁻¹)	309	108	106
Total Nitrogen (g kg ⁻¹)	22	8	7
Available P (mg kg ⁻¹)	415.91	416.29	373.22
Total P (mg kg ⁻¹)	1664.98	4069.76	5475.43
Available K (mg K ₂ O kg ⁻¹)	3296.88	1676.05	882.58
Zn (ppm)	33.19	33.03	33.02
Cu (ppm)	25.19	25.08	25.01
Water holding Capacity (mm m ⁻¹)	176.21	155.32	145.54
Porosity (%)	71.61	77.27	72.83
рН	8.79	8.51	8.37

within the soil for plant growth (Yusuf, 2010; Adamu and Aliyu, 2012). Diatomite is naturally porous and can absorb up to 150% of its own weight in water (Yıldız, 2008). The values measured for water holding capacity and porosity of the BSDS samples were comparable with fertile soil. Water holding capacity between 110 and 210 mm m⁻¹ (Pam and Brain, 2007) and total porosity should range between 30 and 47% (Moore et al., 1998). Water holding capacity has declined over dumping time slightly, which may be related to the decline in organic carbon content of BSDS over time.

3.1.2. BSDS alkalinity and its potential for treatment of acidic soils

The pH values indicate that all BSDS samples were slightly alkaline, starting at 8.79 in fresh BSDS and declining to 8.37 in the two-year old sample (Table 1). Luque et al. (1990) found that the pH of brewery waste sludge from three South American breweries was highly variable, ranging from 6.5 to 11.5, due to differences in water source and processing technique. Given that the greatest quantity of nutrients are available when soil pH is between 5 and 8 (Belinda, 2000), the use of BSDS as a soil amendment may affect the availability of both macro- and micronutrients. Consequently, if used to maintain soil fertility, BSDS may need to be combined with chemicals that lower pH, or for crops that tolerate alkalinity. On the other hand, BSDS could be used to neutralize slightly acidic soils, as an alternative to liming. In Ethiopia, 40% of cultivated land is characterized by acidic soils (Mesfin, 2007), so the use of BSDS to raise pH would often help to improve soil fertility. Furthermore, the fact that the pH of BSDS declines over time may be an important consideration in applying it to fields, as older BSDS may be more appropriate on neutral or alkaline soils.

3.1.3. Ionic balance of BSDS over time

Concentrations of cations and anions were generally higher in fresh BSDS samples than the 2 months and 2 years old BSDS samples (Fig. 1). One exception is bicarbonate (HCO_3^{-2}) , which was lower in fresh BSDS than in the other samples, indicating that its concentration increases after dumping. However, our results indicate that the concentrations of all other cations $(K^+, Mg^{2+} \text{ and } Ca^{2+})$ and anions $(Cl^- \text{ and } SO_4^{-2})$ decrease slightly (by no more than 0.02 ppm) after dumping. This trend may be attributed to the slight alkalinity of BSDS and a low concentration of dissolved organic matter, allowing the ions to bond and precipitate (Bikash and Sanjay, 2015). The relatively high concentration of sodium in the fresh BSDS may be attributed to the fact that glass bottles in the brewery are washed with sodium hydroxide and the wastewater from this process may be included in the BSDS.

3.1.4. The nutrient content of BSDS and its potential as a soil amendment

Analysis of physicochemical properties of BSDS collected at



Fig. 1. Ionic balance of BSDS (brewery spent diatomite sludge) samples. A = fresh BSDS, B = two-month old BSDS, and C = two year old BSDS.

different times since dumping confirms our expectation of both physical and chemical changes over time (Table 1). According to Metson (1961) and Frank (1990), soils with concentrations of >20 ppm available phosphorus and >400 ppm available K are considered to have high fertility. Available P and K were found to be higher than these values in each of the three BSDS samples. The release of P from particles is slow and steady (Wang et al., 2015). Although available P increased over the course of two years and K decreased, in general, BSDS appears to have high concentrations of P and K and therefore has great potential to be used as a soil amendment for soils that are deficient in these nutrients.

