

STRONTIUM EXCHANGE CHARACTERISTICS OF SOILS FROM THE OGOTORUK CREEK WATERSHED IN ALASKA¹

J. L. MORTENSEN, E. C. MARCUSIU, AND N. HOLOWAYCHUK

*Department of Agronomy, Ohio Agricultural Experiment Station,
and The Ohio State University, Columbus 10*

The distribution and fate of strontium-90 in soil is determined by such factors as ion-exchange and fixation mechanisms, leachability, uptake by plants, erosion, complexing by organic matter, etc. Properties of the soil such as pH (Haghiri and Sayre, 1961), kind and amount of clay minerals (Jones and Haghiri, 1962; McLean et al., 1960), amount of organic matter (Nishita et al., 1956), and base status (Klechkrovsky, 1957; McHenry, 1958; Prout, 1958) have been shown to affect such factors as strontium-90 ecology in soil.

The purpose of this study was to investigate the strontium exchange characteristics of soils with high organic matter content from the Ogotoruk Creek Watershed area in Alaska.

MATERIALS

The surface horizons or surface organic layers of the ten unclassified soils listed below were used in this investigation. The profile sample designation such as #22 is shown for each of the soils. Pairs of samples from the same Great Soil Group but from different sites were obtained for comparison purposes.

#22 and #107—Very dark grayish brown soils with dark gray or very dark gray subsoil material. Derived in part from stratified sand and gravel.

#24 and #28 —Dark gray mottled soils on silty eolian material.

#26 and #41 —Gray or dark gray soils on silty colluvium mixed with materials derived from calcareous rocks. These two soils are slightly acid and have a base saturation exceeding 75 per cent.

#30 and #91 —Gray or dark gray soils on eolian silty material and on mixed silty materials derived from eolian silts and mudstone and graywacke. These are very acid soils, having a base saturation of about 10 per cent.

#31 and #47 —Very dark grayish brown soils with dark gray or very dark gray subsoils on materials derived from mudstone and graywacke.

METHODS

Soils used in this study were air-dried and crushed to pass a 2-mm sieve. Carbon content was determined by dry combustion and pH was measured with a glass electrode using a soil-water ratio of 1:3.

Frontal analysis chromatography was used to determine cation exchange capacity (Dawson, 1956b). The soils were saturated with hydrogen ions using 0.2 N HCl. Chloride ions were removed by leaching with distilled water and the soils were then air-dried. A slurry containing 10.00 g of soil was transferred to a glass column (1.7 cm x 20.0 cm) which contained a retaining mat of glass wool. Five grams of Hyflo Super Cel were mixed with samples of soil #22, #31, and #41 prior to packing the column. After all of the soil had been transferred to the column, a glass wool mat was placed on the soil surface. Following the removal

¹Journal Paper No. 83-62 of the Ohio Agricultural Experiment Station, published with permission of the Director under Atomic Energy Commission Project AT(11-1)-414.

of excess water above the soil surface, separate columns were leached with 0.2 N barium acetate and strontium acetate. A head of 8.0 cm was maintained above the surface of the soil. Two-ml fractions were collected and the liberated acetic acid was titrated with 0.1002 N NaOH. The titration values were summed as a measure of the cation exchange capacity. Flow rate depended upon the soil and varied from 2 ml/3 min to 2 ml/15 min.

Adsorptivity and leachability of strontium in soils #30 and #41 were determined by a combination of frontal analysis and displacement development chromatography. A slurry of soil (10.00 g of soil #30, 5.00 g of soil #41 plus 5.00 g Hyflo Cel) and distilled water was transferred to a glass column and prepared for chromatography as outlined above. The soils were not saturated with hydrogen ions but were used as they came from the field. The soil in the column was then leached with 0.1 N SrCl_2 containing 4550 counts/min/ml of $\text{Sr}^{90}(\text{Y}^{90})$. A constant head of 9.0 cm was maintained above the soil surface during the collection of 2-ml fractions. The flow rate averaged 2 ml/6 min. When the count rate in the collection tubes reached an equilibrium value the column was leached with distilled water until no activity was detected in the collection tubes. The column was then leached with 0.1 N HCl until all the $\text{Sr}^{90}(\text{Y}^{90})$ desorbed by this reagent had been collected. The column was then leached with distilled water. An aliquot of the solution in each collection tube was placed in an aluminum planchet, dried under a heat lamp and $\text{Sr}^{90}(\text{Y}^{90})$ immediately counted with a windowless flow counter operating in the proportional region. Organic matter in each collection tube was determined by a colorimetric method following the addition of a $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ mixture (Dawson, 1956a). One ml of the material in the collection tubes following the leaching of the column with 0.1 N HCl was titrated with 0.1002 N NaOH. Plotting counts/min/ml, optical density and ml 0.1002 N NaOH versus fraction number permitted graphical visualization of the breakthrough curves of concentration of $\text{Sr}^{90}(\text{Y}^{90})$, organic matter and acidity.

