Ms. 4420

INFLUENCE OF CLAY MINERAL TYPE AND ORGANIC MATTER CONTENT ON THE UPTAKE OF ^{239}Pu AND ^{241}Am BY PLANTS

by B. N. VYAS and K. B. MISTRY

Biology and Agriculture Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

KEY WORDS

Americium Concentration ratio *Hordeum vulgare* L. Kaolinite clay Montmorillonite clay Organic matter Plant uptake Plutonium

SUMMARY

The uptake of ^{239}Pu and ^{241}Am from different clay mineral-organic matter-sand mixtures simulating contrasting soil types was examined in growth chamber experiments. The mixtures represented various combinations of organic matter (0, 5 and 10%), kaolinite (1:1 type) and montmorillonite (2:1 type) clay minerals, each at the levels of 5, 10 and 25%, and purified quartz sand (as filler).

Results indicated a marked reduction in uptake of both ^{239}Pu and ^{241}Am with increase in organic matter as well as clay content of the mixtures. The Pu Concentration Ratios (CRs) ranged from (2.5 – 7.0) $\times 10^{-3}$ in the case of kaolinite-organic matter mixtures, and from (0.9 – 5.5) $\times 10^{-3}$ in the case of montmorillonite-organic matter mixtures. The corresponding values of Am Concentration Ratios (CRs) obtained were (1.9 – 725.4) $\times 10^{-3}$ in the case of kaolinite-organic matter mixtures, and between (0.7 – 3.5) $\times 10^{-3}$ for the montmorillonite-organic matter mixtures.

Reduction in the uptake of ^{241}Am with increasing clay content was more pronounced in the montmorillonite clay-organic matter mixtures as compared to that in the case of kaolinite-organic matter mixtures. While similar qualitative reduction in ^{239}Pu CRs with increasing clay content was observed, the reduction was less marked than in the case of ^{241}Am. The values for Am CRs were higher than the corresponding Pu CRs in kaolinite based mixtures whereas in the case of montmorillonite-organic matter mixtures Pu CRs exceeded the Am CRs.

Increasing organic matter content and its interaction with both kaolinite and montmorillonite clay minerals were found to be equally effective in reducing the uptake of ^{239}Pu as well as ^{241}Am by plants.

INTRODUCTION

There is considerable contemporary interest in studies on the behaviour of ^{239}Pu and ^{241}Am, the long-lived and highly radiotoxic transuranic radionuclides, in soils and the soil-plant system due to their production, use and releases associated with expanding nuclear power industry. Among the edaphic factors influencing the transfer of these hazardous radionuclides from contaminated soils to plants, clay and humus are of considerable significance. The capacity of

Plant and Soil 59, 75–82 (1981). 0032-079X/81/0591-0075$01.20.
© *Martinus Nijhoff/Dr. W. Junk b.v. Publishers, The Hague, Printed in The Netherlands.*

soils to adsorb and exchange ions with the soil solution is greatly governed by the clay-humus complex, the formation of which in turn depends on the type and content of clay minerals as well as organic matter content.

There is very little quantitative information concerning the interaction of soil organic fraction with different clay minerals and its impact on the availability of the transuranic radionuclides, ^{239}Pu and ^{241}Am. The present paper reports on studies using simulated soil mixtures aimed at examining the interaction between organic matter and two major clay minerals occurring in a wide spectrum of agricultural soils, *viz* a montmorillonite (2:1 layer type) and a kaolinite (1:1 layer type) clay, in relation to their influence on the uptake of ^{239}Pu and ^{241}Am by barley (*Hordeum vulgare* L.) plants.