The amounts of organic carbon (3.09%) and total nitrogen (0.22%) were much higher in fresh BSDS than in the two older samples, indicating a rapid loss of these nutrients in the first two months after dumping. According to Metson (1961) and Frank (1990) medium soil fertility is indicated by 4% organic carbon and 0.225% total nitrogen, whereas low soil fertility is indicated by 2% organic carbon and 0.125% total nitrogen content. Therefore, in terms of carbon and nitrogen, fresh BSDS is in the low to medium fertility range, and drops to low fertility after only two months. Losses of organic carbon are expected during decomposition resulting from the activity of microbial populations (Mondini et al., 2003). During decomposition, some carbon is released as CO₂ and some is assimilated or immobilized by microbial communities (Fang et al., 2001; Cabrera et al., 2005). The loss of nitrogen may also be attributed to microbial utilization of nitrate compounds and denitrification as ammonia gas (Quan et al., 2006; Barjinder and Saini, 2013).

Finally, concentrations of zinc and copper are similar to those of a soil in the normal fertility range. Soil with 10–120 ppm zinc and 10–25 ppm copper is normal and non-toxic for plant growth (Alloway, 1990). The concentrations of zinc were approximately 33 ppm for zinc and 25 ppm for copper and did not decline over time, indicating that the use of BSDS as an organic fertilizer would not be toxic for plant growth, and could be a source of these micronutrients in otherwise deficient soils.

3.1.5. Potentially toxic trace elements in BSDS

The analysis of BSDS samples revealed that arsenic and cadmium were present, although below the detection limits (Table 2). The concentrations of lead (1.16 ppm) and nickel (31.12 ppm) in BSDS samples were much lower than the standards established for land application (840 ppm for lead and 420 for Ni) (Sonon and Gaskin, 2012). Moreover, the concentrations of these metals in BSDS were lower than those typically found in inorganic phosphorus fertilizer. For example, DAP used in Chile contained 4.9–14.5 ppm lead; DAP in Saudi Arabia contained 11.2–16.4 ppm lead and 52.2–73.4 ppm nickel (Modaihsh et al., 2004; Mauricio et al., 2009). The concentrations of trace metals also fall below the standard set for agricultural soil by the FAO and Ministry of the Environment of Finland (Randhawa et al., 2014; Toth et al., 2016). This suggests that BSDS from the BGI brewery can be safely used for agricultural purposes.

3.1.6. Effect of age of BSDS for field application

Overall, it appears that fresh BSDS is the most appropriate for field application. First, the concentrations of essential macro- and micronutrients were highest in fresh BSDS (Table 1). Second, the high concentration of bicarbonate in the older samples deters us from using it as organic fertilizer, as bicarbonate can cause iron deficiencies leading to yellowing of leaves. In addition, bicarbonate binds with other nutrients and reduces their availability to plants, and causes the formation of crusts on the surface of soils, which reduces infiltration rates (VBI, 1998). In our analysis, the only counter-indication for use of fresh BSDS is the slightly higher alkalinity, which may be offset by addition of acidic amendments or use on acidic soils.

3.2. Impact of BSDS application on physicochemical characteristics of post-harvest soil

As we would expect from our analysis of BSDS, experimental additions to a clay soil resulted in many changes in its

Fable 2 Analysis of trace metals in Borland Graphics Interface (BGI) brewery spent diatomite sludge (BSDS). The detection limit of the machine was 0.0							
Trace metals	Concentration (mg l	(g ⁻¹)					
	Fresh BSDS	Two month BSDS	Two years BSDS	^a MRLs (mg kg ⁻¹)			
Cd	Not detected	Not detected	Not detected	1.50			
As	Not detected	Not detected	Not detected	_			
Pb	1.16	1.17	1.19	100.00			
Ni	31.12	31.15	31.18	70.00			

Δinaliv	ric of	trace metals in	Borland Cu	applies Interface		brower	r cnont	distomite	chudaa		The detection	limit of	the machine	was 0.02 m	$\alpha k \alpha^{-1}$
Allaly:	515 01	trace metals n	I DUI Idillu Gi	applies interface	(DGI)	Dieweiy	spent	ulatollille	Sludge	(DSDS)). The detection	IIIIIII OI		Was 0.02 III	ig kg .

