

Kinetics of Non-exchangeable Potassium Release in Selected Soil Orders of Southern Iran

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Abstract

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Non-exchangeable K release can greatly influence soil K fertility. This study was carried out to study the release of non-exchangeable K from 22 surface and subsurface soils of southern Iran using successive extraction with 10 mmol/l of CaCl₂ and oxalic acid in a period of 2–1368 h at 25 ± 1°C. Alfisols, Aridisols, Entisols, Inceptisols, Mollisols, and Histosols were among the studied soil orders. Illite, smectite, chlorite, vermiculite, kaolinite and palygorskite clay minerals were identified. The amount of non-exchangeable K varied from 95 to 506 mg/kg. Results showed that CaCl₂ and oxalic acid released 60 and 55% of non-exchangeable K from soils, respectively. The discontinuity in slope was found when the cumulative amount of released K was plotted versus time, supporting the multi-reactive nature of K exchange sites. The cumulative K release in soils ranged from 87 to 300 mg/kg for CaCl₂ and 78 to 300 mg/kg for oxalic acid which was well described by simplified Elovich and power function equations. The *b* constant of simplified Elovich as an index of non-exchangeable K release rate was in the range of 10 to 36 mg/kg for CaCl₂ and 11 to 36 mg/kg for oxalic acid. The highest *b* constant was measured in Inceptisols and Alfisols, while the lowest values were found in Entisols and Histosols. In conclusion, the K release pattern was similar for both extractants and affected by clay content and type, and soil depth.

Keywords: calcium chloride; clay mineralogy; kinetic equations; organic acid

Potassium, as the seventh most frequent element of the Earth crust (2.6% of weight), is an essential nutrient for humans, animals, and plants. Soil potassium could be divided into soluble, exchangeable, non-exchangeable, and structural forms. The major proportion of soil potassium is structural (90–98%), whereas soluble and exchangeable (0.1–2%) and non-exchangeable potassium (2–10%) constitute only a small portion of total soil K. Non-exchangeable K is released to exchangeable forms to meet plant needs of potassium (SPARKS & HUANG 1985). MARTIN and SPARKS (1983) suggested that the release of K from non-exchangeable to exchangeable form could be limited when the concentration of K in the soil solution exceeds 1 mmol/l. WANG *et al.* (2011)

showed that the critical level of soluble K for the release of non-exchangeable K could be related to the type of clay minerals and content of Ca²⁺ and Na⁺ in the soil solution. JALALI (2006) stated that the calcareous soils of Iran containing sufficient exchangeable K and K-bearing minerals are capable of releasing sufficient K for optimal plant production. However, exchangeable K is not always a reliable estimation of plant availability of potassium in calcareous soils. The interaction of soil mineralogy, textural characteristics, and biological processes may influence the release of potassium in different soil orders (SIMONSSON *et al.* 2007). Therefore, the research on the rate of non-exchangeable K release seems necessary in such soils.

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Several equations including zero order, first order, Elovich, parabolic diffusion, and power function have been used to describe the kinetics of non-exchangeable K release and to evaluate soil K availability for plant growth (SRINIVASARAO *et al.* 2006; WANG *et al.* 2011). JALALI and KHANLARI (2014) described the K release from some calcareous soils of western Iran using Elovich, parabolic diffusion and power function equations. HOSSEINPUR and MOTAGHIAN (2013) studied the release of non-exchangeable K from 10 calcareous soils of central Iran using 10 mmol/l CaCl_2 . They reported that the release of non-exchangeable K was well described by parabolic diffusion, power function and simplified Elovich. The *b* constant of kinetic equations clearly showed the release rate of non-exchangeable K and its availability.

Many crops, especially deep-rooted crops, can obtain a substantial amount of K from lower layers of soils, but the release of non-exchangeable K in subsoil samples has been investigated to a lesser extent. We hypothesized that soil physicochemical properties and clay mineralogy are quite different in various soil orders and soil depths, which in turn affect the release of non-exchangeable K related to soil classification. Data about non-exchangeable K content and its release related to clay minerals and soil development are highly valuable for fertility management of soils. However, limited data are available for soils of southern Iran. The aims of the present research were to study: (1) the non-exchangeable K release rate in 22 surface and subsurface soils with different clay mineralogy and soil properties using CaCl_2 and oxalic acid extractants, and (2) the rela-

tionship between K release rate and selected physicochemical properties and clay mineralogy of soils.

