Sodic Soil Reclamation Potential of Gypsum and Biochar Additions: Influence on Physicochemical Properties and Soil Respiration

Eric Schultz, Amitava Chatterjee, Thomas DeSutter, and David Franzen

Soil Science, North Dakota State University, Fargo, North Dakota, USA

ABSTRACT
Reclamation of sodic soils is proving increasingly vital as greater land area becomes salt-affected in the northern Great Plains of the United States. Flue gas desulfurization gypsum (FGDG) can be an agriculturally important resource for increasing land productivity through the amelioration of sodic soils. Biochar is also considered as an aid in reclaiming degraded soils. In this incubation study, two rates of FGDG (33.6 Mg ha\(^{-1}\) and 66.2 Mg ha\(^{-1}\)), two rates of biochar made from sugar beet (Beta vulgaris L.) pulp (16.8 Mg ha\(^{-1}\)), and one rate of FGDG combined with one rate of biochar (33.6 Mg ha\(^{-1}\) ea.) were applied to a sodic soil. Soil physicochemical properties, including cationic exchange, pH, electrical conductivity (EC\(_e\)), sodium adsorption ratio (SAR\(_e\)), total organic carbon (TOC), water retention, and soil respiration rate, were assessed during and at the end of the incubation period. Addition of FGDG to sodic soil increased EC\(_e\) from 3.5 to 8.4 dS m\(^{-1}\) and decreased SAR\(_e\) from 16 to 9. Biochar addition to sodic soil increased TOC from 62.2 to 99.5 µg g\(^{-1}\) and increased soil respiration rate (mg C kg\(^{-1}\) soil day\(^{-1}\)) on every measurement period. When FGDG and biochar were both added to the sodic soil, TOC did not significantly improve; however, EC\(_e\) increased from 3.5 to 7.7 dS m\(^{-1}\), SAR\(_e\) decreased from 16 to 9, and soil respiration rate increased for all measurements. The results confirm there is potential for FGDG and biochar to reclaim sodic soils alone, and applied in combination.

ARTICLE HISTORY
Received 30 October 2016
Accepted 21 July 2017

KEYWORDS
Biochar; gypsum; land reclamation; sodic soil; soil respiration

Introduction
Globally, excess salts affect over 30% of agricultural land and the salt-affected land area has been continuing to grow (Rengasamy 2006). According to Szabolcs (1989), there were 932.2 million ha of total salt-affected soils worldwide, of which 581.0 million ha were classified as sodic soils. Currently, sodic soils represent 1.9 million ha in the northern Great Plains region of the USA alone (He et al. 2015). Sodic soils are defined in the USA by a sodium adsorption ratio (SAR) from a saturated paste extract of 13 or greater, an exchangeable sodium percentage (ESP) greater than 15, an electrical conductivity (EC) from a saturated paste extract of less than 4 dS m\(^{-1}\), and pH of 8.5 or greater (Richards 1954). These chemical characteristics adversely affect soil physicochemical and biological properties (Rengasamy 2006; Ritz and Haynes 2003) and the soil–plant interactions (Harris 1980; Nelson and Ham 2000).

The primary limitations of sodic soils are physical impedance for root growth and limiting root functions such as nutrient and water uptake (Cairns 1962; Curtin and Naidu 1998). Sodic soils suffer from slaking and swelling (Rengasamy and Sumner 1998), which disperse clay particles and soil organic matter (Backstrom et al. 2004; Norstrom and Bergstedt 2001) and deteriorate the soil.
structure, resulting in poor water and air movement (Levy, Shainberg, and Miller 1998; Nelson and Ham 2000; Shaw, Coughlin, and Bell 1998) and decreased microbial activity (Rietz and Haynes 2003; Yuan et al. 2007). Poor plant growth on sodic landscapes results in physiological deserts, or slickspots (Hopkins, Sweeney, and Richardson 1991), and decreased organic matter inputs, leading to slow soil carbon (C) turnover (Chatterjee et al. 2015).

With shrinking agricultural land, reclamation and amelioration of sodic soils are important to maintain or increase the productivity of salt-affected soils (Nelson and Ham 2000; Oster and Jayawardane 1998). Gypsum is a common amendment for sodic soils reclamation because of its (i) moderate solubility, (ii) ability to replace sodium ion (Na⁺) on the exchange sites with calcium ion (Ca²⁺), and (iii) low cost and widespread availability (Murtaza et al. 2009, 2013; Oster 1993; Qadir et al. 2006; Sakai, Matsumoto, and Sadakata 2004). Gypsum also improves soil aggregation and structure (Franzen, Rehm, and Gerwing 2006), besides being a potential source of sulfur (S, 18–19%) and Ca (23–24%) (DeSutter, Lukach, and Cihacek 2011; Franzen and Lukach 2007; Franzen, Rehm, and Gerwing 2006).