^a FAO MRL (Maximum Residual Limit) value.

^b TV (Threshold value) heavy metal concentration values standards of the MEF (Ministry of Environment of Finland, 2007).

physicochemical characteristics, including improvements for agricultural production (Table 3). Except for electrical conductivity and pH, all other physicochemical parameters showed changes that enhance soil fertility. Our results confirm those of several previous studies, including Ramya et al. (2015), who showed that the addition of BSDS improved organic carbon content and water holding capacity as a result of its high organic matter content and high cation exchange capacity. Erdem and Sozudo (2002) provided evidence that brewery sludge amendments raise the pH of acidic soils and increase the organic carbon content, concentrations of exchangeable cations, and soluble cations and anions. Therefore, our analysis of the physicochemical impacts of BSDS application indicates that its use as a soil amendment is not only an 'environment-friendly' disposal mechanism for industrial waste, but a viable way to improve the quality of agricultural soils.

3.3. Field scale experiment on BSDS application as soil amendment

3.3.1. Grain yield

For both teff and wheat, addition of BSDS resulted in significantly higher yields than observed for the control (no fertilizer added) and use of FYM, but significantly lower than those resulting from the use of RIF (Fig. 2, Table 4). For both cereals, an approximately two-fold increase in grain yield was observed following the addition of BSDS when compared to the control. Increases in yield compared to FYM were 1.3 fold for wheat and 1.5 fold for teff. Nevertheless, the effect of BSDS on yield of both cereals was far lower than the effect of RIF. This is the first evidence that the use of BSDS improves yields of teff (2.45 t ha⁻¹), a staple crop in many parts of Ethiopia that is central to local food traditions. The use of BSDS also resulted in wheat yield of 2.65 t ha⁻¹. Our results correspond with those of Luque et al. (1990), who reported a

Table 3

Physicochemical characteristics of soil before and after application of brewery spent diatomite sludge (BSDS).



^bTVs (mg kg⁻¹)

1.00 5.00 60.00

50.00

Fig. 2. Box plot showing cereals yield among the different treatment groups (control, farmyard manure, BSDS = brewery spent diatomite FYM = sludge; RIF = recommended inorganic fertilizer). Boxes represent the mean \pm standard error and whiskers represent two standard deviations.

significant correlation between the doses of BSDS and yields of corn, sorghum and groundnut, as well as Iliescu et al. (2009), who observed that application of BSDS on wheat and tomato seedlings increased vegetative mass and yields. Thus, the use of BSDS as an organic fertilizer could contribute to the productivity, and therefore the food security of farming communities in rural areas. As the cost of inorganic fertilizers rise, BSDS may provide a more affordable option, with fewer long-term negative consequences for soil and

