Potash Review

Monthly communications by the International Potash Institute, Berne (Switzerland)

Subject 4

Soil Science
46th suite

February 1971

Adsorption and desorption patterns of potassium, rubidium and cesium in various soils at macro and trace concentrations

K. Smierzchalska

Agricultural Isotopic Laboratory, Polish Academy of Sciences
Warsaw, Poland

Introduction

This paper contributes to the problem of the use of chemically similar elements potassium, rubidium and cesium as well as their isotopes for studies on some processes going on in soils or fertilizer-soil system, especially such as adsorption and migration of the ions. It would be also of great importance to predict the behaviour of these elements on the basis of the experimental data obtained with another one of similar chemical properties. These considerations would be particularly valuable for potassium being one of the principle plant nutrients, as well as for cesium being a dangerous radionuclide in the contamination hazard.

Rubidium is placed in the periodic system between the two elements–potassium and cesium, and because of its suitable radioisotope Rb^{86} is considered as a standard element. The use of Rb^{86} in the studies on potassium behaviour has been investigated by a number of workers and their results were reviewed and published together with research carried out by the author previously (16).

Recently, the behaviour of cesium, its adsorption and release by various soils were investigated too. This problem is of importance because of soil contamination with Cs^{137} being a long-living constituent of fallout. The adsorption capacities of soils and clay minerals, especially for irreversibly adsorbed cesium, as well as the influence of other cations on its adsorption pattern were studied by many authors (1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 14, 17, 18, 19).

Materials and Methods

The adsorption patterns of potassium, rubidium and cesium have been studied on 18 soils; nine of them (seven Polish soils and two Yugoslav soils) were analysed in the Agricultural Isotopic Laboratory of PAS, situated at the Agrochemistry Department of the Agricultural University in Warszawa. The studies on the other nine soils were carried out in the Institute of Nuclear Sciences in Agriculture (ITAL), in Wageningen, The Netherlands*. Among these soils there were six Dutch soils,

---

* The determinations were carried out during the author's stay at ITAL, in 1969.

while the others derived from Italy, France and Germany. All these soils were included in the research programme of the ITAL. The soil types studied at this Institute were similar to those investigated in Poland.

The determination of the soil capacities for potassium, rubidium and cesium adsorption (total, exchangeable and nonexchangeable) was carried out with the same method as reported previously (16). Soil samples (5 g of soil) were equilibrated with potassium, rubidium or cesium solutions at concentration corresponding to 2,56 meq/100 g of soil, at the soil/solution ratio of 1:2,5.

The radioisotopes K^{42} or K^{43} have been used for potassium labelling, Rb^{86} for rubidium and Cs^{137} for cesium labelling.

The exchangeable cations were determined after equilibration with ammonium ions; the neutral *N* $AcNH_4$ solution was added to the soil suspension system previously equilibrated for one hour with cations to be adsorbed, and after another one hour of equilibration the liquid supernatant was separated and its radioactivity measured.

The stepwise release of the cations adsorbed by soils was also determined. The three extractions of soil samples with fresh extractant solution were carried out. The following procedure was applied: After the equilibration of the soil with a solution of adequate cation under investigation (performed in the same way as previously), the soil was separated from the solution and washed with small portions of distilled water. Then the soil was equilibrated with ammonium acetate solution for one hour, and the radioactivity of the liquid supernatant determined. The procedure was repeated three times. The results are reported in Figure 1.

Using the above described equilibrium techniques the adsorption and desorption patterns of the cations, applied in trace amounts were determined at the doses used for labelling the elements when studied at macro-concentration. They were: for $K^{42} = 1,3 \times 10^7$ cpm/5g of soil, for $Rb^{86} = 1,9 \times 10^7$ and for $Cs^{137} = 1,6 \times 10^7$.

The influence of various carriers on the adsorption patterns of the isotopes under investigation was considered, too.

