Binary Exchanges of Calcium, Magnesium, and Potassium on Thermally Desorbed Soil

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Thermal desorption (TD) remediates hydrocarbon-contaminated soil by heating the soil (200–500°C) to volatilize the hydrocarbons, effectively removing the contaminant from the soil. Knowledge of the effects of TD on remediated soil for agricultural crop production are limited, but cation exchange capacity (CEC) and selectivity for cations can be good indicators of plant productivity potential. In this study, the CEC and selectivity of cations of TD-treated and untreated topsoil and subsoil were compared using binary exchange measurements of Ca–Mg, Ca–K, and Mg–K. The tested soils were illite and smectite-dominated Mollisols that were collected near an active TD-remediation site in northwest North Dakota. Vanselow selectivity coefficients and Gibb's free energies (ΔG_{ex}) were computed. For all three exchanges, significant differences were observed in ΔG_{ex} between the untreated and TD-treated topsoil. In the Ca–Mg exchange, both the untreated and TD-treated topsoil preferred Ca, whereas both TD-treated and untreated subsoils preferred Mg. For the Ca–K and Mg–K exchanges, all treatments preferred K. Cation exchange capacity values were significantly greater in the untreated subsoil of the Ca–Mg exchange and the untreated topsoil and subsoil of the Ca–K exchange than in the TD-treated soils. The differences may be caused by contrasts in soil organic C and mineralogy. Although CEC and ΔG_{ex} differed between untreated and TD-treated soils, the cation selectivities were not altered, suggesting that the magnitude of the differences may not require alternative fertility management to retain previous soil productivity.

Abbreviations: CEC, cation exchange capacity; ΔG_{ex}, Gibb's free energy; *I*, ionic strength; K_V, Vanselow selectivity coefficient; SOC, soil organic C; SS, subsoil; SS-TD, thermal desorption-treated subsoil; TD, thermal desorption; TD-TS, thermal desorption-treated topsoil; TS, topsoil

Modern society is dependent on energy, which is most often satisfied by extracting fossil fuels, including oil (Lehmann, 2007). However, this creates a risk of oil spills that can contaminate soils with a broad range of hydrocarbons (Khamehchiyan et al., 2006). The properties of hydrocarbon fluid and the nature and topography of the terrestrial environment influence the mobility of an oil spill (Osuji et al., 2005). Crude oil has been reported to be increasingly destructive to soil biota and crop growth through its negative effects on soil conditions, microorganisms, and plants (Baker, 1978; Osuji et al., 2005). Attempts to reclaim crude oil-contaminated soils have included additions of poultry manure, sawdust, or lime or Ca and Mg applications (Osuji et al., 2005; Sayed and Zayed, 2006; John-Dewole and Sanni-Awal, 2013). Bioremediation has been used to facilitate recovery efforts by the use of aerobic respiration of microorganisms that transforms petroleum hydrocarbons to CO_2 and water, or other less toxic substances. A simpler method of bioremediation is in situ land-farming that utilizes soil microorganisms and the standard farming procedures of irrigation and aeration to reduce petroleum hydrocarbon concentrations (Onwurah et al., 2007).

Core Ideas

- **Thermal desorption is used to remediate contaminated soil.**
- **Thermal desorption can alter Gibb's free energies.**
- **Thermal desorption at 350°C did not change cation selectivity.**

Soil Sci. Soc. Am. J.
doi:10.2136/sssaj2017.01.0028
Received 19 Jan. 2017.
Accepted 26 Apr. 2017.
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An alternative method that reliably reduces hydrocarbon concentrations in contaminated soil to desirable levels is TD.

Thermal desorption remediates hydrocarbon-contaminated soils, preserving the remediated soil for reuse and eliminating the liability of a landfill (Hamby, 1996). In the TD process, contaminated soil is heated to between 200 and 500°C in a chamber in which hydrocarbon desorption is facilitated by volatilization, removing the contaminant from the soil to achieve a desired concentration. The treated soil then exits the chamber, is quenched with water, and cooled. The volatilized hydrocarbon gases are routed from the chamber and through a filtration unit where the dust and particulates are removed. After filtration, the hydrocarbon gases enter a secondary chamber where they are combusted and converted to CO_2 and water vapor. The remediated soil can then be returned to the original excavation site at the discretion of the end-user (Hamby, 1996).

One potential impact of heating the soil during the TD process may be changes to CEC caused by alterations in soil mineralogy or loss of soil organic matter (Bonnard et al., 2010; O'Brien et al., 2016). The temperature threshold for clay deterioration is normally above 500°C (Pape et al., 2015). For instance, kaolinite structure begins to degrade at 530°C, whereas bentonite, which is often composed of smectite minerals, does not deteriorate through heating until temperatures reach over 700°C (Tan et al., 1986). The CEC of a soil is a measure of its ability to hold and exchange nutrients like Ca, K, and Mg and is a good indicator of soil fertility (Mukherjee et al., 2011; Jeffery et al., 2011). The fate of nutrients in soil is influenced by the ionic radius, valence, the degree of hydration, and the selectivity of the exchanger for one cation over another (Teppen and Miller, 2006; Rigon et al., 2015). Thus any changes to CEC or cation preference may require alternative nutrient management strategies.

