

TRACE ELEMENT AND TRACE RADIONUCLIDE

COMPOSITION OF SNOW AND RAIN ^{1/}

by

R. W. Perkins and R. J. Engelmann ^{2/}

Introduction

The foreign material contained in a raindrop or snowflake is a mixture of the substances responsible for their original nucleation plus those scrubbed from the atmosphere during their descent to the earth. Information relating to the birth and to the subsequent environment of a snowflake or raindrops could therefore be obtained, if the composition and abundance of their trace materials were known. Also, a knowledge of the composition of snow and rain would provide the basic information necessary to predict what tracer materials would be most sensitive as atmospheric tracers of ice crystal nucleation (rainout) and for precipitation scavenging (washout). Analytical methods have been developed and applied which utilize new ultra-sensitive and selective methods in the determination of several trace elements and trace radionuclides which are present in rain and snow. This present work describes the measurement techniques, the observed concentrations, and the origins of several trace materials which have been measured in rain and snow. The possible use of these natural materials plus the use of artificial tracers in describing atmospheric phenomena are considered.

Nature and Origin of Atmospheric Aerosols

The natural atmospheric aerosols range in size from slightly less than 0.001μ diameter for small ions (consisting of a cluster of 10 to 30 molecules around an ion) to about 20μ diameter for the giant particles. Between these extremes lie the Aitken particles with diameters less than 0.1μ micron, the large particles with diameters between 0.1 and 1μ , and the giant particles with diameters greater than 1μ . The large and giant particles account for the main aerosol mass. Also, since water vapor supersaturations in the atmosphere are always small, normally only the giant and large nuclei serve as condensation nuclei for rain or snow formation.

Physical constituents of aerosol particles in the atmosphere vary from dry insoluble dust particles to clear droplets of salt solution. Identified sources of these aerosols include mineral dust from the continents, sea spray from the oceans, man-made particles from combustion and other processes, reactions of atmospheric gases to form particles, and injection of extraterrestrial dust into the stratosphere. It has been pointed out (Junge 1963) that the role of soil material in atmospheric aerosols is certainly underestimated and its role as condensation nuclei in continental cloud formation has still to be assessed.

The atmospheric aerosols become tagged with both the natural and artificial radionuclides in the atmosphere which can serve as tracers in studying the chemical and physical behavior of aerosols. The natural cosmic-ray produced radionuclides and the daughters of radon are natural constituents of the atmosphere which attach themselves to the aerosols and can thus serve in studying atmospheric aerosol processes. Numerous fission and activation produced radionuclides from nuclear testing are also attached to these aerosols and are useful tracers.

The giant and large aerosol particles serve as condensation nuclei and thus an analysis of cloud or rain water could provide information on the composition of these nuclei. Such an analysis is not valid for those elements which are in a gaseous state (e.g. SO_2 , NH_3 and NO_2) since they would condense along with water vapor during the condensation process in a cloud. A rain or snow sample collected well below the cloud would

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^{2/} Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, Washington.

contain material washed from the air as well as that which participated as condensation nuclei in the cloud. However, this washout process does not modify the relative composition of the precipitation residue unless the large and giant particles below the cloud are different from those within the cloud which served as condensation nuclei.

Measurement Techniques for Trace Elements and Trace Radionuclides

Through the recent developments of multidimensional gamma ray spectrometry (Perkins, 1965) it is possible to make direct measurements of numerous trace elements and trace radionuclides in the residue from a rain or snow sample. The trace radionuclides are measured directly while the trace elements are measured following neutron activation. The multidimensional gamma ray spectrometers have been described in detail earlier (Perkins 1965, Perkins and Robertson 1965) and only a brief description of their operation is considered here.

