NUREG/CR-0758
ANL/ES-69

NUREG/CR-0758
ANL/ES-69

CONTAMINATION OF THE HUMAN FOOD CHAIN BY URANIUM MILL TAILINGS PILES

by

R. B. Holtzman, P. W. Urnezis,
A. Padova, and C. M. Bobula III

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. NUCLEAR REGULATORY COMMISSION
under Interagency Agreement DOE 40-550-75

Available from
National Technical Information Service
Springfield, Virginia 22161

NUREG/CR-0758
ANL/ES-69

(Distribution
Code: RE)

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CONTAMINATION OF THE HUMAN FOOD CHAIN BY URANIUM MILL TAILINGS PILES

R. B. Holtzman
P. W. Urnezis
A. Padova
C. M. Bobula III

Radiological and Environmental Research Division

W. E. Kisieleski - Project Leader

Division of Environmental Impact Studies

March 1979
Published: April 1979

Prepared for
Division of Safeguards, Fuel Cycle and Environmental Research
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
Under Interagency Agreement DOE 40-550-75
NRC FIN No. A2046

FOREWORD

The Argonne National Laboratory, under contract with the U.S. Nuclear Regulatory Commission (NRC), Division of Safeguards, Fuel Cycle and Environmental Research, has conducted extensive long-term field studies at operating uranium mills to provide input for the generic environmental impact statement on the U.S. uranium industry being prepared by the NRC.

The field study program originally was designed to achieve the following objectives:

(1) To provide measurements that could be used to characterize and to estimate the rates of release of airborne radioactive effluents (source terms) for uranium milling activities.

(2) To provide data that could be used to verify predicted offsite environmental concentrations of radionuclides based on source terms and dispersion calculations.

(3) To evaluate the potential radiological significance of food ingestion pathways for airborne effluent released from uranium mills, focusing primarily on ingestion exposures associated with grazing animals and locally raised food crops or garden produce.

(4) To test, demonstrate, and evaluate environmental monitoring methods and techniques in order to provide information to develope guidance for monitoring programs.

In this report, results of the pilot study undertaken to assess and predict the potential radiological impact of food ingestion pathways are detailed. The study was designed to determine the levels of the long-lived nuclides in the uranium decay series--uranium, thorium-230, radium-226, and lead-210--that might enter the food chain of man from milling operations. The levels of human intake of these radionuclides from the food chain, water, and atmosphere near uranium operations are compared to those in control areas distant from mines and mills.

The overall study was conducted by the Environmental Impact Studies Division; information for this report was gathered and calculated in cooperation with the Radiological and Environmental Research Division at Argonne National Laboratory. Harry Landon of the NRC was the funding officer monitoring the activity; active direction was received first from Paul Magno* and subsequently from Hubert Miller of the NRC.

**Now with EPA.*

TABLE OF CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

We thank those who helped in this project, particularly Mr. William Gray and Mr. Elrod Leany of the Anaconda Company and Mr. James Cleveland of the Kerr-McGee Nuclear Corporation and their co-workers and members of the Argonne National Laboratory Division of Environmental Impact Studies, especially Mr. Leonard Link, Dr. Walter Kisieleski and Dr. Michael Momeni.

ABSTRACT

A study is in progress to estimate the contamination of the human food chain by uranium, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po originating from tailing piles associated with uranium ore processing mills. Rabbits, cattle, vegetables, and grass were collected on or near two uranium mill sites. For controls, similar samples were obtained from areas 20 km or more from the mining and mill operations. For the onsite rabbits the mean ^{226}Ra concentrations in muscle, lung, and kidney of 5.5, 14, and 15 pCi/kg wet, respectively, were substantially higher than those in the respective tissues of control animals (0.4, 1.5, and 0.2 pCi/kg). The levels in liver did not differ significantly between the groups. The concentrations in bone (femur and vertebra) were about 9000 and 350 pCi/kg ash for the onsite and offsite animals, respectively. The levels of ^{210}Pb and ^{210}Po did not differ significantly for a given tissue between the two groups, except that the ^{210}Pb level in the kidney was greater in the onsite group.

For cattle the results are less complete, but the data indicate that the concentrations in muscle, liver and kidney do not differ greatly between those grazed near the pile and the controls. The levels of ^{226}Ra, and possibly of ^{210}Pb, appear to be greater in the femur of the animals near the piles. Vegetables from a residential area on a mill site contained substantially greater concentrations of ^{226}Ra and ^{210}Pb than those reported for standard New York City diets.

Grass and cattle dung from land irrigated by water containing 60 pCi/L ^{226}Ra from uranium mines had concentrations of ^{226}Ra and ^{210}Pb 50 and 8 times, respectively, those in control samples.

It is estimated that doubling the normal concentrations in meat and vegetables of uranium and daughter products could increase the dose equivalent rates to the skeletons of persons consuming these foods by 30 or more mrem/yr.

CONTAMINATION OF THE HUMAN FOOD CHAIN BY URANIUM MILL TAILINGS PILES*

R. B. Holtzman, P. W. Urnezis, A. Padova,** and C. M. Bobula III

INTRODUCTION

This study was undertaken to obtain data on the possible contamination of the human food chain by radionuclides in tailings piles from uranium ore processing mills. These data are to be used for a generic environmental impact statement on uranium milling operations (UMOGES) sponsored by the U.S. Nuclear Regulatory Commission. The nuclides of interest are the long-lived members of the ^{238}U decay series, namely ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po, shown in Figure 1. Other naturally occurring nuclides, such as those in the ^{235}U and ^{232}Th series, were not considered because the abundance of ^{235}U in ores is low relative to that of ^{238}U. The ^{232}Th abundance in ores from the regions considered is also low. This being a pilot study, it was necessary to limit the scope.

The long-lived nuclides may enter the food chain through soil and inhalation. They are on dust particles from the mill or on resuspended particles from the tailings that may be deposited on soil and vegetation or be inhaled by animals. ^{210}Pb and ^{210}Po are of particular interest as decay products of ^{222}Rn, which emanates into the atmosphere. These nuclides may thus form in the atmosphere at atmospheric concentrations greater than those originating from resuspended dust particles. Moreover, the atmospheric residence times of 3 to 10 days for ^{210}Pb are probably much greater than those for resuspended dust, and the radon provides a nonsettling source with a 3.82 day half life that can disperse over long distances.

The importance of these nuclides is best illustrated by the natural case in which ^{210}Po deposited in the human skeleton, and supported by the long-lived ^{210}Pb, produces from 25 to 50% of the background radiation dose to the bone of the general public.[2]

The usual sources of these nuclides for man and the normal input amounts in each route are shown in Table 1.[2,3] The early members of the series are acquired mainly by ingestion through food and water, with about 5 to 10% from inhalation of dust. It is assumed that the breathing rate is 15 m^3/day. For

---

*Work partially supported by the U.S. Nuclear Regulatory Commission and funded through the Argonne National Laboratory Division of Environmental Impact Studies. This report is an updated and expanded version of a previous one in a Radiological and Environmental Research Division Annual Report (Ref. 1).

**Present address: 47 Gordon Street, Rehovoth, Israel.

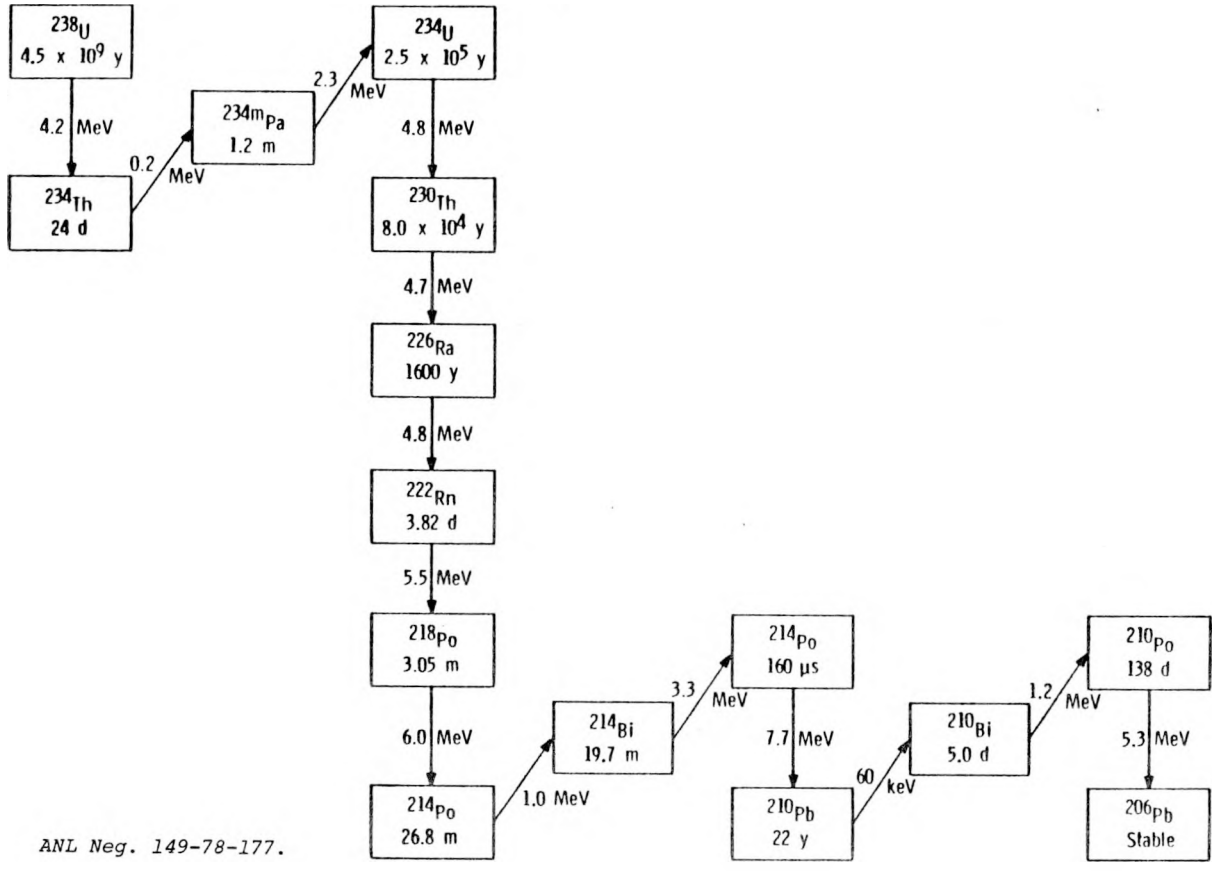

Fig. 1. The ^{238}U Series Decay Scheme.

^{210}Pb it has been estimated that about one half is acquired from ingestion and half from inhalation.[2] About 5% or so may be derived from internal sources, such as ^{226}Ra deposited in the body and ^{222}Rn dissolved in body fluids. The sources of ^{210}Po are more uncertain, but it has been estimated that normally about 90% originates from the ^{210}Pb deposits in the skeleton, and the remainder from ingestion and inhalation.[4]

A model illustrating some (but not necessarily all) of the complexities of the pathways in the body of ^{210}Pb is shown in Figure 2.[5] Thus, this nuclide can enter the body from diet, water, the atmosphere, and cigarette smoke.

Reported here are the results of a survey made of contamination levels of the human food chain to estimate the amounts of contamination produced under extreme conditions, particularly with respect to the nuclides ^{226}Ra, ^{210}Pb, and ^{210}Po. It may be noted that some reported values differ from those in the earlier report[1] due to more recent data, especially ^{210}Pb values determined from two rather than the single analysis available previously.

Table 1. Nuclides of Interest and Sources for Man

Nuclide	Sources	Amount, pCi/d	Fraction from source, %
^{238}U	Ingestion		
	Food	0.45	95
	Water	0.03	5
	Inhalation (dust)	0.0014	-
^{230}Th	Ingestion		
	Food	0.1	~100
	Inhalation (dust)	0.001	-
^{226}Ra	Ingestion		
	Food	1.4	98
	Water	0.03	2 (95)[a]
	Inhalation (dust)	0.001	< 1
^{210}Pb	Ingestion		
	Food	1.4	45
	Water	0.03	5
	Inhalation		
	^{210}Pb	0.3[b]	45
	^{222}Rn daughters		2
	Internal		
	^{226}Ra (50 pCi)[d]		2[e]
	^{222}Rn (15 pCi)[d]		2[e]
^{210}Po	Ingestion		
	Food and Water	1.8	5
	Inhalation		
	^{210}Po	0.07[b] (1.6)[c]	5
	Internal(^{210}Pb) (600 pCi)[d]		90[e]

[a] *In certain regions potable water containing high concentrations of radium may contribute 95% or more of the radium intake.*

[b] *For non-smokers.*

[c] *For smokers.*

[d] *Amount of nuclide in the body.*

[e] *This nuclide in the body contributes this fraction (%) of the body content of nuclide of interest (Column 1).*

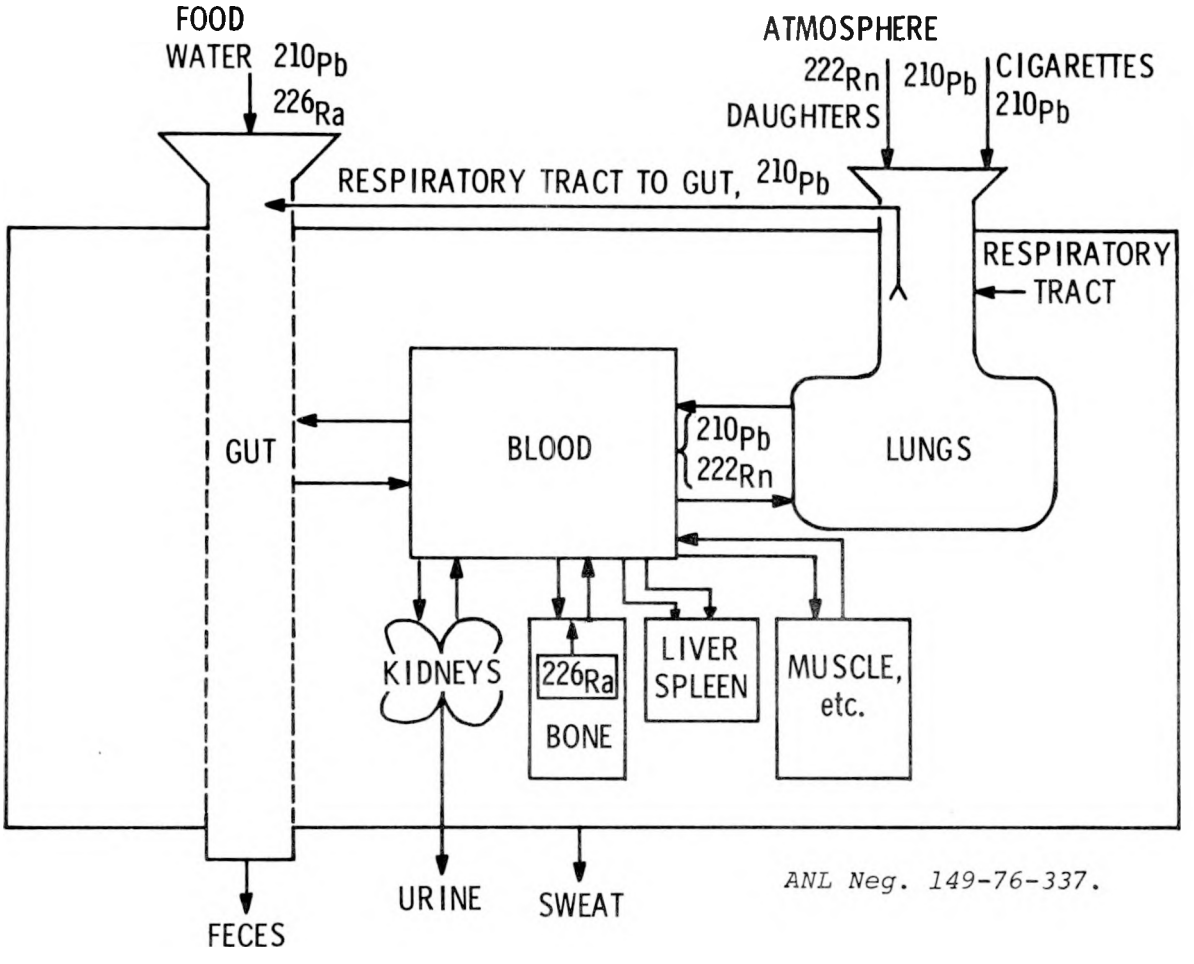

Fig. 2. Model for ^{210}Pb Metabolism in Man.

