

# Soil exchangeable base cations along a chronosequence of *Caragana microphylla* plantation in a semi-arid sandy land, China

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**Abstract:** As a pioneer leguminous shrub species for vegetation re-establishment, *Caragana microphylla* is widely distributed in the semi-fixed and fixed sandy lands of the Horqin region, North China. *C. microphylla* plantations modify organic carbon (SOC), nitrogen (N) and phosphorus dynamics, bulk density and water-holding capacity, and biological activities in soils, but little is known with regard to soil exchange properties. Variation in soil exchangeable base cations was examined under *C. microphylla* plantations with an age sequence of 0, 5, 10, and 22 years in the Horqin Sandy Land, and at the depth of 0–10, 10–20, and 20–30 cm, respectively. *C. microphylla* has been planted on the non-vegetated sand dunes with similar physical-chemical soil properties. The results showed that exchangeable calcium (Ca), magnesium (Mg), and potassium (K), and cation exchange capacity (CEC) were significantly increased, and Ca saturation tended to decrease, while Mg and K saturations were increased with the plantation years. No difference was observed for exchangeable sodium (Na) neither with plantation years nor at soil depths. Of all the base cations and soil layers, exchangeable K at the depth of 0–10 cm accumulated most quickly, and it increased by 1.76, 3.16, and 4.25 times, respectively after *C. microphylla* was planted for 5, 10, and 22 years. Exchangeable Ca, Mg, and K, and CEC were significantly ( $P < 0.001$ ) and positively correlated with SOC, total N, pH, and electrical conductivity (EC). Soil pH and SOC are regarded as the main factors influencing the variation in exchangeable cations, and the preferential absorption of cations by plants and different leaching rates of base cations that modify cation saturations under *C. microphylla* plantation. It is concluded that as a nitrogen-fixation species, *C. microphylla* plantation is beneficial to increasing exchangeable base cations and CEC in soils, and therefore can improve soil fertility and create favorable microenvironments for plants and creatures in the semi-arid sandy land ecosystems.

**Keywords:** cation exchange capacity; soil organic carbon; soil pH; soil fertility; *Caragana microphylla*; ecological restoration

**Citation:** YuGe ZHANG, ZhuWen XU, DeMing JIANG, Yong JIANG. 2013. Soil exchangeable base cations along a chronosequence of *Caragana microphylla* plantation in a semi-arid sandy land, China. Journal of Arid Land, 5(1): 42–50.

*Caragana microphylla* is a long-lived perennial deciduous shrub species, and is widely distributed in the sandy lands of Inner Mongolia, the steppe zone of the Songliao Plain and the mountainous forest zone of North China (Zhao, 2005). As a pioneer leguminous shrub species for vegetation re-establishment, *C. microphylla* is widely distributed in the semi-fixed and fixed sandy lands of the Horqin region (Cao et al.,

2011). It is well adapted to moving sand dunes, resistant to heat, cold, drought, wind erosion, sand burial and hail storm, and forms nitrogen-fixing modules (Yue et al., 2008; Wang et al., 2010).

Many researches related to *C. microphylla* plantations focused on plant productivity (Ma et al., 2004), cycling of soil C and N, P, and K nutrients (Su and Zhao, 2003; Su et al., 2005; Kondo et al., 2012), soil

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Received 2012-04-15; revised 2012-07-11; accepted 2012-11-07

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fauna (Jiang et al., 2007), or soil microbial activities (Cao et al., 2008, 2011). Only a few involved soil exchangeable base cations and cation exchange capacity (CEC).