The typical spectrometry system consists of a 4096 channel analyzer used in a 64 x 64 channel grouping arrangement in conjunction with two anticoincidence shielded NaI(Tl) detectors of equal size (See Figure 1). One of the detectors (which is 4 inches thick by 6 inches in diameter) has a 4 inch light pipe of pure sodium iodide which serves to shield the detector from gamma radiation originating in its phototube. The anticoincidence annulus in this case is a 11½ inch diameter by 12 inch long NaI(Tl) crystal with a 6½ inch diameter center hole to accommodate the principal detectors. The sample to be measured is sandwiched between the two 6 inch diameter detectors. The signals from the two detectors are fed to the two separate analog to digital converters of the analyzer for energy and coincidence analysis and from there to the memory storage unit. When a single photon interacts with one of the detectors, the event is stored on the corresponding X or the Y axis of the memory. When two photons are emitted simultaneously, each interacting with a separate detector, the event is stored in an energy-energy plane at a point uniquely characteristic of the two energies. The spectrum of Co⁶⁰ (Figure 2) illustrates the manner of storage. The normal spectrum of Co⁶⁰ as seen by one of the detectors is shown for comparison. With a detection system of this type the unique decay characteristic of many radionuclides are readily resolvable thus permitting a far greater sensitivity for detection and direct measurement of many minor radioactive constituents. In addition the background interference for many radionuclide measurements is several orders of magnitude lower.

The trace elements in precipitation result in part from continental dust and sea spray. Following neutron activation of soil or sea water several trace elements can be measured by direct counting of the daughter radionuclide mixture on the multidimensional gamma-ray spectrometers. Figure 3 presents a gamma-ray spectrum of soil showing the energy regions in which 7 trace elements are measured. These elements can be measured at levels of less than 10⁻⁹ grams per sample and are easily measured in the residue from rain or snow. Figure 4 presents a spectrum of neutron activated sea water showing the energy regions in which 10 trace elements are simultaneously measured from their daughter radionuclide concentrations.

Natural atmospheric aerosols become tagged with radionuclides which have resulted from nuclear weapons testing and the measurement of the radionuclides on both the airborne aerosols and on those deposited in precipitation provides information on precipitation processes. In Figure 5 the energy areas used in our measurements of 13 radionuclides on the airborne aerosols are indicated (Perkins and Robertson 1965).

Trace Elements in Precipitation

The condensation nuclei responsible for the precipitation process plus those washed from air below the cloud are present in precipitation reaching the earth. If one assumes that the composition of the condensation nuclei in the cloud is the same as that of the aerosol washed from the air below the cloud then an analysis of the residue in rain or snow represents that of the condensation nuclei. Table I presents the measurement of 7 trace elements in fresh snow and compares them with the trace element composition of the earth's crust and of sea water.

The snow sample values are the average of a few samples collected in the Cascade Mountains near White Pass. It is interesting that while the trace elements in the snow are of comparable concentrations to those in sea water that the major element, sodium, is

40,000 times higher in sea water than snow. A more meaningful comparison of the relative concentrations of the trace elements in snow, the earth's crust and sea water can be made by normalizing all trace element values to a sodium value of 10,000 units for the three materials. (See Table II). It is evident that the elemental composition of snow is comparable to the earth's crust and not to that of sea spray. To arrive at the observed composition for the snow residue from a mixture of earth's crust and sea salt would require that the mixture have a very small or no sea salt component. Silver has been used as a cloud seeding agent and subsequently measured in the resulting precipitation. Studies (Schaefer and Fuquay 1965) in the AgI seeding of supersaturated supercooled air in the Old Faithful region of Yellowstone Park resulted in easily measurable concentrations of silver in the precipitation which was produced.