EXPERIMENTAL METHODS

Collection

Specimens of the food chain and some related samples listed in Table 2 were collected in the Grants, New Mexico, uranium mining district (shown on the map of northwestern New Mexico in Fig. 3), and from the vicinity of two mills, Kerr-McGee Nuclear Corporation and the Anaconda Company.

The Anaconda site is particularly useful for this study because only milling is done here, and a company village is situated within a few kilometers of the mill. The residents raised vegetables in an otherwise barren region. The Kerr-McGee site is less suitable because several mines are very close to it, thus making it difficult to separate mine contamination from that due to the tailings.

Table 2. Specimens for Analysis

Sample	Description	Number
Jack rabbit (blacktail)	*Lepus californicus*, Anaconda tailings pile, collected 7/77	3
	Same as above, but from a control area, Sanchez Ranch near San Rafael, N.M., collected 7/77	2
Cottontail rabbit	*Sylvilagus audubonii (?)*, Anaconda site, collected 7/77	1
Cattle	Grazed in open pasture adjacent to Anaconda property. North, east and west, collected 7/77	2
	1. Black cow, age ∿10 yr 2. Red cow, age ∿3 yr	
Cattle (controls)	Grazed about 20 miles north of Anaconda mill, collected 7/77	2
	3. Brown, age 9 4. Black, age 8	
Cattle bones (miscellaneous)	1. Found at San Mateo Creek	2
(controls)	2. Phillips ore storage area	1
Vegetables	From gardens in Anaconda site residential area, collected 8/77	5
Grass	From various places, collected 6/77.	
	mine-water irrigated, Kerr-McGee	2
	control, Kerr-McGee	2
	control, San Mateo Creek	2
	Anaconda mill site	2
	Phillips pile, vicinity at 75, 200 and 1000 meters	3
Cow dung	Uranium mine water irrigation at Kerr-McGee site, Ambrosia Lake, N.M., collected 6/77	5
Cow dung (controls)	San Mateo Creek, collected 6/77	4

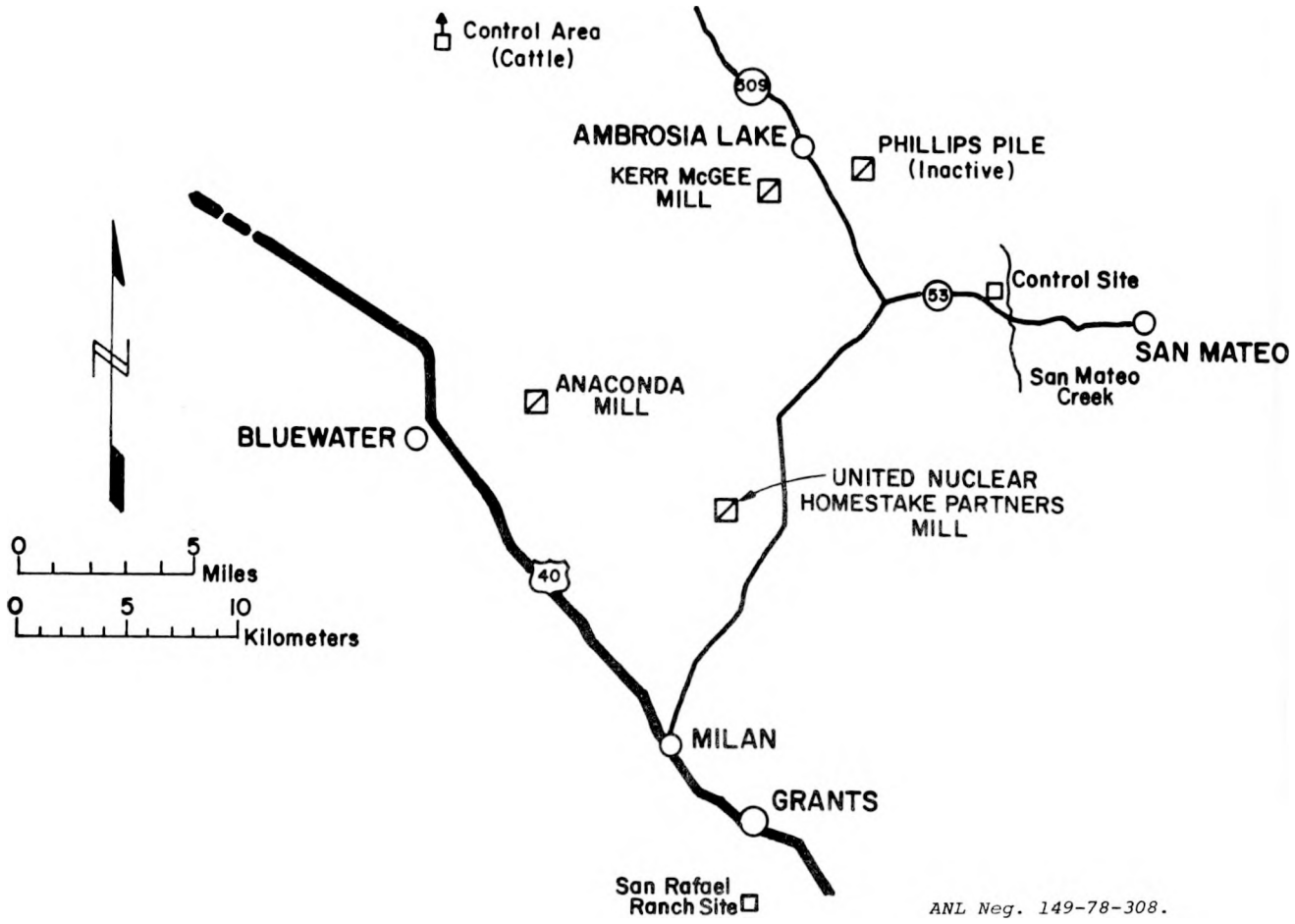

Fig. 3. Location of Sites Studied in the Grants, New Mexico, Uranium Mining District.

Wild animals hunted and eaten by the local residents were represented by jack and cottontail rabbits [*Lepus californicus* and *Sylvilagus auduboni* (?)] collected on the site of the Anaconda mill within a few hundred meters of the tailings pile, as shown in the circles on the map, Figure 4. Domesticated animals were represented by two head of cattle that had grazed most of their lives in a field adjacent to the Anaconda property, up to the fence on the northeastern section, as shown in Figure 4.

Where possible, control samples were collected from areas similar to the tailings area, but at least 15 km from the mining and milling areas (Fig. 3). We obtained two head of cattle raised about 40 km from the Anaconda site and two rabbits from a ranch near San Rafael, N.M., about 30 km away. Some miscellaneous cattle bones of unknown origin, which may serve as controls, were obtained from near San Mateo Creek.

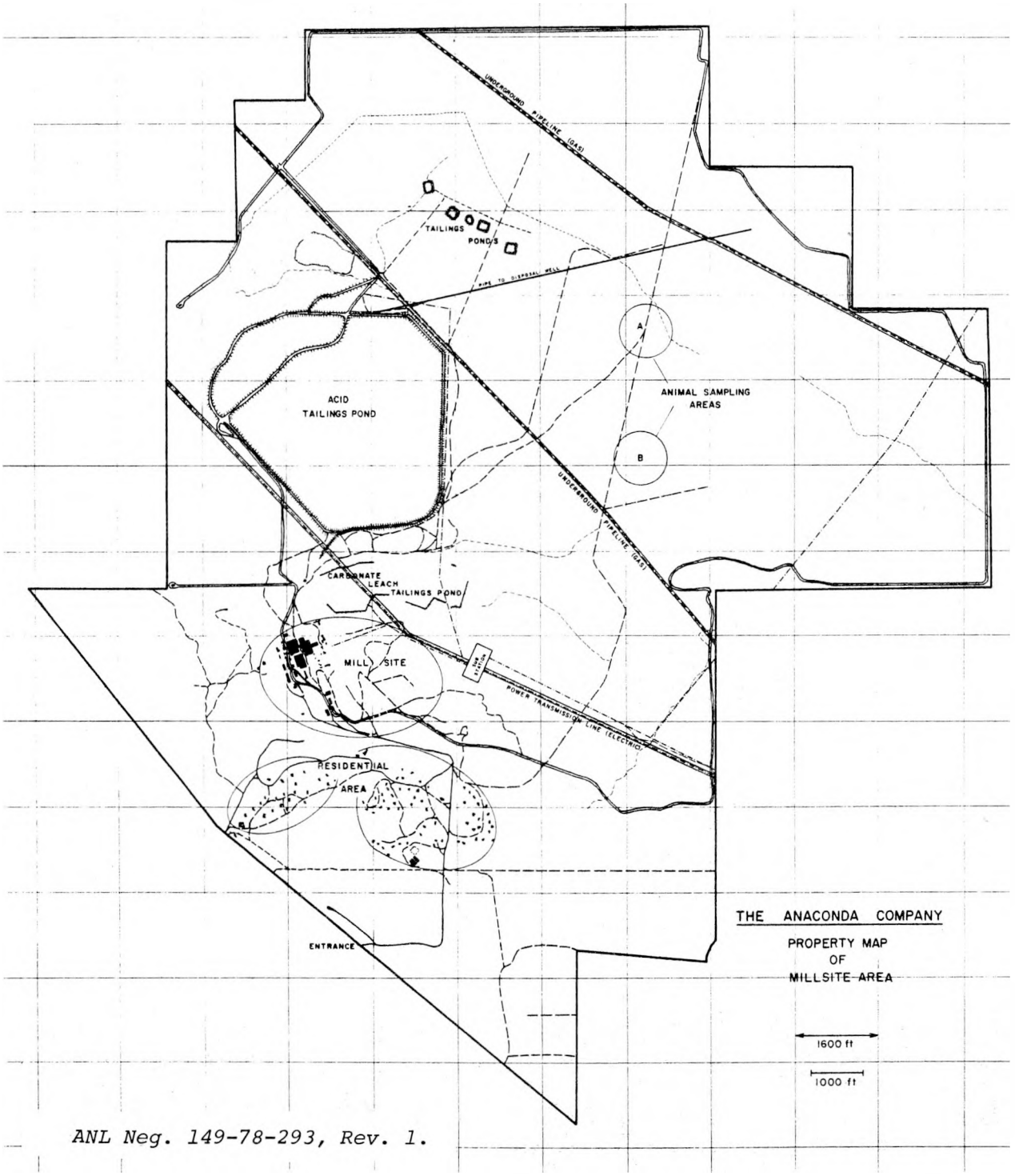

Fig. 4. Map of Anaconda Company Mill Site and the Residential Areas. Circles show where rabbits were captured. The cattle grazed on the northern and eastern boundaries.

Also collected were specimens of vegetables grown in the Anaconda residential area (see Fig. 4) and grass and other plants from the Kerr-McGee and Anaconda sites. Some grass was also collected from the vicinity of the Phillips (now United Nuclear Corporation) tailing pile near Kerr-McGee. While this pile is inactive, it is similar to the active ones, but it provides more extreme conditions, such as a lush grass growth near the pile and cattle grazing within a kilometer or so of the leeward side of the pile. It is from a carbonate rather than acid process mill.

Analytical Techniques

The samples were processed as summarized here. The detailed analytical procedures are given in Appendix A.

After dissection, the samples were processed, either by freeze-drying or heat-drying at 100°C. They were then oxidized in a low-temperature asher which uses oxygen plasma, or wet-ashed in nitric and perchloric acids. These procedures prevent volatilization of both ^{210}Pb and ^{210}Po.

The ^{226}Ra was determined from an aliquot fraction of the dissolved samples by the radon emanation method of Lucas.[6,7]

The ^{210}Pb and ^{210}Po were determined by first converting an aliquot of the dissolved samples to hydrochloric acid solution from which the ^{210}Po was plated onto a silver disk. The disk was then counted in an alpha counter. After several months' wait to allow the 138-day ^{210}Po to grow in from the ^{210}Pb, the solution was replated and counted. The Bateman equations of radioactive decay and growth were then used to calculate the amounts of both the ^{210}Po and ^{210}Pb at the time of collection.[8]

Calcium was also determined, to estimate the mineral content of bones and as a measure of the mineral content of other biological materials, by flame atomic absorption spectrophotometry with a Perkin Elmer Model 303 instrument.[9,10]

Results

The available results of analyses of the rabbit tissues are shown in Table 3 for the individual rabbits, the cottontail (CT1A) along with the three jackrabbits (JR1A, JR2A, and JR3A) from the Anaconda mill site. The last two columns are data from the control animals (JR1C and JR2C) from the offsite ranch.

The concentrations of ^{226}Ra in muscle are higher by factors of 2 to 30 in the onsite than in the offsite animals, while in kidney they are 10 or more times greater. Differences are not apparent in liver because one control value is low and the other high, and the differences for ^{210}Pb and ^{210}Po in onsite and control animals are not significant. These differences and similarities are seen in the mean values in Table 4, where the mean concentrations of ^{226}Ra are much greater in the onsite animals, except in liver. Because of the wide variability and few samples the means are not necessarily statistically different ($P > 0.05$). However, the fact that all or most of the levels in the exposed animals are greater than those in the controls is a strong indication of significant differences.

