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INFLUENCE OF CLINOPTILOLITE ON SR90 AND CS137 UPTAKES BY PLANTS

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With the growing use of nuclear energy, it is not improbable that certain areas of the biosphere could become contaminated with radionuclides at biologically hazardous levels. In such an event, it would be necessary to apply various remedial procedures, in order to minimize the transfer of hazardous radionuclides along the soil-plant-animal food chains leading to man. Several of these procedures were reviewed by Reitemeier, James and Menzel (16). As an aspect of these procedures, we have been attempting to determine the effectiveness of applying certain minerals to contaminated soils in reducing the Sr90 and Cs137 uptake by plants.

In our previous work (12) in which the effects of applying minerals (clinoptilolite, "Verxite", bentonite, illite, kaolinite, vermiculite and bauxite) to a soil were examined, it was found that clinoptilolite had the greatest effect in reducing the Sr90 uptake by plants. The plant uptake of Cs137 was increased to a small extent. The application of clinoptilolite also had the deleterious effect of reducing the plant yield. In these experiments, the minerals and the radionuclides were mixed thoroughly into the entire soil mass.

This paper presents the results of two experiments. In experiment I, the objective was to determine the effect of clinoptilolite on Sr90 and Cs137 uptakes by plants from soils contaminated only at the surface. The clinoptilolite was applied to the contaminated surface in this study. The objective of experiment II was to determine the influence of clinoptilolite on the release of Sr90 and Cs137 to plants upon continuous and prolonged cropping of contaminated soils treated with clinoptilolite.

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MATERIAL AND METHODS

Three soils (Hanford sandy loam, Vina loam and Egbert muck) were used for these studies. Their chemical and physical properties are given in table 1 together with those of the clinoptilolite used. These soils and clinoptilolite were of different batches than those used in the previous experiment (12). The properties of the clinoptilolite (Hector, California) are those of the pulverized material that was applied to the soils. The Ca-treated clinoptilolite was prepared in the same way as before (12). Note that the electrical conductivity of the saturation extract of the untreated clinoptilolite was very high, indicating it to be strongly saline. Egbert muck was somewhat saline.

In experiment I, beans (Phaseolus vulgaris, "stringless green pod") and barley (Hordeum vulgare, "Atlas") were used as test plants. Bean plants were grown one per can, while the barley plants were grown two per can. The cans were of one-gallon capacity and were painted on the inside with gray vinyl base paint (Amercoat No. 33) and had a 7-mm. hole at the bottom for drainage. The contents of the cans were in layers as follows (starting from the bottom): 1400 g. of No. 16, washed silica sand; 3,500 g. of uncontaminated soil; 5 g. of soil contaminated with Sr90 and Cs137; 0, 17.5 or 35 g. of untreated or Ca-treated clinoptilolite; and 200 g. of No. 16 silica sand. The purpose of the top layer of sand was to minimize the disturbance of the clinoptilolite and Sr90 and Cs137 contaminated layers when irrigating. Each 5-g. aliquot of the contaminated soil contained 1.5 μc of Sr90 and 1.5 μc of Cs137. The contaminated soil was distributed in a thin layer. The area of the soil surface was 213.3 cm^2. The bean or the barley seeds were planted in the uncontaminated soil about 0.5 inch deep before the contaminated soil, the clinoptilolite and the top sand layers were applied. The plants were

TABLE 1

Chemical and physical characteristics of soils

Soil*	pH**	E.C. Sat. Extr. *mmhos./cm.*	Organic Matter %	Cation Exchange Capacity *meq./100 g.*	Extractable Cations*** K *meq./100 g.*	Na *meq./100 g.*	Ca *meq./100 g.*	Mg *meq./100 g.*	Particle Size Distribution Sand %	Silt %	Clay %
Vina Loam	6.75	1.04	2.72	21.33	1.19	0.10	11.27	5.63	52.19	34.31	13.50
Hanford sandy loam	6.80	1.57	1.99	7.60	0.72	0.21	5.23	1.40	66.08	26.54	7.38
Egbert muck	3.92	14.14	32.89	45.30	1.06	1.62	23.66	7.89	—	—	—
Clinoptilolite (Untreated)	8.10	129.00	—	104.44	13.62	190.70	42.71	3.27	—	—	—
Clinoptilolite (Ca-treated)	8.45	0.73	—	104.44	11.83	10.06	108.09	1.95	68.08	20.42	11.50

* Major clay minerals of soil: Vina, montmorillonite-kaolinite; Hanford, illite.
** Determined on 1:1 suspension with glass electrode.
*** Extractable with neutral N ammonium acetate.

grown to apparent maturity before harvesting. Each treatment was set up in 6 replicates.