Results and Discussion

1. The adsorption and desorption patterns of cations applied at macro concentration.

The total amounts of potassium, rubidium and cesium adsorbed by soils, and the parts in forms easily exchangeable and nonexchangeable against the NH_4 ions (so called nonexchangeable adsorption) are given in Table 1. The data indicate that soils equilibrated with the solution of particular cations adsorbed their amounts depending on the kind of element and the soil properties. These amounts varied for potassium from 20 to 81% of the total dose applied (2,56 meq/100 g of soil), for rubidium 28 to 90% and for cesium 26 to 94%. The major part of the cations adsorbed was readily exchangeable and was removed by NH_4 cations from the soil complex to the solution again. The nonexchangeable part of the cations adsorbed was relatively small for potassium, but greater for rubidium and cesium. It should be emphasized that for the majority of soils, i.e. in 15 out of 18 soils tested, the values of the nonexchangeably adsorbed rubidium and cesium are similar or even the same. When differences occured, they were in favour to the nonexchangeably adsorbed cesium in comparison with rubidium. The only exceptions are three soils of lower values for cesium adsorbed nonexchangeably in comparison with rubidium.

. . .

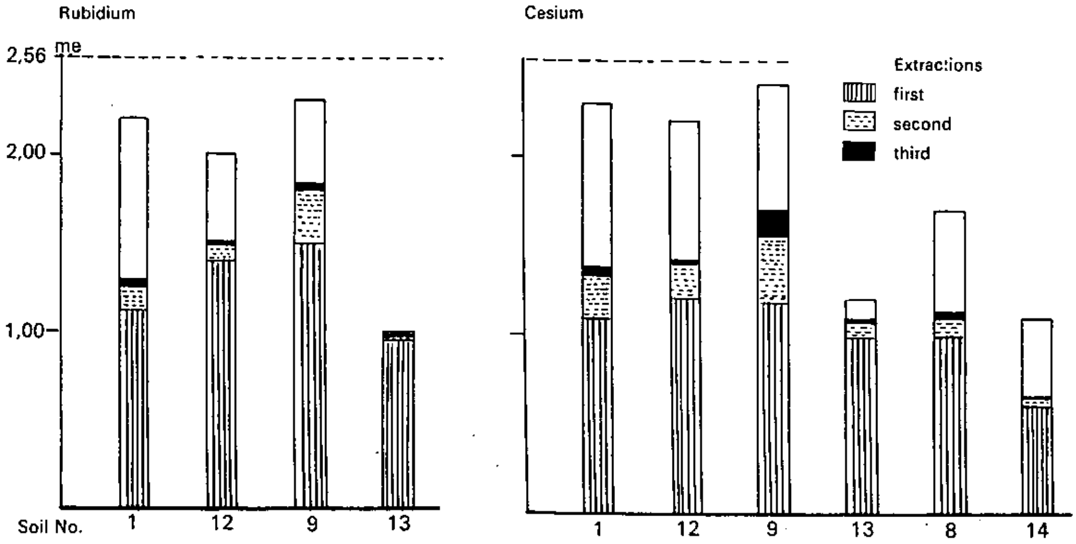

Fig. 1. Desorption of rubidium and cesium in the three repeated extractions with N $AcNH_4$, in % of the total amount of cations adsorbed.

Table 1 Adsorption of potassium, rubidium and cesium by soils in me/100 g of soil, at the dose applied 2,56 me/100 g

