THESIS

^{226}RA CONTAMINATION OF SOIL AND FOLIAGE AS A FUNCTION OF DISTANCE DOWNWIND FROM URANIUM MILL TAILINGS

submitted by

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY DAWN J. SKINNER ENTITLED ^{226}RA CONTAMINATION OF SOIL AND FOLIAGE AS A FUNCTION OF DISTANCE DOWNWIND FROM URANIUM MILL TAILINGS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT

^{226}RA CONTAMINATION OF SOIL AND FOLIAGE AS A FUNCTION OF DISTANCE DOWNWIND FROM URANIUM MILL TAILINGS

This study concerned ^{226}Ra contamination of soils and foliage as a function of distance downwind from a uranium mill tailings pile. In soils the radium contamination was primarily associated with particle sizes < 0.045 mm and mainly found within the 0-0.6 cm soil horizon. The 0-0.6 cm soil horizon showed a decrease in activity concentration with distance. The 0-15 cm and 0-30 cm soil depth samples also showed a significant decrease with distance.

An attempt was made using ultrasonic washing to separate internal from external ^{226}Ra contamination in Artemisia tridentata. Internal contamination appeared to be a larger contributor to total contamination at distances $\leq$ 0.16 km downwind from the tailings pile. At distances > 0.16 km, external contamination became a larger contributor to the total ^{226}Ra contamination.

Concentration ratios (based on total contamination and internal contamination) were determined as a function of distance downwind from the tailings pile. Concentration

ratios appeared to be highly site specific, however higher values (0.8-2.8) were generally associated with distances $\leq$ 0.16 km from the mill. At distances > 0.16 km

In most soil samples ^{226}Ra concentrations approached background levels at a distance of 1.1 km from the tailings pile. Total vegetation contamination approached background at 6.6 km. A trend of decreasing internal and external ^{226}Ra contamination with distance downwind was found to be significant ($P < 5\%$). This study suggested that a combination of root uptake and foliar absorption were responsible for internal contamination and further studies were suggested.

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INTRODUCTION

Previous investigators have surveyed vegetation and soil around uranium mill tailings to determine the extent of radionuclide contamination (Ib82, Ma80, Ko77, Wi75, Wi74). Most previous investigations did not distinguish between internal and external plant contamination. Two primary mechanisms of radionuclide accumulation by plants are root uptake and external deposition of airborne particulates. Quantification of internal and external plant contamination may indicate the relative importance of these two transport pathways.

Exposed uranium mill tailings offer a radioactive source available for wind dispersion. Radionuclides such as ^{226}Ra, ^{210}Pb, ^{210}Po, ^{238}U, and ^{230}Th are abundant in such tailings and of ecological interest. ^{226}Ra is of particular concern because it is a chemical analog to calcium in ecological systems, has a long physical and biological half-life when incorporated in to the skeleton (ICRP59), and due to its alpha emissions and radioactive progeny, it is comparatively radiotoxic (Ma69). In sulfuric acid leached tailings, radium is expected to be in the highly insoluble $RaSO_4$ form. The leachability of $RaSO_4$ from these tailings in water has been reported as 0.08 - 0.15% (Ib81). Once

tailings particles disperse into the normal environment, the chemical form of radium (and other radionuclides) may change by reactions with humic acids (Gj76) or other components of soils. Such changes potentially allow for solubilization, migration and subsequent root uptake by plants. The process of root uptake may be important for reclamation and mitigation strategies long after operational shutdown of a uranium mill is completed. Realistic modeling for dose assessment must account for both deposition and root uptake processes.

In this study, an attempt was made to distinguish the contribution of each process to the ^{226}Ra burdens in sagebrush (Artemisia tridentata) as a function of distance from a uranium mill. Specific objectives included: measurement of plant/soil ^{226}Ra concentration ratios as a function of distance downwind; soil ^{226}Ra concentrations as a function of soil depth and distance downwind; and internal vs. external plant concentrations as a function of distance downwind.

METHODS AND MATERIALS

1. Area description. The uranium mine-mill complex under study is located in the southeastern high plains region in Wyoming at an elevation of about 2200 m. The physiography is gentle, rolling semi-arid land dominated by a grassland-sagebrush association. The annual precipitation

is about 25 cm with snowfall contributing the major portion. Strongest winds prevail from the west.

The thin topsoil (10-15 cm) covers the White River formation of Cenozoic and Mesozoic origin. The majority of the landscape surrounding the mill is used for livestock grazing and recreation (hunting antelope, rabbit, and sage grouse). Sagebrush (Artemisia tridentata) and various grasses and forbs dominate the upland vegetation communities of the area.

The mill is a conventional acid leach operation which has a capacity of 1500 tons of ore per day containing an average uramium content of 0.2 percent. The tailings slurry (approximately 30% solids, 70% liquids) is pumped to an impoundment where solids settle into two particle fractions, sands (> 90 microns) and slimes (< 90 microns). The concentrations of ^{226}Ra are considerably higher in the smaller slime fraction (approximately 540 pCi/g) than in the sand fraction (approximately 200 pCi/g) (Ib82).

2. Site locations, sample collection, and radiochemical analysis. The predominant direction of transport of wind eroded tailings was determined by examination of site specific windrose data (Table 1). Based on these data, a due eastern transect expected to be within the plume of wind-dispersed tailings was designated for an extensive gamma survey. A Ludlum Model 2200 scaler with a 2.5 x 2.5 cm NaI crystal was used for the survey on April 10, 1981. Gamma surveying was completed at several other locations

Table 1. Annual wind rose data for the Uranium Mine, 1978. Values in % of time.

Wind From Direction	(%) 0-7 mph	(%) 8-11 mph	(%) 12-18 mph	(%) 19-24 mph	(%) >24 mph	(%) Totals
N	1.4	1.1	2.2	1.2	.3	6.2
NNE	2.1	1.4	1.3	1.1	.5	6.4
NE	2.8	.7	1.3	.4	.7	5.9
ENE	3.7	1.0	2.0	.4	.8	7.9
E	4.0	2.0	1.7	.4	.5	8.6
ESE	1.6	1.0	1.6	.4	.4	5.0
SE	1.0	1.1	1.3	.7	.7	4.8
SSE	1.1	1.2	1.2	1.0	.4	4.9
S	1.1	.9	1.5	.5	.6	4.6
SSW	.8	.5	.9	.3	.7	3.2
SW	.7	.6	1.2	.7	.5	3.7
WSW	1.2	1.0	1.8	1.1	.7	5.8
W	2.6	3.2	5.7	2.9	2.8	17.2
WNW	1.1	1.0	2.5	1.7	1.1	7.4
NW	.8	.8	1.4	1.2	.8	5.0
NNW	.7	.8	2.1	1.2	.8	5.6
Variable & Calm	.7	0.0	0.0	0.0	0.0	.7
Totals	27.4	18.3	29.70	15.2	12.3	

around the mill to confirm the shape and direction of the plume of deposited tailings.

Five sampling site locations were chosen along the eastern transect based on ease of access and a 50-60% reduction in count rate of the gamma survey meter between adjacent locations. One upwind control site located 3.4 km northwest of the tailings pile was also included in the sampling to serve as a background location. These sites are labeled D_1, D_2, D_3, D_4, and D_5 for the downwind locations and BG for the upwind control (Figure 1). Sites D_1 through D_5 were 0.04, 0.16, 1.1, 3.3, and 6.6 km downwind (east) from the tailings pile.

Four replicate sagebrush samples of approximately 30 grams each were collected at each site on July 16, 1981. Only current annual growth was collected. In addition to the vegetation samples, paired soil samples (30-500 grams) were also collected from the area immediately surrounding the root zones of the plants sampled. In order to infer the distribution of ^{226}Ra in soils, the soil samples were collected as a function of depth strata including 0-0.6 cm, 0-15 cm, and 0-30 cm soil horizons.