MATERIAL AND METHODS

Study area and sampling of soils. The study area is located in Fars Province, southern Iran (Figure 1). The mean annual temperature and precipitation were 17°C and 339 mm, respectively. The area was classified as semi-arid region with xeric moisture and thermic temperature regimes. Forty pedons were studied and eleven representative pedons (Figure 1) were selected for physicochemical, morphological, and clay mineralogical studies.

Physicochemical properties. Particle size distribution was identified using a hydrometer (GEE & BAUDER 1986). Calcium carbonate equivalent (CCE) was determined by the acid dissolution (LOEPPERT & SUAREZ 1996). The method of NELSON and SOMMERS (1982) was used for organic matter measurement. Cation exchange capacity was investigated by 1 mol/l NaOAc, pH 8.2 (CHAPMAN 1965) and HNO_3 extractable K (as total K) was determined with boiling nitric acid 1 mol/l (PRATT 1965) and extractable K was determined with NH_4OAc (MC LEAN & WATSON 1985). Non-exchangeable K content was calculated with the following formula:

$$\text{Non-exchangeable K} = \text{HNO}_3 \text{ extractable K} - \text{NH}_4\text{OAc extractable K}$$

Clay mineralogy. Clay mineralogy was performed on the first and second horizon (total of 22 samples) of each pedon (KITTRICK & HOPE 1963; JACKSON

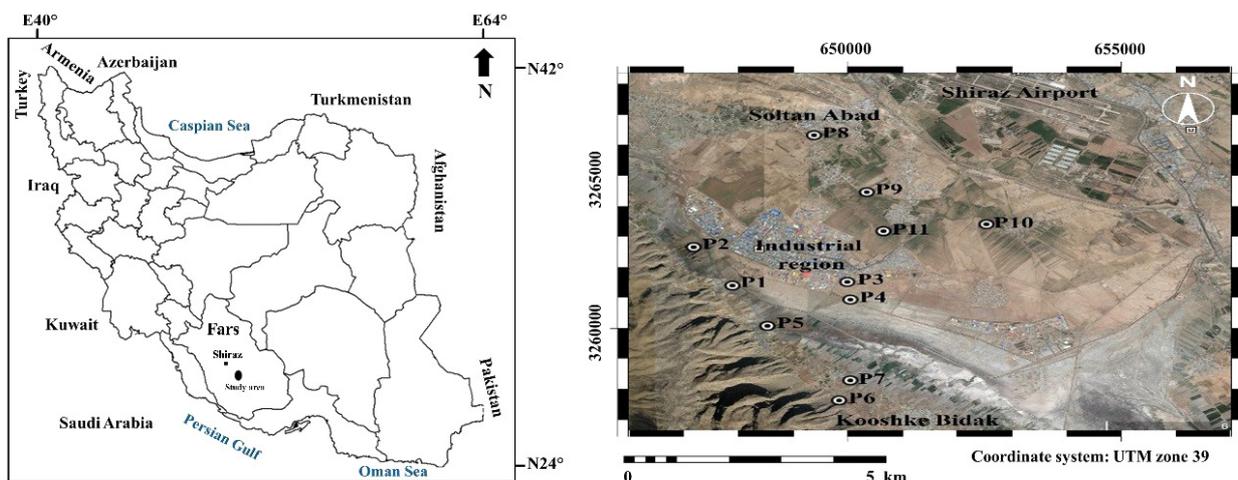


Figure 1. Location of the study area in Fars Province in southern Iran and location of eleven pedons studied in Gharebagh Plain

1975). A 1130 X-ray diffractometer (Philips, Netherlands) with Cu K α target under 40 kV and 30 mA was used for the analysis. Semi-quantitative estimation of clay minerals was performed by comparing the area under each diffractogram in Mg-saturated slide treated with ethylene glycol (JOHNS *et al.* 1954).