In experiment II, Ladino clover (Trifolium repens) was grown in 3500 g. of Hanford sandy loam and 2700 g. of Egbert muck in one-gallon cans painted in the same way as above. Because of the lower bulk density, the volume of Egbert muck was slightly greater than that of Hanford s.l. in the cans. The soils were contaminated with Sr90 and Cs137 (processed carrier-free) each at the level of 500 dis./sec./g. soil. Ammonium nitrate (0.178 meq./100 g.), $Ca(H_2PO_4)_2$ (0.070 meq./100 g.) and K_2SO_4 (0.106 meq./100 g. soil) were applied initially as fertilizers. The radionuclides and the fertilizers were mixed thoroughly into the entire soil mass with and without the addition of Ca-treated clinoptilolite by using a small cement mixer that was sealed to prevent leakage of radioactive dust. When Ca-treated clinoptilolite was added, it was added at the level of 1 g./100 g. soil. The plants were started by planting 20 seeds per can. After the seedlings became established they were thinned to 8 per can. The plants were grown for a total of 322 days (11 July to 9 May) during which eight harvests were made. Each harvest was done at the blooming stage of the plants. Each treatment was set up in seven replicates.

The plants of both experiments were grown in a greenhouse supplied with air filtered through activated charcoal. Irrigation was done with deionized water as needed by weight.

The chemical and physical properties of the soils and the untreated and Ca-treated clinoptilolites were determined by the same procedures that were used previously (12). The Ca and K contents of the plants were determined by the use of 1.5 meter, direct reading emission spectrometer (Applied Research Laboratories). The radioassays were done on plant materials that were ground with a Wiley mill to pass through a 40-mesh screen. A low background gas-flow detector system having an efficiency of 16.3 per cent for Cs137 activity and 15.9 per cent for Sr90 were use for beta particle counting. The Cs137 activity was separated from the Sr90 activity by the use of an automatic deep well gamma counter with a single channel discriminator. The efficiency of the deep well gamma counter for Cs137 was 11.6 per cent. Appropriate corrections for counting efficiency, self-absorption and decay were made on all samples.

RESULTS AND DISCUSSION

Figure 1 shows the shoot tissue yields of the plants grown on Sr90 and Cs137 contaminated soils with and without clinoptilolite treatments (experiment I). In comparison with the control (no clinoptilolite application), the application of untreated clinoptilolite, in general, decreased the average shoot yields of both bean and barley plants. The higher level (35.0 g./can) of the untreated clinoptilolite was consistently more detrimental to the plant yields. The Ca-treated clinoptilolite did not change significantly the average shoot yields of either the bean or the barley plants. This may be surmised by the overlapping intervals formed by adding and subtracting one standard deviation from the means. Comparisons between the untreated and the Ca-treated clinoptilolite treatments indicated that bean and barley plants grown with Ca-treated clinoptilolite showed the higher average yields in Hanford s.l. In Vina l., the bean plants grown with Ca-treated