Table 3. ^{226}Ra, ^{210}Pb, and ^{210}Po (pCi/kg wet)[a] and Ca (mg/kg wet) in Rabbit Tissues from the Mill and Control Sites

Tissue	Nuclide	Mill Site[b]				Control Site[b]	
		CT1A	JR1A	JR2A	JR3A	JR1C	JR2C
Muscle	^{226}Ra	16.5	1.26	3.18	0.95	0.32	0.48
	^{210}Pb	13.7	10.6	1.1	2.9	3.4	6.6
	^{210}Po	-	45.0	8.1	5.2	3.0	9.0
	Ca	386	199	77.0	36.7	56.3	-
Liver	^{226}Ra	42	22.3	8.3	3.5	0.46	28.9
	^{210}Pb	88.7	31.1	80.1	16.3	21.4	65.5
	^{210}Po	22.0	22.8	47.4	-	2.4	56.7
	Ca	319	436	-	232	276	338
Lung	^{226}Ra	27.8	9.6	19.2	0.28	0.96	2.84
	^{210}Pb	21.8	11.0	13.9	48.7	10.8	37.2
	^{210}Po	-0.36	-0.75	1.86	-	-1.3	26.2
	Ca	532	262	118	201	-	295
Kidney	^{226}Ra	29.7	15.4	10.8	4.5	0.37	-1.2
	^{210}Pb	56.1	268	79.9	55.0	21.6	46.4
	^{210}Po	-12.4	-	300	97.1	-	180
	Ca	329	303	206	185	261	345
Femur	^{226}Ra	6100	13800	10500	5650	235	460
	^{210}Pb	1820	547	527	725	656	954
	^{210}Po	820	422	483	-	238	620
Vertebra	^{226}Ra	5830	12100	10900	6130	240	453
	^{210}Pb	2670	1200	1640	496	1830	1210
	^{210}Po	796	-	-	226	29.3	494

[a] *1 pCi/kg = 37 mBq/kg.*

[b] *CT, cottontail rabbit; JR, jack rabbit.*

Table 4. Summary of Nuclide Concentrations in Rabbit Tissues (mean ± S.E.)

Tissue	Nuclide	Mill Site, pCi/kg wet[a]	Control Site, pCi/kg wet
Muscle	^{226}Ra	5.5 ± 3.7	0.40 ± 0.10
	^{210}Pb	7.1 ± 3.0	5.0 ± 1.6
	^{210}Po	19 ± 13	6 ± 3
Liver	^{226}Ra	19 ± 9	15 ± 14
	^{210}Pb	54 ± 27	43 ± 22
	^{210}Po	31 ± 8	30 ± 27
Lung[b]	^{226}Ra	14 ± 6	1.5 ± 0.5
	^{210}Pb	24 ± 9	24 ± 13
Kidney[b]	^{226}Ra	15 ± 5	0.2 ± 0.2
	^{210}Pb	115 ± 51	34 ± 12
		pCi/kg ash	pCi/kg ash
Femur	^{226}Ra	9020 ± 1900	350 ± 110
	^{210}Pb	900 ± 310	800 ± 150
	^{210}Po	1040 ± 470	430 ± 190
Vertebra	^{226}Ra	8700 ± 1600	346 ± 100
	^{210}Pb	1500 ± 450	1500 ± 300

[a] *1 pCi/kg = 37 mBq/kg.*

[b] *Additional analyses of ^{210}Pb are in process.*

The ^{226}Ra levels of about 9000 pCi/kg ash in the bones of the onsite rabbits are greater than in the controls by a factor of 25, while the levels of ^{210}Pb and ^{210}Po are nearly identical in the two groups. Relative to the concentrations of ^{226}Ra, those of ^{210}Pb and ^{210}Po are much lower in the onsite compared to the control animals.

While the concentrations of ^{226}Ra in bone vary between animals, they are essentially identical for femur and vertebra in a given animal. This similarity indicates that the intake of this nuclide throughout the life of the animal was fairly constant. On the other hand, the ^{210}Pb concentrations are generally lower in the femur than in the vertebra (except for JR3A). This difference indicates a recent increase in ^{210}Pb intake, which deposits more readily on cancellous, e.g., vertebra, than in compact bone. The ^{210}Pb concentrations do not appear to be correlated with those of ^{226}Ra.

The calcium concentrations in the soft tissues vary considerably between animals, but they do not differ significantly between the onsite and control groups.

The data on the four head of cattle shown in Table 5 are less complete, but some preliminary conclusions may be reached. The concentrations appear not to differ greatly, except that the ^{210}Pb and ^{210}Po levels in the livers of the onsite animals appear to be much greater than those of the controls. The radium concentrations in the control kidneys are greater than those in one onsite animal, but lower than in the other. The levels of all the nuclides in the lung of Cow 1 are greater than those in Cow 4, a control. The concentrations of nuclides in the stomach contents of one control cow are about the same as those in local non-exposed grasses (*vide infra*).

For the hard tissues, the concentrations of ^{226}Ra in the femurs from onsite are significantly greater than those in the controls, both in femur and teeth. (The very low value of ^{226}Ra in that of Cow 4 appears to be anomalous and is being checked.) The ^{210}Pb levels in the onsite animals are greater than those in the controls, except that in the femur of Cow 3 is somewhat greater than that in Cow 2. This effect may be due to the ages of the animals; Cow 2 from the mill site is only about 3 yr old, compared to 8 to 10 yr for the others. Thus the concentrations in bone may represent the integrated long-term intake of the nuclide, while those in the soft tissues may vary more rapidly.

The nuclide concentrations in the vegetable samples from the Anaconda residential area are shown in Table 6, and as noted, control samples are not available. (Additional vegetables and control samples for these vegetables were obtained this year and are being processed.) However, these samples have high values compared to those reported for foods from New York,[11-13] San Francisco,[11] and other cities in the U.S.[2,3] Both the ^{226}Ra and ^{210}Pb are in appreciably greater concentrations in the mill site samples than in those from New York. This may be the contamination from the tailings or mill, but it may also be due to variant growing conditions for the different regions. Those vegetables exposed to the atmosphere and having large surface-to-volume ratios (peas, green beans and pea pods) have appreciably greater concentrations of ^{210}Pb than do the others. It may also be due to their being legumes.

Results from grass samples collected from possibly contaminated sites are shown in Table 7. The activities in the control samples from the Kerr-McGee and San Mateo Creek sites have concentrations similar to those reported in the midwestern United States.[13] From the Anaconda site the ^{210}Pb concentration is about 15 times that in the control. Those from the inactive Phillips pile, which is similar in structure to the active ones, but from a basic carbonate process, show high ^{226}Ra, but low ^{210}Pb concentrations near the pile. The ^{210}Pb concentration increases in the sample at about 200 m from the pile and then drops in the 1-km sample, even though the latter sample was growing on a sand dune formed from the tailings. The low value of ^{210}Pb in the grass from the 75-m location may be due to damp soil which allows faster growth and less accumulation time for airborne ^{210}Pb.

The concentrations are high in the grass sampled near the Kerr-McGee mine-water storage pond. The mine water contains about 60 pCi/ℓ ^{226}Ra and has a high ^{210}Pb concentration--several hundred pCi/ℓ.

Table 5. Nuclide Concentrations in Cattle Tissues from the Mill and Control Sites

Tissue	Nuclide	Mill Site[a] pCi/kg wet[b] Cow 1	Mill Site[a] pCi/kg wet[b] Cow 2	Control Site[a] pCi/kg wet[b] Cow 3	Control Site[a] pCi/kg wet[b] Cow 4
Muscle	^{226}Ra	1.1	1.2	1.1	1.5
	^{210}Pb	9.5	1.8	28	2.6
	^{210}Po	36	60	80	330
Liver	^{226}Ra	0.87	1.5	1.5	0.3
	^{210}Pb	209	73	31	12
	^{210}Po	230	340	-	-
Kidney	^{226}Ra	220	2.6	25	12
	^{210}Pb	420	41	260	330
	^{210}Po	685	270	1800	-
Lung	^{226}Ra	11.2	-	-	1.0
	^{210}Pb	72	-	-	9.6
	^{210}Po	800	-	-	50
				pCi/kg dry	
Stomach contents (estimate of intake)	^{226}Ra	-	-	-	200
	^{210}Pb	-	-	-	1500
		pCi/kg ash		pCi/kg ash	
Teeth	^{226}Ra	-	-	2000	1100
	^{210}Pb	-	-	1970	1500
Femur	^{226}Ra	3200	5170	2360	208
	^{210}Pb	7000	3080	3550	2020
	^{210}Po	6660	-	8330	1700
				San Mateo Creek	
Mandible, middle section	^{226}Ra			2220	
	^{210}Pb			1560	
	^{210}Po			2070	
Teeth 1,2,3 from tip of above mandible	^{226}Ra			2260	
	^{210}Pb			1840	
	^{210}Po			500	
Teeth 5,6,7	^{210}Pb			1000	
	^{210}Po			497	
Femur (cortical)	^{210}Pb			1170	
	^{210}Po			1170	
		Phillips Ore Storage Area			
Bone (exposed?)	^{226}Ra	61600			
	^{210}Pb	390			
	^{210}Po	525			

[a] *See Table 2 for description of animals.*

[b] *1 pCi/kg = 37 mBq/kg.*

Table 6. ^{226}Ra and ^{210}Pb Concentrations in Vegetables

Sample	^{226}Ra, pCi/kg wet	^{210}Pb, pCi/kg wet
Anaconda Mill Site		
Tomato	1.1	3.5
Peas	1.4	11
Pea pods	3.5	10.8
Green beans	5.9	17
Carrots	5.9	3.3
Beets	10.3	4.1
Mean ± S.E.	4.7 ± 1.5	8.3 ± 2.3
New York City[12]		
Fresh vegetables	0.50	1.1
Canned vegetables	0.65	0.44
Root vegetables	1.4	0.21
Dry beans	1.1	3.0
Mean	0.9	1.2

Table 7. ^{226}Ra, ^{210}Pb and ^{210}Po Concentrations in Grass and Tamarisk (pCi/kg dry)

Sample	^{226}Ra	^{210}Pb	^{210}Po
Exposed			
Anaconda pile	-	4320	2810
Phillips pile - 75 m	22700	2920	-
Phillips pile - 200 m	-	5000	-
Phillips pile - 1 km (dune)	-	10400	3900
Kerr-McGee - grass tops	-	9950	4140
Controls			
Kerr-McGee - grass tops	500	220	-
San Mateo Creek	200	724	718
Tamarisk	-	680	-

We also obtained samples of cattle dung from animals grazed on land irrigated by mine water on the Kerr-McGee site (Table 8). The mean concentration of ^{226}Ra was about 50 times, and that of the ^{210}Pb 8 times those of the control samples from San Mateo Creek. Although these are not actual grass samples, the results are probably representative of the relative nuclide intake of the animals under various conditions.

Table 8. ^{226}Ra and ^{210}Pb Concentrations in Cattle Dung from the Area Irrigated with Water from Uranium Mines (Kerr-McGee mill site)

	Pond Area			Control (San Mateo Creek)	
Sample	^{226}Ra, pCi/kg dry	^{210}Pb, pCi/kg dry	Sample	^{226}Ra, pCi/kg dry	^{210}Pb, pCi/kg dry
1	36000	22800	1	894	2740
2	45600	37600	2	853	2860
3	-	29600	3	-	5090
4	-	32100	4	-	2920
5	-	19800	Mean	870	3400±560
Mean	41000	28300			
		±7200			

DISCUSSION

Normal Dietary Content of $^{238-234}U$, ^{226}Ra, ^{210}Pb and ^{210}Po

To better assess the levels of contamination represented in our data and until more specific data are available on the local dietary intake, they will be compared to the "normal" dietary levels experienced by the U.S. population. While the dietary content of these nuclides could vary significantly with local growing conditions, such as the amounts of water, fertility of the soil, and climatic variations, the "normal" U.S. levels probably are fairly representative of those in the Grants region. This is due to the fact that much of the food originates and is shipped from the same sources as those in San Francisco and New York, e.g., vegetables from southern California and grain from various midwestern states.

The levels of dietary intake have been summarized by UNSCEAR[3] in 1977 and by NCRP[2] in 1975 and in more detail for the United States by Holtzman[15] for ^{226}Ra, ^{210}Pb and ^{210}Po.*

The mean daily intake of ^{238}U was about 0.4 pCi/day in three U.S. cities.[3] (This includes the α-activity from ^{234}U, which is assumed to be in radioactive equilibrium with the ^{238}U; the alpha activity of 1 μg uranium is 0.66 pCi.) This value is similar to those reported from other countries, which ranged from 0.2 to 0.9 pCi/day.

The dietary intakes for ^{226}Ra, ^{210}Pb and ^{210}Po are about 1.4 to 1.6 pCi/day as shown in Table 9. A more detailed list of ^{226}Ra and ^{210}Pb intakes in "standard" diets** in various cities in the U.S. is presented in Table 10, where for adults they range from 0.7 to 1.8 pCi/day for ^{226}Ra and are about 1.2 pCi/day for ^{210}Pb (two values for New York only).

The daily intake of radionuclides from diets submitted by dieticians and others in the United States are shown in Table 11. The results are similar to those of the standard diets, except for a few with over 4 pCi/day reported by Michelson in 1961 and 1965. These latter were teen-age diets and were also associated with high calcium intakes, indicating greater than average total food intakes. Similar ranges of values for ^{226}Ra and ^{210}Pb were obtained in various regions of the U.S. by Michelson et al.[19] in 1961 (Table 12).

Their extensive data summarized in this table indicate that teen-age diets normalized to an adult level of calcium of 1 g/day in cities in the North Central States had higher levels of both ^{226}Ra and ^{210}Pb than did the other regions in January 1961. However, in the May-June collections they were all more uniform and higher in ^{226}Ra (^{210}Pb was not determined in this set). The dietary calcium levels showed no seasonal changes. There were some differences in dietary intake with age, infants and adults being generally lower than teen-agers. Low income teen-agers had more dietary radium than did middle-income teen-agers in January, but less in the May-June diets.

It thus appears that on the average dietary intakes vary little with place and time, although special conditions could change this. However, in actual studies care must be exercised in making and interpreting measurements, since variations do occur as illustrated in a long-term study of ^{210}Pb and ^{210}Po in Figure 5 taken from Holtzman et al.[21] The dietary levels (one 2-day diet in each 6-day period) vary 20% or more from the mean over the 27 periods studied, although the diet was designed to be constant in other factors, such as calorie content, protein and calcium. Also, most of the foodstuffs had been acquired at one time. These variabilities do not appear to be artifacts of analysis in that the analyses were done at different times and not necessarily in order of collection. The ^{210}Pb, in particular, has a periodicity of about 48 days.

Much of the following text and tables are taken and modified from the latter paper.

