THE DETERMINATION OF CONTENT AND ORIGIN OF LEAD IN SURFACE AND GROUND WATERS OF NORTHEASTERN NEW MEXICO

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INTRODUCTION

This study is an attempt to develop a comprehensive understanding of the content, distribution, and origin of lead in surface and ground waters of northeastern New Mexico. In addition, we have attempted to determine the ultimate fate of lead from various sources in the environment. The data result from

(1) sampling: fresh precipitation, wells, streams, rivers, lakes; the biota of streams, rivers and lakes; other plants and animals of the region.

(2) separation of heavy metal contaminants and radionuclides from various samples.

(3) analytical chemical analyses for lead and other heavy metals.

(4) radiochemical analyses of samples for Pb-210 (RaD) and Po-210 (RaF).

An attempt has been made to develop correlative means for determining a relationship among Pb concentrations, RaD concentrations, RaF concentrations, independently, and other factors such as concentrations, time of collection, and elevation of the sample collection.

PART I

SAMPLE COLLECTION AND CHEMICAL ANALYSIS

1. Sampling

The vast majority of samples taken were water samples from streams, rivers, and lakes in the Pecos Wilderness and its periphery. Many other samples from lakes and low streams in the Northeast Plains were also collected. Many of the streams and lakes were sampled seasonally and in systematic fashion; some water systems were checked less frequently. (See Table I.) Some streams in this region were sampled as early as fall 1971 and summer 1972. Systematic sampling of some areas were conducted beginning in summer 1972.

Fresh precipitation (rain and snow) was collected at various times for analysis.

A limited number of wells were sampled.

Fish and biota of some streams and lakes were sampled. (See Table II.) Additional plant and animal samples were collected where it was felt that interesting correlations between the presence of radionucleides and that of the stable elements would result. Some soils samples have been analyzed.

TABLE I

Streams, Rivers, and Lakes Sampled for Water

Surface Water	Site	Sampled
Lake McAlister		seasonally
Storrie Lake		seasonally
Gallinas River	Montezuma	seasonally
Gallinas River	Las Vegas	seasonally
Gallinas River	2 mi. No. Evergreen	summers 72, 73
Montezuma Hot Springs	Montezuma	seasonally
Rito San Jose	9 mi. from C.G.	summers 72, 73
Rito San Jose	Porvenir C.G.	seasonally
Elk Mountain	Elk Mountain	winter 73
Beaver Creek (lower)	Pecos Wilderness	summer 72
Hollinger Creek (lower)	Pecos Wilderness	summer 72
Beaver Creek (upper)	Pecos Wilderness	summer 72
Hollinger Creek (upper)	Pecos Wilderness	summer 72
Sapello Creek	Sapello	seasonally
Maestas Creek	above Rociada	various
Gascon Creek	above Rociada	various
Murphey Lake		seasonally
Pecos River	San Jose	seasonally
Pecos River	Pecos	seasonally
Pecos River	Holy Ghost C.G.	various
Pecos River	Beatty's cabin	summer 72
Lost Bear Lake	Pecos Wilderness	summer 72
North Fork Lake	Pecos Wilderness	summer 72
Lake Kathryn	Pecos Wilderness	summer 72
Middle Fork Lake	Pecos Wilderness	summer 72
Upper Tecolote Lake	Pecos Wilderness	summer 72
Lower Tecolote Lake	Pecos Wilderness	summer 72
Tecolote Creek	various sites	various
Rio La Casa	Pecos Wilderness	summer 72
Rito Sebadilloses	Pecos Wilderness	summer 72
Jack's Creek	Pecos Wilderness	summer 72
Nambe River	Pecos Wilderness	summer 72, 73
Santa Fe River	Santa Fe (above)	seasonally
Rio Grande	Embudo	seasonally
Rio Grande	Lyden	seasonally
Rio Embudo	Embudo	seasonally
Santa Barbara	Santa Barbara C.G.	seasonally
Rio Lucio	Rio Lucio	summer 73, 73
Rio en Medio		summer 72
Rio Pueblo	Tres Ritos	seasonally
Trampas Creek	El Valle C.G.	summer 73

TABLE I (continued)

Surface Water	Site	Sampled
Santa Cruz Lake		seasonally
Black Lake		summer 72, 73
Coyote Creek		summer 72
Cimarron River	Cimarron Canyon	summer 72, 73
Costilla Lake		summer 72, 73
Red River	Questa	various
Red River	at Molycorp	various
Little Rio Grande	So. of Talpa	various
Canadian River	So. of Raton	summer 72
Canadian River	at Sabinoso	summer 73
Conchas Lake		summer 73
Lower Charette Lake		various
Upper Charette Lake		various
Springer Lake		various
Maxwell Lake		various
Stublefield Lake		summer 72
Ute Lake		summer 72
Bluewater Lake		summer 72
Agua Piedra		winter 72
Rio Frijole		winter 73

TABLE II

Streams and Lakes Sampled for Fish

Waters	Samples	No. of samples
Gallinas River	Brown trout	19
Rito San Jose	Brown trout	20
Storey Lake	Rainbow trout	8
Lake McAlister	Rainbow trout	30
Rio Nambe	Brown and cutthroat trout	12
Rio Chiquito	Brown trout	12
Costilla Lake	Trout	5
Bluewater Lake	Rainbow trout	5

2. Chemical Analyses

The preferred methods of analyses for heavy metals in this study have proven to be non-flame atomic absorption spectroscopy. for samples containing extremely small (less than 1.0 ppm) amounts of lead and other metals, flame atomic absorption spectroscopy for samples with greater than 1.0 ppm of lead, and electrochemical methods of analysis for all samples. The more useful electrochemical methods have been anodic stripping voltammetry and polarography; these methods are preferred for referee purposes, however.

We will review the methods of analyses used for (a) water samples, (b) plant and animal tissues, (c) bone samples, and (d) soil samples.

a. Water samples

Most water samples collected, including fresh precipitation, required preconcentration before analysis. Frequently, two or more liters of a particular sample were collected and evaporated to small volumes, usually 100 ml to 200 ml. Only occasionally, however, was it possible to analyze the previously evaporated samples directly. It was usually difficult to analyze the concentrates because (1) high carboniferous or siliceous residues remained which interfered in the analyses or (2) the samples contained lead or other trace metals in fractions of a part per billion.

Subsequent to evaporation, lead in the samples was extracted with ammonium pyrrolidine dithiocarbamate (APDC) into methyl

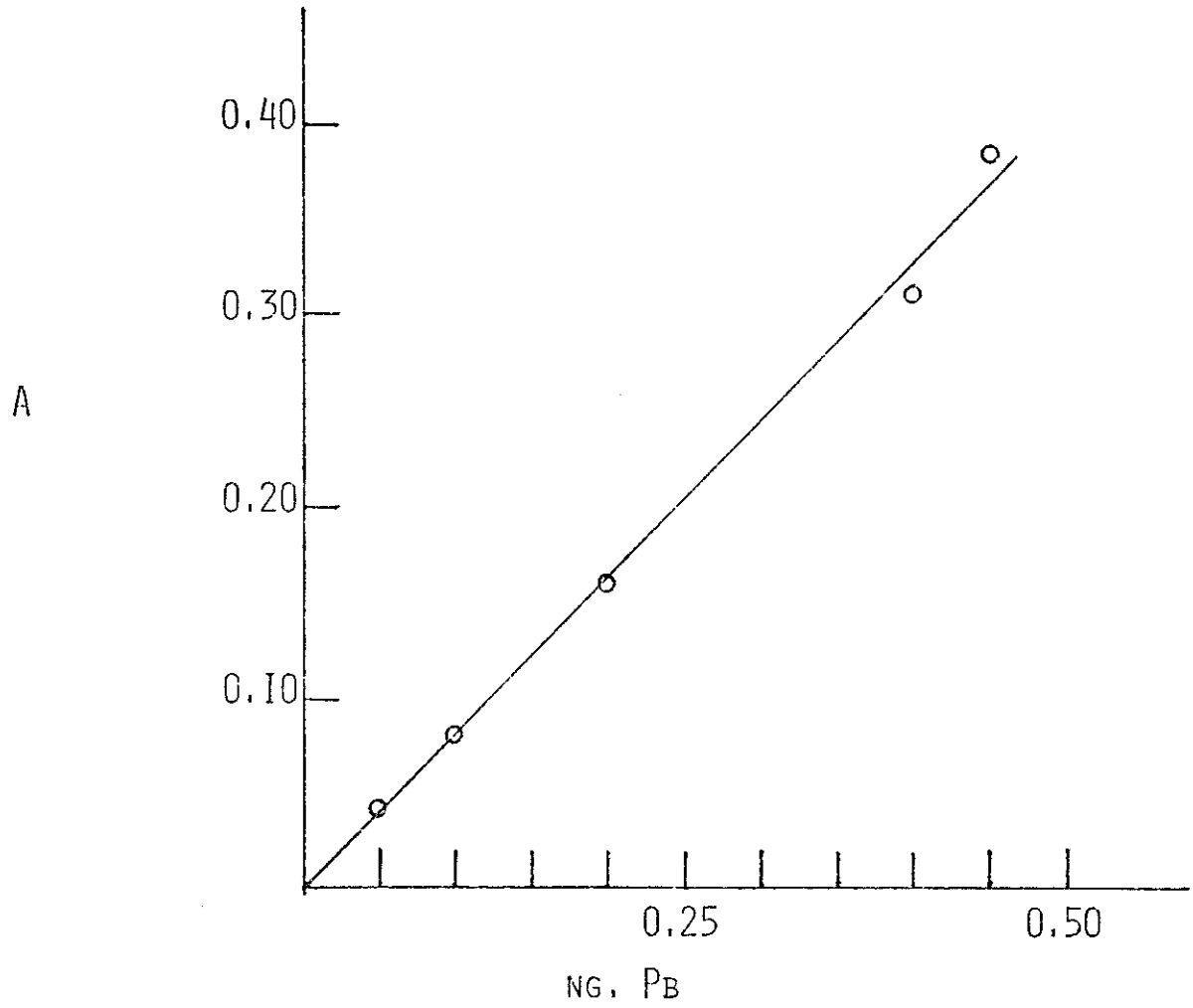
isobutyl keton (MIBK) using a modified method suggested by Parker (1). This liquid-liquid extraction may adequatley be performed by making 100 ml of the water sample one per cent APDC, adjusting the pH of the solution to three, and extracting with 10 ml of the organic solvent.

This method of extraction and concentration of the samples enabled one to analyze the organic layer either in an air-acetylene flance by measuring the resonance absorption of light by the heavy metal atoms or in a carbon furnace also via atomic absorption spectroscopy. Extracts which contained greater than 0.1 micrograms per gram of solution were analyzed with the flame. However, since many more of the samples contained a few parts per billion (or less) of lead in the original sample, the carbon furnace became the preferred method for the vast majority of samples.

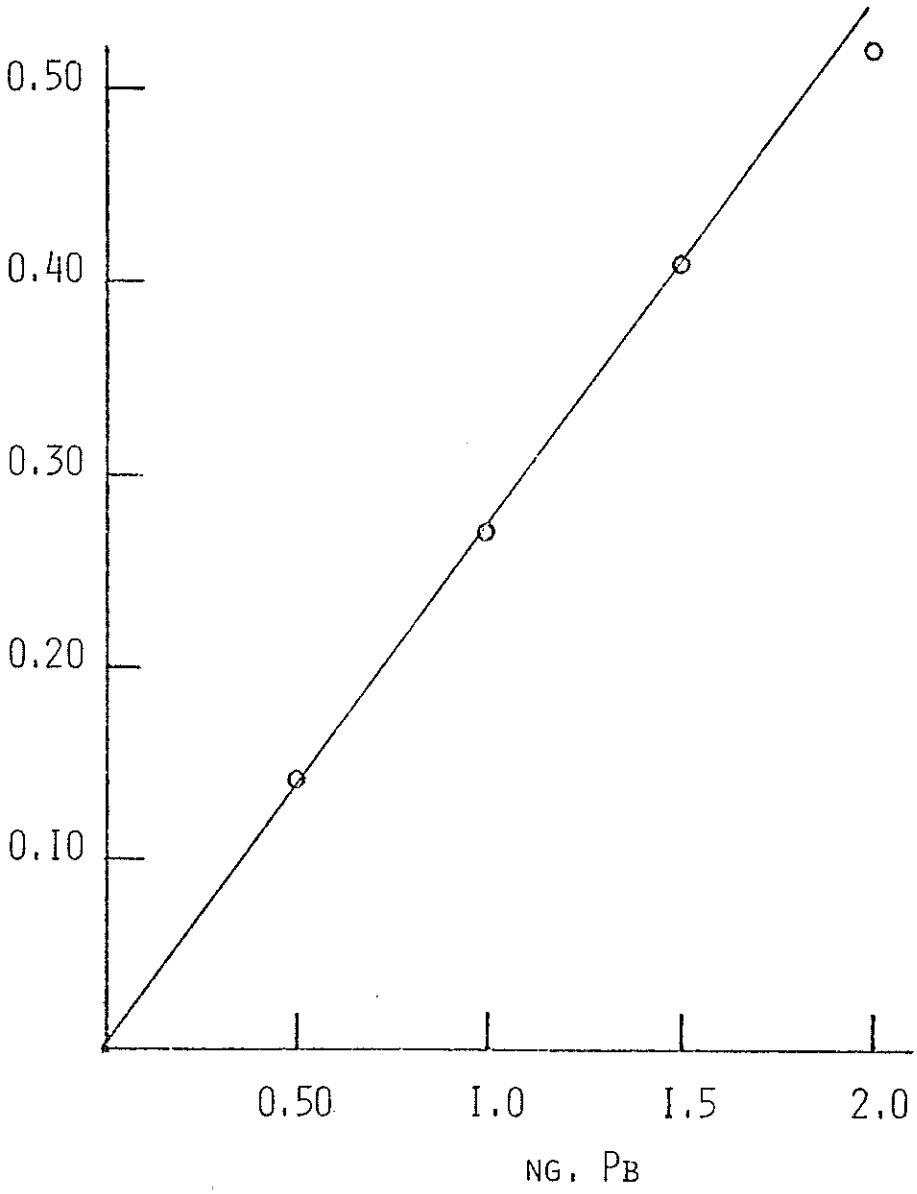
The extracts could be compared to similarly prepared samples which contained generally 5, 10, 20, 50, or 100 ppb of lead. Each of the standard solutions and samples were injected into either a carbon tube or a carbon cup and placed in the Model 1000 Varian Techtron Atomic Absorption Spectrometer. The spectrometer allows the analyst to dry, ash, and atomize the sample in a step-wise fashion with either of the carbon furnaces. (The principal difference in using the carbon cup and carbon tube is that the latter allows 4 to 5 times the sensitivity of the former.)

Resonance absorption of the 217.0 nm line of lead was measured for standards and samples. The absorption signal was read on a

Hewlett-Packard 101B strip chart recorder from which a calibration curve was constructed with each new carbon furnace and used to determine the lead concentrations of the samples. A typical calibration curve, illustrating the extreme sensitivity of the technique may be found in Figure 1.



AA ANALYTICAL CURVE FOR THE DETERMINATION OF PB AT 217.0 NM USING THE CARBON TUBE ATOMIZER.



AA ANALYTICAL CURVE FOR THE DETERMINATION OF PB AT 217.0 NM USING THE CARBON CUP ATOMIZER.

The concentrates often contained concentrations of lead ranging from 0 to 50 ppb which means that the original water samples contained lead in concentrations range from 0 to 0.10 ppb.