The interactions between soil exchange properties and other physical, chemical, and biological properties in soil control plant nutrient availability (Havlin et al., 2004). Calcium (Ca), magnesium (Mg), and potassium (K) are essential elements and important macronutrients in terrestrial ecosystems, and interactions between these dominant base cations and other nutrients, such as nitrogen (N) and phosphorus (P), are potentially important for the health and stability of ecosystems (Lucas et al., 2011). Exchangeable base cations and CEC vary a lot with different organic matter fractions (Oorts et al., 2003), soil particle sizes (van Erp et al., 2001), soil pH (Katou, 2002), land use change (Jiang et al., 2009), cation migration characteristics, the eluviation-illuviation processes, alternative reducing-oxidizing conditions, the selective absorption of cations by plants, and some other pedogenic and anthropogenic conditions (Favre et al., 2002; Jiang et al., 2005). In general, it is well documented that soil CEC increases with clay or soil organic matter (SOM) increases, and the CEC of most soils increases with an increase in soil pH as well. Clay soils of high CEC tend to have a greater water-holding capacity than sandy soils of low CEC, and high CEC soils are more able to retain base cations, while low CEC soils are more likely to be deficient of K and Mg and other cations.

It is basically clear that soil chemical properties such as SOC, N, P, and soil pH, and physical features such as bulk density, water-holding capacity, and biological activities related to soil fauna, microbes and enzyme change a lot under *C. microphylla* plantations or beneath natural shrubs. Our hypothesis was that soil exchangeable cations and CEC would change along with soil physical-chemical and biological properties under *C. microphylla* plantations, and hence, the objectives of this study were to examine the variation in soil exchangeable cations and CEC along a chronosequence of *C. microphylla* plantations, and to identify factors contributing to the variation in base cations and CEC.

## 1 Materials and methods

### 1.1 Study area

The study was conducted at the Wulanaodu Desertification Experimental Station (43°02'N, 119°39'E), Chinese Academy of Sciences, southwestern Horqin Sandy Land of Northeast China. The station is located in a semi-arid continental temperate monsoon zone, with an annual average temperature of 6.3°C, and an average annual frost-free period of 130 days. The average annual precipitation is 340 mm, with 70%–80% occurring during May–September, and the annual pan-evaporation averages about 2,500 mm. The typical landscape is gently undulating moving and semi-moving sand dunes with inter-dune bottomlands. The soil, which is sandy in texture, light yellow in color, loose in consistence, low in organic matter, and susceptible to wind erosion, is classified as Typic Usti-Sandic Primosols in Chinese Soil Taxonomy (CRGCST, 2001) or Haplic Arenosols in FAO Soil Taxonomy (FAO, 1988). *C. microphylla* has been selected as an experimental plant for ecological restoration of non-vegetated sandy dunes since the early 1980s. The experimental sites were enclosed after seeding of *C. microphylla*, and shrubby belts were formed 3–5 years after seeding. Gradually, short grasses, legumes and forbs colonized, and a stabilized shrubby-grass vegetation system was established. In this study, three *C. microphylla* plantations with an age sequence of 5, 10, and 22 a, and adjacent non-vegetated sand dunes (0-a) were selected as experimental treatments.

### 1.2 Sampling and soil analyses

In April 2006, mixed soil samples were collected at the depths 0–10, 10–20 and 20–30 cm. We selected four sampling sites from different sand dunes with the same age of *C. microphylla* plantation. At each site, five sub-samples were collected with a shovel, and were then mixed as one sample. A total of 48 soil samples were collected from four treatments, replicated four times at three soil layers. All soil samples were air-dried and ground to pass through a 2-mm sieve, and the sub-samples were ground to pass through a 0.149-mm sieve for related chemical analysis.

Because the shrubs in this study were established

from non-vegetated sandy dunes, it was assumed that the soils at each site were similar prior to *C. microphylla* plantation. In fact, the data obtained from previous and recent studies at the sites have shown that soil texture and organic matter content were not significantly different in the unstable dunes over time, suggesting that the soils were relatively similar in these characteristics before planting (Cao et al., 2008), and hence the changes of soil properties were assumed to come from the plantation time of *C. microphylla*.