Recently, there has been focus on flue gas desulfurization gypsum (FGDG) as an alternative to mined gypsum for utilization as an amendment of sodic soils (DeSutter and Cihacek 2009; Korcak 1998; Sakai, Matsumoto, and Sadakata 2004). FGDG is a by-product of wet and semidry desulfurization processes of flue gas using limestone in coal-fired power stations (Bolan, Syers, and Sumner 1991; DeSutter and Cihacek 2009; Sakai, Matsumoto, and Sadakata 2004). It is a very pure form of gypsum when produced in this manner (>99%) (Bolan, Syers, and Sumner 1991). There are similarities between FGDG and mined gypsum as a Ca source for replacing Na on soil/clay exchange sites (Clark, Ritchey, and Baligar 2001) and in providing benefits to improve soil physical conditions through amending chemical properties (EC, pH, and SAR) (Korcak 1998). In addition, FGDG has a lower cost than mined gypsum (DeSutter and Cihacek 2009). The potential of FGDG on different salt-affected soils needs to be evaluated before its recommendation to growers.

Besides FGDG, biochar is also often considered as an aid to reclaim degraded soils (Atkinson, Fitzgerald, and Hipps 2010; Lehmann et al. 2011). Biochar is a high-C product of thermal decomposition of organic materials that can be applied to soils (Lehmann and Joseph 2009). Biochar has been shown to positively influence soil through improved pore function (Baronti et al. 2014) and microbial community structure (Lehmann et al. 2011), and increased total C (Rogovska et al. 2014) and field-available water (Jones, Haynes, and Phillips 2010; Rogovska et al. 2014). While biochar has been recently studied extensively examining plant growth components (Drake et al. 2015; Thomas et al. 2013) and soil properties (Herath, Camps-Arbestain, and Hedley 2013; Jien and Wang 2013; Lashari et al. 2013; Thomas et al. 2013), there have been few incubation studies on the effects of biochar and the integrated applications of biochar and gypsum on salt-affected soils.

We have conducted a lab incubation study to determine the (i) physicochemical and (ii) respiration changes of Na-affected soils in response to additions of FGDG, biochar, and both. We hypothesize that FGDG has the potential to change the cationic composition of exchange sites, whereas biochar would supply mineralizable C for microbial growth. Alternatively, we tried to understand the microbial growth of Na-affected soil being limited by an adverse chemical environment or a poor supply of substrates due to slow decomposition (Chatterjee et al. 2015).

Materials and methods

Soil

Bulk soil for incubation was sampled in 2013 from a field site located at 46° 22’N 97° 7’W near Wyndmere, North Dakota, in Richland County. This site was cropped with corn (Zea mays L.) at the time of sampling. The soil was obtained from the 0–15 cm depth. The soil within the field site is classified as a Wyndmere fine-sandy loam (coarse-loamy, mixed, superactive, frigid Aeric Calciaquolls) (Soil Survey Staff 1999) with identifiable highly sodic, nonsaline inclusions present.
Subsequent laboratory analyses were conducted to confirm sodicity as defined by Richards (1954). The sodic soil sample was then air-dried, ground, and sieved (<2 mm).

**Treatment preparation**

This study evaluated the application of two rates of FGDG (33.6 and 67.2 Mg ha\(^{-1}\)), two rates of biochar (16.8 and 33.6 Mg ha\(^{-1}\)), and one rate of FGDG combined with one rate of biochar (33.6 Mg ha\(^{-1}\) of each) to the sodic soil. In addition, the sodic soil was evaluated without amendments. FGDG, previously described and used in DeSutter and Cihacek (2009), DeSutter, Lukach, and Cihacek (2011), and DeSutter, Cihacek, and Rahman (2014), and sugar beet (Beta vulgaris L.) pulp biochar (Char Energy, LLC, Minnesota, USA) chemical properties are shown in Table 1. These amendments were each ground and sieved (< 1 mm).

The seven treatments, all of which contained 1 kg of sodic soil and have associated amendment rates in parenthesis, were (1) sodic soil control, (2) 27 g FGDG (33.6 Mg ha\(^{-1}\)), (3) 54 g FGDG (67.2 Mg ha\(^{-1}\)), (4) 14 g biochar (16.8 Mg ha\(^{-1}\)), (5) 27 g biochar (33.6 Mg ha\(^{-1}\)), and (6) 27 g FGDG plus 27 g biochar (33.6 Mg ha\(^{-1}\) each). Treatment rates for FGDG were similar to the gypsum requirement (GR) outlined by Oster, Shainberg, and Abrol (1999) by the following modified formula:

\[
GR = 0.0086 \left( F \right) \left( D_s \right) \left( \rho \right) \left( CEC \right) \left( SAR_i - SAR_f \right)
\]

where \( F \) is the exchange efficiency factor between Ca-Na and ranges between 1.1 and 1.3 and is unitless, \( D_s \) is the soil depth (m), cation exchange capacity (CEC) in units of mmol c kg\(^{-1}\), \( \rho \) is the soil bulk density (Mg m\(^{-3}\)), and SAR\(_i\) and SAR\(_f\) are the initial and final values for SAR, respectively. Unlike FGDG, biochar has a much wider range of properties and application rates (e.g. 0.2–135.2 Mg ha\(^{-1}\), Glaser, Lehmann, and Zech 2002), and thus, the application rates for biochar in this experiment were determined based on feasibility and comparison purposes. Each of the treatments were combined (with the soil) separately in plastic bags and thoroughly hand mixed to represent