For water samples which contained appreciably more lead (more than 0.2-0.5 ppb Pb), it is possible to use the air-acetylene flame for analysis. It is also possible to analyze these more contaminated samples using a stationary mercury drop electrode, plating the lead on the mercury drop, the measuring the anodic current as the drop is stripped of the Pb present.

The anodic stripping voltammetric method was used principally to monitor results obtained by the atomic absorption method. Aqueous solutions which contain in excess of 50 ppb of Pb may be analyzed by anodic stripping in solutions which contain either 0.1 M KCl or 0.1 M NH_4Ac. In this method the aqueous sample is placed in an electrolysis cell, the lead is deposited cathodically for 25 minutes on a stationary (either hanging or sitting) drop, and then the lead is stripped anodically. The anodic current, which can be measured with extreme sensitivity, is recorded and compared to similar currents produced by the analysis of standard lead solutions.

b. Plant and Animal Tissues.

Plant and animal tissues, including fish tissues, were analyzed after subjecting the samples to various treatments. Frequently, the most common procedure, reported in the literature for analysis of tissues, is to dissolve the sample and to analyze by either atomic

absorption on electrochemical methods. One such method was developed in our laboratory and reported in the literature (2); the method is similar to a procedure reported by Pagenkopf, Neumann, and Woodriff (3). The analysis of solutions of tissues is rapid and presents very few difficulties; however, the preparation of such solutions can often be difficult and time-consuming.

We have recently experimented with a method in which we place previously-weighed, minute amounts of dry tissue in a carbon cup and analyze the samples on the Model 1000 Varian-Techtron Atomic Absorption Spectometer with no further sample preparation. The sensitivity of the method is outstanding and the precision and accuracy are good for dry tissue samples. It is possible in this manner to analyze samples as small as 2-3.0 mg and detect quantities of lead which amount to a few picograms (10^{-12} g) of the metal.

In the solution method, either ground or finely chopped pieces of dry or wet tissue are dissolved in a minimum amount of nitric acid necessary for complete dissolution of the tissue. Typically, 0.1 g to 1.0 g of tissue is all that is necessary for analysis. The dissolved sample is then diluted with water and APDC is added to the aqueous portion. The pH is adjusted to three and the metal is extracted into a layer of MIBK. The MIBK solutions are then analyzed with the atomic absorption spectrometer in the same fashion that water samples are reported to be analyzed earlier in this section.

It is not uncommon to be able to analyze tissues with a widely varying concentration of lead, e.g. 0.010 micrograms/gram tissue to 3-4.0 micrograms/gram tissue.

Tissue samples have also been analyzed by polarography and anodic stripping voltammetery. The sample preparation is unfortunatley tedious and time-consuming and we have found the methods useful only for referee purposes. Fish tissue samples (1.0g) were dissolved in a minimum amount of nitric acid with had been pre-electrolyzed for purification. The tissue solutions were diluted with water to 50 ml and buffered to pH 5 with 1M HOAc: NH_3 solution. The solutions were then passed through a 10 x 100 mm Chelex 100 chromatographic column to remove the lead. The lead was then eluted from each column with 1M HNO_3 and each solution was placed in the electrolysis mini-cell. The solution was then either analyzed polarographically or by anodic stripping voltammetry. The polarographic methods allows analysis of solutions containing approximately 5.0 to 25.0 ppm of Pb. Smaller concentrations of the metal may be analyzed by anodic stripping, as described earlier for water samples. Occasionally, samples were analyzed by anodic stripping which contained as little as 10 ng/g of lead in tissue.

c. Bone samples.

Bone from fish or animals (including teeth samples) were analyzed following the same "wet" procedure for tissue. However, the analysis of bone samples requires special care during the extraction of lead from solutions of bone. It is necessary to carefully adjust the pH of acidic solutions of bone to between

2.0 and 5.0. However, calcium will tend to precipitate and care must be taken that this does not happen. MIBK extracts of the bone solutions may be analyzed in the same way that extracts of water samples were analyzed as described in an earlier section.

It is not possible to analyze aqueos solutions of bone directly with the use of the carbon furnace. The calciferous deposit from an aqueous bone solution, that is left upon ashing, causes the sample to "pop" out of the carbon tube or cup during atomization. For this type of analysis, therefore, the extraction procedure is necessary.

d. Soil samples

A few soil samples were analyzed, generally sediments of river or lake beds. The general procedure for analyzing soils which was followed was to dissolve the sample in hot HNO_3 or mixtures of HNO_3:HCl. The pH of the solutons were then adjusted to 3.0-5.0, the lead was extracted by the same method using APDC and MIBK as the solvent. The extracts were then analyzed either in the air-acetylene flame or by the non-flame spectroscopic method described earlier for water samples.

Analysis of aqueous solutions of soils with the carbon tube or cup generally presents a problem because of the siliceous residues that are left upon ashing the samples. The analysis of organic extracts of the aqueous solutions of soils is in general satisfactory.

e. Other trace metals

An attempt was made to develop methods or to modify existing methods for the determination of Be, Cd, Fe, Mn, V, Ag, and Zn in water samples which were known to contain very minute amounts of these trace metals. Minor modifications of methods recommended by Parker (4, 5, 6, 7) for the analysis of C, Fe, Zn, and Ag proved to be satisfactory for the determinations of sub-part-per-billion concentrations of the metals in water using the carbon tube in atomic absorption analysis. Each of these methods allows the analysis of basically the same extracts which were obtained for the lead analyses. Care must be taken, however, to monitor the metal content of washings left over after each extraction to insure that large traces of either Cd, Fe, Zn, or Ag are not left behind.

The resonance absorption lines used for each analysis are Cd (228.8 nm), Fe (248.3 nm), Zn (213.9 nm), and Ag (328.1 nm).

ANALYTICAL RESULTS AND DISCUSSION

Reliability of Data

The advantage in using atomic absorption spectroscopy, and especially the carbon furnace technique, is illustrated by the following: The calibration curves in Figures 1 and 2 are plots of absorption versus quantity of lead present in the carbon tube or carbon cup. Therefore, it is possible to analyze any sample--aqueous liquid, organic liquid, or solid--and compute the amount of lead present in the sample. The concentration of lead in the sample may then be computed from the known volume or mass of the sample and the analytical result.

This method was used to analyze the large majority of samples--water, biological materials, or soil. Similarly, the same method was used to analyze for other heavy metals-Cd, Fe, Ag, and Zn.

Methods for the analysis of these heavy metals are rapid and yield good precision and accuracy. Of course, the one disadvantage in analyzing for more than one metal is that one must replace the hollow cathode lamp each time for a different metal analysis. One does also use a second lamp with a continuous spectrum to check for non-atomic absorption during the atomization of metal sample. We used a hydrogen lamp.

The accuracy and precision of the use of the carbon cup for analysis of either aqueous or organic solutions, prepared from fresh water samples which had to be pre-concentrated, is illustrated in TABLE III.

TABLE III

LEAD ANALYSIS OF WATER SAMPLES

(Collected 12/72)

SAMPLE	TRIALS	Micrograms Pb/gram H_2O
Sapello Creek	10	0.032 ± 0.011
Embudo River (Apodaca)	10	0.025 ± 0.009
Rio Grande (Lyden)	10	0.095 ± 0.020

The precision which is obtained is remarkable when one considers that these are very minute amounts available for analysis.

Precision is enhanced appreciably as the concentration of Pb in the samples increases. TABLE IV illustrates this and shows also that is is possible to analyze dry solid tissue directly with a great amount of precision. Indeed the precision of the "dry" method is far more practical; it is rapid and, if done carefully. leads to greater precison and accuracy than "wet" methods.

TABLE IV

LEAD CONTENT OF BROWN TROUT
(COLLECTED MAY 1972)

ANALYSIS: ATOMIC ABSORPTION SPECTROSCOPY/CARBON CUP.
SAMPLES ARE DRY POWDER OF MUSCLE TISSUE.

SAMPLE	MICRO G. PB/G.	TRIALS	BACKGROUND CORRECTION
RITO SAN JOSE #4 (PORVENIR CANYON)	0.56 ±.01	10	30%
RITO SAN JOSE #8 (PORVENIR CANYON)	0.12 ±.01	4	55%

ANALYSIS: AAS/CARBON TUBE. PB-APDC/MIBK EXTRACTS OF AQUEOUS HNO_3 SOLUTIONS.

RITO SAN JOSE #4	0.47 ± .09	4

Analysis of Results

Water samples. The outstanding characteristics of these data are (1) the large range of concentrations of lead in the water samples over the period of years from 1971 to 1974, and (2) the amazing purity of the overwhelming majority of the samples collected during this period. Most of the samples are as pure as precipitation which falls in the remotest parts of the world, see, for example, reference (8). Contamination, which did occur in 1971 and in winter of 1973, seems to have been affected primarily by local conditions. A discussion of this phenomenon is included in the final section of this report. Other trends which may have occurred are difficult to detect.

It was found that the concentrations of lead in waters of most small streams were dependent generally on the concentrations of snow at the catch-basins. The concentrations remained generally constant downstream although there was generally some "scrubbing" that occurred. As long as there was not some local introduction of contaminant, therefore, the lead concentrations downstream could often be less than at the catch-basin. In northern New Mexico, however, it is often the case that either a primitive or improved road will follow a stream for some considerable distance and these local effects do have a profound impact on the concentrations of lead in the streams.

The concentrations of Pb in snow at the catch-basins generally depend on the remoteness of the catch-basin. TABLES V, VI, and VII illustrate this point.

TABLE V

LEAD CONTENT OF PRECIPITATION

SAMPLE	Micrograms Pb/kg. H_2O
snow: Puerto Nambe (6/73)	0.017
snow: Porvenir Canyon (4/73)	0.016
snow: Gascon area (4/74)	0.016
snow: Maestas Creek area (4/74)	0.008

(Just a brief explanation here. To be entirely consistent with our units, 1 microgram/kg = 1 ng/g $\cong$ 1 ppb; 1 microgram/gram $\cong$ 1 ppm.)

TABLE VI

LEAD CONTENT OF PRECIPITATION

(COLLECTED APRIL 1973)

SAMPLE	NG. PB/G.
SNOW; 2.5 MI. NORTH OF LAS VEGAS	0.19
SNOW; LAS VEGAS * (3RD FLOOR SCIENCE BLDG.)	0.41

* COLLECTED DURING FIRST 20 MINUTES OF DEPOSITION (AND 4.5 HOURS AFTER PREVIOUS SNOWFALL).

CONTRAST ABOVE DATA WITH

GASCON CREEK (WATER)	0.055

ANALYSES: ATOMIC ABSORPTION SPECTROSCOPY/CARBON CUP. PRECONCENTRATION 215:1.

TABLE VII

LEAD CONTENT OF PRECIPITATION
(COLLECTED JANUARY 1972)

SAMPLE*	NG. PB/G.
SNOW: JOHNSON MESA (REMOTE)	0.17
SNOW: JOHNSON MESA (100 YARDS OFF ROAD)	0.30
SNOW: GALLINAS CANYON (5 FEET OFF ROAD; 5IN. DEEP CORES)	$1\text{-}2 \times 10^3$

* ALL SAMPLES COLLECTED ONE WEEK AFTER SNOWFALL.

COMPARE DATA TO

UPPER GALLINAS RIVER (WATER)	0.20

ANALYSES: ATOMIC ABSORPTION SPECTROSCOPY/CARBON TUBE OR ROD. PRECONCENTRATION 200:1 (ALL BUT THIRD ANALYSIS).

The areas sampled in TABLE V are absolutely inaccessible in winter by motor vehicle. The concentrations of lead in snow are 10 to 20 times less than the concentrations of samples collected nearer to the city of Las Vegas. Comparison of TABLES V and VI illustrates this well.

However, local conditions do influence the condition of the catch-basin. A comparison of TABLES V and VII illustrates this. Johnson Mesa is located approximately 15 miles from a town of any size (Las Vegas) but it is accessible in winter by motor vehicle. The data points in TABLE VII illustrate lead concentrations (1) far off the road, (2) 100 yards from the road, (3) immediately off the road, and (4) in a stream which is followed by the road. The impact on a stream which is followed by a busy road is considerable. A road also affects markedly any catch-basin within which it is located. Thus, the effect of automobile exhausts on local sources of water is well illustrated.

It has been illustrated that precipitation, in relatively undisturbed areas, is very pure. The impact of local automobile roads on the waters of local areas has also been established. One interesting point is that the presence of a local drouth condition, like that of summer 1971, will markedly affect the lead concentration of a small stream that is near a road. This is illustrated in TABLE VIII.

TABLE VIII

LEAD CONTENT

Gallinas River

DATES COLLECTED	SITE	Microgram Pb/kilogram H_2O
4/71	Las Vegas	2.0
6/71	Las Vegas	50.0
7/72	Lourdes	0.007
7/72	Las Vegas	0.026
7/73	Las Vegas	0.005
10/73	Montezuma	0.008
4/74	Canyon	0.030
4/74	Montezuma	0.016
4/74	Las Vegas	0.027

The early data for the Gallinas River were obtained at a time when the stream was almost dry. The summer of 1973, however, the river was at times several times its normal size; thus the road that runs along it up the Gallinas Canyon had a minimal impact when runoff was several times above average.

TABLE IX, TABLE X, AND TABLE XI will merely illustrate that, in general, the waters in northeastern New Mexico are extremely free of lead pollution. Surprisingly, many of the lakes -- McAlister, Storrie, Springer, Maxwell, Stublefied -- are also extremely pure in

this regard in spite of the fact that these are readily accessible to the public.

Well water is in most cases at least as free of lead as surface water, and in the case of wells in the immediate vicinity of Las Vegas, well water is perhaps a bit more pure. The drinking water in Las Vegas is usually even more lead-free than the water in the Gallinas River (at Las Vegas). Some of the wells which were monitored periodically are listed in TABLES XI and XII.

To summarize these results, the amount of lead present in these waters is extremely small. Most lead which is present in the waters is present as a result of co-depositon with rain and snow. This amount is not altered appreciably as the water enters streams, rivers, lakes, and water-wells except in instances in which roads and other vehicular activity infringe on the catch-basin, streams or rivers. Occasionally one finds that some of the lead is "scrubbed out" as precipitation makes its way into bodies of surface and well water.