Table 1. Previous data (O'Brien et al., 2016) collected on particle size distribution, specific surface area, mineralogical analysis and distribution of clay fraction, and soil organic C of untreated and thermal desorption (TD)-treated soils. Standard errors can be found in O'Brien et al. (2016). Reprinted with permission from *Journal of Environmental Quality*.†

	TS	TS-TD	SS	SS-TD
	Particle-size distribution			
	g kg^{-1}			
Sand	473	494	480	490
Silt	335	319	314	322
Clay	192	188	206	188
	Textural class			
	Loam	Loam	Loam	Loam
	Specific surface area			
	m^2 g^{-1}			
	89.6	71.2	93.3	80.0
	Mineral			
	% by weight			
Quartz	48.2	42.3	38.6	40.9
Plagioclase	17.4	16.8	13.9	13.6
Microcline	6.7	3.3	5.2	4.8
Muscovite or illite	6.2	6.0	5.6	6.9
Kaolinite	0.6	0.7	0.7	Trace
Amphibole	Trace	Trace	0.7	Trace
Dolomite	2.1	2.9	4	2.5
Calcite	Trace	0.4	1	1.1
Amorphous	18.9	27.5	30.2	30.1
	Clay fraction			
	% by weight			
Smectite	42	42	57	51
Illite	46	47	33	37
Kaolinite	8	8	7	9
Chlorite	4	3	3	3
	Soil organic C			
	g kg^{-1}			
	28.2	19.8	15.2	10.9

† TS, topsoil; SS, subsoil; TD-TS, TD-treated topsoil; SS-TD, TD-treated subsoil.

The objectives of this study were to determine whether the TD process alters the CEC, cation preference, and the magnitude of preference of an agricultural topsoil and subsoil. The null hypothesis was that no differences would be observed in CEC, cation selectivity, or ΔG_{ex} between the untreated and TD-treated soils. The results of this study will indicate if TD has implications for the preference of major cations in agricultural soil and thus long-term fertility considerations.

MATERIALS AND METHODS

The soil samples were collected in Mountrail County, ND, near an active remediation site that had been contaminated with Bakken crude oil from a pipeline leak (O'Brien et al., 2016). The soils at this site are mapped as Williams–Zahl loams (Williams: fine-loamy, mixed, superactive, frigid Typic Argiustolls; Zahl: fine-loamy, mixed, superactive, frigid Typic Calciustolls) with productivity indices of 76 and 60, respectively. Untreated, noncontaminated topsoil (TS) and subsoil (SS) were collected from uncontaminated stockpiles outside the boundary of the remediation site. Untreated, noncontaminated TS and SS were then treated separately with an RS40 Thermal Desorption/Oxidation unit (Nelson Environmental Ltd., Edmonton, AB, Canada) at 350°C for 15 min to generate TD-treated topsoil (TS-TD) and TD-treated subsoil (SS-TD). This is the same temperature and time used to reduce oil-contaminated soil at the site to less than 500 mg kg^{-1} of total petroleum hydrocarbons.

Previous research (O'Brien et al., 2016) was conducted on the soils to determine particle size distribution, specific surface area, mineralogical analysis and distribution of clay, and soil organic C (SOC). Both treated and untreated TS and SS profiles were classified as loams (Table 1; O'Brien et al., 2016). Particle size distribution was conducted via the hydrometer method (Gee and Or, 2002; ASTM International, 2007). Specific surface area was calculated using the ethylene glycol monoethyl ether retention method (Pennell, 2002). Mineralogical and clay analysis was performed by using X-ray diffraction at a private laboratory (Activation Laboratories Ltd., Ancaster, ON, Canada) and total C and soil inorganic C were evaluated with a PrimacsSLC TOC Analyzer (Skalar Analytical B.V., Breda, The Netherlands); SOC was determined as the difference between total C and soil inorganic C.

Table 2. Binary exchange of Ca–Mg solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated topsoil profile (TS) and the thermally desorbed, noncontaminated topsoil profile (TS-TD).

Exchanger test	Solution composition		TS				TS-TD			
			Exchanger composition				Exchanger composition			
	Ca	Mg	Mg	Ca	CEC	K_v	Mg	Ca	CEC	K_v
	—mol L^{-1}—		—mol kg^{-1}—		$cmol_c\ kg^{-1}$		—mol kg^{-1}–		$cmol_c\ kg^{-1}$	
1	0.019	0.000	0.000	0.064	12.8 (0.6)†	–	0.000	0.048	9.7 (1.1)	–
2	0.016	0.003	0.008	0.055	12.6 (0.7)	0.85 (0.05)	0.008	0.041	9.9 (1.9)	1.11 (0.29)
3	0.013	0.007	0.022	0.047	13.8 (0.5)	0.90 (0.05)	0.018	0.039	11.5 (0.3)	0.90 (0.01)
4	0.008	0.011	0.034	0.036	14.0 (0.4)	0.70 (0.04)	0.031	0.030	12.3 (0.1)	0.77 (0.03)
5	0.006	0.015	0.049	0.024	14.6 (0.3)	0.84 (0.04)	0.044	0.021	12.9 (0.8)	0.87 (0.08)
6	0.000	0.020	0.074	0.000	14.9 (0.1)	–	0.064	0.000	12.9 (0.3)	–
Average					13.8 (1.0)a‡				11.5 (1.6)b	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant differences ($p < 0.05$) between similar columns.