Soil exchangeable Ca, Mg, K and Na were extracted with 1M NH<sub>4</sub>-acetate (NH<sub>4</sub>OAc, pH 7), and the extracts were then analyzed for exchangeable Ca, Mg, K and Na by flame emission at the wavelength of 422.7, 285.2, 766.5 and 589.0 nm, respectively, using atomic absorption spectrophotometer (AAS, Shimadzu, Japan). Because in the study site, soil pH is higher than 7, and the sum of exchangeable cations accounts for more than 99% of the CEC, we just calculated the cation exchange capacity by adding up the total amount of exchangeable Ca, Mg, K and Na measured above. Base saturation (%) was calculated by dividing the charge equivalents of base cations by CEC and multiplying by 100. Soil pH was measured with combined electrodes in a 1:2.5 soil:water suspension. Soil electrical conductivity (EC) was measured using electrodes in a 1:2 soil:water suspension. Soil organic carbon and total nitrogen contents were determined by the dry combustion method using a Vario ELIII Elemental Analyzer (Elementar, Germany). China's national standard soil reference materials (GBW07424 and GBW07458) were adopted through

the digestion, extraction and analysis procedures as a part of the QA/QC protocol.

### 1.3 Statistical analysis

The obtained data were analyzed with SPSS Version 11.5 for Windows, using one-way ANOVA and Duncan's pairwise comparison for means separation, and a significance level of  $P < 0.05$  was chosen for detecting significant differences. Univariate analysis of variance was adopted to test inter-subject effects with plantation year and soil depth as factors. Simple correlation coefficients and linear regression analysis were performed to examine the relationship between some soil chemical properties. Figures were drawn using SigmaPlot 11.0 (Systat Software Inc.).

## 2 Results

### 2.1 Soil exchangeable base cations under different plantation years of *C. microphylla*

Univariate analysis of variance showed that soil exchangeable Ca, Mg, K, and cation exchange capacity (CEC) varied significantly ( $P < 0.001$ ) with different plantation years, and exchangeable Ca, K, and CEC varied significantly at different soil depths, but no difference was observed for exchangeable Na with neither plantation years nor depths. No significant inter-subject effect was tested for exchangeable base cations or CEC (Table 1).

Soil exchangeable Ca, Mg, K, and CEC increased significantly in 5-, 10-, and 23-a *C. microphylla* plantations at 0–10, 10–20, or 20–30 cm soil layer, respectively, but no significant change was observed for ex-

**Table 1** Univariate variance analysis for soil chemical properties in different *C. microphylla* plantation years and at different soil depths

Variable	Plantation year		Soil depth		Plantation year×soil depth	
	<i>F</i> value	<i>P</i>	<i>F</i> value	<i>P</i>	<i>F</i> value	<i>P</i>
Exchangeable Ca	10.07	<0.001	4.24	0.022	0.42	0.862
Exchangeable Mg	5.18	<0.001	1.07	0.355	0.55	0.771
Exchangeable K	35.10	<0.001	22.42	<0.001	2.24	0.061
Exchangeable Na	2.12	0.115	1.00	0.378	0.65	0.701
Cation exchange capacity	22.52	<0.001	8.43	0.001	0.54	0.773
Soil organic carbon	137.58	<0.001	31.11	<0.001	3.72	0.006
Total nitrogen	23.75	<0.001	28.29	<0.001	4.71	0.001
Soil pH	36.93	<0.001	3.34	0.047	0.16	0.987
Electrical conductivity	53.07	<0.001	19.98	<0.001	1.08	0.388

changeable Na, relative to the non-vegetated sand dunes (Fig. 1). As compared with non-vegetated sand dunes (0-a), the average content of CEC at the depth of 0–10 cm increased by 32.56%, 45.35%, and 57.09%, respectively in 5-, 10-, and 22-a *C. microphylla* plantations; exchangeable Ca increased by 29.14%, 38.56%, and 46.11%, respectively in 5-, 10-, and 22-a plantations. Of all the base cations and soil layers, exchangeable K at the depth of 0–10 cm enhanced most quickly, and it was increased by 1.76, 3.16, and 4.25 times, respectively, after 5, 10, and 22 years of *C. microphylla* plantation.