TABLE IX

LEAD ANALYSIS WATER SAMPLES

SUMMER 1973

Water	Site	Pb conc. in micrograms/kilogram
Lake McAlister		.0.008
Mora River		0.013
Sapello Creek	Sapello	0.007
Sapello Creek	Sapello	0.005
Sapello Creek	Sapello	0.025
Pecos River	San Jose	0.018
Pecos River	Pecos	0.019
Nambe River	Nambe	0.001
Namber River	Puerto Nambe	0.014
Santa Barbara	S.B.C.G.	0.029
Rio Pueblo		0.017
Rio Pueblo		0.002
Cimarron River	Cimarron Canyon	0.130
Cimarron River	Cimarron Canyon	0.005
Coyote Creek		0.022
Canadian River	Sabinoso	0.082
Conchas Lake		0.022
Lower Charette		0.004
Upper Charette		0.042
Ute Lake		0.019
Springer Lake		0.007
Stublefield Lake		0.002

TABLE IX (continued)

LEAD ANALYSIS WATER SAMPLES

SUMMER 1973

Water	Site	Pb conc. in micrograms/kilogram
snow	Puerto Name	0.017
Lake Kathryn		0.024
Rio Embudo	Embudo	0.041
Las Brazos		0.022
Rio Chama		0.016
Santa Clara		0.100

TABLE X

LEAD ANALYSIS WATER SAMPLES

SUMMER 1974

Water	Site	Pb conc. in Micrograms/kilogram
Lake McAlister		0.011
Storrie Lake		0.026
Gallinas River	Below Las Vegas	0.086
Gallinas	Montezuma	0.078
Gallinas River	Las Vegas	0.065
Las Vegas City water		0.011
Mora River	Mora	0.024
Sapello Creek	Sapello	0.016
Murphey Lake		0.010
Gascon Creek	Above Rociada	0.007
Maestas Creek		0.006
Pecos River	Pecos	0.011
Nambe River		0.009
Santa Fe River	Santa Fe	0.070
Rio en Medio	Cundiyo	0.008
Santa Cruz Lake		0.010
Trampas		0.006
Rio Pueblo		N.D.
Cimarron River	Micarron Canyon	0.002
Black Lake		0.009
Little Rio Grande	2 mi. So. Talpa	0.008

TABLE X (continued)

LEAD ANALYSIS WATER SAMPLES

SUMMER 1974

Water	Site	Pb conc. in Micrograms/kilogram
Canadian River	Sabinoso	0.007
Conchas Lake		0.007
Lower Charette		0.020
Upper Charette		0.009
Ute Lake		0.004
Springer Lake		0.004

TABLE XI

LEAD ANALYSIS WATER SAMPLES

Water	Site	Date Collected	Pb conc. in micrograms/kilogram
Lake McAlister		1/73	0.008
Storrie Lake		10/73	0.003
Storrie Lake		4/74	0.003
Gallinas River	Montezuma	10/73	0.008
Gallinas River	Lourdes	7/72	0.007
Gallinas River	Las Vegas	4/74	0.027
Gallinas River	Canyon	4/74	0.030
Gallinas River	Montezuma	4/74	0.016
Las Vegas City water		2/74	0.003
Las Vegas City water		10/73	0.003
Mora River	Mora	3/74	0.003
Mora River	Mora	4/74	0.001
Sapello Creek	Sapello	12/73	0.022
Sapello Creek	Sapello	10/73	0.012
Sapello Creek	Sapello	3/74	N.D.
Sapello Creek	Sapello	4/74	N.D.
Rito San Jose	Porvenir C. G.	4/74	0.012
Rito San Jose	Porvenir C. G.	4/74	0.009
Murphey Lake		12/73	0.032

TABLE XI (continued)

LEAD ANALYSIS WATER SAMPLES

Water	Site	Date Collected	Pb conc. in micrograms/kilogram
Rio La Casa		12/73	0.078
Pecos River	Pecos	2/73	0.051
Pecos River	Pecos	12/73	0.111
Pecos River	San Jose	5/74	0.029
Pecos River	H.G.C.G.	5/74	0.008
Pecos River	Pecos	5/74	0.005
Nambe River		12/73	0.127
Nambe River		11/73	0.031
Santa Fe tapwater		12/73	0.011
Santa Fe tapwater		12/73	0.118
Rio en Medio		11/73	0.003
Rio en Medio	Tesuque	12/73	0.011
Santa Cruz Lake		12/73	0.133
Santa Barbara	S.B.C.G.	12/73	0.160
Santa Barbara	S.B.C.G.	11/73	0.005
Santa Barbara	S.B.C.G.	4/74	N.D.
Trampas		11/73	0.063
Rio Pueblo		3/74	0.011
Rio Pueblo		4/74	0.007
Arroyo Hondo		11/73	0.320
Cimarron River	Cimarron Canyon	3/74	0.047
Red River	at Red River	12/73	0.005
Red River	Questa	12/73	0.074

TABLE XI (continued)

LEAD ANALYSIS WATER SAMPLES

Water	Site	Date Collected	Pb conc. in micrograms/kilogram
Conchas Lake		3/74	N.D.
Lower Charette		3/74	N.D.
Springer Lake		3/74	0.005
Tres Ritos	4 mi. west of Trading Post	10/73	0.130
Tres Ritos	Loma Linda Ranch	10/73	0.002
Frijoles		10/73	0.001
Rio Lucio		11/73	0.101
Rio Grande	Lyden	11/73	0.016
Ranchos de Taos		11/73	0.015
Agua Piedra		12/73	0.008
well	Rito San Jose	4/74	0.047
snow		2/73	0.038
Gascon Creek	above Rociada	4/74	0.016
Maestas Creek		10/73	0.009
Maestas Creek		4/74	0.008

TABLE XII

LEAD CONTENT OF WATERS
NORTHEASTERN NEW MEXICO

WATER	DATE COLLECTED	NG.PB/G.
MADRID WELL	2/73	0.048
CONNER WELL	2/73	0.10
AT APODACA	12/72	0.025
SAPELLO RIVER	12/72	0.032
STORRIE LAKE	1/73	0.052
RIO GRANDE AT LYDEN BRIDGE	12/72	0.095
MORA RIVER AT LA CUEVA TRNOFF	1/73	0.16
PECOS RIVER AT LOWER BRIDGE	1/73	0.27
PECOS RIVER AT SAN JOSE	1/73	0.10

Water analysis--other trace metals. Some water samples were analyzed for Pb, Cd, Fe, Ag, and Zn. These analyses are listed in TABLE XII. No discernible patterns are apparent. The presence of silver in the water is probably due to particulates which result from cloud-seeding. An attempt was made to detect dissolved silver in the water but the amounts are to small to be able to detect the monovalent ag ion.

Air analyses. The small amounts of lead in water leads one to suspect that the air is similarly lead-free in this region. We conducted some lead analyses in the Gallinas Canyon and in the vicinity of Las Vegas. We collected air samples on Pb-free paper with a custom-manufactured air pump which we operated with a 12-volt battery.

The analysis of the air deposited samples collected on filter paper was conducted with the atomic absorption spectrometer also. The filter paper pads were leached with nitric acid. The nitric acid solutions were diluted and analyzed with the Model 1000 Varian Techtron Atomic Absorption Sepctrometer in a manner described earlier for analyzing all lead-containing solutions.

The air contained at various times from 0.01 to 0.20 micrograms Pb per cubic meter of air in the very remote areas. The air in the vicinity of Las Vegas contains during daylight hours approximately 1.75 micrograms Pb per cubic meter of air.

It thus becomes apparent that only along roadways does lead deposit after precipitation occurs.

Most animals and humans in the Las Vegas area and in northeastern New Mexico thus ingest lead primarily through the alimentary tract from food and water. This is discussed further in the final section of this report.

Analysis of biological samples.

Biological samples were analyzed to (1) illustrate the magnification in the lead content which occurs in the biota of lakes and rivers and (2) compare the amounts of radioactive nucleides present to the stable lead in these samples. The latter illustration is made in PART II of this report.

The analysis of trout samples is given in the tables following this page. It is interesting that in 1971, when analysis of streams and lakes were yielding 0 to 50 ppb of lead in water, the analyses of fish in these waters were much higher (these analyses are in the low ppm-range). TABLE XIII illustrates fairly high concentrations of lead in fish tissues during a drouth year (1971). TABLE XIV and XV illustrate a considerably improved set of samples as far as concentration of lead in trout are concerned. (These samples were collected from tributaries of the same stream.)

TABLE XII

WATER ANALYSIS OF TRACE METALS

(Cd, Fe, Ag, Zn)

micrograms metal/kilogram H_2O

Water	Date collected	Cd	Fe	Ag	Zn
Gallinas River	10/73	N. D.		0.031	
Storrie Lake	10/73	0.003	0.28	N. D.	0.002
Mora Rive	7/73	N. D.		N. D.	
Sapello Creek	8/73	0.010	10.0	2.04	0.010
Sapello Creek	10/73	N.D.	10.0		0.010
Maestas Creek	2/73	0.006	5.16	0.017	
Gascon Creek	10/73	N. D.	6.60	N. D.	
Rio Pueblo	7/73	N. D.			
Coyote Creek	7/73	0.001		0.005	
Rio Pueblo	7/73	N. D.		0.18	
Tres Ritos	10/73	0.044		N. D.	
Cimarron River	7/73	N. D.		0.042	
Rio Embudo	7/73	N. D.		0.049	
Rio Grande (Velarde)	11/73	N. D.	8.50	N. D.	0.20
Rio en Medio	11/73	N. D.			
Rio Lucio	11/73	N. D.			
Santa Barbara	11/73	0.006			
Red River	12/73	0.001			
Santa Cruz Lake	12/73	0.001			
Pecos River (Pecos)	7/73	0.002	21.0		0.21
Pecos River (Pecos)	11/73	0.001	26.1		0.15
Lake Kathryn	7/73	0.019		0.006	
Rio La Casa	12/73	0.001			
Santa Fe River	12/73	0.001			
Nambe River	11/73	0.005		N. D.	
Agua Piedra	12/73	0.001			
Arroyo Hondo	11/73	0.003		N. D.	

TABLE XII (cont.)

Water	Date collected	Cd	Fe	Ag	Zn
Pot Creek	11/73	0.002			
Ute Lake	7/73	0.001		0.023	
Lower Charette	7/73	0.009		0.53	
Upper Charette	7/73	0.001		.027	
Canadian River	7/73	0.001	0.016		
Springer Lake	7/73	0.002		0.066	
Stublefield Lake	7/73	0.001		0.045	
Conchas Lake	7/73	N. D.		0.023	
Storrie Lake	4/74	0.001	9.2	N. D.	0.036
Mora River	3/74	0.001		0.016	
Las Vegas tapwater	2/74	0.009		N. D.	
Gascon Creek	4/74	0.002		N. D.	
Sapello Creek	4/74	0.001	12.0	0.23	0.02
Maestas Creek	4/74	0.003	3.1	0.20	0.02
Pecos River (H.G.C.G.)	5/74	0.004		0.016	
Rio Pueblo	4/74	0.002		0.001	
Lower Charette	3/74	0.008		0.048	
Upper Charette	3/74	0.002		0.046	

TABLE XIII

LEAD CONTENT OF BROWN TROUT

(COLLECTED ON MAY 1971)

SAMPLE	MICRO G. PB/G. WET	MICRO G. PB/G. DRY
	MUSCLE	MUSCLE
RIO SAN JOSE (PORVENIR CANYON)	0.48	2.0
RIO SAN JOSE (PORVENIR CANYON)	0.45	2.0
RIO SAN JOSE (PORVENIR CANYON)	0.55	2.7

ANALYSES: ATOMIC ABSORPTION SPECTROSCOPY/ C_2H_2 - AIR FLAME. PRECONCENTRATION BY SOLVENT EXTRACTION. ANALYSIS OF PB-APDC/MIBK SOLUTIONS.

TABLE XIV

LEAD CONTENT OF BROWN TROUT
(COLLECTED JUNE 1972)
UPPER GALLINAS RIVER

SAMPLE	MICRO G. PB/G. WET	MICRO G. PB/G. DRY
	MUSCLE	MUSCLE
B	0.016	0.071
C	0.036	0.12
A	0.069	0.28

TABLE XV

LEAD CONTENT OF BROWN TROUT

(COLLECTED MAY 1972)

LOWER GALLINAS RIVER

SAMPLE	MICRO G. PB/G. WET	MICRO G. PB/G. DRY
	MUSCLE	MUSCLE
#10	0.003	0.017
#12	0.005	0.025
#16	0.005	0.037
# 9	0.006	0.026
#14	0.006	0.027
# 8	0.006	0.029
#15	0.007	0.034
# 4	0.008	0.038
# 2	0.009	0.044
#11	0.010	0.057
# 3	0.011	0.046
#17	0.011	0.047
# 5	0.012	0.058
# 1	0.015	0.066
#13	0.016	0.072
#19	0.020	0.084
#18	0.024	0.10
# 6	0.088	0.42
# 7	0.093	0.43

Fish, like vertebrate animals, tend to store lead in bone. Although the phenomenon has been known for a long time (9), it is well illustrated in fish (See TABLE XVI.) Since the techniques, for analyzing both tissue and bone, which were used in this study are almost identical, the introduction of extraneous contamination into the sample is not likely. (It is important to note that only of very high grade of acid solvent was used--ULTREX HNO_3 which contains less than 1 ppb of Pb.)

In summary, the amount of lead in fish is far in excess of what would be expected from the known concentration of the waters which they inhabit.

TABLE XVI

LEAD CONTENT

OF

LAKE RAINBOW TROUT

(Collected May 1971)

SAMPLE	BONE MICRO G. Pb/G.	MUSCLE MICRO G. Pb/G. wet
#1 Lake McAlister	0.50	0.25
#2 Lake McAlister	0.61	-
#1 Storrie Lake	0.72	-
#2 Storrie Lake	1.00	0.17

ANALYSES: Atomic Absorption Spectroscopy/ C_2H_2- air flame, preconcentration by solvent extraction. Analysis of Pb-APDS/MIBK solutions.

TABLE XVII

LEAD CONTENT OF BROWN TROUT
(COLLECTED JULY 1972)

SAMPLE	MICRO G. PB/G. WET	
	MUSCLE	BONE
RIO CHIQUITO	0.30	
RIO CHIQUITO	0.25	
RIO CHIQUITO	0.14	
RIO CHIQUITO	0.19	
RIO CHIQUITO	0.16	
RIO CHIQUITO	0.17	

ANALYSES: ATOMIC ABSORPTION SPECTROSCOPY/CARBON TUBE. SAMPLES IN AQUEOUS HNO_3 SOLUTIONS.

TABLE XVIII

LEAD CONTENT OF RAINBOW TROUT

(COLLECTED AUGUST 1972)

SAMPLE	MICRO G. PB/G. WET MUSCLE
A - BLUEWATER LAKE	0.030
B - BLUEWATER LAKE	0.82
C - BLUEWATER LAKE	0.030

WATER CONTAINED 2.0 - 3.0 NG. PB/G.

ANALYSES: ATOMIC ABSORPTION SPECTROSCOPY/CARBON TUBE.

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PART II

RADIOCHEMICAL ANALYSIS FOR PB-210 AND PO-210 IN ENVIRONMENTAL SAMPLES

Summary of Experimental Approach

Major effort was devoted in this research effort toward the development of analytical techniques which would permit the analysis of Pb-210 (RaD) and Po-210 (RaF) in environmental samples in a rapid, reliable, and economic manner. The types of samples analyzed included water, soil, vegetation, litter and animal tissues including bone. Procedures established for the analysis of these radionuclides which generally include the wet ashing of samples with nitric and perchloric acids[1] were omitted because of costs, time required/analysis, and primarily because of the unavailability of scrubber hoods for this project. Also dry ashing of samples was avoided because of the volatility of RaF under these conditions: it was felt that simultaneous analysis of RaD and RaF was important in tracing the contribution of automobile exhausts to the Pb load in the environment as opposed to that coming from natural sources.

The most common route for the analysis of RaD in environmental samples has been by an indirect method of detecting daughter product activity of Bi-210 (RaE) or RaF because of RaD's weak emissions (61 & 15 KeV end-point energy betas, L-conversion electrons between 30-33 KeV). RaE emits a 1.160 MeV end-point energy beta particle while its daughter, RaF, emits an alpha particle with 5.305 MeV energy. Both of these radionuclides are easily detected by proportional counters, but must be electrodeposited (RaE, RaF) or plancheted in a thin layer (RaE) to be detected with sufficient sensitivity. A great advantage is gained by analyzing for RaD via

RaF because of the low backgrounds encountered in alpha counting, but the detection of RaE for this purpose must be performed under conditions of significant background (less than 1 cpm for alpha counting; about 60 cpm for beta counting) and advantage is gained over counting RaD directly only by the former's ease of detection unless a low background beta-counter is used. A distinct disadvantage in detecting RaF to determine RaD concentrations in samples is the relatively long ingrowth period of RaF (138.4 day halflife for RaF; 5 day halflife for RaE), and by the necessity of having to remove the RaF present initially under most conditions: one is never sure whether unsupported RaF is present in a sample above that which would be present at equilibrium, and under most conditions it is not possible to wait for the sample to approach equilibrium before analysis. Thus, RaF concentration information is usually unavoidably lost in this type of analysis.