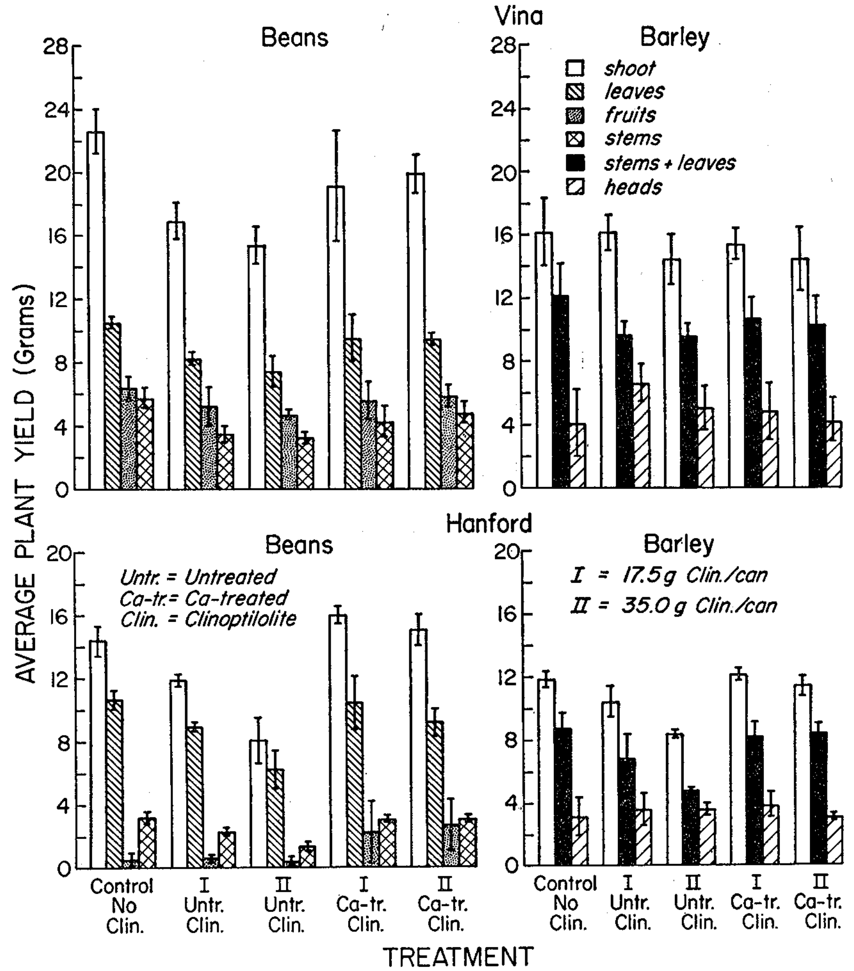

FIG. 1. Average plant yields resulting from surface application of untreated and Ca-treated clinoptilolite to Vina l. and Hanford s.l. contaminated on the surface with Sr90 and Cs137 (Experiment I). The indicated intervals were obtained by adding and subtracting one standard deviation from the average value.

clinoptilolite gave the higher average yields, while the barley plants showed no appreciable difference between the two treatments. In general, the untreated clinoptilolite had an adverse effect on plant growth, while the Ca-treated clinoptilolite had no significant effect. The detrimental effect of the untreated clinoptilolite was probably due to its very high available Na content (table 1).

The average Sr90 content of the different parts of the bean plants was consistently in the following order of magnitude: leaves $\gg$ stems $>$ fruits (fig. 2). The order of the average Cs137 content, which was very small compared to Sr90, was (Cs 137) leaves $>$ fruits $>$ stems. The application of either the untreated or the Ca-treated clinoptilolite reduced appreciably the Sr90 content of the plants grown in either soil. The percentage reduction of Sr90 content ranged from 48 to 70, 54 to 77 and 44 to 77 per cent in the leaves, stems and fruits, respectively, depending on the clinoptilolite treatment and the soil (table 2). The average Cs137 content of the bean plants grown in Vina l. tended to increase or did not change appreciably, but those of the plants grown in Hanford s.l. tended to decrease in most cases. In any case, the changes in the absolute Cs137 activity resulting from the clinoptilolite treatments were