MATERIALS AND METHODS

The composition of mixtures giving various combinations of clay, organic matter and sand employed in the investigation is shown in Table 1. Pure montmorillonite (−250 mesh and having cation exchange capacity 86.25 meq/100 g), a representative of 2:1 type clay minerals, and a kaolinite (−250 mesh and having cation exchange capacity 7.5 meq/100 g) representing 1:1 type clay minerals were used for the experiments. Vegetable compost ground to pass −20 mesh screen with a C/N ratio of 20:1 and cation exchange capacity of 175 meq/100 g was used as a source of organic matter. Pure quartz sand was acid washed, followed by washing in distilled water, dried and passed through a 2 mm sieve. The various levels of organic matter were 0, 5 and 10% whereas each type of clay mineral was added at 5, 10 and 25% (W/W) of the prepared mixture. Purified sand was used as a filler to obtain

Table 1. Experimental design-weight of various constituents in g

Treatments	Organic matter		
	0%	5%	10%
Sand	475	450	425
Clay 5%	25	25	25
Organic matter	–	25	50
Total	500	500	500
Sand	450	425	400
Clay 10%	50	50	50
Organic matter	–	25	50
Total	500	500	500
Sand	375	350	325
Clay 25%	125	125	125
Organic matter	–	25	50
Total	500	500	500

the total weight *i.e.* 500 g of the mixture. Since the addition of the higher levels of organic matter used in the study did not result in major volume variations of the mixtures, it was decided to maintain constant weight rather than constant volume of the mixture. Calculated amounts of sand, clay and organic matter were weighed and mixed in dry state in an end-over-end shaker for $\frac{1}{2}$ hour. The dry mixtures were then transferred in polythene containers and sufficient deionised water was added to achieve 60% moisture equivalent. Pots were incubated at $23 \pm 2°C$ for three days to permit equilibrium between different constituents of the mixtures. At equilibrium, the pH (1: 2.5) values for all the kaolinite clay-organic matter mixtures were 6.5. The pH (1: 2.5) values in the case of all montmorillonite mixtures in the absence of organic matter were 7.5 and in the remaining montmorillonite clay-organic matter mixtures both at 5 as well as 10% organic matter levels were 7.0. Subsequently separate series of pots were labelled with 4 μCi $^{239}Pu(NO_3)_4$ and 5 μCi $^{241}Am(NO_3)_3$ for experiments on Pu and Am, respectively. The activity was intimately mixed and each treatment was replicated three times. In contaminated mixtures, 35 barley (*Hordeum vulgare* L.) seeds were sown and covered with a thin layer of quartz sand to prevent possible formation of aerosols, particularly in the case of Pu. One week after germination, 25 healthy seedlings were retained after thinning and the plants were harvested after 3 weeks of growth. Harvested plants were dried to constant weight at 90°C and radioassay of ^{239}Pu was carried out by thenoyaltrifluoroacetone (TTA) extraction[9] as reported in our earlier studies[12] with Pu. The quantitative estimations of ^{241}Am were made through gamma-ray spectrometry of the 60 keV gamma photopeak using a well type 7.5 × 7.5 cm NaI (Tl) crystal integral line assembly and a Nuclear Data 512-Channel pulse height analyser attached to an oscilloscope and a computer readout typewriter. Since each plant sample obtained only one radionuclide, no interference from the other radionuclide occurred during radioassay. For uptake studies, Concentration Ratios (CRs) were computed as under –

$$CR = \frac{\text{Radionuclide content/g dry tissue}}{\text{Radionuclide content/g clay-organic matter-sand mixture}}$$

All experiments were conducted in growth chambers where temperature was maintained at $23 \pm 2°C$ with relative humidity at $65 \pm 1\%$ and the plants were illuminated for 12 hours at 8000–9000 lux.

RESULTS

Availability of ^{239}Pu

Kaolinite clay-organic matter mixtures

Data on the effect of kaolinite clay and organic matter mixtures on the uptake of ^{239}Pu by barley plants are shown in Table 2. The observed values of Pu CRs for the nine clay mineral-organic matter-sand mixtures examined ranged between $(2.48 - 7.01) \times 10^{-3}$. Data in Table 2 indicate a significant reduction in plant uptake of ^{239}Pu by increasing clay content upto 25% in the case of controls where organic matter was not added. However, increasing clay content at higher organic matter levels (5 and 10%) did not show any further reduction in Pu CRs. Addition of 5% organic matter at lower clay contents (5 and 10%) resulted in decreased values of Pu CRs. Further, no significant differences in the plant uptake of ^{239}Pu and Pu CRs between 5 and 10% organic matter levels were observed at a given clay content.