Each vegetation sample was split into two fractions, one for ^{226}Ra analysis without ultrasonic cleaning, the other for ^{226}Ra analysis with ultrasonic cleaning. This was done to estimate external and internal ^{226}Ra concentrations respectively. Four to five grams of plant material were placed in a Branasonic ultrasonic water bath (50/60 Khz,

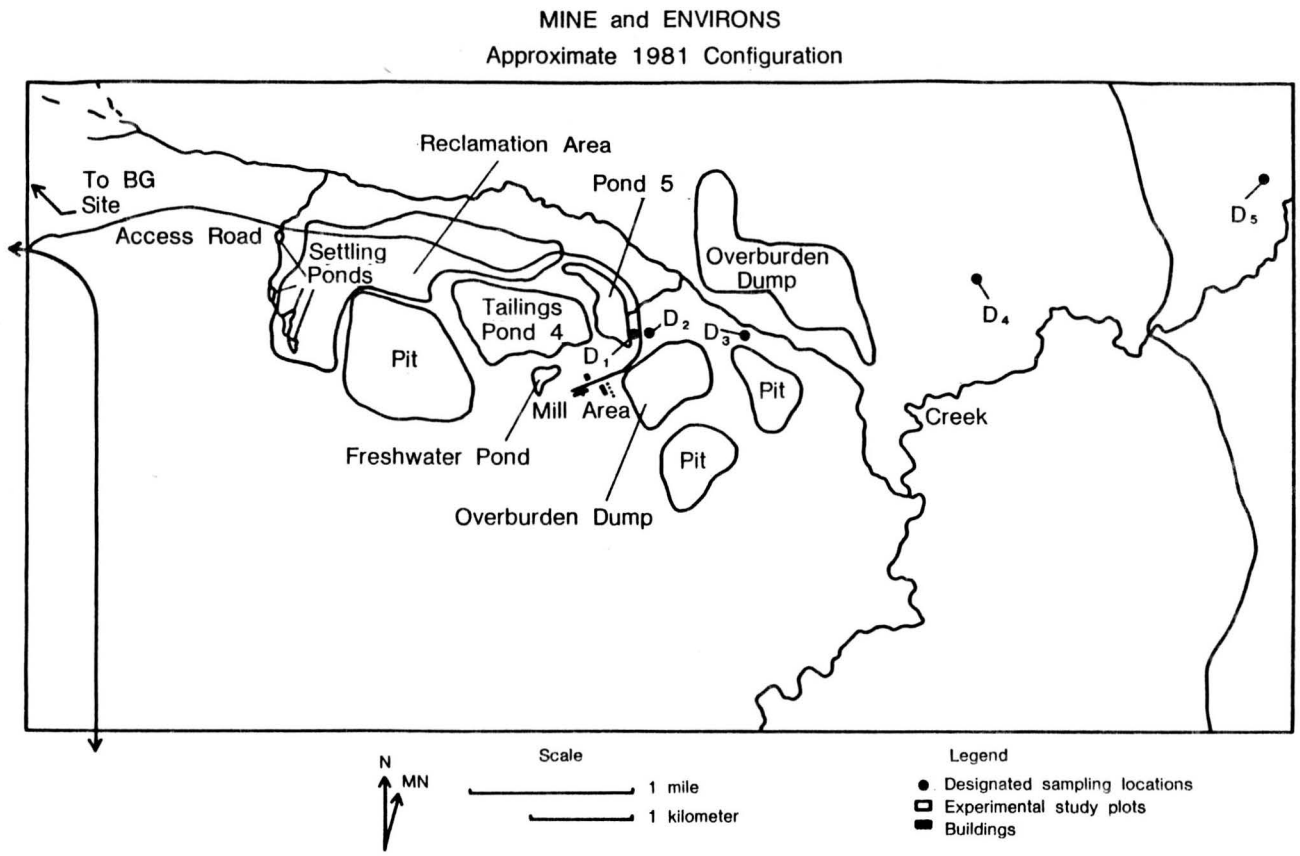

Fig. 1. Map of the uranium mine and environs. Major features, sampling locations, and experimental sites are shown.

model B-22-4, Smithline, Co.) for ten minutes with 1.5 l distilled water and approximately 0.1-0.2 g Sparkleen laboratory detergent. The sample was then strained through a wire mesh screen and placed back into the ultrasonic cleaner with 1.5 l of fresh, distilled water to rinse for an additional ten minute ultrasonic treatment. The rinse was repeated a second time, bringing the total time in the ultrasonic waterbath to 30 minutes. This washing regime was previously determined on the basis of titanium measurements to be 0.74 $\pm$ 0.06% efficient in removing surficial dust on sagebrush (Appendix A). The washed vegetation samples were then oven dried at $< 70^{\circ}C$, dry ashed overnight at $500^{\circ}C$, hot leached in (conc.) HCL (5 ml/5 g plant) and (conc.) HNO_3 (5 ml/5 g plant) for 5-10 minutes. The samples were then diluted with 90 ml distilled water and heated again for twenty minutes. The unwashed vegetation samples were oven dried at $< 70^{\circ}C$. The vegetation was then wet ashed on a sand bath with (conc.) HNO_3, then $HClO_4$, followed by an HF digestion to decompose adhearing silica particulates expected from external deposition. Decompostion was done in batches of ten which included a blank and a ^{226}Ra standard traceable to the National Bureau of Standards (NBS).

Both washed and unwashed vegetation samples were then analyzed for ^{226}Ra activity using the barium-sulphate carrier method as developed by Percival (Pe74). Once vegetation samples were radiochemically processed for ^{226}Ra, the Ba-$RaSO_4$ filters were alpha counted on a gas flow

proportional counter (background 0.06 cpm, efficiency 0.42-0.51 counts/disintegration for ^{239}Pu alpha standard). When low concentrations were expected, larger samples were processed (up to 20 grams) to increase sample activity and improve the minimum detectable concentration (MDC) capability.

The MDC was calculated from the method outlined in the 1980 Health Physics Society Committe Report to the U.S. Environmental Protection Agency (USEPA80) and the efficiency obtained with a ^{239}Pu NBS traceable alpha source.

$$MDC = 4.65 \times K \times S_b$$

where: 4.65 is a constant due to symmetry and statistical considerations

and K = 1/efficiency x yield x count time

$= 1/.48 \times .90 \times 80 = .03$

and S_b = Std. Dev. of background count based on 10 background samples

$= 2.19$ counts

$$MDC = 4.65 \times 0.03 \times 2.19 = 0.31 \text{ dpm}$$

$$= \frac{0.31 \text{ dpm}}{2.22 \text{ dpm/pCi}} = 0.14 \text{ pCi/sample}$$

Each 0-0.6 cm soil sample was particle sized fractioned through dry sieving to < 0.045 mm, 0.045-2.0 mm, and > 2.0 mm. Each 0-15 and 0-30 cm soil sample was particle size fractioned into < 2 mm and > 2 mm. Samples were then sealed with glyptol as used by Parsont (Pa67) (Fisher Scientific's

"Sealit") in steel counting cans (Gencan, Inc. dimensions: diameter 10.6 cm; height 6.4 cm) and allowed to equilibrate for 30 days (97% ^{214}Bi daughter ingrowth after 20 days). The soils were then counted on a 4 x 8 inch NaI crystal (efficiency = 0.047 c/dis for ^{214}Bi) along with standard uranium tailings of known ^{226}Ra concentration using the ^{214}Bi daughter gamma peak at 1.76 MeV. Once ^{226}Ra analysis was completed a weighted average based on particle size contribution was computed (pCi ^{226}Ra/g soil) for all soil samples.