The suggestion of Fairman[2] was explored in this laboratory because it held the most promise in accomplishing our objectives during the research period. This method of analysis allows the simultaneous determination of both RaD and RaF initially present in a sample using liquid scintillation counting. This method of analysis was reported to be nearly 100% efficient for RaF, and 98% efficient for RaD. Background counting rates for the RaD and RaF regions on the counter in our laboratory were 45 and 16 cpm, respectively. Thus, although one sacrifices sensitivity in detecting RaD directly as opposed to RaF, the sensitivity for detection is about the same whether one uses RaE for this determination on a proportional counter or detects RaD using liquid scintillation

counting.

We also explored the suggestion of Fairman in using anion exchange techniques for separating RaDEF mixtures. Unfortunately, we encountered a number of problems when we attempted to use this technique for both RaDEF standards and samples. The use of Dowex-1X-8 anion exchange resin in our experiments resulted in an incomplete removal of RaE and a distinct "tailing" effect was noted in the case of RaF elution. Also the flowrate was diminished considerably in the presence of small amounts of colloidal silica present in environmental samples. Consequently, we abandoned this technique for the analysis of samples in general and used only it only for producing relatively pure RaD for RaDEF solutions as reported earlier.[3] Our research efforts led us to experiment with a direct extraction of these radionuclides into liquid ion exchange media which could be encorporated into a counting "cocktail". Di-2-Ethylhexyl-phosphoric acid (D2EHPA) appeared adequate for this purpose and its use was explored.

The aquisition of an ambient air liquid scintillation counter for use by the project greatly enhanced our efforts to pursue a simultaneous analysis for RaD and RaF. Utilization of the "external standard" mode of operation on the counter (a gamma irradiation source of Cs-137 to determine both chemical and color quenching simultaneously) made it possible to derive spectral change equations for these radionuclides as a function of sample quenching. In addition a technique was developed to separate RaE from the RaDEF mixture which made the spectral separation of RaD and RaF more effective.

While most of the water samples were extracted from evaporates directly, a fusion technique was developed to convert the silica present in environmental samples (and silicates in soils) to soluble silicates, and to oxidize organic matter present in oven-dried samples at temperatures of about 500°C. The oxidation was performed at a lower temperature than is generally employed by using $NaNO_3$ in the fusion technique. Only about 40% of the RaF present in the samples was lost by this method, and made possible its analysis by liquid scintillation counting. In addition to the rapid method of preparation which this fusion technique afforded, it also minimized variations in chemical recoveries by providing a sample matrix which overwhelmed individual sample matrices in most cases. One exception was that of bone.

Sample Preparation For RaDEF Extraction And Separation

Unfiltered water or water which had been passed through coarse filter paper (Whatman No. 500 or equivalent) to remove coarse debris were prepared for RaDEF extraction by placing evaporates (2 - 12 liters evaporated to about 150 ml) in sufficient HNO_3 to make up a 1N solution of the acid. An aliquot of about 60 ml were removed for analysis. Water evaporates were either filtered with coarse filter paper or (if silica was appreciable) the solution was made acid and centrifuged prior to extraction of the radionuclides. Care was taken not to allow colloidal material to be removed in any filtration at near neutral pH values (such as is the case for most surface waters) to allow passage of colloidal lead at this hydronium ion activity.

Other samples including vegetation, animal tissues, soil and soil litter were all oven-dried at 125°C for 24 hours in a vaccuum drying oven prior to further processing. Small animals such as field mice, fish, horned toads, frogs and insects were analyzed whole without removing stomach contents, or separating soft from osseous tissues whatever the case. The dried samples were pulverized to a fine powder prior to fusion. Five gram portions of dried pulverized sample were taken for fusion. Plant, animal, litter, and soil samples were treated in an identical manner; fresh and dried weights were recorded as were initial and final volumes of water samples.

Samples other than water evaporates were fused with a specific fusion mixture consisting of 25 grams NaOH, 5 - 7 grams $NaNO_3$, and 5 grams of dried pulverized sample. The NaOH pellets were melted in aluminum tart pans ($4\frac{1}{2}$" top dia.; 3" bot. dia.), allowed to reach a temperature of about 500°C on a hot-plate (Chromalox, 1500 watts, $8\frac{1}{2}$" dia.), and then the 5 grams of sample were added slowly to form a charred slurry. The aluminum did not react with the fusion mixture if the latter were kept dry, however, if the NaOH was allowed to absorb moisture a reaction and destruction of the pan would result; the pans were disposed of at the end of each fusion run. After the emission of smoke from the melt ceased, 5 to 7 grams of $NaNO_3$ was sprinkled on the melt to oxidize the organic matter present. This last step was performed slowly to avoid production of a flame. When all organic matter was oxridized the melt would assume a green color; the melt was allowed to cool near room temperature. The cooled melt was then placed in 200 ml of 5.6N HNO_3

(70 ml conc. HNO_3 made up to volume) to neutralize all of the NaOH, and to provide a residual hydronium ion activity of about 1.5N. In most cases the amount of silica regenerated gave a very faint colloidal appearance to the solution, however, in the case of some soils centrifugation at about 2000 rpm was required. Some samples also required the addition of an equivalent amount of HCl to dissolve a non-silica colloidal dispersion which would not dissolve in the HNO_3 alone. After solution of the latter the sample would be evaporated down to a low volume to remove most of the HCl added. In all cases a 40 ml aliquot of the fusion solution was diluted to 60 ml with distilled water to use for extraction of RaDEF. Most of the samples were centrifuged prior to this step.

Water samples were acidified to 1N with HNO_3 and 60 ml aliquots were removed for analysis. These samples were not centrifuged prior to extraction of RaDEF.

Extraction Procedure For RaDEF

While only one extraction procedure was developed for fused samples, three such procedures were developed for the analysis of water. Only the final and most efficient procedure for water analysis and the procedure for fused samples will be reported in this section. Discussion of the other two procedures for water analysis will be discussed in later sections.

A liquid ion-exchange medium consisting of 20% v/v of Di-2-ethylhexyl-phosphoric acid (D2EHPA; Union Carbide Corp., New York, New York) in reagent grade toluene was prepared. The 40 ml aliquot of fused sample solution diluted to 60 ml with distilled water or 60 ml of acidified water sample were placed in contact with the

glass electrodes of a pH meter (Zeromatic, Beckman). Some means of sample agitation was provided such as a magnetic stirrer; the sample was contained in a 300 ml beaker. An amount of 0.5 grams of hydroxylamine hydrochloride was added to help stabilize the valence of RaF at (+2), and the pH of the solution was adjusted to 1.1 with 10N NaOH. Twenty ml of 20% D2EHPA solution was added to the solution and the two phases were allowed to equilibrate for about 3-4 minutes using the stirring apparatus to insure proper mixing of phases. The pH was readjusted to 1.1 if necessary; if the pH was overrun, dilute HNO_3 was used for readjustment: HCl was avoided for use in pH adjustments because in caused incomplete separation of RaE and RaF. The two phases were transferred to a teflon separatory funnel (with the top cut off) and the organic phase containing primarily RaE and other radionuclide contaminants was discarded. The pH of the aqueous phase was subsequently readjusted to 4.5 and then 20 ml of fresh D2EHPA solution was added to extract the RaD and RaF present in the sample. The phases were allowed to equilibrate for another 3-4 minutes and the pH of the aqueous phase was adjusted to 4.0 with NaOH as before; another 3-4 minutes were allowed for phase contact. The phases were again separated and the organic phase transferred to a 25 ml scintillation vial (low potassium I vial, Packard Nuclear Chemicals). A volume of 2 ml scintillator cocktail concentrate (10X) was added to the vial to make the sample ready for counting on the LSC (liquid scintillation counter). The scintillator concentrate was prepared by dissolving 40 grams and 1 gram of PPO and POPOP (scintillation grade, Packard Nuclear Chemicals), respectively, in 1 liter of re-

agent grade toluene. The latter chemical dissolves with some difficulty in this amount of toluene.

Sample Counting Procedure

The extracted RaD and RaF in the scintillation vial was placed in the LSC (LS-100C, Beckman) which was equipped with an automatic sample changer, pre-selected counting interval and/or pre-selected error determination. The gain of photomultiplier tube was set at 4.47 on the dashpot, while the three counting channels (to be referred to as red, green, and blue windows) were set at 0-5, 5-8, and 8-10 volts, respectively. The sensitivity of the instrument was set so that the most energetic electronic pulses generated by alpha particles emitted by RaF were below the 10 volt discriminator or the detector. Hence, the majority of electron pulses originating from the decay of RaD registered in the red window, while those pulses produced by RaF decay were almost exclusively registered in the blue window at normal quenching values. The pulses due to RaE were divided in a 14:66:20 percent ratio in the red, green and blue windows, respectively, at a quench value of 16.0 on the detector. Quench values between 11 and 19 were observed for all environmental samples, blanks, and RaDEF standards. Although significant spectral changes (distribution of count rates in the three windows) occurred within this range of quench values, only an insignificant change in RaD counting efficiency was noted, and none at all in the case of RaF. Therefore, it was necessary to develop spectral change relationships as a function of sample quench alone without considering efficiency as a variable.

Finally, each sample was allowed to stand for about 300 minutes prior to counting to allow all short lived daughters originating from Rn-222 to decay off. The counting time on all samples and blanks was set at 100 minutes and/or 1% error at the 99% confidence level. Most samples and blanks counted for 100 minutes.

Derivation of Quench Correction Equations

Relationships to correct for the distribution of counts in the three windows were derived by using multiple and curvilinear regression analysis. Relatively pure RaD obtained from RaDEF standard solution[3], and a RaF standard solution were used to obtain the necessary data. Increasing amounts of 0.1 gram/liter dithizone in chloroform was added to an extract of RaD or RaF in 25 ul increments. This procedure caused a systematic quench increase in the medium containing these radionuclides (see TableI, II). Stepwise multiple regression techniques were applied to the results and the best fit determined in each case. The best fit for determining the fraction of RaD counts in the red window (FLR) as a function of quench (Q) was:

$$FLR = 1.024 - 4.43 \times 10^{-4}Q^{2}, \quad (R=0.88;\ F=30.12,\ 1\&9\ D.F.,\ 99\%c.l.)$$

Similarly the fraction of RaD in the blue window (FLB) was determined to be insignificant at most quench values observed; it was approximated to equal 0.005 throughout the quench range. The fraction of RaF in the red window (FPR) although quite small at low quenching values became significant in the higher quench values observed (it should be noted that the LS-100C prints low numerical values for highly quenched samples and visa versa). The relationship

which best fit the data was:

$$FPR = 1.943 \times 10^{-2} - 4.809 \times 10^{-5} Q^2, \quad (R=0.93;\ F-57.98,\ 1\&8\ D.F.,\ 99\%\ c.l.)$$

The relationship for determining the fraction of RaF counts in the blue window (FPB) was found to be best fit by:

$$FPB = 2.28 - 22.19/Q, \quad (R=0.95;\ F-92.83,\ 1\&8\ D.F.,\ 99\%\ c.l.)$$

The test of hypothesis on all partials ($b_1 = b_2 = b_3 = \ldots = 0.0$) was rejected at the 1% level of confidence, and the test on individual partials were found to be significantly different from 0.0 at this level of confidence. The fraction of RaD in the green window (FLG) and also the fraction of RaF in the green window (FPG) were determined by difference.

Qualitatively the FLR relationship states that as quench increases in the scintillation medium, that most of the electronic pulses generated by RaD decay are confined to the 0-5 volt range of the red window. The FPR relationship, however, states that as quench decreases fewer electronic pulses produced by RaF are degraded below the 8-10 volt range of the blue window. The FPB relationship also shows this effect, but in addition it also illustrates the rather precipitous drop of pulse height voltage as the quenching in the medium increases beyond a certain value. Practically all of these pulses are eventually degraded to the 5-8 volt region of the green window, and very few are degraded any further as can be observed by referring to Table I.

All of these relationships were used as part of a computer program which was developed to make spectral shift corrections as a function of sample quench. This program will be discussed in a later section of this report.

Application of Blank Background Corrections

A series of blank runs including all reagents used in making RaD and RaF analysis were conducted to correct samples for their effect on RaDEF concentrations. The results of these experiments are given in Table III. The average quench values were:

1) 15.88(0.63)

2) 15.45(0.56)

3) 14.79(0.51)

4) 17.99(0.55),

for type 1, 2, 3, and 4 analysis respectively. All of those values lie within the quench correction range mentioned earlier in this report (the values in parenthesis are 1 sigma standard deviations). Methods 1 and 2 are earlier analytical types for determining RaD and RaF in water samples. Type 1 blank consisted of 1 gram $Ca_3(PO_4)_2$ + 0.5 grams $NH_2OH \cdot HCl$, 60 ml 1N HNO_3, and 60 ml HCl + the appropriate amount of 10N NaOH required to neutralize the solution to the desired level. Type 2 blank was identical to type 1 without the $Ca_3(PO_4)_2$. The details of these two methods will be discussed further in sections which follow. As can be seen from inspection of Table III, the standard error for type 4 method which is the fusion type blank is considerably greater than the first two types and significantly different background count rates are recorded in the red and blue window of the detector than for all other types. Furthermore, our analysis of these fusion blanks also showed that some of the counts observed in all windows decayed off with a half-life close to the decay of a secular equilibrium mixture of Rn-222 daughters, RaABCC'. These radionuclides emit alpha

TABLE I

Count Rate Shifting in Red, Green, and Blue Windows As Affected by Quenching Value, RaF

Sample No.	Dithizone* Added, ul	Quench Value	Cpm, Red** Window	Cpm, Grn Window	Cpm, Blue Window
1	0.0	17.09	138	298	21471
2	0.0	16.09	151	722	21604
3	0.025	14.25	204	3190	18234
4	0.050	12.83	265	8190	13303
5	0.075	12.30	247	13082	8754
6	0.100	11.24	270	18651	2866
7	0.125	10.74	284	20117	1412
8	0.150	10.03	308	21226	454
9	0.175	9.34	327	21043	312
10	0.200	9.18	443	21173	34
11	0.225	8.97	441	21173	16
12	0.250	8.38	426	21446	5
13	0.275	8.05	428	21328	0

* Dithizone was dissolved in chloroform at a concentration of 0.1 gram/liter.

** All counts were for one minute

TABLE II

Count Rate Shifting in Red, Green, and Blue Windows As Affected by Quenching Value, RaD

Sample No.	Dithizone* Added, ul	Quench Value	Cpm, Red** Window	Cpm, Grn. Window	Cpm, Blue Window
1	0.0	16.04	3853	344	17
2	0.025	13.79	4062	125	10
3	0.050	12.54	3995	91	17
4	0.075	11.82	4003	59	11
5	0.100	10.91	3874	87	2
6	0.125	10.42	4085	74	2
7	0.150	9.86	4006	71	0
8	0.175	9.22	3966	82	3
9	0.200	8.78	3887	87	2
10	0.225	8.30	3929	81	0

* Dithizone was dissolved in chloroform at a concentration of 0.1 gram/liter.