The leachability of carrier-free $\text{Sr}^{90}(\text{Y}^{90})$ by water-soluble components of soils #30 and #41 was determined by elution development chromatography. A column of 10.00 g of soil was prepared as outlined above. After excess water had been removed from the soil surface, 0.42 microcuries of carrier free $\text{Sr}^{90}(\text{Y}^{90})$ (8.4×10^{-5} mg SrCl_2) in 0.5 ml of distilled water was added to the surface of the soil. Leachate from a column of 20.00 g of soil #30 (or #41 when this soil was being leached) suspended above the column to which $\text{Sr}^{90}(\text{Y}^{90})$ had been added was allowed to drip on the glass wool pad placed on the soil surface of the lower column. The upper column was leached with distilled water in order to provide the water-soluble component for leaching the soil column to which $\text{Sr}^{90}(\text{Y}^{90})$ had been added. The rate of flow from the lower column varied from 2 ml/13.5 min at the beginning of the experiment to 2 ml/1.6 hr at its termination. An aliquot of each 2-ml fraction collected from the lower column was counted for $\text{Sr}^{90}(\text{Y}^{90})$ activity. Following the collection of 173 fractions (346 ml) the soil in the lower column was carefully removed and separated into $\frac{1}{2}$ inch sections. The soil in each section was shaken for 1 hr with 0.1 N HCl and centrifuged. $\text{Sr}^{90}(\text{Y}^{90})$ activity of the supernatant was determined immediately.

RESULTS AND DISCUSSION

The soils used in this study contained considerable organic carbon, and all of them with the exception of soil #22, #31, #47, and #107 could be classified as organic soils. Reaction (pH) of these soils varied between 3.9 and 5.8 (table 1). pH of the less acid soils was no doubt influenced by limestone rocks in the vicinity.

Figure 1 represents the exchange of barium and strontium ions for hydrogen ions on four representative soils used in this study. On high exchange capacity soils (see table 2), the elution curves reached an equilibrium value indicative of maximum liberation of acetic acid from the 0.2 N acetate salts. The asymmetrical

TABLE 1
Carbon content and pH of surface layers of ten soils in Ogotoruk Watershed area, Alaska

Soil	Depth(*)	Carbon %	pH
22	0-4"	8.2	5.0
24	5-0"	26.7	4.2
26	8-0"	20.0	5.7
28	6-0"	30.2	3.9
30	6-0"	26.4	4.2
31	0-4"	14.9	4.4
41	11-0"	30.3	5.8
47	0-5"	15.4	4.5
91	6-0"	26.5	4.1
107	0-4"	14.1	5.0

(*)8-0", 11-0", etc. denotes organic surface layer; 0-4", 0-5", etc. denotes mineral surface layer.