Methods for cation selectivities between Ca and Mg, Ca and K, and Mg and K followed the batch method described by DeSutter et al. (2006). Initially, soils were equilibrated using 2 M $CaCl_2$ for the Ca–Mg and Ca–K exchanges, and 2 M $MgCl_2$ for the Mg–K exchange on a horizontal shaker for 20 min at 180 oscillations min^{-1}. This process was repeated three times to ensure that all exchange sites were saturated with Ca or Mg. After each salt equilibration, soils were rinsed, shaken three times with deionized water to remove excess salts, then allowed to dry at 25°C. After drying, the soils were ground to pass through a 1.0-mm sieve. Solution phases were prepared using six predetermined equivalent fractions of cations. Equivalent fractions ranged from 0:1 (Ca/Mg, Ca/K, or Mg/K) to 1:0 (Ca/Mg, Ca/K, or Mg/K) (Table 2 to Table 7) while maintaining a constant target ionic strength (I) of 0.05 mol L^{-1}. The six solution concentrations were prepared by pipetting appropriate amounts of 2 M $CaCl_2$, 2 M $MgCl_2$, or 2 M KCl solutions into a 1-L volumetric flask and bringing them to volume with deionized water.

Twenty milliliters of equilibrating solution was then added to 1.0 g of Ca- or Mg-saturated soil that had been weighed into 50-mL polypropylene centrifuge tubes. The soil–solution mixtures were shaken for 20 min on a horizontal shaker (180 oscillations min^{-1}) and centrifuged for 20 min at a relative centrifugal force of 650 × *g*. The supernatant was then decanted and discarded. This process was repeated three times. After equilibration, the soil was washed five times with 20 mL of 95% ethanol by shaking for 10 min on a horizontal shaker (180 osc min^{-1}) followed by centrifugation at a relative centrifugal force of 650 × *g*. After the washings were completed, soils were allowed to air-dry overnight to remove any excess ethanol. Calcium carbonate was detected in the soils by placing a drop of 1 M HCl on a sample of the dry soil. To lessen the dissolution of $CaCO_3$, the cations (Ca, Mg, or K) in each soil were extracted with 20 mL of 1 M sodium acetate (adjusted to pH 8.2) by shaking on the same horizontal shaker for 20 min and centrifuging for 20 min at a relative centrifugal force of 650 × *g*. The supernatant was removed through pipetting and saved. Calcium, Mg, or K concentrations were then determined with an atomic absorption spectrophotometer (210/211 VGP, version 3.94C, Buck Scientific, Norwalk, CT). For the Ca–Mg and Ca–K exchanges, unintentionally dissolved Ca from $CaCO_3$ in the soil was accounted for by subtracting the recorded Ca concentration from the 0% Ca equilibrating solution extractions from each proceeding Ca concentration.

Analysis

For the Ca–Mg exchange, the general binary exchange reaction was:

$$CaX_2 + MgCl_2 \leftrightarrow CaCl_2 + MgX_2; \qquad [1]$$

Table 3. Binary exchange of Ca–Mg solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated subsoil profile (SS) and the thermally desorbed, noncontaminated subsoil profile (SS-TD).

Exchanger test	Solution composition		SS				SS-TD			
			Exchanger composition				Exchanger composition			
	Ca	Mg	Mg	Ca	CEC	K_v	Mg	Ca	CEC	K_v
	—mol L^{-1}—		—mol kg^{-1}—		$cmol_c\ kg^{-1}$		–mol kg^{-1}—-		$cmol_c\ kg^{-1}$	
1	0.019	0.000	0.000	0.043	8.5 (1.6)†	–	0.000	0.048	9.6 (0.9)	–
2	0.016	0.003	0.009	0.040	9.9 (1.1)	1.26 (0.14)	0.008	0.026	6.9 (0.7)	1.75 (0.30)
3	0.013	0.007	0.024	0.032	11.2 (0.9)	1.40 (0.03)	0.021	0.031	10.4 (0.6)	1.31 (0.07)
4	0.008	0.011	0.039	0.023	12.4 (0.75)	1.24 (0.03)	0.034	0.022	11.2 (0.6)	1.16 (0.07)
5	0.006	0.015	0.051	0.015	13.3 (0.7)	1.40 (0.06)	0.048	0.013	12.3 (0.9)	1.50 (0.29)
6	0.000	0.020	0.080	0.000	16.0 (0.5)	–	0.068	0.000	13.6 (0.6)	–
Average					11.9 (2.6)a‡				10.7 (2.3)a	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant differences ($p < 0.05$) between similar columns.

Table 4. Binary exchange of Ca–K solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated topsoil profile (TS) and the thermally desorbed, noncontaminated topsoil profile (TS-TD).