^{226}Ra concentration ratios were calculated for both unwashed and washed vegetation using the relationship:

$$CR = \frac{\text{pCi } ^{226}\text{Ra/g dry plant}}{\text{pCi } ^{226}\text{Ra/g dry soil}}$$

The ^{226}Ra concentration used for the washed vegetation concentration ratios was corrected for residual ^{226}Ra surface activity. This was estimated by the ultrasonic removal efficiencies previously determined (Appendix A) for sagebrush.

The calculation of internal ^{226}Ra concentration was computed using the following formula:

$$I = Y - \frac{(Y-X)}{0.74}$$

Where:

I = internal ^{226}Ra sagebrush concentration

Y = the total ^{226}Ra (or unwashed concentration) in sagebrush

X = the washed sagebrush ^{226}Ra concentration

and 0.74 = removal efficiency previously determined (Appendix A) for sagebrush.

The 0-15 cm soil depth (with all particle sizes) was used for the calculation of concentration ratios since this was the horizon containing most of the root mass of sagebrush. Concentration ratios reported in previous investigations (Ib82 and Ib81) have also used this soil horizon.

RESULTS AND DISCUSSION

Most of the radioactivity was associated with the < 0.045 mm particle size fraction in 0-0.6 soil horizon (Table 2). The activity concentrations for this particle size ranged from 285 pCi/g at site D_1 to 4 pCi/g at site D_5. The ^{226}Ra activity concentration at site D_1 approximates the reported value (Ib81) for slimes from mill tailings.

Observed ^{226}Ra concentrations in soil declined with distance downwind and also with soil horizon (Figure 2, Table 2). Most of the ^{226}Ra contamination appeared to be restricted to the top 0-0.6 cm soil layer. The 0-15 cm and 0-30 cm soil horizons had significantly lower ($P < 0.05$)

Table 2. Mean pCi ^{226}Ra/g soil for three particle sizes and horizons as a function of distance downwind from uranium mill tailings.

Site Location (km)	Soil Horizon (cm)	Mean ^{226}Ra Pci/g soil for Particle Size Fraction: (n = 4)*		
		< 0.04 mm	< 2.0 mm	> 2.0 mm
D_1 (0.0 4 km)	0-0.6	285±80	93±23	151±21
	0-15.0		11±2	8±8
	0-30.0		14±11	3±.8
D_2 (.16 km)	0-0.6	36.±6	25±5	40±13
	0-15.0		4±.6	6±1
	0-30.0		5±.8	3±1
D_3 (1.1 km)	0.06	19.±8	9±3	4±.5
	0-15.0		4±.5	4±.5
	0-30.0		3±.7	3±.7
D_4 (3.3 km)	0-0.6	6±2	3±.3	3±.6
	0-15.0		3±.3	2±.2
	0.30.0		2±.7	2±.4
D_5 (6.6 km)	0.0.6	4±2	5±6	3±.6
	0-15.0		2±.1	2±.1
	0-30.0		3±.2	2±.4
BG	0-0.6	8±3	5±.7	6±5
	0-15.0		3±.1	4±.5
	0-30.0		3±.3	4±1

*Particle size for 0-0.6 cm soil horizon was < 0.04 mm, 0.04-2.0 mm and > 2.0 mm. Other horizons as marked in table.

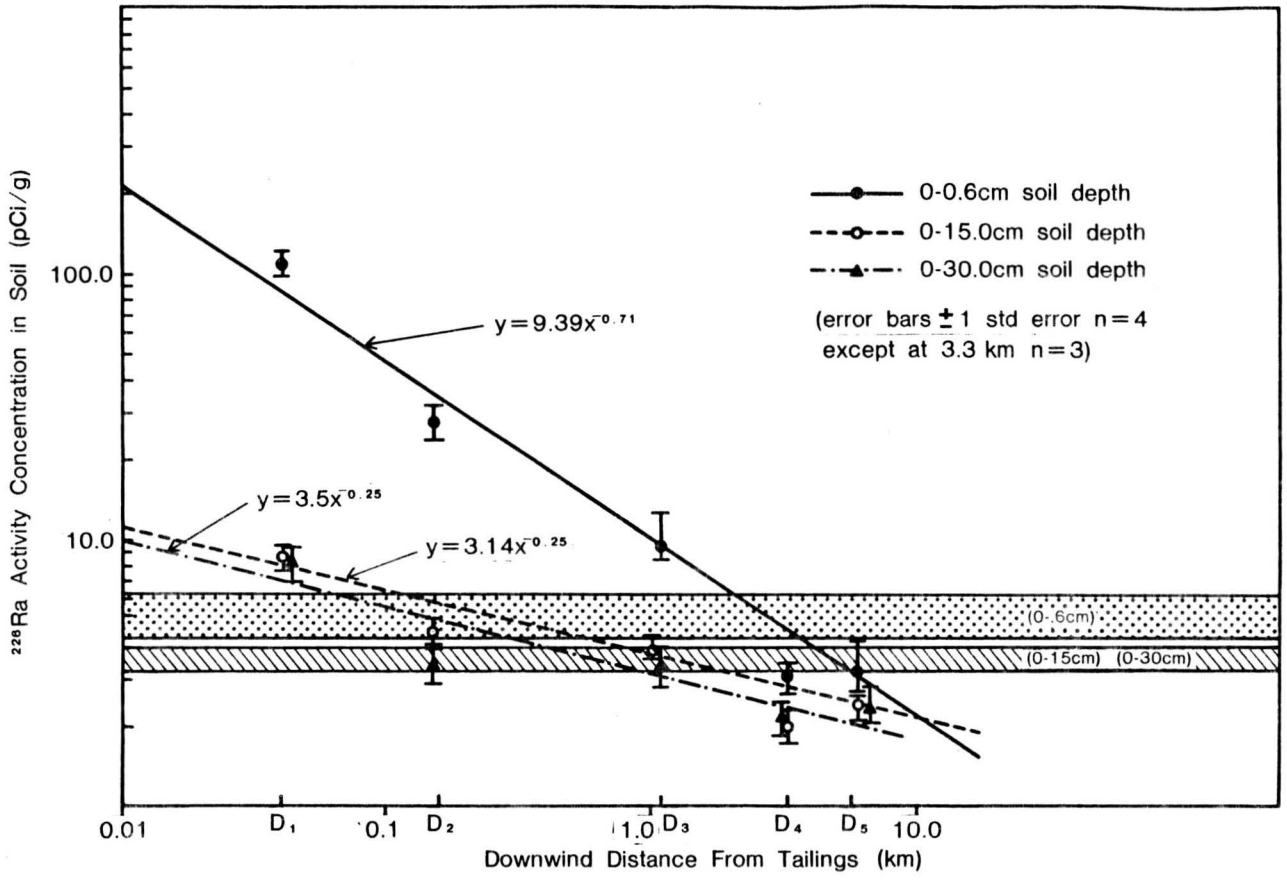

Fig. 2. ^{226}Ra activity concentration (pCi ^{226}Ra/g soil) for three soil horizons as a function of downwind distance (km) from the uranium mill tailings area. Horizontal bars represent background, 67% confidence bands for the mean, for the same three soil horizons.

concentrations of ^{226}Ra than the 0-0.6 cm layer, however, they did not differ significantly from each other. This observation agrees with the data reported by Jaworowski and Grzybowska (Ja77).

The trend of decreasing ^{226}Ra activity concentration with distance was observed for all soil horizons but it was more exaggerated for the 0-0.6 cm layer. A regression analysis of mean activity versus distance on log-log transformed data resulted in the best fit of the 0-0.6 cm data with $R^2 = 0.94$. This was found to have a significant slope ($P < 0.001$) indicating that the decrease in ^{226}Ra activity with distance was a significant trend for soil samples. The 0-15 cm soil depths also showed this trend with an $R^2 = 0.65$, which is significant at the 0.01 level. The comparable 0-30 cm soil depth regression analysis was found significant at the 1% level ($R^2 = 0.77$). The three regression equations are presented in Figure 2.