Parameters	Before application	After application	Change in percent
Sand (%)	12.79	13.4	4.77
Silt (%)	26.05	18.87	-27.56
Clay (%)	60.16	66.03	9.76
Texture class	Clay	Clay	_
pH	6.63	6.84	3.17
Electrical conductivity (mS cm ⁻¹)	0.26	0.11	-57.69
Exchangeable Na ⁺ (meq 100 g soil ⁻¹)	0.42	0.83	97.62
Exchangeable K ⁺ (meq 100 g soil ⁻¹)	0.95	1.01	6.30
Exchangeable Ca^{2+} (meq 100 g soil ⁻¹)	35.35	51.01	44.30
Exchangeable Mg ²⁺ (meq 100 g soil ⁻¹)	12.54	17.44	39.07
Cation exchange capacity (meq 100 g soil ^{-1})	61.30	72.03	17.50
Sum of cations (meq 100 g soil ^{-1})	47.31	69.79	47.52
Organic Carbon (g kg ⁻¹)	0.84	0.89	5.95
Total Nitrogen (g kg ⁻¹)	0.11	0.13	18.18
Available P (mg P ₂ O ₅ kg soil ⁻¹)	24.61	56.38	129.09
Available K (mg K ₂ O kg soil ⁻¹)	371.33	404.54	8.94
Exchangeable Na percentage (%)	0.66	1.16	75.76
Porosity (%)	52.57	63.5	20.79

Table 4

Comparison of grain and biomass yields for wheat and teff treated with BSDS (brewery spent diatomite sludge), FYM (farmyard manure) and RIF (recommended inorganic fertilizer).

Cereals	Treatment	Grain Yield (kg ha ⁻¹)	Comparison groups	Mean difference	T-value	P-value
Teff	Control	1111.1	Control vs. FYM	-0.0440	-3.11	0.036
	FYM	1555.6	Control vs. BSDS	-0.1111	-8.66	0.001
	BSDS	2222.2	Control vs. RIF	-0.2889	-15.92	0.000
	RIF	4000.0	BSDS vs. FYM	0.0666	3.928	0.017
			BSDS vs. RIF	-0.1780	-8.76	0.009
Wheat	Control	1150.0	Control vs. FYM	-0.158	-6.72	0.003
	FYM	1550.0	Control vs. BSDS	-0.270	-11.64	0.000
	BSDS	2400.0	Control vs. RIF	-0.640	-26.90	0.000
	RIF	4000.0	BSDS vs. FYM	0.112	6.95	0.002
			BSDS vs. RIF	-0.370	-22.54	0.000
		Biomass yield (kg ha $^{-1}$)				
Teff	Control	2785	Control vs. FYM	-2067	-241.4	0.000
	FYM	4852	Control vs. BSDS	-3783	-547.9	0.000
	BSDS	6568	Control vs. RIF	-9675	-544.6	0.000
	RIF	12460	FYM vs. BSDS	-1716	-204.6	0.000
			BSDS vs. RIF	-5892	-333.2	0.000
Wheat	Control	2938	Control vs. FYM	-1938	-281.7	0.000
	FYM	4876	Control vs. BSDS	-4226	-793.9	0.000
	BSDS	7164	Control vs. RIF	-9558	-1850.9	0.000
	RIF	12496	BSDS vs. FYM	-2288	-348.9	0.000
			BSDS vs. RIF	-5332	-1128.3	0.000

water quality, and public health.

3.3.2. Biomass yield

Analysis of variance indicated significant differences (p < 0.05) between treatments for biomass yield in both crops (Table 4). For wheat and teff, application of BSDS resulted in significantly higher biomass yields than the control and FYM, but was significantly lower than those obtained from the use of RIF. Similar to the grain yield, a two-fold increase in biomass yield was observed following the addition of BSDS as compared to the control. The increase in biomass yield compared to FYM was only 1.3 fold for wheat and 1.5 fold for teff. However, for both cereals, the effect of BSDS on biomass yield was far lower than the effect due to RIF. This may be explained by the fact that nutrient release from BSDS is slower than that of RIF. Our results support the findings of Luque et al. (1990) and lliescu et al. (2009) who reported a significant increase in the biomass yield of crops following BSDS application.

3.4. Effects of BSDS application on grain protein content

For wheat and teff, the protein content of grains was significantly different between treatments (Table 5). The highest grain protein (12.09% in wheat and 12.53% in teff) was measured in crops treated with RIF, and the lowest in the control (9.98% in wheat and 10.25% in teff). Higher protein content in the RIF treatment could be due to higher grain nitrogen uptake by both crops; nutrients in inorganic fertilizers are more quickly available to plants than those released from organic fertilizers. Lemon (2007) and Blumenthal et al. (2008) have likewise reported enhanced grain protein following the application of inorganic nitrogen.