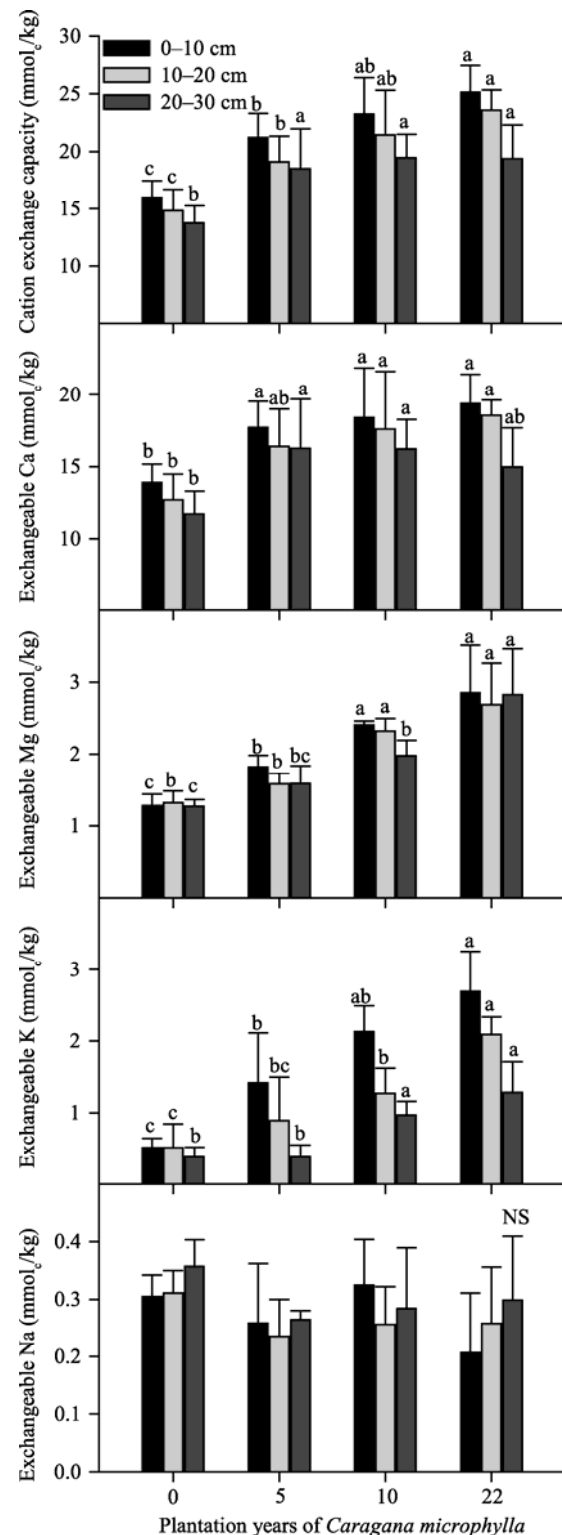
## 2.2 Changes of SOC, total N, pH, and EC

Soil organic carbon (SOC), total N, soil pH, and electrical conductivity (EC) varied significantly ( $P < 0.05$ ) with different plantation years and at different soil depths. Significant inter-subject effects for SOC and total N ( $P < 0.01$ ) were tested taking plantation year and soil depth as factors (Table 1).

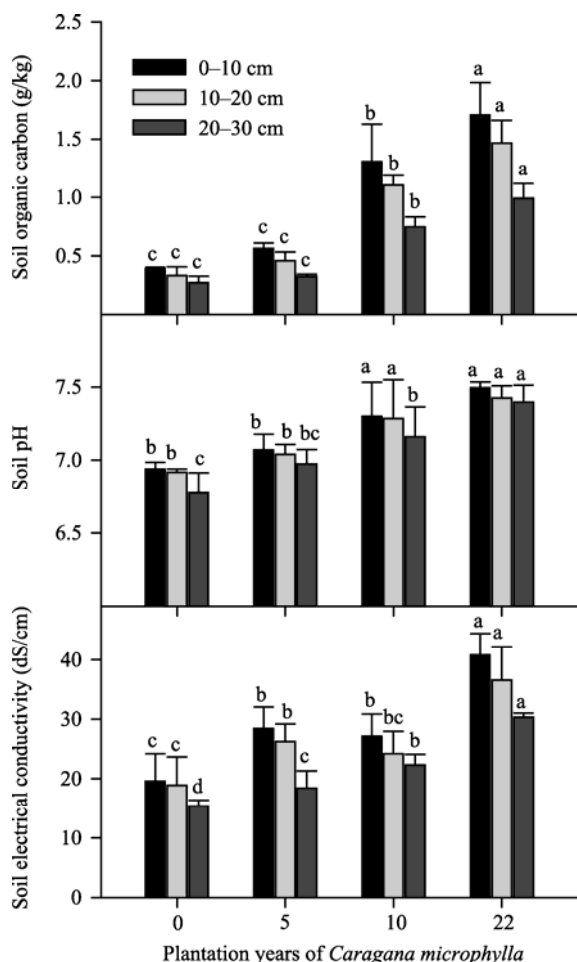
SOC at all the three soil layers was more significantly increased in 10- and 22-a plantations than in 5-a treatment or non-vegetated sand dunes, while it was also greater in 22-a than in 10-a treatment, but no statistical change was observed between 5-a treatment and non-vegetated sand dunes (Fig. 2). Soil total N dynamics was the same as SOC in this study. Soil pH was higher in 10- and 22-a plantations than in 5-a plantation or non-vegetated sand dunes. Soil EC was significantly greater in 22-a plantation than at other three treatments in the three soil layers, while it was greater in 10- and 5-a plantations than in non-vegetated sand dunes at the corresponding layer (Fig. 2).