K-release kinetics. Soluble and exchangeable K was first removed from soil samples using 1 mol/l CaCl₂ for 24 h followed by the centrifugation of suspensions. Excess Cl was removed by water and alcohol (MARTIN & SPARKS 1983). Subsequently, 2 g soil samples in 3 replicates were transferred into centrifuge tubes in two sets containing 20 ml of 10 mmol/l of CaCl₂ and oxalic acid solutions. Samples were equilibrated for 2, 4, 8, 14, 24, 36, 48, 72, 96, 120, 168, 192, 360, 528, 696, 864, 1200, and 1368 h at 25 ± 1°C. After each period, the supernatant was separated and a new portion of extractant was added, shaken, and centrifuged. The K concentration was measured in the supernatant by a flame photometer (Model PFP7, Jenway, UK). The cumulative release of non-exchangeable K with time was fitted to the simplified Elovich equation:

$$Y = a + b \ln t$$

parabolic diffusion equation:

$$Y = a + b t^{1/2}$$

and power function equation:

$$\ln Y = \ln a + b \ln t$$

where:

Y – quantity of K released (mg/kg) at time t

a, b – constants

The above equations were tested using the R^2 analysis and standard error of the estimate by

$$SE = [\sum (Y - Y^*)^2 / (n - 2)]^{1/2}$$

where:

Y^* – calculated content of K released at time t

n – data number

Statistical analyses. Statistical analyses were performed using SPSS software package (Ver. 23, 2016). The means were compared using Duncan's test at $P < 0.05$. Linear regression procedure was used to describe the kinetic equations of non-exchangeable K release. The correlation between K release characteristics and selected soil chemical and physical properties was calculated using Pearson's test.

RESULTS

Soils of Gharebagh Plain were classified as Entisols, Inceptisols, Mollisols, Histosols, Aridisols, and Alfisols (Table 1).

Results of the study showed that the pH of soils ranged from 7.1 to 8.3, EC ranged from 0.8 to 32 mS/cm and the CaCO₃ content ranged from 32 to 8%. The minimum (0.1%) and the maximum (21%) contents of organic carbon were measured in Aridisols and Histosols, respectively. The CEC ranged from 72 in Entisols to 578 mmol(+)/kg in Histosols (Table 2).

The semi-quantitative clay mineralogy in the area is shown in Table 1. The trend of palygorskite < kaolinite < vermiculite < chlorite < smectite < illite was observed for clay mineral content. Palygorskite was found only in saline soils, but other clay minerals were detected in all studied soils. The relative quanti-

Table 1. Classification and clay mineralogy of the studied soils

| Soil pedons | Depth (cm) | Soil order | Smectite | Illite | Chlorite | Vermiculite | Kaolinite | Palygorskite |
|-------------|------------|-------------|----------|--------|----------|-------------|-----------|--------------|
| P1 | 0–30 | Entisols | +++ | ++ | ++ | + | + | – |
| | 30–60 | | + | +++ | ++ | + | ++ | – |
| P2 | 0–20 | Inceptisols | ++++ | +++ | ++ | + | + | – |
| | 20–45 | | +++ | ++ | ++ | + | + | – |
| P3 | 0–15 | Inceptisols | ++ | +++ | ++ | + | + | + |
| | 15–60 | | ++ | ++ | ++ | + | + | ++ |
| P4 | 0–20 | Aridisols | +++ | ++ | ++ | + | + | + |
| | 20–60 | | +++ | ++ | ++ | + | + | + |
| P5 | 0–30 | Histosols | +++ | ++ | ++ | + | + | – |
| | 30–85 | | +++ | ++ | ++ | + | + | – |
| P6 | 0–10 | Entisols | ++ | +++ | ++ | + | + | – |
| | 10–45 | | ++ | ++ | +++ | + | + | – |
| P7 | 0–15 | Mollisols | +++ | +++ | ++ | + | + | – |
| | 15–45 | | +++ | ++ | ++ | + | + | – |
| P8 | 0–20 | Alfisols | ++ | ++++ | ++ | + | + | – |
| | 20–45 | | ++ | +++ | ++ | + | + | – |
| P9 | 0–15 | Inceptisols | ++ | ++++ | ++ | + | + | – |
| | 15–45 | | ++ | +++ | ++ | + | + | – |
| P10 | 0–20 | Entisols | ++ | ++++ | ++ | + | + | – |
| | 20–50 | | ++ | +++ | ++ | + | + | – |
| P11 | 0–20 | Inceptisols | ++ | ++++ | ++ | + | + | – |
| | 20–50 | | ++ | +++ | ++ | + | + | – |