Exchanger test	Solution composition		TS				TS-TD			
			Exchanger composition				Exchanger composition			
	Ca	K	K	Ca	CEC	K_v	K	Ca	CEC	K_v
	—mol L^{-1}—-		—mol kg^{-1}—		cmol$_c$ kg^{-1}		—–mol kg^{-1}—		cmol$_c$ kg^{-1}	
1	0.017	0.000	0.000	0.047	9.3 (0.9)†	–	0.000	0.044	8.7 (0.4)	–
2	0.014	0.010	0.023	0.037	9.6 (0.2)	22.12 (0.41)	0.024	0.034	9.2 (0.1)	27.94 (1.44)
3	0.010	0.022	0.036	0.031	9.7 (0.3)	8.67 (0.54)	0.035	0.027	9.0 (0.1)	9.84 (0.08)
4	0.007	0.030	0.049	0.026	10.1 (0.1)	6.51 (0.03)	0.048	0.021	9.0 (0.1)	7.90 (0.11)
5	0.003	0.042	0.066	0.020	10.6 (0.1)	2.86 (0.06)	0.062	0.015	9.3 (0.1)	3.66 (0.30)
6	0.000	0.051	0.102	0.000	10.2 (0.1)	–	0.094	0.000	9.4 (0.0)	–
Average					9.9 (0.6)a‡				9.1 (0.3)b	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant difference ($p < 0.05$) between similar columns.

Table 5. Binary exchange of Ca–K solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated subsoil profile (SS) and the thermally desorbed, noncontaminated subsoil profile (SS-TD).

Exchanger test	Solution composition		SS				SS-TD			
			Exchanger composition				Exchanger composition			
	Ca	K	K	Ca	CEC	K_v	K	Ca	CEC	K_v
	—mol L^{-1}—		—mol kg^{-1}—		cmol$_c$ kg^{-1}		—mol kg^{-1}—		cmol$_c$ kg^{-1}	
1	0.017	0.000	0.000	0.404	8.0 (0.1)†	–	0.000	0.035	6.9 (0.1)	–
2	0.014	0.010	0.030	0.031	9.3 (0.2)	43.56 (2.84)	0.024	0.027	7.8 (0.1)	36.98 (1.86)
3	0.010	0.022	0.043	0.022	8.7 (0.3)	17.75 (1.06)	0.040	0.019	7.8 (0.2)	18.89 (0.98)
4	0.007	0.030	0.059	0.022	10.3 (0.2)	10.39 (0.14)	0.053	0.017	8.7 (0.1)	11.86 (0.38)
5	0.003	0.042	0.074	0.008	9.0 (0.4)	9.77 (2.29)	0.068	0.008	8.5 (0.3)	8.24 (1.39)
6	0.000	0.051	0.108	0.000	10.8 (0.1)	–	0.102	0.000	10.2 (0.1)	–
Average					9.3 (1.0)a‡				8.3 (1.0)b	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant differences ($p < 0.05$) between similar columns.

Table 6. Binary exchange of Mg–K solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated topsoil profile (TS) and the thermally desorbed, noncontaminated topsoil profile (TS-TD).

Exchanger test	Solution composition		TS				TS-TD			
			Exchanger composition				Exchanger composition			
	Mg	K	K	Mg	CEC	K_v	K	Mg	CEC	K_v
	—mol L^{-1}—		—mol kg^{-1}—		cmol$_c$ kg^{-1}		—mol kg^{-1}–		cmol$_c$ kg^{-1}	
1	0.024	0.000	0.000	0.058	11.7 (0.2)†	–	0.000	0.064	12.7 (0.8)	–
2	0.020	0.010	0.023	0.044	11.0 (0.1)	22.06(0.76)	0.025	0.050	12.6(0.2)	20.91 (0.85)
3	0.016	0.019	0.039	0.037	11.4 (0.4)	14.67 (0.91)	0.037	0.038	11.3 (0.9)	13.29 (0.87)
4	0.010	0.029	0.052	0.028	10.8(0.9)	9.25 (0.33)	0.052	0.029	11.1 (0.4)	8.50 (0.67)
5	0.005	0.036	0.073	0.023	12.0 (0.5)	5.87 (0.38)	0.069	0.024	11.7 (0.0)	5.17 (0.25)
6	0.000	0.043	0.102	0.000	10.2 (0.6)	–	0.094	0.000	9.34 (0.1)	–
Average					11.2 (0.7)a‡				11.5 (1.2)a	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant differences ($p < 0.05$) between similar columns.

Table 7. Binary exchange of Mg–K solution and exchanger compositions, cation exchange capacity (CEC) of the soils, and Vanselow selectivity coefficients (K_v) for the untreated, noncontaminated subsoil profile (SS) and the thermally desorbed, noncontaminated subsoil profile (SS-TD).