In order to determine the distance downwind that soil ^{226}Ra concentrations became indistinguishable from upwind control site concentrations, each soil sample concentration was compared by t-test to upwind control soil values. The 0-0.6 cm soil horizon was indistinguishable from upwind control at site locations D_3, D_4, and D_5 ($P = 0.10$, 0.12, and 0.18, respectively). The comparable t-test on control versus site location for the 0-15 cm soil horizon was insignificant at site D_2 ($P = 0.055$). No significant difference between control and test sites were found for the

0-30 cm soil horizons at any of the site locations. The control site (all soil depths) was tested for significant differences from reported values of 3.08 ± 0.775 (Ib81) for this area, and no significant differences were found. P-values were calculated as P = 0.10, 0.44, and 0.49, respectively for the 0-0.6 cm, 0-15 cm, and 0-30 cm soil depths. The inference was that the control was not significantly different from reported background concentrations and was considered a representative background site.

The total ^{226}Ra activity concentration (unwashed samples) found for sagebrush followed the same trend as soil of decreasing activity with distance (Figure 3). The background control washed sagebrush ^{226}Ra concentration was tested for differences from comparable, previously published values (Ib81) and no significant difference was found (P = 0.25). This provided evidence that vegetation samples at the control site were equivalent to background.

The unwashed sagebrush data were fit best by a log-log transform of activity vs. distance ($R^2 = 0.90$; $p < 0.01$). The significant slope confirmed the obvious trend of decreasing activity with distance. These samples were tested for significant differences from unwashed background control sagebrush samples. This was computed to determine the distance at which total ^{226}Ra activity concentration on sage vegetation became indistinguishable from background levels. Significant differences were found between BG and

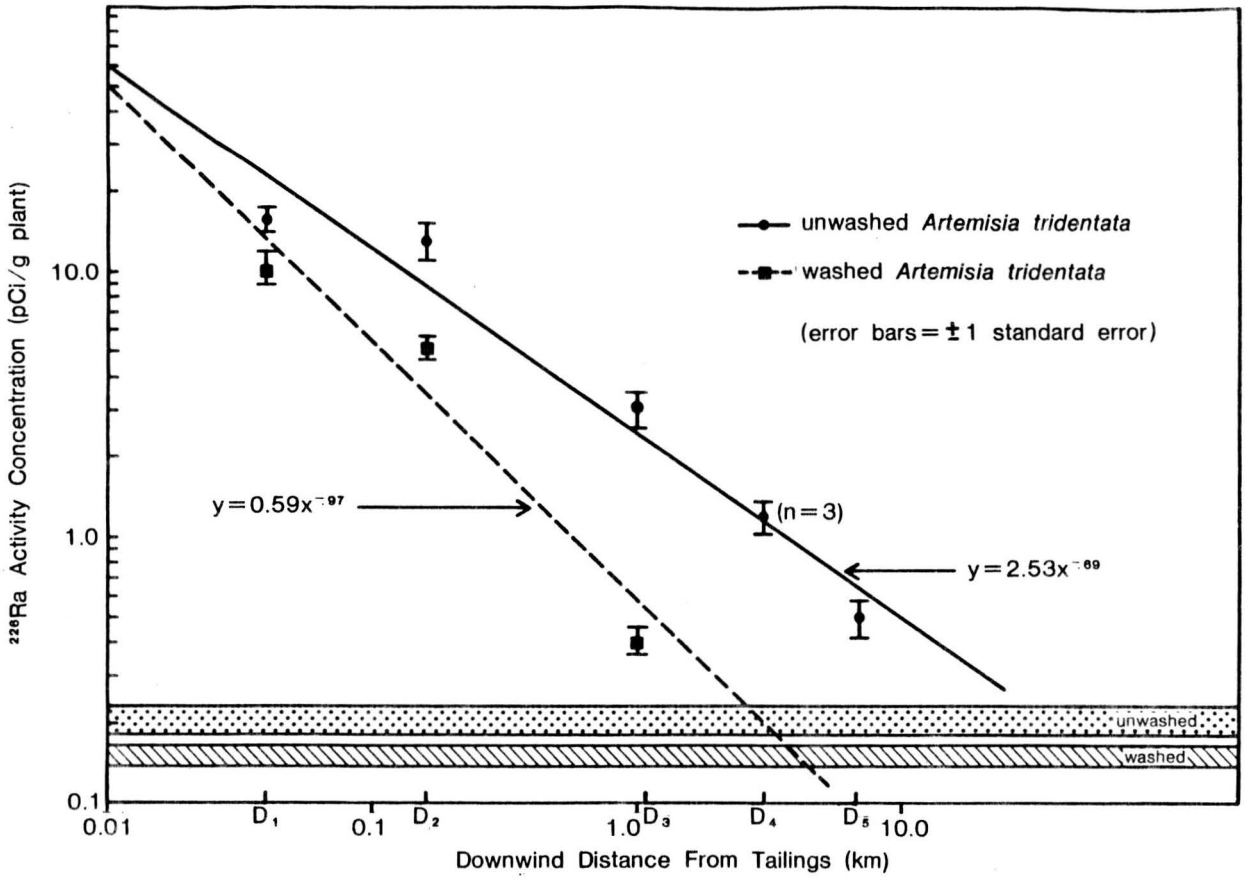

Fig. 3. ^{226}Ra activity concentration (pCi/g plant) in Artemisia tridentata as a function of distance downwind (km) from a uranium mill tailings area. Horizontal bars represent corrected washed and unwashed background sagebrush, 67% confidence bands; n = 4 unless marked.

sites D_1, D_2, D_3, and D_4 ($P \leq 0.01$). No significant difference was found between site D_5 (6.6 km) and BG ($P = 0.08$). This suggests that total ^{226}Ra activity concentration in sagebrush becomes statistically indistinguishable from background at a distance $\geq$ 6.6 km downwind from the mill site.

The trend of decreasing internal contamination with distance was also observed (Figure 3). A linear regression analysis on the log of the means versus log distance yielded an equation ($Y = 0.59X^{-0.97}$) which had a significant slope ($R^2 = 0.998$, $P < 0.05$). This indicated a decrease of internal ^{226}Ra contamination with distance (to 1.1 km downwind), but there may be no significant decrease after this distance. The data for the internal contamination after 1.1 km were suspect due to cross contamination and were discarded as invalid. Significant differences were found between washed sagebrush samples at the background location and site locations D_1, D_2, and D_3 ($P \geq 0.0026$).