** All counts were for 1 minute

TABLE III

Blank Background Corrections for Environmental Sample RaD and RaF Determinations

Method Type	No. Obsv.	Cpm, Red Window	s** r	Cpm, Grn. Window	s g	Cpm, Blue Window	s b
1	5	43.85	0.68	30.58	0.35	14.76	0.34
2	5	45.38	0.51	31.11	0.88	14.53	0.87
3	10	43.71	0.87	30.62	1.69	14.35	0.96
4	10	46.02	1.21	30.72	1.85	16.06	1.06

** 1 sigma standard deviation

Note: Types 1 & 2 blanks are for older procedures used in water analysis.

and beta particles, and gamma rays. The source of this contamination is probably due to the larger amounts of NaOH which are used in the type 4 method. This conclusion is supported by the difference between type 4 and type 3 blanks; the latter not using NaOH in such large quantities. Another source of contamination may be the larger quantities of HNO_3 used in type 4 method.

Decay Corrections

All samples were corrected for the decay and build-up of RaF and the decay of RaD. Since the time lag between the collection of a sample, its preparation, and its time of analysis varied from several days to over one year in some cases, the proportion of supported and unsupported RaF in biotic components and water would be expected to change to a degree dependent on this time lag. Correction for the decay of RaD although small was computed by taking the quotient:

$$A_{\cdot} = A/e^{-\lambda_1 t},$$

where;

$A_{\cdot}$ = RaD activity at the time of collection, cpm

λ_1 = the RaD decay constant in day^{-1} (equal to ln2/(22 X 365)

A = RaD activity at time of analysis, cpm

t = time lag between collection and analysis, days

Correction for the build-up of RaF due to decay of RaD was performed by subtracting the ingrowth term from the amount present at the time of analysis:

$$A_i = (A/e^{-\lambda_1 t})\ (1.0 - e^{-\lambda_2 t})$$

$$A_{\cdot\cdot} = (A_u - A_i)/e^{-\lambda_2 t}$$

where:

A_i = RaF activity ingrowth in the sample from decay of RaD

λ_2 = the RaF decay constant in day^{-1} (equal to ln2/138.4)

A_u = the supported and unsupported RaF present in the sample at the time of analysis

A_{oo} = the RaF activity in the sample at the time of collection

The second RaF equation above merely converts the observed amount of RaF in the sample to the time of collection. If secular equilibrium existed in the sample before analysis, then the RaD/RaF count ratio would be very close to unity. If, however, the time interval between collection and analysis was such that the initially present RaF decayed below the sensitivity of the detector, then this adjustment would indicate an absence of this radionuclide at the time of collection which may or may not have been the case. Also the error term for this calculation would be significantly larger than for determining RaD or RaF alone, hence, long intervals of time between the collection and analysis of a sample were avoided wherever possible.

Finally, a correction for the amount of RaE produced in a sample after the second extraction and during counting was applied to the data by lumping it with the amount of RaE which was unavoidably extracted into the counting medium at pH = 4.0. This topic will be covered in a later section.

Extraction Efficiencies

A key factor in the determination of RaD and RaF in environmental samples was the development of liquid extraction techniques which could remove interferring RaE activity from that of these two radionuclides as well as other contaminants. Another report[3] gave

a procedure for isolating RaD in D2EHPA after having been previously separated from a RaDEF standard solution using anion exchange resin. Because of the problems encountered using an ion exchange column, a new technique using liquid ion exchange medium exclusively was developed to effect these separations as previously described. Two procedures (type 3 & 4) and the other two (type 1 & 2) have been referred to in the section on blank corrections. The latter procedures involve a double extraction: the RaDEF is first extracted from 1N HNO_3 (60 ml) which has been partially neutralized to pH - 4.0 with 10N NaOH (about 10 ml). The organic phase (20 ml D2EHPA, 20% v/v in toluene) containing RaDEF and other radionuclides is then placed in 1N HCl (60 ml), the pH is adjusted to 2.0 with NaOH to remove RaE and other contaminants, and is then discarded. The aqueous phase is contacted with new organic medium and the pH is adjusted to 5.0 with NaOH. The organic phase is then treated as previously described for the analysis of RaD and RaF. A total of 1 gram of $NH_2OH \cdot HCl$ is added to these samples: $\frac{1}{2}$ gram during the first extraction out of HNO_3, and $\frac{1}{2}$ gram during the next two extractions out of HCl. Table IV gives the results of some of our recovery experiments for these procedures. As mentioned earlier types 3 & 4 for water and other environmental samples, respectively, were our final selection of methods. It should be noted that the pH adjustment for both these methods is very critical during the first extraction procedure as can be seen by inspection of recoveries for type 3 and type 3A standards. The latter first extraction was conducted at pH = 1.3 while the former was conducted at pH = 1.1. The amount of RaF which is taken up by

TABLE IV

Recovery And Separation Expériments Of RaDEF From Blank solutions of Types 1, 2, 3, and 4*

No. Sample	Type Blank	% Rec. RaD	% Rec. RaF	% Rec. RaE
1	1	53 (5)	74 (4)	12 (9)
2	1	73 (4)	73 (4)	26 (4)
3	1	74 (4)	77 (4)	20 (5)
4	2	49 (5)	84 (5)	14 (12)
5	2	43 (6)	70 (5)	12 (12)
6	3	84 (4)	63 (4)	11 (7)
7	3	88 (4)	68 (4)	11 (7)
8	3	88 (4)	64 (4)	13 (7)
9	4	78 (4)	79 (4)	20 (4)
10	4	69 (4)	81 (4)	32 (3)
11	4	74 (4)	78 (4)	29 (3)
12	3A**	89 (4)	26 (5)	15 (40)
13	3A	79 (4)	36 (5)	30 (20)
14	3A	87 (4)	34 (5)	5 (13)

* Solutions were spiked with 5000 cpm each of RaD, RaE, and RaF from standard RaDEF solution.

** Type 3A blanks were identical to type 3 blanks except that the first extraction to remove RaE was performed at pH = 1.3 rather than at pH = 1.1.

D2EHPA increases substantially within this pH range which results in lower RaF recoveries in the second extraction due to its absorption in the first contact at the lower pH values. The recovery of RaD, however, is not affected significantly. The addition of NH_2OH prior to phase contact at the lower pH values lowers the amount of RaF which is removed during this step. About 10% of the RaF is removed during the first extraction at pH - 1.1.

The amount of Ca^{++} present in a sample of most environmental samples excluding bone and some soils does not affect the recoveries of RaD and RaF. However, a precipitate will form in the second extraction at pH - 4.1 (types 3 & 4) if concentrations of Ca^{++} are greater than about 4000 ppm and the recoveries of both RaD and RaF are lessened considerably. Hence, the fusion technique or the technique for water as such are not generally applicable to this type of sample. As a rule any sample which gives a visible precipitate (a colloidal appearance can be excluded) will give lower recoveries of both these radionuclides. One method which was developed to cope with this problem was to precipitate the calcium salts out of solution at pH - 4.5 after the initial RaE separation at pH - 1.1. The precipitate was then redissolved in 0.1N HNO_3 and extracted as before at pH - 4.0 using NaOH to neutralize the acid. <u>However</u>, the pH must be adjusted very gradually with the organic phase present to present re-precipitation and loss of these radionuclides (this ordinarily requires about 20 minutes instead of the usual 3 minutes for equilibration to occur). Samples up to at least 7000 ppm (equivalent to about 1 gram $Ca_3(PO_4)_2$/sample) can be analyzed by this method with about the same chemical re-

coveries as noted before for type 4 samples.

The presence of large amounts of silica and silicic acid in environmental samples such as soils and some water evaporates also may present problems with type 3 and type 4 extraction procedures. This problem arises because not all of the soluble silicates and/or silicic acid or silica resulting from the acidification part of the fusion procedure is removed in the centrifugation process or in the first extraction step. As a consequence, these substances interfere with proper phase separation at pH 4.0, and the two phases may need to be centrifuged apart. RaD and RaF recoveries are not noticeably affected except when a small amount of calcium salts precipitate out with it. A small amount of silica dispersed in the organic phase also does not interfere with the recovery of these two radionuclides. Our experiments indicate that up to 3000 ppm silica...etc. (which appears to be the solubility limit for silica in the acidified fusion solution) can be separated without centrifugation.

Samples containing both significant quantities Ca^{++} and silicates are most difficult to analyze by type 4 procedure. However, a preliminary precipitation as described for high Ca samples, and redispersement of the precipitate in 0.1N HNO_3 and extraction at pH 4.0 can also yield high recoveries of RaD and RaF. Again the addition of NaOH must be very slow to make the final adjustment. Sample blanks containing as much as 7000 ppm Ca^{++}, and 3000 ppm silica have been successfully analyzed by this method. Consequently, one gram bone samples prepared by the fusion method can be analyzed by type 4 procedure, or a type 3 procedure can be worked out as

well without any loss in separation efficiencies for the radionuclides of interest.

The fusion technique described previously also causes losses of RaF from a sample. Our procedure involves a maximum temperature of about 500°C during the fusion, however, a lower temperature is probably satisfactory: the NaOH melt requires a temperature of 319°C to remain molten, and to char the organic matter present in the sample. In addition the added $NaNO_3$ requires a temperature of 380°C to decompose and begin oxidation of the charred organic matter. A temperature of between 400-450°C appears adequate for this purpose, although we were not able to test the hypothesis. A lower fusion temperature would lower the amount of RaF lost through volatilization.

Three experiments involving fusions spiked with RaDEF solution yielded an average recovery for RaF of 60(4)% which indicates that about 40% of this radionuclide is volatilized during the fusion procedure at 500°C. The RaD yields were not significantly affected by this process, although some losses of RaE were recorded. Five experiments on environmental samples of leaves, deer droppings, deer mice, trout, and harvester ants which were spiked with RaDEF solution post-fusion yielded an average recovery of 82(7)% for RaD and 74(8)% for RaF. Hence, recoveries of 40-50% overall are expected to occur for RaF for the entire fusion-extraction process. RaD recoveries almost entirely dependent on the liquid extraction procedure with D2EHPA.

Decontamination From Other Radionuclides

The selectivity of D2EHPA for the alkaline earths (excluding Ra) has been well established by McDowell[4]. At the pH of the second

extraction in our procedure it is not expected that Sr-90 would be taken up very effectively by D2EHPA; Ra-226 would also be expected to fall into this category at pH 4.0. Contamination from U-238 and daughters Th-234, Pa-234, and U-234 was also not expected in the second extraction since these radionuclides bind very strongly to D2EHPA in acid media comparable of the pH of our first extraction step[5]. The tri-positive radionuclide Y-90 was expected to extract with the RaE in the first extraction. Table V gives the results of decontamination experiments with these radionuclides mentioned above. In the case of the radium experiment the activity was allowed to decay for 300 minutes to remove short-lived activity. The extraction in the first step (pH 1.1) had a window distribution almost identical to RaE. If it is assumed that the latter radionuclide was RaE, then the amount of Ra-226 present in the first two windows of the second extraction can be considered negligible (RaD), and the RaF present in this solution as a result of ingrowth would occupy the blue window. The overall contamination due to Ra-226 would thus be reduced to about 3% and all of this would be restricted to the third window at normal quenching values for the samples.

The experiment involving U-nitrate shows an almost quantitative removal of U-238, Th-234, Pa-234, and U-234. The residual activity appears to be derived from contamination of funnel and glass electrodes of the pH meter; also incomplete separation of the phases at pH 1.1, as well as absorbed radionuclides. It does not appear to be a significant source of contamination.

Sr-90 decontamination results are not as clearly defined as those radionuclides previously considered. It is noted that the

TABLE V

Decontamination Experiments On Liquid Extraction Procedures Involving Radionuclides Found in Environmental Samples

Isotope Used	Amount Added Cpm	Cpm Recovered 1st Extr.	Cpm Recovered 2nd Extr.	Percent Rec. 2nd Extr. By Window Red	Green	Blue
Ra-226 + daughters	110000[1]	9672	21782	6.4	2.2	11.0
U-238 + daughters	444000[2]	396935	10576	0.4	0.7	1.1
Sr-90 + Y-90	966[3]	114	211	2.3	10.5	8.7

1. Ra-226 was stored in polyethylene bottle @ 0.1 uCi/ml and contained an unknown quantity of both short and long-lived daughters RaABCC'C''DEF (see text).
2. 0.316 grams of Uranium nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ to give about 111,000 dpm each of U-238, Th-234, Pa-234, and U-234.
3. A Sr-90 standard solution containing 483 dpm/ml of solution in secular equilibrium with Y-90.
4. Both of the aliquots taken from the standard solutions and the uranium nitrate were placed in fusion blank solutions of type 4 (see text).

distribution of counts in both the first and second extractions are very similar. This probably indicates that Sr-90 is not actively removed by the D2EHPA at either pH 1.1 or 4.0, and that Y-90 is not completely removed by the first extraction as expected. As can be seen in Table V most of the activity is concentrated in the green and blue windows of the analyzer with a spectral distribution similar to that of RaE.

If one assumes that the levels of Sr-90 in the soils of this area are about 1 dpm/gram[6], then the analysis of a soil sample for RaD and RaF would result in a count rate increase of about 0.2 cpm in the blue window and about one-fourth that in the red window where the majority of RaD counts occur. In the absence of significant fallout from nuclear bomb detonations during the last few years, the Sr-90 levels in plants are highly dependent on that present in soils. Although plants are slight concentrators of Sr-90 from soils, particularly in soils with low Ca concentrations, these levels will be highly dependent on the total amount of Ca in the sample analyzed as well as the amount of Ca in the soil. It is not expected that plants will contain Sr-90 in higher concentrations than does the surrounding soil, although there may be exceptions particularly over areas that are very granitic. Bone may be an exception because of its high Ca content with respect to that for most soils, and by the fact that it is derived from food-chain transfer. The levels of Sr-90 in trout skeletons from high mountain lakes were seen to vary considerably depending on the Ca concentration of the water[7] (5 - 200 pCi/gram with a mean of 46 pCi for about 20 lakes). The concentrations were found to be inversely related to

Ca concentrations and lakes with Ca levels of about 20 ppm had trout with Sr-90 burdens in their skeletons of about 5 - 10 pCi/gram ash. Since most of the data for this research has been conducted from areas where the water and other environmental samples have been far removed from the snowpack, and where ground water has contributed to the mineral content of the water, it is expected that the levels of Sr-90 in trout bone and that from other animals would fall into the lower range of values reported by these authors. Even lower values can be expected because of the absence of significant fallout, the difference in fallout between Colorado and New Mexico, and the geological differences between the two states in terms of limestone abundance in the high country. Finally, our samples containing bone were homogenates of entire animal carcasses which in effect lowered the amount of bone analyzed/sample. An estimate of between 0.2 - 0.5 cpm increase in count rate in the blue window due to Y-90 in made on the basis of available information from the study area for osseous tissue, and plants from locations of low soil Ca. Reduction of this error by computer techniques will be described in the next section.

RaD - RaF Concentration Calculations And Discussion of Error

The concentration of RaD and RaF in a Given sample was calculated by computer programming which incorporated all correction information, quench spectral shifts, and the proper conversion factors. In addition this program provided a systematic calculation of error during the reduction of data to the final form. The products of statistics were treated in the following manner:

$$A(a) \times B(b) \times C(c) \times D(d)\ldots = ABCD\ldots(E)$$

where,

$a,b,c,d,\ldots$ = the standard error of the statistic $A,B,C,D,\ldots$

E = the standard percent error of the product $ABCD\ldots$, which was computed in the following manner:

$$E = ((a/A)^2 + (b/B)^2 + (c/C)^2 + (d/D)^2 + \ldots)^{\frac{1}{2}}$$

In most cases products of statistics were part of or could be reduced to a linear combination:

$$D(d) + F(f) + G(g) + H(h) + \ldots = (D + F + G + H + \ldots)(E')$$

where

$d,f,g,h,\ldots$ = the standard error of a statistic $D,F,G,H,\ldots$

E' = the standard error of the sum $D + F + G + H + \ldots$ which was computed in the following manner:

$$E' = (d^2 + f^2 + g^2 + h^2 + \ldots)^{\frac{1}{2}}$$

The program would compute the standard percent error from products of statistics, convert them to standard errors, and combine them linearly as described above. A check was provided to see if any statistic was equal to or less than zero: if such were the case both the statistic and its standard error were reset to zero to exclude it from further calculations. If the final value attained for the calculation was not significantly different at the 68% confidence level, then it would be reflected in the final calculation of its error.