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>FGDG(^{+})</th>
<th>Biochar(^{\ddagger})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N, %(^{\circ})</td>
<td>0.01</td>
<td>2.56</td>
</tr>
<tr>
<td>C, %(^{\circ})</td>
<td>0.16</td>
<td>67.7</td>
</tr>
<tr>
<td>EC, dS m(^{-1}) g(^{-1})</td>
<td>2.60</td>
<td>1.48</td>
</tr>
<tr>
<td>pH, 1:1 DI water</td>
<td>7.5</td>
<td>9.2</td>
</tr>
<tr>
<td>P, (\mu g) g(^{-1})</td>
<td>22</td>
<td>2103</td>
</tr>
<tr>
<td>K, (\mu g) g(^{-1})</td>
<td>480</td>
<td>9906</td>
</tr>
<tr>
<td>Ca, %(^{\circ})</td>
<td>24.3</td>
<td>0.7</td>
</tr>
<tr>
<td>B, (\mu g) g(^{-1})</td>
<td>171</td>
<td>108.8</td>
</tr>
<tr>
<td>Cu, (\mu g) g(^{-1})</td>
<td>&lt;0.8</td>
<td>32.1</td>
</tr>
<tr>
<td>Mo, (\mu g) g(^{-1})</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Na, (\mu g) g(^{-1})</td>
<td>50</td>
<td>2346</td>
</tr>
<tr>
<td>Zn, (\mu g) g(^{-1})</td>
<td>4.3</td>
<td>102.9</td>
</tr>
<tr>
<td>As, (\mu g) g(^{-1})</td>
<td>&lt;2.6</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Cd, (\mu g) g(^{-1})</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr, (\mu g) g(^{-1})</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Ni, (\mu g) g(^{-1})</td>
<td>2.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Pb, (\mu g) g(^{-1})</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Se, (\mu g) g(^{-1})</td>
<td>2.1</td>
<td>&lt;50</td>
</tr>
</tbody>
</table>

\(^{+}\) Flue gas desulfurization gypsum byproduct from the Powder River Basin (sub-bituminous coal) from Wyoming, USA. (Adapted from Potential agricultural uses of flue gas desulfurization gypsum in the northern Great Plains, DeSutter and Cihacek 2009.)

\(^{\ddagger}\) Biochar from Char Energy, LLC, Ada, Minnesota, USA. Analyzed by Agvise Laboratories, Benson, Minnesota, USA.

\(^{\circ}\) Determined using direct combustion.

\(^{\ddagger}\) Determined by saturated slurry extract.

\# Determined by perchloric acid digestion and inductively coupled plasma spectrometry.
incorporation of the amendments. Deionized water was added to achieve 20% gravimetric water content. Gravimetric water content was used for simplicity in maintaining the water content on a mass basis throughout the experiment. After mixing, the treatments were transferred to thin (0.004 mm) plastic bags and placed in polyvinyl chloride (PVC) pipe microcosms for incubation. The PVC microcosms were sealed on the bottom and the top was machined so that a rubber gasket made an airtight seal with the carbon dioxide (CO$_2$) efflux soil chamber, described below. Each core was lightly tapped on the laboratory bench to allow for settling.

**Cation exchange resin strips**

After transferring the treatments into separate PVC microcosms, cation exchange resin strips (part #3009776, type AR204SZRA, GE Water & Process Technologies, Trevose, Pennsylvania, USA) were added. The cation exchange resin strips were cut from a membrane packaged with propylene glycol (C$_8$H$_{18}$O$_3$) antifreeze solution. The membranes were placed into holders that exposed equal surface areas (3.5 cm x 2.5 cm) on both sides of the resin strip to the soil. Preparation of resin strips included flushing the membrane surface with deionized water while in the holders and re-charging the resin strips with hydrogen (H$^+$) ions by submergence in 0.2 M hydrochloric acid (HCl) solution prior to inserting into the soils (Sherrod, Belnap, and Miller 2003). Around 5-cm-deep slits were made in the soil prior to adding the resin strips, allowing for easier placement and complete covering of the strips. Once placed in the slits, the soil was pressed together gently to close the slits against each side of the resin strip, creating the greatest contact area between the strip and the soil. One cation exchange resin strip was placed in each of the 30 PVC microcosms.