Concentrations ratios were calculated for sagebrush based on corrected washed and unwashed data (Figure 4). The values appear to be highly site specific with a calculated range of 0.01 to 2.8. Concentration ratios obtained at distances $\geq$ 1.1 km based on unwashed vegetation ranged from 0.2 to 1.0, approximating previously reported values (Ib82). The concentration ratios for locations near the tailings source, however, were considerably higher (1.5-2.9 unwashed and 1.1-1.3 washed, corrected) than literature values

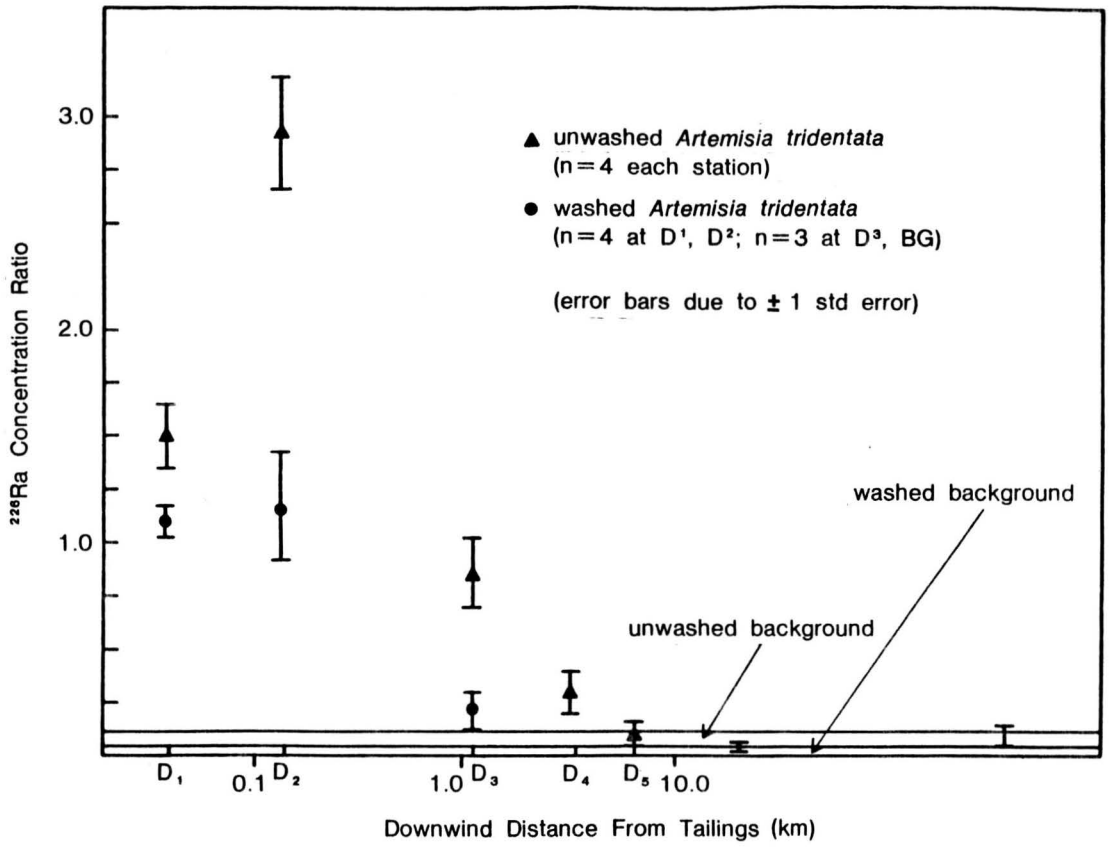

Fig. 4. ^{226}Ra concentration ratios for unwashed and corrected washed Artemisia tridentata as a function of downwind distance. Horizontal lines represent background sagebrush values.

(0.02-0.8) (Ib82). This may be attributable to foliar absorption of ^{226}Ra from adhearing slimes. Since we did not attempt to distinguish between root uptake and foliar absorption, no conclusive statements can be made about the predominant mechanism that might explain the unexpectedly high internal concentrations.

A calculation based on the amount of soil removed by ultrasonic cleaning (determined by Ti tracer analysis) (Appendix A) and the amount of ^{226}Ra removed (determined by analysis for ^{226}Ra of washed and unwashed vegetation) yields an estimated ^{226}Ra activity concentration in the solids removed from the plants. The calculation can be accomplished as follows: If 72 micrograms Ti are ultrasonically removed per gram of plant material (Appendix A) and 10 pCi of ^{226}Ra are removed/g plant material and there is 4.1 mg Ti/g soil then:

$$\frac{0.072 \text{ mg Ti/g plant}}{4.1 \text{ mg Ti/g soil}} = 1.76 \times 10^{-2} \frac{\text{g soil removed}}{\text{g plant}}$$

then

$$\frac{10 \text{ pCi removed/g plant}}{1.76 \times 10^{-2} \text{ g soil/g plant}} = 570 \text{ pCi/g soil}$$

The 570 pCi ^{226}Ra/g soil strongly suggests that the contamination on the surface of the plant material may be slimes from fugitive mill tailings.

To elucidate the relative contributions of external and internal contamination as a function of distance, a ratio of internal contamination to total contamination was calculated (Figure 5). A regression analysis on means yielded a significant slope ($R^2 = 0.996$, $P < 0.05$). Unfortunately, some data are missing (sites D_4 and D_5) because of suspected cross contamination within the laboratory. The internal contamination apparently made a proportionately larger contribution to total contamination at sites closer to the mill tailings. The calculated internal to external ratio for the background site was 0.75, which did not follow the trend shown in Figure 5. No definite conclusion can be drawn from the incomplete data, but it appears that the internal contamination may not make a large contribution (< 25-35%) to total contamination at distances greater than 1.1 km downwind from the tailings.

Increasing external contamination with distance might be understood by examination and study of aerosols. Smaller particle sizes are transported farther distances (Ha81, Ba72). Also it has been reported that smaller particle sizes have longer weathering half-times on plants than larger particles (Ca76, Ca78, Ca80, Lo71). These two factors may explain the observed trend.

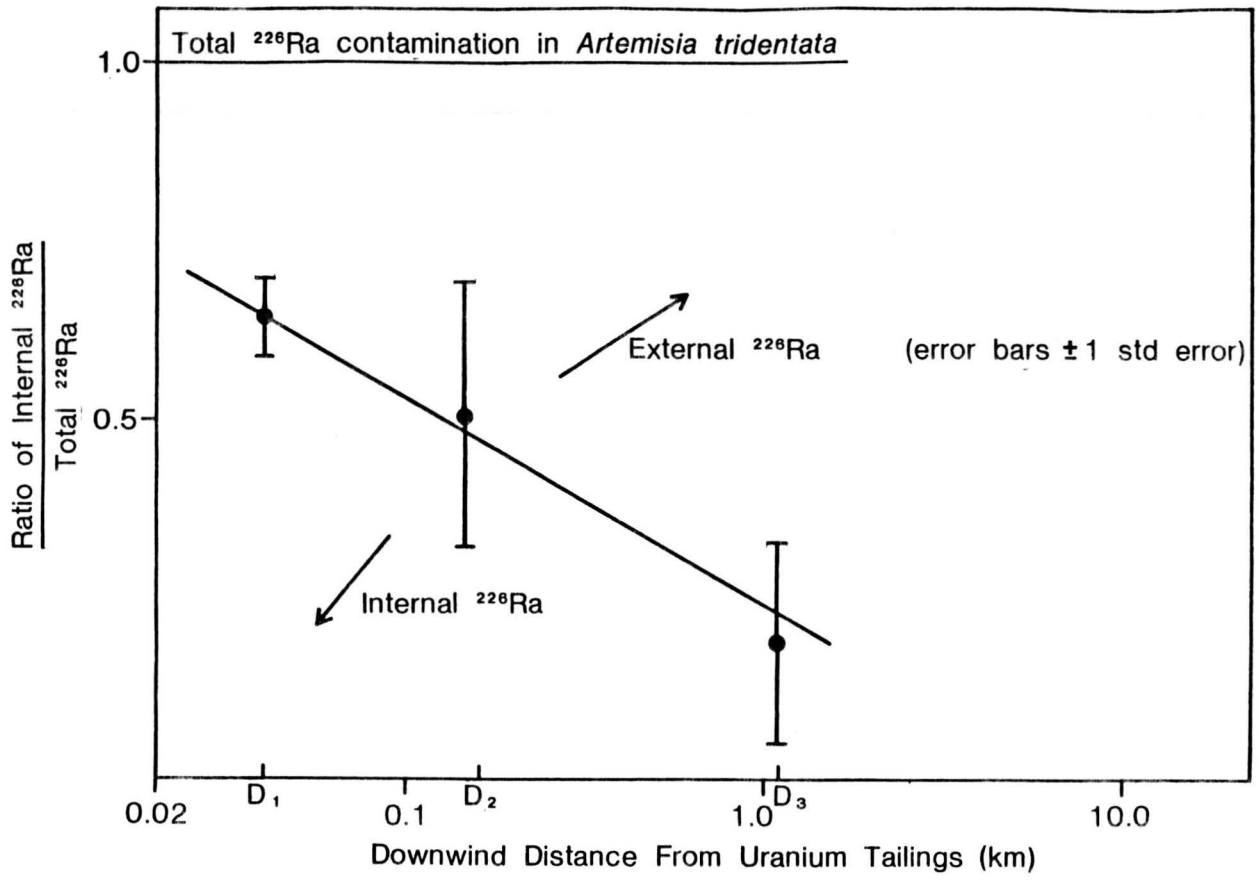

Fig. 5. The ratio of internal to total ^{226}Ra contamination in Artemisia tridentata as a function of distance downwind (km) from a uranium mill tailings area.