## 2.3 Relationships between exchangeable base cations and other chemical properties

Linear regressions of exchangeable Ca, Mg, and K, and CEC with SOC, total N, soil pH and EC in soils under *C. microphylla* plantations were performed, and the results showed that soil exchangeable properties increased with the increase of SOC, total N, soil pH, and EC (Fig. 3). No Linear regression was tested between exchangeable Na and SOC, N, pH, or EC.



**Fig. 1** Exchangeable base cations and cation exchange capacity (CEC) at different soil layers under different plantation years of *Caragana microphylla*. Values above the column of a single figure followed by different letters in the same soil layer are significantly different at  $P < 0.05$  according to Duncan's Multiple Range Test. NS means no significant difference at  $P < 0.05$ .



**Fig. 2** Soil pH, electrical conductivity (EC), and soil organic carbon (SOC) at different soil layers under different plantation years of *Caragana microphylla*. Values above the column of a single figure followed by different letters in the same soil layer are significantly different at  $P < 0.05$  according to Duncan's Multiple Range Test.

### 3 Discussion

#### 3.1 Variation in soil exchangeable base cations with different plantation years

The obtained data showed that exchangeable Ca, Mg, K, and CEC were significantly and positively correlated with the plantation year (Table 2), indicating an accumulation of soil cations along a chronosequence of *C. microphylla* plantation.