–: 0 or trace; +: less than 15%; ++: 15–25%; +++: 25–35%; ++++: 35–45%

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Table 2. Range of soil physiochemical properties

| Soil pedons | Soil subgroup (USDA) | pH _{H₂O} | EC (mS/cm) | CaCO ₃ | OC | CEC mmol(+)/kg | Sand | Clay |
|-------------|----------------------|------------------------------|------------|-------------------|-----------|----------------|-----------|-----------|
| | | | | (%) | (%) | | (%) | (%) |
| P1 | typic Xerortents | 7.1–7.7 | 8.8–23.8 | 46.0–87.5 | 0.2–11.9 | 72–368 | 34.2–61.2 | 10.0–20.6 |
| P2 | vertic Haploxerepts | 7.2–7.8 | 5.4–9.1 | 32.0–72.5 | 0.13–1.1 | 84–271 | 18.0–59.4 | 15.4–38.8 |
| P3 | typic Haploxerepts | 7.8–8.0 | 4.4–18.7 | 45.0–51.5 | 0.2–0.9 | 115–154 | 23.4–37.8 | 15.4–24.4 |
| P4 | typic Haplosalids | 7.7–8.3 | 3.6–32.2 | 35.0–45.0 | 0.13–0.80 | 168–284 | 16.2–25.2 | 24.4–40.6 |
| P5 | hydric Haplofibrists | 7.4–7.5 | 3.6–29.1 | 45.0–63.0 | 14.4–21.4 | 458–578 | 37.8–44.2 | 15.4–19.8 |
| P6 | typic Xerortents | 7.8–8.1 | 0.8–2.1 | 53.5–66.0 | 1.6–0.3 | 112–155 | 45.0–55.6 | 19.0–22.6 |
| P7 | typic Haploxerolls | 7.8–7.9 | 0.8–1.9 | 58.5–61.5 | 0.4–2.6 | 158–232 | 15.0–37.2 | 17.6–42.8 |
| P8 | typic Haploxeralfs | 7.4–8.3 | 3.5–8.7 | 43.5–49.5 | 0.3–1.1 | 196–308 | 14.4–23.4 | 35.2–55.0 |
| P9 | typic Calcixerepts | 7.6–7.7 | 2.8–4.2 | 44.5–49.5 | 0.2–0.8 | 152–198 | 16.2–27.0 | 26.2–35.2 |
| P10 | typic Xerofluvents | 7.7–7.9 | 3.3–7.8 | 47.0–50.7 | 0.15–0.7 | 134–188 | 10.8–22.8 | 22.8–32.5 |
| P11 | typic Calcixerepts | 7.8–7.9 | 0.8–1.9 | 50.5–61.5 | 0.18–0.9 | 202–218 | 15.6–21.5 | 34.5–40.0 |

EC – electrical conductivity; OC – organic carbon; CEC – cation exchange capacity

ties of inherited vermiculite, chlorite, and kaolinite were similar in all of the soils. On the other hand, both pedogenic and inherited sources for illite and smectite could be plausible.

Non-exchangeable K release. The overall results showed that the studied soils contained large amounts of non-exchangeable K except Histosols (pedon 5) and subsoil layer of Entisols (pedon 1). The maximum content of non-exchangeable K (506 mg/kg soil) was found in the surface layer of Inceptisols having vertic properties (pedon 2) with a high amount of clay (41%) and relatively low calcium carbonate (37%), whereas the minimum content (95 mg/kg soil) was

measured in the subsoil of Entisols (pedon 1) with low clay (10%) and high calcium carbonate contents (88%) (Table 3). The release of non-exchangeable K by both the extractants was higher in surface soil compared to subsurface soil (Table 4). CaCl₂ and oxalic acid released more K in surface soils compared to subsurface soils (22 and 28%, respectively) from non-exchangeable positions (Table 4).