No.	Soil	Site	pH	O.m. %	CEC me	Potassium			Rubidium			Cesium		
						Total	Exch.	Non-exch.	Total	Exch.	Non-exch.	Total	Exch.	Non-exch.
1	Black earth	Chylice (P)	6,9	2,7		1,63	0,99	0,64	2,26	1,14	1,12	2,30	1,15	1,15
2	Peat soil	Ablasserwaard (N)	4,5		59,4	1,88	1,26	0,62	2,11	1,17	0,94	2,29	1,30	0,99
3	Forest soil	n/Sarajevo (Y)	5,5	14,6		2,02	1,23	0,78	2,27	1,19	1,08	2,34	1,26	1,08
4	Clay soils	Grouw (N)	4,6		34,9	1,92	1,36	0,56	2,23	1,13	1,10	2,34	1,21	1,13
5		Alkmaar (N)	6,7		40,5	1,70	1,15	0,55	2,14	1,16	0,98	2,30	1,09	1,21
6		Porto Tolle (I)	7,3		25,4	1,62	1,28	0,34	2,09	1,41	0,68	2,29	1,24	1,05
7	Loess soils	Amiens (F)	6,9		22,1	1,57	1,32	0,25	1,98	1,42	0,56	2,12	1,44	0,68
8		Lublin (P)	6,7	2,0		1,06	0,54	0,52	1,61	1,08	0,53	1,73	1,41	0,32
9	Terra rossa	Mostar (Y)	4,7	3,1		1,94	1,35	0,58	2,34	1,13	1,21	2,40	1,12	1,28
10	Terra fusca	Bari (I)	6,2		31,1	2,08	1,48	0,60	2,32	1,40	0,92	2,32	1,40	0,92
11	Loamy soils	Ahrweiler (G)	5,1		14,0	1,41	1,17	0,24	1,76	1,31	0,45	1,92	1,38	0,54
12		Bialystok (P)	6,8	1,6		1,38	0,98	0,40	1,99	1,25	0,74	2,19	1,32	0,87
13	Sandy soils	Siedlce (P)	5,0	1,9		0,67	0,50	0,17	1,16	1,01	0,15	1,18	1,04	0,14
14		Chylice (P)	5,0	0,9		0,62	0,33	0,29	1,06	0,89	0,17	1,07	0,89	0,18
15		Amersfoort (N)	5,1		26,0	1,00	0,83	0,17	1,37	1,09	0,28	1,27	1,04	0,23
16		Hilversum (N)	4,4		14,1	0,81	0,66	0,15	1,02	0,86	0,16	1,06	0,83	0,23
17		Rzasnik (P)	4,3	1,4		0,48	0,34	0,13	0,71	0,58	0,13	0,66	0,57	0,09
18		Polesie (P)	4,5	0,9		0,52	0,49	0,03	0,73	0,60	0,13	0,67	0,49	0,18

Soils derived from the countries: I=Italy; F=France; G=Germany; N=Netherlands; P=Poland; Y=Yugoslav.

The differences between the two pairs of cations nonexchangeably adsorbed may be illustrated by calculating the ratios: Rb/K and Cs/K. Among the soils tested only one showed the values for these ratios significantly lower than unity, amounting to 0,58 and 0,62, respectively, i. e. sandy soil (no. 17). However, for the other 16 soils (sandy soil no. 18 was excluded) the values for Rb/K ratios range from 0,94 to 2,24.

For many soils the values for Cs/K ratios are similar, or only insignificantly higher in comparison to the values for Rb/K. They are less than unity only for three soils which have shown some lower capacities for nonexchangeably adsorbed cesium in comparison to rubidium.

The marked differences in the extent of the adsorbed cations exist between soil types. For the fine soils the adsorption capacities are much greater than for light, sandy soils. These adsorption capacities of soils are connected with their sorption complex. Some part of nonexchangeably adsorbed cations may be fixed by clay minerals, present in fine soils. The significance of clay minerals in the fixation processes of monovalent cations under investigation were reported by many authors (3, 5, 6, 8, 11, 14, 15, 17, 18).

The data dealt with the desorption patterns of rubidium and cesium, stated in three stepwise extractions (Figure 1) indicate that the largest percentage of cations adsorbed went back into solution during the first equilibration with extractant solution. In the next one it was much lower and in the third extraction a further decrease could be observed. The fine soils adsorbed rubidium and cesium twice as much as sandy soils. Both elements were also more strongly fixed by fine soils than by sandy soils. Almost all rubidium, adsorbed by the sandy soil, no. 13 was extractable during the first extraction amounting to 96%. During the second extraction 2,3% was released, and in the third one only traces. The same soil adsorbed cesium similar to rubidium and a small difference occurred only in favour of cesium. Cesium was stronger fixed than rubidium, reflecting the fact that a higher percentage of the adsorbed cesium remained nonextractable.