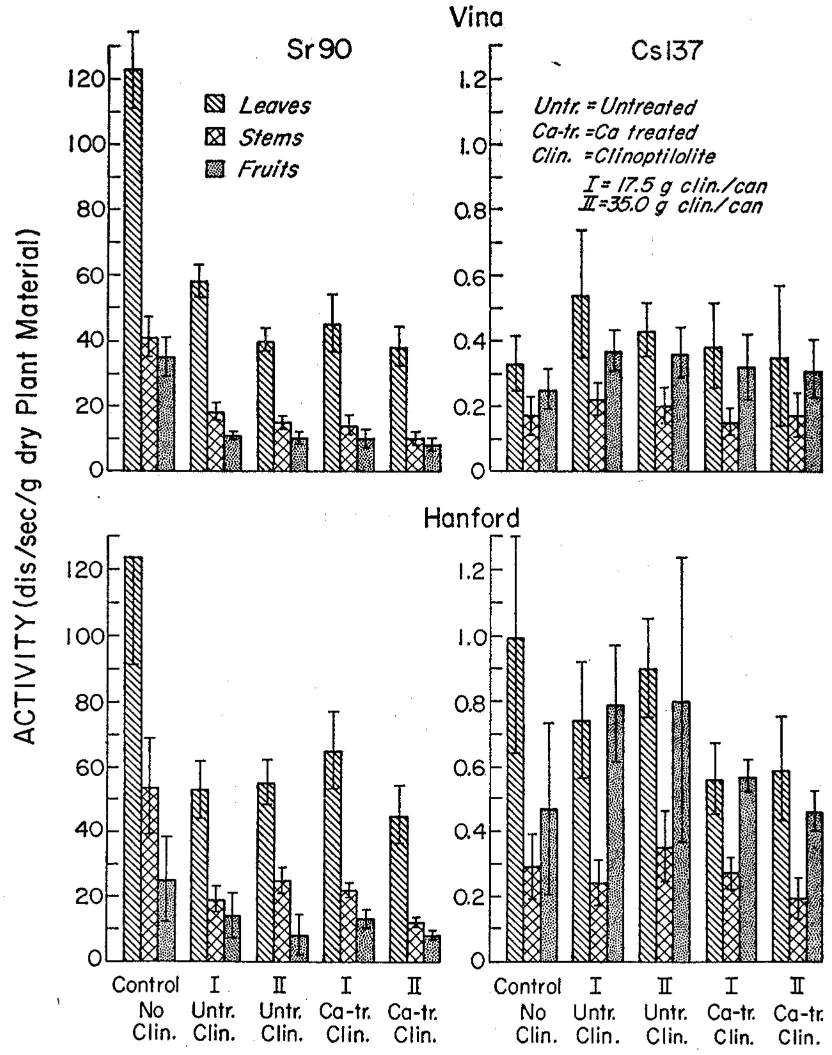

FIG. 2 Average Sr90 and Cs137 contents of bean plants grown in Vina l. and Hanford s.l. The indicated intervals were obtained by adding and subtracting one standard deviation from the average value.

very small. They range from −0.43 to + 0.21, −0.10 to + 0.06 and −0.01 to + 0.33 dis/sec/g. for the leaves, stems and fruits, respectively.

The average Sr90 content of barley plants was reduced also by the application of untreated or Ca-treated clinoptilolite (fig. 3). The percentage reduction under the various treatments ranges from 57 to 77 and 57 to 79 for the leaves and stems, and the heads, respectively (table 2). In the majority of the treatments, the average Cs137 content was reduced also. The reduction of Cs137 content of the plants, however, is not of practical significance, since Cs137 accumulation by the plants was very small without the clinoptilolite treatment.

Figure 4 shows the average yields of Ladino clover grown in contaminated Hanford s.l. and Egbert muck with and without clinoptilolite treatment for a prolonged period of time (experiment II). Except for the fourth harvest, the

TABLE 2

Percentage changes of average Sr90 contents of bean and barley plants resulting from surface application of clinoptilolite to surface contaminated soils

Soil	Treatment*	Beans**			Barley**	
		Leaves	Stems	Fruits	Leaves and stems	Heads
Vina l.	Untr. Clin. I	−53	−67	−69	−69	−72
	II	−68	−70	−72	−73	−79
	Ca-tr. Clin. I	−63	−60	−71	−57	−57
	II	−70	−73	−77	−65	−75
Hanford s.l.	Untr. Clin. I	−58	−66	−44	−69	−62
	II	−56	−54	−68	−77	−68
	Ca-tr. Clin. I	−48	−60	−55	−65	−62
	II	−64	−77	−68	−72	−72

* Untr. Clin. = Untreated clinoptilolite; Ca-tr. Clin. = Ca-treated clinoptilolite. I = 17.5 g. clin./can; II = 35.0 g. clin./can.
** Minus sign indicates decrease.