Interestingly, the protein concentration of wheat treated with BSDS (11.23% in wheat and 11.38% in teff) was higher than that of the control, but slightly lower than those treated with RIF, and higher than threshold levels for product quality. Mariani et al. (1995) reported that wheat with 13% protein content could provide excellent products whereas wheat with protein content below 11% gives products of inferior quality. These data suggest that application of BSDS not only improves grain and biomass yields of wheat and teff but also the grain protein content, meaning that BSDS as an alternative to RIF may enhance the nutritional benefits of low-input agroecosystems.

4. Conclusion

Understanding the physicochemical properties of BSDS is critical to assess its agronomic value and support its efficient use and sustainable management. Our study showed that freshly dumped BSDS contained high concentrations of many macro- and micronutrients essential for crop growth, and increased the water holding capacity and porosity of soils to enhance crop productivity. We

Table 5

Comparison of protein content of wheat and teff treated with BSDS (brewery spent diatomite sludge), FYM (farmyard manure) and RIF (recommended inorganic fertiliz	zer).
---	-------

Cereals	Treatment	^a Protein content (%)	Comparison groups	Mean difference	T-value	P-value
Teff	Control	9.98	Control vs. FYM	-1.3	-25.2	0.000
	FYM	11.41	Control vs. BSDS	-1.25	-48.4	0.000
	BSDS	11.23	Control vs. RIF	-2.11	-71.7	0.000
	RIF	12.09	FYM vs. BSDS	0.18	13.7	0.020
			BSDS vs. RIF	-0.86	-33.3	0.000
Wheat	Control	10.25	Control vs. FYM	-1.3	-33.9	0.000
	FYM	11.55	Control vs. BSDS	-1.13	-26.2	0.000
	BSDS	11.38	Control vs. RIF	-2.28	-66.8	0.000
	RIF	12.53	FYM vs. BSDS	0.17	3.7	0.020
			BSDS vs. RIF	-1.15	-27.4	0.000

^a Calculated: a factor of 6.25 was used to calculate protein from Nitrogen.

have also shown that freshly dumped BSDS obtained from the BGI brewery contained suitably low concentrations of potentially toxic trace elements (e.g., As, Cd, Pb, Ni) compared to the standards set for land application. Our findings suggest that the spent diatomite of BGI brewery could be safely used for agricultural purposes without unintended environmental impacts. Moreover, the results from our field trials on wheat and teff demonstrated that the use of BSDS doubled the vields of these crops when compared without any fertilizers application, and was 50% higher than yields achieved with farmyard manure. Therefore, land application of BSDS would offer an effective strategy to divert brewery waste from landfills and open fields and contribute to long-term soil productivity by recycling nutrients and organic matter in agricultural systems. We recommend further study on the combined use of BSDS alongside other organic and inorganic fertilizer sources, as well as on the rate and time of application, in order to provide farmers with specific guidelines regarding the optimal use of BSDS.

Acknowledgments

The authors wish to thank Jimma University, Samara University and BGI, Ethiopia for their financial and logistic support. We also thank the staff of Water Works Design and Supervision Enterprise Laboratory Service Sub-Process Soil Fertility Section and the Geological Survey of Ethiopia, Laboratory Center for providing support to conduct the laboratory analysis. The authors would also like to thank three anonymous reviewers whose comments helped to improve our manuscript. Finally, the authors are grateful to the farmers at our study site for their assistance as we conducted field experiments.