**Incubation**

The microcosms were incubated in the dark at 25$^\circ$C. CO$_2$ efflux was measured over a 52-day incubation period. The first efflux measurement was performed 12 days after the beginning of the incubation. The thin soil sample bag draped over the edges of the PVC microcosms was loosely folded, in order to prevent an anaerobic environment, on top of the soil. The PVC microcosms were weighed every 5–8 days and deionized water was added on a mass basis to maintain the target gravimetric water content (20%) throughout the duration of the experiment. The cation exchange resin strips were replaced once, following procedures outlined by Sherrod, Belnap, and Miller (2003), during the 52-day incubation period, on day 28. Resin strips were rinsed with deionized water to remove any soil residue and placed in individual capped tubes filled with 100 mL of 2 M HCl solution completely submerging the strips to desorb all ions, and then refrigerated until analysis of cation concentrations (Sherrod, Belnap, and Miller 2003).

**Soil respiration**

Soil respiration was measured by quantifying the headspace CO$_2$ concentration within each PVC microcosm using a PP Systems EGM-4 infrared gas analyzer equipped with an SRC-1 Soil Respiration Chamber (PP Systems, Amesbury, MA, USA). The SRC-1 Soil Respiration Chamber is shown in Figure 1 and was placed on top of the PVC microcosms.

The CO$_2$ efflux was measured every 4–12 days for a total of seven times over the duration of the incubation experiment. Prior to measuring CO$_2$ efflux, the loosely folded bag on top of the soil was opened to refresh the headspace in the cores with a fan for approximately one-half hour. The CO$_2$ efflux is the rate of increase in CO$_2$ concentration in the headspace measured over a continuous 125-second period from which the CO$_2$ respiration rate (g [CO$_2$] m$^{-2}$ h$^{-1}$) is calculated. Readings from the infrared gas analyzer were made and corrected for headspace volume by following the recommended settings of the manufacturer (PP Systems, Amesbury, MA, USA). The CO$_2$ respiration rate (g) for each measurement was converted to mg of C respired per kg of soil per day using the following equation:
Figure 1. Setup of SRC-1 Soil Respiration Chamber (A), which is equipped with an EGM-4 Infrared gas analyzer (B) (PP Systems, Amesbury, MA, USA), used to quantify headspace CO$_2$ concentration. Also featured in (A) are other PVC microcosms containing treatments within thin (0.004 mm) bags loosely folded on top of the soil.

\[
X = \frac{\text{Atomic weight of Carbon} \times A \times 24 \times 1000}{\text{Atomic weight of CO}_2 \times \text{Mass of soil (g)}}
\]

where \(X\) is mg C kg$^{-1}$ soil day$^{-1}$, \(A\) is CO$_2$ respiration rate (g [CO$_2$] m$^2$ h$^{-1}$), 24 represents the hour to day conversion, and 1000 represents the g to mg conversion.

**Chemical properties**

At the conclusion of the incubation experiment, a 150 g soil sample was destructively taken from each PVC microcosm. Deionized water was then added to each sample while stirring with a spoon until it reached the criteria for saturation defined in USDA Handbook 60 (Richards 1954). Saturated pastes were then allowed to equilibrate for 12 h before solution phases of the saturated pastes were extracted under suction using a Buchner funnel and vacuum pump. The pH was determined using a pH meter (13–636-AB15B, Fisher Scientific), EC$_w$ from a Hach conductivity meter (Sension 378; Hach Co., Loveland, CO, USA), and Ca, Mg, and Na concentrations using atomic absorption spectrophotometry (Model 200A; Buck Scientific, Inc.). SAR$_w$ was then subsequently calculated as
\[ \text{SAR}_{\text{e}} = \frac{\text{C}_{\text{Na}}}{\sqrt{\left(\frac{\text{C}_{\text{Ca}} + \text{C}_{\text{Mg}}}{2}\right)}} \]

where C represents the concentration of a particular cation indicated by the subscript (mmol, L\(^{-1}\)) (Richards 1954). Total soluble organic C (TOC) was measured using a TOC-V CPH total organic C analyzer (Shimadzu Scientific Instruments, Chiyoda-ku, Tokyo). Cation exchange resin strips were removed from refrigeration and shaken for 1 h (Sherrod, Belnap, and Miller 2003). The strips were removed from the solution, and the solution was used for quantifying cation calcium, magnesium, potassium, and sodium (Ca, Mg, K, and Na) concentrations using atomic absorption spectrophotometry (Model 200A; Buck Scientific, Inc.).

**Physical properties**

Particle size analysis was determined using the hydrometer method (ASTM 152-H Soil Hydrometer, H-B Instrument Co.) following the procedure of Gee and Bauder (1986). Particle size analysis was performed on sodic soil that was not incubated and the results for the sodic soil were 64.3% sand, 18.7% silt, and 17.0% clay.

The influence of treatments on water retention was determined at applied pressures of \(-33\) kPa and \(-1500\) kPa on soil taken from the PVC microcosms at the conclusion of the incubation, following the procedure outlined by He et al. (2015). Each soil was added to the ceramic plate to the height of the soil-containment ring (5 cm diameter, height of 1 cm) and allowed to saturate for 20 h. Pressure (\(-33\) kPa or \(-1500\) kPa) was then applied for 48 h, followed by determination of the gravimetric soil water content.