CONCLUSIONS AND RECOMMENDATIONS

^{226}Ra was found to be mainly associated with soil particle sizes < 0.045 mm in the 0-0.6 cm soil horizon. The distribution of ^{226}Ra was not homogeneous in soils. Concentrations were not much greater than background at depths of 0-15 and 0-30 cm which represented root zones of plants studied. For the 0-0.6 cm soil depth a significant decrease in ^{226}Ra concentration as function of distance downwind was found.

The total contamination (external + internal) on Artemisia showed a significant decrease of ^{226}Ra activity with distance also. In general, total vegetative contamination approached background levels around 6.6 km downwind from the tailings pile.

Internal contamination was less easily attributed to root uptake than anticipated because of suspected foliar absorption processes. Inhomogenous distribution of ^{226}Ra in soils, insufficient data and methods did not allow these processes to be isolated and quantified.

Concentration ratios for both washed vegetation (internal) and unwashed vegetation (total), showed a distinct difference between sites located close to the mill tailings (0.04-0.16 km) and sites located farther away

($\geq$ 1.1 km). The sites $\leq$ 0.16 km had concentration ratios much greater than either ratios reported in the literature or those calculated at locations > 0.16 km for this study. This phenomenon has also been reported by Ibrahim (Ib81). The use of concentration ratios should be applied with extreme caution and an understanding that this parameter appears to be highly site specific. In this study concentrations ratios were not a strictly linear function of distance, but they showed an appreciable dependence on distance from tailings.

An assessment of the contribution of internal vs. external contamination to ^{226}Ra total contamination was accomplished. The resulting conclusion was that there appeared to be more external contamination than internal contamination on plants tested at sites located $\geq$ 0.16 km from the mill. The relative importance of root uptake vs. aerial deposition was not concisely defined. Internal contamination may be present because of 1. Root uptake; 2. Foliar absorption; or 3. Very tightly bound external material. We could not separate these processes. More research in this area is necessary before these mechanisms can be isolated. A study that might unfold the three pathways, might ideally include a greenhouse root uptake study coupled with a field study such as this one. Some of this work is presently underway at Colorado State University (Ib81).

REFERENCES CITED

Ba72 Baver, L. D., Gardner, W. H., and Gardner, W. R, 1972, "Soil Physics", 4th ed. (New York: John Wiley Sons, Inc.).

Ca76 Cataldo, D. A., and Vaughn B. E., 1976, "Retention, Absorbtion and Translocation of Foliar Contaminants", in: Transuranics in Natural Environments (Edited by M. G. White and P. B. Dunaway), NVO-178.

Ca78 Cataldo, D. A., 1978, "Suspended Particle Interaction and Uptake in Terrestrial Plants", Ecol. Sci. PNL-2500pt 2 UC-11.

Ca80 Cataldo, D. A., Garland, T. R., Wildung, R. E., and Thomas, J. M., 1980, "Foliar Absorption of Transuranic Elements: Influence of Physio-chemical Form and Environment Factors", J. of Environ. Quality 9(3), 364.

Gj76 Gjessing, E. T, 1976, "Physical and Chemical Characteristics of Aquatic Humus", Ann Arbor Science Publisher, Inc., Ann Arbor, Mi. 120 pp.

Ha81 Hakonson, J. E., Watters, R. L. and Hanson, W. C., 1981, "The Transport of Plutonium in Terrestrial Ecosystems", Health Physics 40, 63-69.

Ib81 Ibrahim, S. A. and Whicker, F. W., 1981, "Radioecological Investigations of Uranium Mill Tailings Systems", in: Second Technical Progress Report Oct. 1, 1980-Sept. 30, 1981. U.S. DOE, contract DE-AC02-79EV10305. pp. 70-74. (Colorado State University, Fort Collins, CO).

Ib82 Ibrahim, S. A., Flot, S.L., and Whicker, F. W., 1982, "Concentrations and Observed Behavior of ^{226}Ra and ^{210}Po around Uranium Mill Tailings", International Symposium on Management of Wastes from Uranium Mining and Milling, May 10-14, 1982. Paper #32. Albuquerque, N.M.

ICRP59 International Commission on Radiological Protection (ICRP), 1959, "Report of Committee II on Permissible Dose for Internal Radiation", ICRP Publication 2. Pergamon Press, Oxford. 233 p.

Ja77 Jaworowski, Z. and Grzybowska, D., 1977, "Natural and Radionuclides in Industrial and Rural Soils", Science of the Total Environment 7, 45.

Ko77 Kotsch, J. L., 1977, "^{226}Ra uptake in selected plants and animals at an uranium mill site", thesis. University of Wyoming, Laramie, Wy. 64 pp.

Lo71 Lovaas, A. I. and Johnson, J. E., 1971, "Retention of Near-in Fallout by Crops", in: Survival of Food Crops and Livestock in the Event of Nuclear War (Edited by D. W. Benson and A. H. Sparrow).

Ma80 Marple, M. L., 1980, "^{226}Ra in Vegetation and Substrates at Inactive Uranium mill sites", thesis. University of New Mexico, Albuquerque, N.M. 64 pp. LA-8183-T, thesis (Los Alamos Scientific Laboratories, Los Alamos, N.M.). (also UC-41).

Ma69 Mays, C. W. 1969. "Delayed Effects of Bone Seeking Radionuclides", University of Utah Press, Salt Lake City, Utah. 519 pp.

Pa67 Parsont, M. A., 1967, "The Distribution of ^{226}Ra in an Aquatic Environment", dissertation. Colorado State University, Fort Collins. 121 pp.

Pe67 Percival, D. R. and Martin, D. B., 1974, "Sequential Determination of ^{226}Ra, ^{228}Ra, ^{227}Ac and Thorium Isotopes in Environmental and Process Water Samples", Analytical Chemistry, 46(12), 1742.

USEPA80 United States Environmental Protection Agency, 1980, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1. p. 6-24 - 6-30. EPA 520/1-80-012.

Wi74 Winsor, T. F. and Stahlecker, D. W., 1974, "An Examination of Radionuclide Effluent upon Soil and Biota at the Shirley Basin Uranium Mine", a report to Utah International, Inc. September 26, 1975. (Colorado State University, Fort Collins, CO).

Wi75 Winsor, T. F. and Whicker, F. W., 1975, "^{238}U, ^{226}Ra, ^{210}Pb in Soil and Vegetation at the Lucky Mc Uranium Mine and Mill", a report to Utah International, Inc. September 26, 1975.

APPENDIX A

Ultrasonic Removal of Surficial Radioactivity From *Artemisia tridentata*

Abstract

Surficial radioactive contamination from wind blown uranium mill tailings were ultrasonically removed from sagebrush (*Artemisia tridentata*) leaves with an efficiency of .74 ± .06. Ultrasonic washing for more than 10 minutes (plus two 10-minute rinses) did not remove significantly more of the activity contamination from the leaves. The use of detergent to clean contaminated plants was not a significant aid in reducing either the length of washing time nor the amount of contamination remaining on the leaves that were washed.