Exchanger test	Solution composition		TS				TS-TD			
			Exchanger composition				Exchanger composition			
	Mg	K	K	Mg	CEC	K_v	K	Mg	CEC	K_v
	—mol L^{-1}—		**—mol kg^{-1}—**		cmol$_c$ kg^{-1}		**—mol kg^{-1}–**		cmol$_c$ kg^{-1}	
1	0.024	0.000	0.000	0.065	12.9 (1.2)†	–	0.000	0.068	13.7 (0.0)	–
2	0.020	0.010	0.023	0.050	12.4 (0.9)	17.63 (1.54)	0.026	0.054	13.5 (0.4)	19.25 (0.80)
3	0.016	0.019	0.039	0.041	12.1 (0.8)	12.49 (0.32)	0.043	0.046	13.5 (0.2)	12.20 (0.59)
4	0.010	0.029	0.051	0.036	12.3 (0.7)	6.40 (0.78)	0.056	0.035	12.5 (0.4)	7.44 (0.20)
5	0.005	0.036	0.063	0.024	11.1(0.6)	4.88 (0.71)	0.071	0.024	11.9 (0.3)	5.45 (0.37)
6	0.000	0.043	0.094	0.000	9.4 (0.3)	–	0.105	0.000	10.5 (0.0)	–
Average					11.7 (1.4)a‡				12.6 (1.2)a	

† Values in parentheses are SD.

‡ Different letters after averages indicate significant differences ($p < 0.05$) between similar columns.

for the Ca–K exchange, the general binary exchange reaction was:

$$\mathrm{Ca}X_2 + 2\mathrm{KCl} \leftrightarrow \mathrm{CaCl}_2 + 2\mathrm{K}X; \qquad [2]$$

for the Mg–K exchange, the general binary exchange reaction was:

$$\mathrm{Mg}X_2 + 2\mathrm{KCl} \leftrightarrow \mathrm{MgCl}_2 + 2\mathrm{K}X, \qquad [3]$$

where X represents 1 M of surface negative charge on the exchanger phase. Exchanger mole fractions of Ca (N_{Ca}) and of Mg (N_{Mg}) were defined in homoionic exchange as:

$$N_{\mathrm{Ca}} = \frac{[\mathrm{Ca}X_2]}{[\mathrm{Ca}X_2]+[\mathrm{Mg}X_2]} \qquad [4]$$

$$N_{\mathrm{Mg}} = \frac{[\mathrm{Mg}X_2]}{[\mathrm{Mg}X_2]+[\mathrm{Ca}X_2]}, \qquad [5]$$

and in heteroionic exchange reactions as:

$$N_{\mathrm{Ca,Mg}} = \frac{[\mathrm{Ca{,}Mg}X_2]}{[\mathrm{Ca{,}Mg}X_2]+[\mathrm{K}X]} \qquad [6]$$

$$N_{\mathrm{K}} = \frac{[\mathrm{K}X]}{[\mathrm{K}X]+[\mathrm{Ca{,}Mg}X_2]}, \qquad [7]$$

where brackets represent the concentrations of adsorbed cations in mol kg^{-1}. For each equilibration, the Vanselow selectivity coefficient (K_{v}) for the homoionic exchange reaction (Eq. [1]) was computed from Essington (2004), as:

$$K_{\mathrm{v}} = \frac{\left(\mathrm{Ca}^{2+}\right)N_{\mathrm{Mg}}}{\left(\mathrm{Mg}^{2+}\right)N_{\mathrm{Ca}}}. \qquad [8]$$

Heteroionic exchange reactions (Eq. [2] and Eq. [3]) were computed as:

$$K_{\mathrm{v}} = \frac{\left(\mathrm{Ca}^{2+},\mathrm{Mg}^{2+}\right)N_{\mathrm{K}}^2}{\left(\mathrm{K}^{+}\right)^2 N_{\mathrm{Ca,Mg}}}, \qquad [9]$$

where parentheses indicate activities and N indicates exchanger mole fractions. Activities and I (mol L^{-1}) were determined with Visual MINTEQ, version 3.1 (Gustafsson, 2016) to account for ion pairing (CaCl^{+} and MgCl^{+}). The equivalent fraction of Ca^{2+} or Mg^{2+} ($E_{\mathrm{Ca,Mg}}$) on the exchanger phase for the homoionic reaction was calculated as:

$$E_{\mathrm{Ca}} = \frac{N_{\mathrm{Ca}}}{N_{\mathrm{Ca}}+N_{\mathrm{Mg}}} \qquad [10]$$

The heteroionic reaction was calculated as:

$$E_{Ca,Mg} = \frac{2N_{Ca,Mg}}{2N_{Ca,Mg}+N_{K}}, \qquad [11]$$

where N indicates the exchanger mole fractions. Gibb's free energies (ΔG_{ex}) were calculated for each binary exchange reaction via:

$$\ln K_{\mathrm{ex}} = \int_0^1 \ln K_{\mathrm{v}} \, \mathrm{d}E_{\mathrm{Ca,Mg}} \qquad [12]$$

and:

$$\Delta G_{\mathrm{ex}} = -RT \ln K_{\mathrm{ex}}, \qquad [13]$$

where K_{ex} is the equilibrium exchange constant (Essington, 2004), R is equal to 8.314 J mol^{-1} K^{-1}, and T is the reaction temperature used for this study (298°K). Each reported ΔG_{ex} is the average of three replications. Selectivity diagrams were constructed by plotting the equivalent fraction of the cation (Mg^{2+} for homoionic and K^{+} for heteroionic) in the exchanger phase versus the equivalent fraction of the cation (Mg^{2+} for homoionic and K^{+} for heterionic) in the solution phase (Essington, 2004). Nonpreference isotherms for homovalent exchanges were 1:1 lines; heterovalent equivalent exchange fractions were calculated via:

