Effects of Zeolite and Vermicompost Applications on Potassium Release from Calcareous Soils

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Abstract

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Zeolite and vermicompost applications to soil may improve K fertility of soils. For this purpose, these materials were added to five representative calcareous soils collected from southern Iran. The treatments included (1) control, (2) 20 g/kg zeolite, (3) 20 g/kg vermicompost, and (4) 20 g/kg vermicompost + zeolite (1:1). The samples were incubated for 90 days, and the concentrations of soluble, exchangeable, and non-exchangeable K and K release rate to 0.01M $CaCl_2$ during 240 min (16 successive 15 min extractions of soil samples with $CaCl_2$ solution) were determined. Results indicated that zeolite application increased significantly the concentration of soluble and exchangeable K. Vermicompost application had a positive effect on all forms of K. Cumulative K release was also affected by vermicompost application. Comparison of experimental data to different kinetic models indicated that Elovich, power function, and parabolic diffusion models described well kinetics of K release from all soil samples to 0.01M $CaCl_2$. The *b* values of Elovich equation had significant relationships with NH_4OAc- and HNO_3-extractable K. It is recommended that for K fertility management of calcareous soils, organic and inorganic amendments application to soils should be taken into consideration.

Keywords: available K; Iran; K fertility; kinetic models; non-exchangeable K

Potassium release from calcareous soils has been investigated by many researchers (Munn *et al.* 1976; Havlin *et al.* 1985; Jalali 2005). They concluded that some physical, chemical, and biological properties of soils, land position, soil development, clay mineralogy, and soil moisture and temperature regimes may affect K release rate from calcareous soils. It is assumed that some organic and inorganic soil amendments may affect K dynamics, distribution, release, and fixation. Nowadays, zeolite and vermicompost are widely used for improvement of soil properties.

Zeolites are aluminosilicate minerals (Kithome *et al.* 1998), and many types occur in soils (Tsitsishvili *et al.* 1992). These minerals have been increasingly used for soil remediation (Herwijnen *et al.* 2007), land erodibility control (Andry *et al.* 2009), soil properties improvement (Filcheva & Tsadilas 2002), and nitrogen use efficiency (Tarkalson & Ippolito 2011; Aghaalikhani *et al.* 2012) in recent decades. Vermicomposts are also organic soil amendments that have been successfully used for improvement of soil physical, chemical and biological properties and thereby increasing crop yield (Kamali *et al.* 2010; Kalantari *et al.* 2011; Nada *et al.* 2011).

Potassium release from soils may be affected by these mineral and organic amendments. Jalali (2011) for five calcareous soils of Iran concluded that K release rate was decreased in the following order: vegetables waste > sunflower waste > poultry manure > potato waste > rape waste > sheep manure > fruit waste > tree leaves > weeds residues. Filcheva and Tsadilas (2002) concluded that zeolite increased soil pH and exchangeable K, and compost also increased available phosphorus in low P soils.

Calcareous soils of Iran contain a large amount of available K but with intensive crop production and little or no K fertilizers application these soils may become K-deficient in the future. Therefore, the objectives of the present study were to evaluate the effects of zeolite and vermicompost on K release from five calcareous soils of divergent physicochemical and mineralogical properties and to find the best kinetic models to describe K release from soils treated with zeolite and vermicompost.

MATERIAL AND METHODS

Soils and physicochemical analysis. Soils used in this study were collected from different regions of Fars province, southern Iran. According to different soil and topographic maps and aerial photos, five regions were selected, pits were dug, described (Soil Survey Staff 1993), and classified (Soil Survey Staff 2010). Then surface soils (0–20 cm) were considered for physical, chemical, mineralogical and K release analysis.