Trace Radionuclides from Nuclear Weapons in Precipitation

The tracers introduced into the atmosphere by nuclear testing can be extremely useful in studying precipitation mechanisms. Most of the airborne radioactivity from atmospheric tests is in the stratosphere. This drops into or mixes with tropospheric air and is eventually deposited, mainly by precipitation, on the earth's surface. Figure 6 shows the relative concentrations of 12 radionuclides in the stratosphere (65,000 ft) versus that in the troposphere during early 1965 (Perkins, Thomas and Nielsen 1964). The stratospheric concentrations of these radionuclides exceeds the ground level concentrations by 800 to more than 10,000 times. The concentrations of radionuclides in the troposphere depend on the past history of the air mass but often show major increases with altitude as shown in Figure 7. The major mode of deposition of this activity is by precipitation; however, in areas of low annual precipitations dry deposition becomes important. Figure 8 compares the dry and wet deposition at Richland, Washington for the three summer months of 1964 (Perkins, Thomas, Nielsen 1964). During this period only about 1 inch of rain fell and less than half of the total fallout deposition was carried by the rain (See Figure 8).

The efficiency with which rain and snow remove aerosol particles is only now being investigated; however, the nuclear-weapons-produced radionuclides attached to the aerosol particles provide useful tracers in studying this process. Table III compares the concentrations of several nuclear-weapons-produced radionuclides in rain and snow during a period when the air concentrations of the radionuclides at ground level were comparable. The radionuclide Be^7 is not a nuclear-weapons-produced radionuclide but is produced continuously by cosmic-ray interaction in the atmosphere, and is given further consideration later in this paper. From these limited observations it would appear that snow is significantly more efficient in removing the natural atmospheric aerosols than is rain.

Trace Radionuclides from Cosmic Rays in Precipitation

Radionuclides are produced continuously in the atmosphere by cosmic-ray interactions with the atmosphere. The production rates of these radionuclides vary appreciably with both altitude and latitude but are relatively constant with time. The cosmic-ray produced radionuclides which have been observed to date are summarized in Table IV. The half-lives of these radionuclides range from minutes to millions of years. Their production rates at a given altitude increase rapidly with altitude and are several hundred times greater (per unit weight of air) near the top of the atmosphere than at sea level. These radionuclides are potentially excellent tracers of atmospheric precipitation processes and their use is limited only by their low concentrations which make their measurement very difficult. Table V presents measurements of the short lived radionuclides Cl^{38} (37 min.) Cl^{39} (55 min.) and S^{38} (2.9 hrs.) in rain water (Perkins, et al 1965) during 1964. These values are the first and only reported measurements of Cl^{38} and S^{38} and show the variation in concentration for the various rain samples. These variations must be related to and could serve as tracers of such parameters as the rainout and washout efficiency, the altitude at which condensation occurred, raindrop size, and the rainfall rate. Table VI presents measurements of the concentrations in rain of the two cosmic-ray produced radionuclides Na^{24} (15.1 hr.) and Na^{22} (2.6 yr.) (Perkins 1964). These measurements were made by direct counting of the residue from large volumes of rain water and again show variations which are indicative of the mechanism involved in precipitation. The simultaneous measurement in rain samples of the short lived radionuclides Cl^{38} , Cl^{39} , S^{38} and Na^{24} would be especially helpful since their half-lives are of the right order for studying rates and mechanisms of precipitation processes.

Summary

Numerous trace elements and trace radionuclides are present in the atmosphere which can be used as tracers in studying atmospheric precipitation processes. Multi-dimensional gamma ray spectrometry provides the required sensitivity and selectivity for measuring many of the tracers by direct counting techniques. Trace element measurements of the residues from snow samples indicate that these residues and presumably the condensation nuclei are from the earth's crust rather than from sea spray. Comparisons of the concentrations of airborne radionuclides carried down by rain with those in snow indicate that snow is more efficient in the removal of airborne aerosols. The low concentrations of the trace elements Sc, Ag, Co and Sb in snow residues show that these elements would be very sensitive tracers of atmospheric precipitation processes.