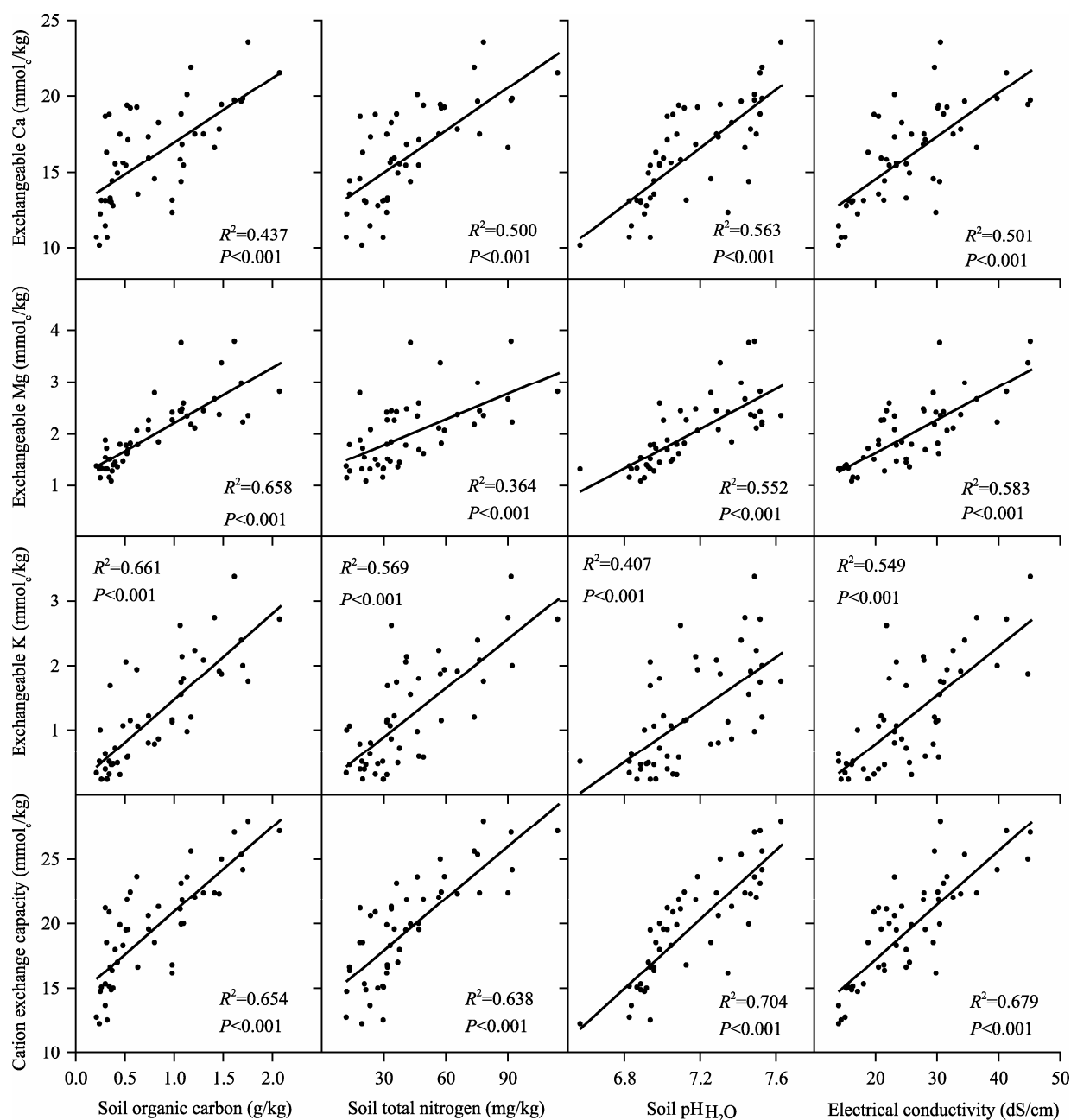
Exchangeable Ca, Mg, K, and Na accounted for 77.07%–87.61%, 8.00%–14.76%, 2.24%–10.70%, and 0.85%–2.60% of CEC, respectively, with different plantation years and at different soil depths (Table 3), so exchangeable Ca was the dominant cation in the

soil of the semi-arid sandy land. Calcium saturation was decreased, while Mg and K saturation were increased with the plantation ages of *C. microphylla* (Table 3).

Dryland soils generally have very high levels of total Ca, reaching more than 5% of the soil by weight and occupying 75%–85% of the CEC sites (Troeh and Thompson, 1993). Hydrated cations are relatively small polyvalent ions and tend to preferentially occupy CEC sites, making Ca less bio-available than other cations that are held less strongly. Because minerals that contain Ca can weather relatively quickly, Ca is subject to leaching (Marschner and Rengel, 2007). Plant uptake and plant litter can accumulate Ca in soil surface (Jobbàgy and Jackson, 2001), and increased exchangeable Ca after *C. microphylla* plantation (Fig. 1), but the comparatively higher leaching rate led to the decrease of Ca saturation in soil with the plantation ages of *C. microphylla* (Table 3).

A same trend was observed for exchangeable Mg accumulated in surface soil as exchangeable Ca, but Mg saturation was slightly increased after *C. microphylla* was planted. This may also due to the co-effect of plant accumulation and different leaching rates of base cations (Jiang et al., 2005) in this plant-soil system.