***"Standard" diet is a sampling of a typical diet, the per capita intake based on total food consumption in the region of interest divided by the population size.*

Table 9. ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po in the Human Diet in the United States[3]

	^{238}U	^{226}Ra	^{210}Pb	^{210}Po
Mean	0.44	1.4	1.4	1.6
Ranges				
3 cities:	0.43-0.46	0.7-2.4	1.3-1.6	-
Other countries:	0.2-0.9	-	-	-
New York	0.43	1.4	1.4	-
Chicago	0.46	-	-	-
San Francisco	0.43	0.9	-	-

Table 10. Daily Radionuclide Intake from "Standard" Diets in the United States

City	Year (Approx)	^{226}Ra, pCi/day	^{210}Pb, pCi/day	Ca, g/day	Ref.
New York	1966	1.6		1.0	11
	1968	1.8		1.0	11
	1970		1.2		12
	1972-73		1.2		13
Infant	1965	0.4		1.35	16
San Francisco	1966	0.76		1.0	11
	1968	0.88		1.0	11
Infant	1965	0.50		1.35	16
Chicago					
Infant	1965	0.58		1.35	16
San Juan, Puerto Rico	1963	0.68		0.51	17

Table 11. Daily Radionuclide Intake from Diets Submitted by Dieticians and Others in the United States[15]

City	Year (approx.)	^{226}Ra, pCi/day	^{210}Pb, pCi/day	^{210}Po, pCi/day	Ca, g/day	Ref.
Boston	1966		1.5[a]			18
	1961	0.7			1	19
	1956	1.7 (excreta)				20
Chicago	1966		1.6[a]			18
Hospital[b]	1967		1.3	1.6	0.22	21
Hospital[b]	1968	0.68	-	-	0.24	22
New Orleans	1966		1.6			18
Los Angeles	1966		1.3			18
Palmer, Alaska	1966		1.4			18
Honolulu, Hawaii	1966		1.4			18
5 cities	1959	2.2-4.4 (1.4-2.4/g Ca)			1.64	23
	mean	1.8/g Ca				
22 cities, 56 teenage diets	1963	5 ∿2.5/g Ca			∿2	24
California	1971-1972	0.4-2.7			1.0	25
20 cities (hospitals) 6 sets July 71-Dec 72	mean	≈1.2				
New York (uranium miner)	1972	-	1.83	-		26

[a] *Results given in pCi/kg. It is assumed that the daily intake is 1.75 kg/day, e.g., as stated in Reference 11.*

[b] *The ^{226}Ra and ^{210}Pb-^{210}Po results are from similar diets in the same metabolic ward.*

Table 12. Daily ^{226}Ra, ^{210}Pb and Ca Intake from Various U.S. Regions (25 major cities) at Different Times[19a]

Region	January 1961			May-June 1961	
	^{226}Ra, pCi/g Ca (≈pCi/d)	^{210}Pb pCi/day (1.75 kg/day adult intake)	Ca, g/d	^{226}Ra, pCi/g Ca (≈pCi/d)	Ca, g/d
Northeast	0.6	1.1	1.8	1.8	2.0
North Central	1.5	1.9	1.9	1.5	1.7
South	0.9	2.1	1.9	1.6	1.3
West	0.8	1.6	1.9	1.7	1.4
Average by age[b]	(pCi/d)			(pCi/d)	
Infant	0.9	-	1.0	1.0	1.2
Low income teenage	2.0	-	1.7	1.8	1.8
Middle income teenage	1.7	-	1.7	2.0	1.6
Middle income adult	0.7	-	0.81	1.9	0.82

[a] *These are mainly diets for teenagers which are probably larger than average for the entire population. It is assumed the average diet contains about 1 g Ca, so that the values of ^{226}Ra/g Ca, etc., will be used.*

[b] *Corrected for a food intake of 1.75 kg/day compared to a mean intake of 3.5 kg/day for these samples.*

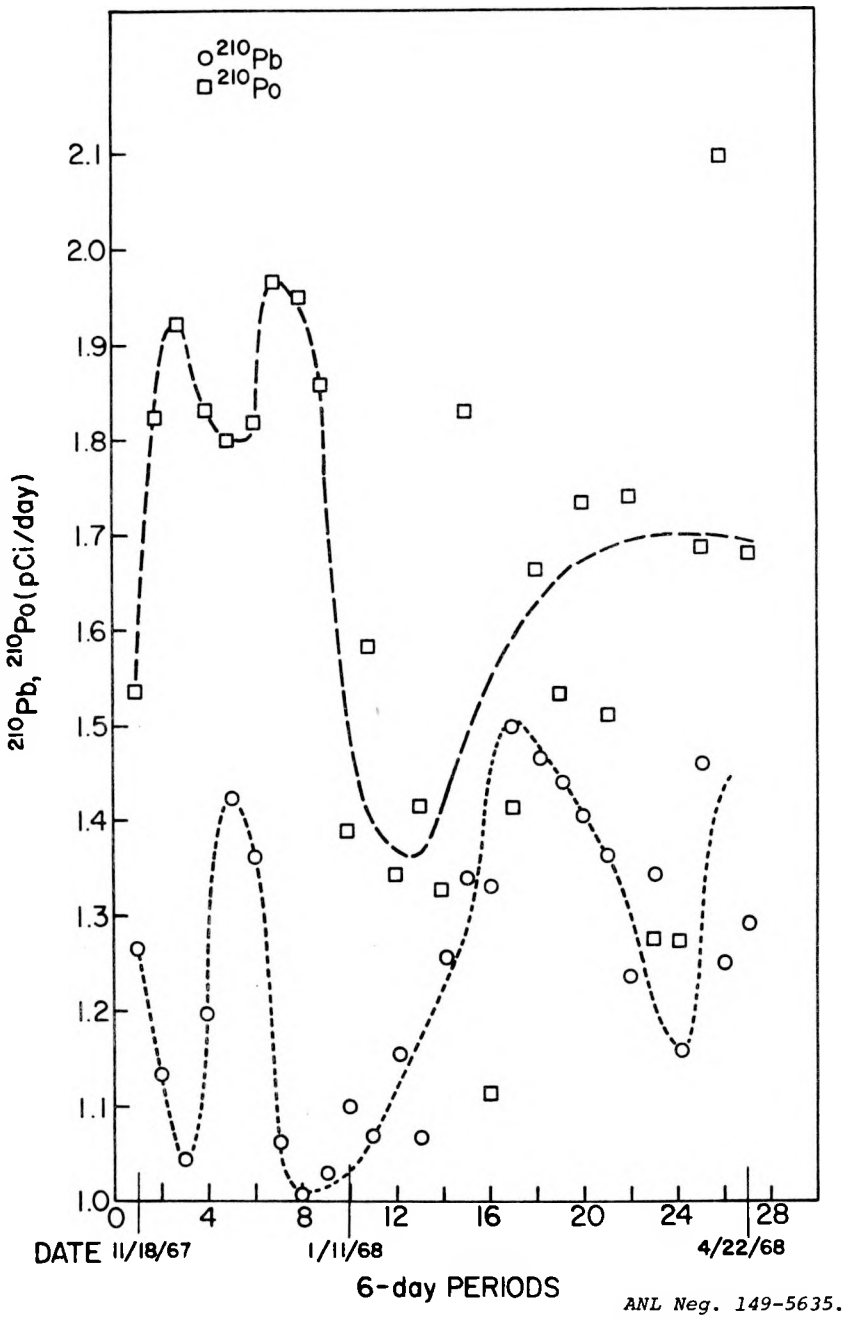

Fig. 5. Daily Contents of ^{210}Pb and ^{210}Po in the Diets of Subjects in a Metabolic Ward.[21]

Foodstuff Categories

Variabilities of total dietary levels between investigators often appear as differences in particular foodstuffs, or foodstuff categories. Thus, many of the recent studies since those of HASL in 1961[11] on diet present data on individual foods (such as Fisenne and Keller,[11] Gloebel et al.,[27] Ladinskaya et al.,[28] and other listed in Tables 13 and 14). For comparison of data from different workers and different countries, the intakes from the individual foods are combined into estimates of intakes for each category of foodstuff. Data from outside the U.S., while not of direct interest do illustrate possible causes of differences in intake. Such comparisons of the levels of ^{226}Ra are given in Table 13, and a similar compilation is given for ^{210}Pb and ^{210}Po in Table 14. As noted earlier the differences in total diet appear to be due to differences in particular categories, the other categories being similar in different countries. All categories are not comparable, but attempts to associate them have been made, such as for Japan (Takata et al.)[32] where not all the categories were covered. Some questions might be raised concerning the paper of Gloebel et al.[27] in that the total yearly food consumption appeared to be low, about 280 kg, compared to about 630 kg in the U.S. and U.S.S.R. Their weights for the foods consumed appeared to be low in most categories, but especially in vegetables and cereals.

Data - This Paper

These results indicate that under the somewhat extreme conditions studied (samples from close to the tailings), contamination is indeed present. Onsite rabbits had higher concentrations of ^{226}Ra in most tissues than did the control animals, although the ^{210}Pb and ^{210}Po levels were not significantly greater. The most significant differences were the ^{226}Ra concentrations in bone. Bone levels represent long-term intake, and if we assume a constant rate of intake, they are probably proportional to the levels in muscle and other soft tissues. Bone is also both a reservoir and a sink for the mineral constituents in the soft tissues, which are probably maintained at levels proportional to those in bone. Measurement of bone levels may be a more accurate measure of the relative nuclide content of the soft tissues of animals sampled because the activities in bone are much higher and thus more easily and accurately determined. The soft tissues probably represent the most important ingestion pathway for man, although if the bones are used for soup, etc., some of the nuclides may be leached from the bones and become an additional source.

While the data on cattle are less complete and definitive than those on rabbits, they indicate some level of increased concentrations of the nuclides. The differences in cattle between exposed and control groups seem to be much smaller than in rabbits, which is to be expected, since the conditions were less extreme. The muscle of both exposed and control animals appeared to have higher concentrations, especially of ^{210}Pb than in the "meat, etc." data in the standard diets (Tables 13 and 14). (The rate of meat consumption is assumed to be about 0.2 kg/day.) The closest approach of the cattle to the tailings is about 2 km, and they can graze several kilometers away from the site boundary fence. Moreover, in winter they may consume fodder not grown near the tailings pile.

Table 13. Comparison of Daily Dietary Intake of ^{226}Ra from Various Classes of Foodstuffs (pCi/day)

Country	United States			India[29]		Italy[30]
City[a]	NYC[11]	SF[11]	SJ[17]	Bombay	Kerala State	Varese
Foodstuff Class						
Cereals	0.58	0.39	0.14	0.42	1.48	0.81
Meat, fish, eggs, poultry	0.46	0.11	0.01	0.05	0.50	0 04
Milk, dairy	0.14	0.05	0.02	0.039	0.19	0.03
Green vegetables, etc.	0.30	0.22	0.53	-	-	-
Root vegetables (vegetables of unknown types)	0.27	0.06		- (0.20)	(0.89)	(0.44)
Water	0.02	0.03	0.01	0.06	0.29	0.07
	1.8	0.9	0.7	0.77	3.35	1.4

[a] *Cities: NYC = New York City; SF = San Francisco; SJ = San Juan, P.R.*

Table 14. Comparison of Daily Dietary Intake of ^{210}Pb and ^{210}Po from Various Classes of Foodstuffs (pCi/day)

Country	U.S.[12] ^{210}Pb	U.S.[13] ^{210}Pb	U.S.S.R.[28] ^{210}Pb	U.S.S.R.[28] ^{210}Po	U.S.S.R.[31] ^{210}Po	Germany[27] ^{210}Pb-^{210}Po ($^{210}Pb/^{210}Po \approx 1.0$)	Japan[32] ^{210}Pb	India[33] ^{210}Po
Foodstuff Class								
Cereals	0.41	-	2.6	1.0	0.9	0.9	0.5	0.93
Meat, fish, eggs, poultry	0.16	0.16	0.74	1.8	0.9	1.5	12 (fish)	0.11
Milk, dairy	0.16	0.15	0.17	0.07	0.2	0.13	-	0.05
Green vegetables, pulses, fruit	0.32	-	-	-	-	1.77	-	-
Root vegetables, potatoes	0.16	-	-	-	-	0.2	-	-
(all vegetables)	(0.48)	-	(2.6)	(1.1)	(0.6)	-	(≈4)	(0.25)
Carbohydrate		0.76	-	-	-	-	-	-
Other	-	0.14	-	-	0.1 (tea)	-	5	-
Water	0.1	-	0.12	0.06	-	0.01	-	-
Daily Totals	1.3	1.2	6.2	4.0	2.8	4.6	17	1.4

The vegetables grown onsite appear to contain higher concentrations of both ^{226}Ra and ^{210}Pb than do other sources, such as those from New York City. With a consumption rate of about 0.5 kg/day, the nuclide intake would be for ^{226}Ra about 2.5 and about 4 pCi/day for ^{210}Pb from this source alone.

The relative concentrations of the nuclides in cattle dung indicate that cattle grazed on land irrigated by mine water may have much higher levels of both radium and ^{210}Pb than others. While these results are not directly applicable to these studies, data on such cattle could be important for more accurately estimating transfer coefficients. Such data are essential for determining the values of the parameters for the system models describing distribution in the environment of nuclides from the tailing piles.

Dose to Man

The effects of contamination on the dose to man may be estimated from the normal dietary nuclide intake, the dietary contribution to the nuclide concentration in man and the resultant dose rates.

Thus, if we assume that the normal body content is associated with a constant intake from the normal diet, then the dose rate per unit intake can be estimated. Only the uranium (which contributes to the total dose[2]), ^{226}Ra and ^{210}Pb intakes will be considered. The relatively short half-life of the ^{210}Po (138 days) allows it to build up much less than does ^{210}Pb in the body for a given constant intake. On the other hand, when considering the dose rates, the alpha-emitting ^{210}Po contributes about 95% or more of the dose equivalent rate from the ^{210}Pb series.[2]

The total dose equivalent rates to man from natural sources are listed in Table 15, which shows that internally deposited radionuclides contribute about 30% of the total dose to soft tissues (as represented by gonads) and about 70% to bone (specifically to the osteocytes).[2] It is assumed that the quality factor, QF, is 10 for alpha particles. Of the dose rates from internal emitters in Table 16, the heavy elements (mainly ^{210}Po) contribute 90% of the dose to the skeleton and about 25% of that to the gonads; ^{40}K contributes most of the remainder. These dose rates are from dietary intakes of about 0.4 pCi/day of U and 1.4 pCi/day each of ^{226}Ra and ^{210}Pb. However, only about one half the bone dose from ^{210}Pb-^{210}Po series is of dietary origin, the remainder being from inhalation from the atmosphere. Also given are the concentrations and dose rates normalized to a daily intake of one pCi for each nuclide (in parentheses).