REFERENCES

1. Junge, C. E., *Air Chemistry and Radioactivity*, Academic Press, New York and London (1963)
2. Perkins, R. W., Thomas, C. W. and Nielsen, J. M. *Radioactive Fallout From Nuclear Weapons Tests Proceedings of the Second Conference, Germantown, Maryland, November 3-6, 1964* pp. 198-221. ed. Alfred W. Klement, Jr.
3. Perkins, R. W., Nucl. Instr. and Meth. 33, pp. 71-76, March 1965.
4. Perkins, R. W. and Robertson, D. E. "Selective and Sensitive Analysis of Activation Products by Multidimensional Gamma-Ray Spectrometry," Proceedings 1965 International Conference: Modern Trends in Activation Analysis, 1965.
5. Perkins, R. W., Thomas, C. W., Hill, M. W., and Nielsen, J. M. Nature 205, p. 790, (1965).
6. Perkins, R. W. and Nielsen, J. M. "Cosmic-Ray Produced Radionuclides in the Environment," Health Physics vol. 11, pp. 1297-1304, 1965.
7. Schaefer, V. J. and Fuquay, J. J. "The Detection of Silver Iodide in Snow by Neutron Activation Analysis," Journal De Recherches Atmosphériques, vol. II, No. 2, pp. 49-52 (1965)

TABLE I

COMPARISON OF THE OBSERVED TRACE ELEMENT CONCENTRATIONS
IN SNOW WITH THOSE IN THE EARTH'S CRUST AND SEA WATER

(concentration, ppm)

<u>Element</u>	<u>Snow*</u>	<u>Earth's Crust</u>	<u>Sea Water</u>
Na	0.29	28,300	10,600
Cu	0.011	70	0.005
Zn	0.004	132	0.01
Co	0.00004	23	0.0005
Sc	0.00001	5	0.00004
Sb	0.0001	1	0.0005
Ag	~ 0.00002	0.1	0.0003

* Average of a few fresh snow samples from the Cascade Mountains.

TABLE II

RELATIVE TRACE ELEMENT CONCENTRATIONS IN
SNOW, THE EARTH'S CRUST, AND SEA WATER

(all values normalized to 10,000 units for Na)

<u>Element</u>	<u>Snow*</u>	<u>Earth's Crust</u>	<u>Sea Water</u>
Na	10,000	10,000	10,000
Cu	380	25	0.005
Zn	140	47	0.01
Co	1.4	8.2	0.0005
Sc	0.3	2.0	0.00004
Sb	3	0.4	0.0005
Ag	~ 0.7	0.04	0.0003

* Average of a few fresh snow samples from the Cascade Mountains.

TABLE III

RADIONUCLIDE CONCENTRATIONS IN RAIN AND SNOW SAMPLESCOLLECTED NEAR RICHLAND, WASHINGTON^a

<u>Radionuclide</u>	dpm/liter of Water		<u>Snow Rain</u>
	<u>Snow*</u> <u>March 1965</u>	<u>Rain**</u> <u>April 1965</u>	
Be ⁷	150	101	1.5
Na ²²	.34	.15	2.3
Mn ⁵⁴	17	16	1.1
Co ⁶⁰	.55	.34	1.6
Y ⁸⁸	~ .06	~ .05	~ 1.2
Ru ¹⁰⁶	100	41	2.4
Sb ¹²⁴	3.3	1	3.3
Sb ¹²⁵	46	32	1.4
Cs ¹³⁷	29	24	1.2
Ce ¹⁴⁴	88	210	.42