Three types of error were considered for the initial variables entered into the program: calculable errors such as count rate, regression line errors for spectral changes, and errors which were estimated with the amount of information known to affect the variance. Calculated errors concerned with counting statistics

were arrived in the following manner:

$$a = (Cpm_A/t_A)^{\frac{1}{2}}$$

where,

a = standard error of count rate A

Cpm_A = count rate of sample A + background count rate in counts/min

t_A = count interval in minutes

Mean regression line errors were obtained by calculating or estimating the error of the regression line throughout the range of the data, and then arriving at a mean value for inclusion into the program. For the RaD spectral equation the error amounted to about 2% while for RaF shifts the error was about 5%. The errors due to blanks were calculated from the estimates obtained by experimental determinations as were the errors due to chemical recoveries for RaD and RaF. The latter were estimated at about 4% while the blank correction errors are given in the text for the various types of samples.

The program also corrected the data for the small amount of RaE which was not separated in the first extraction and appeared with the RaD and RaF in the final extraction. The proportion of RaE scintillations gave electronic pulses which were distrubed in a 14:66:20 percentage ratio at Q = 16 for red, green, and blue windows, respectively as mentioned earlier. The count rate in the green window was determined by the program and the other two were corrected by using the ratio 18:60:22 as a compromise for spectral shift and for the small amount of Y-90 present primarily in the blue window. The latter would over-correct for samples containing

insignificant Y-90. The program also incorporated the stable lead determinations to produce the desired ratios: RaD/Pb and RaF/Pb in fCi/pb or fCi/ppm.

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RESULTS AND DISCUSSION

RaD, RaF, and Stable Lead In Environmental Samples

While All radionuclide analyses are covered in this section, only those stable lead analyses will be discussed which have accompanying RaD and RaF determinations performed on the samples. Discussion of a larger body of information concerning stable lead in the study area will be reserved for another section of this report.

The concentrations of RaD and RaF in various abiotic and biotic components of northern New Mexico ecosystems in addition to other pertinent information are presented in Table VI. Only those values which are significantly different from zero at the 32% level are reported; all others are reported as non-detectable values. The concentration of RaD in surface and some ground waters of the study area ranged from non-detectable (N.D.) values 16% of the time to a maximum value of 4565 fCi/liter in water from the Mora River during one sampling interval. The mean concentration was calculated at 1286 (1120) fCi/liter for the samples analyzed. Similarly, the samples contained RaF from N.D. values in 38% of the analyses to a maximum of 17164 fCi/liter for a sample from the west end of the Santa Fe River. The mean concentration for RaF in the water samples analyzed was calculated at 962 (1696) fCi/liter. All of these samples were collected at a mean elevation of 7666 (1970) feet above sea level with a range from about 12,000 to 5,900 feet.

The concentration of RaD and RaF in samples other than water

TABLE VI

Pb^{210} and Po^{210} Concentrations in Some Rivers, Lakes and Other Environmental Components of Northern New Mexico.

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV. (ft.)
Agua Piedra	Water	539.0 (36)	770.0 (74)	8.175 l.	12-20-73	9000
Black Lake	Water	948.0 (9)	33.0	4.450 l.	12-20-73	8530
Lower Charette	Water	787.0 (18)	N.D.	8.036 l.	3-23-73	6600
Upper Charette	Water	323.0 (62)	N.D.	8.241 l.	3-23-73	6600
Cimarron River	Water	189.0 (89)	5971.0 (45)	8.191 l.	3-23-73	7000
Cimarron River	Water	N.D.	N.D.	4.320 l.	3-23-73	7000
Costilla Lake	Pine Needles	21641.0 (5)	2643.0 (13)	1.000 g/ash	8-1-73	9900
Costilla Lake	Leaves	N.D.	27.0 (4)	4.550 g.	8-1-73	9900
Costilla Lake	Litter	1836.0 (20)	N.D.	57.200 g.	8-1-73	9900
Costilla Lake	Forbs	329.0 (39)	N.D.	100.000 g.	8-1-73	9900
Costilla Lake	Mixed Grasses	2043.0 (13)	10212.0 (11)	57.400 g.	8-1-73	9900
Costilla Lake	Deer Droppings	1437.0 (24)	9428.0 (16)	63.000 g.	8-1-73	9900
Costilla Lake	Mixed Grasses	1910.0 (14)	5213.0 (15)	57.400 g.	8-1-73	9900
Costilla Lake	Mixed Grasses	1894.0 (9)	N.D.	76.400 g.	8-1-73	9900
Costilla Lake	Leaves	N.D.	N.D.	74.500 g.	8-1-73	9900
Costilla Lake	Forbs	206.0 (42)	572.0 (44)	100.000 g.	8-1-73	9900
Costilla Lake	Leaves	7339.0 (5)	N.D.	74.500 g.	8-1-73	9900
Costilla Lake	Moss	15643.0 (6)	N.D.	55.800 g.	8-1-73	9900

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV.(ft.
Costilla Lake	Trout	N.D.	N.D.	157.400 g.	8-1-73	9900
Costilla Lake	Trout	N.D.	N.D.	183.200 g.	8-1-73	9900
Costilla Lake	Mixed Grasses	1986.0 (12)	N.D.	133.800 g.	8-1-73	9900
Costilla Lake	Deer Droppings	683.0 (48)	1042.0 (61)	63.000 g.	8-1-73	9900
Costilla Lake	Forbs	N.D.	N.D.	100.000 g.	8-1-73	9900
Costilla Lake	Deer Droppings	2043.0 (17)	N.D.	63.000 g.	8-1-73	9900
Costilla Lake	Water	1024.0 (35)	N.D.	7.700 l.	8-1-73	9900
El Porvenir	Water	486.0 (25)	171.0 (46)	8.500 l.	8-10-73	7640
Gallinas	Water	2706.0 (21)	481.0 (31)	4.100 l.	10-25-73	6450
Gallinas River	Water	731.0 (27)	N.D.	7.500 l.	8-10-73	6450
Frazer Mountain	Mixed Grasses	1682.0 (16)	N.D.	742.000 g.	7-21-73	12163
Gascon Creek	Water	2909.0 (21)	1111.0 (31)	4.102 l.	10-25-73	8000
Laboratory	Trout	196.0 (4)	N.D.	78.000 g.		6450
Laboratory	Mice (Ash)	N.D.	N.D.	5.000 g.	7-4-74	6450
Laboratory	Mice	N.D.	N.D.	5.000 g.	7-4-74	6450
Lake Katherine	Water	1622.0 (6)	N.D.	8.420 l.	7-27-73	11700
Lake @ Maxwell	Water	420.0 (18)	N.D.	4.400 l.	7-31-73	6000
Las Vegas	Soil	5754.0 (4)	522.0	5.000 g.	6-27-73	6450
Las Vegas	Shortening	N.D.	N.D.	5.000 g.	7-2-74	6450

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV (ft.)
Las Vegas	Tap Water	N.D.	N.D.	9.150 l.	3-21-74	6450
Las Vegas	Ants	N.D.	N.D.	7.130 g.	10-12-73	6450
Lower Pecos River	Water	3009.0 (28)	1435.0 (42)	4.380 l.	6-8-73	7000
Montezuma Hot Springs	Water	935.0 (14)	379.0 (25)	7.450 l.	8-10-73	7000
Mora River@Bridge	Water	N.D.	934.0 (76)	4.675 l.		7785
Mora River	Water	460.0 (32)	904.0 (47)	7.150 l.	3-23-73	7785
Mora River@Bridge	Water	4565.0 (5)	N.D.	4.675 l.		7785
Mount Walter	Mixed Grass & Moss	2010.0 (19)	N.D.	794.800 g.	7-21-73	9000
Murphey Lake	Water	N.D.	607.0 (42)	8.040 l.	12-20-73	7880
Nambe River	Water	2343.0 (15)	1313.0 (26)	7.450 l.		7000
Nambe River	Water	N.D.	1.0 (4)	4.550 l.		7000
Pecos River	Water	N.D.	N.D.	4.050 l.	6-18-73	8000
Puerto Nambe	Pine Needles	38070.0 (5)	6028.0 (9)	1.000 g./Ash		7000
Red River (Moly)	Water	326.0 (58)	N.D.	7.795 l.	12-20-73	13000
Red River	Water	225.0 (54)	307.0 (36)	12.200 l.	8-23-73	9000
Red River	Water	559.0 (28)	297.0 (50)	12.100 l.	8-23-73	9000
Red River Pond	Water	356.0 (33)	30.0 (40)	12.300 l.	8-23-73	9000
Rio Frijole	Water	N.D.	N.D.	8.750 l.	9-8-73	8000
Rio Frijole	Water	2819.0 (25)	61.0 (62)	4.090 l.	11-3-73	8000
Rio La Casa	Water	1344.0 (13)	N.D.	8.565 l.	12-20-73	8000

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV.(ft)
Rio Lucio	Water	2614.0 (14)	432.0 (23)	4.000 l.	11-3-73	7500
Rio En Medio	Water	1225.0 (30)	1464.0 (70)	4.222 l.	11-3-73	7000
Rio Nambe	Water	2960.0 (27)	772.0 (38)	3.526 l.	11-3-73	7000
Rio Santa Barbara	Water	942.0 (21)	N.D.	8,540 l.	2-20-73	9000
Rio Santa Barbara	Water	N.D.	N.D.	4.350 l.	7-31-73	9000
Rio Santa Barbara	Water	2907.0 (27)	1615.0 (25)	3.580 l.	11-21-73	9000
Santa Cruz Lake	Water	1755.0 (11)	N.D.	8.500 l.	9-8-73	7180
Sapello Creek	Water	3237.0 (5)	1193.0 (5)	4.497 l.	10-25-73	7000
Sapello Creek	Water	N.D.	1687.0 (43)	4.700 l.		7000
Springer Lake	Water	N.D.	1414.0 (8)	7.425 l.	3-23-74	5900
Storrie Lake	Sediment	N.D.	10321.0 (41)	283.800 g.	6-1-73	6840
Trampas	Water	1781.0 (49)	1414.0 (33)	4.039 l.	11-3-73	9720
Tres Ritos	Water	2054.0 (34)	1942.0 (35)	4.450 l.	6-8-73	9113
Tres Ritos	Water	N. N.D.	1628.0 (57)	5.000 l.	6-8-73	9113
Tres Ritos L.L.	Water	1479.0 (46)	N.D.	4.634 l.	10-25-73	9113
Stublefield Lake	Water	1163.0 (28)	N.D.	4.320 l.	7-31-73	6000
Canadian River	Water	1856.0 (20)	N.D.	4.087 l.	7-31-73	6135

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV. (ft.)
Taostas (snow)	Water	2020.0 (11)	N.D.	2.480 l.	2-22-73	8880
Ute Lake E. of Dam	Water	N.D.	8491.0 (48)	4.550 l.	7-28-73	6000
Storrie Lake	Water	251.0 (56)	548.0 (80)	8.061 l.	4-24-74	6840
Springer Lake	Water	1624.0 (21)	5699.0 (36)	4.150 l.	7-31-73	5900
Cimarron River	Water	2866.0 (15)	N.D.	3.390 l.	7-31-74	7000
Lower Charette	Water	N.D.	N.D.	4.400 l.	7-30-73	6600
Rio Pueblo	Water	1560.0 (22)	3794.0 (44)	4.110 l.	7-30-73	8800
Montezuma	Bat Urine	41.0 (28)	N.D.	60.000 l.	7-16-74	7000
Montezuma	Bats	126.0 (32)	152.0 (38)	54.000 g.	7-16-74	7000
Montezuma	Bat Guano	487.0 (6)	N.D.	71.100 g.	7-16-74	7000
Las Vegas	Pine Needles	N.D.	N.D.	142.000 g.	7-15-74	6450
Las Vegas	Pine Needles	N.D.	N.D.	72.000 g.	7-15-74	6450
Las Vegas	Pine Needles	5.0 (6)	N.D.	153.000 g.	7-30-74	6450
Las Vegas	Oil (old)	131.0 (6)	N.D.	5.000 g.	7-30-74	6450
Costilla Lake	Deer Mice	267.0 (4)	N.D.	16.300 g.	8-1-73	9900
Coyote	Sediment	1826.0 (8)	268.0 (67)	120.000 g.	8-2-74	7500
Laboratory	Trout	96.0 (8)	N.D.	179.200 g.	8-1-73	6450
Costilla Lake	Litter	552.0 (18)	N.D.	1.000 g.	8-1-73	9900

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV.(ft.)
Costilla Lake	Trout	59.0 (16)	N.D.	168.900 g.	8-1-73	9900
Costilla Lake	Trout	N.D.	N.D.	329.200 g.	8-1-73	9900
Costilla Lake	Trout	90.0 (10)	N.D.	216.000 g.	8-1-73	9900
Las Vegas	Ants-Harvester	N.D.	N.D.	7.150 g.	10-12-73	6450
Las Vegas	Ants	N.D.	N.D.	32.000 g.	6-23-74	6450
Las Vegas	Ants	23.0 (59)	N.D.	32.000 g.	6-23-74	6450
Las Vegas	Soil	29.0 (4)	N.D.	18.500 g.	6-24-74	6450
Las Vegas	Ants	N.D.	N.D.	32.000 g.	6-23-74	6450
Las Vegas	Ants	166.0 (17)	N.D.	5.000 g.	7-7-74	6450
Las Vegas	Horned Toads	66.0 (7)	N.D.	78.750 g.	6-20-74	6450
Las Vegas	Soil	411.0 (9)	N.D.	120.000 g.	6-25-74	6450
Las Vegas	Ants	N.D.	315.0 (14)	20.000 g.	7-7-74	6450
Las Vegas	Ants	N.D.	N.D.	42.000 g.	7-7-74	6450
Las Vegas	Ants	103.0 (12)	N.D.	42.000 g.	7-7-74	6450
Las Vegas	Oil (new)	N.D.	N.D.	5.000 g.	7-30-74	6450
Elk Mountain	Water	3942.0 (24)	4409.0 (55)	19.000 l.		11800
Murphey Lake	Trout	N.D.	N.D.	107.000 g.	8-1-74	6450
Sapello River	Water	N.D.	N.D.	8.200 l.	4-24-74	7000
Maestas Creek	Water	N.D.	N.D.	8.700 l.	4-24-74	8880

TABLE VI (cont.)