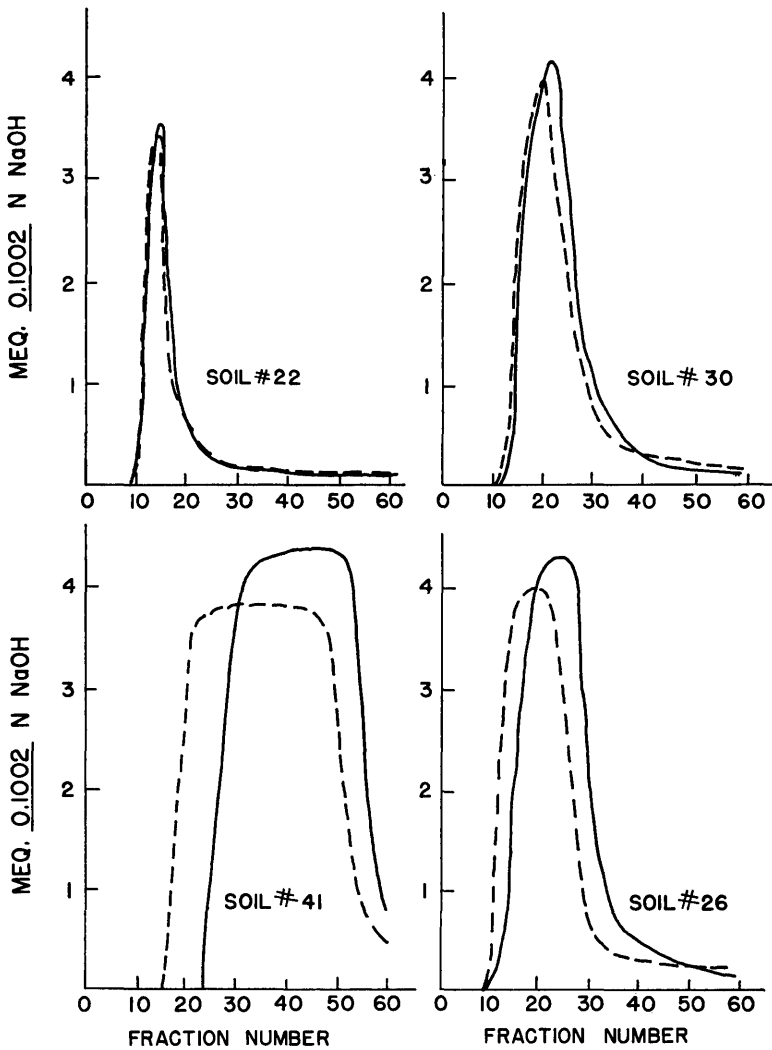


FIGURE 1. Titration of acetic acid liberated by barium acetate (—) and strontium acetate (---) from some hydrogen saturated Alaska soils.

trailing edge of the elution curves has been attributed (Dawson, 1956b) to release of H^+ from phenolic hydroxyls of organic matter, but the degree of ionization of carboxyl groups could very well have differed with change in pH. Hydrogen ions were more rapidly replaced by strontium than by barium, but total exchange capacity as determined with strontium acetate was slightly lower than that determined with barium acetate. Wiklander (1955) found little difference in the replacing power of Sr^{++} and Ba^{++} for H^+ from humus although Ba usually precedes Sr in the lyotropic replaceability series.

The cation exchange capacity for the soils used in this study varied from 23.7 me/100 g to 127.3 me/100 g (table 2). If the two samples (#26 and #41)

TABLE 2
Cation exchange capacity of surface layers of ten soils in Ogotoruk Creek Watershed area, Alaska

Soil	Cation exchange capacity	
	Sr me/100 g	Ba me/100 g
22	22.2	23.7
24	61.8	62.0
26	64.1	70.1
28	65.8	68.5
30	51.0	53.4
31	41.4	36.5
41	125.7	127.3
47	43.2	43.9
91	49.4	50.4
107	46.1	49.5

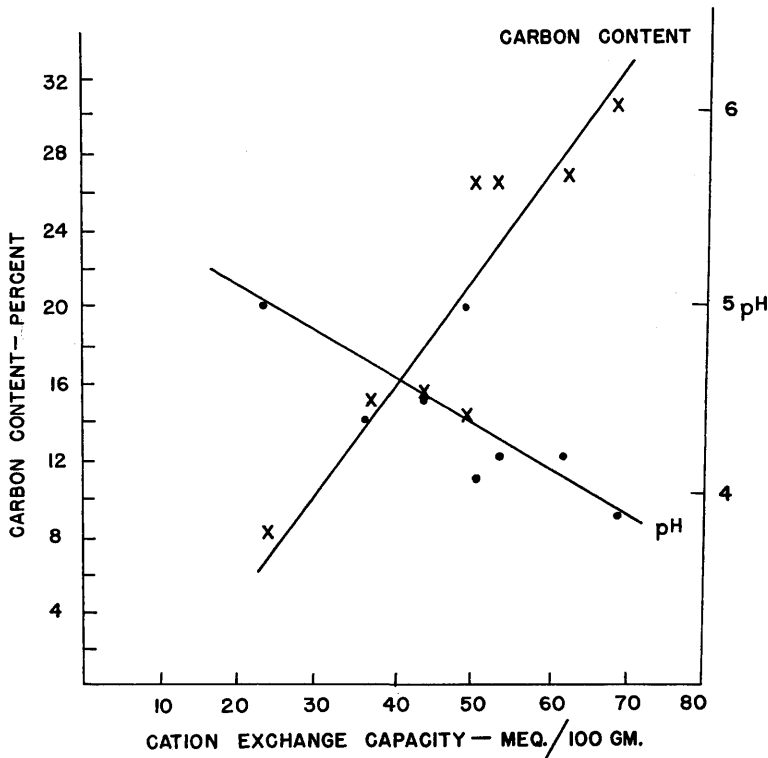


FIGURE 2. Effect of carbon content and pH on cation exchange capacity of some Alaska soils (correlation lines drawn, not calculated).