* 0.1 inches of snowfall - 3-27-65

** 0.175 inches of rainfall - 4-19-65

a Measurements by C. W. Thomas, Battelle-Northwest
Richland, Washington

TABLE IV

Cosmic Ray Produced Radionuclides			
Radionuclide	Half-life	Radiation	Reference**
Be ¹⁰	2.7 x 10 ⁶ y	β^- 555 KeV	Arnold (1956)
Cl ³⁶	3.1 x 10 ⁵ y	β^- 714 KeV	Davis and Schaeffer (1955)
C ¹⁴	5568 y	β^- 156 KeV	Libby (1952)
Si ³²	~ 500 y	β^- 100 KeV	Lal, Goldberg and Koide (1960)
H ³	12.3 y	β^- 18 KeV	Faltings & Harteck (1950)
Na ²²	2.6 y	β^+ , γ 1.28 KeV	Marquez, Costa & Almeida (1957)
S ³⁵	88 d	β^- 167 KeV	Goel (1956)
Be ⁷	53 d	β^-, γ 480 KeV	Arnold & Al Salih (1955)
P ³³	25 d	β^- 246 KeV	Lal, Narasappaya & Zutshi(1957)
P ³²	14.3 d	β^- 1.724 MeV	Marquez and Costa (1955)
Na ²⁴	15.1 hr	β^-, γ 1.38 + 2.76 MeV	Rodel (1963)
S ³⁸	2.9 hr	β^-, γ^* 1.6 + 2.16	Perkins, Thomas, Hill, Nielsen(1965)
Cl ³⁹	55 min	β^-, γ 0.246 + 1.266	Winsberg (1956)
Cl ³⁸	37 min	β^-, γ 1.6 + 2.16	Perkins, Thomas, Hill, Nielsen(1965)

* Radiation due to the Cl³⁸ daughter

** Summarized in a recent review by Perkins and Nielsen 1965

TABLE V
 CONCENTRATIONS OF THE COSMIC RAY PRODUCED RADIONUCLIDES
 Cl^{38} , S^{38} and Cl^{39} in Rain Water^a
 (dpm liter⁻¹)

<u>Date</u>	<u>Volume, liters</u>	<u>Collection Time, Minutes</u>	<u>Cl^{38}</u>	<u>S^{38}</u>	<u>Cl^{39}</u>
7/29/64	5.10	50	147 ± 15	13 ± 5	200 ± 17
7/30/64	6.64	15	~ 18	4 ± 2	~ 10
8/1/64	3.5	50	9 ± 5	b	15 ± 3
8/1/64	1.8	10	31 ± 12	b	28 ± 5
8/12/64	2.2	5	42 ± 13	~ 7	62 ± 12
8/18/64	10.0	40	55 ± 9	b	53 ± 3

^a The plus or minus values are the standard deviations for the measurements

^b Not measured

TABLE VI
 Na^{22} AND Na^{24} CONCENTRATIONS IN RAIN WATER
 (dpm liter⁻¹)^a

<u>Date</u>	<u>Sample Volume (liters)</u>	<u>Na^{24}</u>	<u>Na^{22}</u>
6/15/64	60	0.70 ± 0.13	0.36 ± 0.03
6/17/64	6.64	2.22 ± 0.25	0.25 ± 0.04
6/18/64	14.32	0.59 ± 0.09	0.19 ± 0.02