Time-dependent cumulative K released from soils using CaCl₂ and oxalic acid is plotted in Figure 2. The trend of the cumulative K release pattern was non-linear and almost similar by the two extractants. The K release pattern was characterized by an initial

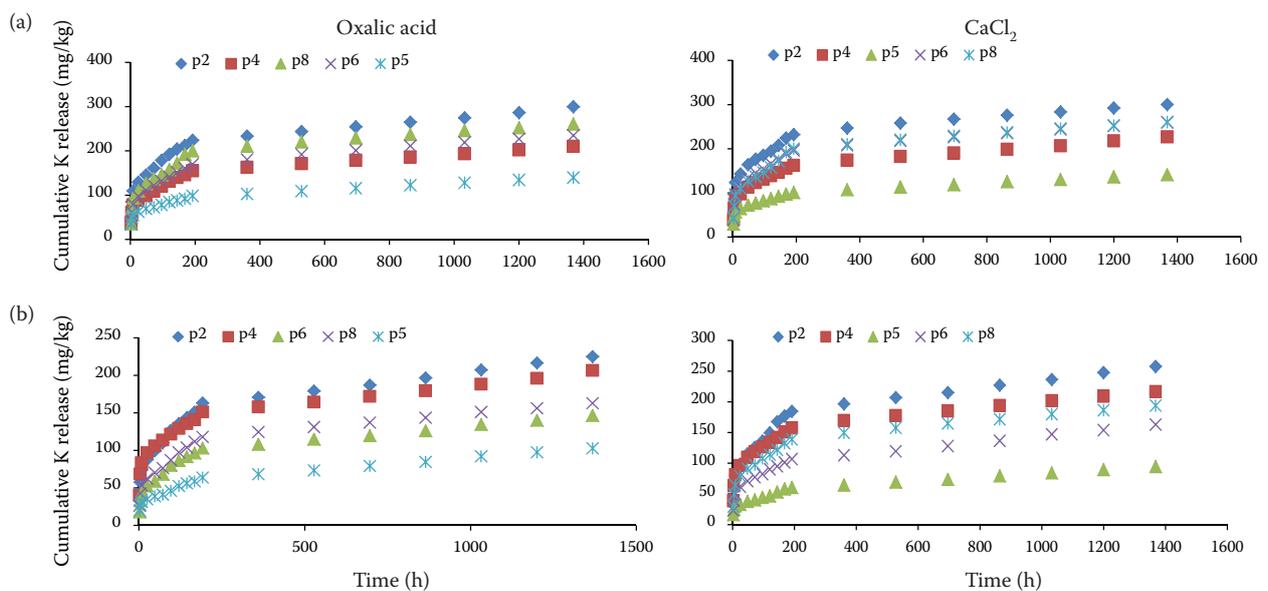


Figure 2. The trend of cumulative K release by CaCl₂ and oxalic acid for selected top soils (a) and subsoils (b)

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fast reaction (2–192 h), followed by a slow reaction (192–1368 h) showing different mechanisms controlling the K release process.

The cumulative content of non-exchangeable K release after 1368 h using CaCl₂ and oxalic acid (Table 3) showed that CaCl₂ released more non-exchangeable K than oxalic acid. The percentages of non-exchangeable K release which are defined as [(cumulative K released × 100)/(non-exchangeable K content)] were 60 and 55% for CaCl₂ and oxalic acid, respectively (Table 3).

The maximum percentages of non-exchangeable K release were measured in the subsurface horizon of Entisols (pedon 1) which were 91 and 82% using CaCl₂ and oxalic acid, respectively. The minimum percentages of non-exchangeable K release were found

in the subsoil of Inceptisols (40 and 50%), when oxalic acid and CaCl₂ were used as extractants (Table 3).

The surface soils showed greater cumulative released K compared to subsurface samples. The mean contents of released K by CaCl₂ in surface and subsurface samples were different (226 and 183 mg/kg, respectively). The amounts of K released from surface and subsurface samples by oxalic acid were measured as 210 and 164 mg/kg, respectively (Table 4).

Modelling of non-exchangeable K release. Different mathematical models were tested to describe the kinetics of non-exchangeable K release for CaCl₂ and oxalic acid extractants over 1368 h. The coefficient of determination (R^2) and standard error (SE) values showed that the three equations used in the study could be fitted well to the K release data. Simplified