of higher pH are excluded, cation exchange capacity was positively correlated with carbon content and acidity, i.e., negatively correlated with pH (fig. 2). Carbon content and pH were also related. Organic matter in soils of lower pH apparently did not decompose as rapidly as that in less acid soils, thus more of it was retained and hence contributed to higher cation exchange capacity.

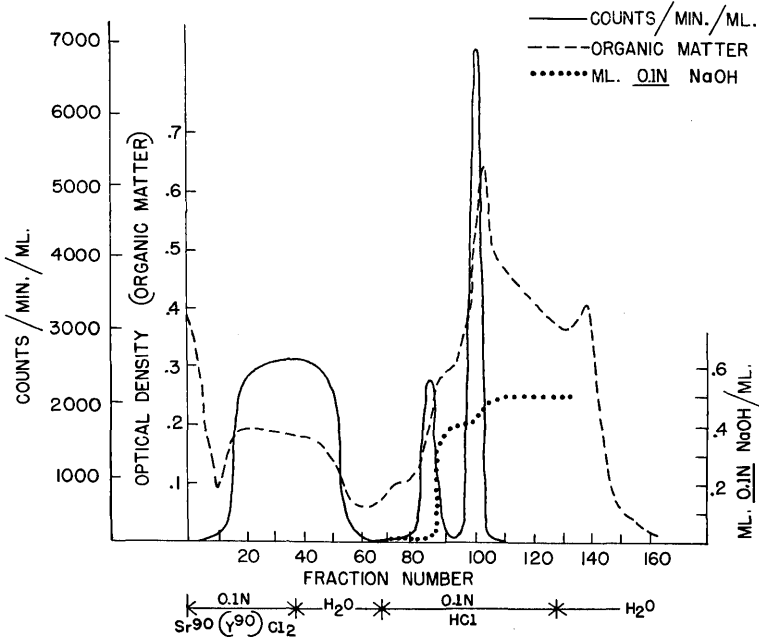


FIGURE 3. Adsorbability and leachability of Sr⁹⁰(Y⁹⁰) in soil #30.

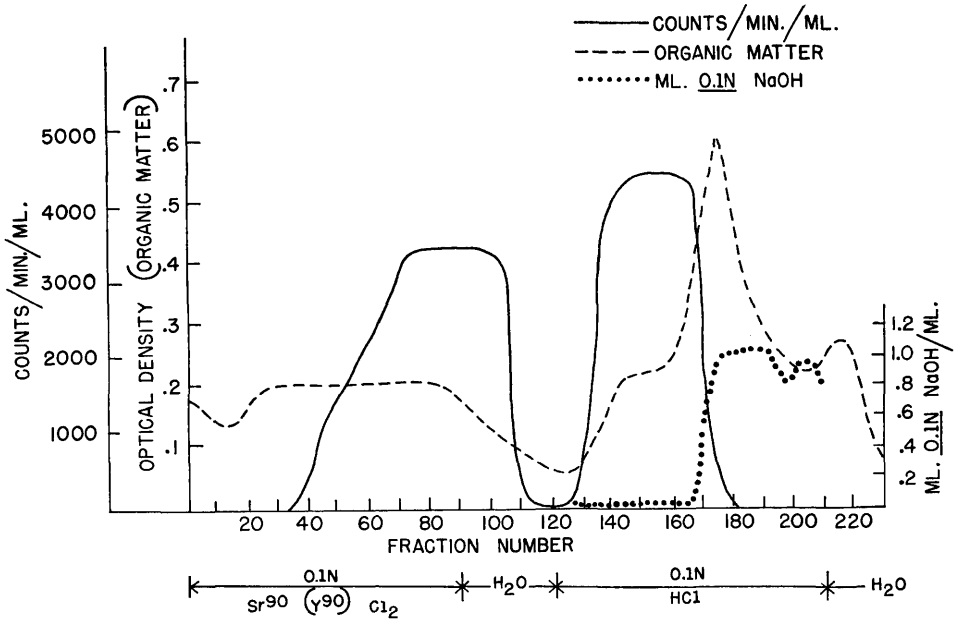


FIGURE 4. Adsorbability and leachability of Sr⁹⁰(Y⁹⁰) in soil #41.