The dose from food may be estimated from the locally grown foods that are affected, viz. meat (beef) and vegetables. Rabbit will not be considered because of the uncertainties in the consumption rates. It is assumed that meat consumption is about 0.2 kg/day[11] and the normal concentrations in beef are 0.4, 0.5 and 1.0 pCi/kg for ^{238}U, ^{226}Ra and ^{210}Pb, respectively (Table 17). The concentrations in beef muscle are probably lower than these, but inclusion of organs, such as liver, could raise the mean intake values to the ranges assumed here.[3] Thus, about 7% of the ^{226}Ra and 15% of the ^{210}Pb is from meat. Consequently, the doses from these dietary sources are about 1 mrem/yr from ^{226}Ra (7% of 16 mrem/yr) and 5 mrem/yr from ^{210}Pb (15% of 30 mrem/yr). Similarly, the ^{234}-^{238}U pair contributes about 2 mrem/yr.[2] The total skeletal

Table 15. Natural Dose Equivalent Rates (NCRP 1975)[2], QF = 10

Source	Gonads, mrem/yr	Bone (osteocytes), mrem/yr
Cosmic radiation	28	28
External terrestrial	26	26
Internally deposited radionuclides	27	115
Rounded total	80	170

Table 16. Dietary Intake and Dose Equivalent Rates[2]

Nuclide	Diet, pCi/day	Concentration in human bone[3], pCi/kg[a]	Dose rate, mrem/yr[a] Osteocytes	Gonads
$^{234-239}U$	0.4[b]	7 (17.5)	12 (30)	0.8 (2)
^{226}Ra	1.4	8 (5.7)	16 (11)	0.2 (0.14)
(^{228}Ra)[b]	1.1	4 (3.6)	19 (17)	0.3 (0.3)
^{210}Pb	1.4	60 (43)	1 (0.7)	0.1 (0.07)
^{210}Po	1.6	60 (38)	60 (38)	6 (3.8)
Total			108 (97)	7 (6.3)

[a] *Values in parentheses are the values normalized to a daily intake of 1 pCi.*

[b] *A major contribution to bone dose, but not in the ^{238}U series.*

Table 17. Dose Rates Due to Consumption of Meat[a] Containing "Normal" (New York City) Concentrations of Radionuclides

Nuclide	Concentration, pCi/kg	Intake Rate, pCi/d	Dietary Fraction, %	Skeletal Dose Rate, mrem/yr
$^{234-238}U$	0.7	0.08	16	2
^{226}Ra	0.5	0.1	7	1
$^{210}Pb(^{210}Po)$	1	0.2	15	5

[a] *Assumed intake of 0.2 kg/day.*[11]

dose rate from the consumption of meat is thus about 8 mrem/yr. Since the ^{226}Ra levels in the control cattle are about twice and the ^{210}Pb levels 2½ to 30 times those above (geometric mean of about 10), very small differentials in the concentrations would lead to a 25 mrem/yr increase in skeletal dose. Thus, based on Table 17 the ^{226}Ra rate from controls would be about 2 and for ^{210}Pb about 50 mrem/yr.

It will be noted that for a given intake the ^{210}Pb appears to be the most significant nuclide in dose production, over twice that of ^{226}Ra. In addition, the ^{210}Pb concentrations in food are substantially greater than those of the radium, twice in the "standard" diets and 2 to 25 times in our controls. While the concentrations in the soft tissues of the onsite animals were not higher than those of the controls, those in bone were about 50 to 100% greater in the onsite bones. This effect indicates that in the long run, the concentrations in soft tissues would also be greater. Thus, a 50% excess of nuclide concentrations in the exposed animals would represent an increased exposure to a regular consumer of 25 mrem/yr from the ^{210}Pb, alone. The radium and uranium would add about an additional 5 mrem/yr.

A similar effect occurs with the locally grown vegetables. In the "standard" New York City diet they contribute about 32% (0.57 pCi/d) of the ^{226}Ra (Table 13) and 37% (0.48 pCi/d) of the ^{210}Pb (Table 14) which represent bone doses from Table 16 of 6.3 and 18.2 mrem/yr for the respective nuclides. The New Mexico vegetables, while not necessarily the same as those in the standard diet or distributed similarly, appear to have ^{226}Ra and ^{210}Pb concentrations more than four times those from New York City. Consequently, the increased doses would be, respectively, approximately 20 and 55 mrem/yr (three times the New York City doses) for a total of 75 mrem/yr.

It, thus, appears that under the extreme conditions assumed, individuals consuming the meat and vegetables from this area exclusively could receive substantial skeletal doses from the nuclides in these foods of up to 100 mrem/yr. Soft tissue doses are probably about 10% or 10 mrem/yr. Moreover, even if only a fraction is due to mill exposure, e.g., 25%, and the remainder to the natural local conditions, the contribution of the mill to the dose could be substantial relative to the USEPA standards.[34] This poses a problem in that because of sample variability a 25% increase in concentration may be difficult to demonstrate. One solution might be to obtain fecal collections from residents, which would represent an integrated dietary intake.

The actual exposure to the residents in this area is probably substantially less than the above figures. Only a small fraction of the homes (<5%) on the Anaconda site have gardens and these probably supply only a fraction of the yearly food for these families. Use of cattle grazed near the mill as a food source would affect only a few families, and even in such cases some of the meat they consume probably comes from distant sites.

The overall population exposure, averaged over the entire area is probably small, also. This average is probably less than 0.1 mrem/yr skeletal dose to the population, in the Grants area with the assumption that 0.1% of the meat and vegetables consumed are grown in the "exposed" sites, as represented by our samples, i.e., cattle raised adjacent to the mill and vegetables grown on the mill site. A similar argument would apply to dose commitment, that is the

commitment would not be substantially greater than that from natural sources over a given period of time.

CONCLUSION

These results show that some contamination of the human food chain is likely. The degree is probably not large since the sampling was designed to exaggerate the contamination level. Rabbits were from near the mill tailings within the perimeter fence and cattle were from fields close to the tailings. Because of the incomplete results on cattle, the level of contamination is uncertain. Vegetables may reflect some influences of the mill. In any case, in the region under study, which has a small population and limited agriculture, it appears that, with an admixture of foods from outside the region, contamination of diet may be small.

We expect to finish these measurements soon to obtain more definite conclusions on the effects of tailings on cattle and, specifically, to determine uranium and ^{230}Th concentrations, and to obtain more specimens and better information on them. Acquisition of feed samples for the cattle would aid in estimating transfer coefficients. In particular analysis of samples from cattle, grass, and soil from grazing land irrigated by mine water will aid greatly in estimation of transfer coefficients in these studies.

REFERENCES

1. R. B. Holtzman, P. W. Urnezis, A. Padova and C. M. Bobula III, *Progress report on a study of contamination of the human food chain by uranium mill tailing piles*, Argonne National Laboratory Radiological and Environmental Research Division Annual Report, July 1977-June 1978, ANL-78-65 Part II, pp. 176-194.

2. National Council on Radiation Protection and Measurements (NCRP), *Natural Background Radiation in the United States*, NCRP Report No. 45 (1975).

3. United Nations Scientific Committee on the Effects of Atomic Radiation 1977 Report to the General Assembly, *Sources and Effects of Ionizing Radiation* (United Nations, New York, 1977), pp. 35-114.

4. R. B. Holtzman, *The source of unsupported ^{210}Po(RaF) in tissue*, Health Phys. 10, 763-764 (1975).

5. R. B. Holtzman, *Application of radiolead to metabolic studies*, in "The Biogeochemistry of Lead in the Environment," J. Nriagu (ed.), Elsevier/North Holland Biomedical Press, Amsterdam, 1978, pp. 37-96.

6. H. F. Lucas, Jr., *Correlation of the natural radioactivity of the human body to that of its environment: Uptake and retention of ^{226}Ra from food and water*, Argonne National Laboratory Radiological Physics Division Report, July-December 1960, ANL-6297, pp. 55-66.

7. H. F. Lucas, Jr., *Alpha scintillation radon counting*, Workshop on Methods for Measuring Radiation in and around Uranium Mills (E. David Harward, ed.) Program Report Vol. 3, No. 9, pp. 69-96, Atomic Industrial Forum, Washington, D.C. (1977).

8. R. B. Holtzman, *Measurement of the natural contents of RaD (^{210}Pb) and RaF (^{210}Po) in human bone. Estimates of whole body burdens*, Health Phys. 9, 385-400 (1963).

9. Perkin-Elmer Corp., *Analytical Methods for Atomic Absorption Spectrophotometry*, No. 303-0152, March 1971.

10. I. M. Fox and R. B. Holtzman, *Standard Procedure for the Analysis of Calcium by Atomic Absorption*, Center for Human Radiobiology procedure, unpublished (see Appendix, this report).

11. I. M. Fisenne and H. W. Keller, *Radium-226 in the diet of two U.S. cities*, USAEC Health and Safety Laboratory Report HASL-224, pp. I-2 to I-8 (1970).

12. R. S. Morse and G. A. Welford, *Dietary intake of lead-210*, Health Phys. 21, 53-55 (1971).

13. D. C. Bogen, G. A. Welford and R. S. Morse, *General population exposure of stable lead and ^{210}Pb to residents of New York City*, Health Phys. 30, 359-362 (1976).

14. R. B. Holtzman, *Natural levels of lead-210, polonium-210, and radium-226 in humans and biota of the Arctic*, Nature (London) 210, 1094-1097 (1966).

15. R. B. Holtzman, *Normal dietary levels of ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po for Man*, submitted to the Proceedings of the Natural Radiation Environment III, held at Houston, Texas, April 23-28, 1978, U.S. Department of Energy.

16. N. A. Harley, J. H. Harley and I. M. Fisenne, *^{226}Ra in infant diet and bone*. In Proceedings of the 11th Annual Bioassay and Analytical Chemistry Meeting held at Albuquerque, New Mexico, Oct. 7-8, 1965, pp. 126-133, Lovelace Foundation and Sandia Corp., Albuquerque, CONF-651008.

17. N. A. Hallden and J. H. Harley, *Radium-226 in the diet and human bone from San Juan, Puerto Rico*, Nature 204, 240-241 (1964).

18. P. J. Magno, P. T. Groulx and J. C. Apidiankis, *Lead-210 in air and total diets in the United States during 1966*, Health Phys. 18, 383-388 (1970).

19. I. Michelson, J. C. Thompson, Jr., B. W. Hess and C. L. Comar, *Radioactivity in the total diet*, J. Nutrition 78, 371-383 (1962).

20. A. F. Stehney and H. F. Lucas, Jr., *Studies on radium content of humans arising from natural radium of their environment*, Proc. Int. Conf. on the Peaceful Uses of Atomic Energy, Vol. II, pp. 49-56, United Nations, New York, 1956.

21. R. B. Holtzman, H. Spencer, F. H. Ilcewicz and L. Kramer, *Metabolic balance of ^{210}Pb and ^{210}Po in unexposed men*. In Proceedings of the Third International Congress of the International Radiation Protection Association, Sept. 9-13, 1973, Washington, D.C. (W. S. Snyder, Ed.), pp. 1406-1411, International Radiation Protection Association and U.S. Atomic Energy Commission, CONF-730907-P2 (1974).

22. H. Spencer, R. B. Holtzman, L. Kramer and F. H. Ilcewicz, *Metabolic balances of ^{210}Pb and ^{210}Po at natural levels*, Radiat. Res. 69, 168-184 (1977).

23. I. Michelson, *Radium-226 in the total diet*, Health Phys. 5, 224-230 (1961).

24. I. Michelson, *Radioisotopes in the 1963 diet*, Health Phys. 11, 56-60 (1965).

25. California State Department of Health, *Estimated daily intake of radionuclides in California diets, July 1971-December 1972*, Radiat. Data and Reports 15, 69-73 (1974).

26. N. Cohen, T. Jaakkola and M. E. Wrenn, *Lead-210 concentrations in the bone, blood and excreta of a former uranium miner*, Health Phys. 24, 601-609 (1973).

27. B. Gloebel, H. Muth and E. Oberhausen, *Uptake and excretion of the natural radionuclides ^{210}Pb and ^{210}Po by man*, Strahlentherapie 131, 218-226 (1966). Also ANL-TRANS-458.

28. L. A. Ladinskaya, Y. D. Parfenov, D. K. Popov and A. V. Fedorova, *^{210}Pb and ^{210}Po content in air, water, foodstuffs and the human body*, Arch. Environ. Health 27, 254-258 (1973).

29. A. S. Chhabra, *Radium-226 in food and man in Bombay and Kerala State (India)*, Brit. J. Radiol. 39, 141-146 (1966).

30. M. de Bortoli and P. Gaglione, *^{226}Ra in environmental materials and foods*, Health Phys. 22, 43-48 (1972).

31. A. P. Yermolayeva-Makovskaya, L. A. Pertsov and D. K. Popov, *Polonium-210 in the human body and in the environment*, UNSCEAR Document A/AC.82/G/L.1260, in HASL Translation, Feb. 1969, pp. 163-170.

32. N. Takata, H. Watanabe and R. Schikawa, *Lead-210 content in foodstuffs and its dietary intake in Japan*, J. Radiat. Res. 9, 29-34 (1968).

33. R. N. Khandekar, *Polonium-210 in Bombay diet*, Health Phys. 33, 148-150 (1977).

34. U.S. Environmental Protection Agency (USEPA), *Environmental Radiation Protection Requirements for Normal Operation of Activities in the Uranium Fuel Cycle*, EPA 520/4-76-016 (1976); and Federal Register 42 (No. 9), 40CFR190, pp. 2858-2861 (Jan. 13, 1977).

APPENDIX A. ANALYTICAL PROCEDURES

I. ASHING OF SAMPLES

Organic material in the samples under study must be removed before analysis of the nuclides and elements of interest can be determined. Because ^{210}Po and to some extent, ^{210}Pb are volatile, the samples are ashed at low temperatures--below 200°C--either by wet-ashing in nitric and perchloric acids or dry-ashing in a low-temperature asher, a device that oxidizes the materials by means of an atomic oxygen plasma produced from molecular oxygen (O_2) in a radiofrequency field.

WET PROCEDURE[1]

This procedure is suitable for dissolution and removal of most organic matter from biological materials, such as bone, animal and human soft tissues, urine, feces, food, and plant tissues. It may also be used for extracting elements of interest from soils and rocks without necessarily dissolving the entire mass.

1. Solid samples are dried at 100°C or freeze-dried. To reduce the volumes to be processed, liquid samples may be evaporated first, or ashed and evaporated simultaneously.

2. Place the sample in a beaker or Erlenmeyer flask and add about 1 ml of concentrated nitric acid for each gram of dry material. If the reaction is too vigorous dilute the acid with water at the rate of 1:1 or greater (v/v).

3. Cover the beaker or flask with a watch glass and allow it to stand for several hours at room temperature to oxidize some material before application of heat.

4. Heat the sample slowly on a hot plate and watch carefully until the reaction starts, as shown by brown fumes of nitrous oxide. The reaction rate can be reduced by cooling the container or adding water.

5. Continue heating until the brown fumes cease or the volume becomes too low--less than about 25 ml. At this time remove the solution from the hot plate, add about 25 ml of nitric acid and continue heating. Repeat this process until no fumes appear on addition of acid and the solution is clear. If the solution does not clear or if fat (not easily oxidized by the nitric acid) is present one may nevertheless go on to the next step.

6. Cool the solution and add 10 to 25 ml of nitric acid and then 10 to 20 ml of 72% perchloric acid ($HClO_4$).

7. Since this step is critical, watch the container carefully after heating commences. (Cold $HClO_4$ is generally not dangerous.) Heat the container slowly. If it becomes darker or begins to react vigorously (e.g., to bubble), cool it, add 10 ml of HNO_3 and then heat again. Continue heating until the white fumes of $HClO_4$ begin to form. The solution is further processed to remove nitrates, which, if present, interfere with the subsequent plating onto the silver disk, i.e., nitric acid dissolves the silver.