The results presented in Figure 1 show that only small differences exist between the total adsorption capacities of fine soils for rubidium and cesium in favour to cesium. Cesium was also more strongly fixed by fine soils in comparison to rubidium the differences, however in the amounts of both cations nonextractable, after three repeated extractions, did not exceed 10%. Some small differences appeared in the desorption patterns of rubidium and cesium between particular extractions on the same soils. As a general trend, there was a lower percentage of cesium released during the first extraction compared to rubidium.

2. The adsorption and desorption patterns of the elements applied in trace amounts as K^{42}, Rb^{86} and Cs^{137}.

The adsorption patterns of the cations applied at microconcentration are presented in Table 2 and Figures 2 and 3. The data indicate much higher adsorption values compared to those when these cations were used at macroconcentration. The total amount of K^{42} adsorbed by six soils under investigation ranged from 62,6 to 90,0% of the total dose applied (Figure 2). A much higher percentage of the adsorbed Rb^{86} amounted to 99,0 to 98,9%, while Cs^{137} was adsorbed almost totally i.e. 99,5 to 99,9% (see table 2).

. . .

Table 2 The adsorption of trace amounts of rubidium and cesium applied as Rb^{86} and Cs^{137}, in % of the total dose used.

No.	Soil	Site	Rb^{86}			Cs^{137}			Ratio, non-exch Cs/Rb
			Total	Exch.	Non-exch.	Total	Exch.	Non-exch.	
1	Black earth	Chylice	98,9	28,5	70,4	99,9	5,9	94,0	1,33
3	Forest soil	n/Sarajevo	98,8	54,2	44,6	99,9	18,0	81,9	1,83
8	Loess	Lublin	93,8	60,4	33,4	99,8	26,6	73,2	2,19
9	Terra rossa	n/Mostar	98,6	56,8	41,8	99,9	22,3	77,6	1,86
12	Loamy soil	Bialystok	97,4	45,6	51,8	99,8	10,0	89,8	1,73
19	Silty soil	Rakowiec	96,8	61,9	34,9	99,5	19,8	79,7	2,28
20		Ciechanów	95,4	63,6	32,8	99,7	21,2	78,5	2,39
13	Sandy soils	Siedlce	96,0	80,1	15,9	99,7	48,1	51,6	3,25
14		Chylice	97,0	79,9	17,7	99,7	48,6	51,1	2,89
21		Maków	97,9	45,4	52,5	99,8	12,7	87,1	1,66
22		Skierniewice	96,9	76,9	20,0	99,5	37,2	62,3	3,12
17		Rzasnik	95,1	86,8	8,3	99,7	71,7	28,6	3,44

The high percentage of cations adsorbed by soils or clay minerals, when applied in trace quantities has been stated by a number of investigators, who also considered reasons and mechanism of this phenomen (1, 3, 11, 12, 14, 18, 19).

Wiklander and *Gieseking* (19) found the increasing adsorption of K^{43} and Sr^{89} by soils, when their concentration decreased and sodium was present as a complementary ion. However this increasing adsorption of radionuclides did not occur when barium was in the solution as a complementary ion. In experiments by *Marckwordt* and *Mousny* (7) small quantities of cesium, applied as Cs^{134}, were adsorbed at 99% by loess and rendzina. A high adsorption of Cs^{137} was stated also by *Nishita et al.* (8, 10), *Schulz et al.* (14), *Jackson et al.* (4).

As for the desorption patterns of Rb^{86} and Cs^{137} adsorbed by 12 soils (Table 2) marked differences have been stated between both elements. Much greater amounts of the isotope Rb^{86} adsorbed were exchangeable and removed back to the solution by NH_4 ions while Cs^{137} was stronger bound in the soil complex. Excluding one sandy, non-typical soil, the percentage of nonexchangeably adsorbed Rb^{86} in 11 soils under investigation varied in the large range of 15,9 to 70,4%, while non-exchangeably adsorbed Cs^{137} varied between 51,1 to 94,0%. Thus, the values of Cs^{137} differed from those of Rb^{86} by the factor of 1,33 to 3,44.