$$E_{\mathrm{K}} = \left\{1 + \frac{1}{\Gamma I}\left[\frac{3}{\tilde{E}_{\mathrm{K}}^2} - \frac{4}{\tilde{E}_{\mathrm{K}}} + 1\right]\right\}^{-\frac{1}{2}}, \qquad [14]$$

where E_{K} is equivalent fraction of K^{+} on the exchange complex; Γ is $\frac{\gamma_{\mathrm{K}^{+}}^2}{\gamma_{\mathrm{Ca}^{2+}\text{or }\mathrm{Mg}^{2+}}}$, where activities and concentrations computed with Visual MINTEQ were used to calculate γ; and $\tilde{E}_K$ is the equivalent fraction of K^{+} in the solution phase (Essington, 2004) given by:

$$\tilde{E}_K = \frac{\{\mathrm{K}^{+}\}}{\{\mathrm{K}^{+}\} + 2\{\mathrm{Ca}^{2+},\mathrm{Mg}^{2+}\}}, \qquad [15]$$

where the braces indicate molar concentrations (mol L^{-1}). If the experimental data lie above the curvilinear nonpreference isotherm, then $K_{\mathrm{v}} > 1$ and the final ion or product is preferred. If the data lie below the nonpreference isotherm, the initial ion or reactant is preferred (Sparks, 2003).

Descriptive statistics were determined for each exchange reaction and a Student's *t*-test was used to compare the noncontaminated TS and SS to noncontaminated, TD-TS and TD-SS. Significant differences were determined with $\alpha = 0.05$ (JMP 8, SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Cation exchange capacities ranged between 8.3 and 13.8 cmol$_{\mathrm{c}}$ kg^{-1}. Similar values were found in Caravaca et al. (1999), with their lowest value at 8.6 cmol$_{\mathrm{c}}$ kg^{-1} in cultivated soils with the clay portion dominated by illite and kaolinite and higher values around 13.8 cmol$_{\mathrm{c}}$ kg^{-1} for an illite- and smectite-dominated clay fraction. The average CEC value in the Ca–Mg exchange for TS was significantly greater than that of TS-TD but no difference was found between SS and SS-TD (Table 2). In the Ca–K exchange, untreated TS and SS both had significantly greater CEC than their TD-treated counterparts. Differences in CEC between untreated and TD soils might be attributed to differences in SOC, with the untreated TS and SS having significantly higher SOC than their TD-treated counterparts (Table 1; O'Brien et al., 2016). Higher SOC is correlated with higher CEC (Rashidi and Seilsepour, 2008); however, in the Mg–K exchange (Table 6 and 7) there were no differences in CEC between the untreated TS

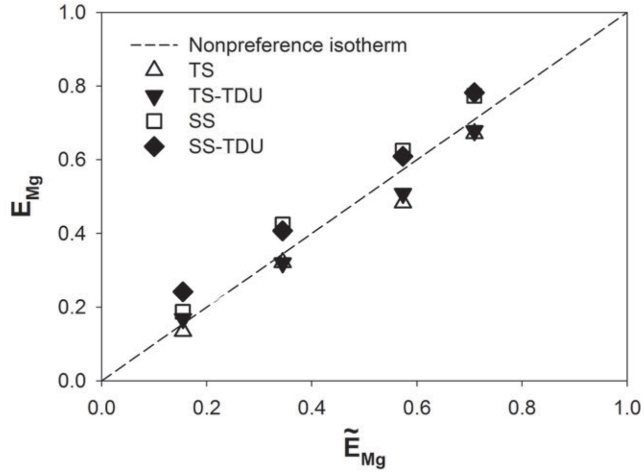

Fig. 1. Calcium–Mg exchange isotherms showing the equivalent fraction of Mg in the solution ($\tilde{E}_{Mg}$) and the exchanger phase (E_{Mg}). Standard deviation values are shown for $E_{Mg} < 0.04$.

or SS and the TD-treated soils. The conversion of SOC within the thermal desorption unit to biochar may have occurred to some extent. If pyrolysis occurred this would lead to greater surface area, negative surface charge, and greater charge density (Lehmann, 2007; Mukherjee et al., 2011; Sizmur et al., 2015). So even though the total SOC was decreased, its reactivity may have increased, offsetting itself; thus CEC was only slightly altered.

Some variation in CEC existed across exchanger cation compositions, which has been reported by many authors (Fletcher et al., 1984; Sposito and LeVesque, 1985; Chung and Zasoski, 1994). The data were deemed satisfactory for calculating ΔG_{ex} with Eq. [12]. Heteroionic plots of $\ln K_v$ as a function of $E_{Ca,Mg}$ were linear and had r^2 values greater than 0.91, whereas for Ca–Mg exchange, the relationships were steady (the slopes of the linear regressions were less than 0.4).