8. Cool the solution and add about 5 ml of concentrated hydrochloric acid and bring the sample to fumes again.

9. Repeat Step 8 three times.

10. After the last fuming, cool the solution and dilute it to 100 to 250 ml in a suitable volumetric flask.

11. Aliquot the samples for the various analyses to be performed.

LOW-TEMPERATURE PROCEDURE

This method uses an oxygen plasma impinging on the oxidizable matter.* The temperature, which depends on the power input, may be kept below 200°C while a reasonable oxidation rate is maintained. When applicable, this method of ashing is preferable to wet ashing because less contamination is likely, since less reagent contacts the sample and it requires less manipulation of the sample. However, it is suitable only for animal and human soft tissues and food and plant materials of low ash content. It is not suitable for bone and its use appears to be inconvenient for excreta. The asher is expensive, about $6000 and it can ash only about 10 to 20 g (dry) per day.

1. Dry the sample at 100°C or freeze-dry it. Place the dry material in a flat borosilicate glass tray. Use less than about 10 g/per tray and spread it as thinly as possible.

2. Place the trays in the chambers and pump down to a vacuum. Dry further under vacuum, if necessary.

3. Adjust the oxygen flow and turn on the power. Adjust the power to 50 to 100 watts.

4. Continue ashing several hours to overnight and then examine the samples. If necessary break up the material daily and continue ashing for one to five days, as necessary.

5. On completion of the ashing, place the ash in a beaker.

   a. If the ashing is complete, dissolve the ash in a small amount of hydrochloric acid.

   b. If the ashing is incomplete, dissolve the ash in nitric acid to complete the process. Subsequently, remove the nitrates by fuming with perchloric and hydrochloric acids, as in Step 4 and the following steps of the wet-ashing procedure.

6. Dilute and aliquot the solutions, as in Steps 10 and 11 of the wet-ashing procedure.

II. DETERMINATION OF ^{226}Ra

^{226}Ra is determined by the radon emanation method of Lucas[2,3] in which the daughter product of ^{226}Ra decay, ^{222}Rn, is collected and determined. The sample containing the radium is dissolved, flushed with radon-free air, and sealed in a flask for several days to allow the radon with its 3.8-day half-life to grow in. The flask is then flushed with radon-free air into a charcoal trap cooled to -78°C which absorbs the radon quantitatively. The radon is then transferred to a counting chamber coated internally with a zinc-sulfide phosphor that produces light pulses when struck by the alpha particles emitted from the radon and its short-lived daughters. The amount of radium in the original sample is calculated from data on the amount of radon in the chamber, the growth time of the radon in the flask, and application of the radioactive growth and decay equations of Bateman.

This method is very specific for ^{226}Ra because ^{222}Rn is the only radon isotope long-lived enough to be detected by this procedure. The limit of detection at 50% uncertainty (in the standard error) which depends on the counter background and reagent contamination is 0.02 to 0.03 pCi in our system.

**We use an International Plasma Corporation IPC 1000 Plasma System, Model 1003 248ANQ, with 2-4 in. dia × 8 in. long reactor chambers with a maximum power input of 300 W.*

METHOD*

The emanation system is shown schematically in Figure A-1.[3] The emanation flask (A) is a one-liter round bottom flask modified by the addition of stopcocks for sealing the flask and glass joints for connection to the system. In one design the bubbler on the left of the diagram enters through a 12/30 tapered joint and is connected to the system through a 18/7 ball joint of with a 24/40 tapered joint and an appropriate adapter. The flush gas of radon-free air enters the flask through a bubbler having a tip opening of 1 to 2 mm.

After passing through the solution and air space in the flask, it then goes through the two traps (B) cooled to -78°C to remove water and acid from the airstream. It then passes through trap (C) containing activated charcoal, also cooled to -78°C. The radon is absorbed on the cooled charcoal. The detailed procedure for the transfer of the radon from the flask to the trap follows:

1. Connect tube F to a vacuum pump and tube E to a source of radon-free air.

2. Place the emanation flask (A) and charcoal trap (C) on the system using vacuum grease on the fittings. Leave the stopcocks closed.

3. Place cooled baths using dry ice and a non-toxic solvent, such as Freon T.A.** in Dewar flasks on the water traps (B) and charcoal trap (C).

4. Open stopcock E and then evacuate the system by opening stopcock at F.

5. Close the stopcock at F, and open the valve on the radon-free air line to bring the system to 3-4 cm Hg above atmospheric pressure. Repeat steps 4 and 5 at least twice.

6. Begin flush by opening stopcock (C) and on outlet of charcoal trap. Adjust flow rate to 1 liter/min using flowmeter (D).

7. Open stopcock above the flask and then the one on the side. Start the transfer of the radon in the emanation flask to the charcoal by closing stopcock E. Continue flushing until the volume of the flush gas is 20 times the volume of the liquid or 10 l, whichever is greater.

8. Stop the flow of the radon-free air, close the stopcocks on the emanation flask and then the stopcock leading to the charcoal trap (inlet stopcock).

9. Record the date and time and remove the charcoal trap and emanation flasks. You may allow the trap to warm to room temperature for analysis at a later date. However, do not close the second stopcock on the charcoal trap until it has reached room temperature or it may explode.

10. Close both stopcocks on the charcoal trap, place it in a dry-ice bath, open the outlet stopcock and evacuate for from 3 to 10 min. Do not evacuate through the inlet stopcock. Close the stopcocks, remove the trap from the cold bath and allow it to warm to room temperature.

TRANSFER OF RADON FROM TRAP TO COUNTING CHAMBER

In this step the radon is transferred from the trap to the counting chamber (Fig. A-2) on a transfer system, such as that shown in Figure A-3 and in the schematic diagram in Figures A-4 and A-5.[4] This system is similar to that of Lucas,[3] except for the replacement of a Sigma pump with a peristaltic pump and the mercury column manometer control with a solid state pressure sensor and controller. The counting chamber is that of Lucas. Details for the construction of the chamber are presented in a recent paper.[3] Radon is transferred from the evacuated trap (C) above to the chamber.

Much of the following detailed procedures were taken from Lucas,[3] with modifications.

***E. I. DuPont de Nemours and Co., Wilmington, Delaware 19898.*

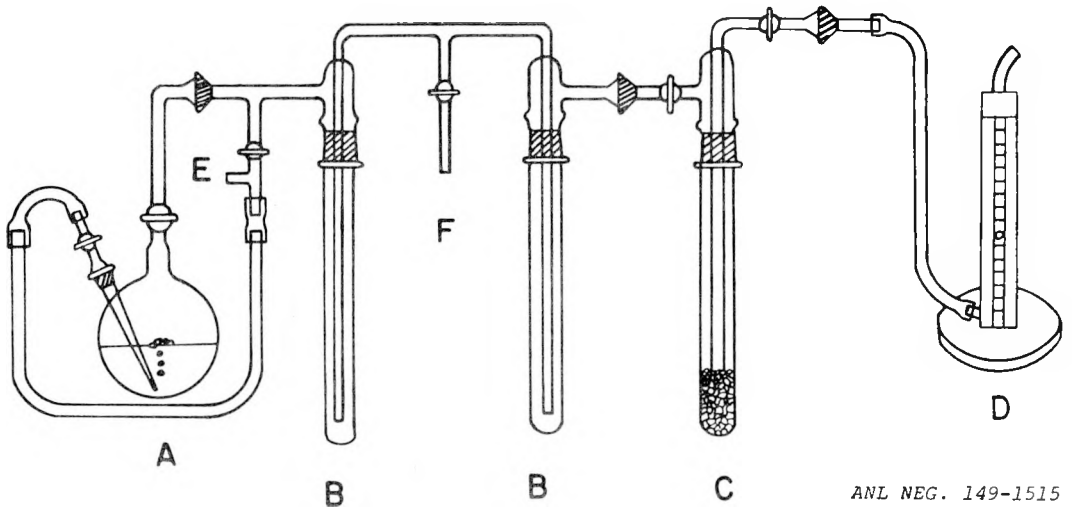

Fig. A-1. Schematic of Radon Emanation System.[3]

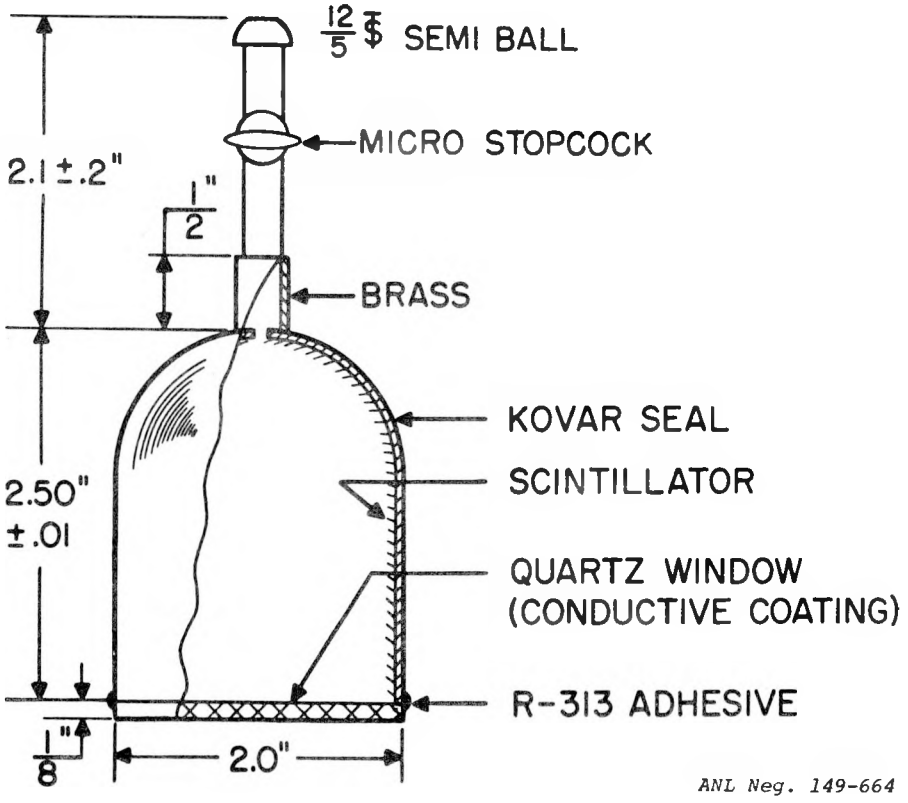

Fig. A-2. Radon Counting Chamber.[3]

Fig. A-3. Radon Transfer System.[4]

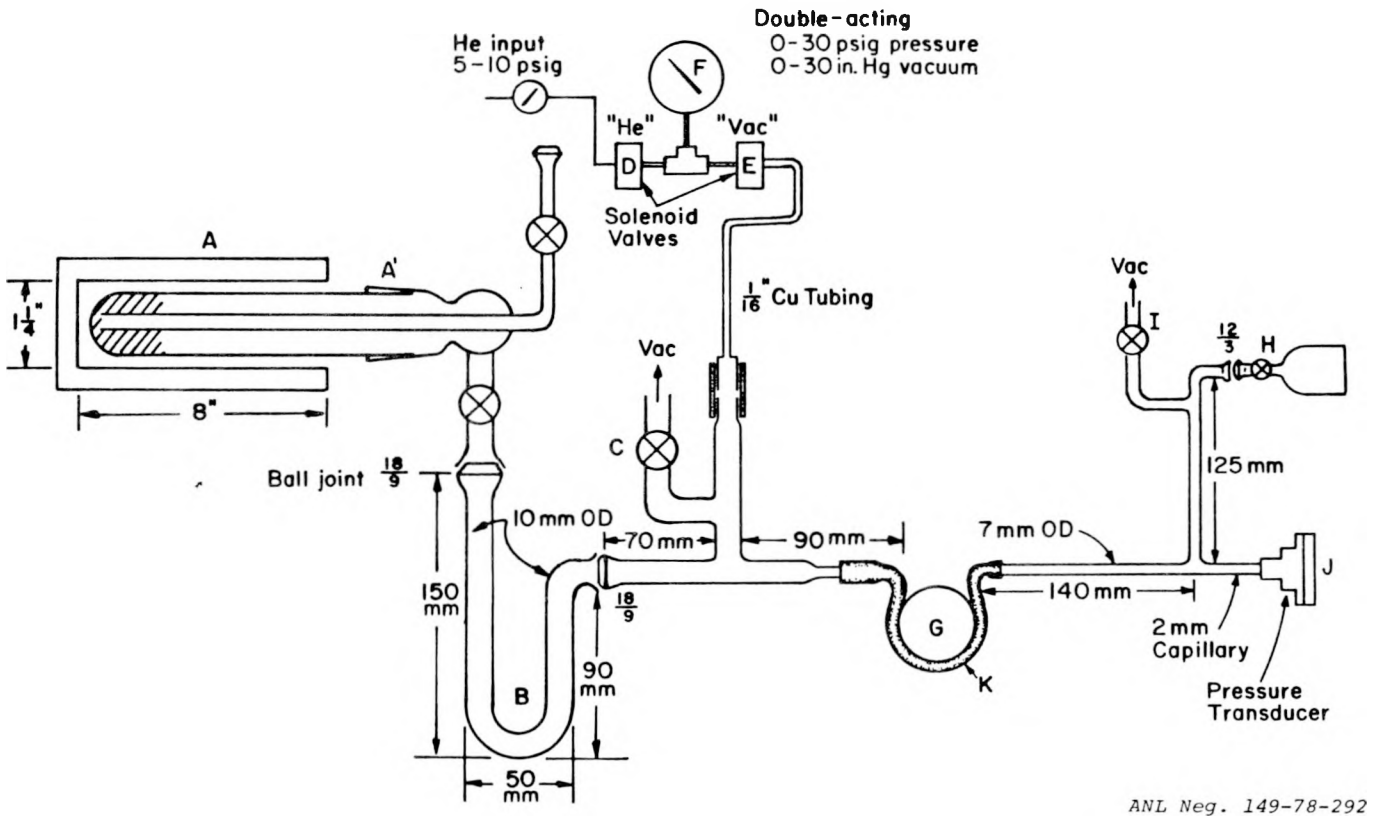

Fig. A-4. Diagram of Radon Transfer System: (A) trap heater (furnace) at 500°C with charcoal trap (A'); (B) water trap at -80°C; (C) stopcock to vacuum pump; (D) solenoid valve to helium reservoir; (E) solenoid valve to transfer line; (F) vacuum-pressure gauge; (G) transfer pump; (H) radon counting chamber; (I) stopcock to vacuum; (J) pressure transducer; (K) rubber tubing.