Due to K fixation and sorption to the cation-exchange sites in soils, K is not easily leached from soils, even over long periods of time. In dryland ecosystems, exchangeable K accumulates at the surface due to upward transport by plants and accumulation of K in plant litter (Jobbàgy and Jackson, 2001). Hydrated K ions are of the same size as ammonium ions and held with about the same strength, whereas they are weakly held relative to Ca and Mg ions. Therefore, K ions are readily exchangeable (Marschner and Rengel, 2007). In this study, no depth effect of exchangeable K was observed in the 0-a treatment, while the surface accumulation effect of exchangeable K was obvious under plantation treatments. Both exchangeable K content (Fig. 1) and K saturation (Table 3) were significantly greater at 0–10 cm than at 20–30 cm soil layer in the plantation treatments.



**Fig. 3** Linear regression of exchangeable Ca, Mg, and K, and cation exchange capacity with soil organic carbon (SOC), total nitrogen (N), soil pH and electrical conductivity (EC) in soils under *Caragana microphylla* plantations (n=48)

**Table 2** Correlations between base cations and plantation year (n=48)

	Correlation coefficient ( $R^2$ )	Significance ( $P$ )
Exchangeable Ca	0.379	0.008
Exchangeable Mg	0.869	<0.001
Exchangeable K	0.762	<0.001
Exchangeable Na	-0.158	0.283
Cation exchange capacity	0.593	<0.001

**Table 3** Cation saturation in different *C. microphylla* plantation years and at different soil depths

Treatment (a)	Soil depth (cm)	Ca saturation (%)	Mg saturation (%)	K saturation (%)	Na saturation (%)
0	0–10	86.89±1.23	8.00±0.86	3.18±0.52	1.92±0.32
	10–20	85.46±1.84	8.98±1.40	3.43±2.23	2.14±0.49
	20–30	85.19±2.09	9.38±1.53	2.83±1.11	2.60±0.25
5	0–10	83.52±3.89	8.61±0.43	6.67±3.35	1.20±0.39
	10–20	85.50±4.05	8.32±0.82	4.96±3.86	1.22±0.21
	20–30	87.61±2.52	8.68±1.07	2.24±1.54	1.47±0.29
10	0–10	78.69±3.95	10.49±1.45	9.40±2.52	1.41±0.39
	10–20	81.52±4.43	11.14±2.38	6.12±2.22	1.22±0.34
	20–30	83.25±2.16	10.22±1.22	5.07±1.34	1.46±0.51
22	0–10	77.13±4.29	11.32±2.08	10.70±1.99	0.85±0.50
	10–20	78.73±1.29	11.31±1.68	8.88±1.14	1.07±0.34
	20–30	77.07±3.94	14.76±3.44	6.56±1.64	1.60±0.69

Note: data in the table are mean±standard deviation for each treatment replicated four times.

Sodium ions are less tightly held to soil particles than K, Ca or Mg. Therefore, Na is more easily leached from soil than the other cations (Marschner and Rengel, 2007); hence no statistical difference was observed among treatments or at soil layers.

### 3.2 Effects of soil organic carbon on exchangeable base cations

Soil particles and organic matter have negative charges on their surfaces, which can be adsorbed by mineral cations, and hence, soil exchangeable cations are highly dependent upon soil texture and organic matter content (Hepper et al., 2006; Gogo and Pearce, 2009). In this study, both exchangeable cations and CEC were significantly and positively correlated with SOC (Fig. 3).

Parfitt et al. (1995) collected 1,043 samples from New Zealand soils, and found that most of the CEC arose from soil organic matter by using multiple regression, and they calculated that CEC was 221–330 cmol<sub>c</sub>/kg per unit C. The CEC of organic matter was found to vary from 35 to 165 cmol<sub>c</sub>/kg in 18 acid forest soil samples in France, and so represented 10%–85% of the total soil CEC in the tipper soil horizons (Turpault et al., 1996). Measurements made on long-term experiments of cultivated soils in sub-Saharan Africa showed that changes in CEC and SOM were positively correlated, but different SOM played unequal roles as contributing to soil CEC (Guibert et al., 1999). The samples from nine field experiments in Germany showed that the CECs decreased with increased equivalent diameters of soil

particles, and varied with C and N contents in the size fractions (Leinweber et al., 1993). The results mentioned above supported that SOM is one of the dominant factors influencing CEC in soils. According to this study, CEC was equivalent to 660 cmol<sub>c</sub>/kg SOC. In the sandy soil, both exchangeable base cations and SOC are lower than in other ecosystems, hence SOC may play more contribution to base cations.