Calcium carbonate equivalents (Salinity Laboratory Staff 1954), organic carbon (Nelson & Sommers 1996), soil pH (Salinity Laboratory Staff 1954), electrical conductivity (Salinity Laboratory Staff 1954), and cation exchange capacity (Chapman 1965) were determined. Different forms of K were determined by methods of Helmeke and Sparks (1996): total K by digestion (110°C) of soil with HF and HCl, water soluble K in the saturated extract, exchangeable K by NH_4OAc (pH 7), and nitric acid-extractable K by extraction of soils with boiling 1M HNO_3 for 1 h. Potassium was measured on all filtrated extracts using Corning 405 flame photometer (Corning Incorporated, Corning, USA). Analyses were carried out in triplicate.

Incubation experiment and K release analysis. The experiment was a completely randomized 5 × 4 × 3 factorial arrangement. It was done in polyethylene pots, with 200 g soil. Treatments consisted of five soils and four soil amendments with three replicates. The soil amendment treatments included 20 g/kg zeolite (Z), 20 g/kg vermicompost (V), 20 g/kg vermicompost + zeolite (1:1) (ZV), and control (C). The samples were incubated at 22 ± 3°C for 90 days. Enough distilled water was added to bring the soil moisture level to field capacity. At the end of incubation time, samples were air-dried and analyzed to determine different forms of K and K release to 0.01M $CaCl_2$.

Potassium release analysis was carried out by successive extraction of 3 g of soil samples with 30 ml 0.01M $CaCl_2$ and 15 min shaking (Hagin & Feigenbaum 1962; Lopez-Pineiro & Garcia Navarro 1997). Then the samples were centrifuged, and the concentration of K was determined in the clear solution. The soil was mixed with a new portion of diluted $CaCl_2$ solution, shaken, and centrifuged. This procedure was repeated 16 times. Potassium release from samples with time was fitted to:

parabolic diffusion model $(q = a + bt^{1/2})$

power function equation $(\ln q = \ln a + b \ln t)$

Elovich equation $(q = a + b \ln t)$

first order reaction $(\ln (q_0 - q_t) = a - bt)$

zero-order reaction $(q_0 - q_t = a - bt)$

where:

q – amount of released K

q_t – cumulative K released at time t

t – time of release

q_0 – maximum K released

a, b – constants

These mathematical models were tested by least squares regression analysis to determine which equation best described K release from soils. Coefficients of determination (r^2) were obtained by least squares regression of measured versus predicted values. The rate constants of K release from soils were calculated on the basis of these models.

RESULTS AND DISCUSSION

According to Table 1, the studied soils belong to Vertisols, Aridisols, Inceptisols, and Entisols. All soils are calcareous. Clay content ranged from 9 to 51% (Table 2). Potassium constituted 0.50–0.99% of the soils. According to Table 2, mixed mineralogy including smectite, mica, chlorite, palygorskite, vermiculite, and quartz has been attributed to the studied soils; however the relative percentage of these minerals is highly variable. Soils 1 and 4 are smectitic, while soil 3 is chloritic. Generally, for K distribution and dynamics in calcareous soils of southern Iran, some

Table 1. Classification, soil moisture and temperature regimes, and physiographic units of the studied soils

Soil No.	Classification*	Soil moisture regime	Soil temperature regime	Physiographic unit
1	Typic Haploxererts	xeric	mesic	piedmont plain
2	Typic Haplocalcids	aridic	thermic	piedmont plain
3	Typic Calcixererts	xeric	thermic	piedmont plain
4	Typic Torriorthents	aridic	hyperthermic	alluvial plain
5	Typic Haploxerepts	xeric	thermic	piedmont plain

*Soil Survey Staff (2010)

Table 2. Some chemical and physical properties and mineralogy of the studied soils

Soil No.	Depth (cm)	Particle size distribution (%)			$CaCO_3$ (%)	OC (%)	pH	EC (dS/m)	CEC (cmol(c)/kg)	Total K (%)	Clay mineralogy (< 0.002 mm)*
		sand	silt	clay							
1	0–20	13	36	51	3	1.2	7.3	0.4	34	0.99	S >> M > V
2	0–20	55	34	11	45	0.8	7.3	3.7	13	0.50	S = M = C > P
3	0–20	15	46	39	31	0.8	7.5	1.2	15	0.85	C > S = P = M
4	0–20	57	34	9	54	0.3	7.6	7.1	5	0.55	S > C > M
5	0–20	21	44	35	47	1.6	7.6	1.4	14	0.73	S = C = M = P

C – chlorite; M – micas; P – palygorskite; S – smectite; V – vermiculite; *Najafi-Ghiri *et al.* (2012)

characteristics like soil temperature and moisture regimes, soil orders, agricultural activity, clay mineralogy, and soil depth are important (Najafi-Ghiri *et al.* 2010, 2011).