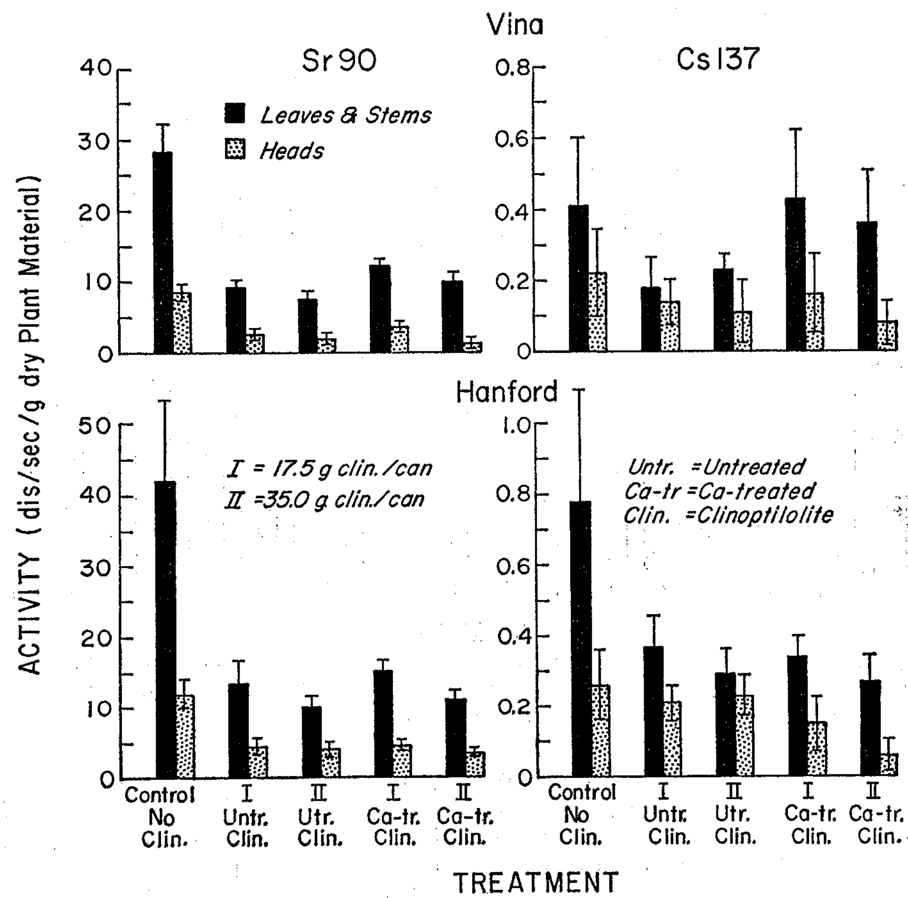

FIG. 3. Average Sr90 and Cs137 contents of barley plants grown in Vina l. and Hanford s.l. The indicated intervals were obtained by adding and subtracting one standard deviation from the average value.