Introduction

Credible assessment and modeling of radionuclide behavior in ecosystems is critically dependent on fundamental knowledge of transport mechanisms and their relative importance. Two primary mechanisms of radionuclide accumulation by plants are root uptake and foliar deposition of airborne particulates. The relative importance of these processes might be assessed in specific field situations if an effective method of separating surficial from internal contamination could be developed.

Plant/soil concentration ratios reported in the literature range over several orders of magnitude for the same plant species and radionuclide. Some investigators report concentration ratios determined on unwashed vegetation, while others report them on washed vegetation. The variability in treatment and analysis leads to confusion in the interpretation of concentration ratios.

This investigation was concerned with the use of ultrasonic water bath cleaning to selectively remove surficial contamination. Most refractory activity on plants in the field is usually associated with surficial dust contamination, therefore removal of the dust particles should remove the surface radioactivity as well. ^{226}Ra and Ti were used to trace surface contamination by wind blown uranium mill tailings. The chemical form of radium in these sulfuric acid leach mill tailings was most likely $RaSO_4$. This form of radium is generally considered insoluble in a water solution, hence foliar adsorption of surficial contamination is not likely significant.

This study was completed to assess ultrasonic cleaning as a method to separate internal and external contamination in sagebrush plants. The method included a detailed study on removal efficiency of surficial ^{226}Ra and titanium by ultrasonic cleaning. Investigators in the past have assumed surficial decontamination by ultrasonic treatment (Ma80), but to our knowledge no detailed report on efficiency, length of washing time, or effect of detergent has been published. This study was designed to partially eliminate these gaps in the literature.

Materials and Methods

Mature, indigenous sagebrush (Artemisia tridentata) plants growing downwind from an active uranium mill site's tailings dam in Wyoming, provided the ^{226}Ra contaminated vegetation samples for the ultrasonic washing study. A large (300 g) surficially contaminated sample (leaves only) was collected from an area .04 - .10 km downwind from the tailings dam. The sample was premixed and then randomly divided into 36 4 g samples for the wash study. Four 4 g samples were retained and analyzed for ^{226}Ra activity without washing. The remaining 32 samples were

split between a detergent group and a no detergent group. Both groups were subjected to the use of a 42 KHz Bransonic ultrasonic cleaner (Smithkline Co. model B-22-4 rated 50/60 KHz).

To assure consistency of operation of the ultrasonic bath, the amplitude of the ultrasonic waves was checked daily with a transducer coupled to an oscilloscope. An aluminum positioning lid with six check positions was constructed to ensure reproducible positioning of the transducer within the bath. The six positions were averaged each day to give a single amplitude and compared to 20 independent control observations. In addition, the frequency of the bath was checked daily and found to be 42 ± 6 KHz. The bath was rated by the manufacturer at 50/60 KHz.

Four wash time lengths were investigated, including 10, 30, 60 and 90 minute wash times. Each was followed by 2 10-minute ultrasonic rinses. Four replicate samples were analyzed for ^{226}Ra after washing for the specified times. The water bath was filled with 1.5 l distilled water and the leaves dispersed into the water by stirring. The leaves were then strained through a wire mesh, placed back into the ultrasonic water bath with 1.5 l clear distilled water and ultrasonically treated for another 10 minutes. This rinse procedure was repeated once more to bring the total ultrasonic treatment time to the wash time plus 20 minutes for all samples tested in both detergent and no detergent treatment groups.

The analysis of ^{226}Ra activity was accomplished by dry ashing the sagebrush samples at 500^{o}C overnight, chemical separation of ^{226}Ra by the barium sulphate precipitate method as used by Kirby (Ki64), and counting the precipitate on a gas flow proportional counter.

Titanium is reported in the literature not to be taken up internally by plants in concentrations greater than 1.0 ppm (He70a). Consequently, titanium has been frequently used as a tracer to measure soil ingestion in deer (Ar79) and cattle (He68, Ma77, Mi75, Ry76). Since this practice has been generally accepted as valid, Ti was used as a tracer for residual surficial soil particles (hence radioactivity) after the ultrasonic cleaning treatment.

A Ti tracer analysis was completed on 8 samples. Four unwashed replicates were decomposed by a HNO_3-$HClO_4$ digest followed by a HF digest for 10 minutes plus two 10 minute clear rinses to solubilize the Ti. The other four replicates were ultrasonically washed and then decomposed in the same manner. Both sets of replicates were then analyzed for total Ti by the CSU Soils Testing Lab with atomic adsorption. In addition, 4 soils and 4 tailings samples were analyzed for Ti also following HF digestion. From these analyses the mass loading of soil onto plants and the efficiency of soil removal by the washing technique was calculated.

Results and Discussion

The mean ^{226}Ra activity concentration (pCi/g of plant material) ± two standard error units (based on a pooled estimate of standard deviation for washed data and an unpooled standard deviation for unwashed) versus wash time is presented in Fig.A-1for the no detergent and detergent treatment groups, respectively. A pooled estimate of standard deviation was used for washed data since there were no significant differences between the 10, 30, 60 and 90 minute wash time data in either group. The one way analysis of variance computed for the no

detergent treatment groups (excluding the 0 wash time samples) gave an F ratio of 2.88 which had a P value of .080. The one way analysis of variance was computed on the detergent treatment group also. The F ratio was calculated to be 3.15 which had a P value of .0645.

Based on the results of the one way analysis of variance it was concluded that there were no significant differences (5% level) between the 10-90 minute wash time samples in either the no detergent or the detergent treatment groups.

Linear regressions were computed for each set of data (excluding 0 wash time). The R^2 value was low in both cases (.17 and .04 for no detergent and detergent respectively). This implies that there is more variability within the data than can be accounted for by the regression analysis. Neither slope was significant ($P > .1$) indicating a lack of trend.

Since no significant differences were found between wash times in either group, each group's washed data were pooled and the mean ^{226}Ra activity concentration differences were 2-tail t-tested for significant differences between the groups. As was observed by examination, there was no significant difference between the detergent and no detergent groups ($P = .16$).

For statistical completion a 1-tail t-test was done on the pooled detergent and no detergent data vs. the unwashed sage data to show that washing for at least ten minutes did significantly reduce the ^{226}Ra activity on the sagebrush leaves. This test showed that the unwashed sagebrush had a significantly greater ^{226}Ra concentration (.1% level) than the sagebrush that had been washed for at least 10 minutes.

To determine the actual removal efficiency of the 10 minute wash (plus two 20 minute clear rinses) a Ti soil tracer analysis was completed. The four replicate unwashed sagebrush samples had 97.8 ± 6.2 ppm (standard deviation) Ti as compared to the 25.5 ± 4.12 ppm for the washed samples. This gives a calculated removal efficiency of .74 ± .06 (standard deviation).

Titanium content in soil was not significantly different from Ti in tailings. The residual mass value for soil on plants can be calculated from knowledge of the Ti in soil (or tailings) if the assumption is made that Ti is not taken up by plants (< 1 ppm) (He70b). Since the washed vegetation averaged 25.5 μg Ti/g plant and the soil averaged 4.1 mg Ti/g soil then:

$$\frac{.0255 \text{ mg Ti/g plant}}{4.1 \text{ mg Ti/g soil}} = 6.2 \times 10^{-3} \text{ g soil/g plant.}$$

The mass loading value of soil on sagebrush can be similarly calculated from knowledge of Ti analysis of unwashed sage and Ti content in soil. The unwashed sage sample averaged 97.8 ± 6.2 μg Ti/g plant (n = 4). The value for Ti content in soil, as above, was 4.1 mg Ti/g soil. The mass loading value is the ratio:

$$\frac{.0978 \text{ mg Ti/g plant}}{4.1 \text{ mg Ti/g soil}} = 2.39 \times 10^{-2} \text{ g soil/g plant}$$

or

23.9 mg soil/g plant

This mass loading value of soil onto plants is within the range of values reported by Dreicer (DR81) for tomato plants.