References

- Access Capital Research, 2011. Ethiopia: Macroeconomic Handbook 2011/12. Addis Ababa, Ethiopia.
- Adamu, G.K., Aliyu, A.K., 2012. Determination of the influence of texture and organic matter on soil water holding capacity in and around Tomas irrigation Scheme, Dambatta Local Government Kano State. Res. J. Environ. Earth Sci. 4, 1038–1044.
- Alloway, B.J., 1990. Heavy Metals in Soils. Wiley, New York.
- Barjinder, B., Saini, M.S., 2013. Effect of age and seasonal variation on leachate characteristics of municipal solid waste landfill. Int. J. Res. Eng. Technol. 2, 223–232.
- Belinda, L., 2000. Understanding Soil pH. http://www.dpi.nsw.gov.au/-data/assets/ pdf-file/0003/167187/soil-ph.pdf (Accessed 19 January 2016).
- Bikash, A., Sanjay, N.K., 2015. Qualitative study of landfill leachate from different ages of landfill sites of various countries including Nepal. Journal of environmental science. Toxicol. Food Technol. 9, 23–36.
- Black, C.A., 1965. Methods of Soil Analysis, Part I. American Society of Agronomy, Madison Wisconsin, USA.
- Blumenthal, J., Baltensperger, D., Cassman, K., Mason, S., Pavlista, A., 2008. Importance and Effect of Nitrogen on Crop Quality and Health. Agronomy & Horticulture - Faculty Publications. http://digitalcommons.unl.edu/agronomyfacpub/ 200 (Accessed 16 June 2016).
- Bray, H.R., Kurtz, L.T., 1945. Determination of organic and available forms of phosphorus in soils. Soil Sci. 9, 39–46.
- Cabrera, M.L., Kissel, D.E., Vigil, M.F., 2005. Nitrogen mineralization from organic residues, Research opportunities. J. Environ. Qual. 34, 75–79.
- Chapman, H.D., 1965. Cation exchange capacity. In: Black, C.A., Ensminger, L.E., Clark, F.E. (Eds.), Methods of Soil Analysis (Agronomy 9). American Society of Agronomy, Madison Wisconsin, pp. 891–901.
- Chopra, S.H., Kanwar, J.S., 1976. Analytical Agricultural Chemistry. New Delhi, India. Clemens, A., 2010. Coming to grips with depth filtration. Brauwelt Int. 28, 165–167.
- Crosier, J.D., 2014. Agricultural Utilization of Brewers' Spent Grains & Sawdust: Effects on Fertility of Soils and Productivity of Crops. Master's thesis. Ohio University.
- Day, P.R., 1965. Particle fraction and particle size analysis. In: Black, C.A., et al. (Eds.), Methods of Soil Analysis, Part 2. American Society of Agronomy, pp. 545–567.
- Delibacak, S., Okur, B., Ongun, A.R., 2009. Influence of treated sewage sludge applications on temporal variations of plant nutrients and heavy metals in a Typic Xerofluvent soil. Nutr. Cycl. Agroecosystem 83, 249–257.
- Erdem, N., Sozudo, S., 2002. Effect of brewery sludge amendments on some chemical properties of acid soil in pot experiments. Bioresour. Technol. 84, 271–273.

Fang, M., Wong, M.H., Wong, J.W.C., 2001. Digestion activity of thermophilic

bacteria isolated from ash-amended sewage sludge compost. Water Air Soil Pollut. 126, 1–12.

- Fillaudeau, L., Blanpain-Avet, P., Daufin, G., 2006. Water, wastewater and waste management in brewing industries. J. Clean. Prod. 14, 463–471.
- Fontana, M., Buitti, S., 2009. Amino acids in beer. In: Victory, R.P. (Ed.), Beer in Health and Disease Prevention. Elsevier Inc., Academic Press, pp. 273–284.
- Frank, B., 1990. Agricultural Compendium. FAO and Booker (MTs).

Iliescu, M., Faraco, M., Popa, M., Cristea, M., 2009. Reuse of residual kieselguhr from beer filtration. J. Environ. Prot. Ecol. 10, 156–162.