The natural zeolite used in this study was composed of about 90% clinoptilolite and had a pH of 7.31, CEC of 189 $cmol^{(+)}$/kg, soluble K of 80 mg/kg, exchangeable K of 6100 mg/kg, non-exchangeable K of 7460 mg/kg, and total K of 2.6%. Vermicompost was prepared from kitchen waste and had a pH of 7.27, soluble K of 1.33%, exchangeable K of 141 mg/kg, and organic carbon of 37.5% (with no nonexchangeable K).

Different forms of potassium. Changes in soluble, exchangeable, and nonexchangeable K after treatment of soils with zeolite, vermicompost, and vermicompost + zeolite and 90 days incubation at field capacity moisture condition are shown in Table 3. Soluble K in the soils ranged 7–63 mg/kg (mean of 28 mg/kg), and significantly increased to 17–252 mg per kg (mean of 154 mg/kg) with vermicompost application, 13–57 mg/kg (34 mg/kg) with zeolite application, and 10–83 mg/kg (mean of 58 mg/kg) in vermicompost + zeolite application. Exchangeable K in the soils ranged 100–426 mg/kg, and significantly increased with all treatments. Zeolite application had more significant effect on exchangeable K than vermicompost application. Rezaei and Movahedi Naeini (2009) indicated that zeolite application to soil reduced soluble K, but it had a positive effect on available K. Filcheva and Tsadilas (2002) also concluded that zeolite application to soil increased exchangeable K. Zorpas *et al.* (2000) also indicated that zeolite application to vermicompost reduced concentrations of all metals, but increased the concentration of potassium and sodium. Jalali (2011) and Rodriguez *et al.* (2005) concluded that organic residues application to soil had a significant effect on available K.

Potassium release from soils. Potassium release curve for all treatments of the representative soil (soil 3) during 240 min to 0.01M $CaCl_2$ is shown in Figure 1. Release was rapid during the initial phase for all treatments but it reached a nearly constant rate after 45–75 min. This trend has been previously observed for calcareous soils of southern Iran by Jalali and Zarabi (2006) and Jalali (2005). The

Table 3. Contents of water soluble, exchangeable, and nonexchangeable K of the soil samples after 90 days incubation (in mg/kg)

Soil No.	Water soluble K				Exchangeable K				Nonexchangeable K			
	C	V	Z	ZV	C	V	Z	ZV	C	V	Z	ZV
1	7	17	13	10	300	369	421	397	393	458	409	446
2	17	77	30	40	310	550	588	587	456	483	358	417
3	33	236	40	80	112	267	407	400	55	114	33	45
4	33	252	33	77	100	244	435	405	100	129	48	66
5	63	188	57	83	426	668	738	772	144	228	85	157
Mean	28^a	154^d	34^b	58^c	250^a	419^b	518^c	512^c	230^{ab}	282^c	187^a	226^b

C – control; V – vermicompost; Z – zeolite; ZV – vermicompost + zeolite; means in the same rows for each treatment followed by different letters are significantly different at $P < 0.05$ by Duncan's test