### 3.3 Effects of soil pH on exchangeable base cations

According to Fig. 3, CEC increased by about 13.38 mmol<sub>c</sub>/kg as pH increased by 1 unit under *C. microphylla* plantation, of which exchangeable Ca, Mg, and K accounted for about 9.47, 1.92, and 2.64 mmol<sub>c</sub>/kg, respectively. In this study, a negative contribution of soil pH to exchangeable Na was observed, but the relationship between the two variables was not significant.

The sum of positive charges of adsorbed cations that the soil can adsorb at a specific pH is its CEC (Foth, 1990). As soil pH is increased, the surface negative charge on clay colloids increases and repulsive forces between particles dominate (Renault et al., 2009). Thus, soil CEC is dependent on, and is positively correlated with, soil pH (Bortoluzzi et al., 2006).

According to Katou (2002), CEC of variable-charge soils is often expressed as a function of pH and electrolyte concentration. The relationship of CEC (mmol<sub>c</sub>/kg) with pH and ion concentration (EC, dS/cm) in solution could be expressed with the following equation:

$$\text{CEC}=7.964 \text{ pH}+0.218 \text{ EC}-42.897, \\ (R^2=0.878, P<0.001). \quad (1)$$

For variable charge soils, modest changes in electrolyte ionic strength are as important in their effect on CEC as are changes in pH values (Gillman, 1981), and our study also showed the changes of both soluble and exchangeable cations in soil under *C. microphylla* plantation.

### 3.4 Effects of plant-soil interaction on base cations

Figure 3 showed that the increase of CEC accompanied with the increase of both pH and SOC. It could be deduced that both pH and SOC were dominant factors contributing to base cations in soils under *C. microphylla* plantation.

In sandy land ecosystems, *C. microphylla* plantation can form a fertility island as soils under plants show higher concentrations of N and organic matter, through N-fixation, carbon-nitrogen interactions, spread of shrubs, and return of plant litters to soil surface (Perroni-Ventura et al., 2010). The fertility island creates a favorable microenvironment for creatures, hosts creatures ranging from bacteria, fungi and nematodes to beetles (Jiang et al., 2007; Cao et al., 2008), and promotes nutrient and water availability for plant growth. The uplift of nutrients from deep soil layers by plants leads to surface accumulation of nutrients under *C. microphylla* shrubs (Jobbàgy and Jackson, 2004). The accumulation of organic matter and N modifies soil physical and biological properties, and is beneficial to clay formation. Both organic matter and clay can provide more CEC sites and result in accumulation of exchangeable base cations in topsoil (Havlin et al., 2004). In brief, the variation in exchangeable base cations and CEC is controlled by the interaction of plant and soil, and the interaction of soil physical, chemical, and biological properties, which in turn controls plant nutrient availability in the sandy land ecosystem.

## 4 Conclusions

Soil organic carbon and pH were the main factors influencing the variation in exchangeable Ca, Mg and K, and CEC. As a nitrogen-fixation species, *C. microphylla* benefits the formation of fertility islands in

soils, and hence increases SOC content and nutrient availability. Owing to the increase of SOC and soil pH, exchangeable Ca, Mg and K, and CEC increased significantly along a chronosequence of *C. microphylla* plantation. Exchangeable Ca was the dominant cation in the soil of the semi-arid sandy land. Due to the preferential absorption of cations by plants and different leaching rates of base cations, Ca saturation was decreased, while Mg and K saturation were increased with the plantation ages of *C. microphylla*. The results suggest that *C. microphylla* plantation is beneficial for enhancing soil fertility and is an active way to the ecological restoration of semi-arid sandy lands in North China.

## Acknowledgements

The work was supported by the National Key Basic Research Program of China (2011CB403204) and the Natural Science Foundation of China (31000200). The authors thank the members of the Wulanaodu Desertification Experimental Station under the Chinese Academy of Sciences for technical assistances.

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