In the Ca–Mg exchange, the TS and TS-TD preferred Ca, as shown by the K_v values being predominantly less than one (Table 2 and Eq. [1]) and the lines below the 1:1 line of nonpreference (Fig. 1). Jensen and Babcock (1973) reported K_v values of 0.61 at $I = 0.001$ and 0.010 in Ca–Mg exchange, which were similar to the values in this study. Previous studies using soils dominated by montmorillonite and illite clays have observed Ca preference over Mg, which is often contributed to the organic matter's affinity for Ca (Van Bladel and Gheyi, 1980; Curtin et al., 1998). In pure montmorillonite clay, Ca and Mg have equal affinities for exchange sites; however, when SOC is present in the exchanger system, the preference shifts toward Ca (Sposito et al., 1983). With less SOC and a shift toward a smectite-dominated clay fraction (Table 1), both the SS and SS-TD soils preferred Mg over Ca, as shown by the K_v values being greater than one (Table 3) and preference lines above the nonpreference line (Fig. 1).

In the Ca–K and Mg–K exchanges, all treatments preferred K, as indicated by the K_v values >1 (Table 4 to Table 7) and the preference lines above the nonpreference line (Fig. 2 and Fig. 3). Similar values were observed by Jensen and Babcock (1973), with K_v values of 12.0 and 22.9 in Ca–K and Mg–K exchanges, respectively, at $I = 0.01$ in a Yolo loam. Similar findings of K preference over Ca or Mg have been observed in a variety of soils consisting of mica, smectite, and kaolinite clays (Sinanis et al., 2003; DeSutter and Pierzynski, 2005). Vanselow selectivity coefficients of 9.90 and 23.81 were found in two smectite Ca–K exchanges by Shainberg et al. (1987) using $I = 0.062$ mol L^{-1}, similar to the values of K_v found in our study and similar to our I (Table 4). As stated in Shainberg et al. (1987), illite has a high affinity for K, which may explain the K preference in these soils. Similar to previous findings (Jensen and Babcock, 1973; Sinanis et al., 2003; Agbenin and Yakubu, 2006), the soil's preference for K was higher at lower degrees of K exchanger composition for both Ca–K and Mg–K exchanges, which indicates that the higher selectivity sites for K are filled first, followed by low selectivity sites. This selectivity has been attributed to the heterogeneity of adsorption sites and to the fact that the cationic mixture on the exchanger phase does not behave as an ideal solid–solution mixture (Sinanis et al., 2003; Agbenin and Yakubu, 2006). In the Ca–Mg system, K_v was constant and independent of exchanger composition.

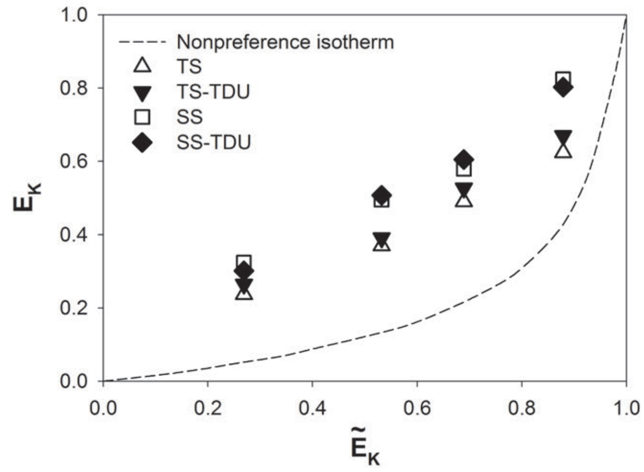

Fig. 2. Calcium–K exchange isotherms showing the equivalent fraction of K in the solution ($\tilde{E}_K$) and the exchanger phase (E_K). Standard deviation values are shown for $E_K < 0.03$.

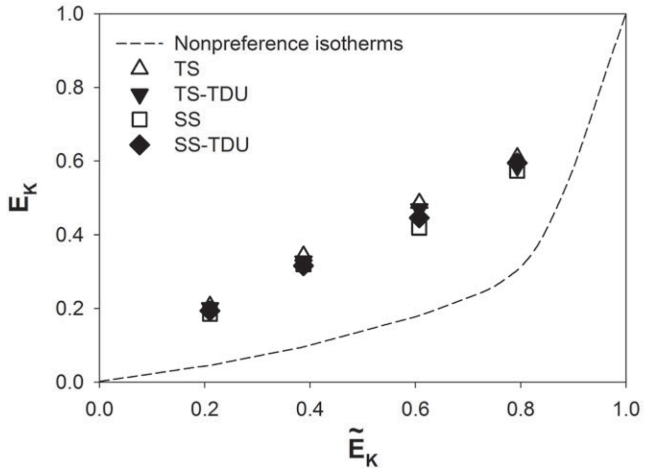

Fig. 3. Magnesium–K exchange isotherms showing the equivalent fraction of K in the solution ($\tilde{E}_K$) and the exchanger phase (E_K). Standard deviation values are shown for $E_K < 0.03$.