Table 2. Effect of clay (5, 10 and 25%) and organic matter (0, 5 and 10%) interactions on uptake (*p*Ci/g) and Concentration Ratio (CR)* of ^{239}Pu by 3 week-old barley (*Hordeum vulgare* L.) plants

Type and clay (%)	^{239}Pu uptake (*p*Ci/g dry wt)				Concentration Ratio (CR)* × 10^{-3}			
	0**	5	10	L.s.d. ($p=0.05$)	0	5	10	L.s.d. ($p=0.05$)
Kaolinite (1:1)								
5	48.99	20.05	17.42	13.60	7.01	2.86	2.48	1.94
10	23.70	24.01	20.58	5.09	6.78	3.43	2.94	0.73
25	20.53	19.35	21.20	7.72	2.94	2.75	3.01	1.10
L.s.d. ($p=0.05$)	13.67	6.45	6.48	–	1.95	0.92	0.93	–
Montmorillonite (2:1)								
5	38.39	22.70	15.78	11.47	5.50	3.02	2.10	1.53
10	21.34	16.92	6.57	7.03	3.05	2.25	0.88	0.94
25	17.26	15.65	9.37	4.51	2.32	2.01	1.26	0.60
L.s.d. ($p=0.05$)	11.49	7.01	4.49	–	1.53	0.93	0.60	–

* CR = Concentration ratio = $\frac{\text{Radionuclide content/g dry tissue}}{\text{Radionuclide content/g clay-organic matter-sand mixture}}$

** Per cent organic matter (0, 5 and 10%)

Montmorillonite clay-organic matter mixtures

Data on uptake of ^{239}Pu by plants from montmorillonite clay-organic matter mixtures are reported in Table 2. The Pu CRs range between (0.88 – 5.50) × 10^{-3} for the different clay mineral-organic matter-sand mixtures. Results, in general, indicate a reduction in Pu CRs with increasing clay content upto 25% at all three organic matter levels studied. However, at 5% organic matter the differences in Pu CRs between 5 and 10% clay content were not significant. It is noteworthy that increasing the organic matter content upto 10%, in combination with 10% clay content resulted in lowest value of Pu CR.

Availability of ^{241}Am

Kaolinite clay-organic matter mixtures

Results on the uptake of ^{241}Am from kaolinite clay-organic matter mixtures presented in Table 3 show a trend similar to that obtained for ^{239}Pu *i.e.* ^{241}Am uptake by plants was decreased by elevating clay content upto 25% at 0 and 5% organic matter levels. Am CRs at 25% clay were reduced from (725.46 – 284.26)

Table 3. Effect of clay (5, 10 and 25%) and organic matter (0, 5 and 10%) interactions on uptake (*p*Ci/g) and Concentration Ratio (CR)* of ^{241}Am by 3 week-old barley (*Hordeum vulgare* L.) plants

Type and clay (%)	^{241}Am uptake (*p*Ci/g dry wt)				Concentration Ratio (CR)* × 10^{-3}			
	0**	5	10	L.s.d. ($p = 0.05$)	0	5	10	L.s.d. ($p = 0.05$)
Kaolinite (1:1)								
5	6883.90	30.57	25.60	737.45	725.46	3.22	2.69	116.60
10	6283.03	22.80	27.36	745.80	662.14	2.40	2.88	117.90
25	2697.40	17.95	23.55	293.43	284.26	1.89	2.48	46.41
L.s.d. ($p = 0.05$)	1089.06	6.60	8.77	–	172.12	1.00	1.40	–
Montmorillonite (2:1)								
5	33.72	13.60	13.81	6.26	3.55	1.43	1.45	0.99
10	17.61	13.86	7.11	2.54	1.85	1.48	0.74	0.40
25	13.56	6.51	6.42	1.76	1.43	0.68	0.67	0.28
L.s.d. ($p = 0.05$)	15.49	1.57	2.49	–	2.45	0.25	0.39	–

* CR = Concentration ratio = $\frac{\text{Radionuclide content/g dry tissue}}{\text{Radionuclide content/g clay-organic matter-sand mixture}}$

** Per cent organic matter (0, 5 and 10%).

× 10^{-3} and from (3.22 – 1.89) × 10^{-3} at 0 and 5% organic matter levels, respectively. However, change in clay content at the highest organic matter level (10%) did not show any significant effect on Am CRs. Increase in organic matter upto 5% at a given clay content resulted in a very marked reduction in the uptake of ^{241}Am. Subsequent increase in organic matter content upto 10% in combination with the three clay mineral levels did not show further reduction in Am CRs. The values for Am CRs depending on clay mineral and organic matter content ranged from (1.89 – 725.46) × 10^{-3}.