LOCATION	TYPE	Pb^{210} fCi/l.(g.)	Po^{210} fCi/l.(g.)	ORIG. QUANT.	DATE COLLECTED	ELEV.(ft.)
Gascon Creek	Water	316.0 (15)	N.D.	8.300 l.	4-24-74	8000
Santa Fe River, East	Water	817.0 (13)	17764.0 (8)	8.300 l.	8-8-73	8000
Santa Fe River, West	Water	537.0 (19)	7035.0 (16)	7.800 l.	8-8-73	8000
Las Vegas	Water	623.0 (15)	739.0 (35)	9.000 l.	2-20-74	6450
Mora River	Water	133.0 (38)	N.D.	8.000 l.	4-24-74	7785
Costilla Lake	Soil	496.0 (6)	N.D.	18.500 g.	8-1-73	9900

TABLE VII

Pb^{210}/Pb and Po^{210}/Pb Ratios in Some Biotic and Abiotic Components of Northern New Mexico

LOCATION	TYPE	Pb^{210}/ppm	Po^{210}/ppm	DATE COLLECTED	ppm	ELEVATION (FT.)
Costilla Lake	Pine Needles	15457.0	1883.0	8-1-73	1.4	9900
Costilla Lake	Leaves	N.D.	10.0	8-1-73	2.7	9900
Costilla Lake	Litter	227.0	N.D.	8-1-73	8.1	9900
Costilla Lake	Forbs	1645.0	N.D.	8-1-73	0.2	9900
Costilla Lake	Mixed Grasses	10217.0	51058.0	8-1-73	0.2	9900
Costilla Lake	Deer Droppings	2847.0	18857.0	8-1-73	0.5	9900
Costilla Lake	Mixed Grasses	6366.0	17375.0	8-1-73	0.3	9900
Costilla Lake	Mixed Grasses	306.0	N.D.	8-1-73	6.2	9900
Costilla Lake	Leaves	N.D.	6477.0	8-1-73	0.3	9900
Costilla Lake	Forbs	86.0	283.0	8-1-73	2.4	9900
Costilla Lake	Leaves	7339.0	N.D.	8-1-73	N.D.	9900
Costilla Lake	Moss	3815.0	N.D.	8-1-73	4.1	9900
Costilla Lake	Trout	N.D.	N.D.	8-1-73	0.9	9900
Costilla Lake	Trout	N.D.	N.D.	8-1-73	3.3	9900
Costilla Lake	Mixed Grasses	903.0	N.D.	8-1-73	2.2	9900
Costilla Lake	Deer Droppings	683.0	1042.0	8-1-73	N.D.	9900

TABLE VII (cont.)

LOCATION	TYPE	Pb^{210}/ppm	Po^{210}/ppm	DATE COLLECTED	PPM.	ELEVATION (FT.)
Costilla Lake	Forbs	N.D.	16.0	8-1-73	0.05	9900
Costilla Lake	Deer Droppings	6810.0	N.D.	8-1-73	0.3	9900
Frazer Mountain	Mixed Grasses	94.0	N.D.	7-21-73	9.7	12163
Laboratory	Mice (Ash)	N.D.	N.D.	7-4-74	0.1	6450
Laboratory	Mice	N.D.	2.0	7-4-74	0.1	6450
Laboratory	Trout	68.0	N.D.		2.9	6450
Las Vegas	Soil	5754.0	522.0	6-27-73	N.D.	6450
Las Vegas	Shortening	N.D.	4.0	7-5-74	0.2	6450
Las Vegas	Ants	N.D.	N.D.	10-12-73	4.3	6450
Mount Walter	Mixed Grasses	1117.0	N.D.	7-21-73	1.8	9000
Puerto Nambe	Pine Needle (Ash)	21150.	3348.0		1.8	7000
Storrie Lake	Sediment	N.D.	2517.0	6-1-73	4.1	6450
Montezuma	Bat Urine	9.0	N.D.	7-16-74	4.4	6450
Montezuma	Bats	15.0	18.0	7-16-74	N.D.	6450
Montezuma	Bat Guano	70.0	N.D.	7-16-74	7.0	6450
Las Vegas	Pine Needles-Old	N.D.	N.D.	7-15-74	3.6	6450
Las Vegas	Pine Needles-New	N.D.	N.D.	7-15-74	13.6	6450
Las Vegas	Pine Needles-Old	3.0	N.D.	7-30-74	1.4	6450

TABLE VII (cont.)

LOCATION	TYPE	Pb^{210}/ppm	Po^{210}/ppm	DATE COLLECTED	ppm.	ELEVATION (FT.)
Las Vegas	Oil (Used)	16.0	N.D.	7-30-74	8.0	6450
Costilla Lake	Deer Mice	205.0	N.D.	8-1-73	1.3	9900
Coyote	Sediment			8-1-73	Tr.	7500
Laboratory	Trout	188.0	N.D.	8-1-73	0.51	6450
Costilla Lake	Litter	173.0	N.D.	8-1-73	3.19	9900
Costilla Lake	Trout	2808.0	N.D.	8-1-73	0.0325	9900
Costilla Lake	Trout	N.D.	N.D.	8-1-73	0.1949	9900
Costilla Lake	Trout	7246.0	N.D.	8-1-73	0.0081	9900
Las Vegas	Harvester Ants		N.D.	10-12-73	N.D.	6450
Las Vegas	Harvester Ants			6-23-74	N.D.	6450
Las Vegas	Harvester Ants	6.0	N.D.	6-23-74	4.1	6450
Las Vegas	Soil	8.0	N.D.	6-24-74	3.57	6450
Las Vegas	Harvester Ants	N.D.	N.D.	6-23-74	0.51	6450
Las Vegas	Harvester Ants	205.0	N.D.	7-7-74	0.81	6450
Las Vegas	Horned Toads	6600.0	N.D.	6-20-74	0.011	6450
Las Vegas	Soil	122.0	N.D.	6-25-74	3.36	6450
Las Vegas	Harvester Ants	N.D.	583.0	7-7-74	0.54	6450
Las Vegas	Harvester Ants	25.0	67.0	7-7-74	0.53	6450
Las Vegas	Harvester Ants	195.0	N.D.	7-7-74	0.53	6450

TABLE VII (cont.)

LOCATION	TYPE	Pb^{210}/ppm	Po^{210}/ppm	DATE COLLECTED	ppm.	ELEVATION(FT.)
Las Vegas	Oil (New)	N.D.	N.D.	7-30-74	1.6	6450
Murphey Lake	Trout	N.D.	N.D.	8-1-74	N.D.	7880
Costilla Lake	Soil	488.0	N.D.	8-1-73	0.081	9900

TABLE VIII

Pb^{210} and Po^{210} Ratios In Some Rivers, Streams and Lakes of Northern New Mexico.

LOCATION	Pb^{210}/ppb	Po^{210}/ppb	DATE COLLECTED	ppb.	ELEVATION (FT.)
Agua Piedra	67338.0	96248.0	3-23-73	0.0080	9000
Cimarron River	401.0	12705.0	3-23-73	0.4700	7000
Gallinas	338310.0	61386.0	10-25-73	0.0080	6450
Gascon Creek	242420.0	92549.0	10-25-73	0.0120	8000
Las Vegas	14480.0	30167.0	3-21-74	0.0028	6450
Lower Pecos River	158369.0	75529.0	6-8-73	0.0190	7000
Mora River (Bridge)	N.D.	7182.0		0.1300	7785
Mora River	153418.0	301432.0	3-23-74	0.0030	7785
Murphey Lake	10511.0	18971.0	12-20-73	0.0320	7869
Nambe River	167351.0	93757.0		0.0140	7000
Pecos River	N.D.	47159.0	6-18-73	0.0190	8000
Red River (Moly)	69386.0	27172.0	12-20-73	0.0047	9000
Rio Frijole	2818954.0	60920.0	11-3-73	0.0010	8000
Rio La Casa	17231.0	N.D.	12-20-73	0.0780	8000
Rio Lucio	25885.0	4282.0	11-3-73	0.1010	7500
Rio En Medio	408288.0	488123.0	11-3-73	0.0030	7000
Rio Nambe	95481.0	24908.0	11-3-73	0.0310	7000

TABLE VIII (cont.)

LOCATION	Pb^{210}/ppb	Po^{210}/ppb	DATE COLLECTED	ppb	ELEVATION (FT.)
Santa Barbara	5887.0	N.D.	2-20-73	0.0080	9000
Santa Barbara	581405.0	323088.0	11-21-73	0.0050	9000
Santa Cruz Lake	13199.0	N.D.	9-8-73	0.1330	7180
Sapello Creek	N.D.	67488.0		0.0250	7000
Springer Lake	N.D.	201964.0	3-23-74	0.0070	5900
Storrie Lake	N.D.	3440336.0	6-1-73	0.0030	6450
Trampas	28274.0	22879.0	11-3-73	0.0630	9720
Tres Ritos	120796.0	114241.0	6-8-73	0.0170	9113
Tres Ritos	3080.0	10855.0	6-8-73	0.1500	9113
Stublefield Lake	612354.0	N.D.	7-31-73	0.0019	6000
Canadian River	22643.0	N.D.	7-31-73	0.0820	6135
Maestas (Snow)	53155.0	N.D.	2-22-73	0.0380	8880
Ute Lake E. of Dam	5619.0	446343.0	7-28-73	0.0190	6000
Storrie Lake	83618.0	182623.0	4-24-74	0.0030	6450
Springer Lake	232047.0	814108.0	7-31-73	0.0070	5900
Cimarron River	573275.0	N.D.	7-31-73	0.0050	7000
Lower Charette	25677.0	N.D.	7-31-73	0.0040	6600
Rio Pueblo	821231.0	1996862.0	7-30-73	0.0019	7000

TABLE VIII (cont.)

LOCATION	Pb^{210}/ppb	Po^{210}/ppb	DATE COLLECTED	ppb.	ELEVATION (FT.)
Elk Mountain	3942.0	4409.0		0.23	11800
Sapello River	830.0	N.D.	4-24-74	0.56	7000
Maestas Creek	16547.0	N.D.	4-24-74	0.02	8880
Gascon Creek	1434.0	N.D.	4-24-74	0.22	8000
Santa Fe River, East	939.0	20418.0	9-8-73	0.87	8000
Santa Fe River, West	2686.0	35174.0	9-8-73	0.20	8000
Maestas (Snow)	53155.0	N.D.	2-22-73	0.03	8880
Las Vegas Tap Water	2308.0	2738.0	2-20-74	0.27	6450

TABLE IX

Correlation Matrix for Variables Used
In Regression Analysis of Water Samples.

1,2	1,3	1,4	1,5	1,6	1,7
.1117	(.2725)*	.08001	.2222	(.3585)	.0311
	2,3	2,4	2,5	2,6	2,7
	.0853	.2846	(.3656)	.1531	(.4311)
		3,4	3,5	3,6	3,7
		(.0100)	.2021	.1059	.1954
			4,5	4,6	4,7
			(.0455)	.0248	(.0508)
				5,6	5,7
				.2338	.1978
					6,7
					.1775

1 - RaD
2 - RaF
3 - Time of Collection
4 - Elevation
5 - ppb of Pb
6 - RaD/ppb
7 - RaF/ppb

* Values in parenthesis are significant at the 10% level of confidence.

collected in the study area gave mean concentrations of 1065(2584), and 620(2012) fCi/gram, respectively. The concentrations varied from N.D. for RaD and RaF to maximum values of 15643 and 10321 fCi/gram for these radionuclides, respectively. While only 36% of the samples contained N.D. levels of RaD, 75% registered N.D. levels of RaF. The mean elevation for collection of these samples (8033) was slightly higher than that for water samples because of the large contribution of samples from Costilla Lake at about 9900 feet above sea level. A small number of the samples included substances of both abiotic and biotic types were obtained from the laboratory or were collected from the vicinity of Las Vegas, New Mexico. Such items collected included were leaves from the city park, certain items from the local grocery store, and mice and trout from the laboratory. In addition, a number of harvester ants were collected from colonies around the city of Las Vegas in connection with a related study by a graduate student. Motor oil (both new and used) were also analyzed to compare with environmental samples.

Some of the information in Table VI in conjunction with the measured levels of Pb in most of the samples were used to construct RaD/Pb and RaF/Pb ratios which are presented in Tables VII, and VIII respectively for water and other environmental samples. One can appreciate immediately the large difference between Pb concentrations in water (in ppb), and those of other samples. The values of RaD/Pb range from N.D. levels to 2,818,954 fCi/ppb and 10,217 fCi/ppm for water and other environmental samples, respectively. The values reflect much larger ratios for water in general with plants and soils following in that order. A similar

trend is evident for RaF/Pb ratios, but the much larger of N.D. concentrations of RaF (about 75%) in these samples precludes any accurate description of the data. The RaF/Pb ratios varied from predominantly N.D. levels to 1,996,862 fCi/ppb and 51,058 fCi/ppm for water and other environmental samples, respectively.

The reduced data was organized for treatment by simple linear and multiple regression analysis. The variables chosen for inclusion into these analyses were:

1) RaD concentration, fCi/liter
2) RaF concentration, fCi/liter
3) Time of collection, days
4) Elevation, feet above sea level
5) ppb of Pb
6) RaD/ppb, fCi/ppb
7) RaF/ppb, fCi/ppb

The only samples analyzed by these methods were the water samples because they were the only ones collected from a broad enough geographical area, and with sufficient frequency to permit analysis of the type to be described. The time of collection was transformed into a regression variable by assigning a "day number" to each collection date. The day number was determined by comparing the time elapsed in days from a fixed reference date (May 15,1971). The day number was further transformed to correspond to a given date during one hypothetical year. That is, a given date such as August 10,1971, 72, 73, and 74 would have approximately the same day number, after allowance for the number of days in a given year. If any of the variables were to vary in cyclical manner throughout the year, then the data could be made to fit a polynomial such as:

$$X = b_0 + b_1 TC = b_2 TC^2 + \ldots$$

where,

X = variable fitted to the time period of collection

TC = the day number of the sample collection date

$b_0, b_1, b_2, \ldots$ = multiple regression coefficients.

Thus, any cyclical trend in the variable of interest in addition to other correlative variables could be embodied in an equation of the type described above.

Elevation data was read from a topographic map to the nearest 40 foot isoline; in many cases a coarser approximation was necessary. The other variables employed were taken from Table VI, VII, and VIII without any further transformation. A one to one simple regression correlation matrix was determined for these variables and is presented in Table IX. As can be seen by inspection of the table only 1/3 of these values (correlation coefficients) were significant at the 90% level of confidence. In some cases the total regression coefficient for the significant correlations were not significant beyond the zero intercept.

While a correlation between RaD concentrations and the RaD/ppb, Pb ratios was expected (1,6), the correlation between RaD concentration and the elevation of collection (1,3) proved to be one of the strongest relationships established for RaD as will be shown later in this section. RaF concentrations correlated significantly with the elevation of the sample, but not with the time of sample collection in opposition to RaD data; and the Pb concentrations in the water samples correlated very poorly (although significantly) with elevation, and with RaF as mentioned. It is interesting to note with respect to experimental design that the relationship

between the time of sample collection and the elevation (3,4) is the lowest correlation coefficient obtained whether the value was significant or not. A highly correlative relationship between these two variables would have affected any further developement of analysis utilizing multiple regression techniques. For the purpose of this discussion the only relationship which adds to our understanding of the fate of RaD in the environment is the relationship (1,3) which states:

$$RaD = 1923\ (323) - 3.359\ (1.809)\ TC,$$

$$(R=0.27;\ F=3.45,\ 1\&43\ D.F.,\ 90\%\ c.l.)$$

where,

RaD = fCi/liter of RaD

TC = day number of collection period.

Only 7.5% of the total sum of squares is explained by this variable although both the zero intercept and the partial regression coefficient are significantly different from zero at the 99 and 90% confidence levels, respectively. As will be shown RaD concentrations do not appear to correlate well with any single variable or combination of variables employed, and they probably reflect a great deal of biological and other microenvironmental variations which our simple relationships are not able to explain with the information on hand.

A general failure of simple linear regression techniques to explain the variations in RaD, RaF, and stable lead concentrations led to the consideration of finding possible interaction terms. Using the correlation matrix as a guide our efforts led to stepwise multiple regression of possible significant interaction terms

along with independent variables to find relationships which would explain these variables. Only the aforementioned variables were considered as dependant variables.