^a The ± values are the standard deviation

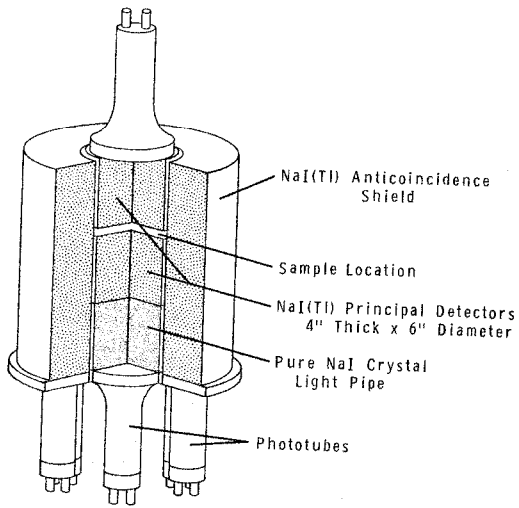


FIGURE 1
SODIUM IODIDE DETECTOR SYSTEM FOR MULTIDIMENSIONAL
GAMMA-RAY SPECTROMETRY

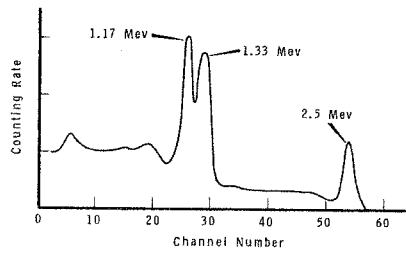
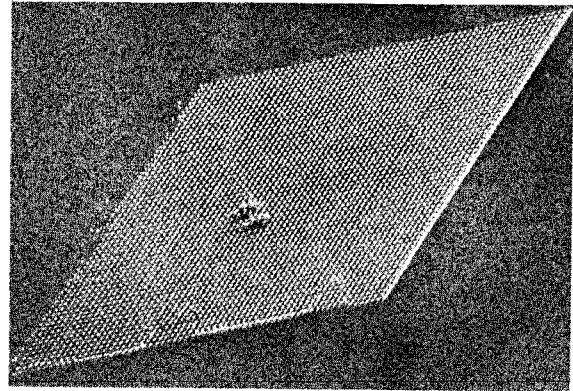


Figure 2
Co⁶⁰ SPECTRA

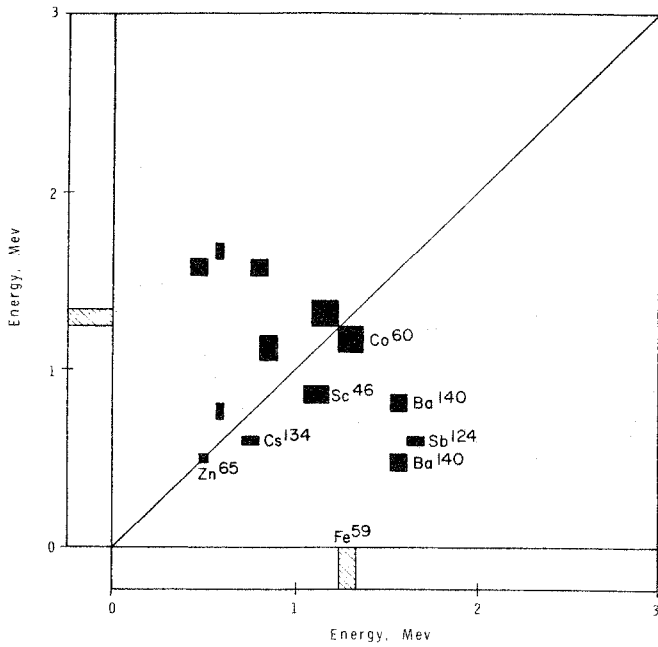


FIGURE 3
ENERGY AREAS USED IN THE DIRECT MEASUREMENT OF 7
RADIONUCLIDES IN SOIL (COLUMBIA RIVER SEDIMENTS) FOLLOWING
NEUTRON ACTIVATION