Montmorillonite clay-organic matter mixtures

Data in Table 3 on the plant uptake of ^{241}Am from montmorillonite clay-organic matter mixtures reveal effects similar to those observed in the case of ^{239}Pu. Data indicate that increasing clay content upto 25% at higher organic matter levels (5 and 10%) was effective in reducing the uptake of ^{241}Am by plants. However, in case of control (no organic matter) reduction in Am CRs with increase in clay content was not statistically significant. The addition of 5% organic matter over

control was effective in decreasing the plant uptake of ^{241}Am at all clay mineral levels. Increase in organic matter content upto 10% further reduced the uptake of ^{241}Am only in combination with 10% clay. The values of Am CRs for the various clay mineral-organic matter-sand mixtures ranged from $(0.67 - 3.55) \times 10^{-3}$.

Relative availability of ^{239}Pu and ^{241}Am

It is evident from Tables 2 and 3 that plants removed more of ^{239}Pu as well as ^{241}Am from kaolinite clay-organic matter mixtures as compared with those grown in montmorillonite clay-organic matter mixtures. The observed CRs for both transuranic radionuclides were higher in kaolinite based mixtures. In this context, it is noteworthy that Am CRs for plants grown in kaolinite system in the absence of organic matter were greater than the corresponding Am CRs in montmorillonite by two orders of magnitude. In general, the addition of 25% clay in the absence of organic matter was highly effective in reducing the uptake of the two radionuclides.

Addition of 5% organic matter with reference to control in both kaolinite and montmorillonite systems appears to markedly influence the plant uptake of the two transuranic radionuclides. Further increases in organic matter upto 10% were, in general, less effective. It is of interest to note (Tables 2 and 3) that the values for Am CRs in the case of plants grown in kaolinite clay-organic matter mixtures were significantly higher than those of Pu CRs. In contrast, higher Pu CRs than Am CRs were obtained for plants grown in montmorillonite based mixtures.

DISCUSSION

It is evident that increasing clay mineral content has reduced plant uptake of both the transuranic radionuclides. This reduction in uptake can be attributed to the fact that due to increase in clay content there is effective increase in surface area and the cation exchange capacity of the growth medium; this effect being greater in the case of 2:1 layer type minerals. Increased surface area probably results in greater adsorption and fixation of the radionuclides on the exchange sites rendering the nuclides less available for plant uptake. The higher values of Pu and Am CRs for the plants grown in kaolinite clay mixtures suggest that both Pu and Am ions were relatively less strongly bound in the kaolinite clay-organic matter mixtures and as a result were available to a greater extent for absorption by plants. These observations serve to explain the findings of our earlier studies[12,13] which indicate significantly lower plant uptake of ^{239}Pu and ^{241}Am

from an alkaline medium black soil (Pellustert) having higher cation exchange capacity and predominance of montmorillonitic clay in comparison to that from a laterite soil (Oxisol) with predominantly kaolinite clay and low cation exchange capacity. Higher uptake of ^{241}Am by bush beans (*Phaseolus vulgaris* L.) and maize (*Zea mays* L.) from a Troup sandy loam soil having low cation exchange capacity compared to that from a Dothan sandy clay loam soil with relatively higher cation exchange capacity has also been reported[3].

Marked effects of the clay mineral type on the comparative uptake of Pu and Am by plants demonstrated in the present study (Tables 2 and 3) offer a possible explanation of the variations in the relative magnitude of Pu CRs and Am CRs reported in literature[1,4,10,11] for plants grown in different soils.