Table 3. Cumulative amount of K release, percent of non-exchangeable K release, and b constant from the Elovich equation with 10 mmol/l CaCl₂ and 10 mmol/l oxalic acid

| Soil pedons | | Non-exchangeable K (mg/kg) | Cumulative K released (mg/kg) | | Non-exchangeable K released (%) | | b from Elovich equation (mg/kg/h) | |
|--------------|---------|-------------------------------|----------------------------------|-------------|------------------------------------|-------------|--|-------------------|
| | | | CaCl ₂ | oxalic acid | CaCl ₂ | oxalic acid | oxalic acid | CaCl ₂ |
| P1 | topsoil | 299.9 | 179.7 | 152.7 | 59.9 | 50.9 | 18.5 | 23.0 |
| | subsoil | 94.9 | 86.6 | 77.7 | 91.2 | 81.9 | 9.5 | 10.6 |
| P2 | topsoil | 505.7 | 300.0 | 299.9 | 59.3 | 59.3 | 36.3 | 35.5 |
| | subsoil | 444.4 | 257.8 | 225.2 | 58.0 | 50.7 | 28.3 | 33.1 |
| P3 | topsoil | 403.9 | 216.1 | 203.9 | 53.5 | 50.5 | 25.1 | 27.1 |
| | subsoil | 280.5 | 154.7 | 156.1 | 55.2 | 55.6 | 18.4 | 18.9 |
| P4 | topsoil | 386.7 | 226.7 | 210.0 | 58.6 | 54.3 | 25.4 | 26.9 |
| | subsoil | 356.6 | 216.7 | 206.4 | 60.7 | 57.9 | 22.9 | 25.9 |
| P5 | topsoil | 163.6 | 141.5 | 139.7 | 86.5 | 85.4 | 15.0 | 15.9 |
| | subsoil | 143.3 | 94.9 | 102.6 | 66.2 | 71.6 | 12.1 | 11.2 |
| P6 | topsoil | 462.7 | 259.8 | 234.5 | 56.1 | 50.7 | 29.6 | 32.0 |
| | subsoil | 314.0 | 163.0 | 146.5 | 51.9 | 46.7 | 19.0 | 19.8 |
| P7 | topsoil | 329.9 | 189.5 | 148.8 | 57.4 | 45.1 | 18.1 | 26.7 |
| | subsoil | 373.5 | 205.4 | 205.2 | 55.0 | 54.9 | 26.5 | 27.1 |
| P8 | topsoil | 451.8 | 260.4 | 260.9 | 57.6 | 57.7 | 33.5 | 33.0 |
| | subsoil | 357.1 | 193.9 | 162.9 | 54.3 | 45.6 | 20.5 | 24.4 |
| P9 | topsoil | 418.2 | 242.8 | 210.2 | 58.1 | 50.3 | 26.2 | 29.7 |
| | subsoil | 443.8 | 254.9 | 194.2 | 57.4 | 43.8 | 21.0 | 35.3 |
| P10 | topsoil | 405.4 | 237.7 | 234.3 | 58.6 | 57.8 | 29.8 | 31.4 |
| | subsoil | 354.1 | 178.7 | 162.4 | 50.5 | 45.9 | 20.5 | 22.6 |
| P11 | topsoil | 426.4 | 234.5 | 212.6 | 55.0 | 49.9 | 27.0 | 29.4 |
| | subsoil | 415.8 | 209.6 | 164.8 | 50.4 | 39.6 | 21.1 | 30.1 |
| Max. | | 505.7 | 300.0 | 299.9 | 91.2 | 85.4 | 36.3 | 35.5 |
| Ave. topsoil | | 386.7 | 226.2 | 209.8 | 60.1 | 55.6 | 25.9 | 28.2 |
| Ave. subsoil | | 325.3 | 183.3 | 164.0 | 59.2 | 54.0 | 20.0 | 23.5 |
| Min. | | 94.9 | 86.6 | 77.7 | 50.4 | 39.6 | 9.5 | 10.6 |

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Table 4. The mean comparison of illite content, non-exchangeable K content, cumulative K release, and *b* constant in surface and subsurface soils

| Parameter | Topsoil (<i>n</i> = 11) | | Subsoil (<i>n</i> = 11) | |
|--|--------------------------|------|--------------------------|------|
| | mean | SD | mean | SD |
| Illite (%) | 31.5 ^a | 8.5 | 24.5 ^b | 5.2 |
| Non- exchangeable K (mg/kg) | 386.8 ^a | 28.3 | 298.1 ^b | 16.8 |
| <i>b</i> constant Elovich (CaCl ₂) (mg/kg/h) | 28.2 ^a | 1.6 | 23.8 ^a | 2.5 |
| Cumulative K released by CaCl ₂ (mg/kg) | 226.2 ^a | 13.3 | 185.4 ^b | 17.3 |
| <i>b</i> constant Elovich (oxalic acid) (mg/kg/h) | 25.9 ^a | 2.0 | 20.0 ^b | 1.6 |
| Cumulative K released by oxalic acid (mg/kg) | 209.8 ^a | 14.7 | 162.4 ^b | 13.3 |