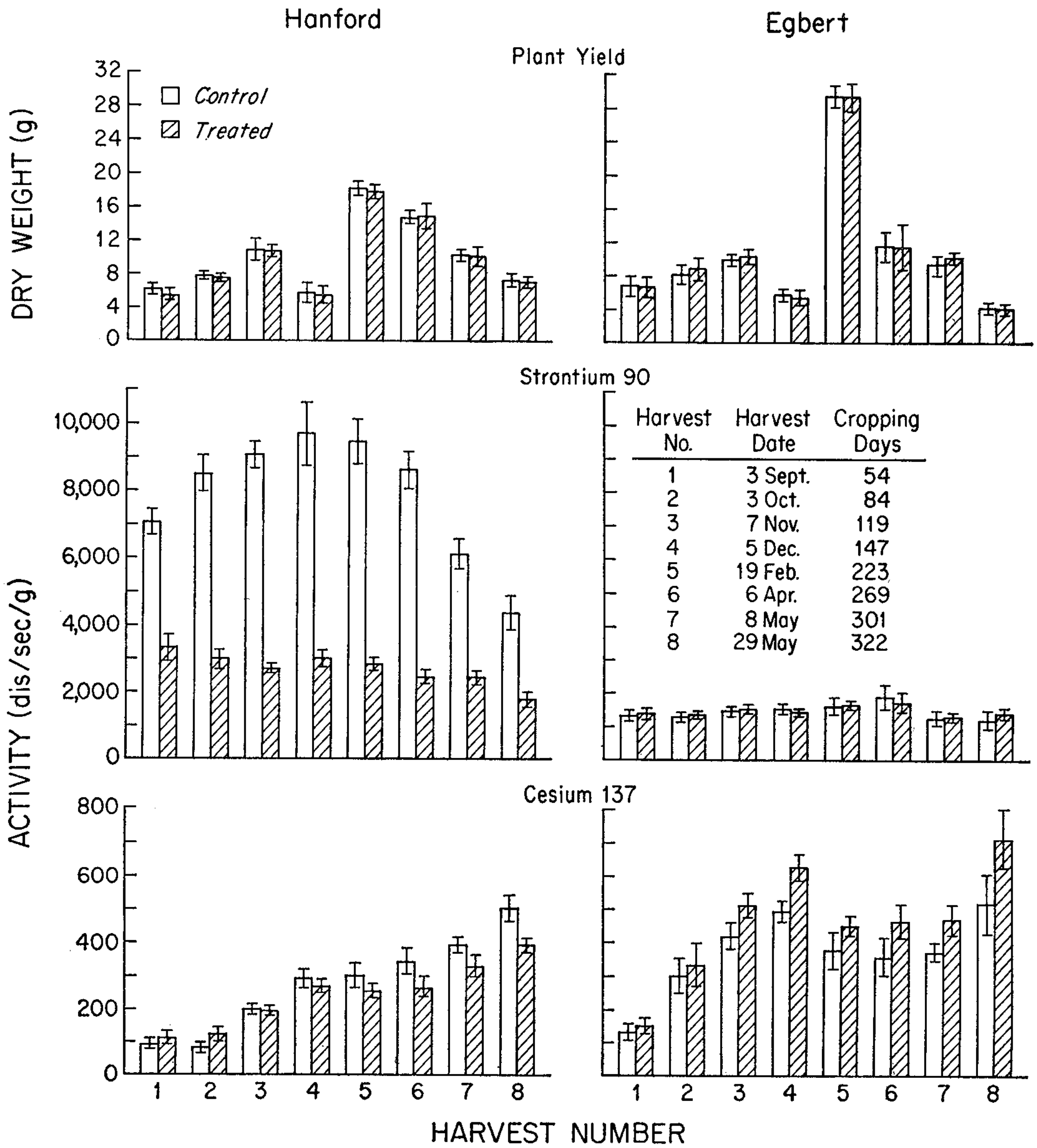

FIG. 4. The average yields and the Sr90 and Cs137 contents of Ladino clover grown in contaminated soils with and without clinoptilolite treatment (Experiment II). The indicated intervals were obtained by adding and subtracting one standard deviation from the average value.

yields increased to a peak at the fifth harvest and then declined. The reduced yield for the fourth harvest is considered to be a climatic effect, since the plants grown in both soils showed the same growth trends. As mentioned previously, all harvests were done in the blooming stage of the plants. The general yield increase that occurred initially was due to the size increase of the plant crowns with successive harvests. The yield decline after the fifth harvest was probably due to the decline of certain available plant nutrients resulting from the prior cropping. Surface application of NH_4NO_3 Ca $(H_2PO_4)_2$ and K_2SO_4 (at the same levels used initially) were made immediately after the sixth harvest, but the plant yields for the subsequent harvests continued to decline,

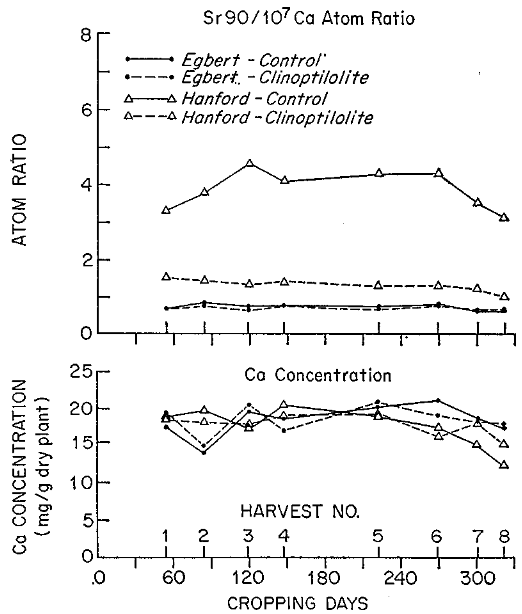

FIG. 5. Average Ca contents and Sr90/10^7Ca atom ratios of Ladino clover.