- IPCC, 2006. In: Eggleston, H.S., Miwa, K., Srivastava, N., Tanabe, K. (Eds.), Guidelines for National Greenhouse Gas Inventories — a Primer, Prepared by the National Greenhouse Gas Inventories Programme. IGES, Japan.
- Jackson, M.L., 1958. Soil Chemical Analysis. Engle Wood Cliffs, New Jersey.
- Johnson, M., 1997. Management of Spent Diatomaceous Earth from the Brewing Industry. Thesis. the University of Western Australia.
- Kanagachandran, K., Jayaratne, R., 2006. Utilization potential of brewery waste water sludge as an organic fertilizer. J. Inst. Brew. 112, 92–96.
- Kanagachandran, K., 2004. Biogas generation from brewery wastes, Demonstration at a laboratory scale. Tech. Q. Master Brew. Assoc. Am. 41, 394–397.
- Klute, A., Dirksen, C., 1986. Hydraulic conductivity and diffusivity: laboratory methods. In: Klute, A. (Ed.), Methods of Soil Analysis, Part 1, pp. 687–734. Agronomy monograph No. 9, ASA and SSSA, Madison Wiscosin.
- Lemon, J., 2007. Nitrogen Management for Wheat Protein and Yield in the Esperance Port Zone. Department of Agriculture and Food, State of Western Australia. Luque, O., Bracho, O., Maier, T.W., 1990. Utilization of brewery waste water sludge
- for soil improvement. Tech. Q. Master Brew. Assoc. Am. 27, 5–9. Madejo'n, E., Burgos, P., Lo'pez, R., Cabrera, F., 2003. Agricultural use of three organic
- residues: effect on orange production and on properties of a soil of the Comarca Costa de Huelva (SW Spain). Nutr. Cycl. Agroecosystem 65, 281–288.
- Mariani, B.M., D'Egido, M.G., Novaro, P., 1995. Durum wheat quality evaluation: influence of genotype and environment. Cereal Chem. 72, 194–197.
- Mathias, T., Mello, P., Servulo, E., 2014. Solid waste in brewing process: a review. J. Brew. Distill. 5, 1–9.
- Mauricio, M., Fabia, N.A., Raul, C.N., Marcia, C., Mauricio, E., 2009. Trace element composition of selected fertilizers used in Chile: phosphorus fertilizers as a source of long-term soil contamination. Soil Sediment Contam. 18, 497–511.
- Mbagwu, J.S.C., Ekwealor, G.C., 1990. Agronomic potential of brewers' spent grains. Biol. Wastes 34, 335–347.
- Mesfin, A., 2007. Nature and Management of Acidic Soil in Ethiopia. Addis Abeba, Ethiopia.
- Metson, A.J., 1961. Methods of Chemical Analysis of Soil Survey Samples. Wellington, New Zealand.
- Ministry of the Environment, Finland, 2007. Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007, March 1, 2007).
- Modaihsh, A.S., Al-Swailem, M.S., Mahjoub, M.O., 2004. Heavy metals content of commercial inorganic fertilizers used in the Kingdom of Saudi Arabia. Agric. Mar. Sci. 9, 21–25.
- Mondini, C., Dell'Abate, M.T., Leita, L., Beneditti, A., 2003. An integrated chemical, thermal and microbiological approach to compost stability evaluation. J. Environ. Qual. 32, 2379–2386.
- Moore, D., Hall, D., Russell, J., 1998. Soil water. In: 'Moore, G. (Ed.), Soil Guide, a Handbook for Understanding and Managing Agricultural Soils, pp. 80–94. Bulletin No. 4343, Agriculture Western Australia.
- Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of Available Phosphorus in Soils by the Extraction with Sodium Bicarbonate. Circ. 939, Department of agriculture, U.S.
- Pam, H., Brain, M., 2007. Interpreting Soil Test Results. NSW Department of Natural Resources, Australia.
- Price, G.W., Voroney, R.P., Chong, C., 2009. Crop performance on soils receiving annual paper mill biosolid amendments with and without supplementary nitrogen. Can. J. Soil Sci. 89, 269–279.
- Quan, D., Zhang, Y., Zhao, Y., 2006. Long-term operation of a compost-based biofilter for biological removal of n-butyl acetate, p-xylene and ammonia gas from an air stream. Biochem. Eng. J. 32, 84–92.
- Ramya, N., Srinivas, T., Aruna Lakshmi, K., 2015. Studies on effect of brewery waste water sludge (BWS) on morphology and yield of Chilly (*Capsicum Annuml*) plant. Int. J. Pharm. Sci. Res. 6, 405–409.
- Randhawa, M.A., Ahmad, G., Anjum, F.M., Asghar, A., Sajid, M.W., 2014. Heavy metal contents and their daily intake in vegetables under peri-urban farming system of Multan, Pakistan. Pak. J. Agric. Sci. 51, 1025–1031.
- Rigby, H., Smith, S.R., 2014. The nitrogen fertiliser value and other agronomic benefits of industrial biowastes. Nutr. Cycl. Agroecosystem 98, 137–154.
- Rowell, D.L., 1994. Soil Science: Methods and Applications. Addison Wesley Longman Limited, England.
- Rowell, D.L., 1997. Soil Science: Method and Application. Addison Wesley Longman Group, UK, Singapore.
- Sahlemedhin, S., Taye, B., 2000. Procedure for Soil and Plant Analysis. National Soil Research Centre, Ethiopian Agricultural Research Organization, Addis Ababa, Ethiopia.
- Snyman, H.G., van der Waals, J., 2004. Laboratory and Field Scale Evaluation of Agricultural Use of Sewage Sludge. Report to the Water Research Commission on the Project "Laboratory and field scale evaluation of agricultural use of sewage sludge. March, 2004, Pretoria 0001, South Africa.
- Sonon, L.S., Gaskin, J., 2012. Metal Concentration Standards for Land Application of Biosolids and Other By-products in Georgia. Bulletin No. 1353. University of