The addition of organic matter in various combinations with clay minerals depressed the uptake of ^{239}Pu and ^{241}Am. Our present findings are compatible with reports indicating decreased plutonium uptake by soybeans (*Glycine max*)[6], and lower ^{241}Am uptake by bahiagrass (*Paspalum notatum*)[8] and rice (*Oryza sativa* L.)[2] on application of organic matter to soil.

Very little solubilization of plutonium and americium by fulvic acid which is the more soluble fraction of soil humic compounds has been reported[7]. The authors report that what little solubilization occurs is probably due to complex formation and/or colloidal peptization. However, the resulting solutions are unstable and over a period of few days most of the plutonium and americium precipitate due to colloid coagulation or hydrolysis[7]. Evidence that plutonium reacts with natural fulvates to form insoluble complexes has been provided[5] which lends support to the view that fulvic acid fractions of organic matter tend to remove plutonium from solution and lower its solubility in soils.

Results of our studies employing clay mineral-organic matter-sand mixtures which represent the clay mineral types and content as well as organic matter content likely to occur in a wide range of cultivated soils describe, in quantitative terms, the influence of these major soil constituents on the transfer of Pu and Am from soils to plants. Further, the present data would help to elucidate the variability in the relative uptake of Pu and Am by plants from contaminated soils reported in literature.

Received 19 May 1980. Revised August 1980

REFERENCES

1 Adams, W. H., Buchholz, J. R., Christenson, C. W., Johnson, G. L. and Fowler, E. B. 1975 Studies of plutonium, americium and uranium in environmental matrices. USAEC Doc. LA-5661. 24 p.

2 Adriano, D. C. 1979 Factors affecting the availability of americium-241 to the rice plant. J. Agric. Food Chem. **27,** 1369–1375.
3 Adriano, D. C., Delaney, M. S., Hoyt, G. D. and Paine, D. 1977 Availability to plants and soil extraction of americium-241 as influenced by chelating agent, lime and soil type. Environ. Exp. Bot. **17,** 69–77.
4 Au, F. H. F., Leavitt, V. D., Beckert, W. F. and McFarlane, J. C. 1977 Incorporation of transuranics into vegetable and field crops grown at the Nevada Test Site. *In* Transuranics in desert ecosystems. Eds. M. G. White, P. B. Dunaway and D. L. Wireman. USDE Doc. NVO-**181.** pp 1–15.
5 Bondietti, E. A., Reynolds, S. A. and Shanks, M. H. 1976 Interactions of plutonium with complexing substances in soils and natural waters. *In* Proc. Symp. Transuranium Nuclides in the Environment, IAEA, Vienna, pp 273–287.
6 Cataldo, D. A., Routson, R. C., Wildung, R. E. and Garland, T. R. 1976 Uptake and distribution of plutonium in soybean tissues as a function of time following germination. USDA Doc. BNWL-2000 pt 2.
7 Cleveland, J. M. and Rees, T. F. 1976 Investigation of solubilization of plutonium and americium in soil by natural humic compounds. Environ. Sci. Technol. **10,** 802–806.
8 Hoyt, G. D. and Adriano, D. C. 1979 Americium-241 uptake by bahiagrass as influenced by soil type, lime and organic matter. J. Environ. Qual. **8,** 392–396.
9 Moore, F. L. and Hudgens, J. E. 1957 Separation and determination of plutonium by TTA extraction. Anal. Chem. **29,** 1767–1770.
10 Romney, E. M., Wallace, A., Gilbert, R. O. and Kinnear, J. E. 1976 ^{239,240}Pu and ^{241}Am contamination of vegetation in aged fall-out areas. *In* Proc. Symp. Transuranium Nuclides in the Environment, IAEA, Vienna, pp 479–491.
11 Schulz, R. K., Tompkins, G. A., Leventhal, L. and Babcock, K. L. 1976 Uptake of plutonium and americium by barley from two contaminated Nevada Test Site soils. J. Environ. Qual. **5,** 406–410.
12 Vyas, B. N. and Mistry, K. B. 1978 Studies on the uptake of plutonium from major Indian soils and its distribution in plants. J. Environ. Qual. **7,** 533–536.
13 Vyas, B. N. and Mistry, K. B. 1980 Uptake of Am-241 from major Indian soils and its distribution in plants. Environ. Exp. Bot. **20,** *in press.*