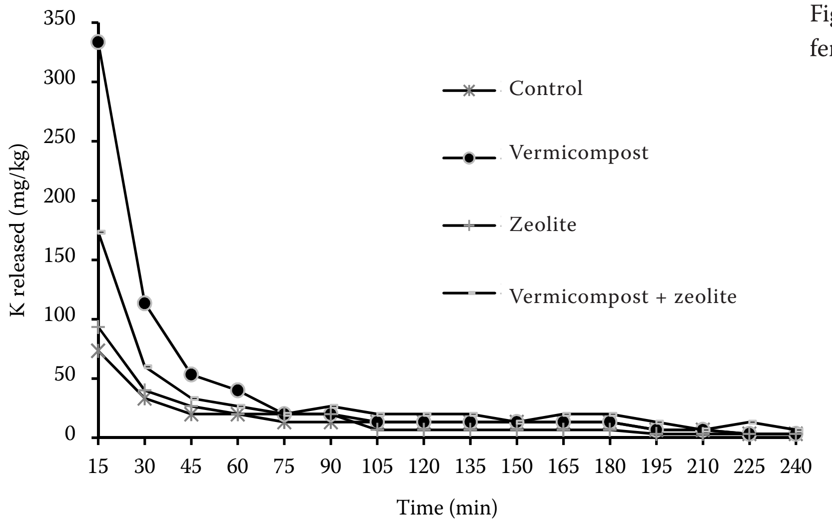

Figure 1. Potassium release curve for different treatments of soil 3

rapid phase of vermicompost treatment continued for 75 min while this time for vermicompost + zeolite, zeolite, and control treatments was 60, 45, and 45 min, respectively. A similar trend was found for other soils. The final constant rate was from 0.1 to 0.9 mg/kg/min. The highest and lowest values exhibited soils 5 and 3, respectively.

Cumulative K released to 0.01M $CaCl_2$ during 240 min is shown in Table 4. The highest amount of K was released from soil 5 while the lowest value was determined for soil 3. Significant and positive relationships ($P < 0.05$) were found between cumulative K release and soluble and exchangeable K ($r = 0.52$ and 0.62, respectively). The effects of zeolite, vermicompost, and vermicompost + zeolite on K release are shown in Table 4. Generally, zeolite had no significant effect on K release, although in soil 2 zeolite application increased cumulative K release significantly. On the other hand, zeolite decreased K release from soils 1 and 5. Addition of vermicompost (with or without zeolite) significantly increased K release from all soils. The effect of vermicompost application was more sensible than vermicompost + zeolite application. The average increase in cumulative K release with application of vermicompost was 88%; while this value for vermicompost + zeolite was 45%. The lowest increase in cumulative K release with application of vermicompost was observed for soil 1. Soil 1 is smectitic with minor content of K-bearing minerals (micas). In a study, Najafi-Ghiri and Abtahi (2012) concluded that high-clay smectitic soils in southern Iran had a high capacity for K fixation; and this may reflect that some released K may be fixed by smectites.

Decrease in K release with zeolite application may be explained by the fact that zeolite had a high affinity toward K ions (Barros & Arroyo 2004; Panuccio *et al.* 2007). As mentioned previously, zeolite used in this study had a high ratio of exchangeable to soluble K (6100:80), and this may reflect the high tendency of zeolite for K adsorption.

Vermicompost had a lower affinity toward K. With application of vermicompost, some K ions may be fixed by K-fixing minerals like smectites, but a high proportion of K ions may be soluble in soils; and this reflects more K release from soils treated with vermicompost especially in the early period of the experiment.

Description of K release by kinetic models. The coefficient of determination (R^2) and the standard error of the estimate (SE) of various kinetic models are shown in Table 5. According to these data, Elovich, parabolic diffusion, and power function models describe very well the kinetics of K release from soils. A successful application of these models to K release from calcareous soils of Iran has been previously reported by Jalali (2007). Rezaei and

Table 4. Cumulative K released (mg/kg) by 16 successive extractions with 0.01M $CaCl_2$ during 240 min

Soil No.	Treatments			
	C	V	Z	ZV
1	533.6	580.3	493.6	593.6
2	320.2	960.5	420.2	727.0
3	273.5	680.3	273.5	493.6
4	286.8	780.4	293.5	446.9
5	847.1	1254.0	760.4	1020.5
Mean	452.2^a	851.1^c	448.2^a	656.3^b