The data concerning the desorption of Cs^{137} in the three, stepwise extractions (Figure 4) show that similarly to the desorption of cesium applied at macroconcentration, the greatest percentage was released during the first extraction and much less during the second and third. The quantities however, of Cs^{137} replaceable differed significantly from the values stated in the macroconcentration. The total amount of Cs^{137} released during the three stepwise extractions did not exceed 5% of the total dose adsorbed by black earth. It is interesting to note that this value is the same as the one reported previously (Table 2), obtained with the equilibrium method i.e. when the NH_4 ions were introduced to the soil suspension equilibrated previously with Cs^{137}. The amount of Cs^{137} desorbed from loamy soil during all the three extractions amounted to 15%. A much higher percentage of Cs^{137} was removed from loess and terra rossa soils; it amounted to 45,3 and 49,2%, respectively. Sandy

. . .

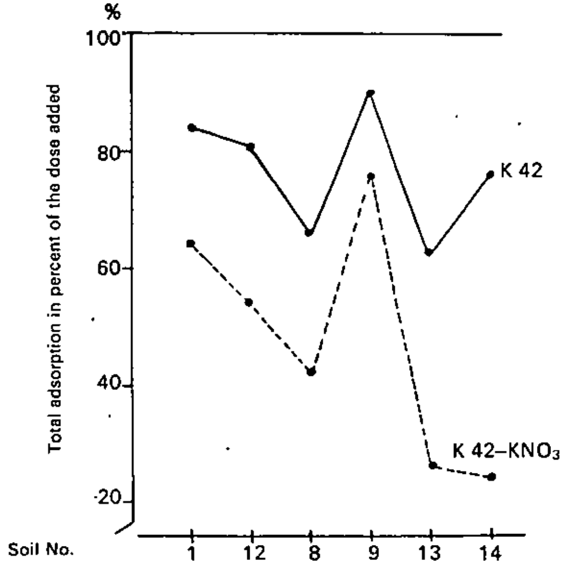

Fig. 2. Adsorption of K^{42} applied in trace amount and in the presence of natural potassium.

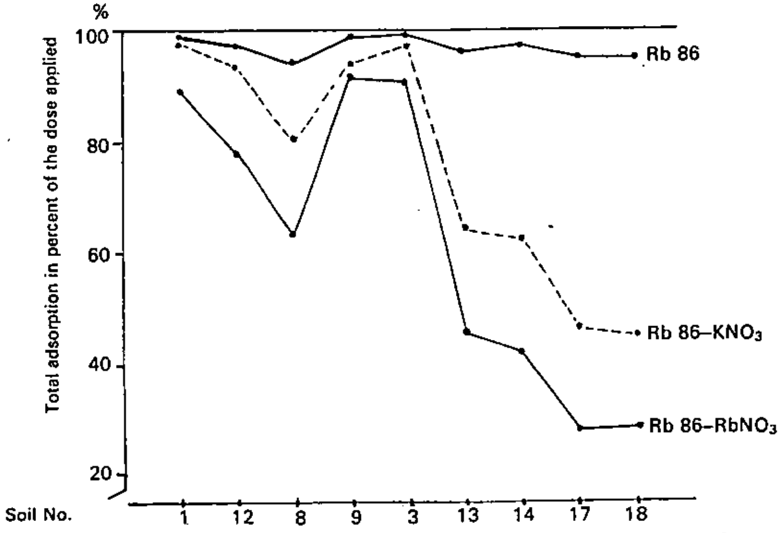

Fig. 3. Adsorption of Rb^{86} applied in trace amount and in the presence of natural potassium and rubidium.

. . .

soils released about 65% of adsorbed Cs^{137}. For these last four soils the values for Cs^{137} extractable, obtained by repeated extractions, were higher than those stated when the equilibrium methode was used (Data reported in Table 2).

