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KINETICS OF ADSORPTION AND DESORPTION OF CESIUM IN AN ORGANIC MATTER RICH SOIL SATURATED WITH DIFFERENT CATIONS

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We attempted to analyse the effect of dominating exchangeable cations on the adsorption and desorption kinetics of cesium in an organic matter rich soil from Bikini Islands. The top soil (0-25 cm) and sub-soil (25-40 and 40-60 cm) samples were taken from representative sites in Bikini Atoll. The organic matter content ranged from 55 to 9 g/kg in the 0-25 and 40-60 cm depth. The major source for cation adsorption in the Bikini soils is the organic fraction and Ca is the predominant exchangeable cation. Oxide contents including amorphous Al- and Fe-oxides were extremely low, being basically undetectable.

The kinetic studies were conducted using stirred-flow reactor chamber developed by Carski and Sparks (1985). With this technique, 1 g of Ca-, K- or Na-saturated soil was placed in the chamber and then 0.02 N CsClO₄ was passed through the soil at a flow rate of 1 ml/min using a peristaltic pump. Since practically no clay minerals exist in these soil samples, we are assuming film diffusion would be the major type of mass transfer. Under these conditions, the ratio of the adsorption rate constant (K_a) to the desorption rate coefficient (K_d) would equal the exchange equilibrium constant, K_{eq} . Using this relationship, we could then obtain the standard Gibbs free energy for Cs-Ca, Cs-K and Cs-Na exchange, ΔG° using the relationship $\Delta G^\circ = -RT \ln K_{eq}$.

Adsorption kinetics were continued until an apparent equilibrium in Cs adsorption occurred. After adsorption, Cs was desorbed with 0.02N perchlorate solution of either Ca, K or Na. Similar to adsorption, the desorption studies were carried out until an apparent equilibrium was attained.

Cesium adsorption and desorption on Ca-, K- and Na-saturated soils was completely reversible since approximately equal amounts of Cs were adsorbed and desorbed (Table 1). The kinetics of Cs-K and Cs-Ca exchange were rapid with an approach to equilibrium occurring in about 16-24 min. Cesium adsorption was highest in the 0-25 cm depth when Na was on the exchange site. The lower adsorption of Cs in the surface soil depth when Ca was the predominant exchangeable cation is due to the preference of Ca over Cs on organic colloids. The organic matter content was quite high in the 0-25 cm depth.

The preference for Ca over Cs is also reflected in the $+\Delta G^\circ$ value (815 J/mol) in the top two depths of Bikini soils. In the lower depth, Cs is preferred over Ca ($\Delta G^\circ = -1328$ J/mol) and in this horizon, organic matter content was dropped off considerably. Adsorption of Cs decreased with depth for all the three exchange systems and was particularly lower in the 40-60 cm depth. The decrease in Cs adsorption with depth is attributable to the lower amount of humic material in the lower depths.

Table 1. Total amount of cesium adsorbed and desorbed on Ca-, K- and Na-saturated surface and subsoils of Bikini Atoll

Depth (cm)	Amount of Cs Adsorbed or Desorbed					
	Cs-Ca Exchange		Cs-K Exchange		Cs-Na Exchange	
	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
	-----cmol/kg-----					
0-25	3.104	3.098	4.688	4.645	6.330	6.318
25-40	3.599	3.550	1.682	1.729	3.400	3.390
40-60	0.767	0.744	1.726	1.453	1.935	1.931

Adsorption and desorption rate constants (K_a and K_d , respectively) and half-times ($t_{1/2}$) for adsorption and desorption showed that irrespective of cation saturation, the rate of Cs adsorption was more rapid for lower Bikini soil horizon. Also the total amount of Cs adsorbed was lowest in this horizon, particularly in Cs-Ca system. When Ca is the predominant ion, Cs desorption was slowest from 40-60 cm depth. This again indicates that as humic material decreases in quantity, Cs is more strongly preferred and less easily leached. In fact, in the upper horizons, where humic materials were more prevalent, Cs desorption was faster than Cs adsorption.

The relative rates of adsorption and desorption of Cs as characterized by the half-time, $t_{1/2}$ show that for both Ca- and K-saturated soils, Cs adsorption was much faster in the 40-60 cm depth. It further shows that desorption of Cs was much slower in this horizon when the dominant cation is Ca^{2+} .

References :

Carski, T.H. and D.L. Sparks, 1985. A modified miscible displacement technique for investigating adsorption-desorption kinetics in soils. Soil Sci. Soc. Am. J. 49 : 114-116