^{a,b}Means in the same rows followed by different letters are significantly different at $P < 0.05$; SD – standard deviation

Elovich equation and power function were selected as the best equations describing the kinetics of K release by CaCl₂ and oxalic acid (Table 5).

DISCUSSION

Despite the high total K content, low availability of K in many soils has been frequently reported. Potassium in soil is divided into soluble, exchangeable, non-exchangeable and structural forms. Plant uptake and leaching have been known to deplete soluble and exchangeable K. In such conditions, non-exchangeable K, which is less available to plants, could gradually be released to readily available (soluble and exchangeable K) forms (NAJAFI-GHIRI *et al.* 2010). The maximum K release was observed in the surface horizon of Inceptisols (Table 3), due to the presence of vertic properties (pedon 2) caused by illite and higher content of non-exchangeable K (Tables 1 and 3). On the other hand, the minimum K release was measured in the subsurface horizon of an Entisol with low clay and high calcium car-

bonate contents. Supporting this conclusion, the positive correlation was found between clay content ($r = 0.67^{**}$ for CaCl₂ and $r = 0.64^{**}$ for oxalic acid) and K release. In contrast, the non-exchangeable K release was negatively correlated with CaCO₃ content ($r = -0.81^{**}$ for CaCl₂ and $r = -0.78^{**}$ for oxalic acid), probably due to its dilution effect. The effects of clay type, clay content and non-exchangeable K content on K release were also reported by other researchers (AJIBOYE & OGUNWALE 2008; NAJAFI-GHIRI *et al.* 2012).

The contents of non-exchangeable K and cumulative release of non-exchangeable K in surface soils were significantly higher than in subsurface soils, which could be due to the higher content of illite and lower CaCO₃ content in surface soil. The illite content of surface soil was higher than in subsurface soil (Table 4). The higher illite content on the surface could be attributed to addition of K fertilizers and transformation of smectite to illite together with high weathering of primary mica minerals to illite (SRINIVASARAO *et al.* 2006; SIMONSSON *et al.* 2009).

Table 5. Coefficient of determination (R^2), standard error of the estimates (SE), and *a* and *b* constants describing the kinetics of non-exchangeable K for soils

| | Elovich | | | | Parabolic | | | | Power function | | | |
|-------------------------|---------------------|-----------------------|-------|-------|---------------------|--|-------|-------|---------------------|-----------------------|-------|------|
| | <i>a</i> (mg/kg) | <i>b</i> (mg/kg/h) | R^2 | SE | <i>a</i> (mg/kg) | <i>b</i> (mg/kg/h ^{-0.5}) | R^2 | SE | <i>a</i> (mg/kg) | <i>b</i> (mg/kg/h) | R^2 | SE |
| CaCl₂ | | | | | | | | | | | | |
| Max. | 25.46 | 36.31 | 0.98 | 11.27 | 104.84 | 5.76 | 0.98 | 26.62 | 4.03 | 0.28 | 0.98 | 0.05 |
| Min. | -4.65 | 9.48 | 0.89 | 5.64 | 14.35 | 1.68 | 0.87 | 3.09 | 2.23 | 0.19 | 0.93 | 0.05 |
| Ave. | 7.76 | 23.02 | 0.96 | 8.48 | 58.04 | 3.76 | 0.92 | 14.10 | 3.43 | 0.25 | 0.96 | 0.10 |
| Oxalic acid | | | | | | | | | | | | |
| Max. | 35.76 | 35.51 | 0.99 | 14.39 | 117.82 | 5.77 | 0.96 | 26.71 | 4.21 | 0.31 | 0.98 | 0.11 |
| Min. | -16.21 | 10.60 | 0.92 | 5.38 | 22.04 | 1.79 | 0.86 | 4.68 | 2.56 | 0.20 | 0.94 | 0.08 |
| Ave. | 7.54 | 26.30 | 0.97 | 8.73 | 66.68 | 4.18 | 0.91 | 17.30 | 3.52 | 0.26 | 0.96 | 0.10 |

A higher amount of CaCO_3 and its dilution effect may also be responsible for the lower non-exchangeable K release in subsurface soil compared to surface soil.