3. The influence of various carriers on the adsorption patterns of K^{42}, Rb^{86} and Cs^{137}.

The effect of potassium, rubidium and ammonium on the adsorption pattern of K^{42} and Rb^{86} was considered being in equilibrium solution of the concentration of 2,56 me/100 g of soil. The results presented in Figures 2 and 3 show, that the presence of carriers influenced the adsorption of isotopes, depending on soil types and kind of carriers applied.

The addition of the same element or one of the same properties decreases the adsorption of radionuclides through the mass effect. Thus K^{43} applied together with natural potassium behaves in the same way and its adsorption pattern is connected with soil properties, mainly their capacities for potassium fixation. Therefore, the adsorption of K^{42} was high on fine soils and much lower on sandy soils.

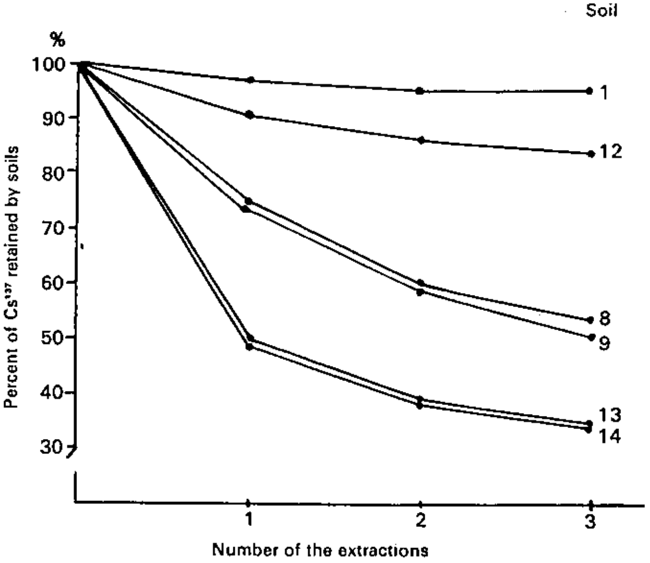

Fig. 4. Percentage of Cs^{137} retained by various soils after repeated extractions.

The NH_4 ions given as a carrier instead of natural potassium in equivalent amount did not influence the K^{42}. When differences occurred, they were small and not significant. For that reason the data are not presented in Figure 2.

The results given in Figure 3 show that the adsorption of Rb^{86} was more affected by the presence of natural rubidium than natural potassium and the effects were connected with the soil types. Rb^{86} applied with natural rubidium behaves in the same way. When potassium is applied as a carrier both cations are competing in

. . .

taking sites at the soil adsorption complex. When natural potassium was used together with Rb^{86} the adsorption size of radioisotope differed quantitatively, but its adsorption pattern was similar. These results comparing the data for adsorption pattern of K^{42} applied with natural potassium (Figure 2) are of interest from a methodical point of view, when the problem of the usefulness of Rb^{86} as a tracer for potassium is considered.

The effect of natural cesium on the Cs^{137} adsorption was similar to that of rubidium on the Rb^{86} adsorption. It can be stated in comparing the data reported in Table 1 and 2 that Cs^{137} applied in trace amount was adsorbed to 99%, while in the presence of natural cesium 70 to 90% was adsorbed by fine soils and 25 to 45% by sandy soils.

The findings of *Nishita et al.* (9) showed that the addition of natural cesium decreased the amount of Cs^{137} adsorbed from 75 to 45%, while the presence of natural potassium did not influence the adsorption pattern of Cs^{137}. The effect of various cations on the adsorption pattern of Cs^{137} was investigated recently in regard to problem of soil and plant contamination with Cs^{137}.

Summarizing the results obtained, it may be concluded that the adsorption and desorption of cations under investigation followed similar patterns. When differences occurred they were of quantitative values. Rubidium and its isotope Rb^{86} may be successfully used in some researches with potassium or cesium e.g. on their adsorption or migration processes in soils. Also the behaviour of one element may be provided on the basis of experimental data obtained with another one. It is necessary to establish the possible differences between the elements or those caused by experimental conditions.