indicating perhaps some other nutrient was limiting. In any case, the important point to note is that although the plant yields varied somewhat from harvest to harvest, the yields of plants grown in the clinoptilolite-treated soil were not significantly different from that of the untreated soil. The application of Ca-treated clinoptilolite (1 g./100 g. soil), therefore, did not have any deleterious effect on the growth of these plants.

The application of Ca-treated clinoptilolite was quite effective in reducing the Sr90 concentration in the plants grown in Hanford s.l. (fig. 4). Depending on the harvest time, the average Sr90 concentrations in the clover plants grown with clinoptilolite treatment were 59 to 69 per cent less than that of the control plants. Furthermore, with clinoptilolite treatment, the average Sr90 content generally declined with successive harvests, whereas without clinoptilolite treatment, the average Sr90 contents increased to a maximum for the fourth harvest and then declined. In other words, the application of Ca-treated clinoptilolite prevented the increase of Sr90 uptake by the plants. With clinoptilolite treatment, the Sr90/10^7 Ca atom ratios of the plants also tended to decrease with successive harvests (fig. 5). This tendency indicates that the decrease of available Ca in the soil was almost commensurate with that of Sr90. The average Sr90 concentrations of the plants grown in both the untreated and the clinoptilolite-treated Egbert muck were drastically less than that of the plants grown in Hanford s.l. and was fairly constant during the experimental period (fig. 4). Furthermore, the application of clinoptilolite had no appreciable effect on the Sr90 contents of the plants. The Sr90/10^7 Ca atom ratios in the plants grown in this soil remained virtually constant also (fig. 5). In general, these results indicate that the application of Ca-treated clinoptilolite may be effective in reducing Sr90 uptake by plants from mineral soils but not from organic soils.

The effect of the application of Ca-treated clinoptilolite on the Cs137 contents of the clover plants was very small (fig. 4). However, certain trends of the effect of soil type were observable. The average Cs137 contents of the plants grown in the clinoptilolite-treated Hanford s.l., though not significantly, were lower than those of the control plants after the third harvest. On the other hand, the average Cs137 contents of the plants grown in Egbert muck were consistently greater than those of the control plants. The Cs137 was taken up more readily from Egbert

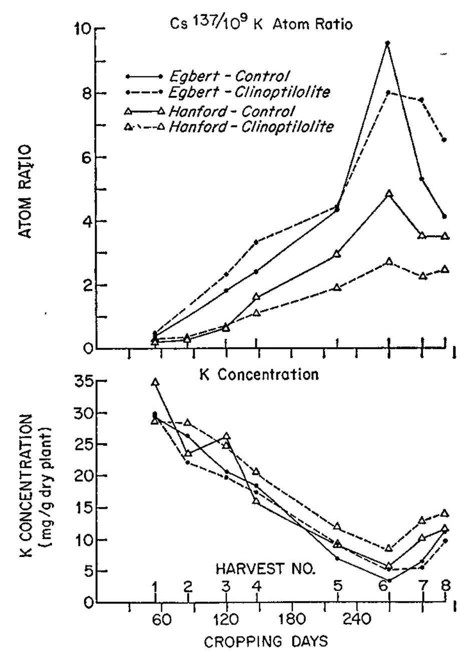

FIG. 6. Average Cs contents and Cs137/10^9K atom ratios of Ladino clover.

muck than from Hanford s.l. The uptake of Sr90 with respect to soil type was vice versa. Perhaps, the important behavior of Cs137 was that its availability to plants increased with increasing cropping time. This was particularly well illustrated by the plants grown in Hanford s.l. This effect is considered to be caused primarily by the reduction of available K in the soils. Figure 6 shows that K concentration in the plant generally decreased progressively with increasing cropping time through the sixth harvest. The increase shown by the seventh and the eighth harvests was caused by the application of KNO_3 as fertilizer to the soil surface immediately after the sixth harvest. The Cs137/10^9 K atom ratio in the plant increased as K content decreased and vice versa when the K increased. The influence of K in reducing Cs uptake by plants has been reported previously (2–11, 13–15).