**Statistical analyses**

Seven treatments consisting of two different amendments (FGDG and biochar) at two application rates each and a combination of both biochar and FGDG were arranged as a completely randomized block design with five replications. Mean values of seven treatments were separated using Fisher’s Least Significant Difference test at 95% significance level. All statistical analyses were conducted using SAS Enterprise Guide 4.3 (SAS Institute Inc., Cary, NC, USA).

**Results**

**Cation exchange resin strips**

Cation concentrations obtained 28 days after incubation (Table 2) showed significant effects from all treatments on K\(^+\) concentration. Additions of FGDG significantly decreased K\(^+\) concentration, while the biochar and FGDG + biochar significantly increased K\(^+\) concentration. The concentration of Na\(^+\) was significantly reduced by FGDG and FGDG + biochar and not significantly influenced by biochar.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>Na(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodic control</td>
<td>430 ± 61(^a)</td>
<td>209 ± 14(^a)</td>
<td>2.43 ± 0.36(^a)</td>
<td>137 ± 24.8(^a)</td>
</tr>
<tr>
<td>FGDG (33.6 Mg ha(^{-1}))</td>
<td>433 ± 29(^b)</td>
<td>200 ± 26(^ab)</td>
<td>1.82 ± 0.19(^b)</td>
<td>79.0 ± 10.7(^b)</td>
</tr>
<tr>
<td>FGDG (67.2 Mg ha(^{-1}))</td>
<td>450 ± 28(^a)</td>
<td>201 ± 25(^ab)</td>
<td>1.86 ± 0.36(^a)</td>
<td>79.0 ± 10.9(^a)</td>
</tr>
<tr>
<td>Biochar (16.8 Mg ha(^{-1}))</td>
<td>359 ± 35(^b)</td>
<td>180 ± 17(^b)</td>
<td>3.68 ± 0.31(^a)</td>
<td>124 ± 33.2(^ab)</td>
</tr>
<tr>
<td>Biochar (33.6 Mg ha(^{-1}))</td>
<td>381 ± 23(^bc)</td>
<td>181 ± 19(^bc)</td>
<td>5.21 ± 0.66(^a)</td>
<td>117 ± 15.8(^bc)</td>
</tr>
<tr>
<td>FGDG + Biochar (33.6 Mg ha(^{-1}) ea.)</td>
<td>427 ± 18(^ab)</td>
<td>178 ± 19(^b)</td>
<td>4.67 ± 0.49(^a)</td>
<td>98.8 ± 13.2(^bc)</td>
</tr>
</tbody>
</table>

\(^{1}\)FGDG = Flue gas desulfurization gypsum. Letters are used to indicate significant differences (\(p < 0.05\)) between treatments within columns.

Table 2. Average (mean ± standard deviation, \(N = 5\)) of cation concentrations (\(\mu\)g g\(^{-1}\)) obtained from cation exchange resin strips 28 days after incubation for seven treatments\(^1\). Treatment rate accompanies the treatment type(s) in parenthesis.
only. Minimal influence was observed on Mg$^{2+}$ concentration by all treatments, whereas Ca$^{2+}$ concentration was not significantly different for FGDG with and without biochar, but biochar alone significantly reduced Ca$^{2+}$ concentration. Cation exchange resin strips obtained 52 days after incubation (Table 3) resulted in relatively similar relationships among cation concentrations. Potassium (K$^+$) concentration once again was significantly increased with biochar and FGDG + biochar, and not significantly influenced by FGDG additions. Applications of FGDG and FGDG + biochar significantly reduced Na$^+$ concentration and biochar alone had no significant effect on Na$^+$ concentration. Exchangeable Mg$^{2+}$ concentration was again minimally influenced by treatments. The highest FGDG rate and FGDG + biochar significantly increased Ca$^{2+}$ concentration, whereas biochar alone did not influence the Ca$^{2+}$ concentration.

### Respiration

Biochar had the most significant effects on respiration rate, alone and with FGDG (Table 4). Treating Na-affected soils with FGDG had no significant effect on the respiration rate. Biochar and FGDG + biochar additions significantly increased the respiration rate 12, 19, 23, and 52 days after incubation. When biochar was added at the higher rate alone and in the FGDG + biochar addition, the respiration rate increased significantly 28 days after incubation. Respiration rate was also significantly increased by each biochar treatment 32 days after incubation, while only the higher biochar rate significantly increased respiration rate 43 days after incubation.