Summary

The adsorption patterns of the cations under investigation applied at macroconcentration and in trace amounts as K^{42}, Rb^{86} and Cs^{137} were investigated on various soils, using the wet equilibrium technique. The total potassium adsorbed at the concentration corresponding to 2,56 me/100 g of soil, varied in large size; it was much greater for the fine soils than the sandy ones. The significant part of the total adsorbed potassium was readily exchangeable. The adsorption pattern of rubidium and cesium were similar, however, differed from potassium. The values for non-exchangeably adsorbed rubidium differed from potassium by the factor 0,94 to 2,24. The marked differences in adsorption pattern occurred when cations were applied in trace amounts. They were adsorbed to a much greater extent and fixed more strongly by the soil complex. However, the behaviour of cations investigated followed similar patterns, and differences observed were of quantitative value.

Bibliography

1. *Barbier G., Duval L.:* Sur l'échange des cations présents en minime proportion. Application à la retention du strontium et du césium radioactifs dans le sol. Ann. Agron No 6, pp. 695–712 (1958).
2. *Coleman N.T. et al.:* Ion-exchange reactions of cesium. Soil Sci. Soc. Amer. Proc. *27*, 283–289 (1963).
3. *Coleman N.T., Le Roux F.H.:* Ion exchange displacement of cesium from soil vermiculite. Soil Sci. *99*, 243–250 (1965).

...

4. *Jackson W.A. et al.:* Effect of various cations on cesium uptake from soils and clay suspensions. Soil Sci. *99*, 345–353 (1965).
5. *Keppel H.:* Morphological, physiological and environmental conditions affecting the accumulation of long-lived radionuclides from fission products by plants. Proc. of a Seminar on Environmental Contamination by Radioactive Materials, Vienna (1969).
6. *Mackenzie R.C.:* Potassium in clay minerals. Potassium Symposium, pp. 123–143 (1955).
7. *Marckwordt U., Mousny J.M.:* Availability of radiocesium in relation with ammonium fertilization and potassium status of two soil types from Allonvile. Intern. Report, Euratom Joint Research Centre, Ispra.
8. *Nishita H. et al.:* Fixation and extractibility of fission products contaminating various soils and clays. Soil Sci. *81*, 317–326 (1956).
9. *Nishita H. et al.:* Influence of K and Cs on the release of Cs^{137} from three soils. Soil Sci. *89*, 167–176 (1960).
10. *Nishita H. et al.:* Influence of stable Cs and K on the reactions of Cs^{137} and K^{42} in soils and clay minerals. Soil Sci. *94*, 187–197 (1962).
11. *Sawhney B.L.:* Sorption and fixation of microquantities of Cs by clay minerals: effect of saturating cations. Soil Sci. Soc. Amer. Proc. *28*, 183–186 (1964).
12. *Sawhney B.L.:* Cesium sorption from diluted solutions. Soil Sci. Soc. Amer. Proc. *29*, 25–28 (1965).
13. *Shone M.G.T.:* Radioactive tracers in the study of soil/plant relationships. Proc. of the Symposium on the Use of Isotope and Radiation in Soil-Plant Nutrition Studies. IAEA/FAO, Ankara, pp. 217 to 231 (1965).
14. *Schulz R.K. et al.:* On the soil chemistry of cesium 137. Soil Sci. *89*, 16–27 (1960).
15. *Schuffelen A.C., v.de Marel H.W.:* Potassium fixation in soils. Potassium Symposium, pp. 157–201 (1955).
16. *Smierzchalska K.:* The use of the isotope methods (rubidium 86) in the studies on the potassium behaviour in soils and its recovery by plants. Potash Rev. 1–10, May (1968).
17. *Titljanowa A.A.:* O poviedieni cezija i rubidija w poczwach. Poczw. *3*, 53–62 (1962).
18. *Titljanowa A.A.:* Sorpcija cezija sloistymi poczwiennymi mineralami. Poczw. *12*, 88–95 (1964).
19. *Wiklander L., Gieseking J.E.:* Exchangeability of adsorbed cations as influenced by the degree of saturation and the nature of the complementary ions with special reference to trace concentrations. Soil Sci. *66*, 377/384 (1948).