Figures 3 and 4 illustrate a considerable difference in the adsorbability and leachability of strontium in soils of different cation exchange capacity and pH, but of similar carbon content. Considerably more $\text{Sr}^{90}(\text{Y}^{90})\text{Cl}_2$ was required to saturate soil #41 than soil #30. The larger saturation requirement was no doubt due to a greater cation exchange capacity and higher pH. Several workers (McHenry, 1958; Prout, 1958; Rhodes, 1957) have shown that more Sr^{90} is adsorbed by soils of higher pH than lower pH. The shape of the $\text{Sr}^{90}(\text{Y}^{90})\text{Cl}_2$ breakthrough curve for soil #41 suggests that several kinds of replacement reactions

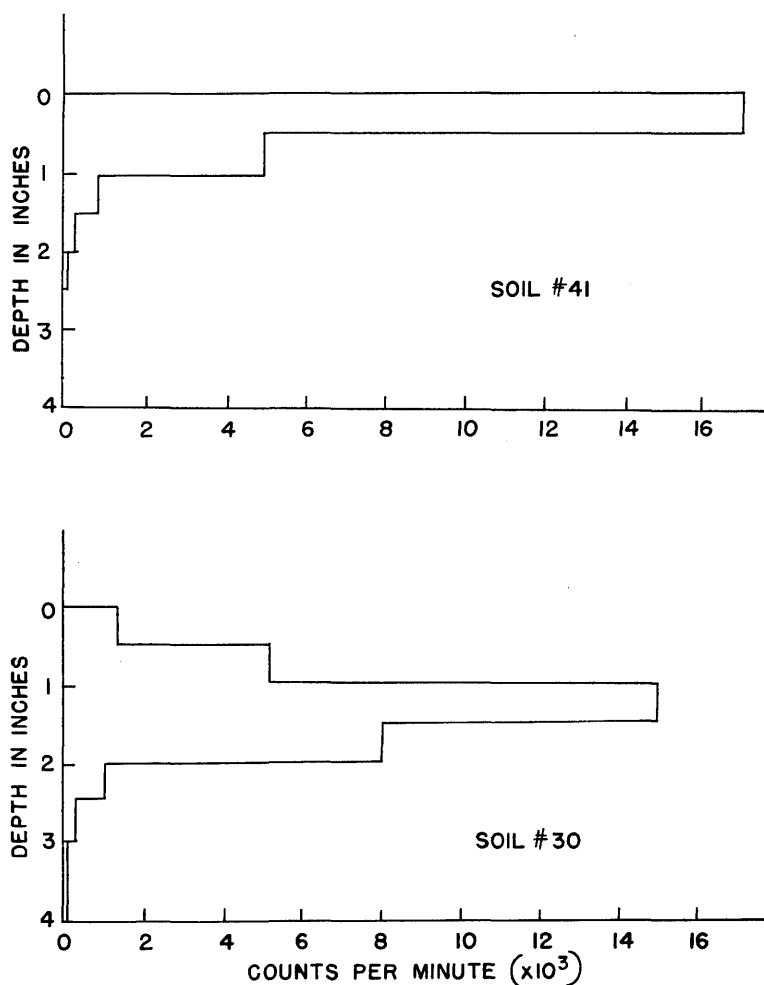


FIGURE 5. Leachability of carrier free $\text{Sr}^{90}(\text{Y}^{90})$ in soils #30 and #41.

probably occurred. Shulz et al. (1958), have shown that for short contact times, Sr is retained in soil in water soluble and exchangeable forms, but the relatively high amount of Sr used in this study may have caused some replacement of Ca from soil minerals.

$\text{Sr}^{90}(\text{Y}^{90})$ was eluted by 0.1 N HCl from soil #41 as a single large peak (fig. 4), but two peaks of $\text{Sr}^{90}(\text{Y}^{90})$ were eluted from soil #30 (fig. 3). The second peak was present in fractions which contained considerable organic matter and the

$\text{Sr}^{90}(\text{Y}^{90})$ in this second peak may have been present as complexes of organic matter solubilized by 0.1 N HCl. Two inflection points in the HCl breakthrough curves were associated with maximum $\text{Sr}^{90}(\text{Y}^{90})$ desorption which suggests that $\text{Sr}^{90}(\text{Y}^{90})$ was displaced from at least two types of complexes by hydrogen ions.