### Table 3. Average (mean ± standard deviation, N = 5) of cation concentrations (μg g$^{-1}$) obtained from cation exchange resin strips 52 days after incubation for seven treatments$^1$. Treatment rate accompanies the treatment type(s) in parenthesis.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>K$^+$</th>
<th>Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodic control</td>
<td>355 ± 23$^a$</td>
<td>247 ± 28$^b$</td>
<td>3.12 ± 0.96$^c$</td>
<td>93.0 ± 21.6$^d$</td>
</tr>
<tr>
<td>FGDG (33.6 Mg ha$^{-1}$)</td>
<td>404 ± 50$^{abc}$</td>
<td>215 ± 21$^{abc}$</td>
<td>2.45 ± 0.50$^c$</td>
<td>63.0 ± 10.5$^c$</td>
</tr>
<tr>
<td>FGDG (67.2 Mg ha$^{-1}$)</td>
<td>436 ± 68$^a$</td>
<td>238 ± 30$^{ab}$</td>
<td>2.31 ± 0.49$^c$</td>
<td>69.7 ± 18.8$^{abc}$</td>
</tr>
<tr>
<td>Biochar (16.8 Mg ha$^{-1}$)</td>
<td>376 ± 23$^{ab}$</td>
<td>224 ± 13$^{abc}$</td>
<td>5.23 ± 0.46$^b$</td>
<td>88.2 ± 14.1$^{abc}$</td>
</tr>
<tr>
<td>Biochar (33.6 Mg ha$^{-1}$)</td>
<td>360 ± 32$^a$</td>
<td>208 ± 14$^{bc}$</td>
<td>7.64 ± 2.47$^a$</td>
<td>77.7 ± 16.0$^{abc}$</td>
</tr>
<tr>
<td>FGDG + Biochar (33.6 Mg ha$^{-1}$ ea.)</td>
<td>418 ± 49$^{ab}$</td>
<td>201 ± 40$^c$</td>
<td>5.58 ± 0.83$^b$</td>
<td>57.0 ± 21.6$^c$</td>
</tr>
<tr>
<td>P = 0.0396</td>
<td>P = 0.0762</td>
<td>P &lt; 0.0001</td>
<td>P = 0.0221</td>
<td></td>
</tr>
</tbody>
</table>

$^1$FDGG = Flue gas desulfurization gypsum. Letters are used to indicate significant differences (p < 0.05) between treatments within columns.

### Table 4. Respiration rates of six treatments for seven readings 12, 19, 23, 28, 32, 43, and 52 days after incubation. The treatment rate accompanies the treatment type(s) in parenthesis.

<table>
<thead>
<tr>
<th>Days after Incubation</th>
<th>12</th>
<th>19</th>
<th>23</th>
<th>28</th>
<th>32</th>
<th>43</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodic control</td>
<td>0.16 ± 0.10$^{a,d}$</td>
<td>0.25 ± 0.03$^{b}$</td>
<td>0.11 ± 0.10$^{d}$</td>
<td>0.17 ± 0.14$^{d}$</td>
<td>0.11 ± 0.06$^{d}$</td>
<td>0.24 ± 0.10$^{d}$</td>
<td>0.13 ± 0.09$^{d}$</td>
</tr>
<tr>
<td>FGDG (33.6 Mg ha$^{-1}$)</td>
<td>0.12 ± 0.11$^{b}$</td>
<td>0.12 ± 0.09$^{b}$</td>
<td>0.12 ± 0.12$^{d}$</td>
<td>0.20 ± 0.11$^{dd}$</td>
<td>0.12 ± 0.16$^{dd}$</td>
<td>0.11 ± 0.04$^{d}$</td>
<td>0.08 ± 0.03$^{d}$</td>
</tr>
<tr>
<td>FGDG (67.2 Mg ha$^{-1}$)</td>
<td>0.16 ± 0.28$^{b}$</td>
<td>0.18 ± 0.09$^{d}$</td>
<td>0.14 ± 0.09$^{d}$</td>
<td>0.04 ± 0.04$^{d}$</td>
<td>0.09 ± 0.10$^{d}$</td>
<td>0.13 ± 0.07$^{dd}$</td>
<td>0.11 ± 0.06$^{d}$</td>
</tr>
<tr>
<td>Biochar (16.8 Mg ha$^{-1}$)</td>
<td>0.58 ± 0.31$^{a}$</td>
<td>0.54 ± 0.17$^{d}$</td>
<td>0.46 ± 0.20$^{d}$</td>
<td>0.33 ± 0.13$^{d}$</td>
<td>0.47 ± 0.24$^{dd}$</td>
<td>0.31 ± 0.20$^{d}$</td>
<td>0.35 ± 0.16$^{d}$</td>
</tr>
<tr>
<td>Biochar (33.6 Mg ha$^{-1}$)</td>
<td>0.66 ± 0.43$^{d}$</td>
<td>0.48 ± 0.25$^{d}$</td>
<td>0.48 ± 0.14$^{d}$</td>
<td>0.68 ± 0.18$^{dd}$</td>
<td>0.59 ± 0.21$^{d}$</td>
<td>0.66 ± 0.26$^{d}$</td>
<td>0.52 ± 0.10$^{d}$</td>
</tr>
<tr>
<td>FGDG + Biochar (33.6 Mg ha$^{-1}$ ea.)</td>
<td>0.59 ± 0.30$^{d}$</td>
<td>0.55 ± 0.12$^{d}$</td>
<td>0.45 ± 0.09$^{d}$</td>
<td>0.51 ± 0.21$^{d}$</td>
<td>0.33 ± 0.15$^{d}$</td>
<td>0.38 ± 0.14$^{d}$</td>
<td>0.37 ± 0.08$^{d}$</td>
</tr>
</tbody>
</table>