Georgia and Fort Valley State University, USA.

Stocks, C., Barker, A.J., Guy, S., 2002. The composting of brewery sludge. J. Inst. Brew. 108, 452–458.

- Tarraso'n, D., Ojeda, G., Ortiz, O., Alcañiz, J.M., 2008. Differences on nitrogen availability in a soil amended with fresh, composted and thermally-dried sewage sludge. Bioresour. Technol. 99, 252–259.
- Toth, G., Hermann, T., Da Silva, M.R., Montanarella, L., 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. Environ. Int. 88, 299–309.
- UN, 2015. Transforming Our World: the 2030 Agenda for Sustainable Development. United Nations. https://sustainabledevelopment.un.org/.../transformingourworld/ publica (Accessed 8 February 2016).
- VBI, 1998. Bicarbonate Bad Guy in Western Soil, Water. Verdegaal brother inc. http://www.verdegaalbrothers.com/ph-in-soil.pdf (Accessed 20 February 16).
- Walkley, A., Black, C.A., 1934. An examination of different methods for determining soil organic matter and the proposed modification by the chromic acid titration method. Soil Sci. 37, 29–37.
- Wang, Y., Lin, Y., Chiu, P.C., Imhoff, P.T., Guo, M., 2015. Phosphorus release behaviors of poultry litter biochar as a soil amendment. Sci. total Environ. 512, 454–463.
- Yıldız, N., 2008. Diatomite: a New Substrate for Hydroponics. International Meeting on Soil Fertility Land Management and Agroclimatology, Turkey.
 Yusuf, M.A., 2010. Soil Survey and Classification Lecture Series. Geography
- Yusuf, M.A., 2010. Soil Survey and Classification Lecture Series. Geography Department Bayero University, Kano, Nigeria.