In the present experiment, the application of K to the soil increased the K content of the plants but did not reduce the Cs137 content. In fact, the Cs137 content increased in the plants of the seventh and eighth harvests (fig. 4). This apparent contradiction of the previously established fact could be explained by the differential distribution of the applied K in relation to that of the root mass. Since the K was applied to the surface, it was localized in the upper levels of the soil mass. The plant roots in the lower levels of the soil mass were not exposed to the applied K. In the zone of the applied K, the root absorption of K increased and that of Cs137 very likely decreased, while in the lower levels, the absorption of Cs137 continued to increase with the depletion of K. The latter mode of absorption was dominant since there was an increase of Cs137 uptake. The decrease of the Cs137/10^9 K atom ratio shown by the seventh and the eighth harvests (fig. 5) indicate the enhanced absorption of K at the surface levels relative to the net absorption of Cs137.

GENERAL DISCUSSION

The effect of the clinoptilolite on Sr90 and Cs137 is due to the cation sieve properties of the mineral. The sieve properties are largely determined by the structure of the mineral, which is considered to be a species of zeolite (1). The mineral is one of the "open" zeolites, or those zeolites that can accept any of the alkali or alkaline earth metal cations (2). The molecular structure of zeolites, in general, is characterized by definitely arranged network of cavities linked by apertures. The shape and the size of the cavities and the diameter of the apertures depend on the variety of zeolite. The water molecules and exchangeable ions lie in the cavities and can pass through the aperatures. The primary factor determining the sieve properties of a particular zeolite is the diameter of the apertures. The effective diameter of the apertures depends to some extent on the temperature and the exchangeable cations. According to Ames (2), there are at least three mechanisms responsible for the cation sieve properties, i.e. the exclusion of certain cations due to their inability to enter the zeolite lattice in appreciable amounts because of their size, the inability of the negative charge distribution on the zeolite to accommodate a given cation and the interactions between the presence or absence of structural water and cations of the alkali and alkaline earth metal series.

In the present experiments, Sr90 was more selectively sorbed by clinoptilolite used than was Cs137. The clinoptilolite had only little, if any, effect on Cs137 available to plants. These results appear to contradict those of Ames (1), who showed that the selectivity of clinoptilolite for Cs is markedly greater than for Sr using a column loading technique. This apparent discrepancy may be explained by the presence of the soil in the present experiments. The selective sorption of Cs137 by the soil colloids may have been much stronger than by the clinoptilolite and thus made clinoptilolite relatively ineffective. This statement also implies that Sr90 was sorbed more strongly by the clinoptilolite than by the soil colloids.

SUMMARY

An experiment was conducted to determine the effect of clinoptilolite on the Sr90 and Cs137 contents of bean and barley plants grown in soils contaminated at the surface (experiment I). An experiment was also conducted to determine the release of Sr90 and Cs137 to clover plants upon continuous and prolonged cropping of a contaminated soil with and without clinoptilolite treatment (experiment II).

In experiment I, clinoptilolite was found to decrease the average Sr90 contents of plants. The percentage reduction of Sr90 contents of the different parts of the bean plants ranged from 48

to 70, 54 to 77 and 44 to 77 per cent in the leaves, stems and fruits, respectively, depending on the amount of clinoptilolite application and the kind of soil. The percentage reduction of Sr90 in barley plants under various treatments ranged from 57 to 77 and 57 to 79 for the leaves and stems and the heads respectively.

In experiment II, eight harvests of clover were obtained. The application of Ca-treated clinoptilolite was effective in reducing Sr90 contents of the plants grown in the mineral soil used, but it had no effect in the organic soil. Depending on the harvest time, the average Sr90 contents of the plants grown in the treated mineral soil were 59 to 69 per cent less than that of the control plants. Clinoptilolite was effective in maintaining the reduced Sr90 contents of the plants throughout the experimental period. The Cs137 contents of the plants were not changed appreciably by the application of clinoptilolite.

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Sr/Ca
Cs/K

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