P = 0.0078 P < 0.0001 P < 0.0001 P < 0.0001 P < 0.0001 P < 0.0001 P < 0.0001

$^1$Values represented in table are means of five replications for each treatment with standard deviations. Standard deviations followed by different letters indicate significant differences between treatments (p < 0.05) for each column pertaining to that reading (days after incubation) within each column. Least significant differences (mg C kg$^{-1}$ soil day$^{-1}$) for each day after incubation reading: 12: 0.37; 19: 0.18; 23: 0.17; 28: 0.19; 32: 0.21; 43: 0.20; 52: 0.12.
Table 5. Soil chemical properties for seven treatments from saturated paste solutions. The treatment rate accompanies the treatment type(s) in parenthesis.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>EC&lt;sub&gt;e&lt;/sub&gt;</th>
<th>SAR&lt;sub&gt;e&lt;/sub&gt;</th>
<th>TOC &lt;sub&gt;µg g&lt;sup&gt;-1&lt;/sup&gt;&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodic control</td>
<td>8.3 ± 0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.5 ± 0.60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16 ± 2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>62.2 ± 1.73&lt;sup&gt;cd&lt;/sup&gt;</td>
</tr>
<tr>
<td>FGDG (33.6 Mg ha&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>8.0 ± 0.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.4 ± 0.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9 ± 3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>50.2 ± 3.57&lt;sup&gt;cd&lt;/sup&gt;</td>
</tr>
<tr>
<td>FGDG (67.2 Mg ha&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>8.0 ± 0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.2 ± 0.84&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8 ± 2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>51.2 ± 3.54&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Biochar (16.8 Mg ha&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>8.3 ± 0.1&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>3.4 ± 0.41&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13 ± 2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>81.4 ± 13.9&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Biochar (33.6 Mg ha&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>8.4 ± 0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.4 ± 0.29&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14 ± 2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>99.5 ± 9.35&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>FGDG + Biochar (33.6 Mg ha&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>8.1 ± 0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.7 ± 0.56&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9 ± 1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>68.9 ± 15.9&lt;sup&gt;bc&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Values represented in table are means of five replications for each treatment with standard deviations. Standard deviations followed by different letters indicate significant differences between treatments (<i>p</i> < 0.05). Least significant differences: pH: 0.10; EC: 0.80; SAR<sub>e</sub>: 2.07; TOC: 12.6.

Chemical properties

Soil pH ranged from 8.0 to 8.4 (Table 5) and FGDG with and without biochar significantly lowered the pH from 8.3 (control) to 8.0, 8.0, and 8.1, respectively, while the higher biochar rate significantly raised the pH from 8.3 (control) to 8.4. Soil EC<sub>e</sub> was markedly influenced by FGDG, with FGDG and FGDG + biochar significantly increasing EC<sub>e</sub> by 4.9, 4.7, and 4.2 dS m<sup>-1</sup>, respectively. Biochar at either treatment rate did not significantly influence the EC<sub>e</sub>. SAR was significantly decreased with all treatments. Biochar significantly increased TOC by 19.2 and 37.3 µg g<sup>-1</sup>, respectively, while FGDG and FGDG + biochar did not significantly influence TOC.

Water retention

Water retention was only significantly influenced by FGDG (Figure 2). FGDG significantly decreased water retention at −33 kPa, while only the lower FGDG rate significantly decreased water retention at −1500 kPa.

![Figure 2. Water retention for −33 kPa and −1500 kPa means for five replications of each treatment. The vertical bars represent standard deviations. Letters above bars indicate significant differences between treatment means within −33 kPa (p = 0.0047) and −1500 kPa (p = 0.0260). † Flue gas desulfurization gypsum treatment rate of 33.6 Mg ha<sup>-1</sup>. ‡ Flue gas desulfurization gypsum treatment rate of 67.2 Mg ha<sup>-1</sup>. § Biochar treatment rate of 16.8 Mg ha<sup>-1</sup>. ¶ Biochar treatment rate of 33.6 Mg ha<sup>-1</sup>.](image-url)
Discussion

We found significant changes in the soil exchange compositions and microbial activity of Na-affected soils in response to FGDG and biochar additions. Our results support that FGDG alters the cationic compositions of the exchange sites and that biochar supplies mineralizable C for microbial growth.