The dissolution patterns of organic matter by 0.1 N HCl from the two soils were similar. Elution with water following the HCl treatment resulted in a small increase in organic matter solubility in both soils, but no $\text{Sr}^{90}(\text{Y}^{90})$ was detected in fractions containing this organic matter peak.

Figure 5 shows that carrier free $\text{Sr}^{90}(\text{Y}^{90})$ is much more leachable in soil #30 than in soil #41. Leaching waters in soil #30 would be more acidic than in soil #41 and thus more capable of moving $\text{Sr}^{90}(\text{Y}^{90})$ into lower depths of the profile or releasing it into drainage water. The higher exchange capacity of soil #41 would also reduce the leachability of $\text{Sr}^{90}(\text{Y}^{90})$, (Miller and Reitemeier, 1957; Thornthwaite et al., 1960).

It is apparent that soils of the Ogotoruk Watershed area in Alaska, particularly those having high exchange capacity and base status, are capable of adsorbing considerable quantities of $\text{Sr}^{90}(\text{Y}^{90})$. Leaching waters from the more acidic soils should leach $\text{Sr}^{90}(\text{Y}^{90})$ more deeply into the profile and release it more readily into drainage waters than would be the case in the less acid soils. Schulz et al. (1959), have shown that acidic solutions are more effective than solutions of calcium salts in leaching strontium from soil surfaces. The leaching of fallout Sr from acidic organic soils may occur in a relatively short period of time since Larsen (private communication) has recently shown that sample #41 contained considerably more fallout Sr^{90} in the upper 4 inches of the profile than did sample #30. Fission product ecology in soils of the area is apparently governed largely by pH and cation exchange capacity.

ACKNOWLEDGMENT

The analytical assistance of R. Asebrook is gratefully acknowledged.

LITERATURE CITED

- Dawson, J. E. 1956. Department of Agronomy, Organic Soils Laboratory, Chemical Methods, Cornell University.
- . 1956. Organic soils. *Adv. Agron.* 8: 377-440.
- Haghiri, F. and J. D. Sayre. 1961. Strontium 90 uptake by plants as influenced by soil types and liming. *Soil Sci. Soc. Amer. Proc.* 25: 120-123.
- Jones, J. B. Jr., and F. Haghiri. 1962. Reducing the uptake of Sr^{90} by plants on contaminated Ohio soils. *Ohio J. Sci.* 62: 97-100.
- Klechkrovsky, V. M., Ed. 1957. On the behavior of fission products in soil. AEC-TR-2867.
- McHenry, J. R. 1958. Ion-exchange properties of strontium in a calcareous soil. *Soil Sci. Soc. Amer. Proc.* 22: 514-518.
- McLean, E. O., T. G. Arscott, and V. V. Volk. 1960. Adsorption and release of strontium from clays and soils with equilibration, isotopic tracer and plant uptake techniques. *Soil Sci. Soc. Amer. Proc.* 24: 453-457.
- Miller, J. R. and R. F. Reitemeier. 1957. Rate of leaching of radiostrontium through soils by simulated rain and irrigation water. U. S. Dept. Agr., A.R.S. Research Report No. 300. 000 p.
- Nishita, H., B. W. Kowalewsky, and M. H. Larsen. 1956. Influence of soil organic matter in mineral uptake by barley seedlings. *Soil Sci.* 82: 307-318.
- Prout, W. E. 1958. Adsorption of radioactive wastes by Savannah River plant soil. *Soil Sci.* 86: 13-17.
- Rhodes, D. W. 1957. The effect of pH on the uptake of radioactive isotopes from solution by a soil. *Soil Sci. Soc. Amer. Proc.* 21: 389-392.
- Schulz, R. K., R. Overstreet, and K. L. Babcock. 1958. On the soil chemistry of radiostrontium. *Hilgardia* 27: 333-342.
- Schulz, R. K., J. P. Moberg, and R. Overstreet. 1959. Some experiments on the decontamination of soils containing strontium 90. *Hilgardia* 28: 457-475.
- Thornthwaite, C. W., J. R. Mather, and J. K. Nakamura. 1960. Movement of radio-strontium in soils. *Science* 131: 1015-1019.
- Wiklander, L. 1955. Cation and anion exchange phenomena, p. 107-148. *In* Bear, F. E., [Ed.], *Chemistry of the Soil*. Reinhold Pub. Co., New York.