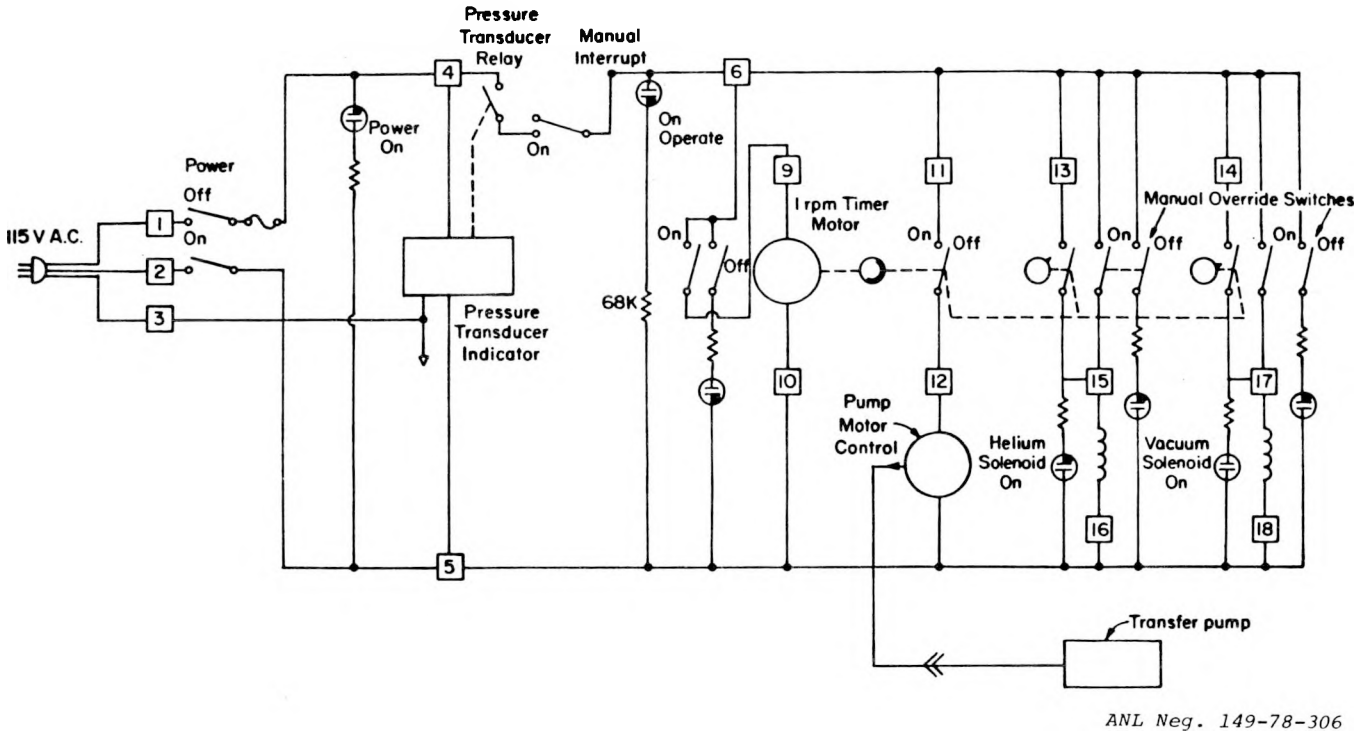

Fig. A-5. Schematic Diagram of the Electrical Circuitry of the Radon Transfer Apparatus. The numbered squares are terminals on terminal strips.

1. Evacuate the radon counting chamber connected at point H, Figure A-4.

2. Connect the evacuated charcoal trap (A^1) containing the sample to the water trap (B) cooled with dry ice. Place the trap heater (furnace) A operated at about 500°C over the trap.

3. Evacuate the lines by opening the stopcocks to the vacuum pump at C.

4. Flush the lines and counting chamber with helium at least 3 times by opening the solenoid valves D and E and operating the transfer pump G.

5. Evacuate the system and counting chamber again and close the stopcocks at C and I.

6. Open the charcoal trap to the system and add about 15 to 20 ml of helium (STP) to the system. This is done by opening D to a helium resevoir maintained at about 5 to 10 psig (tank of helium gas connected to a regulator valve). Close D and open E to the system.

7. Switch on the timer which then activates the transfer pump for 50 sec. to transfer the helium with entrained radon into the counting chamber. The pumping rate is such that in 50 sec. the gas on the trap side of the line will be transferred almost completely, so that a "good" vacuum of about 29 in (740 mm) Hg is attained.

8. Steps 6 and 7 are repeated four additional times until the pressure in the chamber side of the system is about one atmosphere. The pressure of the helium and the transfer rate are adjusted to fill the counting chamber in approximately 5 cycles. On opening the solenoid valve E to the evacuated line, the vacuum on gauge F should be about 24 to 24 1/2 in (610 to 622 mm) Hg. Note that the pressure is appreciable because the gauge chamber now contains the helium for flushing.

9. On completion of the cycle, when the pressure in the chamber is approximately atmospheric, the time is interrupted. Close the stopcock on the counting chamber and remove the chamber for counting.

Notes on the Emanation and Transfer Procedures by H. F. Lucas, Jr.[3]

Process the samples in order of increasing ^{226}Ra content since about 0.3% of the radon will be absorbed by the rubber tubing* and will be released while transferring subsequent samples. The amount of radon absorbed by the tubing increases as either the pump rpm or the inside diameter of the tubing is decreased. A pump speed of 400-600 rpm is recommended (Sigma pump) (600 rpm for the Masterflex pump. - RBH). At this speed the tubing must be lubricated with castor oil to prevent overheating of the tubing.

The air used for flushing the radon from the emanation flask to the charcoal trap may be obtained by storing for 60 days or longer. The concentration of ^{222}Rn in 220-cubic-foot cylinders, after aging, has been found to range from 0.2 to 5 fCi/l. This radon is derived from the ^{226}Ra on the walls of the cylinders, and thus the ^{222}Rn concentration in the air from the cylinder increases as the cylinder pressure is reduced. However, less than 0.06 pCi ^{222}Rn will be obtained from 12 liters and a correction can be made. Radon-free air may be obtained by absorbing the residual water on magnesium perchlorate (Anhydrone), and the radon on charcoal cooled to -80°C. Copper tubing should be used between the outlet of the charcoal trap and the inlet to the emanation system, since both carbon dioxide and radon have a high rate of permeability through rubber. A ^{222}Rn blank of about 2 fCi is obtained for every 20 cm of rubber tubing. All tubing must be replaced regularly or at first sign of cracking, otherwise higher blanks are obtained.

The rate of removal of ^{222}Rn from the emanation flask is nearly independent of the bubble size so that fritted bubblers are not required. In any case glass frits should not be used

---

Rubber tubing, pure latex, amber (or black), Cat. No. R-8480, 1/8" wall, 3/16" ID, SGA Scientific Inc., 2375 Pratt Blvd., Elk Grove Village, Ill. 60007.

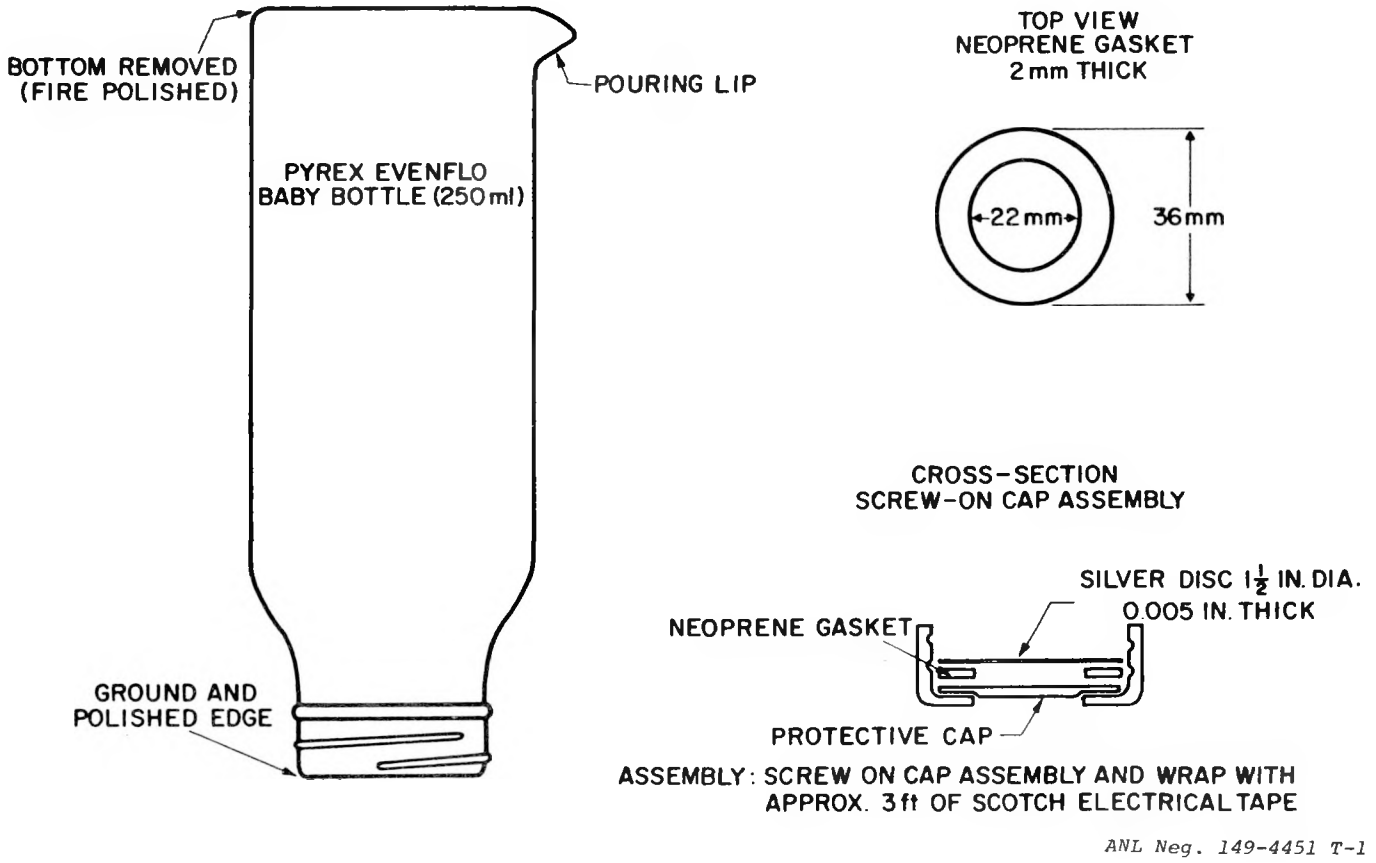

Fig. A-6. ^{210}Po Sample Plating Holder.

with low-level samples because the glass contains appreciable amounts of ^{226}Ra that are leached from the large areas of exposed surfaces in the frit. Successive samples of radon from water samples ranging from 0.1 to 20 liters and for flushing rates from 0.5 to 2 liters/min have shown that about 50% of the radon is removed by a flush volume equal to twice the sample volume. A flush volume equal to 10-20 times the sample volume is suggested.

Radon Counting System

The amount of radon transferred to the radon counting bottle is determined by counting the scintillations as the alpha particles from radon and its daughters strike the inner surface of the bottle. The light pulses are detected and counted by a 2 in. diameter photo-multiplier (PM) tube (EMI 9856KA, RCA 6655 or Dumont 6292) and a scaling circuit. This counting system is checked weekly with a small scintillating source, which tests the scaling circuit and verifies the gain and discriminator settings. In addition, instrumental noise is checked each weekend to assure that the system is in good operating condition.

The background counting rate of each counter bottle is determined at monthly or more frequent intervals. A running mean and standard error for 10,000 minutes of counting time are determined and processed for input to the computer program.

To count a sample, proceed as follows:

1. Stop previous count. Record date, time and total count on sample card.

2. Turn off the high voltage. This is absolutely essential. If the high voltage is left on during the following steps, damage or destruction of the photomultiplier tube usually results.

3. Remove the light-tight cover and the counting bottle. This requires the use of both hands; one for lifting the cover, the second to grasp the counter bottle before it has any chance of falling to the floor.

4. Clean the window of counter bottle and of the PM tube with soft (facial) tissue.

5. Place the bottle on the end of PM tube, centering it carefully and replace the cover. Step 5 like Step 3 is a two-handed operation.

6. Turn on high voltage. Record the counter number on the sample card, start the count, and record the date and time.

The results are calculated by a computer program that determines the amounts and concentration of ^{226}Ra and the statistical errors.

III. DETERMINATION OF ^{210}Pb AND ^{210}Po

This procedure for the determination of both ^{210}Pb ($T_{\frac{1}{2}}$ = 22 yr) and ^{210}Po ($T_{\frac{1}{2}}$ = 138.38 days) is based on the removal and quantitative determination of the ^{210}Po at two times separated by approximately four months.[1] After oxidizing (ashing) the sample at a low temperature (below 200°C), removal of nitrates and adjustment of the resulting solution to a concentration of about 0.5 N hydrochloric acid, this solution is heated and stirred for several hours to plate the ^{210}Po almost quantitatively onto a silver disk that is then counted in an alpha counter to determine the ^{210}Po. The plating and counting procedure is repeated after several months during which time the ^{210}Po has grown in from its parent ^{210}Pb. These counting data are then used to calculate both the ^{210}Pb and ^{210}Po activities initially present in the sample by use of the Bateman equations for radioactive growth and decay.

This procedure is quite general in that it works for almost any type of sample that can be dissolved. Samples containing no organic substances usually do not require ashing, such as clean ground water and rain water. Although urine has been plated without ashing, there is much evidence in this case that recovery was incomplete.

EXPERIMENTAL METHODS

Plating

The sample holder is an 8-ounce Pyrex glass (250 ml) baby nursing bottle (Fig. A-6). A glassblower removed the bottom, polished the edge and put on a pouring lip. The lip of the bottle where the cover screws on is polished smooth with a fine glass grinding compound (used for polishing stopcocks). A silver disk 1½ inches (3.581 cm) diameter and 0.005 inch (0.127 mm) thick is placed against the polished portion of the bottle, a neoprene rubber gasket is placed over the disk and the bottle cap is screwed on. The silver is soft enough to form a good seal on the bottle lip.

Analytical Procedure

1. Adjust the volume of the sample to about 200 ml and the pH to 0.5 N (pH = 0.3) by adding concentrated HCl dropwise.

2. Place the silver disk in the bottle neck (see above) and tighten the cap. Check the seal by adding about 50 ml of water to the bottle and allow it to stand about 15 min. If the seal is poor, water will appear in the cap lip. If no water is visible the seal may be further tested by placing the edge of absorbent paper in the lip. A leaky cap should be tightened, or possibly the disk replaced with a new one.

3. After obtaining a good seal, wrap the edge of the cap and adjacent bottle with 3/4-in. wide vinyl electrical tape to prevent the heating water from contacting the edge of the disk.

4. Place the sample in the bottle and add 200 to 300 mg of ascorbic acid. This is to reduce Fe^{+3} to Fe^{+2} ions in solution and prevent interference with the plating of the Po onto the silver.

5. Place the bottle in a water bath at about 95°C, cover with a watch glass with a slot or hole for the shaft of a glass or plastic stirrer.

6. Stir as rapidly as possible for about 6 hr at a rate just below that at which the solution splashes out of the container.

7. Add water as necessary every few hours to maintain a constant volume in the bottle.

8. After completion of the plating remove the watch glass and stirrer, wash the inner surface of the watch glass with water from a wah bottle and collect the wash water in the sample. Rinse the stirrer and collect the washings in the sample.

9. Pour the sample into a storage bottle and save it. Rinse the bottle several times with a few ml of 1 M HCl and add the rinsing to the sample.

10. Remove the tape from the bottle and remove the disk. Record the time of removal. Rinse the disk with a few drops of 1 M HCl (from a dropping bottle) and dry it on a watchglass heated by the water bath.