The only multiple regression (actually simple curvilinear) analysis which produced a more significant relationship with RaD concentrations than the one mentioned earlier was the regression between RaD and the day number squared.

$$RaD = 1726\ (220) - 0.028(0.005)TC^2\ ,(R=0.31;\ F=4.53\ 1\&43\ D.F.,\ 95\%\ c.l.)$$

Where RaD and TC have the same meaning as described in the previous equation. Although the zero intercept and the partial regression coefficient are significant at the 1% and 5% level of confidence, only 9.6% of the total sum of squares is explained by the regression equation. A combination of TC and TC^2 against RaD did not improve the relationship significantly, leaving only TC^2 as a possible correlate from among a wide field of interaction terms such as will be described in connection with the other two dependant variables.

RaF concentrations were subjected to multiple regression analysis as described above and after a significant number of trials a relationship was derived to best fit the data from the field of variables and interaction terms tested. This relationship may be stated as:

$$RaF = 9647(1914) + 0.03061(0.0142)(TC\ X\ ELV\ X\ PPB) - 0.3791(0.1712)ELEV - 18.84(5.549)TC - 57080(31110)PPB - 0.9329(0.3192)RaD,\ (R=0.81;\ F=6.05\ 5\&16\ d.f.,\ 99.5\%\ c.l.)$$

Where,

RaF = fCi/liter of RaF

Elv = elevation of collection site, feet above sea level.

PTB = ppb of Pb in sample of water

The zero intercept and the partial regression coefficients were all significantly different from zero at the 99.9, 97.5, 97.5, 99.9, 95, and the 99% c.l. About 65% of the total sum of the squares is accounted for by the regression equation (regression sum of squares). The synergistic three way interaction term between the time of sample collection, elevation, and stable lead concentration is interesting in that all 2-way interaction terms become insignificant upon inclusion of the 3-way term into the relationship, leaving the 1-term partials to complete the equation. The total regression coefficients of the variables contained in the above equation: (2,3), (2,4), and (2,5) as shown in Table X show agreement with respect to sign with the partials of these variables as shown in the previous equation. One exception is (2,5) where the lead concentration is positively correlated to RaF by simple linear regression, and has a negative value in the multiple regression equation (m.r.e.) as can be observed. The simple linear regression equation (s.r.e.) for RaF verses stable lead concentration is given as:

$$RaF = 1460(428) + 7933(4211)PPB \quad , (R=0.37,\ F=3.55,\ 1\&23\ D.F.,\ 90\%\ c.l.)$$

Only about 13% of the total sum of squares is accounted for by the regression sum of squares (the regression equation) in this case. A check of total regression coefficients (t.r.c.) for stable lead concentrations with other variables embodied in the m.r.c. (1,5)

(3,5), and (4,5) shows all of them to be negative. A probable explanation for sign reversal in the partial regression coefficient (p.r.c.) for RaF verses stable lead in the m.r.e. is the effective interaction of elevation, time of collection, and RaD concentration with this variable.

The t.r.c. for (2,3), and (2,4) are given in Table X as -1.761 and -0.3265, respectively, although both were insignificant at the 10% level of confidence. There is a very close identity between the partial and the total regression coefficients for RaF verses elevation in both the s.r.e. and the m.r.e. indicating a high degree of independance of this variable from the others employed in the m.r.e. Also, there is agreement in sign between t.r.c. and p.r.c. for (1,2) in both the s.r.e. and the m.r.e., although the former coefficient was insignificant at the 10% level of confidence; its value was calculated at -0.06218. Thus, it appears that the m.r.e. developed to relate to the environmental variables considered is adequate for purposes of our discussion which will be considered later in this section. It shoul be noted that a sizeable part of the residual sum of squares or unexplained error is due primarily to the counting and determination errors noted earlier in connection with the section on radiochemical analysis, as can be observed from inspection of Table VI.

The relationship between the stable lead concentrations in water and other environmental variables was the most effective "fit" attained. After a similar trial with various experimental variables consisting of interaction terms and single variables the following relationship was developed for deriving stable lead concentrations in the surface and ground waters considered in this

section:

$$PPB = 0.08898(0.02259) - 3.812(0.7085) \times 10^{-5} RaF - 4.586(1.102) \times 10^{-4} TC + 3.841(0.3915) \times 10^{-7} (RaF)(TC),$$

(R=0.92; F=43.07, 3&21 D.F., 99.9% c.l.)

The zero intercept and all p.r.c. are significantly differently different from zero at the o.1% level, and the regression sum of the squares accounts for 86% of the total sum of squares. Of interest is the independence of stable lead and RaF concentrations on RaD levels, and a very intimate relationship between stable lead concentrations and RaF levels. Again one notices a sign change difference between t.r.c. and p.r.c. in the s.r.e. and m.r.e., respectively, in the case of RaF verses stable lead concentrations (2,5); also there is a reversal noted in the case of (3,5) as shown in Table X. The synergistic effect of the interaction term noted above gives the highest test value noted throughout the test series, and hence, probably controls the relationship to a large extent compared to the interaction term of the previously considered m.r.e. relating RaF to other environmental factors. Thus, while RaF and stable lead have some relationship in the environment, there is only a partial relationship of RaF to RaD, and virtually no significant relationship of RaD to its stable counterpart which would be expected in a natural situation from known RaD/Pb in parent rock material of the substrate. RaD has only a casual relationship with the time of sample collection which appears to be quadratic in nature, however, other more subtle environmental factors appear to govern its behavior in the

TABLE X

Total Regression Coefficient Matrix.

1,2	1,3	1,4	1,5	1,6	1,7
-0.06218	(-3.359)	0.05265	-2511.0	(6.879×10^{-4})	-8.026×10^{-5}
	2,3	2,4	2,5	2,6	2,7
	-1.761	(-0.3265)	(7933.0)	-.0005579	(.002129)
		3,4	3,5	3,6	3,7
		(-5.596×10^{-4})	218.2	-1.820×10^{-5}	-4.673×10^{-5}
			4,5	4,6	4,7
			-884.9	-8.269×10^{-5}	-2.257×10^{-4}
				5,6	5,7
				-3.970×10^{-8}	-4.502×10^{-8}
					6,7
					.2418

1 -- RaD
2 - RaF
3 - Time of Collection
4 - Elevation
5 - ppb of Pb
6 - RaD/ppb
7 - RaF/ppb

* Values in parenthesis are significant at the 10% level of confidence.

watersheds studied. This decoupling of RaD from its stable counterpart as indicated by our statistical analysis poses a serious problem in trying to determine the meaning of RaD/Pb in the environment to determine the source of Pb contamination when water is used as the vector for study. Of course this phenomenon may very well be caused by some man-made disturbance of the type being studied in this research, and another experimental design could attempt to explain the anomaly.

The RaD, RaF, and the stable lead measurements/can at best be in samples other than water looked at in a qualitative manner as the number and type of samples collected do not warrant statistical analysis per se. However, in the absence of any strong relationship between RaD and stable lead concentrations in surface and ground waters of the study area, it becomes desirable to search for other components in these ecesystems which supports the original hypothesis of this research, the results of the stable lead study given in another section, or at least gives direction as to what component serves as the best indicator accomplish this task.

Fortunately, our study consisted of a comprehensive sampling program of one lake in the study area, Costilla Lake. This lake is located on private land, it is not readily accessable to sportsmen, and lies relatively undisturbed throughout the year. The lake is man-made with a dam being built on one end in the early 1930's; it is located in north-central New Mexico in the Sangre de Cristo mountains. The lake is situated in an area of relatively high annual rainfall and would be expected to contain appreciable levels of scavengeable air particulates of both natural and man-made types.

In general we found that plants such as mosses, and other low

lying plants contained the greatest concentrations of RaD with the lowest concentrations occuring in animal tissues obtained from deer mice and trout. Substances derived from plants such as leaf litter and deer droppings showed similar concentrations to plants. This would indicate that there is very little assimilation of RaD by the gut of either deer mice as indicated analysis of their tissues, or by deer, as indicated by the concentrations of both of these radionuclides in their fecal droppings. However, some deposition of RaD and RaF could have occurred prior to collection as it does on other plant surfaces when left standing[8]. For the most part RaD was N.D. in trout from Costilla Lake, and RaF was not detected in any sample analyzed. However, stable lead values in this organism ranged from about 0.01 to 3.3 ppm in whole homogenized fish. The skeleton would contain over 90% of this lead. Costilla Lake soil collected from around the dam area contained about 1.1 ppm stable lead while soils from around the Las Vegas area had soils concentration ranging from N.D. to about 3.57 ppm. The litter above the more mineralized portion of the soil at this lake, however, had Pb concentrations between about 3 to 8 ppm. This is in contrast to the Pb levels in herbaceous plants from the site which measured predominantly around 0.5 ppm, although a maximum of 9.7 ppm is reported for mixed grasses from around the vicinity of Frazer Mountain in the Santa Fe National Forest. Herbaceous plants generally had the highest RaD/Pb ratios reaching a maximum of 10217 fCi/ppm in a mixed grass sample from Costilla Lake. It is also noted that trout from Costilla Lake with the lowest concentrations of Pb generally were the organisms which contained measurable quantities of RaD.

In the study of the harvester ant around the vicinity of Las Vegas, very little if any significant RaD was found in these organisms, although the levels of stable lead ranged from N.D. to 4.3 which approached if they did not exceed the Pb levels in the surrounding soils. The results of these analyses appear to support what was indicated in the water analysis that higher RaD values are observed in samples which contain lower concentrations of Pb, (see (1,5), Table X), although the relationship was not significant at the 10% level of confidence. Thus, a clearly definable difference should be observed when one compares the RaD/Pb ratios of samples containing relatively high and low levels of Pb. A simple model to explain this phenomenon is the isotopic dilution of RaD produced from Rn-222 emanation with Pb particulates derived from near-in or global fallout.

Having failed to relate RaD/Pb ratios in surface and ground waters of the study area to level of Pb contamination from extraneous sources such as from automobile exhausts using other known variables we attempted to find another indicator which might possibly do an effective job. After a close search through our reported analysis which were still in progress at the time, we noticed a significant difference between both RaD and stable Pb levels in pine needles. Pine needles from both Costilla Lake and from Puerto Nambe were analyzed and found to contain 154 and 211 fCi/gram fresh weight yet contained only 0.014 and 0.014 ppm of Pb on a fresh weight basis. However, pine needles from around the vicinity and within Las Vegas produce only one significant RaD value of 5 fCi/gram fresh weight. The Pb values in these samples were measured at 1.04, 3.6, and 13.6 ppm from two samples of old pine needles, and one sample of young pine needles, respectively. The

only detectable RaD concentration was present in the sample with the lowest Pb concentration. Thus, RaD/Pb values for these two types of sites are different by almost 4 orders of magnitude. Active research is now being conducted by a graduate student to test the sensitivity of this plant indicator in attempting to delineate the extent of Pb contamination from man-made sources.

The concluding statements of this section will be to discuss the relative levels of RaD and/or RaF concentrations of Abiotic and Biotic components in the study area in comparison to measurements which have been made elsewhere. In general the levels of RaD in the ground and surface waters of our study area are very similar to the results of a study on the feedwaters to the Colorado River,[9] which reflects the geology of drainage and weathering, and also many other organic and inorganic chemical reactions. In addition the area reflects the global fallout of RaD attached to particulates (an average of 14 atoms/min/cm^2 of the earth's surface if one assumes an annual rainfall of 1 meter) if one considers the average rainfall differences between the various elevations of the sampling. The values observed in grasses and other herbaceous plants compare with RaD and RaF values observed in grass by Hill[10] who developed a linear correlation of RaD with rainfall (R=0.87; positive correlation). This is possibly one variable which we only considered indirectly (using elevation) in our study not taking into consideration rainfall patterns such as those caused by rain shadows and other meteorological factors.

The levels of these radionuclides in animal tissues were far below the levels reported in animal tissues from Alaska[11] where many of these organisms are dependant on lichens as the primary producer. Lichens and mosses serve as very efficient scavengers

of air and particulates as can be observed by comparing the values we observed within the study area with other components. Finally, the concentration of RaD in soils of the study area were not measured extensively enough to make any comparisons with other areas, however, they appear to contain RaF in quantities similar to soils from Colorado[12] and Wisconsin.[8]

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PART III

CONCLUDING DISCUSSION

The data show a large range in concentration of lead in surface water samples over the period 1971 to 1974. Samples taken during summer, 1971, during which drouth existed, showed a concentration of approximatley 50μg Pb/kg water. From that extreme, more favorable precipitation conditions developed in northeastern New Mexico and each year since 1971 most waters have been very pure. Heavy metal concentrations in water in latter years are as low in northeastern New Mexico as they are in the remotest parts of the world. Comparison of the purity of these waters since 1972 can be made, for instance, with ice sheets in Greenland (1) and with Antarctic snows (2). The reader is cautioned, however, that particular local conditions in the remotest areas in northeastern New Mexico, like the Pecos wilderness, for instance, can permit waters which are lead-free and free of other heavy metals. It is not uncommon for waters in the remote areas of northeastern New Mexico to contain less than 1μg Pb/kg water.

Rain and snow which fall in this area are very pure (again containing often less than 1μg Pb/kg water). Precipitation which falls away from cities, towns, and roadways is especially very pure. It is found that most of the contamination, which is "washed out" of the air by rain and snow, is deposited in approximately the first 20 minutes in which precipitation occurs.

It was also found that snow and rain, which fell along even moderately busy roadways, soon contained very large amounts of lead from vehicular traffic. Incidentally, it is known that lead particles are deposited as Pb Br_2, Pb BrCl, Pb (OH) Br, Pb Br_2, and (PbO_2) Pb BrCl but within a short time lead is converted to Pb carbonates, oxide carbonates, and oxides (3). Since these latter compounds solubility depends on the acidity of the water, it must be assumed that much of the lead is carried through the waters as tiny particles. Many of these particles are often smaller than 1 micron in diameter.

In spite of the very small amounts of lead in these waters, the magnification of the concentrations of lead in fish has been illustrated. While the water which the fish inhabit is approximately 1 μg Pb/kg water (or less), fish contain 10 times and 1000 times that amount.

The hypothesis that most lead in waters of this region of New Mexico resulted from automobile exhausts was tested but not to great avail. That is, Ra D/Pb ratios for water did not definitively permit the interpretation that most lead came from this contaminating source. However, lake trout in a remote area (Costilla Lake) did contain large amounts of stable lead (0.01 to 3.3 μg Pb/g whole fish) and virtually no RaD and RaF. Plant life in the Costilla Lake area, however, contain RaD/Pb ratios as high as 10217 f Ci/ppm. This indicates that fish apparently contain lead other than the naturally occurring amounts of the Costilla Lake area.

Pine needles in the Costilla Lake and Puerto Nambe areas, similarly, contained RaD levels which are high compared to the low

amounts of total lead found. Conversely, the finding of high levels of stable lead in pine needles containing low to undetectable levels of RaD such as from urban sites would lead us to conclude that our original hypothesis may be supported by using a vector other than water to look for such correllation. Active research by a graduate student to help us answer this question is now in progress. This investigator is collecting pine needles from specific locations in our original study area to prove whether this biotic component can serve as a good indicator. Our study reveals that the RaD/Pb in water are subject to too many man-made and natural factors which denied us from making any concrete conclusions, however, the methodologies developed for both chemical and radiochemical analysis should provide the investigator with the necessary tools to continue such a search. Finally, the results of our research seem to indicate that RaF/Pb ratios may prove more valuable in this regard than RaD/Pb ratios.

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