The curves of non-exchangeable K release consisted of two phases; an initial fast release phase followed by a slow release phase (Figure 2). The two phases of K release from soils were also reported by SRINIVASARAO *et al.* (2006). HOSSEINPUR *et al.* (2012) stated that the initial fast release of K may be due to the release of K from peripheral edge sites whereas the subsequent slower reaction represented the K release from interlayer sites. Potassium ions could be replaced from edge and planar sites of clay minerals by Ca^{2+} but, due to high ionic radius and hydration energy, Ca^{2+} is not capable of replacing interlayer K. The interlayer K could gradually be released with time. Exudation of organic acids from roots into soil may increase K availability. Oxalic acid is a common organic acid identified in the rhizosphere of calcicole plants (RENGEL & DAMON 2008). The acid can destroy the soil K minerals such as muscovite, biotite, and k-feldspars resulting in the release of K from non-exchangeable forms. However, the release of K by oxalic acid was lower than that by CaCl_2 . The lower released K content by oxalic acid might be due to high pH and CaCO_3 content of the studied soils (Table 3). The soils used in the present study were calcareous, containing more than 30% of CaCO_3 and $\text{pH} > 7.2$. Oxalic acid has two H^+ which are dissociated at $\text{pH} > 4.5$. Thus, the two free negative charges could complexate with cations such as K, Ca, and Na. Unlike malate and citrate, oxalate has a great ability to chelate with Ca and oxalic acid is largely precipitated as Ca-oxalate and thereby a low content of K may be released (TU *et al.* 2007; WANI 2012).

The b constant of the power function equation was measured less than 1 in studied soils showing a decrease in the K release with time (Table 5). It is well documented that the b constant from the Elovich equation can be used as an index of K release rate (HOSSEINPUR & MOTAGHIAN 2013). The positive correlation was found between cumulative K released by CaCl_2 ($r = 0.97^{**}$) and oxalic acid ($r = 0.98^{**}$) with clay content. Also, b from Elovich was positively correlated with cumulative K release by CaCl_2 ($r = 0.61^{**}$) and oxalic acid ($r = 0.65^{**}$). In contrast, the b parameter constant from Elovich was negatively correlated with CaCO_3 content ($r = -0.77^{**}$ for CaCl_2 and $r = -0.72^{**}$ for oxalic acid). HOSSEINPUR *et al.* (2012) stated that different b constants could clearly reflect different K release power of their studied soils.

Comparison of the b constant between oxalic acid and CaCl_2 showed a similar effect of the extractants on releasing K from non-exchangeable positions (Table 5). The clay mineral composition of studied soils was almost similar, but illite seems to control the K release rate of the soils. Our results indicated that the b constant was high in surface layers of Inceptisols and Alfisols with high clay and illite contents (pedons 2 and 8), whereas the lowest b constant was found in the subsurface horizons of Entisols (pedon 1) and Histosols (pedon 5). The high b constant in pedons 2 and 8 might be attributed to the expandable nature of illite which permits K to be released from the edges and wedge areas (SRINIVASARAO *et al.* 2006). The high content of non-exchangeable K in pedons 2 and 8 may also be responsible for the high b constant in these soils (Table 3).

CONCLUSIONS

This study highlighted the relationship between non-exchangeable K release and soil classification, clay mineralogy and soil depth in semi-arid regions of Fars Province. The results showed that soil order, soil depth, and clay type play a significant role in non-exchangeable K content and K release rate. The lowest contents of non-exchangeable K and K release rate were found in subsurface layers of Entisols with high CaCO_3 and low clay contents (pedon 1); while, the highest values were found in Inceptisols with low CaCO_3 and high clay contents, dominated by illite. Results also indicated that the studied soils contained large amounts of non-exchangeable K which could be released to accessible forms. However, the amount of this reservoir has been depleted due to development of irrigated production systems, thus further application of K fertilizer seems necessary in the early future.

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