11. Count the disk in an alpha counter. This laboratory uses a Nuclear Measurements* internal proportional alpha counter with an internal diameter of 2 inches. The alpha counting efficiency is 51%, and the background counting rate is about 0.020 to 0.040 cpm. The disk is usually counted for about 24 hr. Record the starting and ending times and the number of counts.

12. Store the sample about four months (one half-life of the ^{210}Po) to allow the ^{210}Po to grow in from the ^{210}Pb. The amount of time is not important, as long as the exact time is known to ± 1 day.

13. Repeat Steps 1 to 11 for the second plating. The sample may be dark and contain a black or gray precipitate of organic material from the original ascorbic acid. This does not appear to affect the efficiency of the second plating.

Nuclear Measurements Corporation, Indianapolis, Indiana.

Calculation of Results

The results from the two platings and counts are used to calculate both the ^{210}Pb and ^{210}Po from the Bateman equations for radioactive decay and growth.

The equation for the ^{210}Pb activity at the time of collection is:

$$A_1^0 = \frac{A_2(2) - A_2(1)\ (1 - Y)\ e^{-\lambda_2(t_2-t_1)}}{e^{-\lambda_1(t_2-t_1)} - e^{-\lambda_2(t_2-t_1)}} \cdot \frac{\lambda_2 - \lambda_1}{\lambda_2}\ e^{-\lambda_1 t_0}$$

and similarly for ^{210}Po,

$$A_2^0 = A_2(1) - \frac{\lambda_2}{\lambda_2-\lambda_1} A_1^0\ (e^{-\lambda_1 t_0} - e^{-\lambda_2 t_0})\ e^{\lambda_2 t_1},$$

where $A_2(1)$ is the activity of the ^{210}Po from the first separation,

$A_2(2)$ is the activity of the ^{210}Po from the second separation,

λ_1 is the decay constant of the ^{210}Pb, $(8.63 \times 10^{-5}\ day^{-1})$,

λ_2 is the decay constant of the ^{210}Po, $(5.009 \times 10^{-3}\ day^{-1})$,

t_2-t_1 is the time between the first and second separations,

t_0 is the time between collection of the sample and the first separation, and

Y is the yield, the fraction of the ^{210}Po plated, usually 92%.

$A_2(1)$ and $A_2(2)$ are corrected for chemical yields (Y) and detection efficiencies of the counters.

This calculation is usually done by a computer program (POLO) from raw counting data, dates, times and counts. The activities A_1^0 and A_2^0 are calculated along with estimates of errors based on counting statistics.

IV. DETERMINATION OF CALCIUM BY ATOMIC ABSORPTION*

SCOPE

This method is suitable for the analysis of calcium in dry or wet-ashed biological matter dissolved in perchloric, hydrochloric, and nitric acids: a) urine, b) feces, c) diets, d) bone, e) blood (whole, serum, cells, and washes), and f) soft tissue. Lanthanum diluent added to the calcium aliquot acts as a releasing agent and overcomes most of the interferences.

One should be able to analyze 40-60 samples per day, including standards with a precision of the method of about 2% for the optimum and high ranges and about 5% for the low (expanded scale of 3X) range. The sensitivity for 1% absorption is about 0.04 µg/ml, and the detection limit is about 0.01 µg/ml.

REAGENTS

Ca stock solution: 1000 µg Ca/ml in aqueous solution (Fisher Scientific).

Lanthanum stock solution: Wet 58.65 g of La_2O_3 with distilled water. Add 250 ml concentrated HCl very slowly until the oxide is dissolved. Dilute to 1 liter with distilled water. Filter if necessary. This provides a 5% lanthanum solution in 25% (v/v) HCl (3 N HCl).

Lanthanum diluent: Dilute the La stock solution 1:10 with distilled water. 0.5% La in 2.5% HCl (v/v).

---

*By I. M. Fox and R. B. Holtzman.

EQUIPMENT

A Perkin-Elmer 303 Atomic Absorption Spectrophotometer with 3-slot Bollinghead burner and Ca-Zn lamp is used for the measurements.

The solutions are pipetted with Eppendorf automatic pipets which range in volume from 5 to 1000 µl.

An L/I Repipet, 10-ml capacity dispenses the lanthanum diluent. Set to dispense 4.0 ml (9.0 ml for high calcium range).

ANALYTICAL PROCEDURE

Pipet the solutions into 8-ml polyethylene vials with snap caps and 12-ml vials for high-Ca range. Rinse with water and ethanol and dry between runs. If the aliquot is less than 100 µl fill tip with sample, dispense, and rinse with one or two water aliquots; if it is 100 µl or greater, fill tip with sample to wet inner surface, discard, and then dispense aliquot.

Platinum crucibles with flat bottoms are used for the drying step in the procedure for blood. Clean with hot 6 N HNO_3.

Optimum Range, 0-50 µg Ca/ml

Make up aqueous stock standard solutions of 0.5, 1, 2, 3, 4, 5, 7.5, 10, 15, 20, 30, 40, and 50 µg Ca/ml. Suggested volumes for making these solutions are given in Tables A-1 and A-2. One ml of each standard is taken to make up the series for each run. For good accuracy over the entire range, use all thirteen standards. If sample aliquots are known to be high in calcium, greater than 10 µg, for instance, omit the 0.5 - 4 µg standards. Use at least seven standards and a blank to determine the calibration curve.

In addition, stock solutions containing an equivalent amount of lanthanum diluent can be made up. Use a 10-ppm standard to optimize flame and burner adjustments and to monitor the stability of the instrument during the run. A stock blank solution (matrix) is used to adjust the zero on the instrument.

High Range 0-120 µg Ca/ml

Make up aqueous stock standard solutions of 10, 20, 40, 60, 80, 100, and 120 µg Ca/ml. Take 1 ml of each standard to make up the series for each run.

Low Range 0-6 µg Ca/ml

Make up aqueous stock standard solutions of 0.1, 0.25, 0.5, 1, 2, 3, 4, 5, and 6 µg Ca/ml. Take one ml of each standard to make up the series for each run.

Procedure of Optimum Range (0-50 µg Ca in 5 ml final volume)

1. Set up 40-60 numbered, clean, dry polyethylene vials.

2. Aliquot 1.0 ml of each standard into its respective vial.

3. Aliquot 1.0 ml of distilled water for each matrix blank. Set up one blank for each 10-15 vials.

Table A-1. Calcium Standards

Concentration, µg Ca/ml	Source, µg/ml	Volume of Source, ml	Final Volume, ml
120	1000	6	50
100	1000	10	100
80	1000	4	50
60	1000	3	50
50	100	25	50
40	100	20	50
30	100	15	50
20	100	10	50
15	100	15	100
10	100	5	50
7.5	15	25	50
5	100	5	100
4	10	20	50
3	10	15	50
2	10	10	50
1	5	10	50
0.5	5	5	50
0.25	5	5	100
0.1	1	10	100

Table A-2. Calcium Standards in 0.5% Lanthanum Diluent

Concentration of Standard	Amount of Ca in 5 ml, µg	Source Conc., µg/ml	Volume of Source, ml	Volume of 0.5% La Diluent, ml	Final Volume, ml
10	50	100	20	160	200
8	40	100	4	40	50
2	10	10	10	40	50
0.2	1	1	10	40	50
0	matrix blank	0	20	80	100

4. Aliquot the appropriate volume of urine or feces sample (usually less than 200 µl). Volumes greater than 200 µl may exhibit suppression due to the increase in acidity. This suppression can be eliminated if the aliquot is taken to dryness. (See procedure for blood, *vide infra*.)

5. Add water to make a total volume of 1.0 ml.

6. Add 4.0 ml lanthanum diluent and shake to mix.

7. Allow the spectrophotometer to warm-up for 15 min. or until the energy indicator is steady. The usual settings are: lamp current 15mA (or as noted on lamp), wavelength 42270 (vis), gain 4, slit 4, filter out. The flame is slightly reducing (yellowish) with an acetylene flow of 6 (8 psi) and an air flow of 6 + (30 psi). Set the top burner ¼ inch below the bottom of the light beam. The aspiration rate of water is ≅ 5 ml/min. The recorder uses a noise suppression of 2 for the 1X scale, medium chart speed (1-inch. min), scale selector 0-10%, linear, filter 1, range attenuator off, range 10 mV.

8. Block the beam and adjust the zero knob on the recorder to give 100.0% absorption.

9. Aspirate the matrix blank and adjust the full scale knob to give 0.0% absorption.

10. Aspirate water (base line). Note absorption (∿ -0.5%). Aspirate water after each sample. Check the base line and adjust if necessary.

11. Aspirate the 10-ppm stock solution (or high standard on other ranges) and adjust the burner to maximum absorption and minimum noise. Note the absorption, which should be about 80%.

12. Aspirate ∿2 ml from each vial. Adjust the base line or the matrix blank when necessary. The series usually consists of a blank, the standards, 3 to 4 groups of a blank and 9 samples, ending with another blank.

13. Once through the series, check the absorption of the 10-ppm stock solution.

14. Reset the fine wavelength control if the energy meter indicates a decrease. Repeat Steps 8-11.

15. Aspirate the second half of each solution.

16. Finally, recheck the 10-ppm standard. If the instrument is unsteady, more frequent checks of 100.0% absorption, matrix blank, and 10-ppm standard are necessary.

Procedure for High Range (0-120 µg Ca)

Bone samples and large samples of feces and diets are high in calcium. If the sample contains more than 50 µg Ca/5 µl, the use of this range eliminates an intermediate dilution.

The only changes in the previous procedure are to adjust the repipet to dispense 9 ml of lanthanum diluent and to use the larger vials (10 ml final volume).

Procedure for Bloods and Tissue, Low Range (0-6 µg Ca)

Since 500 µl or large aliquots are required, suppression due to the higher acidity begins to be appreciable. The dryness step does eliminate most of the usual suppression and is faster than the method of additions. If an aliquot larger than 1 ml is desired, reduction to 1.0 ml is necessary.

Since washed red blood cells contain virtually no calcium, but are high in salts that supress the calcium absorption, the maximum sample size taken is 0.1 g wet cells per aliquot.

The amount of calcium in the reagents used for wet ashing is negligible for urine, feces, diet, and bone samples, but it should be considered and probably deducted for blood and soft tissue samples that are very low in calcium.

1. Aliquot the samples into platinum crucibles and add three drops of perchloric acid to insure complete wet ashing. Treat blanks and standards in exactly the same manner.

2. Gently take the solution to complete dryness with a heat lamp or hot plate.

3. Add the aliquot of lanthanum diluent and then 1.0 ml water. If the residue remains insoluble, discard.

4. Repeat the aliquot and heat gently.

5. Transfer the solution to a vial.

6. Follow the procedure under "optimum range", except switch to the expanded scale (3X) using a 1-ppm standard as a monitor for Steps 12-16.

7. Aspirate water and with the absorption range knob adjust the base line to read zero. The matrix blank should be ∿3%.

8. Subtract the matrix blank reading from each absorption reading before computing the curve and the concentrations.

If suppression is still causing a large discrepancy, the method of additions can be applied, also.

CALCULATION OF RESULTS

Hand Calculation

Convert absorption readings to absorbance units using the tables in the Perkin-Elmer manual,

$$\text{Absorbance} = -\text{Log}_{10}\left(1 - \frac{\text{absorption}}{100}\right)$$

Construct a calibration curve plotting concentration (in µg Ca/vial) versus absorbance. Determine the calcium concentration in each sample vial. Calculate:

$$\text{mg Ca/unit} = \frac{(\mu\text{g Ca/vial} \times 0.001 \times \text{volume of sample in ml}}{\text{aliquot in ml} \times \text{number of units}}$$

where the "unit" is day, gram, etc.

Computer Calculation

The results may also be calculated by computer programs, AA3 or AACON available in our laboratory written in IBM FORTRAN IV. These were modified from a program supplied by R. Wendt of the Proctor and Gamble Company.

These programs use data from 7 or more standard samples to determine a calibration curve, usually a linear least squares fit to a second order curve. The sample concentrations are then calculated.

REFERENCES FOR APPENDIX A

1. R. B. Holtzman, *Measurement of the natural contents of RaD (^{210}Pb) and RaF (^{210}Po) in human bone. Estimates of whole body burdens.* Health Phys. 9, 385-400 (1963).

2. H. F. Lucas, Jr., *Correlation of the natural radioactivity of the human body to that of its environment: Uptake and retention of ^{226}Ra from food and water,* Argonne National Laboratory Radiological Physics Division Report, July - December 1960, ANL-6297, pp. 55-66.

3. H. F. Lucas, Jr., *Alpha scintillation radon counting.* Workshop on Methods for Measuring Radiation in and around Uranium Mills (E. David Harward, ed.) Program Report Vol. 3, No. 9, pp. 69-96, Atomic Industrial Forum, Washington D.C. (1977).

4. R. B. Holtzman, F. Markun and J. E. Miranda, *Design, construction and operation of a new radon transfer system,* Argonne National Laboratory Radiological and Environmental Research Division, July 1977 - June 1978, ANL-78-65-II (in press).

Distribution for NUREG/CR-0758 (ANL/ES-69)

Internal:

C. M. Bobula III
A. J. Dvorak
P. F. Gustafson
W. J. Hallett
R. B. Holtzman (3)
W. E. Kisieleski (7)
H. F. Lucas, Jr.
M. H. Momeni
A. Padova
R. E. Rowland
J. Rundo
W. K. Sinclair
A. F. Stehney
P. W. Urnezis
A. B. Krisciunas
ANL Contract File
ANL Libraries (3)
TIS Files (6)

External:

USNRC, Washington, for distribution per RE (119)
USDOE-TIC, Oak Ridge (2)
Chief, Office of Patent Counsel, DOE-CH
President, Argonne Universities Association, Argonne, Ill.
J. Abiss, United Nuclear-Homestake Partners, Grants, NM 87020
T. Buhl, New Mexico Environmental Improvement Agency, Santa Fe, 87503
J. E. Cleveland, Kerr-McGee Nuclear Corp., Grants, NM 87020
R. E. Cunningham, USNRC, Silver Springs, MD 20910
W. E. Gray, Mineral Resources Group, Anaconda Company, Denver, 80204
D. W. Hendricks, U. S. Environmental Protection Agency, Las Vegas, NV 89114
E. E. Kennedy, United Nuclear-Homestake Partners, Grants, NM 87020
R. H. Kennedy, USDOE, Washington
H. H. Landon, USNRC, Washington
E. Leany, New Mexico Operations Uranium Div., Anaconda Co., Grants, NM 87020
P. Magno, U. S. Environmental Protection Agency, Arlington, VA 20460
J. Martin, U. S. Environmental Protection Agency, Arlington, VA 20460
J. Martin, USNRC, Washington
H. J. Miller, USNRC, Washington
W. Mills, U. S. Environmental Protection Agency, Arlington, VA 20460
L. C. Schwendiman, Battelle Pacific Northwest Lab., Richland, WA 99352
W. J. Shelley, Kerr-McGee Nuclear Corp., Oklahoma City, OK 73125