Cation exchange resin strips

Preferential adsorption, depending on the supply of each cation, intensity of removal processes, and adsorption strength (Troeh and Thompson 2005), can explain cation concentrations obtained 28 and 52 days after incubation (Tables 2 and 3). Of the influences on adsorption, in this study adsorption strength affected cation exchange the greatest. Adsorption strength, sequenced by relative attractive forces known as the Lyotropic series (Brady and Weil 1999), aluminum (Al$^{3+}$) > Ca$^{2+}$ > Mg$^{2+}$ > K$^+$ = ammonium (NH$_4^+$) > Na$^+$, influenced exchangeable K$^+$ and Na$^+$ the greatest, resulting in the most significant differences in measured cation concentrations. For example, increased exchangeable K$^+$ with the addition of biochar is similar to the findings of Lehmann et al. (2003) and Chan et al. (2007); however, the nonsignificant Na$^+$ concentrations with biochar addition in this study were different from these same studies. Supply of water, directly effecting cations exchanged (and in solution), poured over the top of the microcosms to maintain gravimetric water content at 20% in our study, may also have dictated the measured cation concentrations, thereby influencing the values obtained 28 days after incubation versus the values obtained 52 days after incubation. Equilibrium relations between the adsorbed cations and the soil solution (Lindsay 1979; Troeh and Thompson 2005) effectively determined cation concentrations for the FGDG treatments with this addition of Ca$^{2+}$.

Respiration

Substantially increased respiration for biochar treatments can be mostly attributed to the C added upon the addition of biochar. However, comparing the decreased respiration of FGDG to the biochar, the lightweight, low-density nature of biochar also influenced this increased respiration by reducing the bulk density. Reduced bulk density through the addition of biochar was also determined by Rogovska et al. (2014), which implies increased pore volume and greater soil air exchange. On the contrary, Yu et al. (2014) observed increased bulk density from FGDG treatments. In our study, the decreased respiration can be partially attributed to the components of increased bulk density from FGDG addition as the environmental conditions (i.e. insufficient leaching) were similar to those of Yu et al. (2014) where Na$^+$ was found to recapture its place on the exchange complex from the Ca$^{2+}$. In our study, FGDG addition resulted in respiration that was lower than the sodic soil control as well. These results are consistent with the findings of Clark et al. (2007) and Mavi et al. (2012), where gypsum treatments had lower cumulative respiration when compared directly to a sodic soil control. Similar to Mavi et al. (2012), we conclude that the increased soil organic matter solubility of the sodic soil control versus the FGDG treatments contributed to the greater respiration.

Chemical properties

Significantly decreased SAR$_c$ values for the FGDG treatments indicate Ca$^{2+}$ is within the solution phase and therefore will be competitive for soil exchange sites with Na$^+$. FGDG and biochar have very different Ca$^{2+}$ concentrations, 24.7% versus 0.7% on a mass basis (Table 1). Biochar, therefore, did not influence the SAR$_c$ nearly as much as the TOC. Increased EC$_c$ is also a result of the dissolution of Ca$^{2+}$ and sulfate (SO$_4^{2-}$) of the FGDG. There were definite increases in EC$_c$ for all FGDG treatments, and a slight decrease in the biochar treatments because it is a poor source of soluble Ca$^{2+}$. 
Lehmann et al. (2003) and Chan et al. (2007) previously found that biochar substantially increased soil pH when applied to acid soils. However, in our study, similar to the findings of Lentz and Ippolito (2012), the biochar effect on soil pH was minimal when applied to calcareous soil. Lentz and Ippolito (2012) also found that biochar increased TOC, as expected, with the addition of this high-C (67.7% by weight, Table 1) source.

Water retention

Overall, water retention values at field capacity (~33 kPa) and wilting point (~1500 kPa) resemble results from He et al. (2015), which show decreases in water retention with increasing ECₑ as well as increases in water retention with increased SAR values. We attribute these results to the threshold values developed by He, DeSutter, and Clay (2013) and He et al. (2015), reflecting dispersion and swelling impact on the water retention of soils.

Conclusions

We found that the addition of FGDG and biochar to sodic soil improves soil physicochemical properties and respiration. Higher application rates (33.6 Mg ha⁻¹ of biochar and 67.2 Mg ha⁻¹ of FGDG) did not result in increased improvement in soil physicochemical properties and respiration over lower application rates (16.8 Mg ha⁻¹ of biochar and 33.6 Mg ha⁻¹ of FGDG) of each amendment. However, the positive effects upon the addition of both of these amendments (33.6 Mg ha⁻¹ ea.) show the benefit of FGDG on soil physicochemical properties and the benefit of biochar on respiration. Improving these elements together results in the increased potential of reclamation. Therefore, this research demonstrates that combining FGDG and biochar has an advantage in the reclamation potential of sodic soils over the addition of these amendments individually.

Acknowledgements

We thank Kevin Horsager and Nathan Derby for assistance throughout the chemical analyses. We also thank the two anonymous reviewers for their comments that have greatly improved this manuscript.

Funding

This work was supported by the North Dakota Corn Council.

References