Conclusions

The following conclusions can be inferred from this study. First, ultrasonic washing (for at least 10 minutes) significantly reduced ^{226}Ra activity when washed samples were compared to unwashed Artemisia

tridentata leaves. Secondly, a removal efficiency of surficial material of .74 ± .06 was estimated from Ti analyses. Thirdly, there was no significant (at the 5% level) difference in ^{226}Ra removal among ultrasonic washing times of 10, 30, 60 and 90 minutes (followed by two 10 minute ultrasonic rinses for each case). Thus, there appeared to be no additional benefit in washing plants for more than one 10 minute wash plus two 10 minute rinses to remove surficial ^{226}Ra contamination. This conclusion drastically contrasts with the method of ultrasonically cleaning for 1 hour (Ma80), and may save time for future investigators who must clean plants. Finally, there appeared to be no significant effect of the addition of detergent on activity removal or length of washing time to achieve a given removal.

Although this study did not consider as a variable the number of rinses used, the investigators suspect that this rather than length of washing time has more influence on cleaning efficiency. Also it is suspected that once the labile soil contamination has been removed by washing, significantly more surface contamination is not likely to be removed by increasing the length of washing time. Finally, it is believed that there will be species differences and if species which have gross morphological characteristics different than sagebrush are to be washed, it would be wise to investigate the removal efficiency for a particular washing regime.

REFERENCES CITED

Ar79. Arthur, W. J. III and Alldredge, A. W., 1979, "Soil Ingestion by Mule Deer in Northcentral Colorado." J. Range Mgt. 32(1):67-71.

Dr81. Dreicer, M., 1981, "Rainfall as a Mechanism for Soil Contamination of Plant Surfaces," M.S. Thesis, Colorado State Univ., Ft. Collins. 32 p.

He68. Healy, W. B., 1968, "Ingestion of Soil by Dair Cows," New Zealand J. Agr. Res. 11:487-499.

He70. Healy, W. B., McCabe, W. J., and Wilson, G. F., 1970, "Ingested Soil as a Source of Microelements for Grazing Animals," New Zealand J. Agr. Res. 13(3):503-521.

Ki64. Kirby, H. W., 1964, "The Radiochemistry of Radium," National Academy of Sciences, Nuclear Science Series NAS-NS 3057,

Kl78. Klienvaum, D. G. and Kupper, L. L., 1978, Applied Regression Analysis and Other Multivariable Methods, University of N. Carolina at Chapel Hill, Duxbury Press, North Scituate, Mass.

Ma80. Marple, M. L., 1980, "Radium-226 in Vegetation and Substrates at Inactive Uranium Mill Sites," Los Alamos Scientific Lab., Los Alamos, NM LA-8183-T (also UC-41).

Ma77. Mayland, H. F., Shewmaker, G. E., and Bull, R. C., 1977, "Soil Ingestion by Cattle Grazing Crested Wheatgrass," J. Range Manage. 30(4):264-265.

Me80. Mendenhal, W., and Ott, L., 1980, Understanding Statistics, Duxbury Press, North Scituate, Mass.

Mi75. Miller, J. K., Maosen, F. C., and Hansard, S. L., 1975, "Titanium-44 Metabolism in Ruminants," J. Anim. Sci. 42(1):279 (Abstr.)

Ry76. Ryan, T. A., Joiner, B. L., and Ryan, B. F., 1976, Minitab Student Handbook, Duxbury Press, North Scituate, Mass.

Sn78. Snedecor, G. W. and Cochran, W. G., 1978, Statistical Methods, Iowa State University Press, Ames, Iowa.

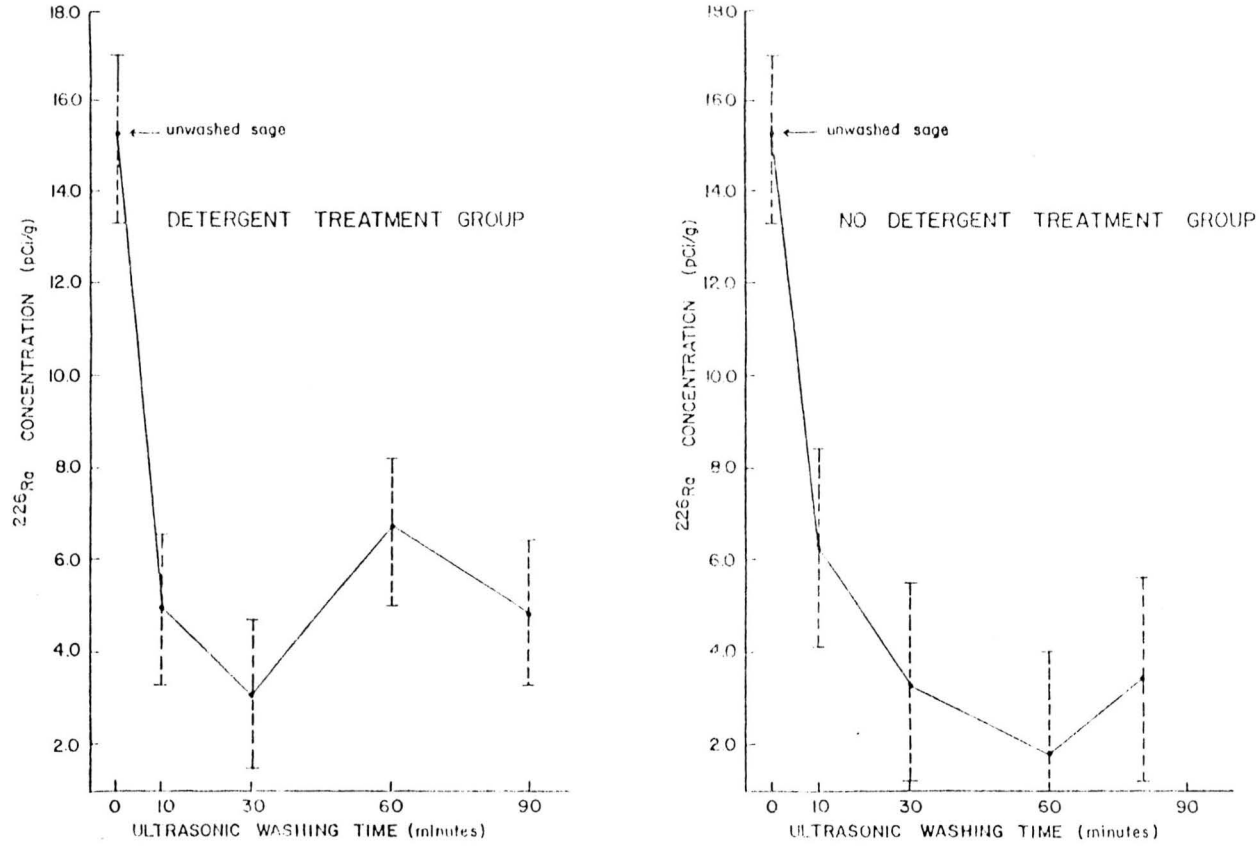

Fig. A-1. ^{226}Ra concentration (pCi/g dry plant) in sagebrush as a function of ultrasonic washing time (minutes) for two treatments. (Error bars due to ± 2 std error units based on a pooled standard deviation for the washed data and unpooled for the unwashed data. n = 4 at each data point).