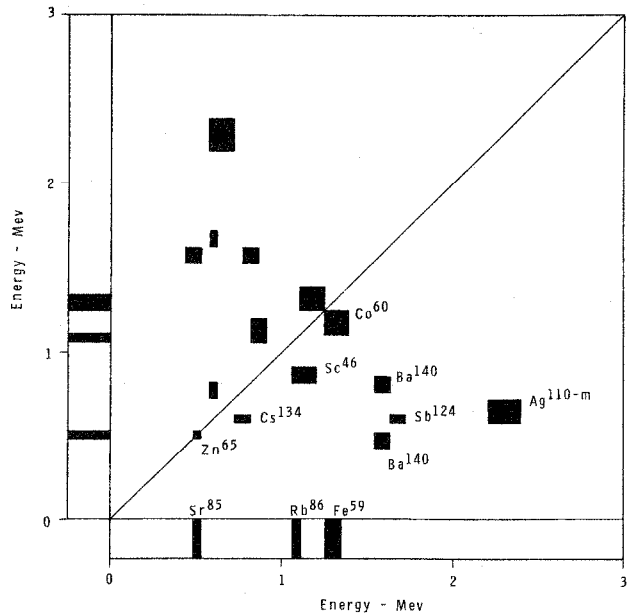


FIGURE 4
ENERGY AREAS USED IN THE DIRECT MEASUREMENT OF 10
RADIONUCLIDES IN SEA WATER

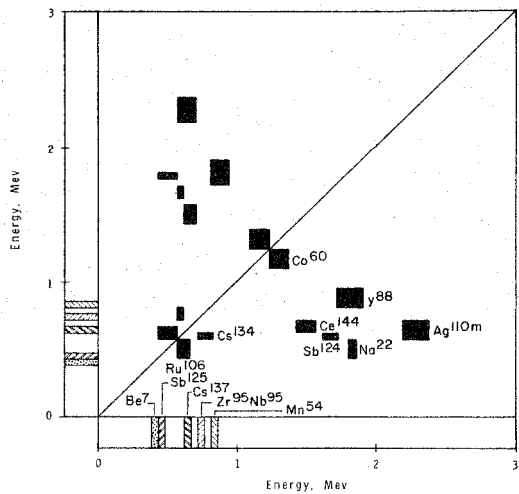


FIGURE 5

ENERGY AREAS USED IN THE DIRECT MEASUREMENT OF 13 AIRBORNE RADIONUCLIDES ON AIR FILTERS

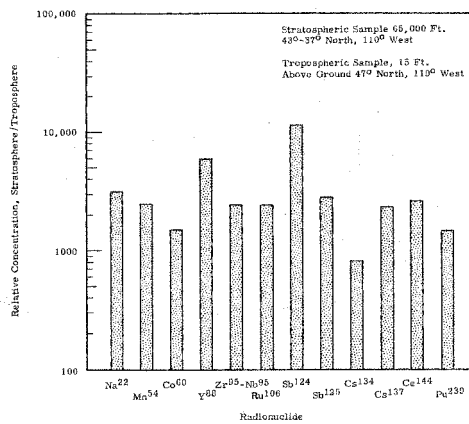


FIGURE 6

Ratios of Radionuclide Concentrations in the Stratosphere to that near Ground Level in the Northwest part of the U.S. in January 1964

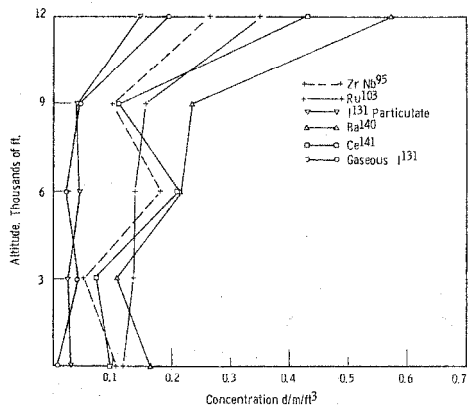


FIGURE 7

Radionuclide Concentration as a Function of Altitude 11/13/62

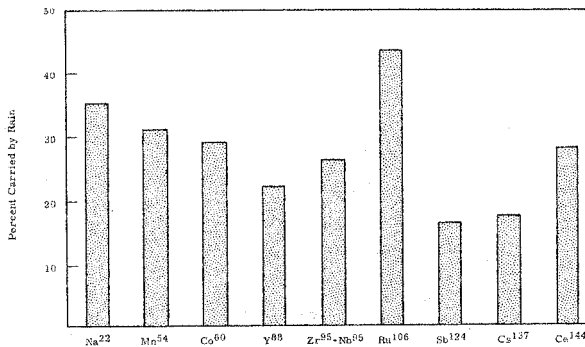


FIGURE -8-

Fraction of Radionuclide Deposition due to Rain during the Summer of 1964. (6-11-64 through 9-15-64)