C – control; V – vermicompost; Z – zeolite; ZV – vermicompost + zeolite; means in the same rows followed by different letters are significantly different at $P < 0.05$ by Duncan's test

Table 5. Coefficient of determination (R^2) and standard error of the estimate (SE) of various kinetic models for different soils and treatments (5 samples with three replicates)

Kinetic models	C		V		Z		ZV	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE
Zero-order	0.932	26.1	0.855	53.1	0.916	25.6	0.917	35.3
First-order	0.936	0.273	0.941	0.297	0.940	0.261	0.929	0.295
Elovich	0.977	16.0	0.985	16.6	0.982	14.5	0.975	20.0
Parabolic diffusion	0.984	11.5	0.941	8.8	0.976	13.2	0.973	15.3
Power function	0.984	0.039	0.965	0.039	0.983	0.040	0.982	0.027

C – control; V – vermicompost; Z – zeolite; ZV – vermicompost + zeolite

Movahedi Naeini (2009) stated that Elovich, first order, zero order, and power function models may describe well K release from zeolite. Stewart *et al*. (1998) concluded that K release from mushroom compost was described using first order and parabolic diffusion equations.

Constants *a* and *b* of Elovich equation may be used as an index of K release rate and initial rate of K release, respectively (Martin & Sparks 1983; Jalali 2007). The constants for five soils as a function of four treatments are shown in Table 6. The *a* value ranged from –614.9 to 120.9 mg/kg. The highest values were found for samples treated with vermicompost, and *a* values for samples treated with vermicompost were significantly ($P < 0.05$) higher than others. Control, zeolite, and vermicompost + zeolite treated samples did not show a significant difference in *a* values.

Table 6. The constants *a* (in mg/kg) and *b* (in mg/kg/min) of Elovich equation for different soils and treatments

Soil No.	Constant	Treatments			
		C	V	Z	ZV
1	*a*	–267.6	–364.4	–365.0	–307.0
	b	144.2	171.0	155.1	163.2
2	*a*	–76.6	120.9	16.1	67.9
	b	71.1	155.6	72.5	122.1
3	*a*	–162.6	29.9	–91.6	–185.8
	b	78.1	120.9	67.4	121.0
4	*a*	–154.4	59.3	–148.7	–131.6
	b	79.5	132.9	78.7	102.6
5	*a*	–614.9	–502.2	–575.3	–586.1
	b	261.8	319.9	236.5	287.9
Mean	*a*	–255.2[a]	–131.3[b]	–232.9[a]	–228.5[a]
	b	126.9[a]	180.1[c]	122.0[a]	159.4[b]

C – control; V – vermicompost; Z – zeolite; ZV – vermicompost + zeolite; means in the same rows followed by different letters are significantly different at $P < 0.05$ by Duncan's test

The highest value of *b* constant was also found for samples treated with vermicompost (mean = 180.1 mg per kg/min). However, there is not a significant difference in *b* constant between control and zeolite treated samples. This is inconsistent with findings of Rezaei and Movahedi Naeini (2009) who concluded that zeolite application to some soils of Iran decreased release rate of K.

A significant and positive relationship ($r = 0.677$, $P < 0.01$) between *b* value and NH_4OAc-extractable K (soluble + exchangeable K) reflects the significance of this parameter in determination of K release rate in calcareous soils. Significant relationships were also obtained between *b* values and HNO_3-extractable K (soluble + exchangeable + non-exchangeable K) and cumulative K release to 0.01M $CaCl_2$.

CONCLUSIONS

Zeolite and vermicompost are not applied for K supply, however secondary effects of these soil amendments on K distribution and dynamics may be important for soil K fertility management. Zeolite and vermicompost application to soils increased available K while this increase for vermicompost was mainly via increase in soluble K. For zeolite, this increase was observed in exchangeable K. Cumulative K release from soils was also affected by zeolite and vermicompost. However, dual application of zeolite and vermicompost had no significant effect on cumulative K release.

For K fertility management of calcareous soils that have a large amount of nonexchangeable K (as a slowly available K) soil amendments application should be taken into consideration.

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