Table 8. Gibb's free energies (ΔG_{ex}) and Vanselow selectivity coefficients (K_{ex}) for the untreated, noncontaminated topsoil profile (TS), the thermally desorbed, noncontaminated topsoil profile (TS-TD), the untreated, noncontaminated subsoil profile (SS), and the thermally desorbed, noncontaminated subsoil profile (SS-TD) of the Ca–Mg, Ca–K, and Mg–K exchanges.

Exchange reaction	Treatment	K_{ex}	ΔG_{ex} (kJ mol^{-1})
Ca–Mg	TS	0.8 (0.01)†A‡	0.52 (0.04)A
	TS-TD	0.9 (0.02)B	0.32 (0.06)B
	SS	1.3 (0.04)a	-0.70 (0.07)a
	SS-TD	1.4 (0.04)b	-0.86 (0.08)b
Ca–K	TS	6.5 (0.13)A	−4.63 (0.05)A
	TS-TD	8.7 (0.14)B	−5.35 (0.04)B
	SS	19.3 (1.52)a	−7.33 (0.20)a
	SS-TD	18.2 (0.33)a	−7.18 (0.04)a
Mg–K	TS	9.8 (0.29)A	−5.66 (0.07)A
	TS-TD	8.6 (0.11)B	−5.35 (0.03)B
	SS	7.3 (0.29)a	−4.92 (0.10)a
	SS-TD	8.2 (0.24)b	−5.21 (0.07)b

† Values in parentheses are SD.

‡ Capital letters indicate significant differences ($p < 0.05$) between untreated and thermal desorption (TD)-treated topsoils within the respective exchange reactions and columns. Lowercase letters indicate significant differences ($p < 0.05$) between untreated and TD-treated subsoils within the respective exchange reactions and columns.

Although the cation preference was not altered after TD, ΔG_{ex} significantly differed in values for all exchanges between the untreated and TD-treated soils, except for Ca–K SS (Table 8). The Ca–Mg exchanges for the TS and TS-TD were 0.52 and 0.32 kJ mol^{-1}, respectively, similar to the 0.44 kJ mol^{-1} value reported by DeSutter et al. (2006) for a soil composed of mica, smectite, and kaolinite clay. The values are slightly higher than the 0.29 kJ mol^{-1} recorded by Jensen and Babcock (1973) at $I = 0.001$ and 0.010 in a Yolo loam and 0.26 kJ mol^{-1} observed by Udo (1978) in a kaolinitic clay at 30°C. The Ca–K exchange ΔG_{ex} values ranged from −4.63 to −7.33 kJ mol^{-1}, which were similar to values found by DeSutter and Pierzynski (2005) in two soils dominated by a mica, smectite, and kaolinite clay fraction that ranged between −4.66 and −5.08 kJ mol^{-1}. Agbenin and Yakubu (2006) observed -3.62 kJ mol^{-1} in the top 0 to 15 cm and −2.43 kJ mol^{-1} at 15 to 30 cm in a savanna soil in northern Nigeria. Udo (1978) observed higher ΔG_{ex} values of −1.65 kJ mol^{-1} at 30°C on a kaolinitic soil clay.

Gibb's free energy values for Mg–K ranged from −4.92 to −5.66 kJ mol^{-1} (Table 8); these values are within the range of values of −5.70 to −6.70 kJ mol^{-1} reported by Sinanis et al. (2003) for mica- and smectite-dominated mineralogies, respectively. Agbenin and Yakubu (2006) reported ΔG_{ex} values of −3.79 kJ mol^{-1} at 0 to 15 cm depth and −2.51 kJ mol^{-1} at 15 to 30 cm depth for Mg–K exchange reactions. Jensen and Babcock (1973) reported ΔG_{ex} values of -1.86 kJ mol^{-1} in Mg–K exchange reactions at $I = 0.001$. With similar directionality and magnitude to comparable soils for related reactions found in the literature, our results indicate that the TD process did not alter the soils' exchanger phase to any great degree. This suggests that although there were significant differences in ΔG_{ex} between untreated and TD-treated soils, the magnitude of the differences may not require alternative fertility management practices.

CONCLUSION

This study examined the effects of TD on CEC and cation selectivity in noncontaminated agricultural TS and SS. Slight variations in CEC in the Ca–Mg and Ca–K exchanges existed between the untreated and TD-treated soils, with the TD treatments having lower CEC values. Vanselow selectivity coefficients indicated that Ca was preferred over Mg when SOC was high, Mg was preferred over Ca when SOC was low, and K was preferred over Ca and Mg for all treatments. Gibb's free energies were significantly different between the untreated and TD-treated soils for each of the three exchanges except Ca–K SS, suggesting different degrees of selectivity after TD treatment. However, no trend was noticed between TD-treated soil and greater or lesser selectivity, but the magnitudes of ΔG_{ex} were similar between treated and untreated soils across all exchanges. Overall, the selectivities between the topsoil and subsoil were not altered after undergoing TD at 350°C. Therefore, if TD is used in an agricultural setting, similar soils undergoing TD at the same temperatures and retention times should not require alternative fertility management to retain their previous productivity.

ACKNOWLEDGMENTS

The authors thank Nelson Environmental Ltd. for assistance in sample preparation and collection. Thanks also to Steve and Patty Jensen for their continued support of this research. This study was funded by Tesoro Logistics Operations, LLC.

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